Archaeological Wood

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Archaeological Wood Properties, Chemistry, and Preservation

Roger M. Rowell, EDITOR
U.S. Department of Agriculture

R. James Barbour, EDITOR
Forintek Canada Corporation

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FOREWORD

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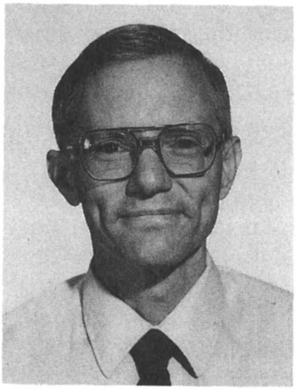


ROGER M. ROWELL is a carbohydrate chemist at the Forest Products Laboratory, U.S. Department of Agriculture, Forest Service, in Madison, Wisconsin. His research involves the enhancement of wood properties through the chemical modification of wood cell walls.

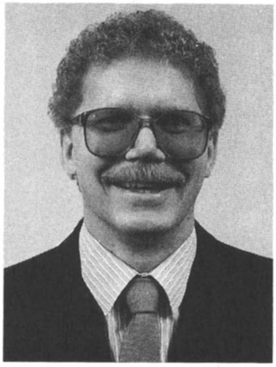
He currently serves as team leader for an International Team on Property Enhancement of Wood Composites Through Chemical Modification, as a team leader at FPL on Property Enhancement of Wood Composites, as professor in the Forestry Department at the University of Wisconsin–Madison, and as research professor, Department of Technical Chemistry, Chalmers University of Technology, Goteborg, Sweden.

His research has included cooperative studies in the Unites States, Brazil, Denmark, New Zealand, France, Germany, Poland, Switzerland, Japan, China, Malaysia, Great Britain, Finland, and Sweden. In 1967 he was an honorary research fellow in the Chemistry Department at Birmingham University, Birmingham, England. For part of 1985 he was a guest professor, Forest Chemistry Department, Beijing Forestry University, Beijing, China, and for part of 1985 and 1986 he was a National Science Foundation exchange professor at the Wood Research Institute, Kyoto University, Uji, Japan. For part of 1986 he was a guest professor, Department of Wood Science, University College of North Wales, Bangor, United Kingdom. For part of 1988 he was a guest research fellow at the Forest Research Institute, Rotorua, New Zealand.

In addition to authoring more than 90 publications and receiving five patents, Rowell has presented numerous papers at national and international scientific meetings, organized national and international symposia, and has been active in consulting and technology transfer of his research worldwide.

Rowell is a fellow in the International Academy of Wood Science, a member of the Sigma Xi Honorary Research Society and the American Chemical Society, where he served as chairman of the Cellulose, Paper, and Textile Division in 1980.

Rowell received his B.S. degree in math and chemistry in 1961 from Southwestern College in Kansas. He received his M.S. and Ph.D. in biochemistry from Purdue University in 1963 and 1965, respectively.



R. JAMES (Jamie) BARBOUR is a wood scientist with Forintek Canada Corporation's eastern laboratory in Ottawa, Ontario, Canada. His research involves the evaluation of wood quality problems encountered by the Canadian wood products industry in the processing of the existing resource, as well as those expected in the utilization of the managed resource that is currently being grown.

He became involved in the conservation of archaeological wood as an undergraduate botany student at Washington State University. He began by making species identifications of wood recovered from the Hoko River Site, which is located on the Olympic Peninsula in Washington. He soon realized that there was a need for further research into the properties of archaeological wood and how these properties influence the outcome of various conservation treatments. This was the topic of his master's thesis, which was written at the University of Washington in Seattle, Washington.

Barbour's research in the area of the conservation of archaeological wood has included work on the microstructural properties of waterlogged wood, the shrinkage and collapse of waterlogged and damp wood during drying, various aspects of the polyethylene glycol (PEG) and sugar treatments to improve dimensional stability, in situ polymerization of water-soluble monomers, and freeze-drying of waterlogged wood. Although his current research is in the area of the industrial utilization of wood, he maintains a healthy interest in the conservation of archaeological wood and hopes to continue to make meaningful contributions to this field.

PREFACE

WOOD HAS PLAYED A MAJOR ROLE throughout human history. Even the earliest humans used wood to make shelters and later to cook their food. Wood also provided tools and weapons. Collective society learned very early the great advantages of wood, which we still recognize today: its strength, workability, wide distribution, renewability, and aesthetics.

To study the uses of wood is to study human history. There is a great need to preserve the wood in the many forms that remain from ancient to modern times, not only because it will be interesting to future generations, but to use it to study the cultures and climates throughout history and to study the wood-aging process itself.

For this book, archaeological wood will be defined in its broadest sense: Any wood that gives information about human development, culture, or climate conditions, or that is used to study the aging process of the wood itself shall be referred to as archaeological wood. This includes woods that are sometimes called historical and prefossilized woods. More restrictive definitions are used in some of the chapters. This different usage reflects the perspective of the individual author. The purpose of preservation of archaeological wood is to save the artifacts for future viewing, study, and reference.

The microstructural, physical, and chemical properties of archaeological wood discussed in this book apply to materials coming from a wide range of environments: wet environments such as bogs, fresh water, and salt water; dry environments such as tombs and dwellings; and variable environments, including historic buildings and outdoor artifacts that exist where weathering has taken its toll.

Present techniques for preserving archaeological wood range from art forms (some have even been referred to as witchcraft) to science. Many methods have been based on empirical approaches rather than hard scientific data. We need to study the changes in microstructural, physical, and chemical properties that occur during the aging process as a result of the environment surrounding the artifact. Familiarity with these changes will lead to an understanding of the mechanisms of degradation. Armed with knowledge of these mechanisms, modern scientists are led along logical paths to develop preservation techniques that will allow the wood to remain, as closely as possible, in its found state, without major modification of its chemistry. Some techniques will cause major changes in the wood's chemistry, and these procedures will need to be carefully recorded for future reference.

We hope that this book will provide some understanding, from a scientific perspective, of archaeological wood, its properties, its chemistry, and its preservation.

We dedicate this book to all past, present, and future scientists who proudly consider themselves archaeological wood preservationists.

Acknowledgments

This book is a result of many hours of effort by many people. We thank all of them for their time and concern for this project. We especially thank Judy Rowell for her efforts as the secretary for the symposium in Los Angeles and also for this book. We also thank the Samuel H. Kress Foundation, whose generosity provided travel funds for the foreign speakers who attended the symposium. Finally, we thank the wonderful staff at ACS Books for their creative ideas, suggestions, hard work, and endless patience.

ROGER M. ROWELL
Forest Products Laboratory
U.S. Department of Agriculture
Madison, WI 53705–2398

R. JAMES BARBOUR
Wood Science Group
Forintek Canada Corporation
Ottawa, Ontario K1G 3Z5, Canada

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Scope and History of Archaeological Wood

Mary-Lou E. Florian

Royal British Columbia Museum, 675 Belleville Street, Victoria,
B.C. V8V 1X4, Canada

Archaeological wood may be defined as dead wood, used by an extinct human culture, that may or may not have been modified for or by use, and that was discarded into a specific natural environment. Such wood has now been removed from this environment, taken out of the sequence of chemical and physical changes that would ultimately have transformed the wood either to a fossil or to dust. The condition of archaeological wood could be near normal or extensively altered. Age alone is meaningless in terms of deterioration, which depends on the type of wood, the environment, and time. Twentieth century society, with a new awareness of the value of the objects of the past and with new technology for handling them, is preserving this wood for posterity. This chapter will present a brief overview of the variable environments of discard, their effects on the properties of the wood, and 20th century attitudes toward technology of wood preservation.

WE CAN ONLY IMAGINE THE DEPTH OF EMOTIONS experienced by those who were there when the Swedish warship, the *Wasa*, broke the surface of the water after 333 years of marine burial. Hearts must have been bursting and tears flowing. The sight of the ship must have conjured up many different thoughts in the people watching: thoughts of its preciousness as an object of antiquity and the incredible tie it forms between the people of today and those of 333 years ago; thoughts about the ship and its fund of information about past ship-building technology; and thoughts of the boat as a museum object and the challenge involved in displaying it.

There must have been thoughts of the excavation procedure, the en-

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gineering feat of raising a 1200-ton ship, the technology of diving, and the thrill of the finds.

Surely a few thought about the material, the wood, now archaeological wood; about the physical and chemical state of the wood and the task of conserving this waterlogged wood; about how the unique burial environment, through some fluke, allowed this wood to evade the natural cycle of deterioration for 333 years; and about the secrets hidden in the wood, such as information about its age and the environment in which it lived, secrets revealed in its unique growth patterns.

I am sure that the most overpowering emotions stemmed from the feeling that this ship is a link to human society of a different century. Attractive as the social aspect is, the topic of this book is wood, archaeological wood. We see the *Wasa* as a heritage and research object, as a cultural and environmental informant. More basically, it is deteriorated material that we have retrieved from a specific environment. The ship must now be preserved in the new environment in which we have placed it.

Over the years attitudes toward objects or "finds" have changed. In the past, archaeological excavations were done for looting and for curiosity. Today such projects are undertaken with scientific discipline to obtain accurate information about human material culture and interrelationship with the environment. Sophisticated scientific techniques are used to extract this information, and legislation is in place to protect archaeological sites and objects. Conservation is now a standard procedure to prevent the object's deterioration after excavation and potentially to preserve it for posterity.

In the past, "after the wreck was excavated, the conservation department was consulted." Now conservators are occasionally a part of the core group before excavation. The conservator's task is to ensure that the objects are protected during and after excavation, are handled appropriately, are secured for transport, are stored correctly and undergo analysis prior to conservation treatment, and are appropriately treated and stored or exhibited.

What Is Archaeological Wood?

For this introductory overview chapter, I will define archaeological wood as dead wood, used by an extinct human culture, that may or may not have been modified for or by use, and that was discarded by intent or accident into a specific natural environment. This may be too narrow a definition. Often, living and dead trees that have been culturally modified in the past (such as Australian aboriginal carved trees, bark-stripped western redcedar trees, and trees showing survey marks) are categorized as archaeological. Ancient living trees such as the bristlecone pines, the giant redwoods, and other species are also categorized as archaeological.

Archaeological wood is excavated most commonly from marine and wet terrestrial burial sites. However, surface finds may be related to recently exposed sites or to unique environments such as the Arctic and Australia. Wood is found in ancient structures that are still standing, such as the pyramids and Chinese temples. The environments that preserve ancient wood vary from wet to dry, and thus archaeological wood ranges from waterlogged to desiccated.

Buried archaeological wood is the same as ancient wood (often called paleontological wood). Both have been deposited in natural environments and have undergone changes there. Normally these changes would eventually turn the wood to dust, humus, or coal, or would mineralize it, depending on the environment of the burial site. But occasionally the wood appears to be stabilized in a strata, like a buried time capsule. It reaches an equilibrium within the strata's unique environment that allows the wood to apparently survive.

Most archaeological buried waterlogged wood is in the early process of diagenesis. Diagenesis is the natural process in which sedimentary materials are slowly compacted and eventually will form rock. In this natural process of change, 2000 or even 25,000 years is a short period.

The chemical and physical state of archaeological wood may vary from near normal to disintegration. This variability may even be present in a single piece of archaeological wood because of centripetal degradation, with which the inside of the piece of wood is near normal and the exterior is degraded. The variability can be explained by any number of factors, such as the wood species, the history of use and fabrication, the time buried, and the burial environment.

Characteristics of Archaeological Wood

Purpose of Analysis. The chemical and physical characteristics of archaeological wood are analyzed for two basic reasons: to understand the process of deterioration and to assist in designing a logical conservation treatment to stabilize the wood. For example, depending on its condition, when wet or waterlogged wood is dried, it may go through drastic dimensional changes because of cell wall and cell collapse or shrinkage. This change must be prevented to retain the integrity of the object.

Chemical Changes. Various chemical changes may have occurred in archaeological wood. Such wood may be normal chemically (that is, contain the same ratios and amounts of the basic chemicals, the biopolymers lignin, cellulose, hemicellulose, and pectin, and the extractives and inorganic chemicals) or it may have altered amounts and ratios of the chemicals. Archaeological wood can be solely cellulosic or lignitic, or any combination of these. The organic chemicals may be replaced by inorganic chemicals, and the wood may be mineralized.

Archaeological wood that is dry when excavated does not present the problems involved in drying waterlogged wood. The intensity, in terms of analysis and treatment of dry wood, has been very little compared with that of waterlogged wood. Therefore, the following discussion will center on waterlogged wood.

Squirrel and Clarke (*1*) compared analyses published between 1977 and 1987, of archaeological waterlogged oak from boat remains of various ages. Their samples, ranging from the 1st to the 17th century A.D., included the *Mary Rose*, the boat they were researching.

The analyses (*1*) showed that as water content within a sample increased, the relative amounts of cellulose decreased and of lignin increased. However, there were exceptions. Comparisons were also made between the outer and the central portion of each sample. Generally, the outer portion showed the greatest moisture, inorganic content, and loss of biopolymers. The central portion showed, in some cases, near-normal amounts of the chemicals. The exceptions were probably caused by the varying burial environments of the archaeological woods or by lack of standard methods of analysis.

Method Standardization. Hoffmann (2) discussed the need to standardize the methods of analysis in 1981. He recommended the use of the standard procedures designed for analysis of fresh wood by the Technical Association of the Pulp and Paper Industry (TAPPI). Although some minor problems with the methods would be expected because of modification of degraded chemicals, he felt that the procedures would give an adequate characterization of archaeological wood. Hoffmann encouraged the use of these analytical methods so that in the course of time enough analysis would be done to confirm relationships between analysis and response to specific treatments.

Seifert and Jagels (3), using the TAPPI standards recommended for archaeological wood, undertook extensive chemical analysis of wood elements of different wood species. Their samples came from the *Ronson* ship's bow excavated from a landfill in the New York Harbor after a burial of approximately 240 years.

There were problems in the analysis. The authors stated, "Summation of the chemical constituents should yield 100%. Most of the totals exceed 100%. This indicates a problem with one or more aspects of the analysis . . . the lignin analysis may be suspect. Cellulose may also be too high." High iron content was found in some samples, and this may have influenced the analysis.

The TAPPI methods were designed for normal wood chemicals. A method of characterizing and quantifying degraded chemicals would seem more appropriate and may solve some of these problems.

Altered Chemicals. Hedges et al. (*4*) used a more refined analysis for the altered chemicals present. They analyzed for individual saccharides of the three polysaccharides (cellulose, pectin, and hemicellulose) and for the phenols of lignin. This approach led to a greater understanding of degradation information, which may be vital in understanding potential conservation treatments.

Hedges et al. (*4*) analyzed buried white oak (approximately 25,000 years old) and red alder and Sitka spruce (2500 years old). All of these samples were considered to be in the dynamic process of diagenesis. The oak was excavated in a drill hole, 100 m deep in sediment off the continental slope of Louisiana. The alder and spruce were excavated from a deposit contemporaneous with a 2500-year-old archaeological site on the Hoko River bank on the Olympic Peninsula of Washington State. This wood, even though not artifact material, illustrates the changes that would affect archaeological wood of this age in this environment.

Remarkably, the spruce showed no significant losses or degradation of biopolymers. The alder, taken from the same excavation horizon as the spruce, was significantly altered, as was the oak. The simple phenols of lignin and the neutral sugar products of carbohydrates were quantified by capillary gas chromatography. The results from the buried wood were compared to those of their modern counterparts.

The sugar and phenol analyses showed that there were chemical degradation and losses. In the alder and oak, respectively, 90 and 98% of the polysaccharides and 15 and 25% of the lignin was lost or degraded. Approximately 75% of the degraded biopolymers had been lost from the two samples.

The analyses showed that the vanillyl and *p*-hydroxyl lignin units were the most stable, followed by the syringyl lignin groups. Of the neutral sugars analyzed, arabinose, galactose, fucose, and rhamnose are least degraded, followed by glucose, mannose, xylose, lyxose, and ribose, the most degraded.

The biopolymers in decreasing order of stability are lignin, pectin, α-cellulose, and hemicellulose. Hedges et al. (*4*) suggested that the inferred order of polysaccharide preservation may be related to the ultrastructure of the wood cells and not to intrinsic chemical stability.

Wayman et al. (5) reported some unique patterns of cellulose retention. In a sample of wood buried for 10 million years, 22% of the cellulose was retained. In another sample of wood buried 30 million years, 30% of the cellulose was retained. In a third sample 100 million years old, there was no cellulose; only lignin remained.

Inorganic Materials. During petrification, the types of inorganic substances that replace organic substances will depend on the burial environment. Phosphates and silicates have been found in petrified wood from the marine environment, and calcium minerals in samples from terrestrial and cave environments. High iron contents are always associated with shipwrecks. All these impregnates will influence the analytical methods and conservation treatments.

The conservator should know the location of the inorganic materials. In some cases iron compounds may be located throughout the cell wall. Other times it can be precipitated in specific regions, such as in bordered pit membranes (Figure 1), where it would influence the permeability of the wood.

Moisture Content. In a specific circumstance (a treatment problem of a group of oak timbers), the moisture content and the amount of internal sound wood core were used instead of chemical analyses to assess degradation (*6*). The wood condition has been classified as follows: Class I, the most deteriorated wood, contains over 400% water ([weight of water] / [oven-dry weight of wood] × 100) and virtually no core; Class II is 185–400% water, with a core present; and Class III is less than 185% water, with only the surface degraded. The analyses included moisture contents and the pin test to determine the extent of sound wood.

In degraded wood the biopolymers may be altered (*4*, *5*). There may be losses in bound water, losses or increases in side chains, and bonding and depolymerization. With other changes the chemical characteristics may be altered, crystallinity may be lost, solubilities and rates of oxidation and

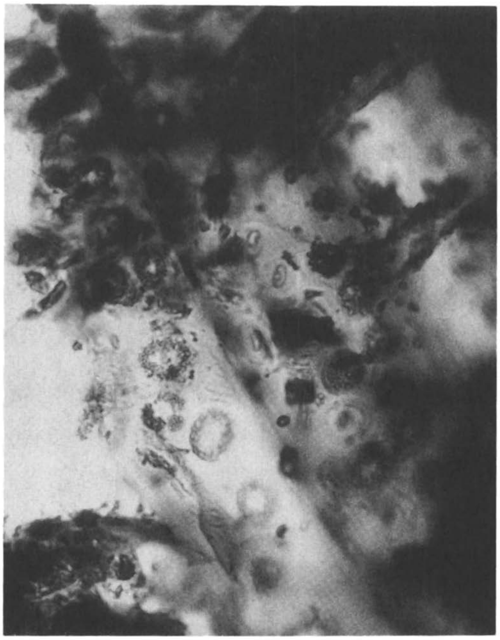

*Figure 1. Light microscopy photomicrograph of radial section of white oak (*Quercus alba* group) from unidentified marine wreck from New Brunswick, Canada. Iron salts have precipitated inside pits (5-μm diameter) on the radial walls of small vessels and in ray parenchyma cells.*

hydrolysis may change. These alterations will be expressed as loss of strength, permeability, hygroscopicity, and other physical changes.

To summarize, the analytical information of archaeological or ancient wood shows variability in chemical changes and losses that may result from the burial environment, the wood species, sapwood or heartwood, outer or inner wood, anomalies in growth, and certainly the methods of analysis. The stability of wood biopolymers has been found to be (in decreasing order): lignin, pectin, cellulose, and hemicellulose. As a rule, increase in moisture content indicates increase in degradation.

Future Directions. Hoffmann (2) wrote in 1982, "It is hoped that in the course of time enough analysis will be done to confirm relationships between analysis and response to specific treatments." In 1987, Grattan and Clarke (*7*) stated, "We are able to analyse wood chemically and give it a detailed biological description, but at present it is very difficult, except in the most general terms, to understand what this predicts for the treatment."

Other information may help to solve treatment problems in the future. One important chemical constituent has been overlooked: the protein, extensin, associated with the primary wall (*8*). Extensin is a structural protein similar to collagen. It may have a quinone tannage, which gives the strongest known cross-links to protein and makes it insoluble. Extensin is located (1–5%) in the most persistent part of the cell wall, the middle lamella–primary wall complex. Its presence there must have something to do with the persistence of this complex.

Pectin analysis also needs more refining and emphasis. Pectic substances are a group of related substances (protopectin, pectin, and pectic acids), each with specific chemical characteristics (*9*). Both the protopectin and the pectic acid, pectinic acid, form insoluble complexes with metals, especially calcium. These too, like the protein, are concentrated in the persistent middle lamella–primary wall complex.

The most significant information in the gross analytical studies is the fact that lignin, even though altered, is the chemical constituent present in highest amounts in the most degraded woods.

Lignin makes up to 15–35% of fresh wood, with 60–80% of the lignin located in the secondary wall. The middle lamella–primary wall complex has the higher concentration (0.6–0.9 g/g), as compared to the secondary wall (0.2–0.3 g/g). In the cell wall, lignin, hemicellulose, and pectin fill the interstices between the cellulose microfibrils. Lignin may be bound to hemicelluloses, the most unstable of the biopolymers in wood, and thus hemicellulose loss would expose the lignin to chemical changes.

The popular polyethylene glycol (PEG) treatment forms hydrogen bonds mainly with the carbohydrate polymers. In archaeological wood (*10*), the carbohydrate polymers, cellulose and hemicellulose, may no longer be present or, if present, only in reduced amounts. Future treatments should be designed for lignin, the major biopolymer that remains.

The colloidal nature of biopolymers has been overlooked. In waterlogged wood, lignin must be in the form of a colloidal hydrated gel, which on drying must cause some dimensional changes. We should be looking into colloidal chemistry for answers to dimensional stability of this colloid (9).

Micromorphological Changes. Chemical analyses are gross analyses. Wood is a tissue, a complex of cells. Its integrity is dependent on tissue and cell integrity and thus cannot be understood by gross analyses alone.

The story of histological analyses involves techniques, light microscopy, fluorescent microscopy, polarizing microscopy, scanning and electron microscopy, and selective staining and removal of the wood biopolymers. Histological analyses of degraded wood show the results of the chemical losses and changes reflected on the cellular and tissue level (*2*, *4*, *11*, *12*). On the cellular level, changes in thickness of specific layers of the cell walls, fungal lytic troughs, bacteria pitting, and inorganic precipitates are observed. On the tissue level, selective losses such as parenchyma cells of the longitudinal and radial wood rays, separation of growth rings, and tracheids are observed.

Cell types may show variable resistance to degradation. For example, a piece of oak from a Late Middle Ages marine wreck in the Netherlands was completely waterlogged. Histological examination using polarized light shows that very little crystalline cellulose is present (Figure 2). The remaining crystalline cellulose is associated with the middle lamella–primary cell wall complex and the tyloses of the large vessels (*13*). The tyloses of the vessels are intact (Figures 3 and 4), show no changes, and even have air that was trapped there during the wood's growth hundreds of years ago. Adjacent to these cells are fiber cells with only amorphous chemicals. These fiber cells are hydrated and swollen to the extent that there is no longer a cell lumen. On drying, the vessels do not collapse or shrink, like those of the adjacent fibers. Other examples of cell type variation can be seen in Figures 5 and 6.

Variations may also occur within one cell. An example is the electrolytic action of iron oxide on surfaces of cell walls, which causes autooxidation of the cellulose beneath it (Figures 7A and 7B).

Fluorescence microscopy shows the location of lignin in the cell walls (*14*). This technique was developed as a method for determining PEG penetration. The presence of PEG inhibits the fluorescence of the lignin when the tissue is reacted with cobalt thiocyanate (*15*).

Scanning electron microscopy (SEM) before and after histochemical extraction of lignin with peracetic acid has shown the location of cellulose and lignin and the persistence of the middle lamella–primary wall complex in archaeological wood buried for 2500 years (*11*).

In the past, information about the micromorphological changes and lo-

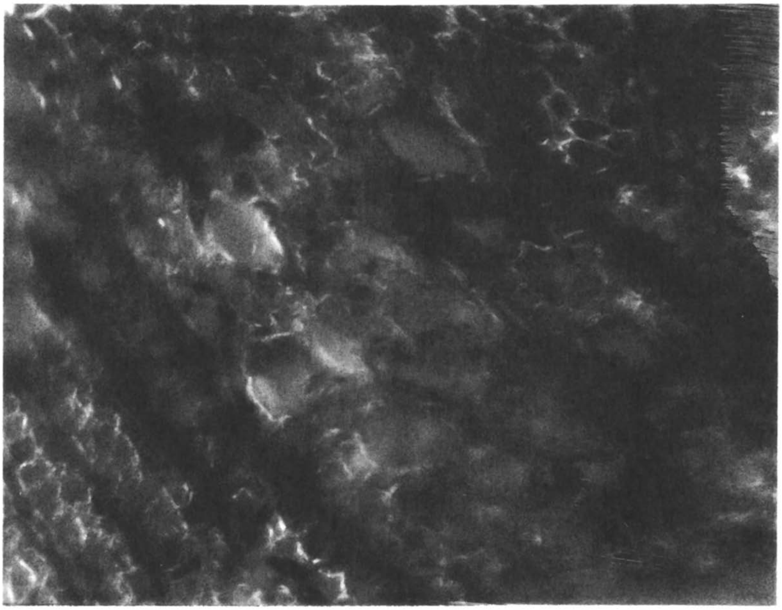

Figure 2. Polarized light micrograph of transverse section of white oak from Krabbendijke, *a marine wreck from the late Middle Ages in the Netherlands. Persistent birefringent crystalline cellulose is restricted to the primary wall–middle lamella complex of fibers and small vessels.*

cation of remnant polymers has been mainly descriptive and used for documentation. This information has value in determining responses to drying and permeability.

Responses to Drying. Waterlogged wood, if allowed to dry without treatment, may go through dramatic dimensional changes and distortions. The information on the chemical losses and micromorphological changes can explain this dramatic response to drying and changes of physical strength.

Barbour and Leney (*16*) demonstrated that dimensional changes result from two distinct actions, shrinkage and collapse. Shrinkage occurs in the cell wall, and collapse means the folding over of the cell walls against each other (Figures 8–10). Collapse occurs as a result of capillary drying tension above the fiber saturation point. Cell wall shrinkage occurs below the fiber saturation point because of desorption and resultant dimensional change.

Florian (*13*) has shown that the drying and subsequent shrinkage of the amorphous chemicals that often fill and bulk the lumen (Figure 11) of very degraded waterlogged wood cells also may contribute to cell wall collapse.

Shrinkage in badly degraded wood is isotropic and may result in radial,

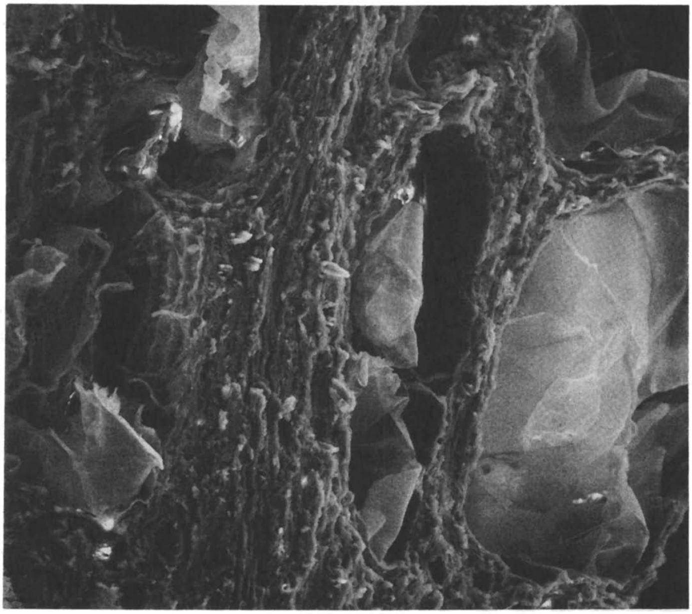

Figure 3. Scanning electron micrograph of transverse section of air-dried waterlogged white oak from the marine wreck Krabbendijke, *late Middle Ages, Netherlands. The fibers and small vessels have collapsed, but the large vessels show minimal collapse and intact tyloses.*

tangential, and longitudinal cracks that cause cuboidal cracks and exfoliation. Collapse is expressed by longitudinal cracks oriented radially or tangentially, and by depressions and distortions.

The most devastating aspect of drying is that the forces of drying vary within one piece of wood. The more degraded surface undergoes more dramatic changes than the core. This variation sets up new drying stresses from the differential strengths. Sometimes the reverse occurs. For example, oil-penetrated archaeological wood from a Thule site shows less dimensional change on the surface than on the inside. This condition reflects the greater amount of water in the core than on the surface, where the water has been replaced by the oil (Figures 12–14).

Changes in Physical Strength. Strength characteristics will obviously be altered to variable degrees because of losses and changes of structural chemicals and loss of cell and tissue integrity.

In many situations, the strength of archaeological wooden objects is not a concern. There are exceptions. If the object is a weight-bearing component, strength must be considered. For example, the strength of the ribs of the *Wasa* was determined to ensure that they have enough residual strength to support the superstructure. Strength is also a problem with ancient wooden

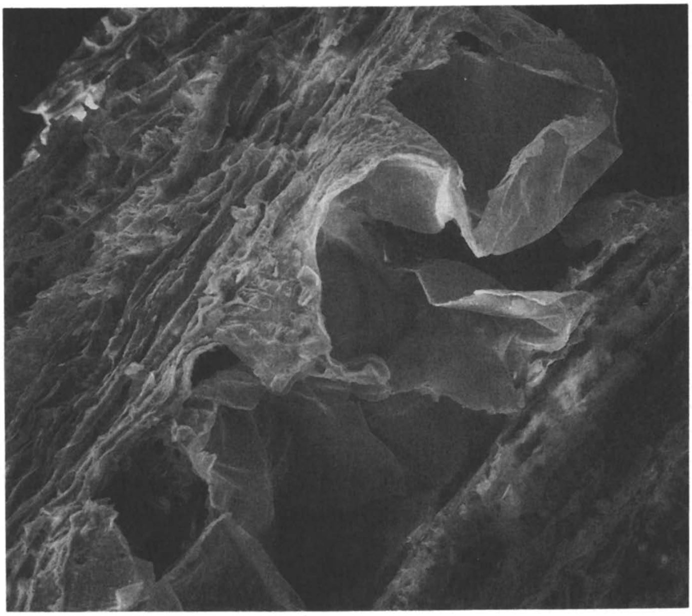

Figure 4. Scanning electron micrograph of longitudinal section of air-dried waterlogged white oak from the marine wreck Krabbendijke, *late Middle Ages, Netherlands. The fibers and small vessels have collapsed, but the large vessels show minimal collapse and intact tyloses.*

buildings. For example, 900-year-old timbers in the Chinese temples have lost 30–50% of their mechanical strength, probably as a result of loss of molecularly bound water. The wood has become deformed by stress, but its tissue integrity has not altered.

What are the strength changes in dried waterlogged archaeological wood? Physical mechanical strength characteristics can be altered to variable degrees by loss of structural chemicals or tissue integrity. For example, a 6000-year-old oak sample from the Somerset Levels, England, is completely waterlogged. The intrusive action of the water has dissolved most of the crystalline structural chemicals, and the wood is now a cellular network of amorphous chemicals (Figures 15A and 15B). On drying, this wood had little mechanical strength; it became distorted because of cell wall shrinkage, shrinkage of the amorphous materials, and collapse of cells as a result of loss of water bulking and adhesive forces in tissue. Distortion and cracking also occurred because of differential strengths of adjacent tissues and cells (such as thin-walled parenchyma cells adjacent to thick-walled fiber cells) (Figure 16).

Surfaces of wood may be exposed to weathering or to soft rot if they are in contact with the ground prior to burial. On excavation, these surfaces will

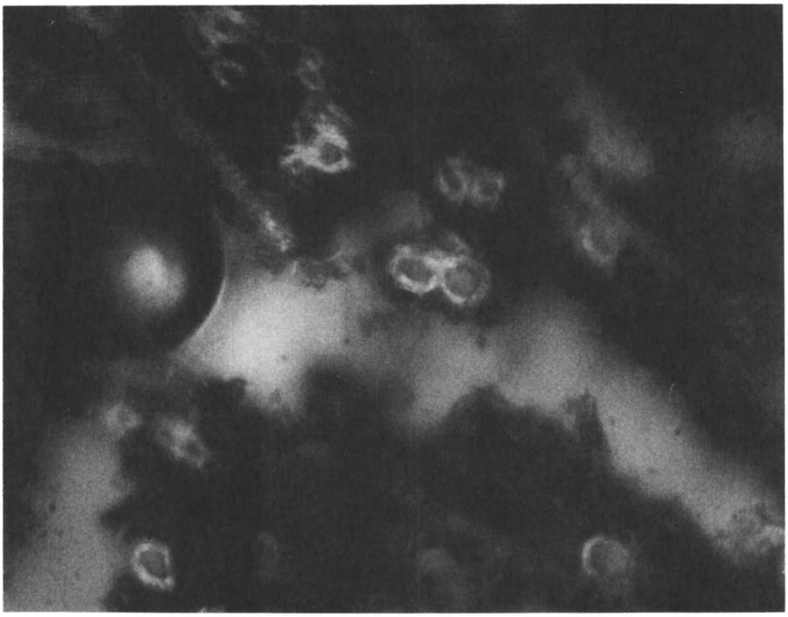

Figure 5. Polarized light microscopy photomicrograph of wet mount of waterlogged wood from a prehistoric habitation site, 100 B.C.–100 A.D., Japan. The hydrated wood shows differential degradation of cell types. Only a few isolated cells have retained birefringent cellulose.

have lost their tissue integrity and will exfoliate as shells of cells shrink and collapse on drying. This is the situation of spruce wood from a 1200–1400 A.D. wooden trackway excavated from a bog in Norway (Figures 17 and 18). This wood also shows loss of tissue integrity because of selective loss of pectic substances and lignin from the middle lamellar region (Figure 19).

Environmental Influences on Degradation

In the history of stabilization of archaeological wood, there have been few if any efforts to describe the burial environment and relate it to the condition of the wood. The first chapter on the marine environment in Pearson's textbook (*17*) on conservation of marine archaeological objects is an important step forward.

We are all aware of the influence of environmental factors. Prior to burial and during early stages of burial, some degradation may occur because of selective enzymatic hydrolysis by a specific anaerobic microorganism. Degradation may also result from ultraviolet adsorption of photochemically sensitive chemicals, such as lignin. Degradation after burial may be a result of ground water leaching and the acid–base and oxidizing–reducing charac-

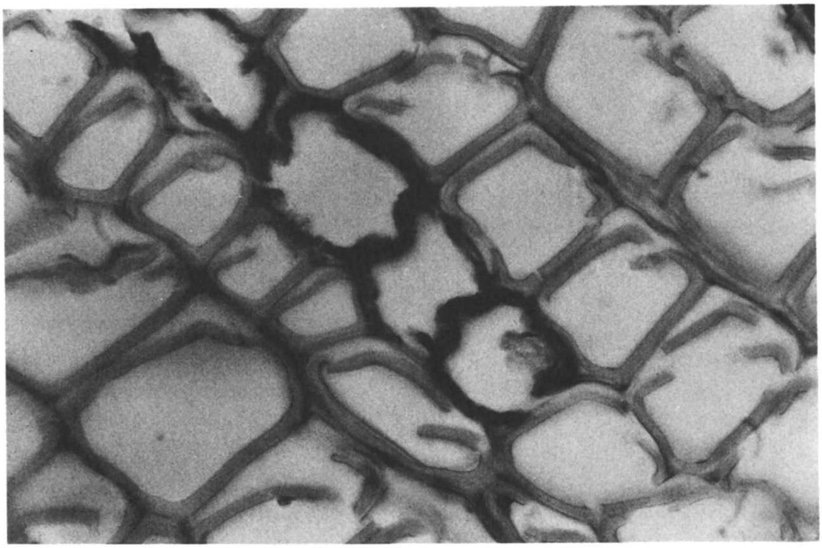

Figure 6. Light microscopy photomicrograph of Chamaecyparis nootkatensis *from the 2500-year-old wet terrestrial Lachane site, Prince Rupert, B.C., Canada. The histological transverse preparation shows the deterioration of the S_2 and S_3 cell wall layers of a few isolated tracheids. The fracturing of these cell wall layers in the normal tracheids is an artifact of the histological preparation.*

teristics of this water. Other factors include temperature, pressure, and various environmental parameters.

Inherent characteristics of the wood will influence its environmental interaction (e.g., the wood species; the presence of heartwood or sapwood; the plant part such as root, branch, or wood; and anomalies in growth) (*18*).

Certainly the environmental history of use and method of fabrication of an object will influence its environmental interaction. Weathered surfaces, the orientation of the tissue on the exposed surfaces, mechanical damage from pounding or stress, and changes caused by heating will influence the degradation patterns.

Changes in archaeological wood result from specific interactions between the wood and the burial or discard environment. Thus it is important that the parameters of the burial environment be recorded.

The Marine Environment

We may think in general of marine or terrestrial wet and dry sites, but microenvironments within these provide unique conditions. Microenvironments in a marine burial site may include anaerobic sediments, aerobic sediments, sediment–seawater interface, and others (*19*) (Figure 20). Dif-

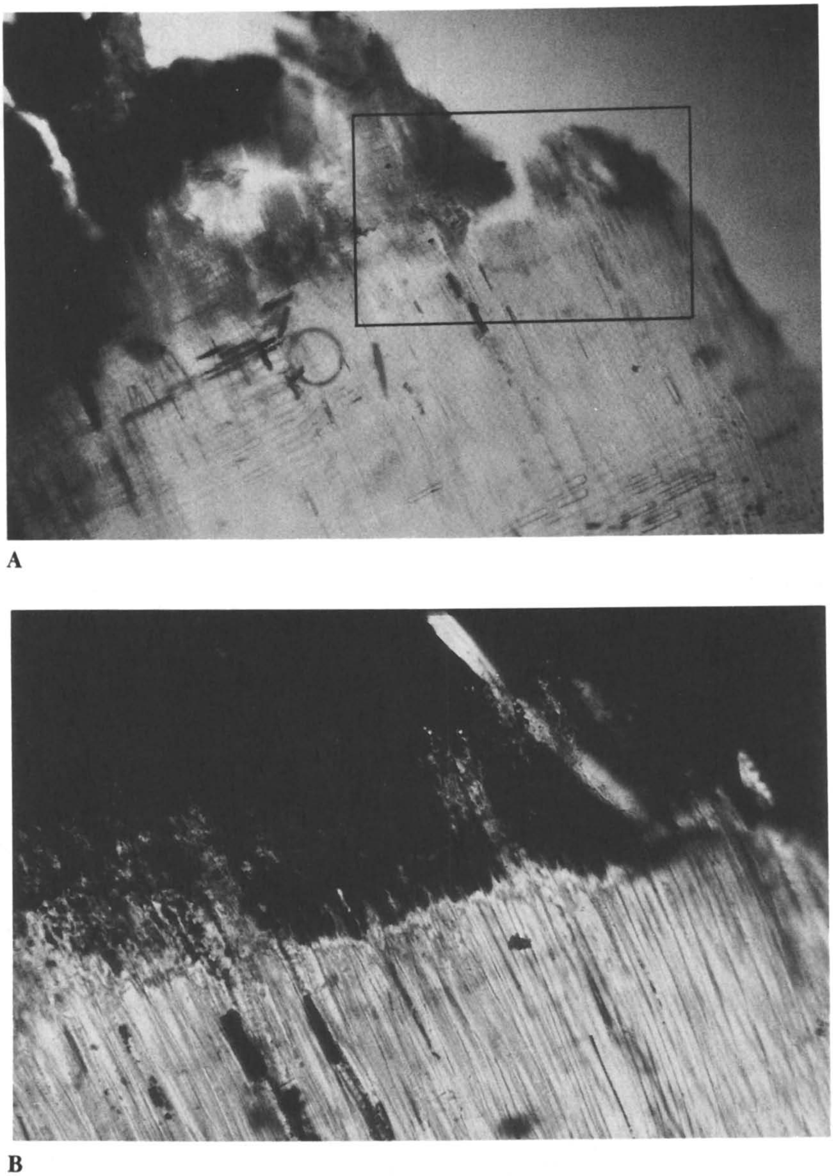

Figure 7. Light microscopy photomicrograph of iron-impregnated waterlogged southern hard maple wood, from the historic marine wreck, the Thos. J. Lipton, *Gambier Island, B. C., Canada. A. An opaque iron oxide precipitate can be seen on the the surface of the irregular upper edge of the wood fragment. B. Polarized light photomicrograph of the outlined area. Below the iron oxide, the cellulose of the fibers has been dissolved or hydrolyzed with acid formed in electrolytic activity. Normal birefringent cellulose is present on the other side of the front of hydrolysis.*

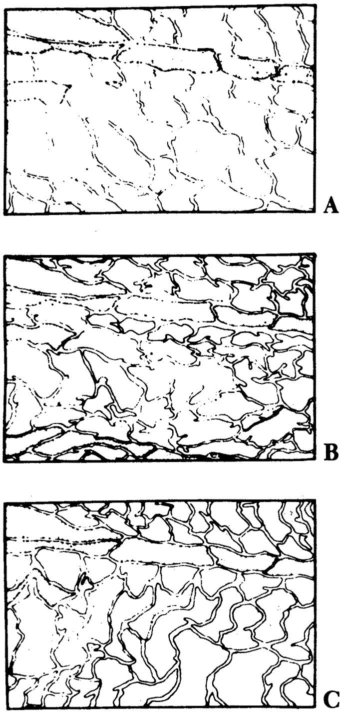

Figure 8. Artist's conception of collapse in a sample block. A. Fibers much as they appear after freeze-drying. B. How the same cells actually collapse tangentially. C. How the cells would appear if they collapsed radially rather than tangentially. (Reproduced with permission from ref. 16. Copyright 1981 International Council of Museums.)

ferent patterns of degradation will occur in each microenvironment. Fungal activity will occur at the sediment–seawater interface. Aerobic or anaerobic bacterial activity will occur in the sediment, depending on the oxidizing or reducing characteristics of the sediment (Figure 21). No microorganisms will be active more than 1 m deep in the sediment.

Depending on the salinity, temperature, and depth of the seawater, certain teredo species will riddle the wood. Such patterns of degradation can also indicate past environmental history. For example, a ship originating from warm waters may have specific teredo species that are not endemic to the cold waters in which it was wrecked. Such anomalies can indicate trade routes.

Smaller environments can exist even within one of these microenvironments. For example, within one piece of wood associated with metal, there can be regions of an electric field that would cause hydrolytic or alkaline degradation of cellulose or lignin.

Seawater is basically uniform around the world. The major variations that do occur are in regions located close to land and are often influenced by terrestrial water runoff. Most of the underwater archaeological sites are located in these regions. This situation may change with the advent of deep-diving technology.

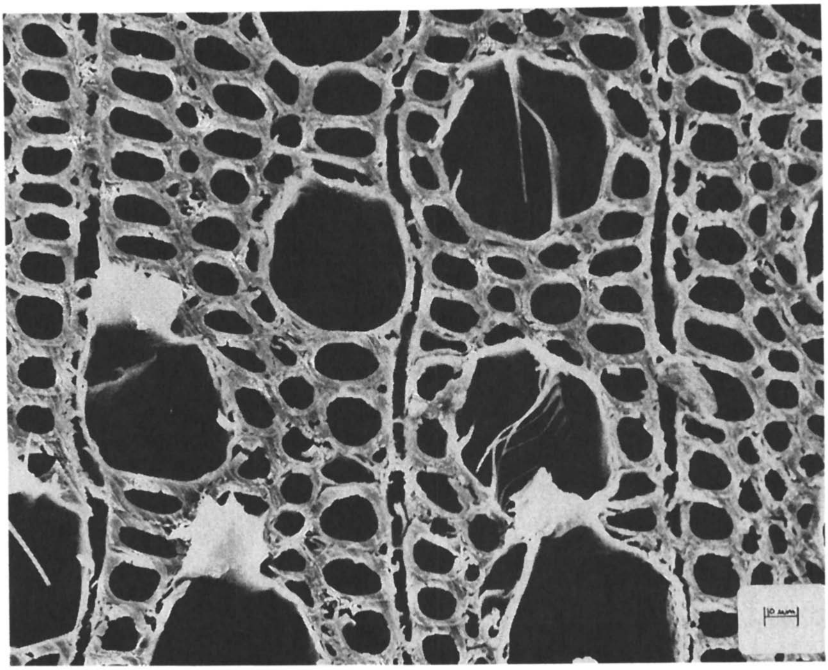

Figure 9. Scanning electron micrograph of transverse surface of air-dried normal undegraded alder wood, for comparison with Figure 10. (Reproduced with permission from ref. 16. Copyright 1981 International Council of Museums.)

Seawater is a strong buffering solution of salts. The salts present must influence the chemical changes of the colloidal biopolymers that occur in marine archaeological wood.

Terrestrial burial environments also are variable and may have microenvironments. Preserved wood is commonly found in acid peat bogs, but rarely found in shell middens. Is this because of different degradation rates or different use patterns of past human environments? We have to be cautious in our interpretations.

If a tally was taken as to what burial site characteristics give the best preservation, the obvious characteristics would be rapid burial at a depth that would eliminate light, oxygen, and anaerobic bacteria. The rapid burial would be in sediment. In a sense, this would package the wood and prevent physical or mechanical damage, as well as slowing the rate of water movement.

Archaeological wood degradation patterns are specific for specific burial sites. Wood in the marine reducing environment, a few centimeters deep in the sediment, will show typical bacterial damage and iron salt precipitation. The region of ground contact of terrestrial wood will have the surface

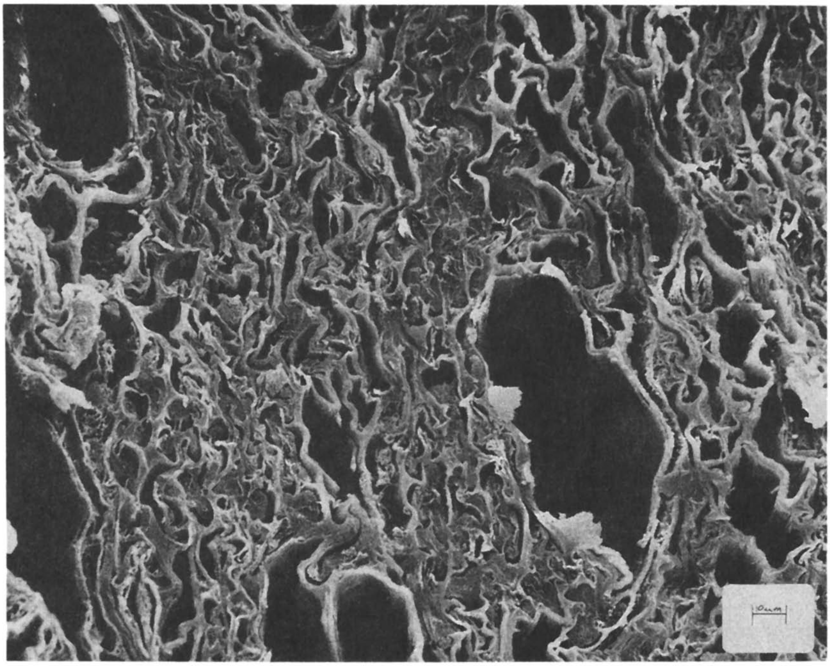

Figure 10. Scanning electron micrograph of transverse surface of degraded alder wood approximately 2500 years old from terrestrial Hoko River wet site, Olympic Peninsula, Washington. The wood shows both collapse and shrinkage. Compare with Figure 9. (Reproduced with permission from ref. 16. Copyright 1981 International Council of Museums.)

degraded by soft rot. Weathered wood will have the characteristic surface layer of cellulose cell shells associated with a fungus, and ponded wood (logs floating in fresh water) shows losses of pectic substances and enlarged pits. Thus micromorphological changes can be used to interpret the environmental history of archaeological wood.

Treatments for Archaeological Wood

Ethics. Conservators are professional people, often with graduate degrees from university programs in conservation, and are thus knowledgeable about the material, treatments, and storage. All their decisions are tempered by their professional ethics. Conservation treatments must not destroy the integrity of the object, its aesthetics, and its research potential. In addition, the treatments should be reversible. These seem to be impossible constraints, but Grattan and Clarke (7) point out that most small objects can be treated while still adhering to a truly ethical approach.

The decision for conservation treatment may be based on the need to

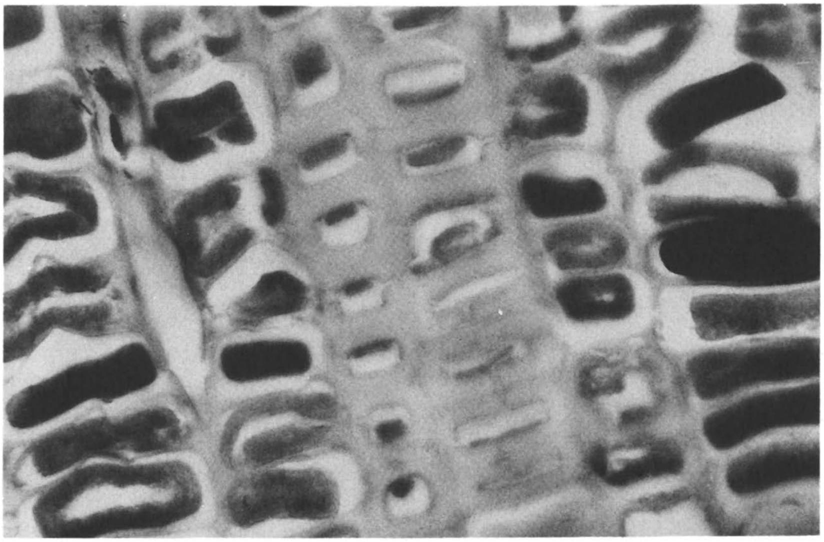

Figure 11. Light microscope photomicrograph of Thuja plicata *from 2500-year-old wood from the wet terrestrial Lachane site, Prince Rupert, B.C., Canada. The histological transverse preparation shows the sequence of deterioration of the* S_2 *and* S_3 *cell wall layers of tracheids. In the first stages the presence of enlarged pits associated with dark amorphous material suggests bacterial activity. The amorphous remnants of the cell walls cause shrinkage on drying.*

prevent dimensional change, to preserve research information, to stabilize for longevity, and even in preparation for exhibits where aesthetics are uppermost. These decisions are usually made by the curator of the object, but preferably with the consensus of the conservator.

Waterlogged Wood. Conservation treatments for waterlogged wood have been designed mainly to prevent the dramatic dimensional changes caused by cell collapse and cell wall shrinkage during drying. Waterlogged wood varies so much because of degree of degradation and permeability, growth anomalies, species differences, and history of use that it is impossible to have one general treatment. It seems that each piece of wood has its own requirements.

Over the years since the first recorded treatment of archaeological wood with alum by C. F. Herbst, in the middle of the 19th century, a number of types of treatments have been used: impregnation and bulking, polar solvent drying, slow air-drying, freeze-drying, and in situ polymerization.

Impregnation and bulking involves replacing the waterlogging water and filling the cell wall and lumen and all cavities in the wood with an inert chemical to prevent drying stresses. The chemicals used have been the water-soluble alum, PEG, and sugars. Polar solvents have been soluble rosin, sodium silicate, tetraethoxy silicate (TEOS), wax, and resins.

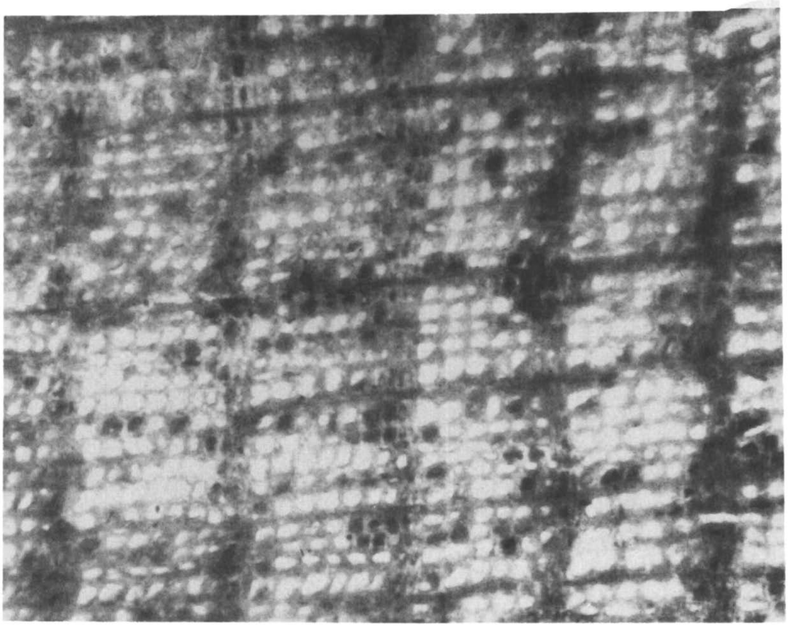

Figure 12. Light microscopy photomicrograph of transverse section of Picea *sp. from a 1200 A.D. Thule site, Herschel Island. The preparation was stained with an oil stain, Sudan III. The stained oil is seen as dark deposits, mainly in the latewood tracheids.*

Polar solvent drying by using acetone and alcohols involves the slow replacement of the waterlogging water with increasing concentration of the solvents. The low surface tension of the solvents lowers the capillary tension forces that cause collapse during the evaporation of the waterlogging water from the wood.

Slow drying by simple air-drying or drying in situ under constraint prevents some shrinkage and drying stresses. Freeze-drying involves the freezing of the waterlogging water. The water is then sublimed, and sublimation eliminates the contractive forces of evaporating water.

In situ polymerization involves the use of monomers that are used as impregnants. When the monomers are inside the wood, they are polymerized by the use of hardeners, γ radiation, or other free radicals.

Development of PEG Treatments. The history of preservation or conservation treatments is a story of success and failures that has been related in detail by Grattan and Clarke (7). This history of conservation treatments is told in the context of the dedicated people who strived to stabilize this unpredictable material. A few of their names are mentioned in the following paragraphs on treatments.

By far the most common treatments have used PEG. The development

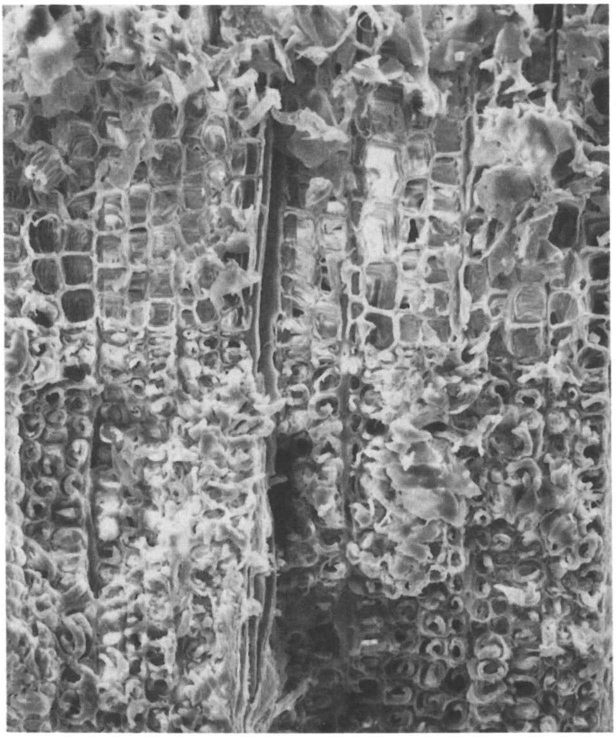

Figure 13. Scanning electron micrograph of transverse section of air-dried Picea *sp. from a 1200 A.D. Thule site, Herschel Island. The fractured surface shows oil-swollen secondary cell walls of latewood tracheids separated from the primary wall complex. This is shown in detail in Figure 14. The earlywood tracheids appear normal.*

of PEG treatment is a saga of molecular weights, percents, temperatures, relative humidities, and ships (*7*).

In the late 1960s and early 1970s, Brorson-Christensen, the National Museum of Denmark with the Skuldelev Viking ships, and Barkman with the Swedish warship *Wasa* developed PEG treatments for the waterlogged wood of these ships. The treatments were sprayed or painted on the wood, or the wood was immersed in a solution of PEG 3350 (molecular weight). Christensen categorized the wood in classes, according to degradation, and a specific regime was designed for each class. Class III, the most degraded, was treated according to the Moren and Centerwall standard aqueous PEG 3350 tank method treatment (*20*). In some treatments, Christensen deviated from the use of aqueous solutions to use the polar solvents 2-methyl-2-propanol and butanol, and also developed the technique of freeze-drying after treatment. Butanol was used instead of water to facilitate the transport of PEG into the wood. In the late 1970s De Jong, in the Netherlands,

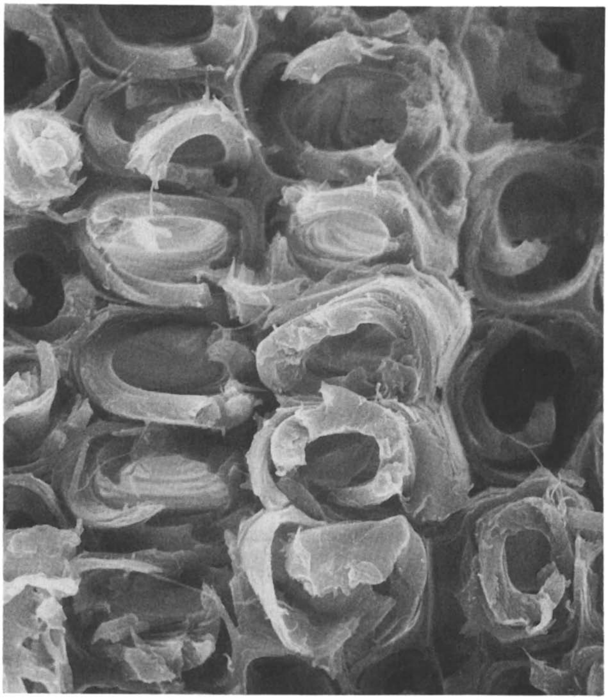

Figure 14. Same as Figure 13, but enlarged.

developed PEG treatments with low molecular weights (1000–1450) and used Christensen's polar solvent, 2-methyl-2-propanol. However, he used slow drying, not freeze-drying, after the treatment (*21*).

The next major ship was the *Cog*, a large medieval merchant ship, 24 m long, 30 tons of wood. It was immersed in a tank of PEG 200 and will be treated later with PEG 3000 or 4000. Conservator D. Noach calculated that it would take 25 years for penetration (*7*).

The long time required for penetration makes the treatment expensive. In the past, enzyme and chemical pretreatments have been used in an attempt to decrease this time, but without success. Lower molecular weights of PEG were also tried.

Grattan of the Canadian Conservation Institute has done work on comparisons of many variations in pretreatment and treatments and has contributed to a better understanding of penetration and freeze-drying pretreatments (*7*).

Low-molecular-weight PEGs, such as PEG 400, are being used in conjunction with freeze-drying. Ambrose showed that the PEG 400 alters the freezing behavior of water and thus reduces the damaging volumetric expansion (*22*). Other impregnants are also being suggested because of the hygroscopic characteristics of PEG 400.

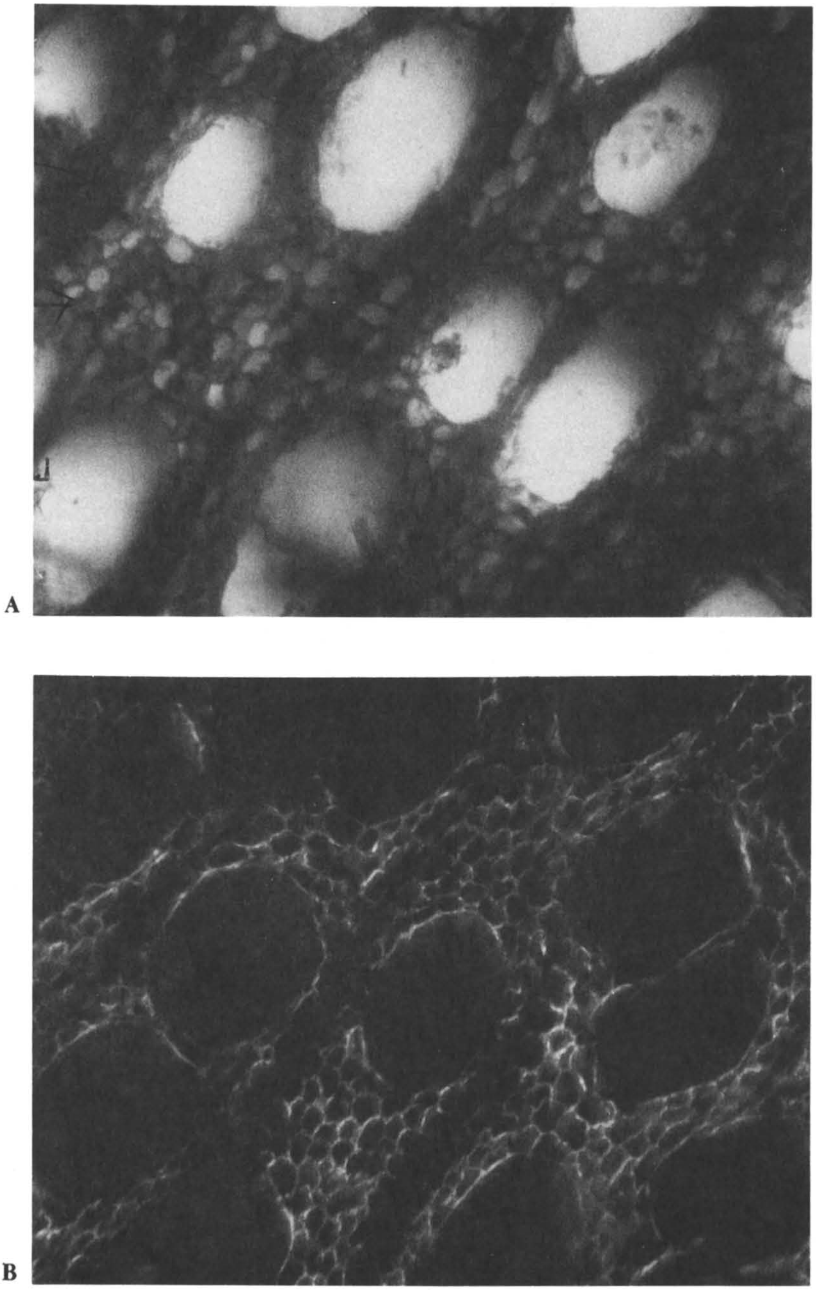

Figure 15. Wet preparation of waterlogged Salix *sp. wood from Somerset Levels, 6000-year-old Sweet Track site, England. A. Light microscopy photomicrograph. The hydrated wood cells contain amorphous cell wall remnants that can be seen by comparison with Figure 15B. B. Polarized light microscopy photomicrograph. The birefringent primary wall–middle lamella complex can be seen in the hydrated wood cells.*

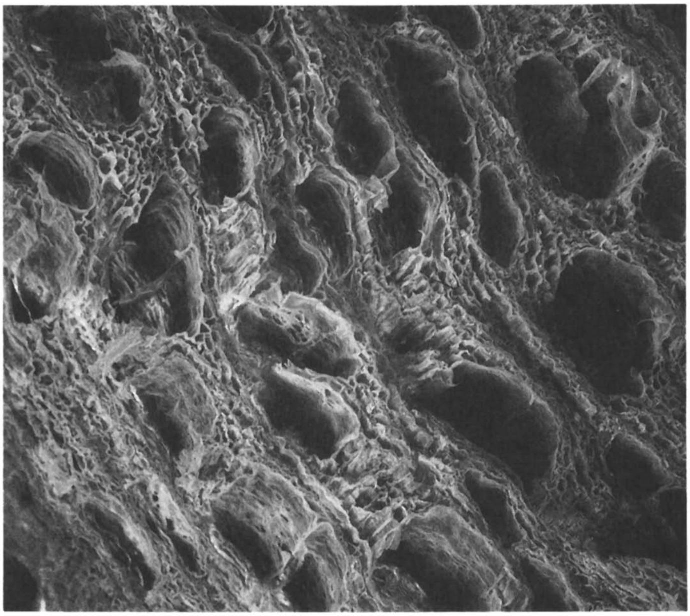

Figure 16. Scanning electron micrograph of air-dried waterlogged Salix *sp. wood from Somerset Levels, 6000-year-old Sweet Track site, England. Collapse and shrinkage have occurred on drying.*

PEG treatments have shown erratic results, lack of or slow penetration, and hygroscopicity. Thus, recent trends have been away from use of PEG treatments.

Sugars are now being tested for conservation of waterlogged wood because of their antishrink properties in wood and their ability to lower the vapor pressure of the waterlogging water. Sucrose-treated wood has the appearance, weight, and much of the strength of nondegraded wood. Sugar methods require more research because of reported erratic responses (7).

International Comparative Waterlogged Wood Project. Grattan and Clarke (7) expressed concern that conservators were working in isolation and that the lack of a standardized approach to research, analyses, and methods of evaluation made it impossible to extrapolate from the published information to other pieces of archaeological wood. Because of this concern, Grattan and Schweingruber initiated the International Comparative Waterlogged Wood Project in 1983. In this project conservators from all over the world analyzed or treated the same eight waterlogged archaeological wood samples in their own laboratories. The results of the project were presented by the participants at a meeting in Fremantle, West Australia, in September 1987. A review of the project has been published (23) and the proceedings from the Fremantle Conference are forthcoming. A videotape and the sam-

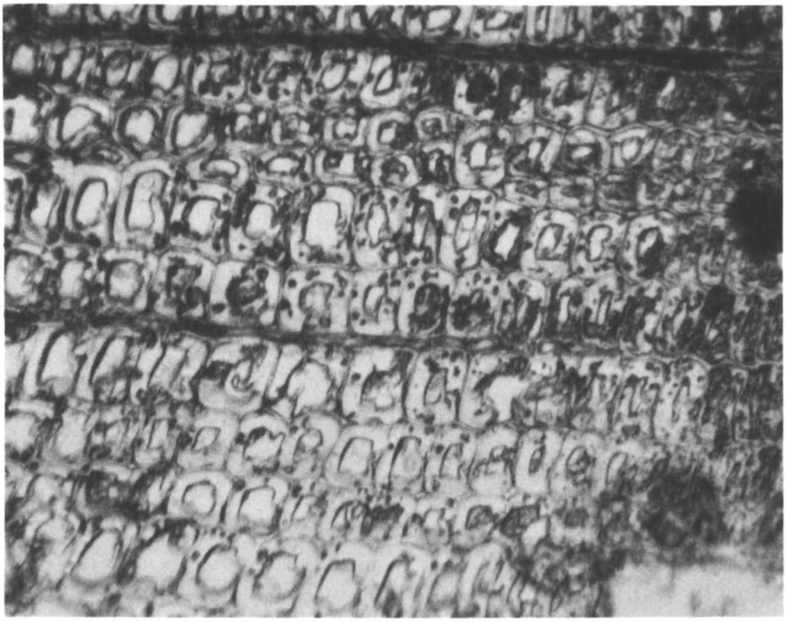

Figure 17. Light microscopy photomicrograph of transverse section, wet preparation of 1200–1400-year-old waterlogged Picea *sp. wood from wooden trackway excavated from a bog site in Central Norway. Soft-rot bore holes are present in the* S_2 *layer of tracheid walls.*

ples will be kept at the University of Trondheim under the care of Roar Saeterhang. It was a significant example of cooperative effort to try to solve the problems of lack of communication between conservators dealing with waterlogged wood.

Dry Wood. Archaeological dry wood does not have the problems of waterlogged wood. Thus, the intensity of research in terms of analyses and treatments has not been comparable. Strength characteristics are considered if the wood is a weight-bearing member. The solution to loss of strength for such components is replacement or reinforcement with epoxy or similar materials.

Some dry archaeological wood may be riddled by insect activity and require consolidation. Hillman and Florian (*24*) have described a sandwich type of deterioration of boards of a bentwood box. The boards are virtually a sandwich of paper-thin outer surfaces between which the wood is completely riddled with lyctid beetle galleries and tunnels filled with frass. This porous material is easily consolidated.

The weathered surface of archaeological wood, still in the natural outdoor environment, is often considered as a candidate for treatment. Before treat-

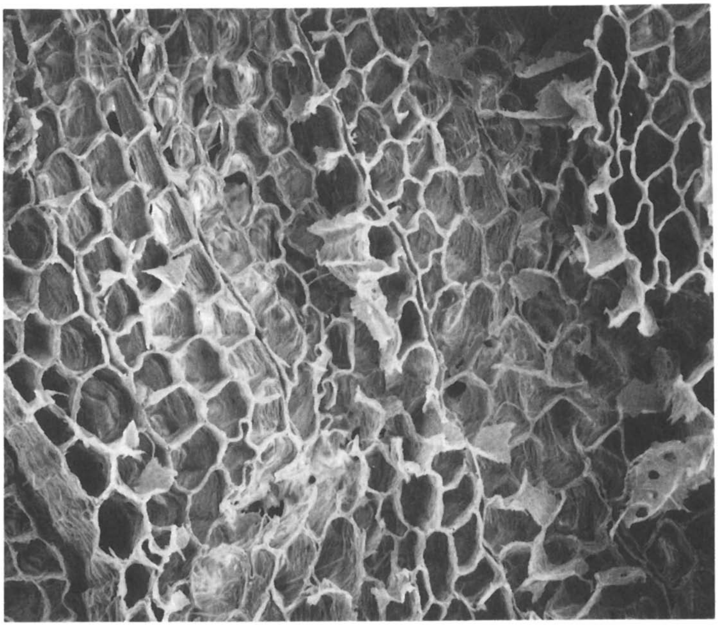

Figure 18. Scanning electron micrograph of transverse surface of air-dried 1200–1400-year-old waterlogged Picea *sp. wood from wooden trackway excavated from a bog site in Central Norway. The insides of the tracheid walls appear fibrillar because of losses by soft-rot lytic troughs. The porous nature of the cells has prevented major collapse, but isodiametric shrinkage has occurred.*

ment, an understanding of this surface is imperative. The weathered surface is a result of a sequence of events leaves less than a millimeter of almost pure cellulose cell shells. These ultraviolet-light-resistant shells protect the sensitive lignin beneath. This delicate surface is consolidated by a ubiquitous fungus, *Aureobasidium pullulans* (*25*). This fungus utilizes mainly hemicelluloses and produces a gel that could help to hold the cells together (*26*).

The rates of weathering of this surface have been recorded for some wood species. Often these rates are for milled wood, not logs in the round. The rates are low—a few millimeters in a hundred years.

Surface treatments have been formulated for kiln-dried or freshly milled wood in service. The success of these treatments is in their ability to make a continuous waterproof region that is almost impossible with a weathered surface. Also, these surface treatments need continuous refinishing maintenance, which causes surface losses. Many treatments incorporate a fungicide that will interfere with the consolidating fungus, and the delicate surface will exfoliate more rapidly.

Maybe in the future there will be successful nonintrusive treatments

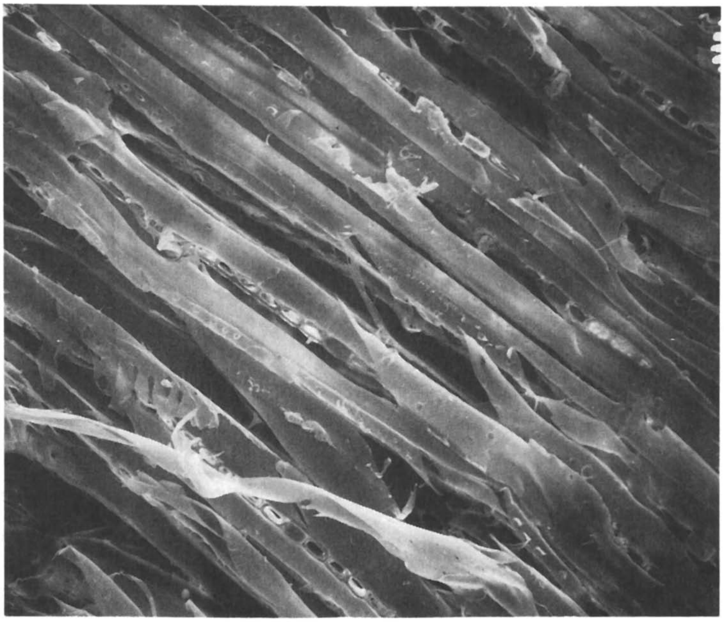

Figure 19. Scanning electron micrograph of tangential surface of air-dried 1200–1400-year-old waterlogged Picea *sp. wood from wooden trackway excavated from a bog site in Central Norway. Shrinkage has caused separation of the tracheids.*

for weathered wood in a natural outdoor environment. However, the most appropriate treatment now is to protect the wood in the natural environment from excessive wind and rain, but not from sunlight. This can be done by altering the natural environment around it or by building wind and rain shields (27).

Storage of Archaeological Wood

I have not been able to find any references in the literature that report whether archaeological wood after excavation and treatment can support biodeteriorating organisms, insects, or microorganisms.

In sediments or soil, a hierarchical sequence of succession of organisms is involved in breakdown of organic materials. Once the altered archaeological wood is removed from the sequence of successions, dried and treated, and placed into a new environment (such as a museum), museum pests such as wood beetles may not infest this wood.

The literature reports uses of biocides in conservation treatments, often during storage. We are now aware of the health hazards of biocides. Should we be using these without a demonstrated need for them? The smell of the storage tank water is no reason to expose oneself to carcinogens, mutagens,

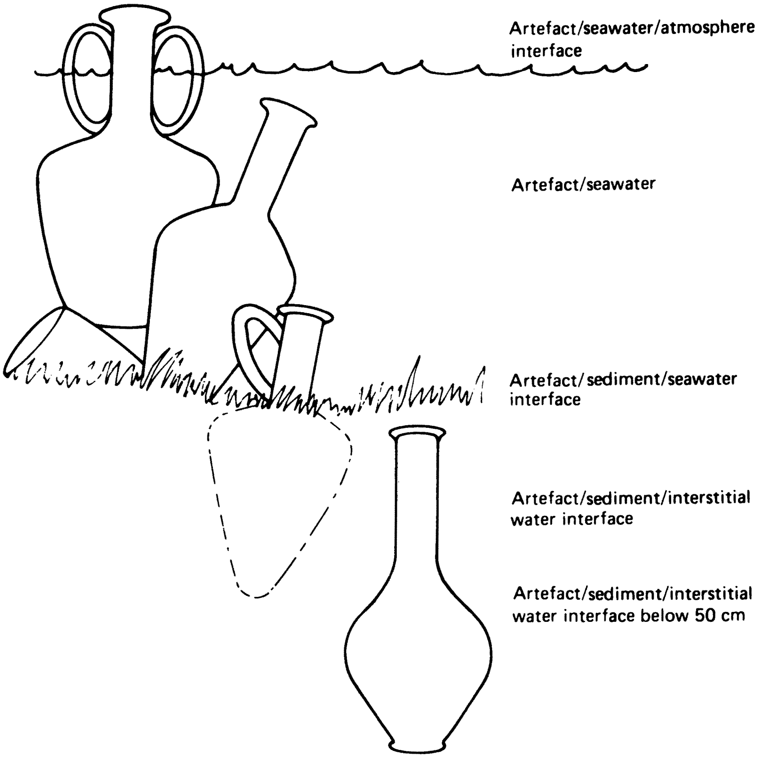

Figure 20. Microenvironments in a marine burial site. Each interface (i.e., artifact–seawater–atmosphere interface, artifact–sediment–seawater interface, etc.) has specific environmental parameters that dictate a specific type of deterioration. (Reproduced with permission from ref. 9. Copyright 1987 Butterworths.)

or toxic chemicals and the wood to interventive chemicals that may increase its deterioration.

Some excavated wood has been reburied after thorough research of the object and also of the reburial site. Jespersen (28) stated that "there was no room for extended storage of 34 tons of wood" in her museum. Her solution was "long-term storage in nature": reburial. A detailed geological and microbiological analysis of potential sites was undertaken to locate a suitable environment. A future analysis of this long-term storage will be most interesting.

Alternatives to Excavation

In the past, some precious objects have been destroyed by disastrous treatments that were the state of the art at the time and done with best intentions. Today conservators proceed with caution and carefully test all treatments.

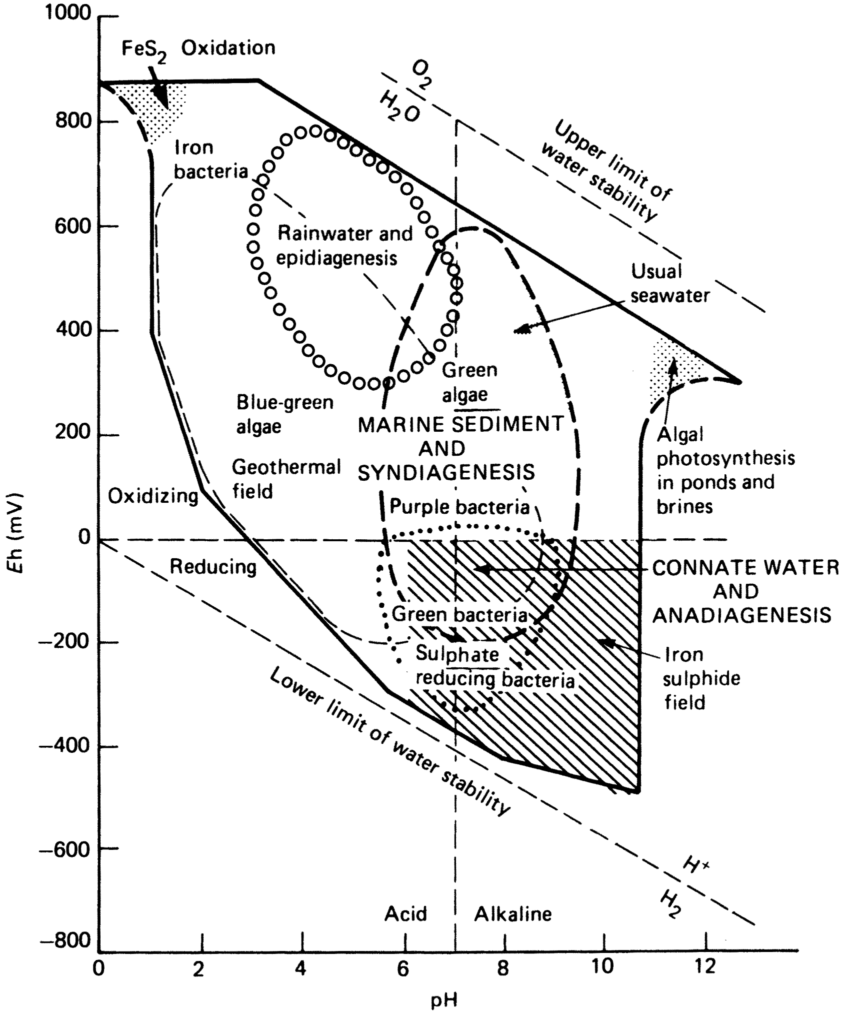

Figure 21. The specific microenvironments defined by specific Eh *(oxidizing or reducing ability) and pH support specific microorganisms and oxidizing or reducing chemical activity. (Reproduced with permission from ref. 9. Copyright 1987 Butterworths.)*

Often the treatments are expensive and require extensive physical facilities that are difficult to acquire. Although conservators are impatient and have an insatiable curiosity, waiting is sometimes best. They are preventing excavation of vulnerable materials that cannot be stabilized at this time.

In September 1988, Ireland announced a moratorium on excavation of the Spanish galleons that lie off her coast. Such sites as these, the *Titanic*, and others are being recorded with sophisticated magnetic resonance and other methods of imagery.

The Future

With regard to archaeological wood, its variations, its need for stabilization, and the treatments available, there are still many unanswered questions and needs for better treatments.

Chronological age means little in terms of preservation. The magic of the age is in reference with past societies. It is exciting to see a climbing pole with wear marks made 300,000 years ago.

Changing attitudes toward the object or finds have already been discussed. Larger and larger objects that require special conservation treatment are being excavated.

Conservation ethics have changed. A present concern is the use of the object for research. Most analytical methods are destructive. Any intrusive treatment, even as simple as using an algicide in storage water for waterlogged wood, can alter the research potential of the object (for example, distort the ^{14}C date). And what about yet-to-be-devised analyses? Many treatments alter the aesthetics of the object, and many treatments are not reversible. Conservators with their code of ethics may seem to have put unusually unrealistic constraints on methods of stabilizing archaeological wood, but this is not necessarily the case.

The future for archaeological wood is bright. People are aware of its value and significance as material culture of the human past. Conservators are aware of the variable nature of the material of the object.

Conservators and wood scientists together will be doing meaningful analyses to provide usable information for determining logical stabilization and preservation.

The contributions in the following chapters hold the key to the future of archaeological wood.

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2

Structure and Degradation Process for Waterlogged Archaeological Wood

Per Hoffmann[1] and Mark A. Jones[2]

[1]**Deutsches Schiffahrtsmuseum (German Maritime Museum),**
D–2850 Bremerhaven, Federal Republic of Germany
[2]**The Mary Rose Trust, HM Naval Base, Portsmouth PO1 3LX, United Kingdom**

Cross sections of waterlogged archaeological woods generally show two or more distinct zones of progressive degradation. Light and electron microscopy, supported by chemical analysis of the respective tissues, demonstrate an abiotic chemical degradation process advancing from the wood surface inward. Following an excessive swelling, the secondary cell wall starts to loosen because of hydrolysis of carbohydrates. The cell walls lose their fluorescence and birefringence. Finally the residual lignin skeleton collapses, and only a granular debris is left. Tertiary walls, and especially the system of compound middle lamellae, are quite resistant and keep up the original dimensions of the tissue as long as this is completely filled with water.

WATERLOGGED ARCHAEOLOGICAL WOOD refers to wood that has been excavated by archaeologists—regardless of size, species, age, or state of preservation—and is more or less completely filled with water. It is understood implicitly that the wood has been waterlogged for a considerable time, from decades to millions of years. Even very old wooden artifacts are often marvelously well preserved when excavated from below the water table, but they are very unstable once exposed to the ambient climate. They shrink, warp, and crumble in a frightening way, destroying the joy that only hours or days before lit the faces of the excavators.

Obviously, this kind of archaeological wood must have a structure different from that of fresh wood. The conservator who has to find a way to

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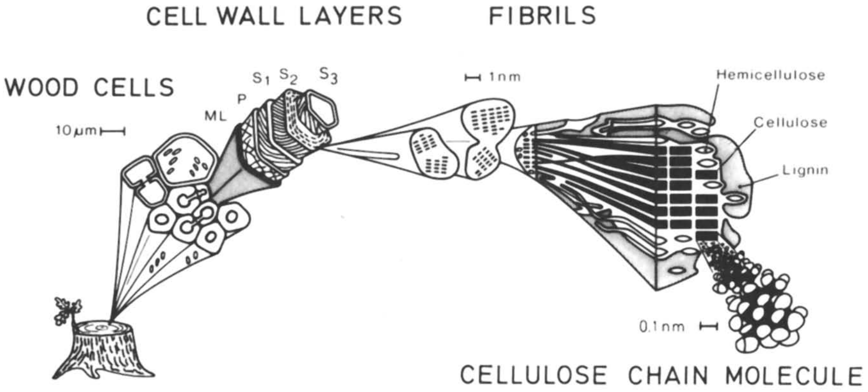
The Structure of Wood Cell Walls

Very long cellulose chain molecules built of up to 15,000 glucose units combine to form strands with a largely crystalline structure. Surrounded by shorter carbohydrate chain molecules (hemicelluloses) and lignin (an amorphous high-molecular-weight polymer of aromatic compounds), cellulose strands form fibrils. In the growing cell, fibrils are laid down onto the middle lamella, which separates the newly formed cells, in discernible layers (p, primary wall; S_1, S_2, S_3, *outer, inner, and terminal secondary walls, respectively). This principle is the same for all cells, but the thickness of the individual cell wall layers may differ among cell species. Within and between fibrils, the void spaces and capillaries in the cell walls can be filled with water or air. During heartwood formation, they can partly be filled with secondary extractives.*



stabilize such wooden artifacts must know the structure and even the ultrastructure of the material in order to choose or develop tailor-made conservation methods. For more than 60 years botanists and wood scientists have published physical, chemical, light microscopic, and electron microscopic data about degraded wood, fossil wood, and wood in the process of carbonization. Rosemarie Kommert gave a comprehensive and detailed synopsis of the relevant literature up to 1975 (*1*). Only relatively few recent publications deal with the visual evidence of the natural chemical degradation of waterlogged wood (*2–8*).

The objective of this chapter is to follow the process of abiotic chemical degradation as it takes place within a piece of wood by examination of a series of tissues taken at increasing distances from the wood surface. Chemical analysis of the tissues under investigation is indispensable for interpretation of the optical evidence. Standard analyses for the main wood constituents were made of the respective tissues to supplement the microscopic evidence and to determine which constituents are still present and which have been degraded from the structures examined. Four hardwoods and one softwood have been investigated to see if there are variations among species.

Degraded wood can be quite tricky to section. The micrographs shown are typical of what can be obtained in a conservation laboratory where microscopy is only one of many occupations.

Materials and Methods

Several archaeological excavations provided samples of waterlogged European oak (*Quercus* sp.), European ash (*Fraxinus excelsior* L.), Dutch elm (*Ulmus campestris* L.), white-poplar (*Populus alba* L.), and European spruce (*Picea abies* (L.) Karst). The timbers were 400–2000 years old and had been covered by marine sediments. Cross sections were cut from timbers 10–20 cm in diameter and samples were taken from macroscopically discernible zones of different states of degradation, as well as from the border between these zones (Figure 1).

For light microscopy, small cubes were embedded in polyethylene glycol 2000. Sections of 12–15 μm were cut, taken off with scotch tape, double stained with chrysoidine–acridine red and astra blue on the tape (*9*). After the sections were mounted on glass slides, the tape was dissolved off with xylene. The sections were examined in translucent and polarized light. For fluorescence microscopy a blue UV illumination was provided with a combination of a 450–490-nm exciter filter and a 520-nm barrier filter. For scanning electron microscopy (SEM), samples were fixed in 5% glutaraldehyde–0.1 M sodium cacodylate (pH 7.2), postfixed in 1% osmium tetroxide–0.1 M sodium cacodylate (pH 7.2), dehydrated in ethanol and acetone, dried in a critical point drier (Polaron), gold coated, and examined in a scanning electron microscope (Joel T 20 and T 35).

Chemical analysis for the main constituents of wood was carried out on tissues taken from the different zones of each wood sample and on fresh wood of the same species according to the standards of the Technical Association of the Pulp and Paper Industry (TAPPI Standards Nos. 12, 15, 203, 204, 207, 212, and 222). Chlorite-holocellulose was determined as proposed by Wise et al. (*10*). Results are listed in Table I and Figure 1. In the cases where the sum of the determined constituents is less than 100%, this discrepancy reflects the presence in the wood of soluble degradation products of carbohydrates or acid-soluble lignin fragments that are not retained on the filters used in the analysis. The density R_g (g/cm^3) is based on dry weight and waterlogged volume, and can be calculated from the maximum water content (u_{max}) by the formula:

$$R_g = \frac{100}{u_{max} + 66.7}$$

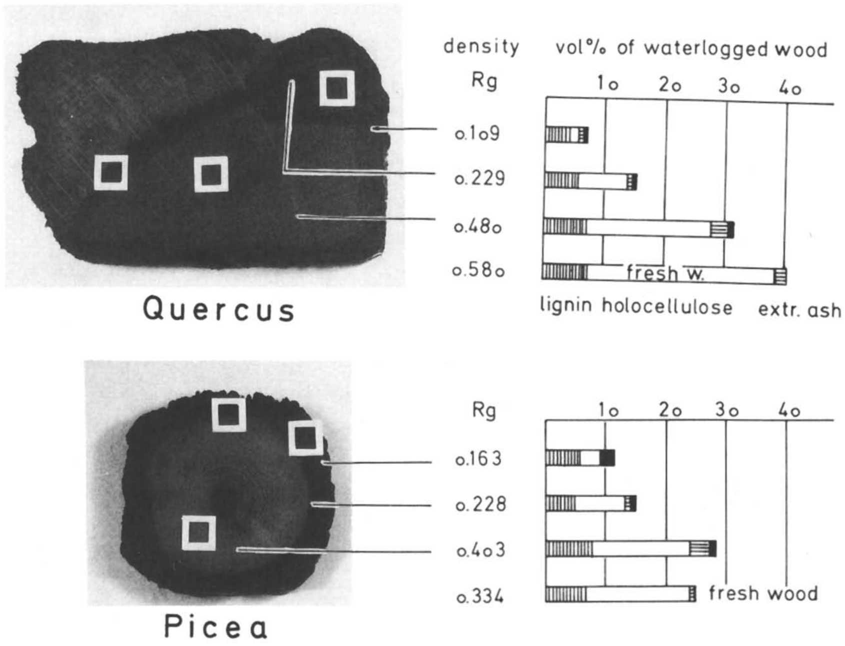


Figure 1. Cross sections of waterlogged archaeological woods showing zones of slight and heavy degradation, and the composition of the main wood constituents. Squares indicate where samples were taken for microscopy.

Structure of Waterlogged Archaeological Wood

Freshly cut cross sections of waterlogged archaeological wood display some sort of zonation in most cases. Two or more zones can be distinguished by differences in color or hardness (checked by pricking with a pin). Where there are no different zones visible, either the wood will be very soft throughout or it will be about as hard as fresh wood. In the latter case there will probably be a very thin zone of softer tissue around the hard wood, even if it is only 1–2 mm thick.

The harder portions of the cross section often have a woolly appearance attributable to fibers protruding from the surface. The softer portions tend to look very clean-cut, indicating that the fibrous structure of the tissue has undergone a thorough modification (Figure 2). The tensile strength of the fiber cells has disappeared. You can easily extract water from such a tissue by squeezing the wood in your hands. The zoning pattern of archaeological wood, a hard core surrounded by softer tissue, suggests that the degradation process proceeds from the surface inward.

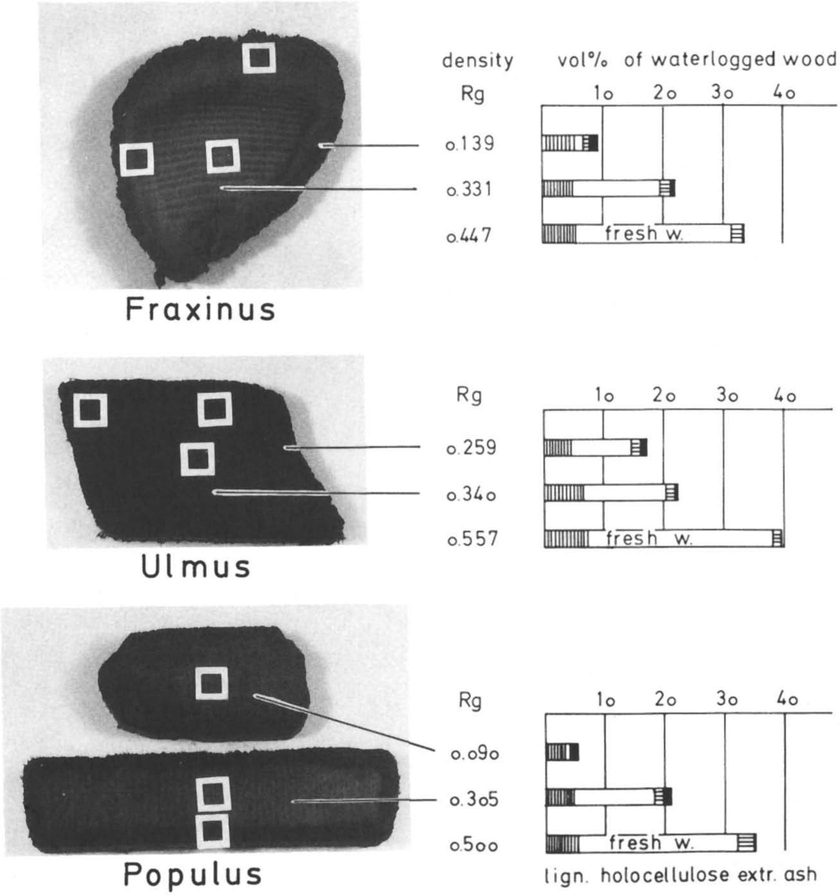


Figure 1.—Continued

European Oak. In fresh wood, lignified cell walls appear red after the double staining with chrysoidine–acridine red and astra blue. They do not absorb the blue stain. Under polarized light, sound tissue shows bright birefringence, which results from the crystalline arrangement of cellulose chain molecules in the cell walls. When the tissue is illuminated with UV light, a strong yellow-green fluorescence arises from all parts of the cell walls. On microscopic sections from the hard inner core of archaeological oak, the secondary cell walls of all cell types take on the astra blue stain. The whole tissue looks brown to blue. This can be interpreted as an indication that the secondary cell wall ultrastructure has been loosened so much that now the larger molecules of the astra blue (MW 1000) can enter. In fresh wood only the smaller molecules of the red dye (MW of chrysoidine, 249; acridine red, 465) find a way into the cell walls. The loosening of the cell

Table I. Chemical Analysis of Archaeological and Fresh Woods

Sample	u_{max}[a]	*Solubility in 1% NaOH*	*Hot Water Extracts*	*Ethanol–Benzene Extracts*	*Lignin*	*Holocellulose*	*Ash*	*Sum of Components*
Quercus								
fresh wood	105.6	19.9	4.6	–	19.2	89.2	0.1	104.1
archaeological wood								
inner part	141.5	19.0	9.1	–	22.6	62.9	2.6	97.2
outer part 1	369.9	25.7	4.9	–	34.8	52.9	5.1	97.7
outer part 2	850.7	50.1	10.9	–	53.6	19.5	10.6	94.6
Fraxinus								
fresh wood	142.9	23.9	6.4	–	17.0	78.7	0.6	102.7
archaeological wood								
inner part	216.8	14.4	7.8	–	22.3	61.8	2.4	94.3
outer part	650.9	44.6	9.9	–	55.5	15.9	13.4	94.7
Ulmus								
fresh wood	112.9	18.3	3.4	–	19.1	81.7	0.3	104.5
archaeological wood								
inner part	227.6	17.2	6.2	–	28.8	60.6	2.1	97.7
outer part	319.2	27.3	7.9	–	27.7	58.5	6.1	100.2
Populus								
fresh wood	133.5	22.2	7.8	–	16.6	78.5	0.5	103.4
archaeological wood								
inner part	260.9	14.4	6.4	–	23.0	66.5	5.5	101.4
outer part	1046.7	62.2	6–10	–	55.4	13.3	21.8	~100
Picea								
fresh wood	232.7	9.1	3.5	0.4	28.6	76.1	0.4	109.0
archaeological wood								
inner part	181.2	9.5	1.9	1.1	28.0	68.2	1.7	100.9
outer part 1	371.3	19.8	4.4	1.5	31.5	54.2	4.7	96.3
outer part 2	546.0	44.0	–	–	52.4	29.1	17.5	99.0

NOTE: All values are in percentages on nonextracted wood.

[a] Maximum water content.

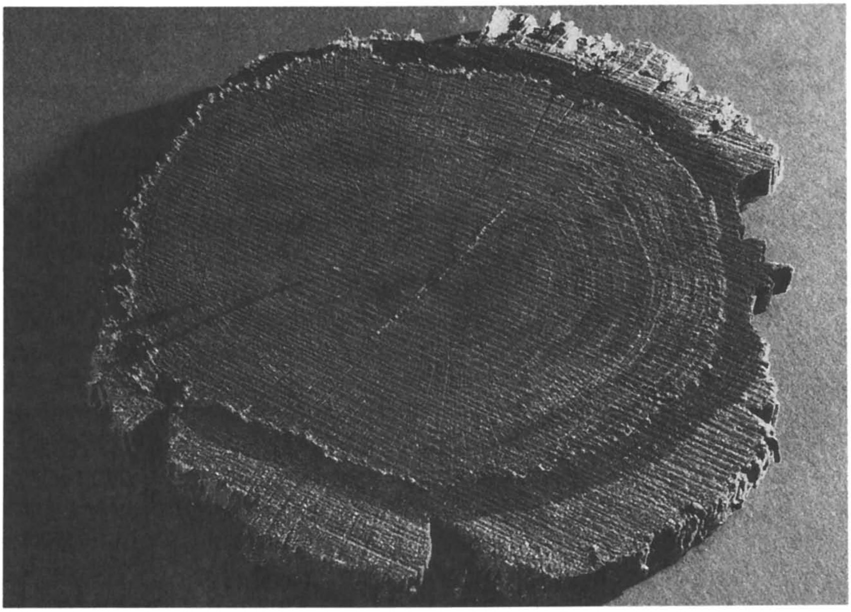


Figure 2. Oak with a central portion of "woolly" appearance surrounded by clean-cut highly degraded heartwood and sapwood.

wall structure is mainly a result of swelling. However, chemical analysis reveals small losses of carbohydrates in this state, probably caused by hydrolysis of hemicelluloses. This hydrolysis, too, enhances the accessibility of the interior of the cell walls.

Bednar and Fengel (*11*) deduced some modification of the cell wall constituents from the increased density in transmission electron microscopy (TEM) of secondary cell walls in this state. Especially in fiber cells, the swelling of the S_2 layer can be so extensive that it bulges into the lumen and sometimes even fills it completely. This swelling starts from the lumen side of the S_2 and stops at the S_2–S_1 boundary (Figure 3).

The fluorescence of woody tissue reacts very sensitively to structural changes. The swelling of the S_2 is reflected by a reduction in fluorescence. Often the examination of fluorescence images gives more information than translucent light microscopy. Figure 4 shows swelling in the cells indicated, although it is not so clearly seen in the normal light (cf. Figure 3).

In the inner region of the soft parts of wood surrounding the hard core we find the S_2 and S_3 layers of fiber cells shrunken and detached from the S_1 (Figure 5). These residues show no fluorescence and no birefringence. They contain nearly no carbohydrates and represent the degenerated lignin skeletons of the S_2. Mostly they appear to be granular and amorphous, but sometimes a lamellation is seen, or a mixture of both (Figure 6). Degraded

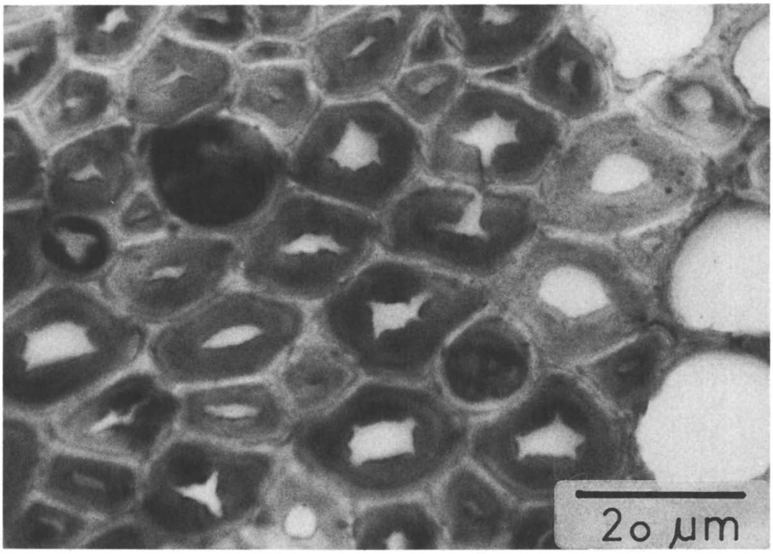


Figure 3. Oak; swollen S_2 in fiber cells, heavily stained and bulging into the lumina.

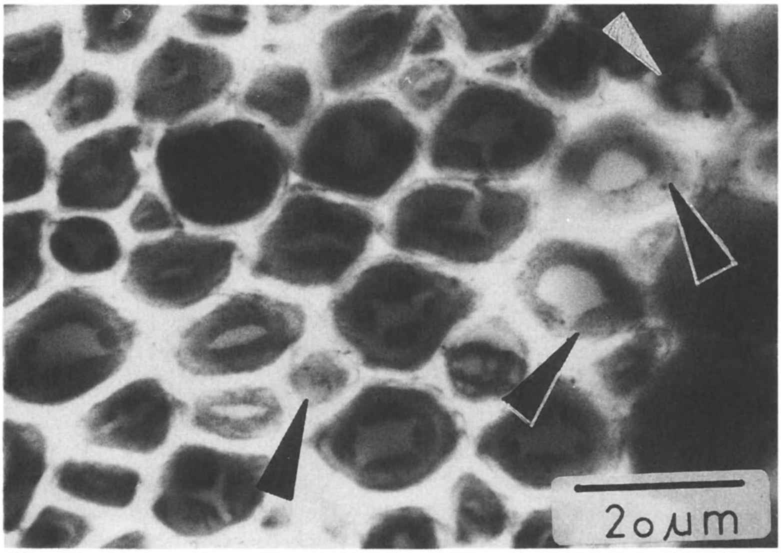


Figure 4. Same as Figure 3; fluorescence image, swelling of S_2 disturbs the natural fluorescence. Beginning of process seen in cells indicated.

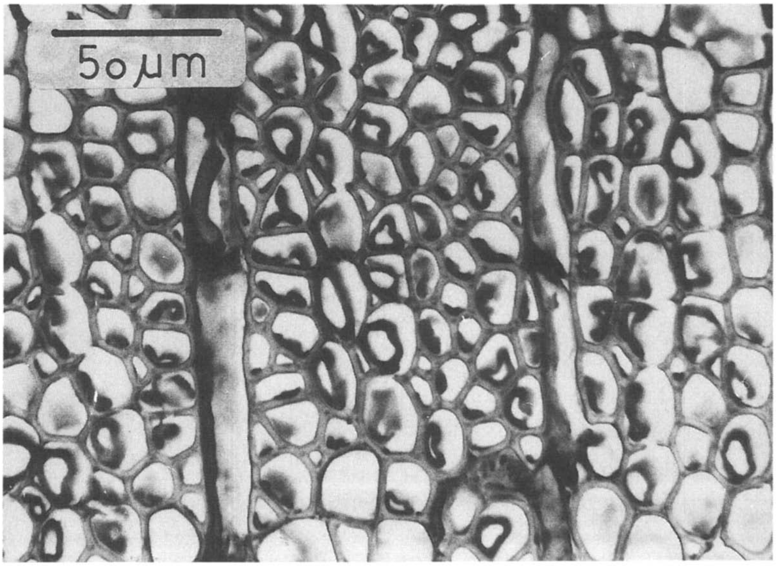


Figure 5. Oak; S_2 *and* S_3 *heavily degraded, shrunken, and detached from middle lamellae (ML) and* S_1*.*

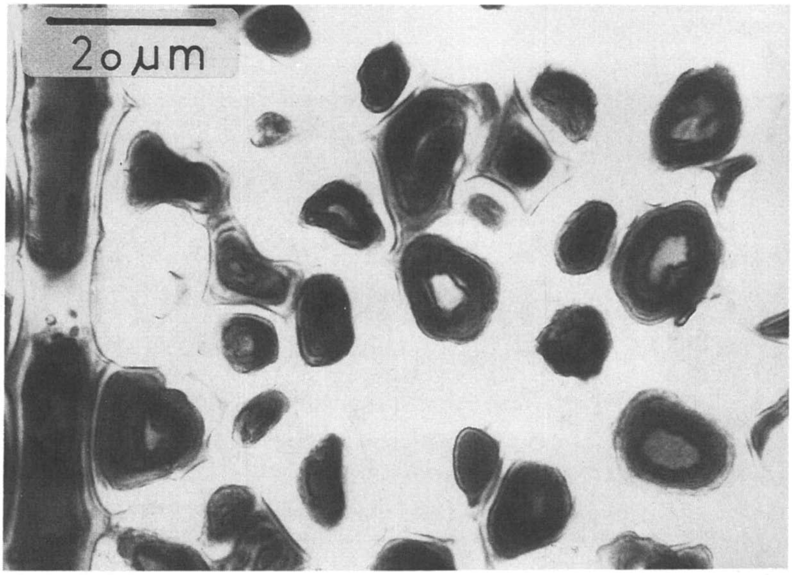


Figure 6. Oak; lamellation in swollen and degraded S_2 *of fiber cells. ML and* S_1 *have vanished through overexposure during the development of the photo to make the lamellation visible.*

S_2 in the other cell types still adhere to the compound middle lamellae (CML) and S_1, and are thus less conspicuous.

In this state the S_1 layers still contain crystalline cellulose, as can be seen from their birefringence (Figure 7). Such a tissue has lost half or more of its original substance, the losses being mainly carbohydrates. Finally, in the softest parts of the wood cross section, even the S_1 have vanished (Figures 8 and 9). What remains is a fragile system of middle lamellae that is easily ruptured during the preparation of microscopic sections. S_2 residues are still found in the lumina of fiber cells, either in a dense coagulated form or beginning to dissolve into cloudy structures. The high alkali solubility of this tissue indicates that the lignin macromolecules are breaking down. The S_3, however, is often found still intact.

Parts of the original amount of lignin have vanished, and only minute amounts of carbohydrates are present (cf. Figure 1). In all, only one-seventh of the original wood substance is left. Barbour and Leney (*5*, *6*) have published exciting scanning electron micrographs that show that the small amounts of carbohydrates present in what is virtually a lignin skeleton of the former wood structure form a thin continuous sheet in the middle lamellae. This sheet contains cellulose in crystalline form and stays intact until the wood is degraded to a density R_g of about 0.1 g/cm^3 or less. Fengel (*12*) has shown cellulose microfibrils to have survived for 20 million years in a very degraded *Taxodioxylon* wood from a lignite deposit. *Taxodioxylon* is a conifer thought to be closely related to redwood (*Sequoia* sp.).

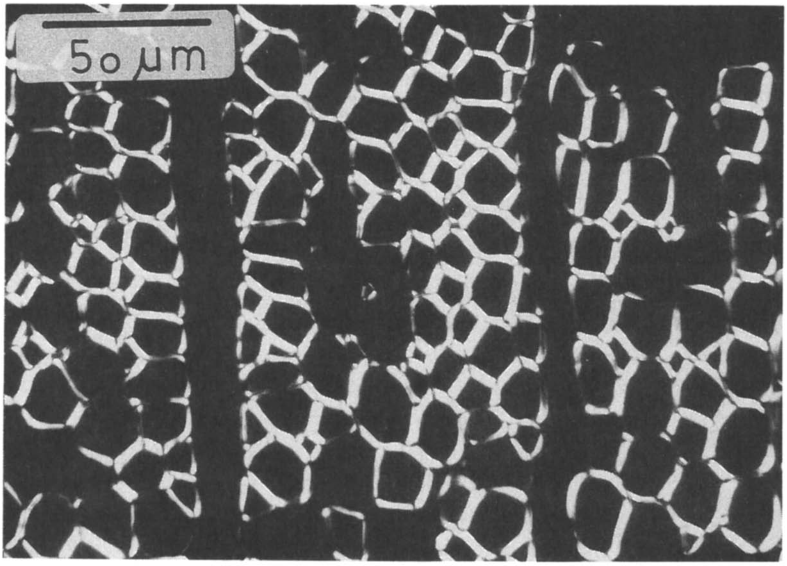


Figure 7. Same as Figure 5; nondegraded S_1 show bright birefringence.

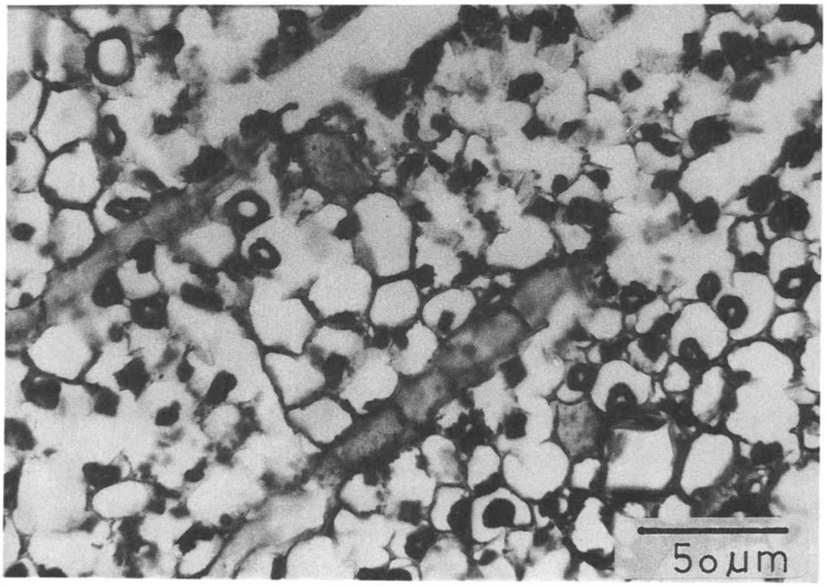


Figure 8. Oak, heavily degraded; system of ML with ruptures and residues of secondary cell walls.

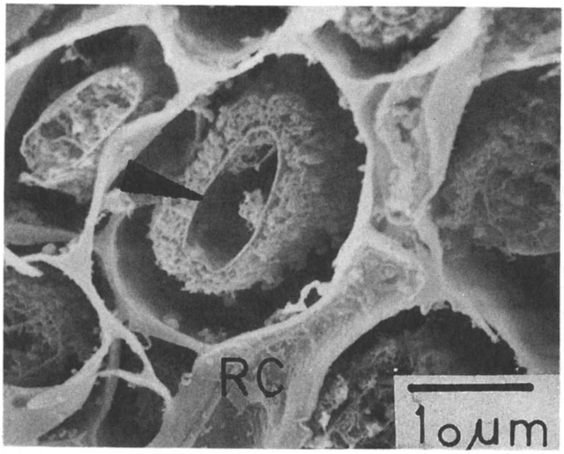


Figure 9. Oak, heavily degraded; dissolving lignin skeletons of S_2 in system of ML; S_3 layer still intact (arrow); RC, ray cells; scanning electron micrograph.

With the support of the water filling it, the frail system of middle lamellae maintains the structure and shape of the wood. Waterlogged timber that is this deteriorated can even be handled—with great care. When the last structural carbohydrate film in the middle lamellae breaks down, the degradation of the wood structure can be considered finished. What remains of the lignin has no structural strength and will crumble under the slightest impact.

To get an idea of the dynamics of the chemical degradation in the various cell types and how the process advances into the wood, it is helpful to look at the borderline between the areas of slight and heavy degradation. The distinct degradation front is parallel to the wood surface, and it is not visibly influenced by the anatomical planes of the wood. In polarized light under crossed nichols, the transition from the area of strong birefringence to that with practically no birefringence at all is quite sharp (Figure 10).

A closer look reveals only slightly swollen fiber cells in direct contact with cells that have heavily degraded secondary cell walls. Relatively sound looking cells may even be totally surrounded by degraded ones without being affected (Figures 11 and 12). In the sample of Figures 11 and 12, even the S_1 seems to have been degraded at the same time as the S_2.

The breakdown of the swollen fiber cell wall is a process that proceeds from cell layer to cell layer. Apparently the carbohydrates in one cell must be almost totally dissolved before the next cell is attacked. Individual cells or small clusters of cells may remain relatively intact for some time behind the degradation front. This phenomenon could result from small differences in the degree of lignification, packing density of the lignocellulose complex, and content of extractives incrusting the cell wall.

At the degradation front the transformation of the cell walls is so sub-

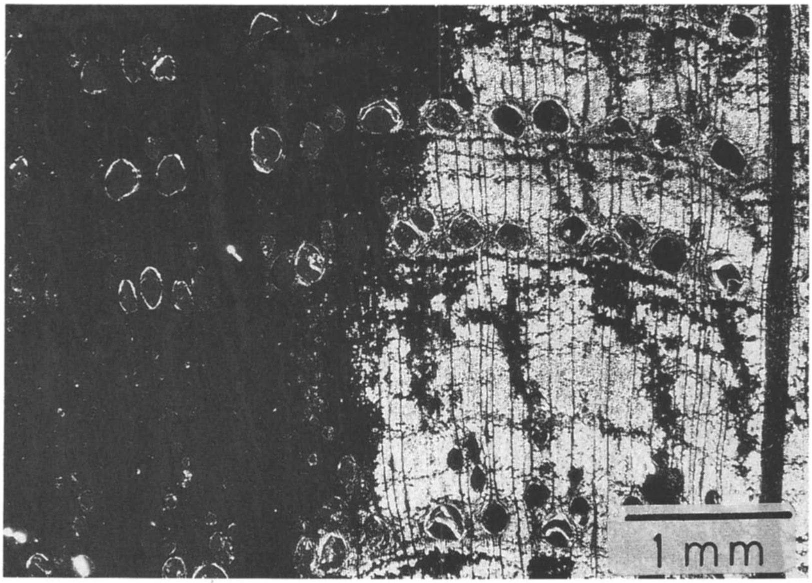


Figure 10. Oak; slightly degraded tissue with birefringence (right) and heavily degraded tissue without birefringence (left).

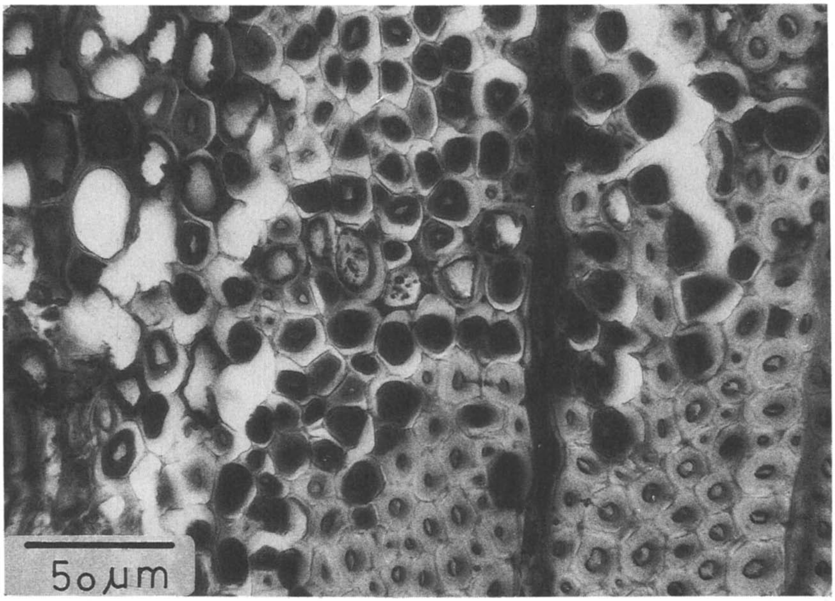


Figure 11. Oak; degradation front between slightly (right lower part) and heavily (left upper part) degraded tissue; light micrograph.

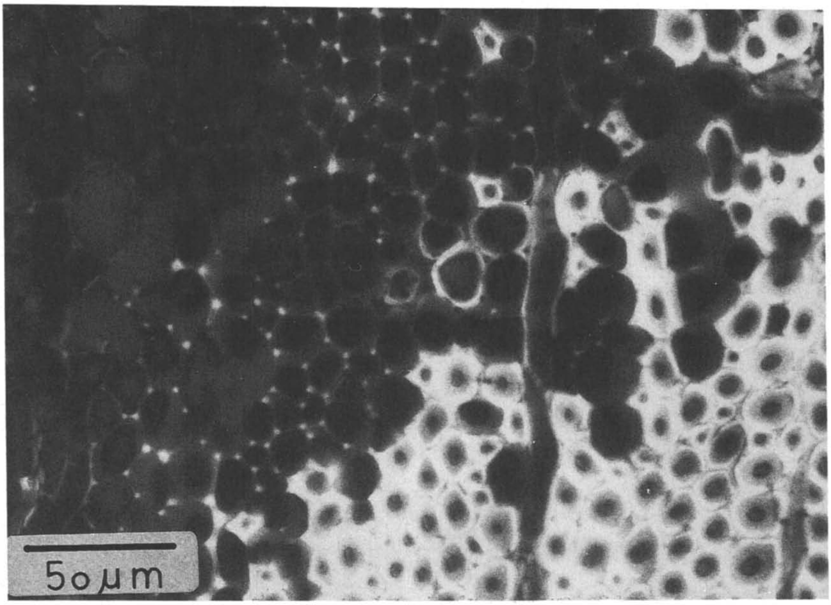


Figure 12. Same as Figure 10; fluorescence image.

stantial that the only structures that react to UV light are cell corners and middle lamellae, pit membranes, and a thin lining in pit chambers (Figure 13). Barbour and Leney (*5*, *6*) reported a similar resistance of intervessel pit membranes in heavily degraded red alder (*Alnus rubra* Bong). Fengel et al. (*13*) found intact-looking pit membranes in 20-million-year-old *Taxodioxylon*.

Cell corners, CML, and pit membranes are structures with heavy incrustations that mask and protect a relatively low content of structural carbohydrates. They are thus quite resistant to a hydrolytic attack.

Degradation begins first in latewood vessels and parenchymateous cells. They may lose their birefringence long before degradation begins in neighboring fiber cells (cf. the dark areas surrounded by birefringent areas in Figure 10). Large springwood vessels have the most resistant cell walls of all cell types in oak. They may show a bright birefringence indicating a high content of nondegraded crystalline cellulose even several millimeters outside the degradation front (Figure 10).

European Ash. A section from the interior of waterlogged ash looks red and blue after double staining. The secondary cell walls of fiber cells are swollen and blue, whereas the walls of the large springwood vessels and of the parenchyma cells surrounding the vessels have absorbed only the red stain. The cell walls of the thick-walled latewood vessels and of the tracheids look red, with areas showing some blue discoloration.

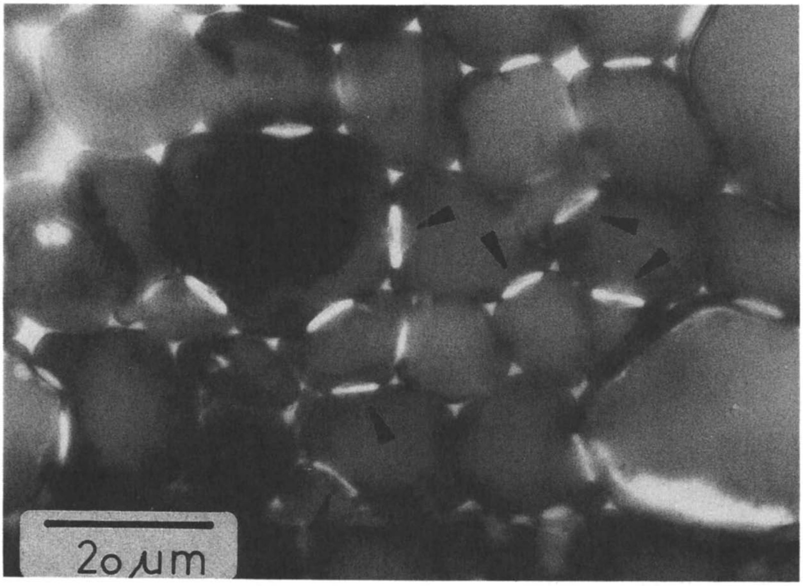


Figure 13. Oak; heavily degraded tissue; only cell corners, ML, a lining in pit chambers, and pit membranes react to UV light with fluorescence.

Under UV light the initial phase of cell wall degradation becomes quite clear (Figure 14). The secondary cell walls of springwood vessels and parenchyma cells appear bright yellow, indicating a nonswollen state. In most fiber tracheids the fluorescence changes from yellow to green, a sign of loosening of the ultrastructure. This process starts in the middle of the S_2 and spreads, but does not affect the S_1 (Figure 15). The tertiary wall, however, is finally included in the swelling. In the thick-walled latewood vessels, the transformation of the S_2 and S_3 starts from the lumen and spreads in a diffusionlike pattern (Figure 16).

In fiber cells, the process seems to have advanced farther. The S_2 and S_3 emit green fluorescence that has already disappeared in some areas, a result indicating a degradation of the cell wall. This degradation starts at the S_1–S_2 interface in cell corners. It spreads along the interface into the S_2, leaving the S_1 unaffected.

No separation of the S_2 from the S_1 occurs at this stage (Figure 17). The same pattern of degradation occurs in fiber tracheid walls once they are swollen. The tissue examined here has lost about one-third of its initial substance, all losses being carbohydrates.

We have not come across this pattern of initial cell wall degradation in other woods. However, the pattern is in accordance with the well-known fact that at the S_1–S_2 interface the ultrastructure is not as densely packed as in the rest of the secondary cell. This condition especially applies to cell corners. In addition, this area is rich in hemicelluloses, which are the car-

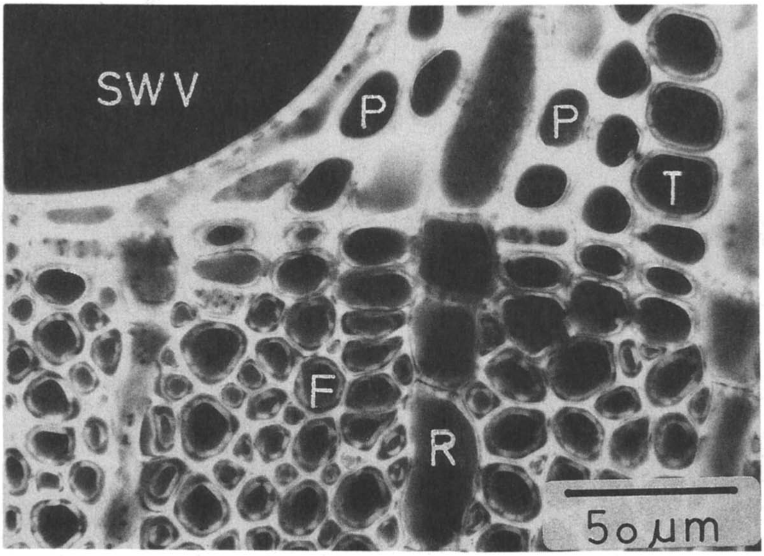


Figure 14. Ash, slightly degraded; fluorescence image; SWV, springwood vessel; P, parenchyma cells; T, tracheids; F, fiber cells; R, ray cells.

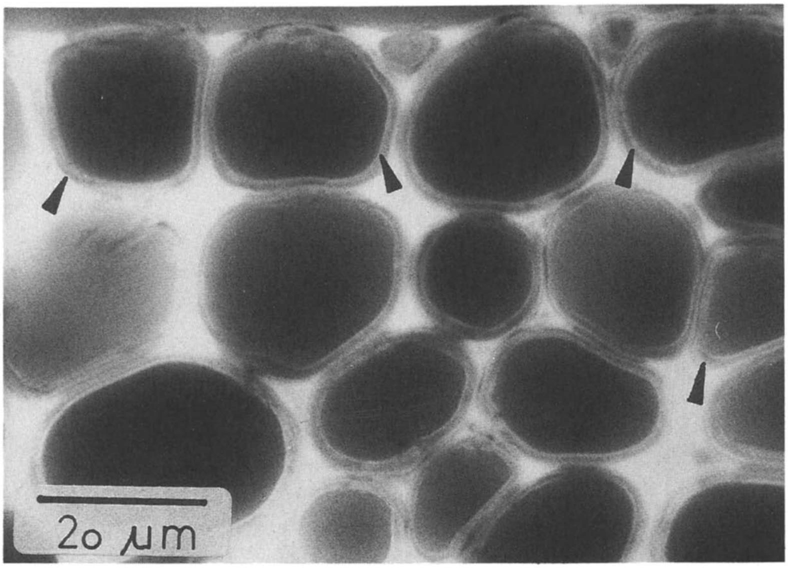


Figure 15. Ash, as in Figure 14; fluorescence image; swelling of the S_2 of fiber tracheids is indicated by a shift of the fluorescence from yellow to green (here: from white to grey).

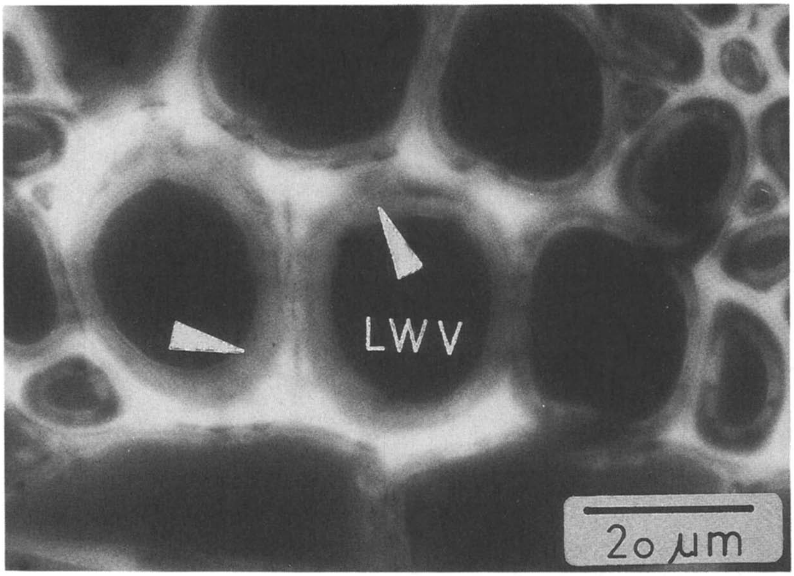


Figure 16. Ash, as in Figure 14; fluorescence image; swelling of S_2 and S_3 in latewood vessels (LWV) advancing from the lumina.

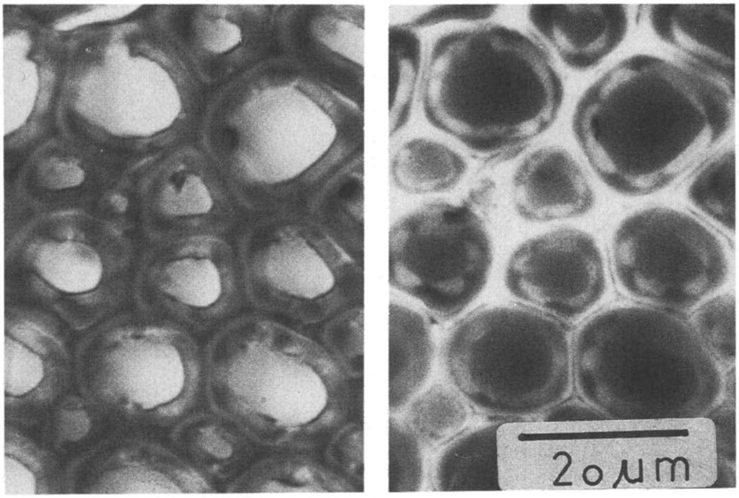


Figure 17. Ash, as in Figure 14; left–light micrograph, right–fluorescence image; the loss of fluorescence in the S_2 of fiber cells, in cell corners, and along the S_1–S_2 interface, is an early indication of beginning cell wall degradation.

bohydrates easiest to hydrolyze (*14*). The S_1–S_2 interface is a weak area in the cell wall and prone to be degraded first.

In ash, as in oak, there is a quite well defined interface between slightly degraded and heavily degraded tissue. This plane is parallel to the wood surface in both ash and oak, and on the whole it is not influenced by the anatomical features of the wood (Figures 18 and 19).

Along the degradation front, there is a substantial breakdown and dissolution of carbohydrates of both S_2 and S_1. About 90% of the carbohydrates still present in the slightly degraded tissue are dissolved here. The residual lignin skeletons of the secondary cell walls appear granular and are detached from the compound middle lamellae. In SEM preparations they often appear as a very flimsy network (Figure 20).

In the thin-walled fibers located between the springwood vessels, cell wall degradation leads to a loss of crystalline cellulose earlier than in the thicker-walled latewood fibers. They start to lose their birefringence before the main degradation front approaches.

The cell walls of springwood and latewood vessels retain crystalline cellulose for some time after the degradation front has passed. The same applies to clusters of parenchymateous cells in the earliest springwood and around vessels (Figure 19). In ash these cells have quite thick walls that obviously are more resistant than fiber cell walls. Together with the very thick walls of the latewood vessels, they are finally broken down from the lumen side (Figure 21).

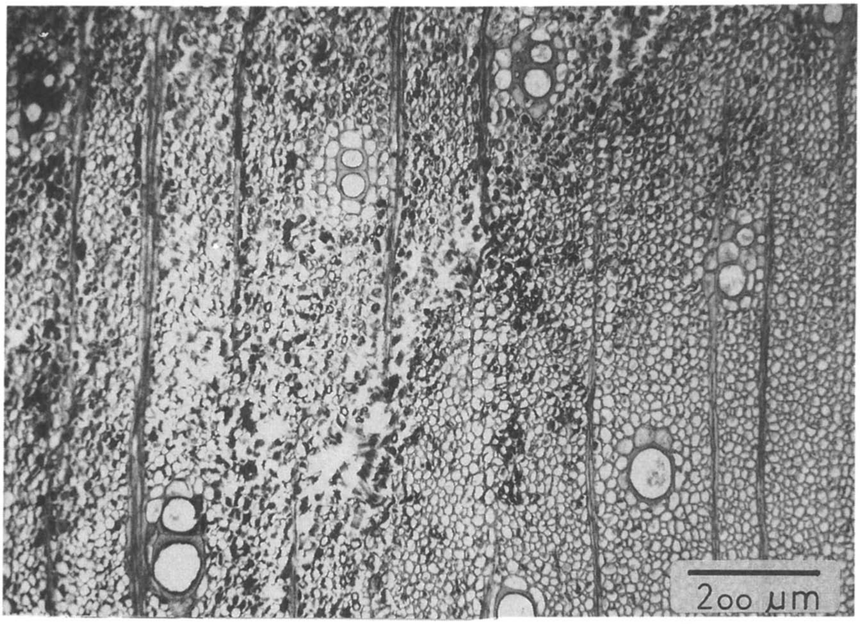


Figure 18. Ash; degradation front between slightly (right lower part) and heavily (left upper part) degraded tissue; light micrograph.

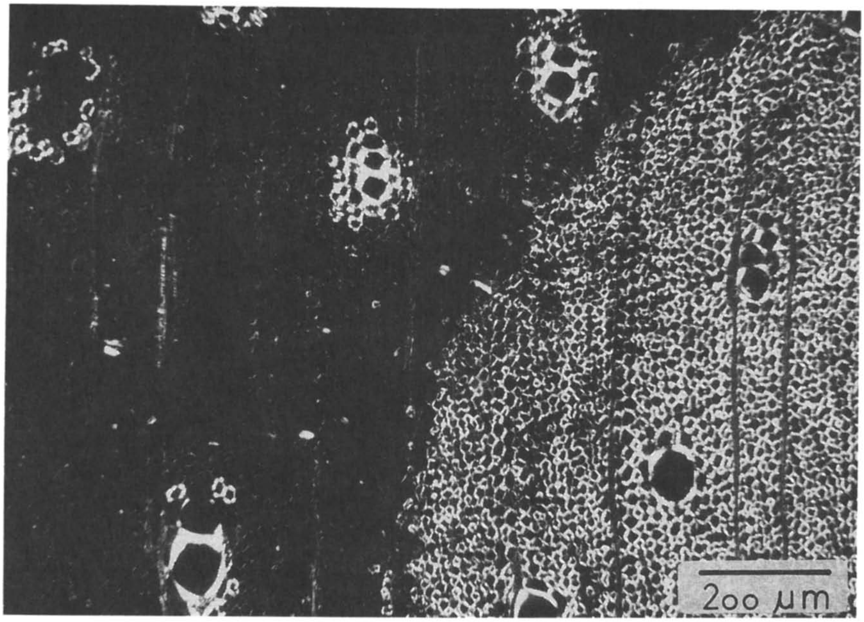


Figure 19. Ash, same as Figure 18; birefringence image.

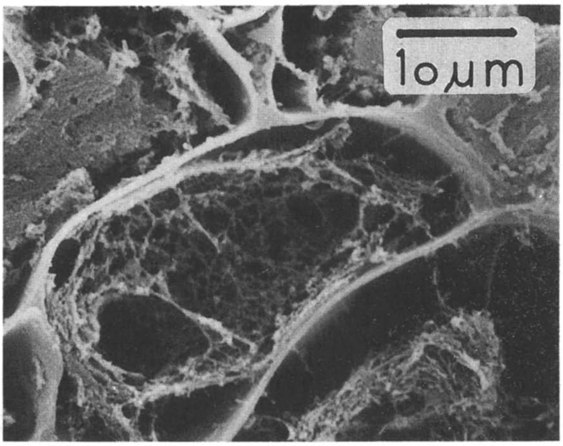


Figure 20. Ash; heavily degraded S_2 skeletons seen as flimsy networks; SEM photo.

In very degraded ash the residual system of compound middle lamellae seems to be quite strong. It may be distorted by physical impact on the wood, but mostly there will be fewer ruptures than in comparable oak (Figure 22).

Dutch Elm. Like oak, elm is characterized by discrete areas with thin-walled vessels, tracheids, and parenchyma cells, and areas of thick-walled fibers. Large earlywood vessels line the border of annual rings.

In sections from the interior of a piece of wood that had been waterlogged for centuries, the fiber walls did not absorb any blue stain, so this indication of a general swelling of cell walls is absent. The whole tissue seems to have taken up more of the red pigments than fresh wood does; even the birefringence is a strong red. There might be a slight loosening of the cell wall ultrastructure, but not enough to give access to the blue stain molecules.

The cell walls of vessels, tracheids, and parenchyma cells, however, have lost their birefringence to a large extent. At higher magnification these cell walls look degraded; dark granular lignin residues adhere to the middle lamellae (Figures 23 and 24). Single fiber cells in the state of advanced degradation, with tubelike dense secondary cell wall debris detached from the middle lamellae, occur preferentially in the vicinity of the tracheid areas (Figure 25).

The tissue discussed here has already lost about half of its carbohydrate content, more than one-third of its initial material. It is hard to imagine that

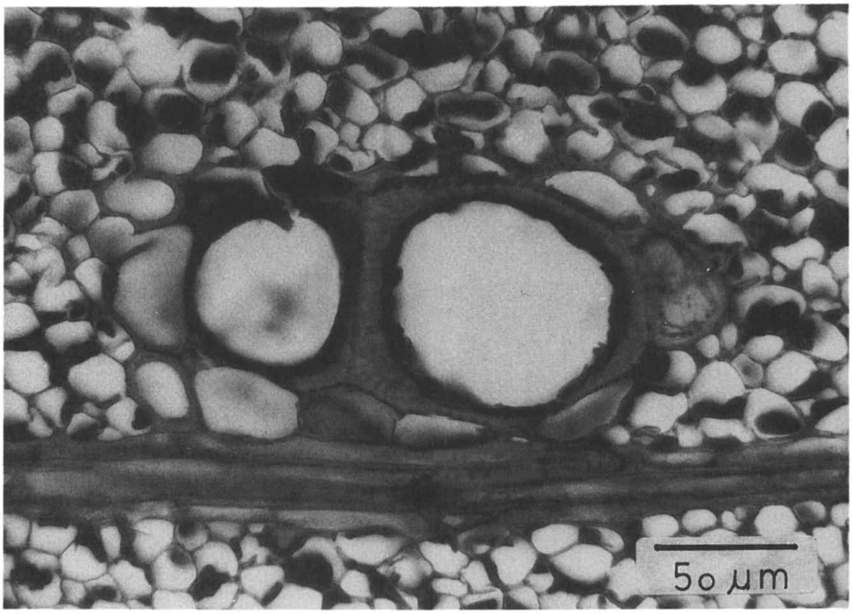


Figure 21. Ash; a pair of latewood vessels being broken down from the lumina, surrounded by heavily degraded tissue.

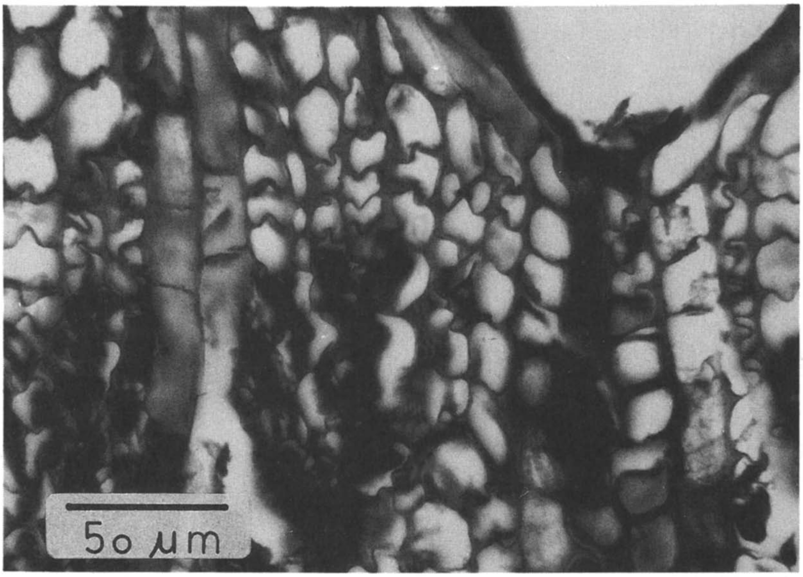


Figure 22. Ash, heavily degraded tissue; the system of ML distorted but without ruptures.

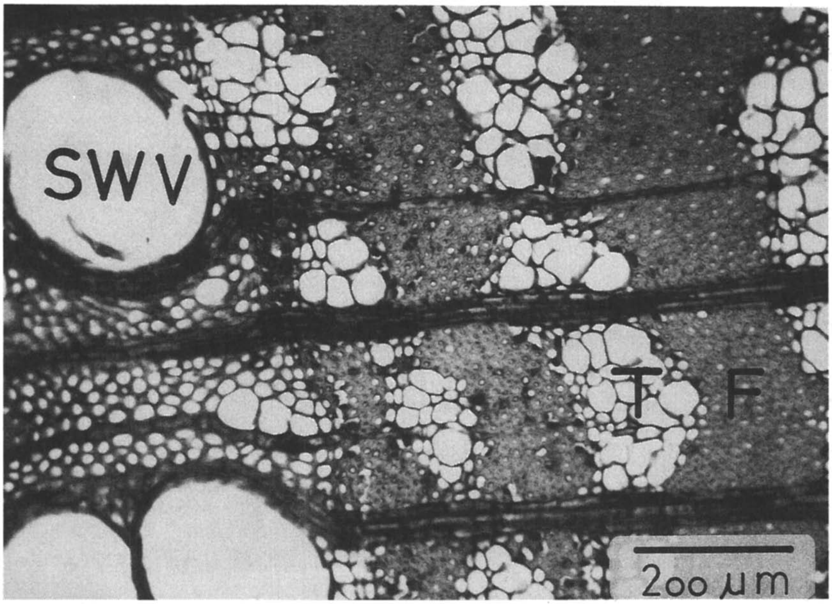


Figure 23. Elm, slightly degraded; alternate areas of latewood vessels and tracheids, T; fibers, F; springwood vessel, SWV.

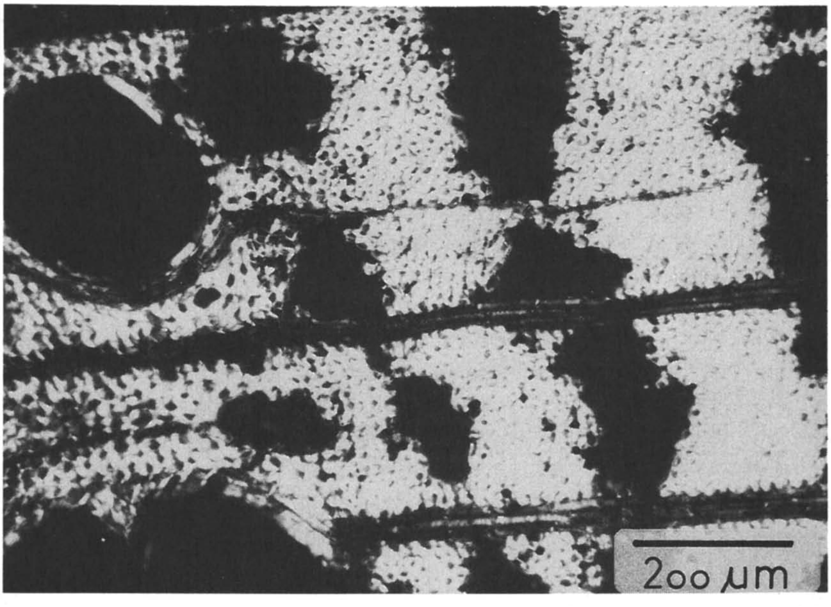


Figure 24. Elm, same as Figure 23; birefringence image; lack of birefringence in tracheid areas indicates cell wall degradation.

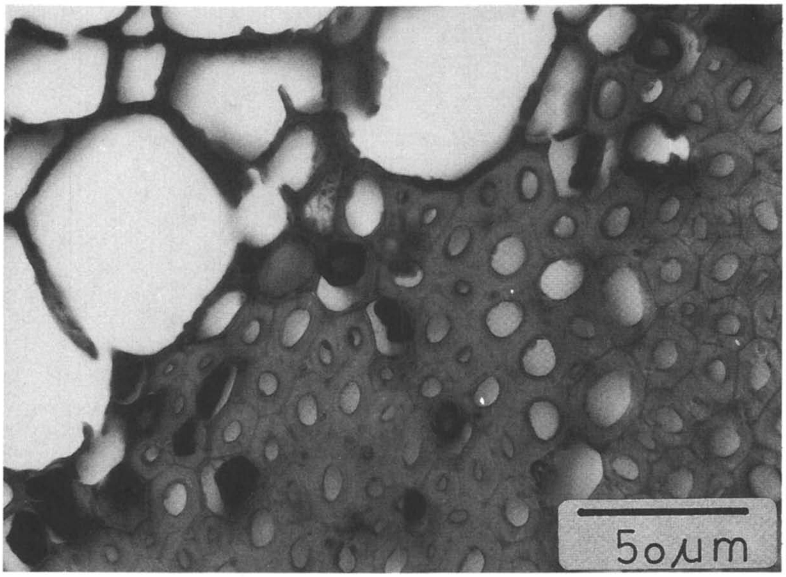


Figure 25. Elm, slightly degraded; individual heavily degraded fiber cells near tracheid area.

such an amount could originate only from the relatively thin walls of the vessels and parenchyma cells and the few degraded fiber cells. Perhaps some hemicelluloses have been dissolved from fiber cell walls without the resulting voids being large enough to let the blue stain molecules enter. A general reduction of the fluorescence might be an indication in this direction.

In elm there is no distinct interface between slightly and heavily degraded wood, although macroscopically there may be a difference in color. There is a transition zone where the degradation of fiber cells increases rapidly. Clusters of degraded cells develop, grow, and then form larger areas of degraded tissue (Figure 26).

In this transition zone we find secondary cell walls that take up blue stain, which indicates that they are strongly swollen. But evidently this state does not last very long. Breakdown of carbohydrates seems to set in immediately, with a detached granular lignin skeleton left behind (Figure 27). This thorough degradation starts at the lumen and comprises the whole secondary cell wall (S_2 and S_1). The residual system of compound middle lamellae is very frail and brittle and is easily ruptured.

White-Poplar. Poplar is a diffuse porous wood composed of vessels surrounded by fiber cells. There are rays, and a few axial parenchyma strands along the border of the annual rings, but on the whole it is a more homogeneous wood than the species examined so far.

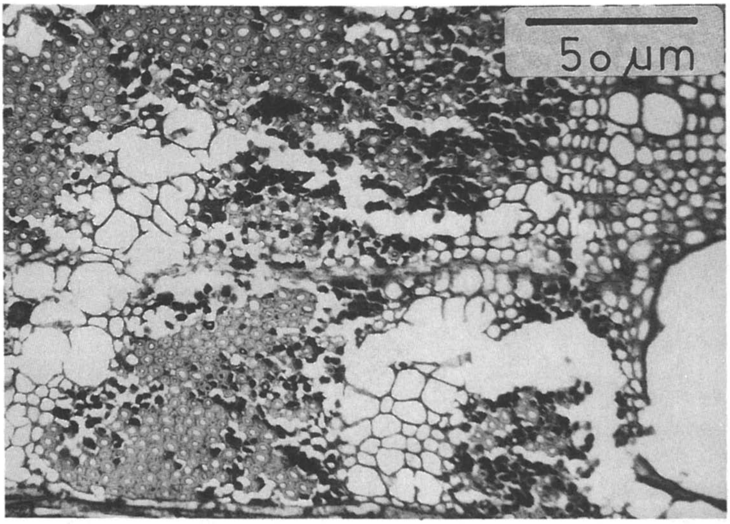


Figure 26. Elm, transition zone between slightly (left) and heavily (right) degraded tissue.

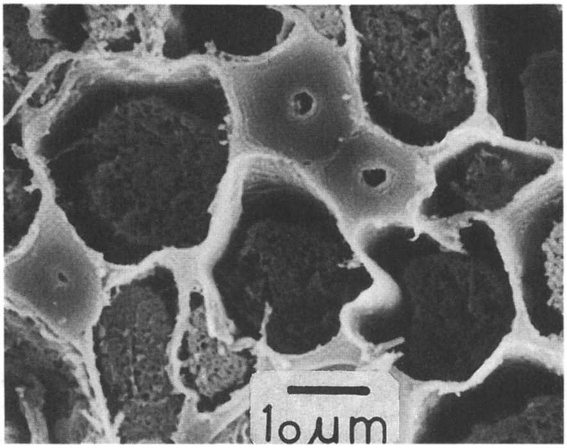


Figure 27. Elm, transition zone; totally degraded cells next to nondegraded ones; lignin residues granular and detached from ML system; SEM photo.

In the interior of the archaeological piece of poplar discussed here, the tissue has already lost half of its carbohydrates. Vessel cell walls have been degraded, and the walls of earlywood fibers are in the process of being broken down. The latewood fibers, however, do not take on any blue stain and do not look swollen (Figure 28). The breakdown of the secondary cell walls clearly proceeds from the lumen side. In the initial phase it is restricted

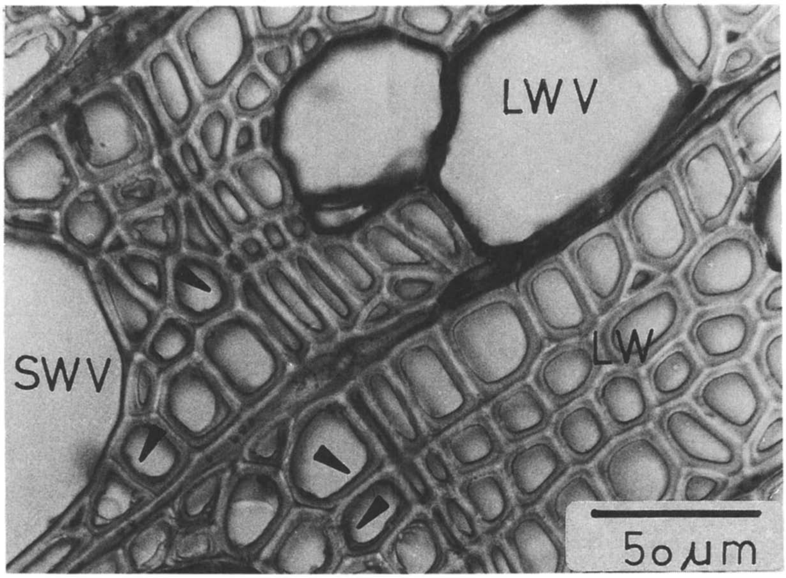


Figure 28. Poplar, slightly degraded; latewood (LWV) and springwood (SWV) vessels with degraded S_2; springwood fibers with S_2 being degraded from the lumen side (arrows); latewood fibers (LW) still unaffected.

to the S_2 and S_3. In the vessels, where all of the S_2 has been transformed to a dense, granular debris, nonaffected S_1 layers are discernible. Again, one cell might undergo complete degradation while the neighboring cell is not affected at all. In poplar, as in elm, the substantial breakdown of cell walls does not occur along a well-defined frontline. In the transition zone the areas of slight and heavy degradation intermingle in diffuse cloudy patterns (Figure 29).

In the case of poplar, the border of the annual rings influences the progress of degradation. The latewood is obviously much more resistant than the earlywood. Polarized light also reveals that not all vessel cell walls are degraded at an early state. Some keep their birefringence longer than the surrounding fiber cells (Figure 30). In the end nearly all carbohydrates have been dissolved, and the lignin residues of the secondary cell walls start to disintegrate.

The tissue in Figure 31 consists of only 14% of its original substance; 2% of the carbohydrates are left, presumably in the middle lamellae. Its density is only 0.09 g/cm^3. Nevertheless, in the waterlogged state, it still looks like wood.

European Spruce. Spruce is a coniferous wood composed of only tracheids (thin-walled in the springwood and thick-walled in the latewood), parenchyma cells in the rays, and thick-walled epithelium cells around resin

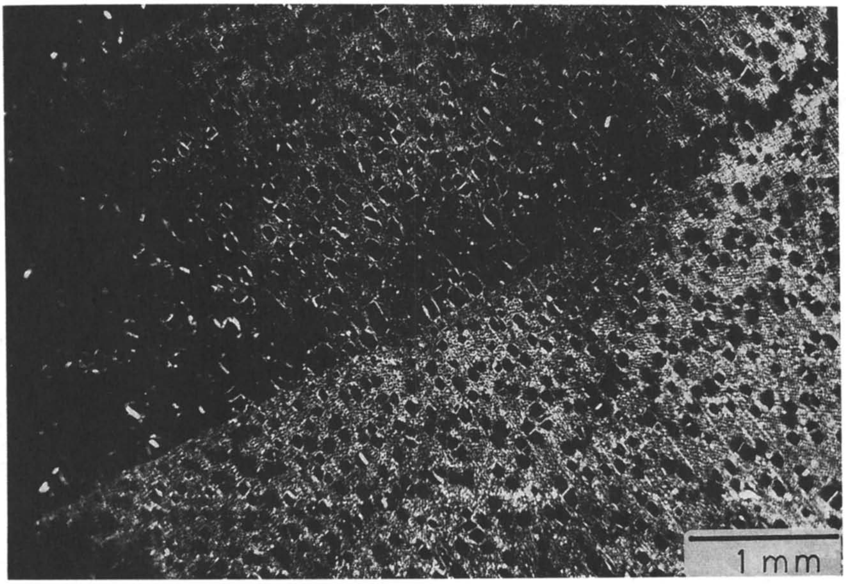


Figure 29. Poplar, transition zone between heavily degraded (left) and slightly degraded (right) tissue. The wood surface is vertical some distance outside the picture to the left; birefringence image.

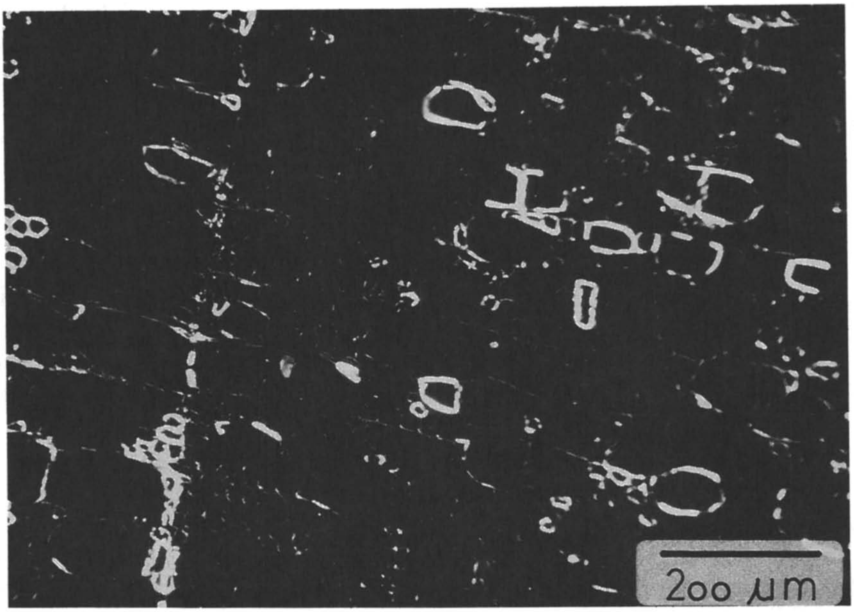


Figure 30. Poplar, heavily degraded; vessels and individual fiber cells still with birefringence, surrounded by tissue totally broken down.

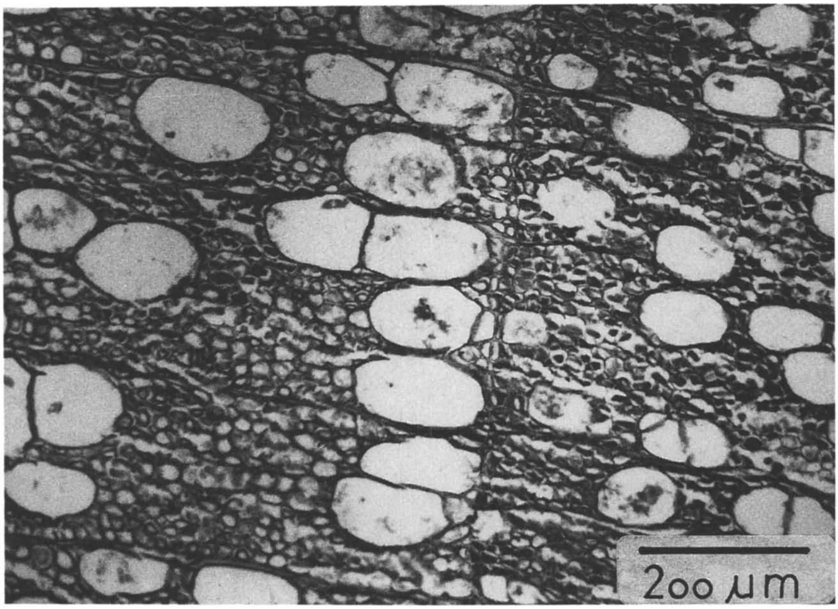


Figure 31. Poplar, heavily degraded; only 14% of the original wood substance is left. The density, R_g, *is 0.09 g/cm³.*

canals. Even after centuries of waterlogging, there are no signs of extensive swelling of secondary cell walls. But a weakening of the S_1 is indicated as now and then cell walls are split in this region, probably as an artifact arising from the sectioning of the sample (Figure 32).

The degradation of secondary cell walls starts from the lumen and transforms the cell wall structure directly to the well-known granular residue (Figure 33). In the wood examined here, no cell walls had taken up astra blue stain. This lack of color indicates that there was no extensive swelling prior to degradation. In a series of electron micrographs, Fengel (*15*) demonstrated the same degradation pattern very clearly in a fossil spruce. It seems that the density of the S_1 is loosened somewhat while the S_2 is being degraded to an electron-dense debris. Then the S_1, too, is degraded. When the degraded secondary cell wall shrinks and splits off from the middle lamellae, the granular residue is still sheathed with a smooth lamellar structure on the outside (maybe a last lignin-rich layer of the S_1) and on the lumen side by the residue of the S_3 layer (Figure 34).

There is no distinct degradation front in spruce. The process starts in individual cells. Most tracheids are broken down within a range of several annual rings (Figure 35). For a very long time the parenchymateous cells of the resin ducts survive unchanged, and so do the ray cells.

The degradation of secondary cell walls also affects the bordered pits.

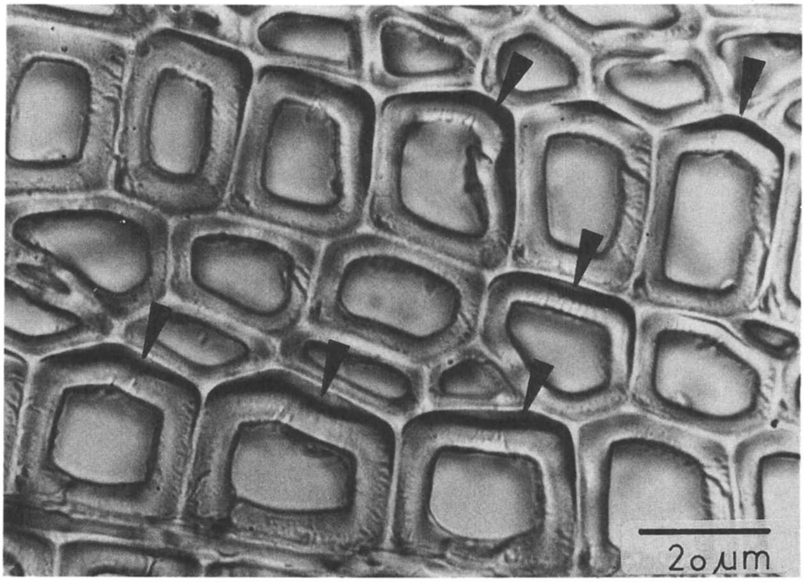


Figure 32. Spruce, slightly degraded; cell walls split in the S_1 (arrows).

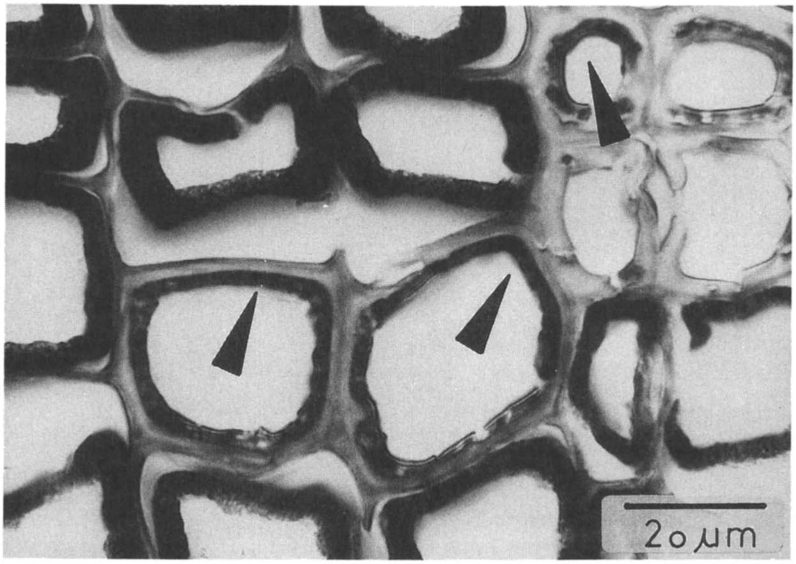


Figure 33. Spruce; tracheids with cell wall degradation proceeding from the lumen (arrows), and tracheids with totally degraded secondary cell walls.

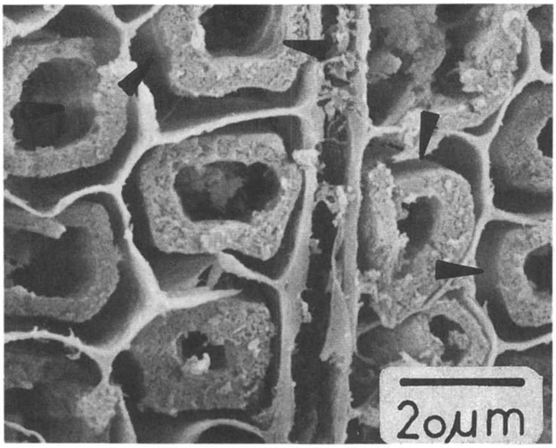


Figure 34. Spruce, heavily degraded; the S_2 skeletons are sheathed with smooth lamellar structures and S_3 layer residues. SEM photo.

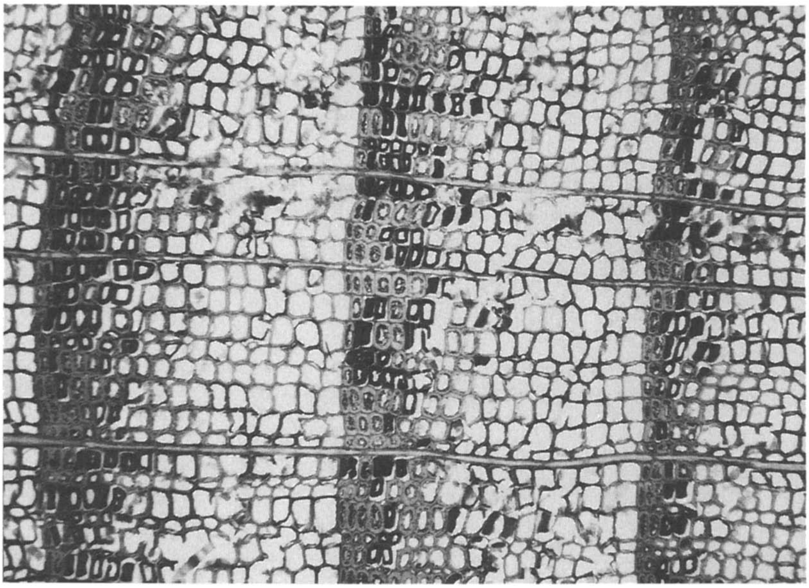


Figure 35. Spruce; transition zone between slightly (right) and heavily (left) degraded tissue; degraded cells appear black.

The pit chambers are reduced to what ontogenetically is called the initial pit chamber, and the pit membranes are dissolved or detached. Fengel (*15*) reports pit membranes in fossil spruce to be quite resistant. However, in tissues where all secondary cell walls have been degraded we have not seen any pit membranes in bordered pits.

Conclusions

The degradation pattern of waterlogged oak as described in this chapter is based on the examination of dozens of timbers from excavations in sea water and rivers, from peat bogs and clay soils. The survey of the other species, however, is restricted to the samples presented here. This study is only a first attempt to broaden our knowledge about the degradation behavior of wood to include all the species that archaeologists and conservators need to handle. Similarities in the observed degradation patterns, together with the evidence already published, allows us to draw a general sketch of what happens during the degradation of waterlogged wood.

In deciduous species, swelling of secondary cell walls loosens the ultrastructure of the lignocellulose complex, and hydrolysis of hemicelluloses begins. This process seems either to spread quite rapidly or to occur about simultaneously throughout the piece of wood. In spruce, no swelling was observed.

Then the cellulose in the inner layers of the secondary cell walls, the S_2 and S_3, is attacked either from the lumen side or from the S_1–S_2 border. Its crystalline structure is broken down, and the chain macromolecules are degraded and dissolved. The residual lignin skeleton degenerates to a granular debris that might shrink and come loose from the S_1, which is still intact and adheres to the middle lamellae. The thin S_1 is then degraded, until finally only the system of compound middle lamellae remains.

The substantial degradation of the secondary cell walls begins at the surface of the wood and slowly proceeds into it. The process develops to its final stage in individual cells independent of whether the same takes place in adjacent cells. Completely degraded and nondegraded cells are found next to each other.

There are slight differences in resistance between cell types. These are not exactly the same in all species. Sometimes vessels and parenchyma cells are more resistant than fibers, sometimes less. The distribution of different types of carbohydrates and lignins varies among cell wall layers and among cell types. Hedges and his group (*16*) have been able to correlate differences in resistance of cell types and cell components with the resistance toward degradation of the main cell wall substances composing them. *p*-Hydroxyl and vanillyl lignin structural units are the most resistant, followed by syringyl lignin units, followed by pectin, then α-cellulose, and finally hemicelluloses.

On the whole, the total breakdown of secondary cell walls proceeds as a front parallel to the wood surface. The interface between degraded and nondegraded areas is sharp in oak and ash, and more diffuse in elm and poplar. In spruce it resembles a transition zone several millimeters thick, in which more and more cells become affected until the whole tissue is uniformly and completely degraded.

Nothing exact can be said about the speed with which the degradation proceeds into the wood. This speed depends on the burial conditions of the individual piece of wood, on the chemical nature of the ground water attacking it, and on the wood species. Wood species differ in anatomical structure, in permeability, and to some degree in chemical composition. The nature and the amount of extractives that incrust the cell wall ultrastructure help to mask and protect the carbohydrates against hydrolysis, and probably also play an important role in degradation.

In the end, all that is left of the former wood is the frail system of middle lamellae containing small amounts of still-crystalline cellulose. Disintegrating lignin residues are enclosed in this cellular and brittle wood skeleton. As long as it stays waterlogged—that is, bulked with and supported by water—this structure has a certain physical strength. It still carries the anatomical characteristics of the wood it once was.

The degradation pattern outlined in this chapter has several implications with regard to the conservation of waterlogged archaeological wood. Depending on the state of tissue degradation, it may need only a treatment to block off the extensive shrinkage that swollen and minimally degraded wood undergoes on drying. Other specimens will need physical strengthening and treatment to avoid the collapse of highly degraded tissue.

Timbers that contain both slightly and highly degraded tissue need special attention. The wood in the two zones behaves differently and will tend to split along the degradation front during conservation treatment. In many cases such timbers will need a double treatment, with separate steps designed for optimal stabilization of the respective wood zones.

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3

Structure and the Aging Process of Dry Archaeological Wood

Thomas Nilsson and Geoffrey Daniel

Department of Forest Products, Swedish University of Agricultural Sciences, Uppsala, Sweden

This chapter is based both on results reported in the literature and on recent studies of the effect of aging on the structure of dry archaeological wood. Various insects cause major structural breakdown in dry wood, but enclosure of wood or the presence of toxic extractives in wood appear to have protected many artifacts from attack by insects. Under dry conditions, the effects of age on wood structure appear minimal up to an age of 4400 years. Structural changes are observed only at the ultrastructural level when using transmission electron microscopy. Delaminations in the middle lamella region or in the secondary cell walls are the most commonly reported phenomena. Fissures and loosening of fibers have also been observed.

WOOD CELLULOSE AND HEMICELLULOSES represent a rich nutrient source that can easily be exploited by numerous insects and wood-degrading fungi and bacteria. The third main wood component, lignin, affords some protection to carbohydrates, particularly against purely cellulolytic microorganisms.

All wood-degrading fungi and bacteria need water for their life processes and as a medium for the distribution of their degrading enzymes. Wood with a moisture content below fiber saturation will not be degraded by microorganisms. Insects that feed on or nest in wood are, however, fully capable of more or less complete destruction of the structure of dry wood.

Wood never (or very rarely) stays dry in nature. As a part of the carbon cycle, dead trees are degraded by an immense variety of microorganisms and insects. Even wood that is only intermittently wet is degraded, albeit

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at a slower rate. Only when waterlogged under completely anaerobic conditions, or when frozen, does wood escape significant degradation by biological agents.

Wood has been used by humans for a very long time. When they started to build shelters and later more elaborate houses into which wooden artifacts were brought, an environment was created in which wood could remain dry for at least as long as the dwelling lasted. Religious belief has contributed more than anything else to keeping very ancient wood dry. Such wood comes almost exclusively from temples, pyramids, or tombs. The oldest samples of dry wood seem to be 4000–5000 years old, not a remarkable age, considering the fact that some living trees are reported to be more than 4500 years old.

Extreme care must be taken when observing the structure of reputedly dry wood. There are no means to ascertain that the wood has been dry throughout its history. Leaks, flooding, or other events may have soaked the wood on one or more occasions. Fairly wet conditions and the presence of desert bugs in the chamber containing the Cheops boat No. 2 prove that not all apparently dry sites have been protected from moisture (*1*). Occasional wetting of wood may lead to microbial attack that could be misidentified later as structural changes due to aging. Seasoning of timber prior to its use also represents an opportunity for microbial attack to produce structural changes.

We have always observed at least some fungal hyphae in the samples of dry wood examined here, indicating infection and growth of fungi within wood at some stage. A good knowledge of microbial decay patterns will help to discriminate between structural changes of microbial origin and those likely to be the result of a nonbiological process.

Very few published reports deal with structural changes in wood caused by aging. These reports are reviewed in the first part of this chapter. The sparsity of available information forced us to undertake further studies, which are reported in the second part of the chapter. The third part contains a brief review of the known structural changes in dry wood resulting from insect attack.

Review of Earlier Studies

A fairly large number of reports deal with structural changes in ancient woods, extending to petrified wood. Only a few reports, however, concern dry wood.

Täckholm (*2*) reports that the wooden artifacts found in the tomb of Hetepheres, Cheops' mother, had shrunk by 10%, but no details of structural changes were mentioned. Several other authors (*3–5*) have mentioned that ancient dry wood has been in a remarkably good condition, also without providing any details.

Narayanamurti et al. (6) examined a piece of teak that was 1800 years old. The wood originated from a beam in a Buddhist monastery. Parts of the wood were described as being so soft that it broke during attempts to cut it. Fungal attack was noted in some parts of the wood. It is not clear from the report if the authors suggest that the fiber deterioration, illustrated in two micrographs, was caused by fungal attack or by aging. In our opinion, the appearance suggests microbial attack. X-ray diffraction studies indicated no difference between recent and ancient wood.

Chowdhury et al. (7) reported on the results of a study of four samples of ancient wood from India. One of the samples, teakwood, was taken from a Buddhist cave, where it had been exposed to atmospheric conditions for 2200 years. Chemical analyses showed a reduced cellulose and pentosan content. Light microscopic studies suggested that the only difference between the ancient and recent wood was helical fissures in the fiber walls of the former. A significant difference, however, was found in the birefringence of the two samples. The birefringence, considerably lower in the ancient wood, indicated a loss in crystallinity of the cellulose.

The most extensive and careful study of the ultrastructure of ancient wood was carried out by Borgin et al. (8). Three of the examined samples, each more than 4000 years old and originating from pyramids in Egypt, represented wood that presumably had been kept dry. The timber species were *Juniperus phoenicea*, *Pinus pinea*, and *Acacia nilotica*. Their ages were approximately 4100, 4300, and 4400 years, respectively. The samples were examined by using light microscopy, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Fracture studies were also carried out. No attack by microorganisms was observed in any of the samples. Borgin (9) had reported earlier that the ancient samples of *Pinus pinea* and *Acacia nilotica* were macroscopically indistinguishable from recent wood. The only difference was a slight change in color.

Changes in the ultrastructure of ancient *Juniperus phoenicea* were apparent, although the macroscopic structure was intact (8). The most typical change was separation of the inner layer in the wood cell walls (S_2) from the outer layer and the primary cell walls (S_1–P). The microfibrils in S_1 were loosened and wavy. Fracture studies indicated failures in the middle lamella region. Large amounts of phenolic substance were observed in the parenchyma cells.

The wood of *Pinus pinea* was reported (8) as being "almost intact". Microtomy for the SEM studies showed that the cell walls often bent over, making it difficult to obtain a smooth surface. Weakening of the middle lamella was evident by the separation of individual tracheids or rows of tracheids from each other. TEM studies revealed delamination in the middle lamella–S_1 region, where the fibrils in S_1 were loosened.

The wood of *Acacia nilotica* also appeared macroscopically intact, but TEM studies revealed delamination and fissures in S_2 and the middle lamella.

Loosening of fibrils was also evident in this sample. Fractures occurred not only in the middle lamella region, but also in the fiber walls. Vestures in vessel pits were similar to those in recent wood.

The authors state (*8*) that "the amount of crystalline material in almost all samples had been reduced." Presumably, this includes one or more of the samples from the pyramids. The examined samples had been selected because they appeared macroscopically sound. The changes observed at an ultrastructural level were attributed to a weakening of the wood material. It was further suggested that the stresses involved during preparation for microscopy (i.e., trimming and cutting) could result in the delaminations and cracks observed. Such effects were, however, rarely observed with samples of new wood.

The authors stated (*8*) that the middle lamella and the matrix of the cell wall is effected by chemical changes such as oxidation and hydrolysis to a higher extent than the cellulose microfibrils. Ultrastructural changes would then be expected to occur in areas rich in hemicelluloses, lignin, or pectic substances. Later, Borgin et al. (*10*) found that the lignin in the ancient wood samples had been oxidized. A decrease in lignin content was evident when the samples were analyzed by a hydrochloric acid procedure.

Recent Studies

Materials and Methods. The ancient wood samples were donated by R. Rowell (Forest Products Laboratory, Madison, Wisconsin, U.S.A.) and J. Amber (British Museum Research Laboratory, London, United Kingdom). All the samples were assumed to have been kept dry according to the information available. The macroscopic structure of all the samples appeared intact. Some characteristics of the samples are provided in Table I. Recent wood samples for comparison were obtained only for Douglas fir.

All samples were examined with light microscopy. Sections were stained with either aqueous safranine or a solution of Chlorazol Sky-Blue (Imperial Chemical Industries, Ltd., U.K.) in lactophenol. Polarized light was occasionally employed.

For TEM small sticks (~3.0 × 5.0 × 0.5 mm) of the various wood samples were removed with a scalpel from the specimen material. They were immediately placed in freshly prepared aqueous 1% w/v $KMnO_4$ and left for 1 h at room temperature. After continuous washing with distilled water to remove leachable $KMnO_4$, the samples were dehydrated by using ethanol and then an ethanol–acetone series (10% steps). They were flat embedded in Spurr's epoxy resin after infiltration (*11*). Resin polymerization proceeded at 70°C for 24 h. Then selected material was sectioned with an ultramicrotome (Reichert FC4). The sections were collected by using formvar-coated copper grids. Additional samples were infiltrated and embedded directly in Spurr's resin without pre-$KMnO_4$ staining or dehydration. After

Table I. Some Characteristics of the Sample Materials

	Species					
No.	*Common Name*	*Scientific Name*	*Code Number*	*Origin*	*Hardwood or Softwood*	*Approximate Exposure Time, years*
1[a]			(FP–F–5)	Egyptian coffin	Hardwood	3000–4000
2[a]	Douglas fir	*Pseudotsuga* sp.	(FP–H–11)	Chaco Canyon, New Mexico	Softwood	1127
3[a]	Douglas fir	*Pseudotsuga*	(FP–H–4)	Axtec, New Mexico	Softwood	748
4[a]		*Pistacia* sp.	(FP–D–2)	Petra 9, Temple of Dhushares, Jordan	Hardwood	1997–2028
5[b]		*Acacia* sp.	(No. 158–BM–337)	Tomb of Tjanefer, Dra' Abu el-Naga', Thebes	Hardwood	3250–3420
6[b]		*Tamarix* sp.	(No. 283–BM–338)	Pyramidal chapel of the tomb of Roma, Dra' Abu el-Naga, Thebes	Hardwood	3150–3400

[a] Courtesy of R. Rowell, Madison, WI.

[b] Courtesy of J. Amber, British Museum, London, United Kingdom.

sectioning these samples were poststained by using 1% w/v $KMnO_4$. Observations were made with a transmission electron microscope (Philips 201) at varying acceleration voltage.

For SEM small wood pieces (0.5 × 0.5 × 0.5 cm) were removed from the sample material with a razor blade and then mounted on aluminum stubs with double-sided cellophane tape. After coating with gold (Polaron Sputter Coater), samples were examined by SEM (Cambridge S150) at 10 or 20 kV.

Results. Light microscopy revealed hyphae and bacteria in all of the ancient wood samples. Profuse growth was, however, not seen. Only a few of the samples showed signs of actual microbial degradation.

Sample No. 1 was a small piece of unidentified hardwood taken from an Egyptian mummy coffin dating from 1000–2000 B.C. Light microscopy revealed that the wood was degraded by soft rot. Fungal hyphae were common, and typical chains of soft-rot cavities were seen within the fiber walls. Holes in S_2 representing cavities were commonly observed by TEM of transverse sections (Figures 1 and 2). Enzymatic activity appeared to have affected only the immediate regions around the holes. Figures 3 and 4 show that the ultrastructure of the cell walls at a distance from the cavities is similar to what could be expected for recent wood. The middle lamella and all wall layers appear intact. A fibrillar structure is clearly seen in Figures 3 and 4. No marked loosening of wall layers and no delamination was observed. The middle lamella and the vessel wall in Figure 2 appear to be quite porous, a condition suggesting loss of wall substance.

Figure 1. TEM photo showing structure of wood fibers from an Egyptian mummy coffin 1000–2000 years old and the presence of soft-rot cavities (c) within both the S_2 and S_1 layers. Bar: 1.0 µm.

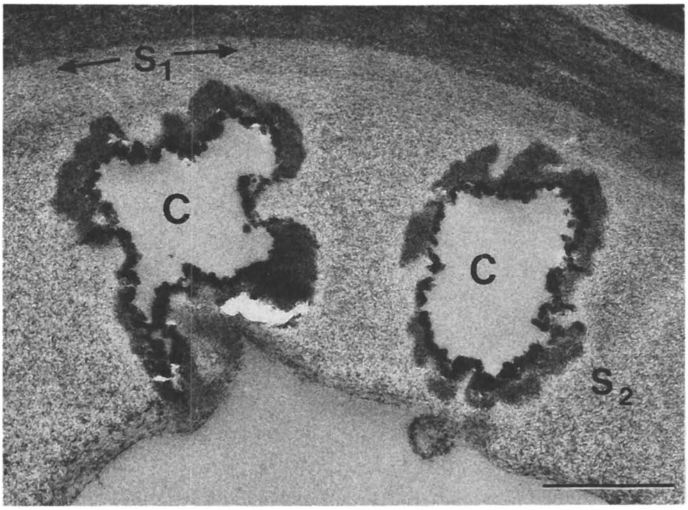


Figure 2. Higher magnification of the soft-rot cavities from Figure 1. Fungal hyphae were absent, but regions of previous enzymatic attack (arrows) are apparent as more darkly staining regions surrounding the cavities (c). Bar: 1.0 μm.

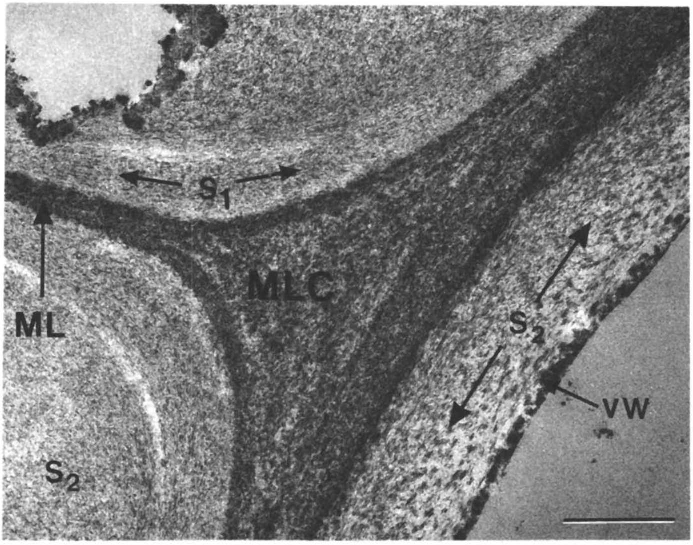


Figure 3. TEM photo showing aspects of the microfibrillar structure of fiber and vessel walls (vw) from the Egyptian mummy coffin. An occasional increase in the electron-lucent appearance of some of the vessel wall layers suggested a loss of wood substance and a possible increase in porosity. (ML, middle lamella; MLC middle lamella corner). Bar: 1.0 μm.

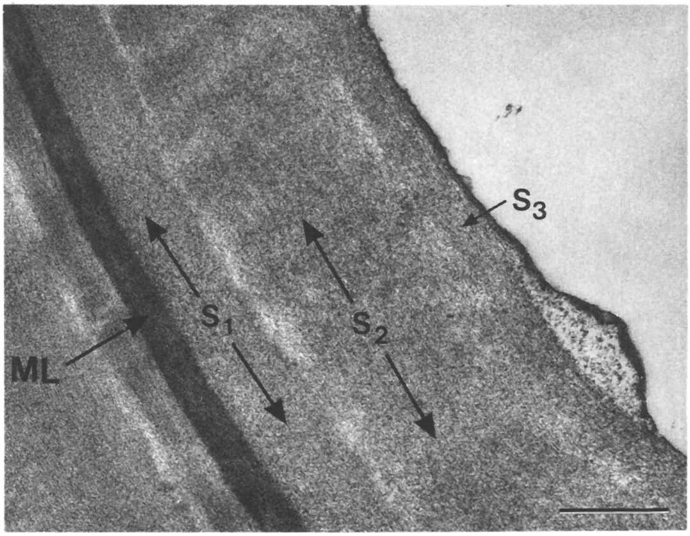


Figure 4. As for Figure 3, but showing a more detailed photo of the secondary cell-wall layers of a fiber. The fibrillar structure generally appeared quite intact, with no obvious delaminations between secondary wall layers. Bar: 2.0 μm.

The two samples of Douglas fir (Nos. 2 and 3, Table I) were studied by using light microscopy and SEM. Slight soft-rot attack was observed in the outermost parts of the youngest sample (No. 3), an indication that the wood had been wet at some time. The SEM studies suggested that the wood structure was indistinguishable from recent wood. Details like bordered pits (Figures 5–8), pit membranes (Figures 9 and 10), crossfields, and spiral thickenings on the tracheid walls (Figures 11 and 12) were identical to those in recent wood. Thus, no effects of aging were revealed.

The hardwood sample from Jordan (No. 4) was identified as a species of the genus *Pistacia*. The wood had remarkably well-developed tyloses in the large-sized vessels (Figure 13). Tylose cell walls were very thick and contained pits. Numerous crystals and spherical bodies were observed within the tyloses (Figures 13–15). Iodine staining indicated that the spheres represented starch grains that were exceedingly well preserved.

TEM studies of transverse sections of the *Pistacia* wood show that the ultrastructure was well maintained (Figures 16 and 17). Swelling of the wall layers, indicated by wrinkling of the S_3 layer, was a common feature (Figures 16 and 17). The middle lamella and all the wall layers, where a well-preserved fibrillar structure was observed, appeared to be intact (Figures 16 and 17). Although separation was occasionally noted within the middle lamella region and the cell wall layers, no distinct loosening at interfaces can be observed in the micrographs presented here. However, splitting of the middle lamella cell corner, caused by sectioning, was often observed (Figure 16).

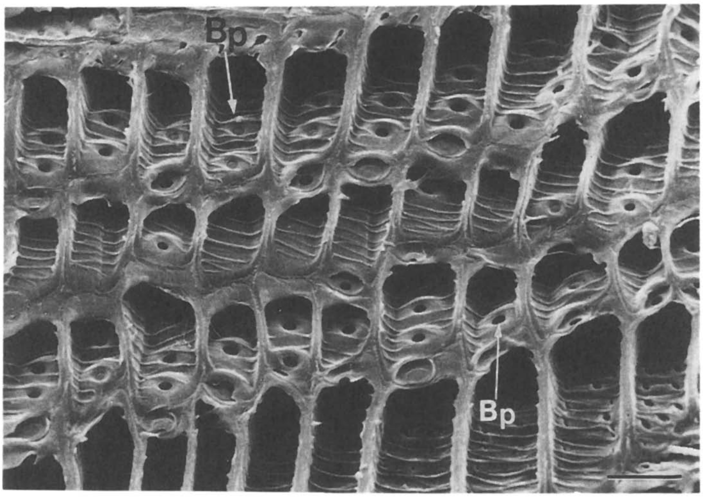


Figure 5. SEM photo showing structural aspects of fibers from 1127-year-old Douglas fir sample from Chaco Canyon, New Mexico. Little difference could be seen between bordered pits (Bp) from this sample and those from recent Douglas fir samples (cf. Figures 7 and 8, see page 76). Bar: 5.0 μm.

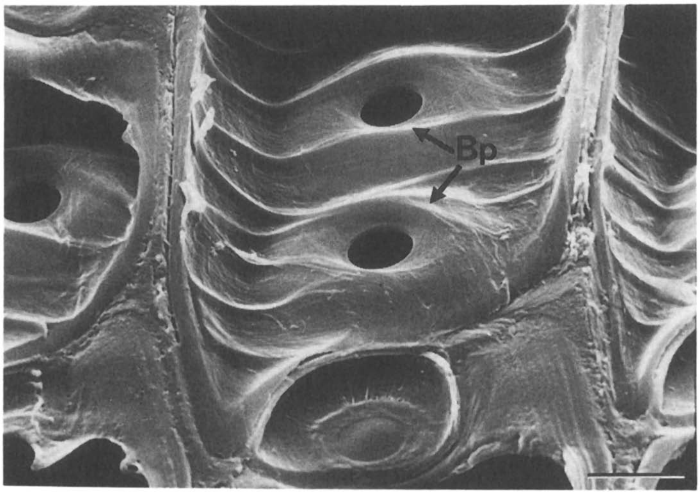


Figure 6. Same as Figure 5. Bar: 2.0 μm.

The ultrastructure of the *Acacia* wood (No. 5, Figure 18) appeared to be as well preserved as that of the *Pistacia* wood. However, splits and checks occurred more often in the *Acacia* samples (Figures 18 and 19). Most occurred in the middle lamella and S_1 regions, but they were occasionally observed within the S_2 cell wall layer (Figure 19).

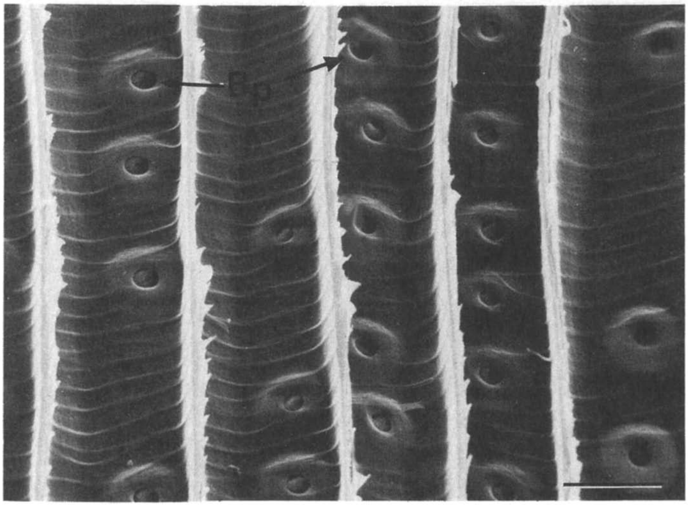


Figure 7. SEM photo showing bordered pits (Bp) from recent Douglas fir sample. Compare with Figures 5 and 6. Bar: 5.0 μm.

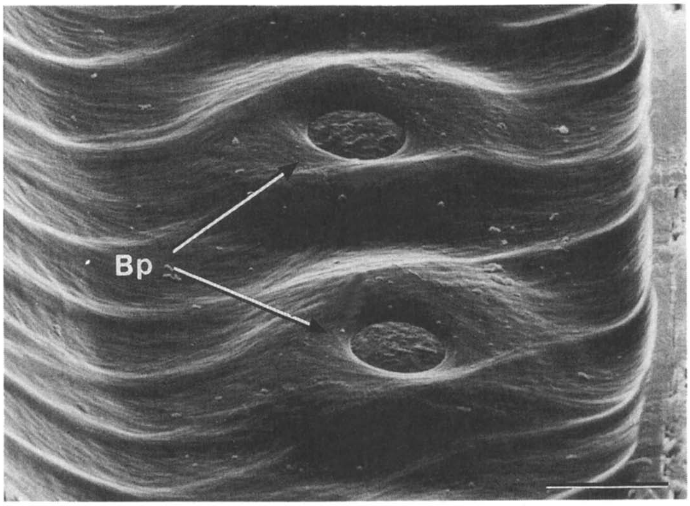


Figure 8. Same as Figure 7. Bar: 2.0 μm.

Figures 20 and 21 give examples of the ultrastructure of transverse sections of ancient *Tamarix* wood (No. 6). A well-maintained ultrastructure was observed, although cracks and splits occasionally occurred.

Structural Changes in Dry Wood Following Insect Attack. A fairly large number of insects are capable of using dry wood as a food resource. Well-known examples are the longhorn beetle (*Hylotrypes bajulus*), the

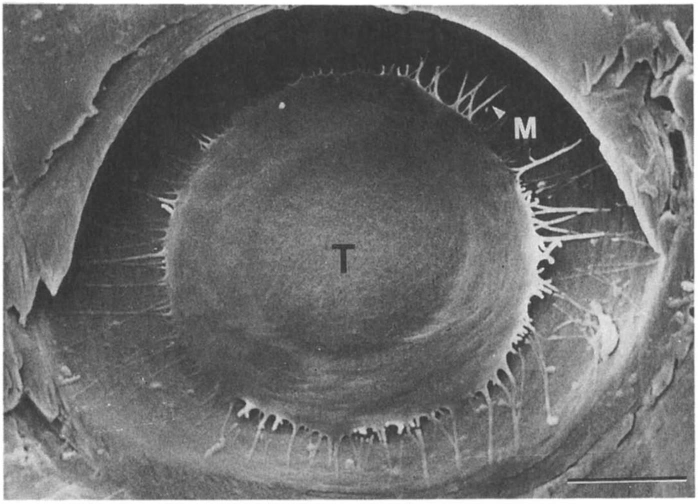


Figure 9. SEM photo showing bordered pit membranes from recent Douglas fir sample. Little difference could be seen between the structures shown here and those in Figure 10. Both had well-preserved margos (M) and tori (T). Bar: 1.0 μm.

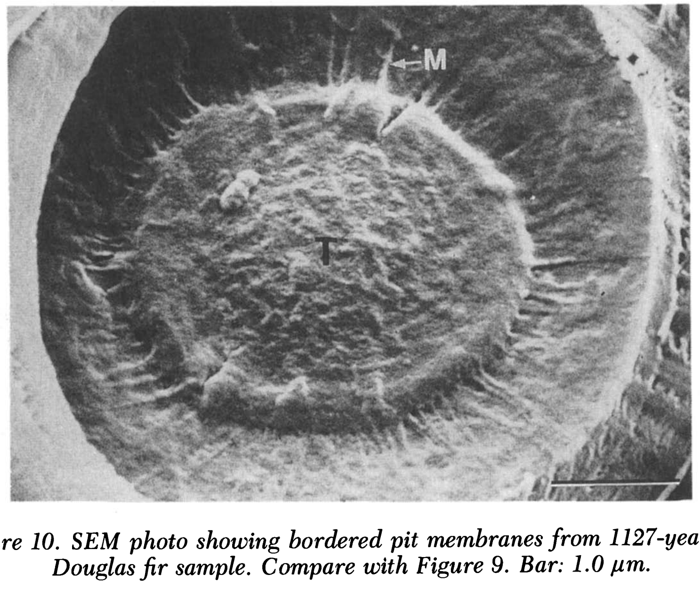


Figure 10. SEM photo showing bordered pit membranes from 1127-year-old Douglas fir sample. Compare with Figure 9. Bar: 1.0 μm.

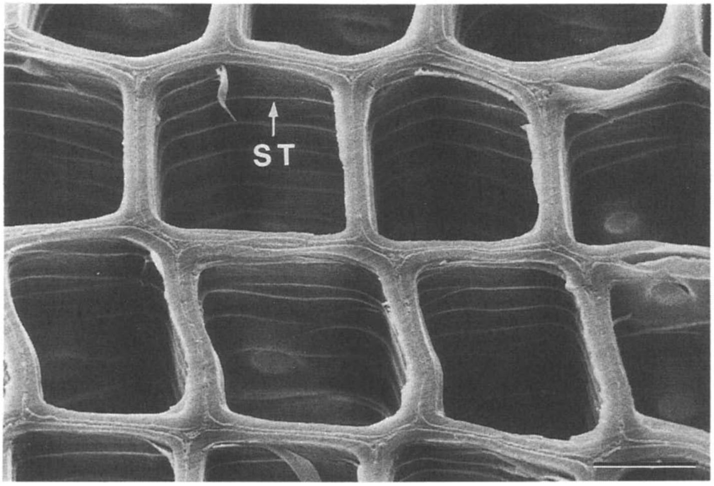


Figure 11. SEM photo showing spiral thickening (ST) in sample of Douglas fir from Chaco Canyon. No obvious differences were apparent between this sample and the recent wood shown in Figure 12. Bar: 4.0 μm.

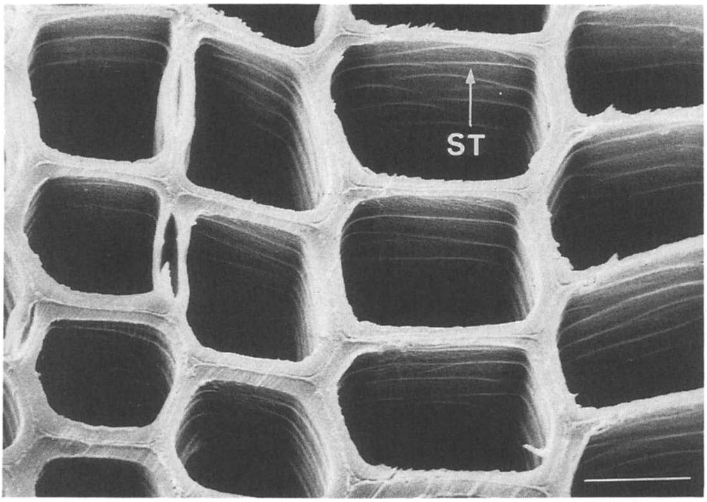


Figure 12. SEM photo showing spiral thickening (ST) in sample of recent wood. Compare with Figure 11. Bar: 4.0 μm.

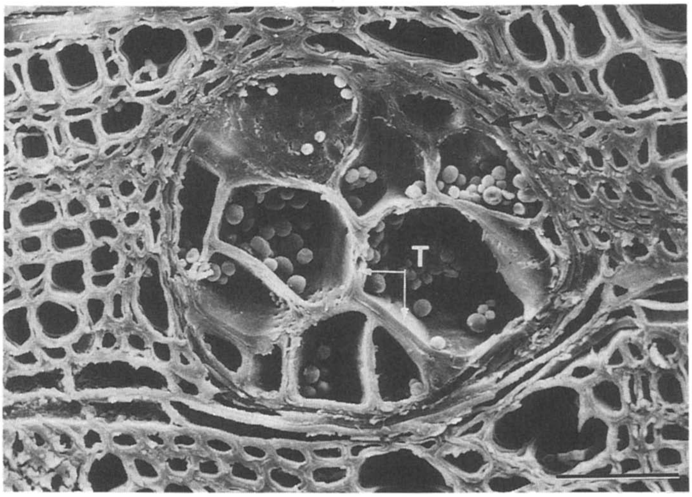


Figure 13. SEM photo showing structural aspects of the hardwood sample Pistacia *(1997–2020 years old) obtained from the Temple of Dhushares, Jordan. Note the characteristic tyloses (T) produced into vessels (v). Bar: 20.0 μm.*

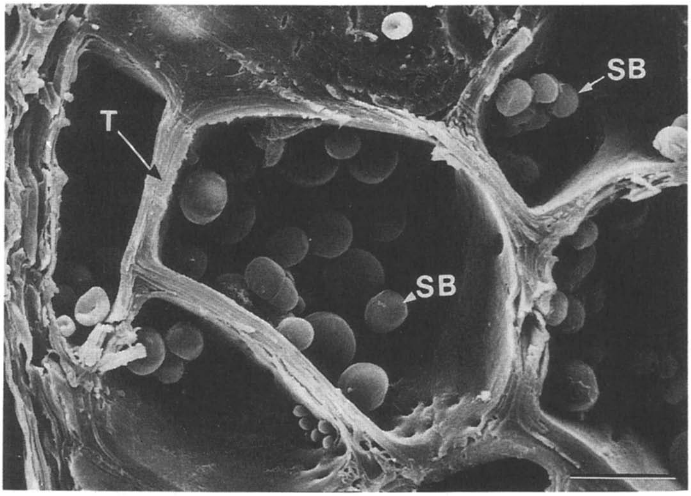


Figure 14. Same sample as Figure 13. Note the association of the tyloses (T) with spherical starch bodies (SB). Bar: 4.0 μm.

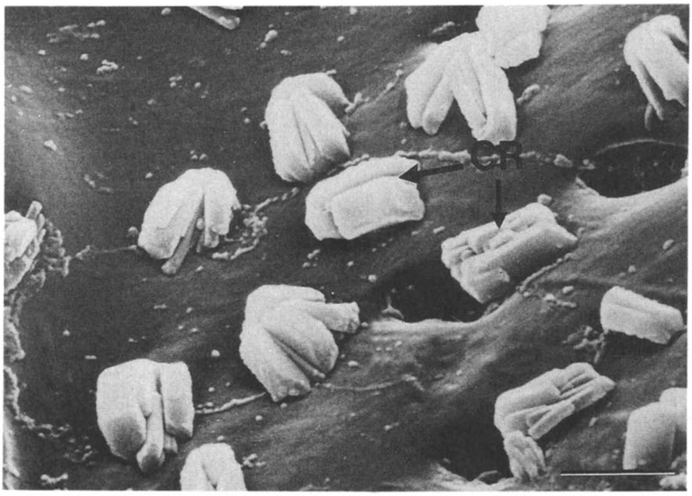
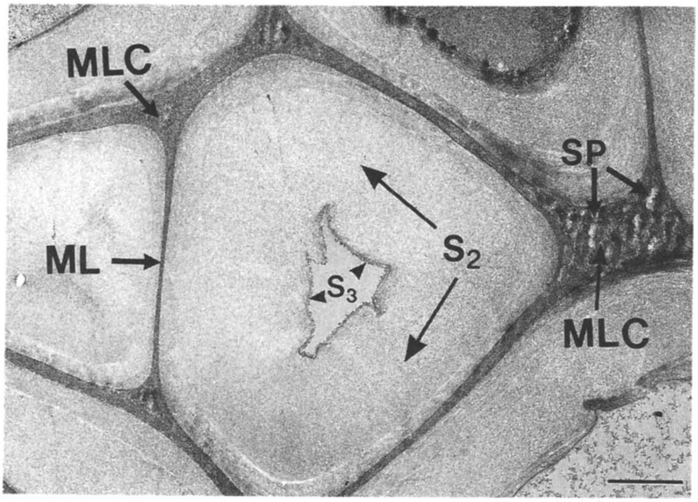


Figure 15. Characteristic crystal (CR) structures found associated with the vessel tyloses from Pistacia. *Bar: 0.5 μm.*



Figures 16. TEM photo showing the well-preserved fibrillar structure of fibers of Pistacia *from the Temple of Dhushares, Jordan. Wrinkling of the S_3 was frequently seen, suggesting some swelling of the S_2 cell-wall layers. Delamination at the cell-wall-layer interfaces, S_1–S_2 and S_2–S_3, was only rarely observed. Splitting (SP) during sectioning of the middle lamella cell corner (MLC, right) was more frequent. Bar: 2.0 μm.*

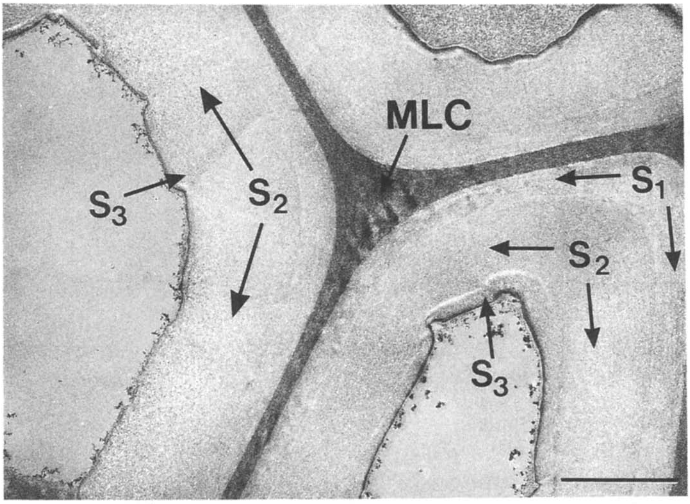


Figure 17. Same as Figure 16. Bar: 2.0 µm.

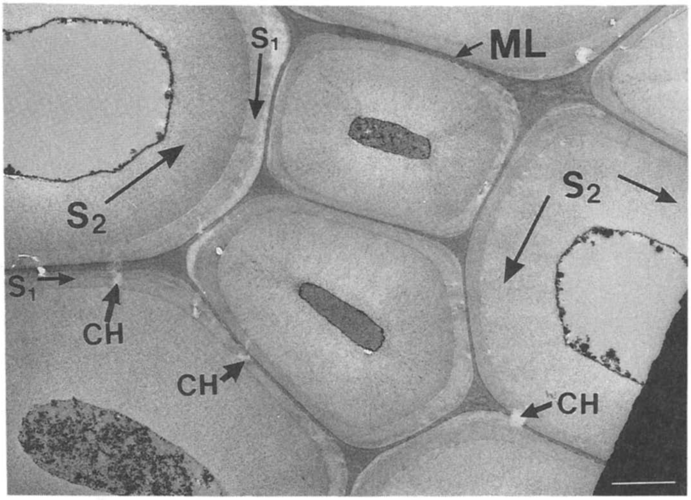


Figure 18. TEM photo showing the structure of fibers from the hardwood Acacia *(3250–3420 years old) from the Tomb of Tjanefer (Thebes). Checks (CH) were frequently noted within the middle lamella (ML) and S_1 cell wall regions and to a lesser extent within the S_2 itself. Bar: 2.0 µm.*

common furniture beetle (*Anobium punctatum*), and several different termite species. Powder-post beetles (*Lyctus* spp.) do not utilize the wood substance but feed on starch present in ray parenchyma cells. Some insects, like the carpenter ants (*Camponotus* spp.), excavate nests in wood but do not use it as a source of food.

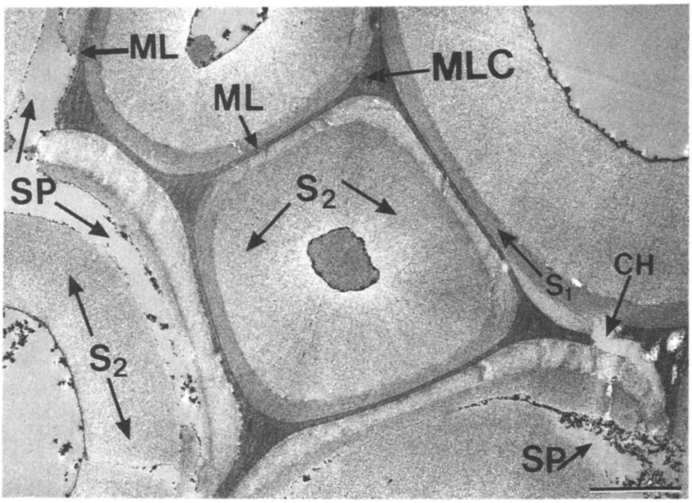


Figure 19. Similar features as shown in Figure 18. Checks (CH) and splits (SP) were frequently noted within the middle lamella (ML) and S_1 *cell wall regions and to a lesser extent within the* S_2 *itself. Bar: 2.0 μm.*

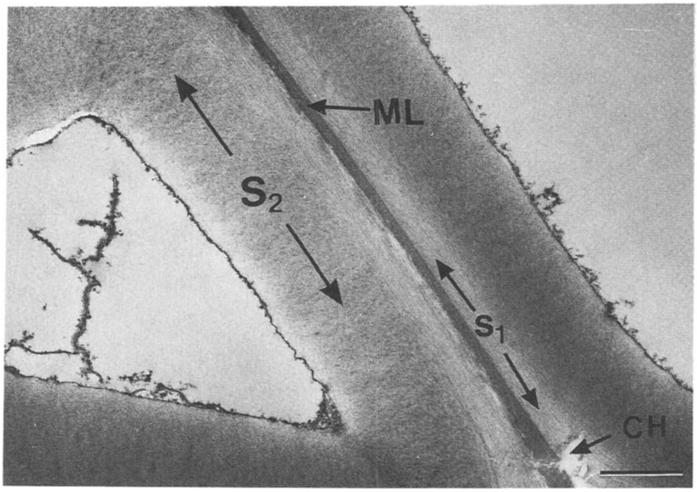


Figure 20. TEM photo showing the structure of Tamarix *fibers (3150–3400 years old) from the Tomb of Roma, Thebes. Unlike* Acacia, *checks (CH) within the secondary cell wall layers and middle lamella regions were less often seen. Bar: 2.0 μm.*

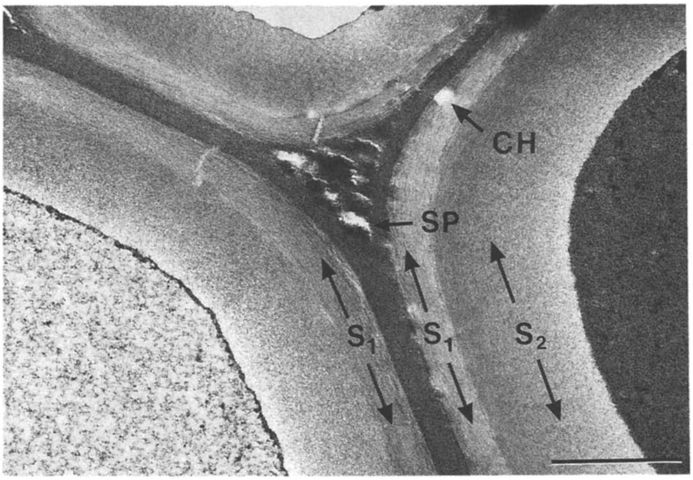


Figure 21. Closer view of sample shown in Figure 20. Unlike Acacia, *checks (CH) and splits (SP) within the secondary cell wall layers and middle lamella regions were less often seen. Splitting (SP) through sectioning of the middle lamella corners (MLC) was more frequently observed. Bar: 2.0 μm.*

In contrast to the small changes brought about by aging of dry wood, insect attack leads to macroscopically visible changes resulting from disintegration and removal of substantial quantities of wood substance. Various descriptive expressions (such as pin-holing, grub holes, powder-posting, and honeycombing) have been used for different types of insect attack in wood.

The damage caused by the longhorn beetle, the furniture beetle, and *Lyctus* species is characterized by extensive tunneling by their larvae throughout the wood structure (Figure 22). The tunnels vary in size, depending on insect species. They are characteristically filled with a flourlike powder, the disintegrated but unutilized wood substance (Figure 22). Extensive boring reduces the wood to a very fragile powdery structure. The surface of attacked timber is generally damaged by numerous exit holes of the adult insects.

Damage to wood structure by termites and carpenter ants has been described as honeycombing. The attack is caused by adult insects, not by larvae. Softer parts of the wood structure are generally preferred to harder and denser parts. This preference is particularly evident in softwoods, where the earlywood is preferentially degraded. The attack results in an extensive network of continuous galleries separated by thin fragments of wood (Figure 23). In contrast to the damage caused by beetle larvae, little or no wood powder can be found in the excavated parts.

Most types of dry timber are attacked by insects. Sapwood is preferred to heartwood, especially if the latter contains toxic extractives. Some ancient timbers have escaped attack by termites because of their content of extrac-

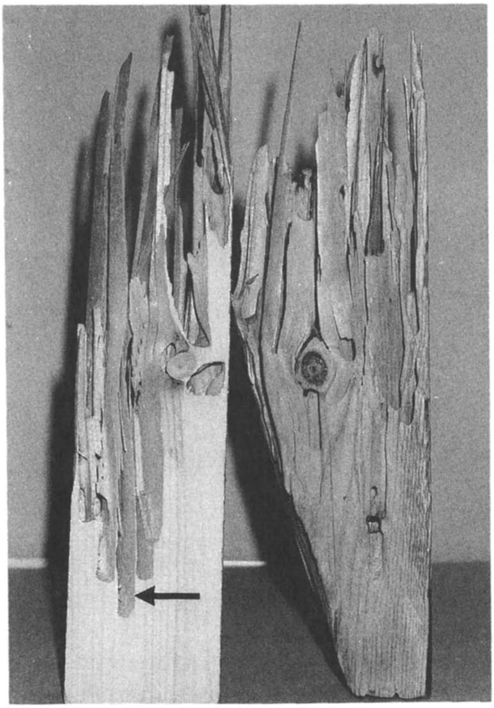


Figure 22. Extensive tunneling is caused by larvae of the furniture beetle. The surface of the timber is generally characterized by the presence of small exit holes that lead to larger tunnels filled with disintegrated powdery wood substance (arrows) resulting from larval activity.

tives, which have proven toxic to termites even today (*3, 4, 12*). Dry wood from ancient Egypt has presumably been protected against insect attack by an effective enclosure of the wood in the various pyramids and tombs.

Discussion

Studies on structural aspects of aging are very limited in the number of samples and number of timber species examined. The results available today indicate that only minor changes occur in dry wood, even at the ultrastructural level, after 3000–4000 years. However, there may be a variation in the effects of aging, depending on timber species. Chemical differences in timber composition (for instance, type and content of extractives) could possibly be important in the aging process.

Oxidation, hydrolysis, photodegradation, and other chemical changes are likely to play a role in the aging process. With the exception of photodegradation, the chemical changes are not likely to lead to a substantial removal of cell-wall substrate in localized areas, as is the case with attack

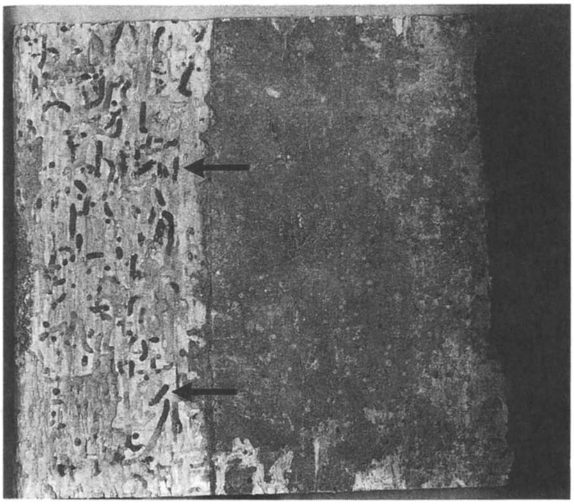


Figure 23. An extensive network of galleries (arrows) produced by carpenter ants during attack on dry wood.

by most wood-degrading microorganisms. These organisms cause thinning of cell walls; they produce bore holes and discrete holes or cavities within wood fiber walls that are easily detected even with an ordinary light microscope. Photodegradation may lead to fairly large voids in the wood microstructure (*13*, *14*). However, ultraviolet light will not penetrate more than 75 μm into the wood (*15*), so any effects will be limited to the outermost fibers. Photodegradation is important in the weathering process of wood (*see* chapter 11) but will most likely not, in the absence of abrasive activities, be significant in the aging process of dry wood. No reference to photodegradation has been found in earlier reports on ancient dry wood.

The action of other chemical changes will not be strictly localized to specific areas within the wood structure. They are more likely to affect all wall layers, although certain parts (like the middle lamella) could be more significantly affected. The chemical changes result in a slow degradation of wood components. The products of degradation will, in the absence of microbial consumption or leaching, still be present unless the conversion proceeds to CO_2 and water. Loss of birefringence of the cellulose indicates a reduction in crystallinity, as reported by Chowdhury et al. (*7*) and Borgin et al. (*8*). Depolymerization of cellulose will probably not significantly affect the visible structure of the cellulose microfibrils unless the degradation has proceeded very far.

Visible changes in wood structure will be small. This expectation is supported by the results of Borgin et al. (*8*) and the present studies. Degradation processes during aging of dry wood obviously lead to a certain weakening of the wood structure. This weakening is revealed by the cracks, delaminations, and loosening of wall layers as a result of the stresses involved during preparations for microscopy (i.e., trimming and sectioning).

In spite of limited research, it seems safe to conclude that the structure of dry wood, in the absence of insect pests, will be remarkably well maintained for at least 4000 years.

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Physical and Mechanical Properties of Archaeological Wood

Arno P. Schniewind

Forest Products Laboratory, University of California, Berkeley, CA 94720

The literature on physical and mechanical properties of archaeological wood is reviewed. The density of wood changes in response to agents of deterioration. Measurement of density and its relationship to other wood properties are discussed. Sorption characteristics are affected by the aging process and by deterioration. Deterioration in turn leads to changes in normal shrinkage and, eventually, the introduction of collapse shrinkage. Mechanical properties also change, and these changes are not usually distributed uniformly through the thickness of wood objects.

ARCHAEOLOGICAL WOOD IS DEFINED HERE as old wood that bears some traces of past cultural activity and that has been buried or otherwise removed from normal service for a period of time. This material may be divided into dry and waterlogged wood in recognition of the circumstances leading to its preservation. In both cases destruction by decay fungi has been avoided because an essential element required for their activity has been eliminated, namely, moisture in the case of dry wood and oxygen in the case of waterlogged wood. Aging processes for both dry and waterlogged wood are discussed in other chapters in this volume.

Subfossil or fossil wood is closely related to waterlogged archaeological wood. Fossil wood may have undergone the same aging and deterioration processes as waterlogged archaeological wood and differs only by the absence of any effects of cultural activity. Fossil wood tends to be older, and therefore it may be useful in extending the time scale beyond the points that are possible with archaeological wood. Collectively, the two types can be referred to as buried wood.

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The counterpart to dry archaeological wood is old historical wood, which covers a more limited time scale. Dry archaeological wood has not been investigated nearly as much as waterlogged wood because it is much rarer. A clear distinction must be made, however, because the deterioration processes are not the same. Waterlogged wood, for instance, typically will lose its hemicellulose fraction first, followed by cellulose, and finally by lignin, which is most resistant (*1*). In dry wood exposed to weathering, on the other hand, lignin will be degraded first (*2*). Dry wood taken from Egyptian pyramids has shown evidence of preferential degradation of lignin by oxidation (*3*).

Density

The density of archaeological wood will at best be equal to the values for recent wood; at worst, it will approach zero as the wood nears total destruction. In general, density will be somewhere between these limits. The degree to which the density deviates from values of recent wood is a measure of the extent of deterioration. However, it is not unusual to find archaeological wood that has significantly lower strength properties than recent wood without showing any reduction in density (*4*, *5*).

Aside from such initial influences as decay or mechanical damage during use, the deterioration of either dry or wet archaeological wood will be related to the specific conditions of its environment, as well as to the length of time it has been exposed to them (*5*). No doubt the archaeological wood that is found, whether in a very dry tomb in Egypt or as waterlogged wood that might be discovered any place in the world, represents a very biased sample in the sense that only the most resistant wood in the most favorable circumstances will be able to survive. For buried wood, survival appears to be most likely in peat bogs or heavy loam or clay soils (*5*).

Measurement of Density. Density of wood is expressed in a number of different ways, and a short explanation may be in order. The density of cell wall substance is generally assumed to be constant, so the density of a piece of wood obtained by measuring its overall weight and volume becomes a measure of wood porosity. Wood density is therefore related to many other wood properties. These relationships would become obscured if the moisture contained in wood were included in the measurements, especially in the case of wood above the fiber saturation point.

Some of the more common ways of expressing wood density are: (1) based on oven-dry weight and volume, where the question of moisture content does not arise; (2) based on weight and volume at 12% or some other level of moisture content, where the weight of the contained moisture is included; or (3) based on oven-dry weight and volume in the water-saturated or green condition, which is especially appropriate for degraded waterlogged wood that is prone to excessive shrinkage during drying. The last of these formulations, sometimes referred to as basic density, has been termed conventional density in International Standards Organization (ISO) standard 3131 (*6*).

All of these measures refer to wood as a whole. Thus, they include wood substance, any contained water, and also void space. Weight determinations are therefore easily made, but volume measurements are more difficult. The usual method is to use a water-displacement method that requires a wax coating when dealing with dry wood. A particular problem arises with severely degraded archaeological wood because it often shrinks excessively. Density based on oven-dry weight and volume, or based on weight and volume at 12% moisture content, is not very meaningful when the density measure is intended as an indicator of other wood properties. Density based on oven-dry weight and wet volume is therefore most appropriate. When determining conventional density, it is possible to dispense with volume measurements altogether by using the maximum moisture content method (*7*).

The maximum moisture content method is based on the assumption that the density of cell wall substance is constant for all species. A value of 1.5 g/cm^3 is usually assumed. Because waterlogged wood is by definition at or near its maximum moisture content, the method requires making certain that all air is replaced by water so that the wood is truly at its maximum moisture content. This step can be done by vacuum–pressure impregnation, after which the moisture content can be determined by oven-drying. The conventional density can then be calculated by:

$$G_f = (M_{\max}/100 + 1/1.5)^{-1}$$

where G_f is the conventional density in grams per cubic centimeter and $M_{\max}$ is the maximum moisture content in percent. Some evidence suggests (*8*, *9*) that the density of the cell wall substance of deteriorated waterlogged wood is lower than that of recent wood, but the differences are small. Especially in wood with very high maximum moisture content, such differences do not affect the calculation significantly.

The use of conventional density is to be preferred over density based on weight and volume at 12% moisture content (air-dry condition) because differences in shrinkage may obscure other effects. For instance, Kommert found that a series of oak finds from 700 to 1600 years old did not greatly differ in their air-dry density from recent wood, although strength was significantly reduced (*10*). This result suggests that there had been deterioration without mass loss. However, the same material was also found to shrink significantly more than recent wood (*11*). Thus, if the comparison had been made by using conventional density, the waterlogged wood would have certainly been found to have a significantly lower value than recent wood.

Measurements on archaeological live oak, for instance, indicated a mass loss of only 8–10% when the comparison was made with density values of oven-dried wood, whereas the mass loss was 26% when calculated from conventional density measurements (*12*). Other authors have expressed similar preferences for using conventional density (*1, 13, 14*).

Survey of Density Values. Taniguchi et al. (*8*) investigated the accessibility (by the hydrogen–deuterium exchange method) and the cell wall density of waterlogged Japanese red pine (*Pinus densiflorus*) dating to between 1192 and 1333 A.D. and of horse chestnut (*Aesculus turbinata*) from the period between the 2nd century B.C. and the 4th century A.D. In both species the accessibility was higher and the cell wall density lower when comparing waterlogged to recent wood. The effect was more pronounced in the Japanese horse chestnut, where the cell wall density as measured with the density-gradient column method was reduced from 1.44 to 1.38 g/cm^3 for the most severely affected portions. In another study (9), 16,000-year-old waterlogged Japanese ash (*Fraxinus mandshurica*) was found to have a cell wall density of 1.45 g/cm^3 in the more severely degraded part, as compared to 1.54 g/cm^3 for recent wood of the same species. Such reductions in cell wall density can be thought of as a result of degradation and leaching-out of carbohydrates from within the three-dimensional lignin network.

Oak is probably the most common species among archaeological finds. This fact is not surprising because oak is widely available, has excellent properties suitable for many uses, and is very durable. Table I shows a collection of density values for buried oak. For the most part the data are for European (white) oak. The ages of the samples as listed are averages when based on radiocarbon dating or minimum values for less precise determinations spanning centuries or millennia. Density values are not uniformly based, as they range from the density of oven-dried wood to conventional density, as indicated. Percentage residual density based on density of recent wood was calculated from values given by the original authors. Table II shows a similar collection of data for buried softwoods and hardwoods other than oak.

The data of Table I, for samples that range in age from 50 to 8500 years, clearly show that age alone is not a good indicator of the mass loss to be expected. This finding is also reflected to a more limited extent in Table II. Residual density values range from 20 to 140% for oak and from 18 to 113% for the other species. Archaeological wood might be higher in density than recent wood for several reasons. For instance, there is a natural variation in wood properties, and we are comparing specific archaeological samples to mean values of recent wood. Thus individual samples could show mass loss and still have a density higher than the average of recent wood. The sample of oak 1100 years old with a density of 872 kg/cm^3 is an example; it had unusually wide growth rings, which in oak generally means higher

Table I. Density of Buried Oak Wood

	Density			
Age, years	*Old wood, kg/m³*	*Residual,[a] %*	*Basis[b]*	*Ref.*
50[c]	767	95	3	49
300	410	75	3	3
330 sap	122	21	3	20
330 heart	462	80	3	20
440	265	49	3	41
440	397	74	3	41
570 sap	150	32	3	43
570 heart	504	94	3	43
700	547	88	2	10
800	661	106	2	10
800	681	109	2	10
810	490	89	3	1
810	530	96	3	1
900	660	102	1	4
900	760	111	2	38
1000 sap	130	20	3	3
1000 heart	620	91	3	3
1000	465	75	2	10
1100	636	102	2	10
1100[d]	872	140	2	10
1500	530	96	3	3
1600	200	36	3	1
1600	400	73	3	1
1600	600	96	2	10
3000	320	49	1	51
4700	665	96	2	52
4700	709	103	2	24
8500	650	97	1	39

[a] Density of old wood relative to that of recent wood.

[b] 1, Oven-dry (OD) weight and volume; 2, weight and volume at 12% moisture content (MC); 3, conventional density (OD weight and green volume).

[c] Live oak.

[d] Wide growth rings.

density. Next, a high ash content is found in much archaeological wood (*see* Chapter 5), which may be interpreted as mineral deposition in the early stages of silicification. With only one exception, where the residual density is 100% or more, the comparison was made on the basis of oven-dried or air-dried wood, where greater shrinkage of archaeological wood can obscure any mass loss that has occurred.

Table II has been divided into softwoods and hardwoods. Residual density values for softwoods tend to be higher than those for hardwoods, but considering the wide diversity of conditions under which these woods had been kept, a categorical conclusion regarding the relative resistance of the

Table II. Density of Buried Wood of Species Other Than Oak

Species	Age, years	Density		Basis[b]	Ref
		Old Wood, kg/m^3	Residual,[a] %		
Softwoods					
Abies alba	900	443	98	2	23
Cunninghamia lanceolata	2100	427	113	2	53
Juniperus communis	2000	540	113	2	53
Picea abies	900	220	58	3	3
Picea abies	100,000	230	61	3	3
Pinus spp.	900	490	100	1	4
Pinus sylvestris	300	240	56	3	3
Pinus sylvestris	900	280	65	3	3
Pinus sylvestris	900	450	105	3	3
Pinus sylvestris	900	260	60	3	3
Pinus sylvestris	10,000	450	105	3	3
Pseudotsuga menziesii	70	410	92	3	54
Taxus baccata	2400	520	72	2	53
Hardwoods					
Alnus rubra	2500	157	42	3	55
Betula odorata	8300	115	21	3	56
Betula spp.	590	94	19	3	20
Betula spp.	3000	190	31	1	51
Bischofia polycarpa	6570	421	90	3	53
Fagus spp.	570	150	27	3	43
Fraxinus mandshurica	16,000				9
Inner portion		400	58	2	
Outer portion		290	42	2	
Tilia spp.	3000	216	44	1	51
Ulmus spp.	900	410	64	1	4

[a] Density of old wood relative to that of recent wood.

[b] 1, OD weight and volume; 2, weight and volume at 12% MC; 3, conventional density (OD weight and green volume).

two groups is not justified. Values for the relatively resistant oak were not included in Table II. Some species of hardwood may be less resistant because of an initially high pentosan content (*15*). The sapwood of durable species such as oak is much more susceptible to degradation than heartwood, as are such nondurable species as beech and alder (*14*).

Sorption Characteristics

Among the major components of wood, hemicellulose is the most hygroscopic and lignin the least hygroscopic, with cellulose in an intermediate position (*16*). The normal pattern of deterioration in waterlogged wood is parallel in that hemicellulose is attacked first, followed by cellulose, and lignin is the most stable (*see* Chapter 5). Accordingly, one might expect that waterlogged archaeological wood with a high lignin content would be less hygroscopic than recent wood. Available data show that this is not the case and that the opposite may be true (*17*). The latter exception can be understood in terms of the increase in accessibility already mentioned and the breakup of the crystal structure in the remaining cellulose.

Dry wood appears to age differently. A study of a variety of species ranging in age from less than 1 year to 3700 years showed that there may be a decrease in hygroscopicity with age, but that the effect is small if it exists at all (*18*). Hinoki (*Chamaecyparis obtusa*) taken from a 1300-year-old temple did, however, exhibit much lower equilibrium moisture content (EMC) values than recent wood (*19*).

Figure 1 shows sorption isotherms for old deteriorated oak from the Bremen Cog and for recent oak. EMC values for recent oak are consistently less than those for old wood, the difference being greatest at relative humidity values greater than 80%. The fiber saturation point (EMC value at approximately 100% relative humidity) of the old wood was more than 50%, a result that explains why waterlogged wood has been found to begin shrinking at equally high moisture content levels (*17, 20*).

A similar sorption isotherm has been published for 2500-year-old waterlogged alder (*21*). EMC values were consistently about twice as great as comparable values for recent wood over the entire hygroscopic range. Additional data collected in Table III include EMC values at or near 100% relative humidity for fir, alder, and a series of oak finds. In many cases the residual density values are greater than 100%, probably because of enhanced shrinkage affecting the determination of air-dry density rather than a com-

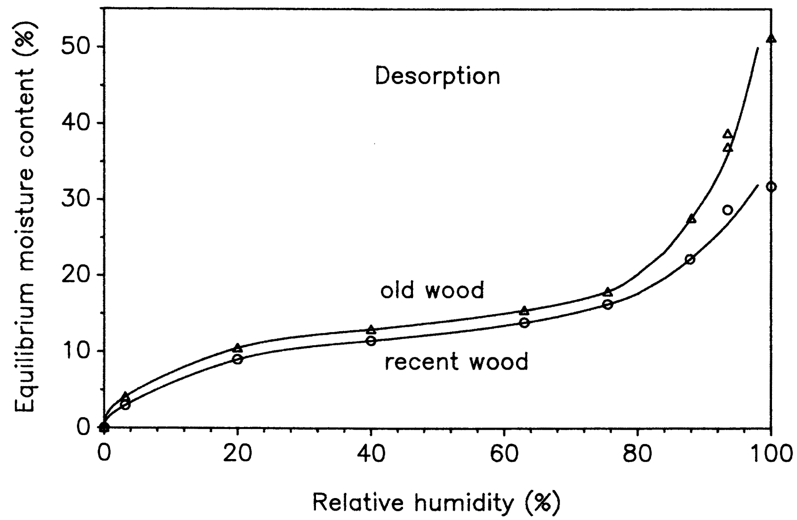

Figure 1. Desorption isotherms for old oak wood from the Bremen Cog and for recent wood. (Adapted from ref. 17.)

Table III. Sorption Characteristics of Buried Wood

		Density		*EMC at 98–100% RH*[c]		
Species	*Age, years*	*Residual,*[a] *%*	*Basis*[b]	*Old Wood, %*	*New Wood, %*	*Ref.*
Abies alba	900	98	2	26.8	23.2	23
Quercus spp.	570	94	3	52.0	32.0	17, 43
Quercus spp.	700	88	2	34.3	30.8	22
Quercus spp.	800	104	2	36.0	30.8	25
Quercus spp.	800	106	2	36.7	30.8	22
Quercus spp.	800	109	2	34.5	30.8	22
Quercus spp.	900	111	2	29.5	23.0	38
Quercus spp.	1000	75	2	36.4	30.8	22
Quercus spp.	1100	102	2	36.3	30.8	22
Quercus spp.	1100	140	2	38.7	30.8	22
Quercus spp.	1600	96	2	33.3	30.8	22
Quercus spp.	4700	103	2	32.0	30.8	24
Alnus rubra	2500	42	3	60.0	30.0	21, 55

[a] Density of old wood relative to that of recent wood.

[b] 1, OD weight and volume; 2, weight and volume at 12% MC; 3, conventional density (OD weight and green volume).

[c] RH is relative humidity.

plete lack of deterioration. However, it does indicate that the deterioration of most of the oak and the fir has not been nearly as severe as the old oak of Figure 1 and the alder (second and last entries, respectively, in Table III). Thus, most of the equilibrium moisture content values at 100% relative humidity are only slightly to moderately higher than those for recent wood. Although the authors concluded in most instances that the hygroscopicity of the archaeological wood was not significantly different from recent wood, in every instance the EMC values for the old wood are greater than for recent wood (*22–25*). The collective evidence therefore suggests that the hygroscopicity of buried waterlogged wood does increase, sometimes dramatically, but that the amount of increase depends significantly on the extent and probably also the mechanism of deterioration. Age alone has no discernible effect on changes in hygroscopicity in the series of oak finds ranging as far as 4700 years old (Recent Stone Age).

Shrinking and Swelling

Little appears to be known regarding the shrinkage of archaeological wood stored under dry conditions. Hinoki from historical structures in Japan up to 1300 years old showed a significant decrease in tangential shrinkage with age (*19*), but the findings on hygroscopicity of other old timbers would suggest little if any change in shrinkage coefficients over time (*18*).

Shrinking and swelling are of particular concern in the case of old waterlogged wood because it often shrinks significantly more upon drying than recent wood. This shrinking can result in the virtual destruction of objects during drying, because the wood may be too weakened to resist drying stresses adequately. Serious fractures, severe distortions, and collapse can therefore occur. The safe drying of waterlogged wood objects is one of the most challenging problems in the conservation of archaeological wood artifacts (*26*).

In recent wood, shrinkage during drying does not begin until the free water contained in the cell cavities and capillary spaces has evaporated and the moisture content falls below the fiber saturation point, which is approximately equal to the moisture content in equilibrium with 100% relative humidity. Shrinkage thus results from the removal of the adsorbed water, also called bound water. Normal shrinkage does not occur uniformly, and this variation gives rise to stresses at several levels. The tendency to shrink with loss of bound water is greater perpendicular than parallel to the cellulose microfibrils. Stresses develop between individual cell wall layers because of differing microfibril orientation.

Stresses may also occur because rays restrain radial shrinkage of other tissues, or because low-density, low-shrinkage earlywood is dominated by high-density, high-shrinkage latewood. These and other morphological factors, such as differences in structure and composition of radial and tangential cell walls, are responsible for shrinkage anisotropy and warping. Stresses can occur if these are prevented from taking place freely. Finally, drying will always proceed from the outside of an object, so that there will be stresses between the surface layers and the interior (*27*).

Healthy recent wood generally has sufficient strength to withstand the various drying stresses with no more than moderate changes in dimension and shape and without excessive checking, provided there is some reasonable control of drying conditions. In severely deteriorated waterlogged wood, two key changes lead to excessive shrinkage and fracturing, no matter how much care is taken in drying.

One of these changes is that the degradation of the carbohydrates is accompanied by a reduction of the crystallinity of the remaining cellulose. Reduced crystallinity not only leads to increased hygroscopicity, but it also allows shrinkage parallel to the cellulose microfibrils. The proportionally greatest increase in shrinkage is therefore in the direction parallel to the grain (*26*).

Second, the strength of the cell walls has also been reduced, and they are therefore less resistant to drying stresses. In particular, cell walls may have become so thin and weak that they can no longer resist the surface tension of receding free-water columns in the cell cavities and thus they collapse. The effect is most pronounced in the tangential direction, where shrinkage of as much as 65% has been observed in waterlogged beech (*17*).

Shrinkage or swelling data for the three principal directions of buried wood, as well as comparative values for recent wood, have been collected in Table IV. Recent wood values were taken from the publications cited, and no attempt was made to provide recent wood values when not provided

Table IV. Shrinkage or Swelling of Buried and Recent Wood

			Shrinkage or Swelling, %							
			Old Wood			*Recent Wood*				
Species	*Age, years*	*Residual Density,*[a] *%*	*T*[b]	*R*	*L*	*T*	*R*	*L*	*Basis*[c]	*Ref.*
Abies alba	900	98	10.4	4.5	1.0	8.6	3.9	0.7	3	23
Acacia spp.	30,000	–	9.6	7.2	4.6	–	–	–	3	57
Acer spp.	–	–	36.2	14.6	7.1	–	–	–	2	48
Alnus spp.	–	–	45.4	20.7	6.3	–	–	–	2	48
Betula odorata	8300	21	67.2	32.3	15.6	–	–	–	1	56
Betula spp.	–	–	47.5	24.9	7.9	–	–	–	2	48
Bischofia polycarpa	6570	90	8.4	4.8	–	8.1	4.5	–	2	53
Fagus spp.	570	27	67.5	8.5	16.0	12.0	6.0	0.3	2	43
Fraxinus spp.	–	–	32.1	12.5	6.1	–	–	–	2	48
Gliricidia spp.	1700	–	33.0	33.0	13.0	–	–	–	1	58
Picea abies	900	58	8.4	4.6	–	4.6	2.2	–	1	3
Picea abies	100,000	61	5.7	4.4	–	4.6	2.2	–	1	3
Picea spp.	–	–	26.0	13.0	6.0	–	–	–	2	59
Pinus sylvestris	300	56	5.6	3.1	–	4.8	2.6	–	1	3
Pinus sylvestris	900	65	4.4	2.8	–	4.8	2.6	–	1	3
Pinus sylvestris	900	105	4.6	2.0	–	4.8	2.6	–	1	3
Pinus sylvestris	900	60	5.6	2.6	–	4.8	2.6	–	1	3
Pinus sylvestris	10,000	105	7.6	4.8	–	4.8	2.6	–	1	3
Quercus spp.	300	75	20.0	6.2	–	5.3	3.0	–	1	3
Quercus spp.	570	94	20.0	9.5	–	10.6	4.8	0.4	2	43
Quercus spp.	570	32	58.5	18.5	11.5	9.4	4.0	0.4	2	43
Quercus spp.	700	88	12.4	7.1	1.0	7.9	4.0	0.6	3	9
Quercus spp.	800	104	15.1	8.0	0.7	7.9	4.0	0.6	3	25
Quercus spp.	800	106	15.1	8.0	1.0	7.9	4.0	0.6	3	9
Quercus spp.	800	109	11.9	6.4	0.9	7.9	4.0	0.6	3	9
Quercus spp.	900	111	20.8	11.5	–	11.3	5.3	–	3	38
Quercus spp.	1000	20	62.2	16.4	–	5.3	3.0	–	1	3
Quercus spp.	1000	75	13.0	6.9	4.0	7.9	4.0	0.6	3	9
Quercus spp.	1000	91	17.1	6.8	–	5.3	3.0	–	1	3
Quercus spp.	1100	102	13.8	9.3	1.2	7.9	4.0	0.6	3	9
Quercus spp.	1100	140	24.9	9.1	1.1	7.9	4.0	0.6	3	9
Quercus spp.	1500	96	15.8	6.6	–	5.3	3.0	–	1	3
Quercus spp.	1600	96	16.0	7.8	1.3	7.9	4.0	0.6	3	9
Quercus spp.	4700	96	11.9	8.0	0.5	8.9	4.3	0.4	1	52
Quercus spp.	4700	103	12.3	5.9	1.0	7.9	4.0	0.5	3	24
Quercus spp., H	–	40	33.0	10.0	10.0	10.6	4.8	0.4	2	59
Quercus spp., H	–	41	47.0	11.0	13.0	10.6	4.8	0.4	2	59
Quercus spp., S	–	24	47.0	14.0	12.0	9.4	4.0	0.4	2	59
Tilia spp.	–	–	71.4	25.8	9.0	–	–	–	2	48
Ulmus spp.	–	–	38.9	13.5	6.9	–	–	–	2	48

[a] Density of old wood relative to that of recent wood.

[b] T, tangential; R, radial; L, longitudinal.

[c] 1, shrinkage from waterlogged to air-dried; 2, shrinkage from waterlogged to oven-dried; 3, swelling from oven-dried to 100% RH.

or to reconcile differences in recent wood values for the same genus. Values for *Bischofia polycarpa* were calculated from shrinkage coefficients by assuming a fiber saturation point of 30%.

Table IV shows that the old wood, with the exception of two Scots pine finds, always shrinks more than recent wood. Age alone does not emerge as a sole factor by which increases in shrinkage can be estimated. Increases in longitudinal shrinkage are most dramatic, with a number of observations of more than 10% shrinkage, yet the shrinkage of recent wood does not exceed 0.6%. Although the radial and tangential shrinkage values of old wood can also increase substantially, the increase is not in the same proportion. As a result, the degree of shrinkage anisotropy of the most severely deteriorated buried wood is substantially reduced. Some samples show a ratio of tangential to longitudinal shrinkage of little over 3, but a factor of at least 10 is characteristic of recent wood. These observations are consistent with loss of cellulose and decrystallization of the remaining cellulose, as the physical organization of the semicrystalline microfibrils is the principal factor determining the anisotropic nature of wood (28).

The largest shrinkage values in Table IV are associated with low values of residual density. Increases therefore appear to be related to the degree of deterioration. This cannot be a simple linear relationship of direct proportionality. Even old wood with little or no apparent mass loss (residual density values of about 100%) can exhibit significant increases in shrinkage. De Jong (29) found that the longitudinal and tangential shrinkage of waterlogged oak was related linearly to maximum moisture content.

Figure 2 is a plot for volumetric shrinkage of waterlogged oak (*1*). It shows that at the same maximum moisture content level (indicating equal values of conventional density and thus no mass loss), the waterlogged wood nevertheless would have more than twice the shrinkage of recent wood. Although there may have been no net mass loss, some wood substance could

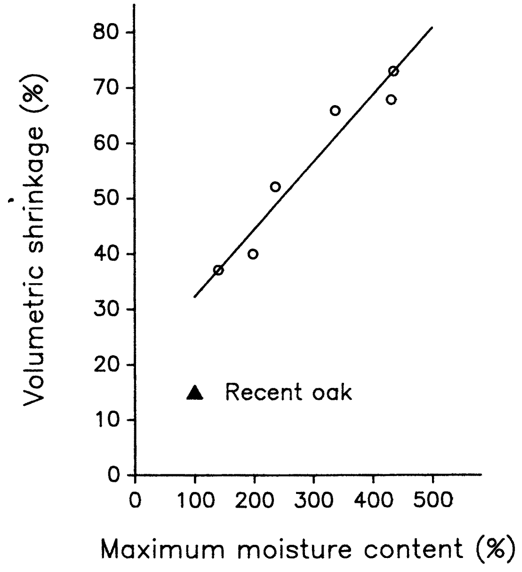

Figure 2. Volumetric shrinkage of archaeological oak wood as a function of maximum moisture content. (Adapted from ref. 1.)

have been lost with simultaneous compensation by the deposition of minerals. In either case, structural changes do occur.

The data of Table IV were used to calculate a shrinkage (or swelling) ratio by dividing tangential, radial, and longitudinal shrinkage values of old wood by the respective value for recent wood. A shrinkage ratio of 2 thus indicates a doubling of shrinkage of the archaeological over the recent wood. The results have been plotted in Figures 3, 4, and 5.

There is considerable scatter in the data, as is hardly surprising because of the variety of species, conditions of exposure, manner of measuring the shrinkage, and the different bases for expressing density. The trend for increasing shrinkage ratio with decreasing residual density (increasing mass loss) emerges quite clearly, particularly for longitudinal shrinkage (Figure 3) where the increase is the greatest, followed by tangential shrinkage (Figure 4), and finally radial shrinkage (Figure 5), where the effect is the least.

Mechanical Properties

The effect of aging on mechanical properties of dry wood has received relatively scant attention. In general, dry conditions of storage or use inhibit most agents of deterioration. Except in the case of insect attack, no major changes in mechanical properties are expected under dry conditions (*14*). Tests of old teak wood that had been in service in a Buddhist monastery for 1800 years showed it to be 14% higher in density and 47% higher in compression strength parallel to grain (hereafter simply referred to as compression

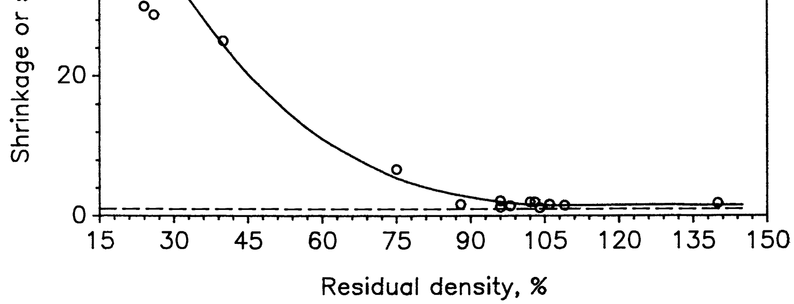

Figure 3. Longitudinal shrinkage ratio of old and recent wood as a function of residual density, from the data of Table IV.

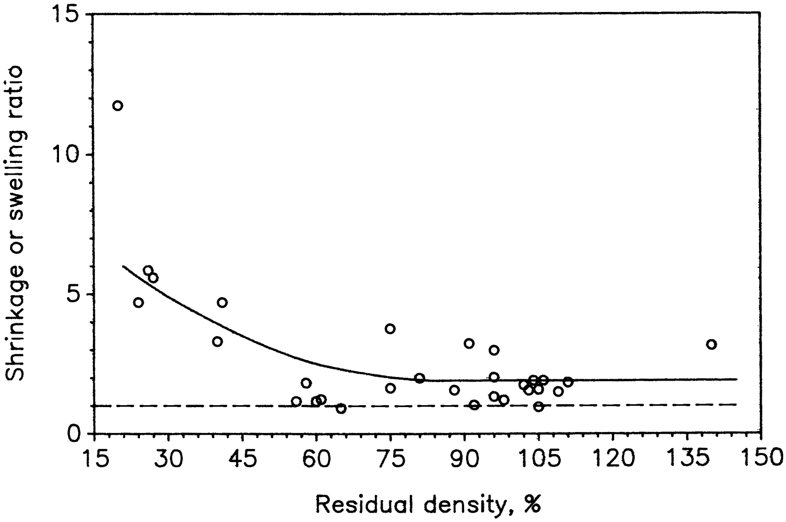

Figure 4. Tangential shrinkage ratio of old and recent wood as a function of residual density, from the data of Table IV.

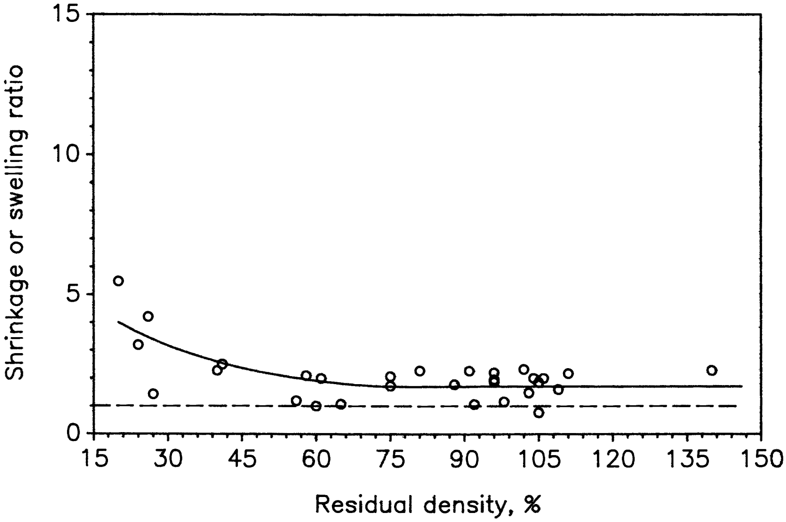

Figure 5. Radial shrinkage ratio of old and recent wood as a function of residual density, from the data of Table IV.

strength) than recent wood (*30*). This case is clearly another example of the dangers inherent in comparing individual samples of old wood to species averages of recent wood, and thus does not allow any conclusions beyond noting that it is consistent with the expectation of little deterioration.

Tests of a 500-year-old sample of *Pterocarpus* spp. taken from an altar, on the other hand, indicated some reduction in bending strength and stiffness and possibly also in compression strength, although the data were somewhat inconsistent (*31*). More extensive tests were made of samples from a roof beam of *Picea abies* that had been in service for 300 years. After adjustment for differences in density, the old wood had the same or slightly higher tensile, compression, and bending strengths and somewhat lower impact bending strength than recent wood (*32*).

A sample of *Pinus pinea* from the Pyramid of Teti, dating to 2350 B.C., was compared with recent wood of the same species. When density differences are taken into account, the old wood had about the same bending strength and stiffness in compression parallel to the grain. Bending stiffness and maximum crushing strength were higher in the old wood. Work to maximum load was lower in static bending and higher in compression parallel to grain when density differences were taken into account. The sum total of the results showed that the wood was remarkably well preserved (*33*).

Results of systematic studies by Kohara (*19*, *34*) are summarized in Figure 6. They show that in the case of hinoki, a softwood, bending and compression strengths increase over the first 200–300 years of exposure and

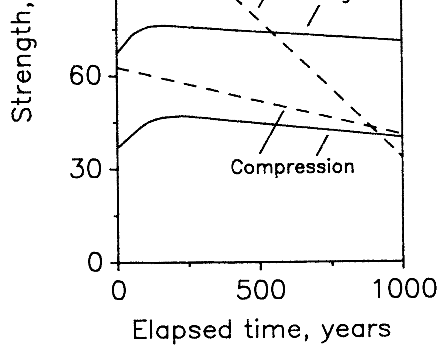

Figure 6. Bending and compression strength of hinoki and keyaki as a function of time during dry exposure. (Adapted from ref. 19.)

subsequently decrease gradually, so that after about 1500 years the strength is again the same as it had been in the beginning. He attributed this behavior to initial increases in cellulose crystallinity, a process that becomes complete in about 300 years. A continual degradation of carbohydrates is responsible for the subsequent decrease in strength. Keyaki, a hardwood, did not show any initial increases; it degraded continuously and at a greater rate than the hinoki. Measurements of the same hinoki timbers used by Kohara gave a plot of the piezoelectric modulus over time very similar to those for strength (*35*, *36*).

Table V lists values taken from the literature of maximum crushing strength in compression parallel to the grain, and static bending strength and stiffness (modulus of rupture and modulus of elasticity) of buried waterlogged wood. In virtually every case, values of residual strength are lower than those of residual density. Therefore, strength losses are not directly proportional to mass losses, and degradation of the quality of the remaining substance also takes place. The few exceptions are for material where there has been little or no apparent mass loss. It may be tempting to attribute the disproportionate strength losses to the accumulation of mineral deposits, which would contribute to density but are not likely to have major effects on strength. However, the deposits do not occur in quantities sufficient to explain more than a fraction of the additional losses in strength.

Early degradation of carbohydrates might indicate that tensile strength and bending strength would be affected more than compression strength parallel to the grain. The data of Table V, however, show about the same residual strength values for compression and bending strength, amounting to an average of 53.2 and 51.4%, respectively (comparing only material where both tests were made). Modulus of elasticity and modulus of rupture values are reduced to about the same extent. The literature on the effects of early stages of decay also indicates that modulus of rupture and modulus of elasticity are affected about equally, but that the effect on compression strength parallel to the grain is less (*37*).

Buried oak 900 years old that was in an excellent state of preservation showed a relationship between density and compression strength that was the same for old and recent wood (*38*). Subfossil oak 8500 years old gave different results, the regressions of compression and tensile strength having about the same slope for subfossil and recent wood. However, the strength of the subfossil wood, which had an ash content of only 1.5%, was much less at equal levels of density (*39*). The data of Table V are plotted in Figures 7 and 8, showing the residual compression strength and residual modulus of rupture, respectively, as a function of residual density. The loss in strength is proportionately greater than the mass loss. The curves shown in the figures were drawn arbitrarily and forced through the point of 100% residual strength and density. The relationships are quite similar for both properties, and it does not appear that results were different for green or air-dried mate-

Table V. Compression and Static Bending Strengths of Buried Wood

				Compression, Parallel to Grain		Static Bending				
						MOR[b]		E[c]		
Species	*Age, years*	*Residual Density, %*	*MC*[a]	*Strength, MPa*	*Residual, %*	*Strength, MPa*	*Residual, %*	*Stiffness, GPa*	*Residual, %*	*Ref.*
Abies alba	900	98	AD	37.1	79	65.2	80	–	–	23
Abies spp.	17	97	AD	41.0	85	75.0	106	–	–	60
Acacia spp.	30,000	–	AD	67.2	71	54.9	29	–	–	57
Betula spp.	3000	31	AD	2.7	5	3.2	2	–	–	51
Bischofia polycarpa	6570	90	AD	34.0	75	66.1	72	6.90	79	53
Cunninghamia lanceolata	2100	113	AD	34.9	97	–	–	–	–	53
Fagus spp.	570	27	G	0.7	2	–	–	–	–	43
Fraxinus mandshurica	16,000	42	AD	11.8	24	11.8	9	0.98	7	9
Fraxinus mandshurica	16,000	58	AD	13.7	28	31.4	23	2.45	17	9
Juniperus communis	2000	113	AD	42.7	107	–	–	–	–	53
Picea spp.	17	98	AD	42.0	93	76.0	99	–	–	60
Pinus spp.	900	100	G	17.0	70	33.7	60	–	–	4
Pseudotsuga menziesii	70	92	G	18.2	77	39.6	76	8.87	75	54
Quercus spp.	330	71	G	16.8	57	34.3	58	–	–	50
Quercus spp.	570	94	G	24.5	66	32.6	49	4.41	45	43
Quercus spp.	700	88	AD	–	–	33.6	47	–	–	10

Quercus spp.	800	106	AD	–	–	74.9	105	–	–	10
Quercus spp.	800	109	AD	45.7	73	80.3	113	–	–	10
Quercus spp.	810	89	G	13.2	43	–	–	–	–	1
Quercus spp.	810	96	G	16.9	55	–	–	–	–	1
Quercus spp.	900	102	G	11.0	35	26.3	40	–	–	4
Quercus spp.	900	111	AD	65.7	112	–	–	–	–	38
Quercus spp.	1000	75	AD	–	–	15.6	22	–	–	10
Quercus spp.	1100	102	AD	–	–	58.2	82	–	–	10
Quercus spp.	1100	140	AD	37.9	60	89.0	125	–	–	10
Quercus spp.	1600	36	G	0.9	3	1.3	2	0.11	1	1
Quercus spp.	1600	73	G	3.8	12	4.3	7	0.83	10	1
Quercus spp.	1600	96	AD	–	–	47.2	66	–	–	10
Quercus spp.	3000	49	AD	9.6	16	2.4	3	–	–	51
Quercus spp.	4700	96	AD	38.5	65	71.0	81	–	–	52
Quercus spp.	4700	103	AD	33.3	56	34.4	47	–	–	24
Quercus spp.	8500	97	AD	44.9	79	–	–	–	–	39
Quercus virginiana	50	95	G	30.9	83	54.3	66	8.89	82	49
Quercus virginiana	240	75	G	13.9	37	33.9	41	5.84	54	12
Taxus baccata	2400	72	AD	33.5	50	–	–	–	–	53
Tilia spp.	3000	44	AD	–	–	2.5	2	–	–	51
Ulmus spp.	900	64	G	9.9	39	19.5	39	–	–	4

[a] Moisture content. AD is air-dry; G is water saturated. [b] Modulus of rupture. [c] Modulus of elasticity.

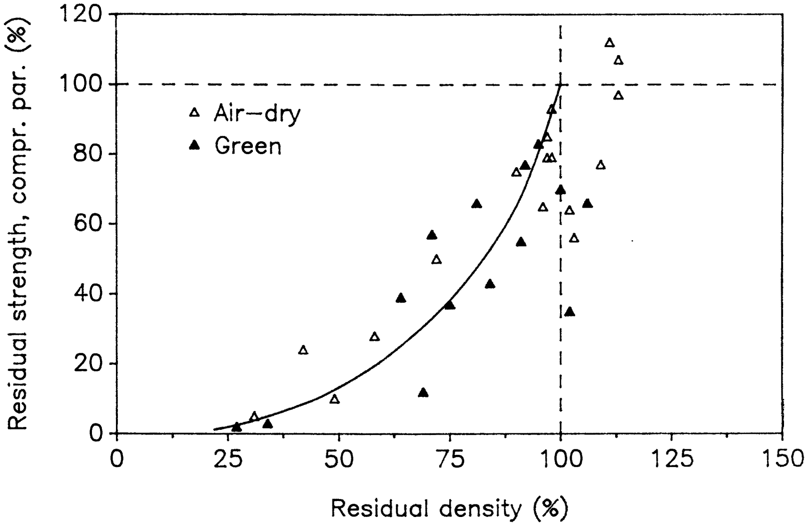

Figure 7. Residual compression strength parallel to grain as a function of residual density, based on data in Table V.

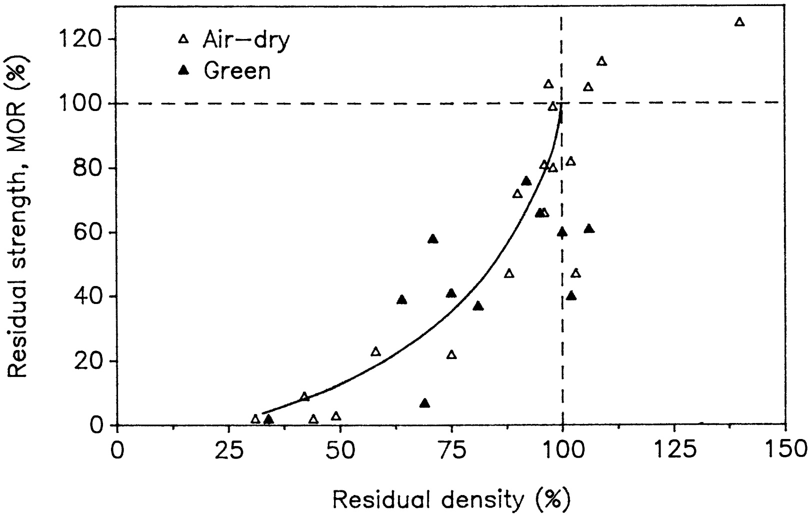

Figure 8. Residual bending strength as a function of residual density, based on data in Table V.

rial. The same type of relationship was found for more limited data of oak only (*1*).

Impact bending strength or shock resistance is recognized as being generally most sensitive to early stages of degradation, including decay (*37*) and thermal degradation (*40*). Available data on impact bending strength, along with a few other miscellaneous properties of waterlogged wood, are shown in Table VI. Although there are some very low values of residual impact bending strength, there are also some astonishingly high ones. Hoffmann et al. (*1*) attributed high impact bending strength values to low stiffness values, and increases in plasticity may contribute as well (*12*). The average residual impact bending strength value from Table VI is 68%, and the average of the matching residual bending strength values from Table V is an almost identical 67%. This agreement indicates that the mechanisms of fungal decay and thermal degradation are not the same as those affecting buried wood.

The deterioration experienced by archaeological wood is not generally uniform. Damage in the *Mary Rose* was distributed in patches (*41*), and it

Table VI. Residual Values of Impact Bending Strength and Other Properties of Buried Wood

			Residual Values Compared to Recent Wood			
Species	*Age, years*	*MC*[a]	*Density, %*	*Impact Bending, %*	*Other Properties, %*	*Ref.*
Abies alba	900	AD	98	71	–	23
Bischofia polycarpa	6570	AD	90	75	80 (shear)	53
Bischofia polycarpa	6570	AD	90	–	74 (hardn.)	53
Bischofia polycarpa	6570	AD	90	–	77 (comp. perp.)	53
Bischofia polycarpa	6570	AD	90	–	95 (tens. perp.)	53
Pseudotsuga menziesii	70	G	92	60	–	54
Quercus spp.	330	G	71	27	63 (hardn.)	50
Quercus spp.	700	AD	88	43	–	10
Quercus spp.	800	AD	106	86	–	10
Quercus spp.	800	AD	109	93	–	10
Quercus spp.	900	AD	111	–	115 (hardn.)	38
Quercus spp.	1000	AD	75	21	–	10
Quercus spp.	1100	AD	102	50	–	10
Quercus spp.	1100	AD	140	121	–	10
Quercus spp.	1600	AD	96	57	–	10
Quercus spp.	1600	G	36	3	–	1
Quercus spp.	1600	G	73	124	–	1
Quercus spp.	4700	AD	96	76	65 (tens. par.)	52
Quercus spp.	4700	AD	96	–	68 (hardn.)	52
Quercus spp.	4700	AD	96	–	95 (shear)	52
Quercus spp.	4700	AD	103	118	–	24
Quercus spp.	8500	AD	97	144	73 (tens. par.)	39
Quercus virginiana	240	G	85	–	46 (hardn.)	12

[a] Moisture content. AD is air-dry; G is water saturated.

is quite common for deterioration to be confined to surface layers of larger members (*1*, *17*). Figure 9 shows how the bending strength of Douglas fir of excavated pilings in the ground for 70 years undergoes substantial increases with distance from the exposed surface (*42*). Although in this case the changes were presumably all within the sapwood, similar differences between inner and outer portions of oak heartwood have also been found (*1*, *43*).

Nondestructive Evaluation

Treatments of deteriorated wood, which are often indispensable, especially for waterlogged wood, must be tailored to the particular properties and state of deterioration of each object (*44*). Therefore, it becomes highly desirable to find appropriate methods of nondestructive evaluation. Some preliminary experiments with ultrasonic pulse measurements appeared to be sensitive to the loss in degree of anisotropy accompanying loss of crystalline structure in cellulose (*45*). However, most published efforts appear to have been focused entirely on hardness measurements (*41*, *46–48*).

Hardness measurements are not always truly nondestructive, and much depends on the particular method chosen. A special method that does not cause any damage has been reported but not described in detail (*48*), but other methods may leave some dents or needle holes (*47*). The latter, although quite unacceptable in some cases, might be considered virtually nondestructive in particular situations, especially with larger objects. An example is the survey conducted on timbers of the *Mary Rose* using a needle impact hardness tester (Pilodyn instrument) (*41*).

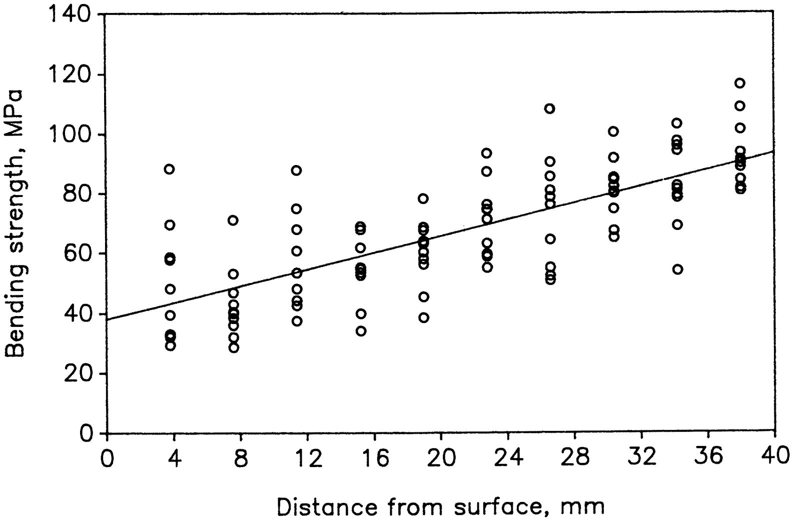

Figure 9. Bending strength of matchstick specimens as a function of distance from pile surface. (Adapted from ref. 42.)

Kazanskaya and Nikitina (*48*) found that their special hardness test showed good correlation with maximum moisture content and also with shrinkage of waterlogged wood. Masuzawa et al. (*46*) used a hardness test method intended for rubber testing and found it to be useful as a nondestructive method for waterlogged wood. Measurements on waterlogged Japanese horse chestnut (***Aesculus turbinata***) dating from the 2nd or 3rd century A.D. gave linear relationships between hardness and maximum moisture content and between radial and tangential shrinkage, as well as a semilogarithmic relationship between hardness and compression strength. All relationships are statistically significant at the 1% level. Maximum moisture content values ranged from 333 to 1053%, with an average of 643%. These values correspond to a range in conventional density from 89 to 250 kg/m^3 (recent wood about 440 kg/m^3), a good range of severely deteriorated wood. Figure 10 shows the plot of maximum moisture content as a function of hardness. There is much variability, but the relationship shows promise for using hardness measurements as a nondestructive method for assessing the degree of deterioration of waterlogged wood.

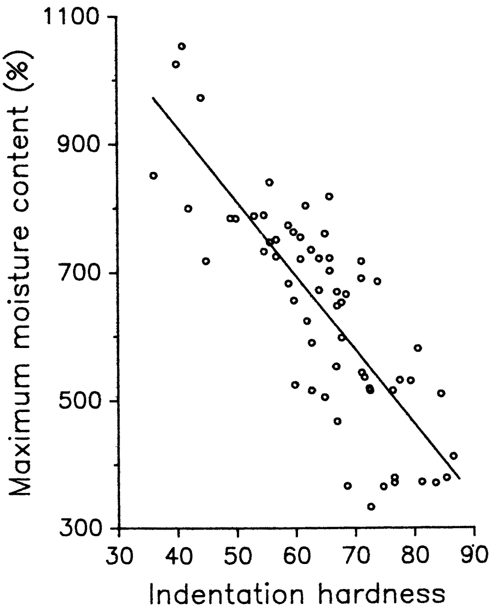

Figure 10. Maximum moisture content of Japanese horse chestnut as a function of hardness. (Adapted from ref. 46.)

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5

The Chemistry of Archaeological Wood

John I. Hedges

**School of Oceanography, WB–10, University of Washington,
Seattle, WA 98195**

Wood is composed of complex mixtures of polysaccharides and lignins whose compositions and relative abundances vary widely among tree and cell types, as well as within the ultrastructure of individual cells. The mechanisms and rates of degradation of these various wood components are dependent on environmental conditions and the microbial flora that they favor. A wide variety of chemical methods is available for characterizing the state of preservation of both archaeological and unworked wood, including determinations of elemental composition, ^{13}C NMR spectra, and chemical degradation products. In general, such chemical analyses of ancient woods show preferential loss of polysaccharides versus lignin, selective degradation of syringyl structural units within hardwood lignins, and elevated levels of nitrogen and ash.

THE AVAILABILITY AND UNIQUE PHYSICAL PROPERTIES of wood have made it the material of choice since antiquity for the fabrication of shelters, tools, transportation devices, and objects of art (*1*). Although wood is among the most resistant of all organic materials, its usual environmental fate is eventual decay. Wooden objects are preserved for long periods of time only under extremely cold, wet, dry, or anoxic conditions. Because wooden artifacts provide a rich and varied record of our early activities and technology, the characterization and preservation of archaeological wood is a subject of wide interest.

The appearance and physical properties of fresh and archaeological woods depend in large part on the chemical composition of the material. In turn, the chemistry of wood is intimately related to its structure. Although all woods comprise primarily polysaccharides and lignins, the types and

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amounts of these organic polymers vary taxonomically, as well as among the different kinds of cells and cell wall layers within a given wood. The microbial degradation of wood is fundamentally a chemical process that often leads to selective alterations of specific compounds and structures. Thus, to understand and treat wood, especially valuable archaeological samples, it is useful to have a basic understanding of the chemistry of this complex solid mixture.

This chapter reviews the chemistry of fresh wood and the compositional changes that it undergoes over time in natural environments. Particular attention is given to characteristic chemical alterations that occur during microbial degradation under conditions that favor different wood-destroying microorganisms. Although the immediate focus of this chapter is on archaeological wood, much of the information on degradation mechanisms and the attending chemical effects is drawn from laboratory and field studies of unworked samples. One of the main goals of this overview is to facilitate the exchange of insights and techniques on the chemistry of degraded wood between geochemists and archaeologists, who often face related problems in sample characterization and treatment.

Wood Chemistry

Sound wood can be thought of as a complex heterogeneous mixture of large organic polymers. Types of polymers and their relative abundance depend on both the cellular microstructures within which they occur and the kind of tree from which they come. The three main chemical constituents of sound woods are cellulose, hemicelluloses, and lignins. Although cellulose is a well-defined single polysaccharide, both hemicelluloses and lignins include a wide variety of individual polymer types. Figure 1 illustrates the fact that cellulose, hemicelluloses, and lignins together typically comprise 95 wt % or more of dry wood (2). Organic substances (such as fats, waxes,

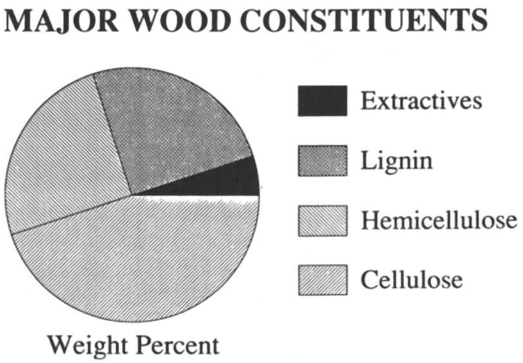

Figure 1. Weight percentages of cellulose, hemicellulose, and lignin in the different cell wall layers of a typical gymnosperm wood.

resins, and simple phenols) that can be extracted with nonpolar solvents ("extractives") account for all but about 1% of the remaining material. A portion of this last percent of wood is inorganic material, which usually is quantified as the "ash" remaining after the sample is heated to approximately 600 °C (*3*).

Cellulose. Cellulose, the main structural polysaccharide of plant cells, makes up approximately 40–45 wt % of wood (*4*). Cellulose is a polymer of D-glucose, a six-carbon reducing sugar. Individual cellulose molecules in wood contain approximately 7000–12,000 glucose residues ($C_6H_{10}O_5$), joined together in a chain by the elimination of one molecule of water between hydroxyl groups on adjacent monomers (*2, 4*). Individual cellulose molecules are on the order of 3–5 μm long (*2*). These molecules are linear as a result of hydrogen bonding between hydroxyl groups within the sugar sequence.

Hydrogen bonding also leads to strong associations among adjacent cellulose molecules, which organize along their long axes to form bundles known as elementary fibrils. These structural units contain approximately 40 cellulose molecules and have a diameter of 2–4 nm (*2, 4, 5*). Elementary fibrils appear to associate into larger parallel structures called microfibrils, which have diameters of 10–30 nm (*4*).

Glucose molecules in fibrils are so regularly aligned that about 70% of the structures are crystalline, as indicated by X-ray diffraction measurements (*4*). The extreme order and high degree of intermolecular association within cellulose fibrils impart great tensile strength and a low solubility in most solvents. The polymer is relatively resistant to hydrolysis and must be pretreated with 12 M sulfuric acid before it can be completely hydrolyzed to glucose by mineral acids (*6*).

Hemicelluloses and Pectins. The second major polysaccharide constituents of wood, hemicelluloses, typically account for 20–30% of the tissue mass. These polysaccharides, first distinguished from cellulose by their solubility in aqueous alkali, were called hemicelluloses because they were thought to be intermediates in cellulose biosynthesis (*7*). Although this hypothesis is not true, the name has persisted and has come to designate most cell wall polysaccharides except cellulose and pectin. Hemicelluloses, also called polyoses, differ from cellulose by having molecular chains that are often branched and much shorter—approximately 100–200 sugar residues per molecule (*7*). In general, hemicelluloses also have less-ordered structures and higher solubilities and are more readily hydrolyzed.

Hemicellulose compositions vary widely among tree species and wood structures. The different major wood hemicelluloses listed in Table I are named for the simple sugars from which they are formed. The major hemicellulose in softwoods is a glucomannan that contributes 10–15% of the wood mass. This polymer consists of an unbranched chain containing about one

Table I. Major Hemicellulose Components of Softwood and Hardwood

Hemicellulose Type	*Amount, % of Wood*	*Composition*		*Residues per Molecule*
		Units	*Molar Ratios*	
Softwoods				
(Galacto)glucomannan	10–15	Mannose	4	100
		Glucose	1	
		Galactose	0.1	
		Acetyl	1	
Galactoglucomannan	5–8	Mannose	3	100
		Glucose	1	
		Galactose	1	
		Acetyl	1	
Arabinoglucuronoxylan	7–10	Xylose	10	100
		4-*O*-MGA[a]	2	
		Arabinose	1.3	
Hardwoods				
Glucuronoxylan	15–30	Xylose	10	200
		4-*O*-MGA[a]	1	
		Acetyl	7	
Glucomannan	2–5	Mannose	1–2	200
		Glucose	1	

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[a] 4-*O*-Methylglucuronic acid.

glucose residue for every four mannose units. It also has small amounts of galactose, which sometimes leads to the designation (galacto)glucomannan.

Gymnosperm woods also contain a galactoglucomannan in which these three sugars occur in ratios of approximately 1:1:3. The galactose occurs as a single-unit side chain to a backbone chain resembling that found in the glucomannan (*2*). Both of the previous polysaccharides contain acetyl groups (one of which is ester) linked to every third or fourth of the backbone glucose and mannose units.

The final major hemicellulose is an arabinoglucuronoxylan, which accounts for 5–10% of softwood (*4*). This polysaccharide has a linear xylose chain onto which arabinose and 4-*O*-methylglucuronic acid units are individually attached. For every 10 xylose units, the molecule contains approximately one arabinose and two 4-*O*-methylglucuronic acid substitutions. The side-chain substituents make this hemicellulose susceptible to acid hydrolysis, but resistant to alkali-catalyzed degradation (*2*).

The major hardwood hemicellulose is a glucuronoxylan that, depending on the particular angiosperm species, constitutes 15–30% of the wood (Table I). The linear backbone of the molecule is formed of xylose units, approximately 70% of which contain *O*-acetyl groups. On average, about 1 in 10 xylose residues is substituted by a single 4-*O*-methylglucuronic acid unit. Although the side-chain linkages are resistant to hydrolysis by acid, the bonds between the backbone xylose units are not. The ester linkages of the acetic acid groups to the xylose chain are particularly sensitive to base hydrolysis and are slowly cleaved, even within the wood of living trees (*2*). The slow hydrolysis of acetic acid from hemicelluloses is thought to contribute toward the weak to moderately acid pH range (3.3–6.4) characteristic of water within most temperate woods (*4*).

Hardwoods also contain minor amounts (2–5%) of a glucomannan, which contains one to two mannose units for every glucose. In general, hardwood hemicelluloses are characterized by high concentrations of xylose and acetic acid structural units, whereas softwood hemicelluloses are relatively rich in mannose.

Pectins are a minor (<1%), but functionally important, polysaccharide component of wood. Pectins constitute the cell wall during early growth and consequently are later found within the middle lamella. Polymers of this type are made up of a backbone that contains predominantly galacturonic acid units, interspersed sometimes with the deoxy sugar, rhamnose (*4*). The carboxyl groups of the galacturonic acid units typically occur as methyl esters or calcium salts. Pectins also contain minor levels (10–25% total) of galactose, arabinose, xylose, and fucose, which are attached as side chains to the uronic acid backbone (*8*). As a class, pectins are characterized by high solubility in neutral water.

Lignins. Lignins are amorphous, cross-linked phenolic polymers that occur uniquely in vascular plants and comprise 20–30% of most wood. Lignins isolated from wood are polydisperse, with molecular weights in the range of thousands to hundreds of thousands (*4*). Lignins are produced almost exclusively from three cinnamyl alcohols, whose structures are shown in Chart I. These structural units have propylphenyl carbon skeletons and differ

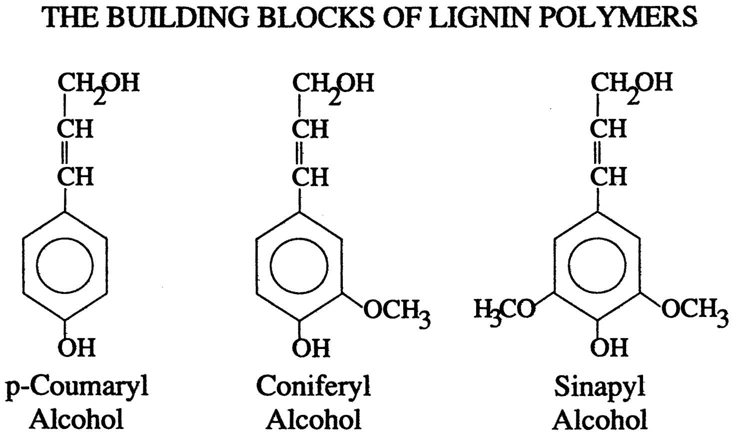

Chart I. The phenolic building blocks of lignin polymers.

from each other only in the number of methoxyl groups ($-OCH_3$) that are substituted on the benzene ring. During lignin synthesis, these monomers are converted to free radicals that couple randomly to form a structurally complex three-dimensional polymer.

The details of lignin structure are beyond the scope of this review. However, the polymer is held together by a wide variety of ether (C–O–C) and carbon–carbon bonds that are intrinsically strong and resistant to hydrolysis. Because of this stability, lignins can be isolated as the residue left when other wood components are dissolved in 72 wt % sulfuric acid. These polyphenols, however, are susceptible to oxidizing reagents and are readily removed from wood by bleaching.

Lignins can be divided into several categories, depending on the extent to which the three cinnamyl phenols in Chart I are incorporated into the final structure. This classification is related to both the type of tree and the type of tissue in which biosynthesis occurs. For example, guaiacyl lignin, which occurs in softwoods, is formed almost exclusively by polymerization of coniferyl alcohol. Gymnosperm reaction wood, which forms in regions of trees that are under compression, also contains relatively high concentrations of *p*-hydroxyl structural units (9) derived from *p*-coumaryl alcohol. In contrast, hardwoods are characterized by guaiacyl-syringyl lignin, which is made by copolymerization of coniferyl and sinapyl alcohols in average overall molar ratios of 4:1 to 1:2 (*2*). The relative proportions of syringyl structural units usually increase with the maturity of the wood (*4*).

The relative abundances of the three different types of lignin structural units have an important effect on the extent of cross-linking within the polymers. The free radical reaction by which lignin polymers are formed can lead to cross-linking on the benzene ring at unmethoxylated carbons that flank the carbon carrying the phenolic oxygen. As a result, lignin polymers containing guaiacyl and *p*-hydroxyl structural units have more cross-linking than those rich in syringyl monomers. For this reason lignin polymers in hardwoods have a lower structural integrity and typically are chemically degraded more easily than softwood lignins.

Chemical Architecture

The types and relative abundances of cellulose, hemicellulose, and lignin vary among wood cell types, between earlywood and latewood, and within individual cell walls. These distributional differences affect the relative resistance of the various components to degradation and are best worked out for spruce wood tracheids and birch wood fibers, which constitute roughly 95 and 80%, respectively, of the volumes of the corresponding woods (*2, 5*).

The relative abundances of the major components in different cell wall layers of spruce (*Picea abies*) tracheids are illustrated in Figure 2. The compound middle lamella (CML) contains 14% cellulose, 27% hemicellulose,

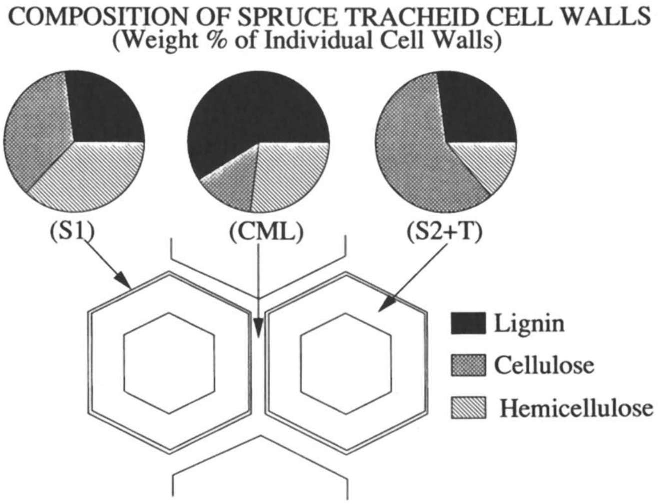

Figure 2. The percentages of cellulose, hemicellulose, and lignin in spruce earlywood tracheids. (Constructed from data in ref. 4.)

and 59% lignin (*4*). The cell corners themselves contain 85% lignin and are by far the most lignin-rich regions of the wood. The thin outer (S_1) secondary wall is composed of almost equal amounts of cellulose and hemicellulose (36%), along with slightly less lignin (27%). The inner (S_2) secondary wall and the tertiary wall that it surrounds are made of 59% cellulose, 14% hemicellulose, and 27% lignin. Thus, the highest levels of cellulose are found in this inner-wall layer, whereas lignin is concentrated in the outer- and between-wall regions. The compositions of earlywood and latewood are quite similar (*4*).

The percentages of total biopolymer that reside within the different cell wall layers are illustrated in Figure 3. These percentages depend both on the compositions described and on the relative volumes of the layers themselves. The relative volumes vary between earlywood and latewood, and will be discussed for earlywood. On the basis of microscopic observation (*4*), the CML region accounts for about 12% of the total tissue volume of spruce earlywood. This wall component contains approximately 4, 21, and 27%, respectively, of the total cellulose, hemicellulose, and lignin in spruce tracheids. The adjacent S_1 layer has a comparable volume and contains 9, 23, and 10% of the total cellulose, hemicellulose, and lignin, respectively.

The S_2 plus tertiary (T) cell wall layers account for about 75% of the tissue volume in earlywood and 80% in latewood. Because of its great thickness, the S_2+T layer contains the majority of the cellulose (87%), hemicellulose (56%), and lignin (63%) in earlywood tracheids. These fractions are even greater for latewood tracheids, which have thicker secondary walls. At the molecular level, arabinans and galactans are concentrated in the CML

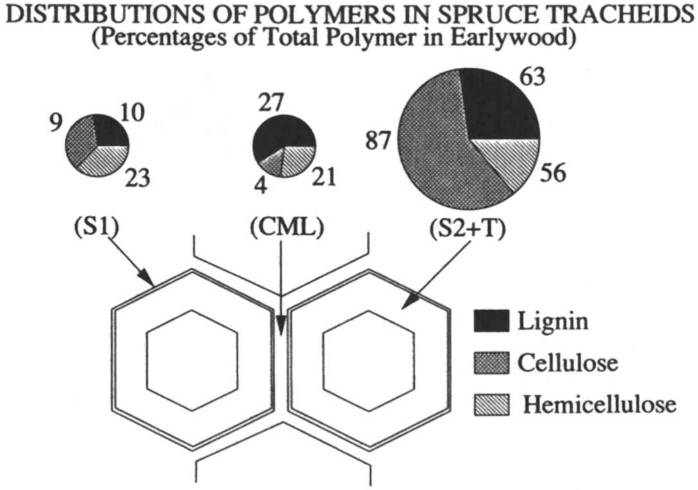

Figure 3. The percentages of the total cellulose, hemicellulose, and lignin that occur within the different cell wall layers of spruce tracheids. (Constructed from data in ref. 4.)

and S_1 layers of softwood tracheids and occur only at trace levels within the inner (S_2+T) cell wall region.

Chemical distributions within hardwoods are more complex because fiber, vessel, and ray cells contain varying levels of syringyl and guaiacyl lignin within their different wall regions. Although the distributions of polysaccharides are not as well known as for softwoods, appreciable information does exist for lignin. As illustrated in Figure 4, the CML between fibers of

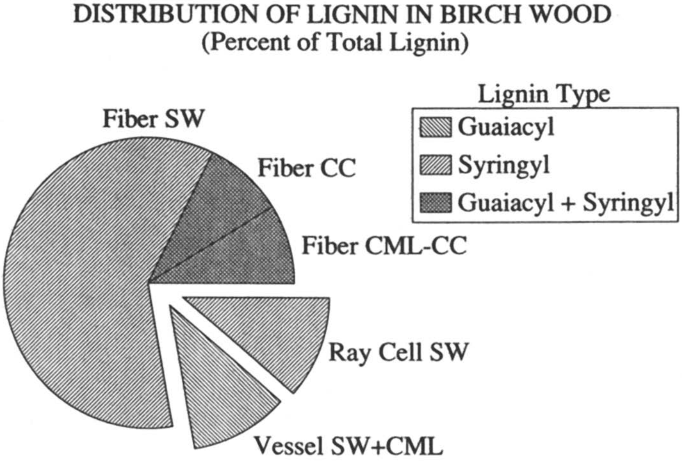

Figure 4. The distribution of lignin within different cell wall components of birch wood. (Constructed from data in ref. 4.)

birch (*Betula papyrifera*) wood is composed of 30–40 wt % of lignin that contains roughly equal concentrations of guaiacyl and syringyl units (*4*). The CML of fibers makes up roughly 5% of the total volume of the wood and contains 9% of its total lignin. The corners of fiber cells have almost twice the concentration of compositionally similar lignin within half the tissue volume and thus contain an additional 9% of the total lignin. The combined secondary walls of birch fiber cells contain only 15–20 wt % of lignin. This layer, however, accounts for almost 75% of the wood mass and as a result holds 60% of the total lignin polymer. Lignin within the secondary wall appears to be primarily of the syringyl type and thus is not extensively cross-linked (*see* previous discussion).

In birch wood, the major portion of the remaining tissue volume is contained within the secondary walls of vessels (9%) and ray cells (10%). Each structure contains 20–30 wt % lignin and holds about 10% of the total lignin in the wood. However, the lignin in the secondary wall (and CML) of vessels is of the guaiacyl type, whereas syringyl lignin predominates within ray cells. Thus, hardwoods are extremely heterogeneous with respect to their lignin distributions, both among and within their cell types.

Although the internal cell wall structures of different woods are not well understood, a variety of models have been proposed (*4*). These models vary in detail, but all have the cellulose fibrils surrounded by hemicellulose, which in turn is embedded within a lignin matrix. Hemicellulose apparently occurs as an interface between lignin and cellulose, but is covalently bonded only to lignin (2). Apparently cellulose and hemicellulose form before lignin is added in a space-filling manner (*4*).

The different main polymers in wood appear to have structural roles that are related to this microarchitecture. Cellulose, an intrinsically rigid crystalline material, provides the reinforcing framework of the cell walls. Theoretical treatments of stress–strain relationships in wood under load indicate that the stiffness of the material is imparted primarily by cellulose fibrils (*10*). The main function of hemicellulose and lignin is to buttress the fibrils. Degradation of any of these wood constituents results in a decrease in the strength of the material.

Chemical Patterns in the Degradation of Woods

Inspection of the global carbon cycle provides a useful backdrop for considering the natural fate of wood. Terrestrial ecosystems accumulate an extremely small fraction of the organic matter photosynthesized within them. Almost all (>99%) of the organic material produced on land is "remineralized" back to carbon dioxide and water within an average half-life of 10–100 years (*11*). The small fraction that escapes is exported by rivers to lakes and coastal marine zones, where a portion of the plant debris becomes waterlogged, sinks, and is incorporated in bottom deposits (*12*).

It is not surprising, therefore, that most archaeological wood is preserved in waterlogged form within peat and sedimentary deposits. The major exception to this scenario is material preserved in sheltered environments such as dry caves or structures where the moisture content of wood remains below the minimum (20–30% of oven-dry weight) necessary for microbial decay (*13*). The lifetime of wood in moist aerobic soils is comparatively short (*14*).

The relatively brief lifetime of wood in most natural environments largely reflects the destructive activities of several types of microorganisms, many of which are specialists in the breakdown of one or more of wood's polymer components. Although biologically mediated, the degradative processes are fundamentally chemical. An in-depth discussion of the different wood-degrading microorganisms and the morphological alterations they cause is presented in other chapters of this book. This chapter concentrates primarily on the characteristic chemical changes caused in wood by the four different broad classes of wood-destroying microorganisms: white-rot fungi, brown-rot fungi, soft-rot fungi, and bacteria.

Fungal Degradation. As shown in Figure 5a, white-rot fungi degrade all the major components of wood. Some species of this subdivision of *Basidiomycetes* preferentially destroy lignin and leave behind a wood residue enriched in polysaccharides, which are white. These obligate aerobes are in fact uniquely able to derive nourishment from the lignin component of wood, although polysaccharides also are always degraded (*16*). Wood decay by white-rot fungi is brought about by a suite of exoenzymes that cause pervasive wastage of the cell wall. The oxidative lignin-degrading enzymes create a variety of chemical changes, including decreases in methoxyl, phenolic, and hydroxyl contents, benzene ring cleavage, and side-chain oxidation (*17*). The remaining oxidized lignin is characterized by elevated oxygen content, greater concentration of carboxyl groups, and elevated yields of acidic chemical degradation products (*17*). In general, white-rot fungi efficiently remineralize intermediates produced in the degradative process so that high concentrations of altered material do not accumulate.

Brown-rot fungi preferentially degrade wood polysaccharides (Figure 5b) and leave behind an altered lignin-rich brown residue. Like white-rot fungi, brown-rot species are *Basidiomycetes* and obligate aerobes. Their major chemical effect on lignin is demethylation of aromatic methoxyl groups, along with limited cleavage and hydroxylation of the benzene ring (*17*). The lignin structure apparently remains relatively intact. In contrast, woods decayed by brown-rot fungi typically suffer extensive loss of hemicelluloses and drastic decreases in the molecular weight of the cellulose fraction. Polysaccharide degradation is apparently mediated in part by a very diffusive oxidative agent, which depolymerizes cellulose more rapidly than it can be remineralized (*16*). The net result is the accumulation of high relative concentrations of altered low-molecular-weight intermediates that exhibit high solubility in water, especially at elevated pH (*18*).

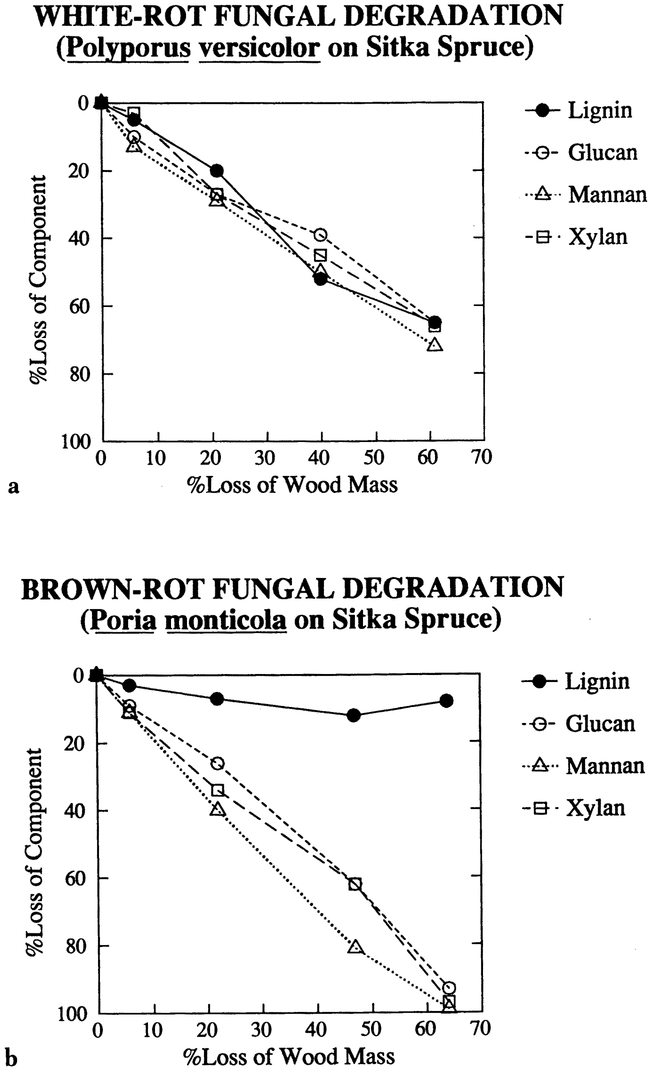

Figure 5. Trends in polysaccharide and lignin content during the degradation of wood by (a) white-rot and (b) brown-rot fungi. (Constructed from data in ref. 15.)

Soft-rot fungi have not been studied as much as the other wood-decaying types and appear to be variable in their patterns of degradative attack. In general, however, it appears that the *Fungi Imperfecti* and *Ascomycetes* that cause this characteristic type of surficial decay are able to degrade lignins as well as polysaccharides. Under most circumstances, soft-rot fungi preferentially attack polysaccharides, but not with pervasive depolymerization such as occurs during brown rot. Wood decayed by soft-rot fungi usually does not contain high concentrations of altered lignins or polysaccharides (*16*). Significantly, fungi that degrade woods in aerobic waters are primarily of the soft-rot type (*19, 20*).

Bacterial Degradation. Bacteria can measurably degrade wood and its lignin component under aerobic conditions (*4*). However, bacteria destroy wood much more slowly than fungi, which are the main agents of decomposition in terrestrial environments. In general, bacteria attack polysaccharides in strong preference to lignin and degrade hemicellulose faster than cellulose (*4*). The observation that delignification greatly accelerates the rate of weight loss from wood undergoing bacterial attack suggests that lignin may act as a physical barrier to degradative enzymes (*21*).

Bacteria are the only common microbial agents of wood degradation that are capable of functioning under anaerobic conditions. This distinction is important for the study of archaeological wood because much of it is recovered from sedimentary environments where anaerobic conditions have prevailed. Even if surrounded by oxygenated water, waterlogged wood should act both as both a sink and a transport barrier for O_2 and lead eventually to internal anoxia.

The rate of wood degradation by bacteria under anaerobic conditions is slow. Benner et al. (22) reported only 1.5 and 4.1% degradation after 246 days under strictly anaerobic conditions. Holt and Jones (23) demonstrated that test blocks of beech wood buried in anaerobic sediments are superficially degraded within months by a variety of rod-shaped bacteria. Others, however, report no measurable degradation of lignin in the absence of molecular oxygen. Little information has been published about the chemical composition of wood that has been degraded by known types of bacteria under anaerobic conditions (*24*).

Chemical Means of Characterizing Woods

Chemical analyses can be a useful tool for determining both the origin of wood and its state of preservation. In the case of archaeological wood, where the wood type tends to be evident morphologically, the degree and type of degradation that the sample has suffered are often the major consideration. Volumes have been written about different chemical methods for analyzing wood (2). This section will focus on selected chemical techniques that have been successfully applied to old woods by archaeologists or geochemists. The discussion will emphasize practical considerations that might help in the selection of analytical techniques for applications to specific types of archaeological wood samples.

Solubility. Solubility-based gravimetric quantification of total cellulose, hemicellulose, and lignin has been by far the most commonly used method for determination of the bulk composition of both archaeological and other old woods. These techniques were developed by wood chemists to isolate, characterize, and quantify the major components of sound wood (*3*). Although the details of the various isolation methods are beyond the scope of this review, the procedures are based on physical isolation via selective solubilizations of other components, followed by weighing of the residue.

Figure 6 illustrates a typical scheme involving removal of lignin from extracted whole wood by bleaching with sodium chlorite; the remaining holocellulose contains both cellulose and hemicellulose. Hemicellulose can then be preferentially extracted from holocellulose by base (4–5% NaOH), leaving behind a relatively pure cellulose residue. Hemicellulose can be determined by difference. Lignin is usually quantified as the residue left after all polysaccharides have been removed by strong acid. Klason lignin, for example, is the insoluble product from the treatment of sound wood with 72 wt % sulfuric acid (*9*).

Because of the extreme structural and chemical complexity of wood, none of the previous gravimetric analyses is completely accurate. Both losses of the desired isolate and contamination are constant problems (*3, 4*). Therefore, changes in chemical composition attending the environmental decomposition of wood can lead to artifacts in gravimetric analyses of the major constituents. For example, degradation of a structural polymer typically increases its solubility in acid and base (*25*), producing erroneously low values

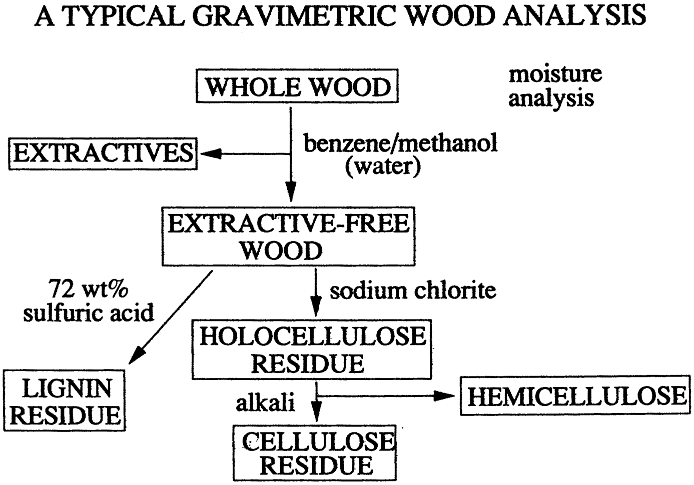

Figure 6. A scheme for the gravimetric quantification of the major wood components by preferential solubilization.

for residues and high results for any component, such as hemicellulose, that might be obtained by difference. In addition, ash levels typically are elevated in woods collected from soils and sediments (*25*, *26*) and can lead to gravimetric errors, especially if derived from recalcitrant mineral precursors such as pyrite. Direct weighing methods typically require gram-size samples so that transfer errors are minimized. Nevertheless, gravimetric analyses provide a comprehensive and direct assessment of the major wood constituents without the need for expensive instrumentation.

Elemental Composition. Elemental (CHN) analysis, a rapid and relatively inexpensive method for characterizing wood composition, has been widely applied to geochemical samples. Within a few minutes an organic elemental analyzer can directly measure the weight percentages of C, H, and N in a wood sample weighing less than 1 mg (*27*). If the ash and water content of the sample are known, then the weight percent of O can be estimated by difference. Ideally, the total measured H and O contents would be corrected for the moisture content of the wood. This approach provides four elemental concentrations that theoretically could be used to calculate the weight percentages of up to an equal number of wood constituents (*28*, *29*).

An application of elemental composition for the characterization of buried woods is illustrated in Figure 7 in the form of a van Krevelen plot of atomic H/C versus O/C ratios (*30*). In this case, buried alder and oak woods can readily be distinguished from their modern counterparts by the lower hydrogen and oxygen contents of the degraded samples. Plots of this type not only illustrate compositional differences, but also can provide crude reaction trajectories between the compositional points for fresh and degraded woods. These trajectories can be used to determine the average elemental composition of the organic material that is being removed or added (*29*).

In Figure 7, the compositional shift corresponds to preferential carbohydrate loss, which leaves a wood residue that is rich in lignin. Corrections for residual water, however, were not made for these samples and only qualitative interpretations are possible. Although nitrogen content is not employed in van Krevelen plots, it can be used to determine the maximum possible protein content of a degraded wood (*28*). Nitrogen also characteristically increases in degrading wood (*31*) and thus has possible application as a diagenetic indicator.

Isotopic Composition. Stable carbon isotope analysis recently has been shown to have application as an indicator of wood degradation (*32*). This method is based on the characteristically low abundance of ^{13}C (approximately 1% of all carbon) relative to ^{12}C in lignins versus polysaccharides (*33*). Preferential removal of polysaccharide carbon leaves a lignin-rich wood with a lowered overall $^{13}C/^{12}C$ ratio. Stable carbon isotope analyses are

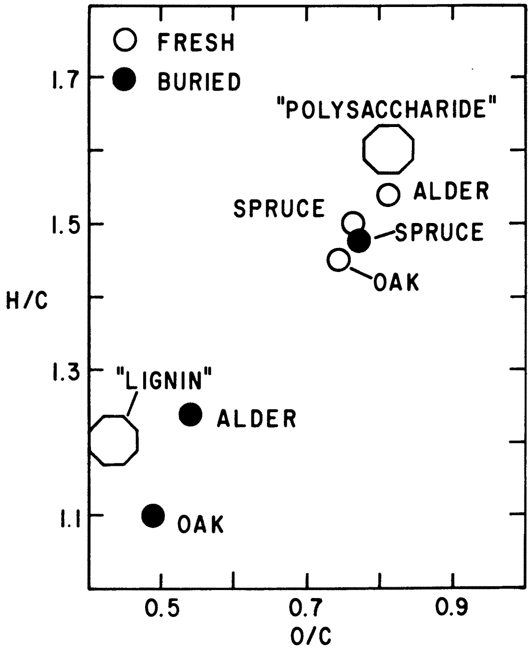

Figure 7. A van Krevelen plot of the elemental compositions of buried woods and their modern counterparts. (Reprinted with permission from ref. 30. Copyright 1985 Pergamon Press.)

possible with milligram-size samples at moderate expense. Because $^{13}C/^{12}C$ measurements often are done as a part of the ^{14}C dating procedure, this compositional information can easily be obtained for some archaeological samples. The main drawback of the technique is that it only offers a single-value characterization, which also should be determined for a fresh wood of the same type to account for species-related variability.

Nuclear Magnetic Resonance. Solid sample ^{13}C NMR is an exciting method for the comprehensive chemical analysis of whole wood. The measurement is made with a nuclear magnetic resonance (NMR) spectrometer, typically operated in the cross-polarization–magic-angle-spinning (CP–MAS) mode for solid samples (*34*). As illustrated in Figure 8 and Table II, this technique provides detailed analyses of the major carbon forms in compositionally complex materials such as wood. At least nine different major carbon types in wood can be distinguished in a typical CP–MAS ^{13}C NMR spectrum and related to different polysaccharide and lignin components. Diagenetic losses of wood components are clearly evident, as any major chemical transformations of the residual material would be. Under proper operating conditions, peak areas reportedly are proportional to the relative

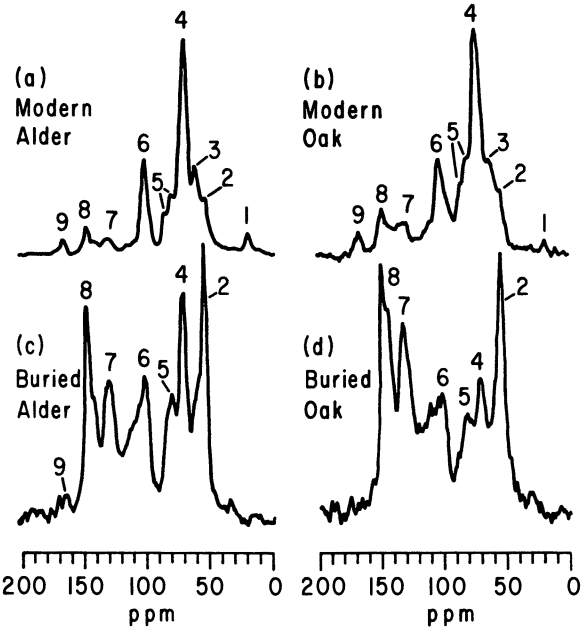

Figure 8. Comparative CP–MAS ^{13}C NMR spectra of two different fresh and buried woods. Assignments of the numbered peaks are given in Table II. (Reprinted with permission from ref. 30. Copyright 1985 Pergamon Press.)

Table II. ^{13}C NMR Peak Assignments for Figure 8

Peak	*Shift, ppm*	*Assignment*
1	20	$-C-^{13}CH_3$ (methyl in acetyl groups of hemicellulose)
2	50	$-O-^{13}CH_3$ (methoxyl in lignin and hemicellulose)
3	60–65	$-C-^{13}CH_2OH$ (C_6 of cellulose and hemicellulose)
4	70–75	$-C-^{13}CHOH-C$ (C_2, C_3, and C_5 of above)
5	80–85	$-C-^{13}CHOC-C$ (C_4 of above plus lignin side chains)
6	100–105	$-C-^{13}CH(OH)_2$ (C_1 of cellulose and hemicellulose)
7	125–135	(non-oxygen-substituted aromatic carbon in lignin)
8	145–155	(oxygen-substituted aromatic carbon in lignin)
9	165–170	$-C-^{13}CO_2R$ (uronic acids and acetate in hemicellulose)

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abundances of the corresponding carbon forms (*34*), which can be identified further by varying the spectral acquisition parameters in a technique called dipolar dephasing (*34*, *35*).

The nondestructive analysis can be made in a matter of minutes to hours on as little as 10 mg of sample. Analysis by CP–MAS NMR does not necessitate dissolution of the whole wood and thus avoids chemical artifacts that can accompany physical separation procedures. The major drawback of the method is that CP–MAS NMR spectrometers are relatively expensive and must be operated by someone who is aware of the potential biases of the measurement.

Chemical Degradation. Molecular-level degradative analyses are being applied increasingly in compositional studies of naturally degraded woods. This final category of analysis incorporates a wide variety of individual methods, many of which have been developed by wood chemists (*3, 9*). Only three techniques will be reviewed here: analysis of sugars by acid hydrolysis, characterization of lignin by CuO oxidation products, and wood compositional surveys by analytical pyrolysis.

Acidic Hydrolysis. Acidic hydrolysis of wood releases individual sugars that can be analyzed by a variety of techniques, including gas chromatography (GC) and high-pressure liquid chromatography (HPLC). For the most part, such analyses have been applied to the neutral sugars, which are more readily hydrolyzed and derivatized than acidic sugars such as uronic acids. A gas chromatographic method for the simultaneous analysis of neutral sugars and uronic acids, however, has recently been published (*36*).

Although many sugars occur in more than one polysaccharide, glucose is derived primarily from cellulose. Mannose and xylose are produced largely by hemicelluloses in softwoods and hardwoods, respectively (*2, 4*). Galactose and arabinose are released from both pectin and some hemicelluloses (*2*). Among the acidic sugars, 4-*O*-methylglucuronic acid characteristically occurs in hemicelluloses (Table I), and galacturonic acid is derived largely from pectin. The yields of different individual neutral sugars therefore can be used as indicators of the relative abundances and total amounts of the various major polysaccharides in a wood sample (*3, 30, 37, 38*).

Such distinctions among cellulose, hemicellulose, and pectin can be especially useful in determining the sites and mechanisms of decay. The major drawbacks of all methods for direct monosaccharide analyses are that they are somewhat tedious and that careful attention must be given to calibrations and overall hydrolysis and recovery corrections if accurate yields are to be determined (*38, 39*).

CuO Oxidation. CuO oxidation analyses have been employed for decades in structural studies of lignins (*9*) and now can be made with as little as 10–20 mg of whole wood (*40*). This relatively clean degradative technique, carried out at elevated temperatures in basic solution, releases a reproducible fraction of the total lignin in the form of simple phenols whose structures are shown in Chart II. These phenols are amenable to analysis by gas chromatography (*40*) and a variety of other methods. The CuO reaction products retain the ring methoxylation patterns of the lignin precursors shown in Chart I and thus clearly distinguish *p*-hydroxylphenyl, guaiacyl (vanillyl), and syringyl structural units.

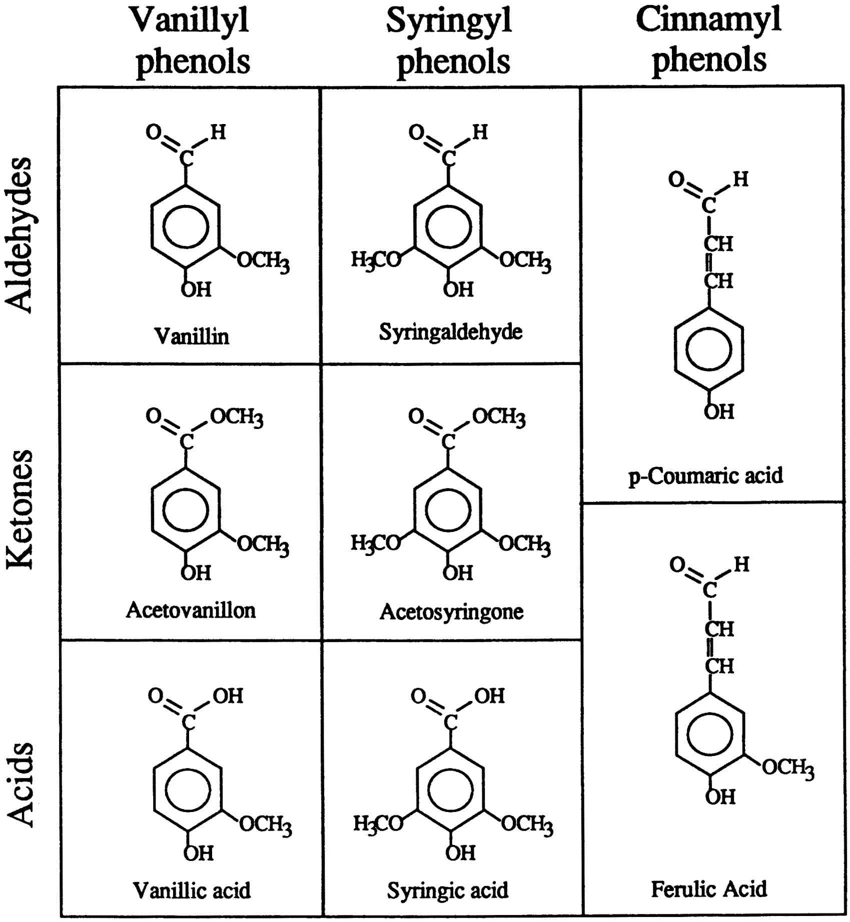

Chart II. Chemical structures of simple phenols that are released by the CuO oxidative degradation of lignins.

Although phenols with different side-chain substitution patterns are produced in remarkably constant relative abundances from sound wood, preliminary results suggest that woods degraded by white-rot fungi give characteristically elevated yields of vanillic acid versus vanillin (*41*). This method, therefore, can provide both compositional and mechanistic information for naturally degraded woods. Its main disadvantage is that analyses are time consuming (two to four samples per day) and require moderately expensive chromatographic equipment.

Analytical Pyrolysis. Analytical pyrolysis is currently one of the most widely used methods for the characterization of degraded woods from natural environments. In this technique, a small sample (<0.1–1 mg) of finely ground whole wood is heated on a wire or filament in the absence of oxygen. The wood pyrolytically breaks down to release volatile compounds, which are then directly quantified by mass spectroscopy (Py–MS) or separated by gas chromatography prior to analysis by mass spectrometry (Py–GC–MS).

A typical Py–GC–MS trace from a wood sample (Figure 9) contains 50–100 individual peaks corresponding to at least that many products. The individual pyrolysis products include furans plus a variety of carbonyl compounds that are typical of polysaccharides, particularly cellulose and hemicellulose (*42*). In addition, many different lignin-derived phenols are obtained that, like the CuO reaction products, retain the methoxylation pattern of the parent structural units and carry diagenetic information on their side chains (*43*). Characteristic pyrolysis products of wood extractives such as resin acids also can be detected (*44*); thus, this analytical method is

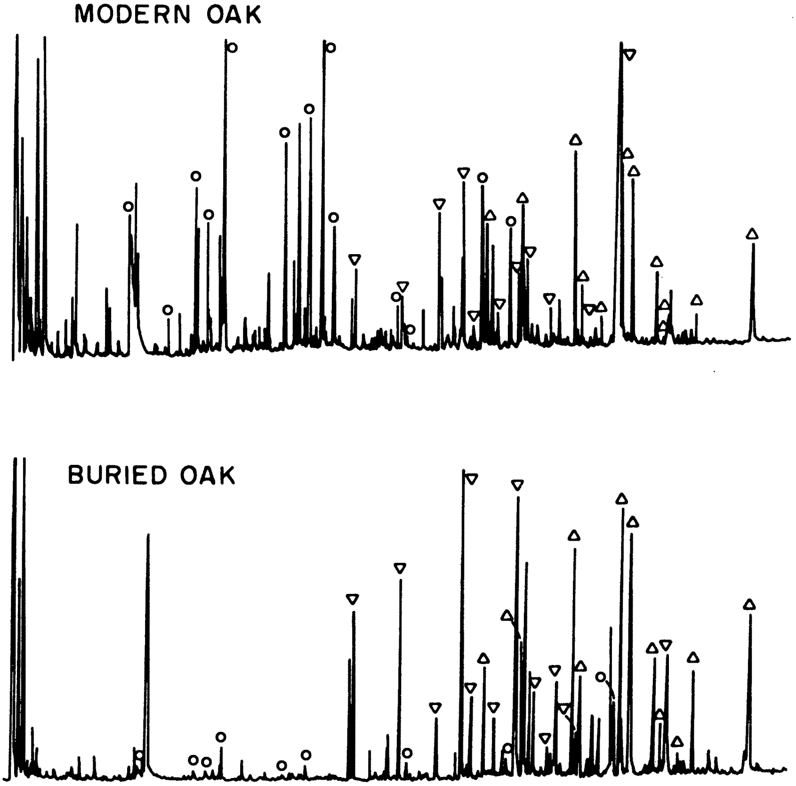

Figure 9. Gas chromatographic traces of the pyrolysis products from recent (upper trace) and buried (lower trace) oak wood samples. Circles represent polysaccharide pyrolysis products, inverted triangles represent guaiacyl lignin pyrolysis products, and upright triangles represent syringyl pyrolysis products. (Reprinted with permission from ref. 44. Copyright 1987 Elsevier Science Publishers.)

extremely broad-based. In addition to these advantages, sample throughput is fast and the mass spectral data are digitized and readily processed by statistical or pattern recognition treatments (*44*).

One of the major disadvantages of most current pyrolysis methods is that, although precise, they do not provide quantitative yield data (e.g., milligrams of product per milligrams of sample) that are useful in determining the overall extent of wood degradation. In addition, the necessary analytical equipment is expensive.

The Chemistry of Ancient Woods

Most chemical characterizations of old woods have been made on nonarchaeological samples (*4, 26*). With the exception of woods that have been treated with synthetic preservatives, however, archaeological and unworked woods should have similar long-term chemical fates in the environment and can be characterized by the same analytical methods. For this reason, both wood types will be discussed together in the following section.

Waterlogged woods constitute a major fraction of all preserved samples. This predominance probably is seen both because wood degradation rates are slower in water than on land and because natural environments other than sediments are usually ephemeral over long time periods. Woods that have been recovered from water ideally would be discussed separately from those that have been preserved subaerially. This is because woods from these two different environments are subject to contrasting types of microbial degradation and spontaneous reactions with ambient chemical agents.

Such clear-cut distinctions, however, are often difficult to make because the early histories of many samples are not well known. In addition, the literature on the chemical composition of dry archaeological wood is so sparse that comparisons to waterlogged counterparts are not very informative. Therefore these two wood types will be discussed together, but distinguished where possible. The focus of the following section will be on chemical properties that most older woods from natural environments hold in common and likely reasons for these characteristics.

Lignin Concentration. Elevated lignin concentration is the most commonly reported chemical property of old woods. This characteristic has now been observed in a variety of woods from such diverse sources as sunken ships (*25, 45, 46*), submerged old pilings (*37, 47*), sediments (*30, 48*), peats (*32, 42*), soils (*49, 50, 51*), and older geologic deposits (*4, 35, 52–54*). The bulk of the evidence for greater lignin concentrations in old versus fresh wood comes from differential solubility–direct weighing measurements such as those given in Figure 10, which also indicate commensurate losses in polysaccharides. Overall, the extents of these inverse trends do not vary with sample age in any clear-cut manner. This observation indicates that

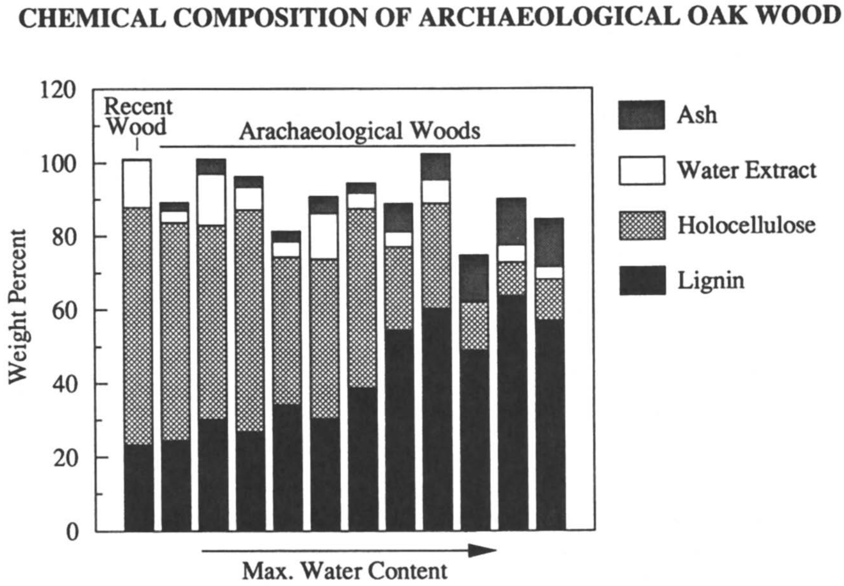

Figure 10. Weight percentages of ash, hot water extract, holocellulose, and lignin in archaeological oak woods. (Constructed from data in ref. 25.)

spontaneous (abiotic) chemical reactions probably are not the primary degradation mechanism for most samples.

Although degradation can affect the solubility characteristics of both the lignin and polysaccharides in wood, there is no evidence that carbohydrates are converted to insoluble alteration products that would interfere with the analysis of Klason lignin. The depletion in polysaccharide and increase in the weight percent of lignin do, however, correspond in absolute magnitude to increased maximal water content (*25*) (Figure 10) and density loss of the wood (*45*). Both of the latter parameters reflect the amount of tissue that has been lost in a given volume of sample. Thus the compositional trends result largely from physical removal of wood components by either solubilization or conversion to gaseous degradation products. Physical erosion is, in fact, the only mechanism by which the mass-normalized concentration of lignin in the sample could be increased. Because cellulose and hemicellulose account for essentially all the remaining mass of wood, the degradative concentration of lignin must result almost exclusively from selective polysaccharide removal.

Mass Loss. The amount of the original wood that has been diagenetically lost cannot be calculated directly from the measured decrease in the weight percentages of holocellulose (or its components) because all constituents of the remnant material are artificially "concentrated" by mass loss.

The density change versus a fresh wood counterpart must either be known (difficult because many degraded woods shrink on drying) or be determined indirectly. One means of indirectly estimating overall mass loss is by the extent to which lignin is concentrated in the degraded wood. If lignin is not removed from the wood during degradation (nor lost in the gravimetric analysis), then the percentage of mass loss from the sample (%ML) can be estimated from the following equation:

$$\%\mathrm{ML} = 100\left(1 - \frac{1}{F}\right) \qquad (1)$$

where F is the ratio of the final ($\%\mathrm{L_f}$) to the original ($\%\mathrm{L_o}$) weight percentage of lignin. The value of $\%\mathrm{L_f}/\%\mathrm{L_o}$ is controlled by the original weight percentage of lignin in the sample. For woods with $\%\mathrm{L_o}$ = 20–25 wt %, $\%\mathrm{L_f}/\%\mathrm{L_o}$ typically will not exceed 4–5. The weight percentage of holocellulose (or its components) in a degraded wood can be multiplied by %ML/100 to obtain the actual percentage of the original component that is preserved in the remnant wood.

For some waterlogged woods it has been possible to demonstrate from density changes that the extent of lignin concentration in individual degraded wood fragments is very close to that expected for conservation of the original polymer (*25*). This result indicates that the lignin component of these woods is absolutely, as well as relatively, resistant to diagenetic removal. In addition, this good agreement demonstrates that the gravimetric method for the analysis of lignin works well for these degraded samples.

Chemical Measurements. Other bulk chemical measurements support the principle of selective polysaccharide loss from old woods. For example, Spiker and Hatcher (*32*) have shown that decreases in the $^{13}\mathrm{C}/^{12}\mathrm{C}$, O/C, and H/C ratios observed for a cedar wood buried in peat are all consistent with preferential polysaccharide loss, which was also evident from analyses by CP–MAS $^{13}\mathrm{C}$ NMR. As shown in Figure 7, alder and oak woods buried in freshwater and marine sediments, respectively, were found to have elemental compositions that closely resembled those of pure lignin (*30*). In this case the differences between the H/C and O/C compositions of the fresh and degraded wood pairs had reaction trajectories that corresponded to that expected for preferential loss of polysaccharides from hardwoods. In both of the previous studies, selective preservation of lignin was confirmed by CP–MAS $^{13}\mathrm{C}$ NMR spectra such as those shown in Figure 8. The same method was used by Hatcher et al. (*47*) to show that a 450-year-old spruce pile from Rotterdam and a spruce log that was buried for 10,000 years in an anaerobic sediment were both depleted in polysaccharide as compared to fresh wood.

Molecular Analyses. Molecular-level analyses of the chemical degradation products of woods also give direct evidence for lignin concentration. For example, Figure 11 shows the elevated yields of phenolic CuO reaction products obtained by Hedges et al. (*30*) from the two buried hardwoods in Figures 7 and 8. In comparison to fresh woods, the mass-normalized yields of total vanillyl phenols from these waterlogged samples were increased by factors of 2.3 for the alder and 3.1 for the oak. When substituted into equation 1, these factors corresponded to minimum calculated losses of 57 and 68%, respectively, of the original mass of the two woods. The chemically estimated mass loss from the alder wood agreed almost exactly with a result of 58% obtained by specific gravity measurements. Because slight chemical alterations of guaiacyl structural units within lignin would be sufficient to decrease the yield of vanillyl phenols, this agreement also is evidence for the great stability of this component in woods from sedimentary deposits. However, Iiyama et al. (*51*) reported decreased relative yields of guaiacyl phenols from ancient hardwoods buried in soils, a result suggesting that lignin was not as well preserved under these conditions.

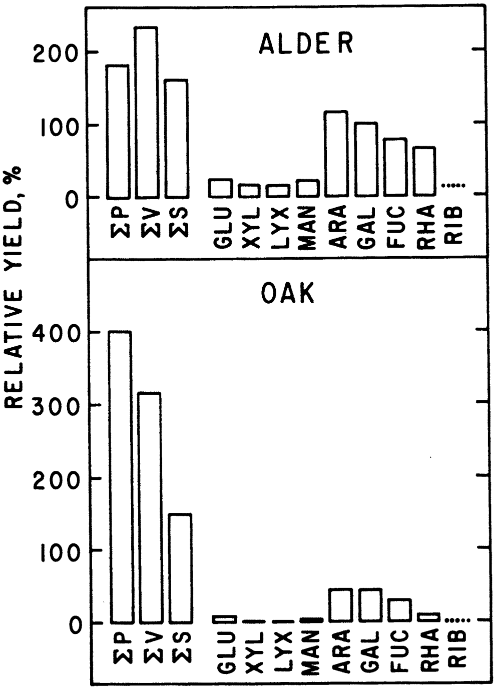

Figure 11. Mass-normalized (ash-free) yields of phenols and neutral sugars from buried alder and oak woods expressed as a percentage of the yield from the corresponding fresh wood. Dotted line indicates no measurable yield. (Reprinted with permission from ref. 30. Copyright 1985 Pergamon Press.)

Neutral Sugars. Evidence that preferential carbohydrate degradation causes elevated lignin levels in old woods also can be seen directly from decreased relative yields of neutral sugars among the acid hydrolysis products of buried woods. This trend has now been reported both for glucose obtained from submerged Baltic redwood piles in Stockholm (*37*) and for neutral sugars produced from ancient woods buried in soils (*51*) and sediments (*30*). In the latter case the percent total mass losses (estimated using the vanillyl phenol concentration factors in Figure 11) were used to calculate that at least 90 and 98%, respectively, of the original polysaccharide in the buried alder and oak woods had been degraded (Figure 12). Pronounced selective loss of carbohydrate from the same samples was also indicated by Py–GC–MS traces such as the pair in Figure 9, which showed that the most outstanding difference between the two pairs of fresh and degraded hardwoods was the lower ratio of polysaccharide to lignin products obtained from the buried samples. In an extensive study, Stout et al. (*42*) reported the same trend

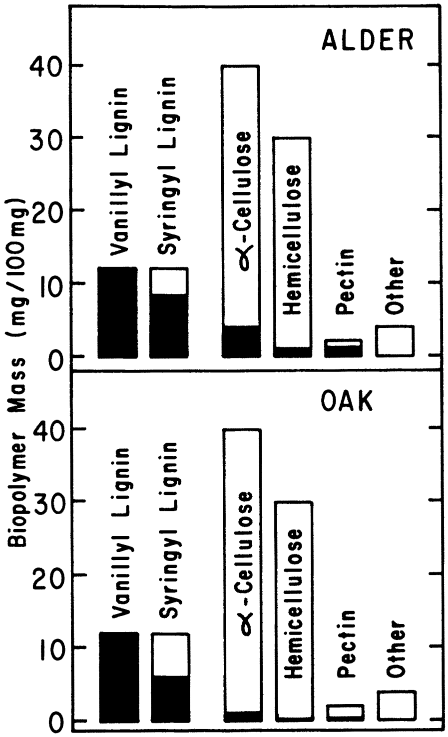

Figure 12. Estimates of the original masses (mg/100 mg) of individual biopolymers in fresh wood (total rectangles) that are preserved undegraded (shaded area) in buried alder and oak wood. The "other" category includes total extractives and minor polysaccharides that are assumed to be lost. (Reprinted with permission from ref. 30. Copyright 1985 Pergamon Press.)

among the pyrolysis products of nine different genera of angiosperm and gymnosperm woods recovered from peats of the southeast United States.

Relative Reactivities. Although it is clear from the previous discussion that holocellulose is extremely reactive in buried woods, a consistent relationship between the relative reactivities of the component polysaccharides is not evident. Published gravimetric analyses of cellulose and hemicellulose indicate variable relative reactivities, possibly resulting in part from the effect of biodegradation on solubility (*45*). Hedges et al. (*30*) reported the stability series for neutral sugars from buried hardwoods shown in Figure 11, in which arabinose, galactose, fucose, and rhamnose were more stable than glucose, which was more stable than mannose and xylose. This relationship and assignments of neutral sugars to specific polysaccharides were used to estimate the overall mass losses illustrated for these samples in Figure 12. These results were taken to indicate that pectin was the most refractory polysaccharide in these woods, followed by cellulose and then hemicellulose.

In a study of various woods in peat, Stout et al. (*42*) observed particularly rapid decreases in specific pyrolysis products of hemicelluloses, such as anhydroxyloses, which also were interpreted to indicate that hemicelluloses are degraded faster than celluloses. The same trend has been reported for ancient oak woods (*4*). However, the composition trends among the neutral sugars obtained by Boutelje and Göransson (*37*) from different depths within submerged redwood piles indicate that hemicellulose is more stable. Preferential cellulose loss was also reported by Iiyama et al. (*51*) for woods from soils and a peat. More comparative analyses of the neutral and acidic sugar compositions of buried woods from a variety of environments will be necessary to resolve the present disparate observations.

Structure and Bonds. The almost universally observed selective degradation of lignin versus polysaccharides in old woods of all types is not surprising. From a chemical standpoint, lignin is the more stable polymer because of its aromatic ring and the fact that the monomers are held together by strong ether and carbon–carbon bonds. These bond types are not nearly as easily hydrolyzed as are the linkages between sugar residues in polysaccharides. Strong oxidizing agents such as peroxide are necessary to extensively break down lignin polymers in the laboratory or biochemically (*17*). As a result of the random and complex structure of lignin, the oxidative agent must be capable of attacking a great variety of intermolecular bonds. Because of the size, irregular shape, and low solubility of lignin polymers, much of the polymer is probably not readily accessible to degradative chemical agents.

Microbiological Degradation. From a microbiological standpoint, selective lignin preservation is to be expected. No microorganisms are known to utilize lignin as the sole nutrient source (*17*). Even white-rot fungi, the only type of microorganism that is known to selectively degrade lignin, also attacks polysaccharides (*18*). Although fungi are common in aquatic environments, white-rot types are not (*20*). Being obligate aerobes, fungi will not attack lignins in anaerobic sediments or within woods if they become internally oxygen-free. Because extensive lignin degradation requires highly oxidative enzymes, rapid lignin degradation by other types of microorganism seems unlikely under reducing conditions. Thus the excellent preservation of lignin in sedimentary waterlogged woods is to be expected, as is the degradation of such material if subsequent exposure to oxygen occurs (*45*). In comparison, polysaccharide hydrolysis does not require molecular oxygen and is within the capacity of a wide variety of microorganisms, including anaerobic bacteria.

Whether the spontaneous hydrolysis of polysaccharides occurs in waterlogged woods at an appreciable rate is a key question that presently is unanswered. Because of the low initial pH of most wood (*4*) and the influence of respiratory carbon dioxide, it seems most likely that spontaneous hydrolysis would occur under acidic conditions. The relative rates of hydrolysis of the β forms of the major aldoses in wood under these conditions are glucose:mannose:galactose:xylose = 1:3:4–5:5–6 (*4*). In general, five-member (furanosidic) ring structures are hydrolyzed more rapidly than six-member (pyranosidic) ones. Electrophilic substitutions on the ring systems, such as by hydroxyl and carboxyl groups, tend to slow hydrolysis (*4*). Thus, if spontaneous hydrolysis of polysaccharides does in fact occur to an appreciable extent in ancient woods, hemicellulose should be degraded more rapidly than cellulose and the galacturonic acid backbone of pectins should be comparably stable.

Preferential Syringyl Lignin Degradation. Depletion in syringyl versus guaiacyl lignin is a second compositional trend often evidenced by molecular-level analyses of ancient woods from a variety of environments, including anaerobic sediments. In spite of the great relative stability of lignins, the determinations of the CuO oxidation products of hardwoods from anoxic sediments shown in Figures 11 and 12 indicate measurable (15–25%) decreases in the yields of syringyl versus guaiacyl phenols (*30*). The Py–GC–MS traces of the same samples in Figure 9 also reveal selective loss of syringyl structural units (*44*). Similar trends have been observed in angiosperm woods from peats (*42*) and soils (*51*). However, CuO analyses of lake sediments indicate that, once deposited, the syringyl and guaiacyl lignins in finely dispersed vascular plant fragments persist at almost constant ratios for 600,000 years (*55*).

Preferential alteration of syringyl lignin is not surprising in soils or oxidized peats because fungi would be present and are known to selectively degrade syringyl versus guaiacyl structural units (*17*, *41*). This pattern could result because the more oxygenated and less cross-linked syringyl units are chemically more reactive or because the fungi selectively degrade regions of the cell wall that are rich in this type of lignin (*56*). Syringyl depletion, however, also has been observed in degraded hardwoods from anoxic marine sediments (*30*) that do not exhibit the increased yields of acidic CuO reaction products that have been obtained from woods degraded by white-rot fungi (*41*). Thus, some degradation of syringyl lignin apparently occurs even under conditions where fungi are inactive. Although bacteria are able to degrade submerged wood under aerobic (*57*) and anaerobic conditions (*58*), it is not clear that these are the agents leading to the degradation of syringyl lignin in reducing sedimentary deposits.

Ash Content. Elevated ash contents are almost always observed in ancient woods from moist environments (*25, 26, 30, 45*). Whereas most sound woods produce less than 1 wt % of ash upon combustion, old waterlogged woods such as those represented in Figure 10 sometimes have ash contents as high as 10% or more. One reason for this trend may simply be that, like lignin, the original mineral components of wood are not efficiently removed during biodeterioration, and thus they are concentrated in the remnant material. This cannot, however, be the only process at work because the concentration factors often are higher than theoretically possible (>5), unless major lignin losses occur.

In addition, one of the commonly reported major elemental components of the ashes from woods in marine sediments is iron, which has very low concentrations in fresh wood (*45*). This iron is probably immobilized as pyrite (FeS_2) and other reduced iron minerals as a result of sulfide released by sulfate-reducing bacteria (*26, 59*). These minerals are significant because they indicate in situ degradation and can affect density measurements in wood. However, from the perspective of the conservator, it is more important that when exposed to oxygen, iron–sulfur minerals tend to oxidize and release sulfuric acid (*26*). For example, Barbour measured a pH of 3.0 in the interstitial waters of a buried alder wood that had been stored for only 6 months at 2 °C (*59*). At such high acidities the hydrolysis of polysaccharides should be expected (*4*). Such mineral phases in buried wood from marine waters can have a deleterious effect any time the material is exposed to molecular oxygen.

Overview

Although most ancient buried woods exhibit elevated ash, nitrogen, and lignin concentrations, other chemical trends are not as yet evident. The general sparseness of clear patterns results partly from the highly variable histories of worked and unworked samples, especially during early periods of burial when environmental changes and microbial degradation usually occur most rapidly. Systematic studies of a wide variety of ancient buried woods will be necessary to better understand the mechanisms of wood degradation that lead to different chemical compositions.

Geochemists and archaeologists both have unique samples and techniques to contribute toward this common goal. For example, many analytical techniques (such as CP–MAS NMR, pyrolysis–MS, CuO oxidation, and CHN determinations) that are in use by geochemists could also be beneficially applied more broadly to archaeological samples. In turn, archaeologists can often provide wood samples of known age or early history that could be used to "calibrate" more extensive geochemical sample sets. Increased communication and cooperation between the geochemists and archaeologists who study ancient woods should be mutually beneficial.

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Biological Degradation of Wood

Robert A. Blanchette[1], Thomas Nilsson[2], Geoffrey Daniel[2],
and André Abad[1]

[1]Department of Plant Pathology, University of Minnesota, St. Paul, MN 55108
[2]Swedish University of Agricultural Sciences, Department of Forest
Products, Uppsala, Sweden

Wood is decomposed by a variety of biological agents, including fungi, bacteria, and insects. Fungi colonize wood and degrade cell wall components to form brown, soft, or white rot. Brown-rot fungi, which degrade primarily the polysaccharide components of wood, leave a lignin framework. White-rot fungi may degrade all cell wall components. The rate and extent of lignin, cellulose, and hemicellulose removal varies among species of white-rot fungi. Soft-rot fungi erode the secondary wall or form discrete cavities within the cell wall. Each type of decay has many forms and can be classified by microscopic and ultrastructural characteristics. Bacteria can directly attack wood to cause erosion, cavitation, and tunneling patterns of deterioration. Bacteria may have a syngeristic or antagonistic effect on other microorganisms that inhabit wood. This chapter reviews the morphological and chemical changes that occur in wood after degradation by different microorganisms and provides information that will help identify the types of deterioration found in wood of historic value.

WOOD IS DECOMPOSED BY MANY DIFFERENT BIOLOGICAL AGENTS if adequate environmental conditions are available. Fungi, bacteria, and insects may all attack wood and use cell wall components or cause mechanical disintegration. Wood in natural environments is usually colonized quickly by microorganisms and insects, and the process of decomposition begins. Structural polymers in wood are gradually reduced to simpler molecules, and finally to CO_2 and water.

This natural recycling of organic matter is an important process in terrestrial and aquatic ecosystems, but it becomes a serious problem when

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wood materials, especially wood of historic value, are disintegrated. Under certain conditions, such as dry environments, archaeological wood may be relatively well preserved (*1*). Often, however, archaeological wood is found in various stages of decomposition (*2–5*). Several reviews discuss the biological, chemical, and biochemical aspects of decomposition (*6–10*). The intent of this chapter is to provide a better understanding of the changes that occur in wood during different types of decomposition by various biological agents, and to reveal the distinct morphological characteristics observed in wood after biological degradation. This information should provide a mechanism to identify the type of degradation that may be associated with archaeological woods and help to ascertain the appropriate conservation needs of the various woods. Information concerning the role of insects in the disintegration of archaeological wood is provided in other chapters in this volume.

The structural features of wood are different among various species of woody plants. General morphological characteristics of sound wood from an angiosperm and gymnosperm are represented in micrographs of *Betula papyrifera* (Figure 1a) and *Pinus monticola* (Figure 1b), respectively. In addition to different types of cells, the cell wall layers within a cell also differ (Figures 3a, 3b, 4a, and 4b).

All wood cells are composed of various ratios of cellulose, hemicellulose, and lignin. In general, angiosperm wood has a lower lignin content than gymnosperm wood (Table I), and the type of lignin monomer in the woods is different (*11, 12*). Both syringyl and guaiacyl units are found in lignin of angiosperms, whereas only guaiacyl-type lignin is present in gymnosperms. Another major difference between the two woods is the type and quantity of hemicelluloses: glucuronoxylan vs. galactoglucomannans (Table I).

Although various tree species have wood that is structurally and chemically distinct, all wood is susceptible to biological degradation. When fungi enter wood, they grow from cell to cell through natural openings, such as simple and bordered pits (Figure 1c) and perforation plates between vessel elements, or they may penetrate directly through the cell wall by producing a bore hole (Figure 1d). Those cells with the most food reserves, such as ray parenchyma cells, are usually colonized first.

Some fungi use only the nutrient reserves in wood storage cells, but do not cause significant cell wall decomposition. These fungi may deteriorate wood by causing only a superficial discoloration on the wood surface or a sap stain within the xylem. The wood may become various shades of blue, brown, green, or red, depending on the type of organism and substrate. Wood-destroying fungi that cause cell wall degradation can be separated into groups, depending on the type of decay produced. White-, brown-, and soft-rot are three categories used to classify the different forms of decay (*13*). Although this classification system is not very precise, considering that there are thousands of species of wood-degrading fungi (*14*), it does provide a

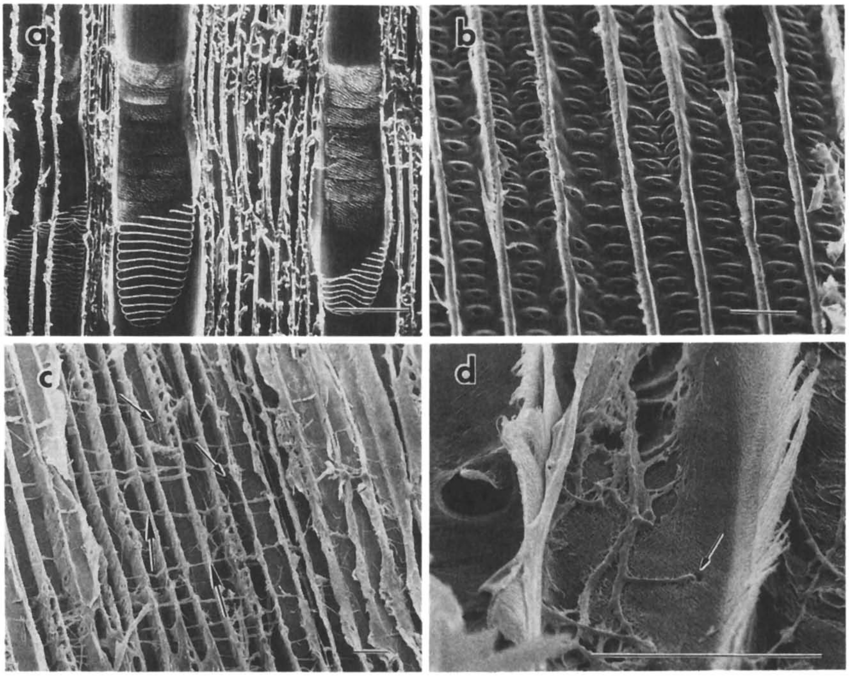


Figure 1. (a) SEM of tangential section of sound Betula papyrifera, *showing vessels with perforation plates and fibers. Bar: 50 μm. (b) SEM of radial section of* Pinus monticola, *showing numerous bordered pits in tracheids. Bar: 50 μm. (Reproduced with permission from ref. 119. Copyright 1980 Society of American Foresters.) (c) SEM of fungal colonization of wood showing hyphae growing in tracheids (small arrows) and traversing cells radially via pit apertures (large arrows). Bar: 50 μm. (d) SEM of hyphae of wood-degrading fungus in tracheid causing an erosion of the cell wall. Hypha can penetrate directly through the cell wall, moving from one cell to another (arrow). Bar: 50 μm.*

mechanism to separate different forms of decay based on gross macroscopic and microscopic differences. Within each type of decay, however, a great deal of diversity exists.

White Rot

White rot in wood results from degradation by basidiomycetes that have the capacity to remove all cell wall components. These fungi cause a definite depletion of lignin from the wood (*13*). Some species are selective and preferentially attack lignin without extensively removing cellulose and hemicellulose, although other species simultaneously remove all cell wall components. A white-rot fungus that previously has received considerable

Table I. Lignin and Wood Sugars in Sound and Decayed *Betula papyrifera* and *Picea mariana*

Fungi and Type of Degradation	*Weight Loss*	*Lignin*	*Glucose*	*Xylose*	*Mannose*
Betula					
Sound	0	19.0	44.9	24.3	2.1
Coriolus versicolor (white rot, nonselective)	65.3	18.8	38.1	18.7	1.6
Phellinus pini (white rot, selective)	17.3	9.7	45.5	23.2	2.3
Fomitopsis pinicola (brown rot)	52.8	39.1	23.2	13.4	trace
Picea					
Sound	0	26.7	48.9	6.9	13.3
Coriolus versicolor (white rot, nonselective)	25.7	25.1	46.0	7.2	13.6
Phellinus pini (white rot, selective)	24.3	17.0	58.9	6.0	11.7
Fomitopsis pinicola (brown rot)	56.0	51.9	24.7	2.7	2.9

NOTE: Percentages reflect 12 weeks of in vitro degradation by various white- and brown-rot fungi.

study, *Trametes versicolor*, is not selective for lignin removal and degrades all cell wall components simultaneously (*15–17*). The decay caused by this fungus has been referred to as a simultaneous rot (*18*).

Lignin and sugar analyses of wood decayed by *Trametes versicolor* indicated that lignin, cellulose, and hemicellulose were removed in approximately the same ratio that these components are found in wood (Table I). After 3 months of in vitro degradation, the resulting wood had approximately the same proportions of cell wall components as sound wood. In contrast, white-rot fungi such as *Phellinus pini* selectively removed lignin but not cellulose from wood. The decayed wood had low lignin and high glucose (representing the cellulose component) percentages (Table I). Other white-rot fungi may remove cell wall components of deciduous and coniferous wood in different ratios, and a variety of different forms of white rot can be found (*10*). In addition, one fungus may be responsible for different types of white rot, selective or nonselective lignin degradation, within the same substrate (*19–21*).

Macroscopic and microscopic differences occur among the two major forms of white rot. Figure 2a shows decay caused by a white-rot fungus that degraded all cell wall substances simultaneously, and thus changed the color of the wood from a normal tan to white. The nonselective attack resulted in a localized erosion of the cells. Gradually, parts of the wall were completely degraded (Figure 2b). A degradation of lignin in some areas resulted in a white pocket rot. These areas of bleached white wood contain cells with no middle lamella, and cells detach from each other (Figure 2d). In wood with advanced white pocket rot, only 1% or less lignin remained in the decayed wood, whereas the glucose content was greater than 80% (*20, 22*).

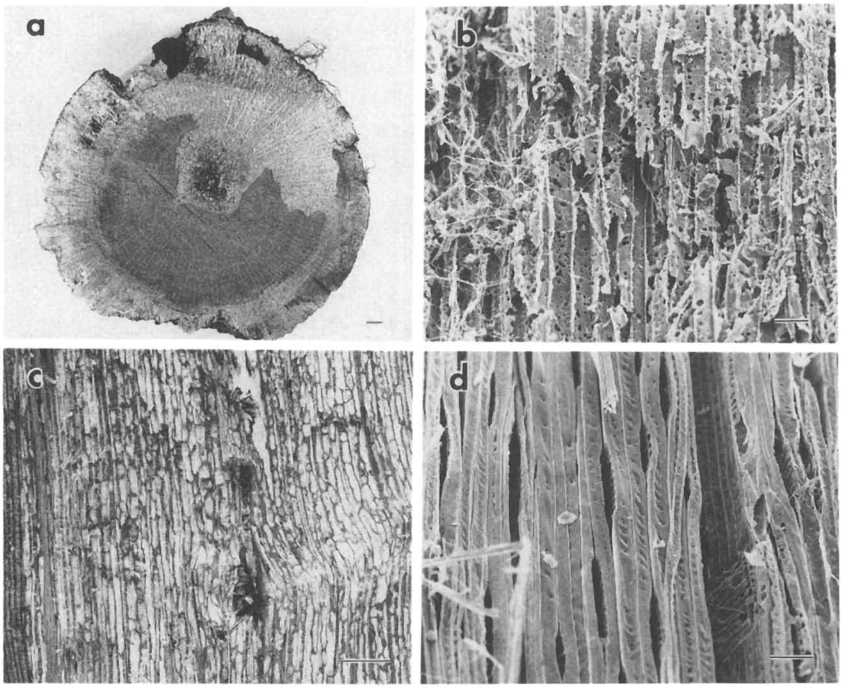


Figure 2. (a) Cross section of an oak log colonized by a white-rot fungus. The decayed wood is white, in contrast to the dark nondecayed wood. Bar: 1 cm. (b) SEM showing morphological characteristics of an advanced stage of white rot where all cell wall components are degraded. Cell walls are severely eroded and numerous holes are present. Bar: 100 µm. (Reproduced from ref. 19. Copyright 1980 National Research Council of Canada.) (c) Longitudinal section of a Pinus *log showing a white pocket rot. White pockets contain cellulose after extensive lignin degradation has occurred. Bar: 1 cm. (d) SEM showing delignified tracheids from a white pocket. Preferential degradation of lignin results in cells that lack middle lamella. Remaining cells consisting of cellulose-rich secondary wall layers separate from each other. Bar: 100 µm. (Reproduced from ref. 19. Copyright 1980 National Research Council of Canada.)*

Fossil Record. The fossil record contains evidence that white-rot fungi have been present since the upper Devonian period (*23*). Fungi with hyphal characteristics of basidiomycetes were found associated with a decay of Callixylon wood that was similar to modern white rot. Cell wall erosion and coalescing of erosion troughs indicated it was the type of white rot that simultaneously degrades all cell wall components. Specimens of *Vertebraria* from the Permian also have been observed with a white rot (*24*). The decay was characterized by cell walls that were progressively reduced in thickness, and eventually the entire cell wall was removed.

Samples of silicified Triassic Period gymnosperms from Antarctica have been reported with evidence of a white pocket rot (*24*). The decayed silicified wood contained well-preserved cells that had been delignified and hyphae with clamp connections, a hyphal type characteristic of basidiomycetes. The hyphae grew from cell to cell via pit apertures that connected adjacent cells, or by direct penetration through the wall via bore holes. The morphological characteristics of the decayed wood were identical to the decay caused in contemporary conifers by fungi, such as *Phellinus pini*, that preferentially degrade lignin (*19*, *25*). The investigations of Stubblefield and others (*23*, *24*) demonstrate that wood degradation resulting from fungi was more common in the geologic past than has been recognized previously. Furthermore, the characteristics of two general forms of white rot, simultaneous removal of all wood components and selective lignin degradation, have changed little from the Paleozoic Period to the present.

Types of Cell Wall Decay. All white-rot fungi can degrade lignin, but the rate and extent of attack and their capacity to degrade cellulose and hemicellulose varies. These physiological differences among fungi result in morphologically distinct types of cell wall decay. When fungi, such as *Trametes versicolor*, degrade the cell walls of wood, the entire secondary wall is degraded from the lumen where the hyphae are located, toward the middle lamella (*10*, *26*).

Within the wood, some cells are attacked to a greater extent than others (Figures 3b, 3c, 4b, and 4c). A progressive thinning of the entire cell wall may occur along the circumference of the lumen, or degradation may be localized to a particular area of the cell. Cells with advanced stages of decay are severely eroded. The secondary wall is often completely removed, and the middle lamella is left between cells (Figure 3d). In other cells, a more concentrated attack occurred in the wall, and localized erosion troughs were evident (Figure 4d). Once the secondary wall and compound middle lamella have been removed, the secondary wall within the adjacent cell is degraded (Figure 4d). These eroded holes in the cell wall demonstrate the localized degradative activity of the enzymes involved.

The removal of lignin appears essential before cellulose and hemicellulose are removed. Histological investigations using lignin-specific stains (*15*, *27*) and specimens fixed in $KMnO_4$ (an electron-dense stain used to observe lignin) for transmission electron microscopy (*28*, *29*) have suggested that lignin is removed before cellulose and hemicellulose are attacked. A stain-free area or less electron-dense zone is observed surrounding the eroded cell wall. Recently, X-ray microanalysis of bromine-treated wood decayed by *Trametes versicolor* showed a precise determination of where lignin was located (*29*). Bromine reacts with lignin to form a lignin–bromine complex that was identified by scanning electron microscopy and X-ray microanalysis. This investigation indicated that lignin was removed from the cell wall before complete cell wall erosion was evident. The delignification, however, was limited to a shallow depth within the cell wall.

Wilcox (*17*) postulated that all cell wall layers of fibers and tracheids in deciduous and coniferous substrates, respectively, could be decomposed simultaneously if all cell layers had equal access to fungal enzymes. Figures 3 and 4 demonstrate the ability of these white-rot fungi to attack the secondary wall layers and compound middle lamellae. The only regions that resist attack and are slow to degrade are the cell corners. Cell corner regions have been found to contain higher concentrations of lignin than other cell wall layers (*29, 30*). This high level of lignin and low carbohydrate content of the cell corners and spatial arrangement within the wall, making it the least accessible region to fungal enzymes, are important factors that allow these regions to persist.

Not all cells within wood, however, are degraded equally. In general, wood fibers from hardwoods decay faster and to a greater extent than tracheids from conifers. Within deciduous wood, the fibers and ray parenchyma cells may be totally degraded while vessels remain relatively free from attack. In a recent study of wood decay under natural conditions, fibers and parenchyma cells in *Acer* and *Tilia* were completely degraded, but vessel elements were not (*31*). Advanced stages of this type of white rot consisted entirely of vessels (Figure 5).

Vessels appear to be extremely resistant to attack by some white-rot fungi, and probably are extremely difficult to degrade by other microorganisms that subsequently colonize the substrate in the forest soil. Several contributing factors may be responsible for the resistance of vessels to attack. These include high concentrations of lignin within the vessel wall, differences in the arrangement of lignin in the wall layers, and lignin monomer composition (*30, 31*). The type of lignin within the walls of different cells may vary considerably. Vessels have a greater ratio of guaiacyl to syringyl units than do other cells (*31*). Several previous studies have demonstrated that guaiacyl lignin is more difficult to degrade by white-rot fungi than syringyl lignin (*32, 33*). This observation may explain the relatively few species of white-rot fungi found on gymnosperms that have only a guaiacyl-type lignin, in comparison to the large number of white-rot fungi that are common on angiosperms. It also helps to explain the unusual phenomena shown in Figure 5, where all fibers and parenchyma can be totally degraded without loss of adjacent vessel elements.

Fungi that cause a selective delignification of wood include many species that occur on gymnosperms, as well as species that can delignify vessel elements along with other types of cells in angiosperms (*34, 35*). One of the most striking morphological differences observed in selectively delignified wood fungi is the extensive loss of middle lamella between cells without destruction of the secondary walls (Figures 3e and 4e). Erosion troughs and thinning of the S_3 and S_2 layers of the secondary wall are not evident. Instead, the secondary wall is delignified, as indicated by the lack of stain (Figures 3e and 4e) or electron density (Figures 3f and 4f), followed by a degradation

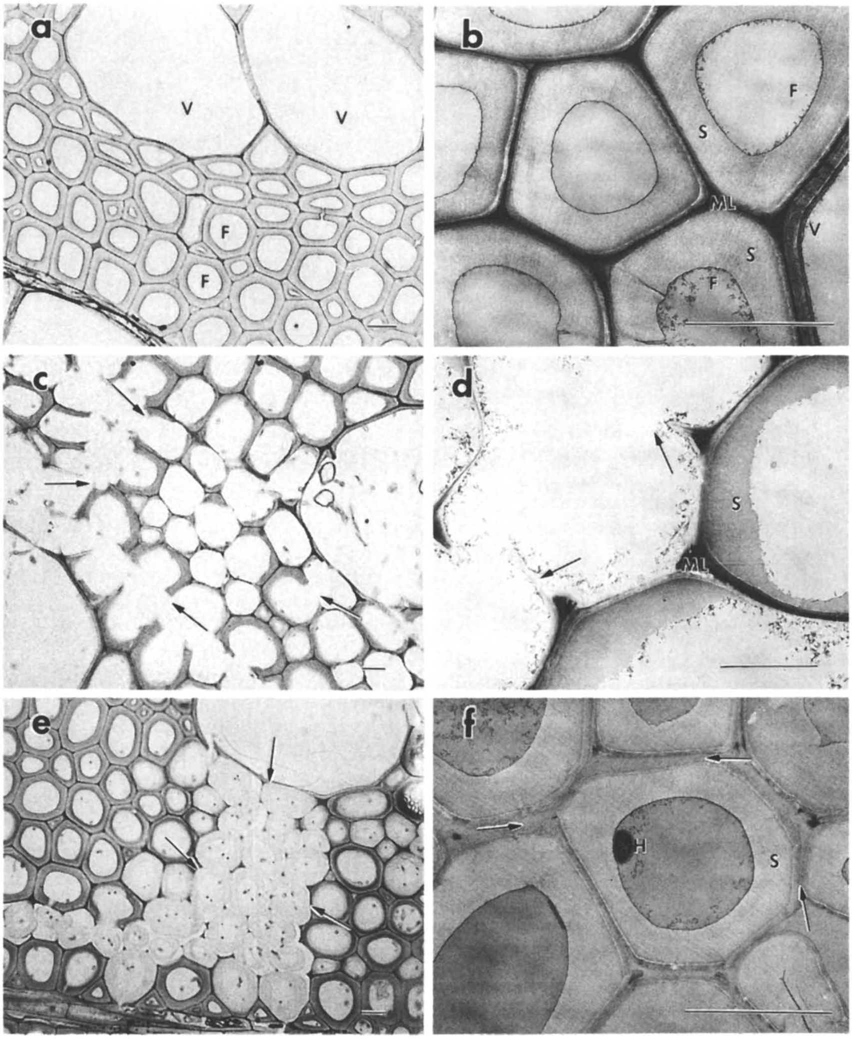


Figure 3. Morphology of sound and white-rotted deciduous wood, Betula papyrifera. *Key: ML, middle lamella; S, secondary wall; F, fiber; V, vessel; H, hypha; bar: 10 µm. (a, b) Sound wood showing fiber and vessel cell walls. Light microscope (LM) and transmission electron micrograph (TEM), respectively. (c, d) Nonselective attack of white rot on cell walls, with erosion of all wall layers caused by* Trametes versicolor. *Cell walls are degraded from the lumen toward the middle lamella. Some cell walls are completely degraded, whereas others exhibit a thinning of the secondary wall. Both secondary wall layers and middle lamella may be degraded (arrows) (LM and TEM, respectively). (e, f) Selective delignification of cells, showing fibers with intact secondary walls but no middle lamella. Delignification is not uniformly distributed throughout all cells but occurs in "pockets" or zones (arrows in e). The loss of lignin in the middle lamella and secondary wall is evident by the lack of electron density. Arrows in f indicate areas void of middle lamella (LM and TEM, respectively).*

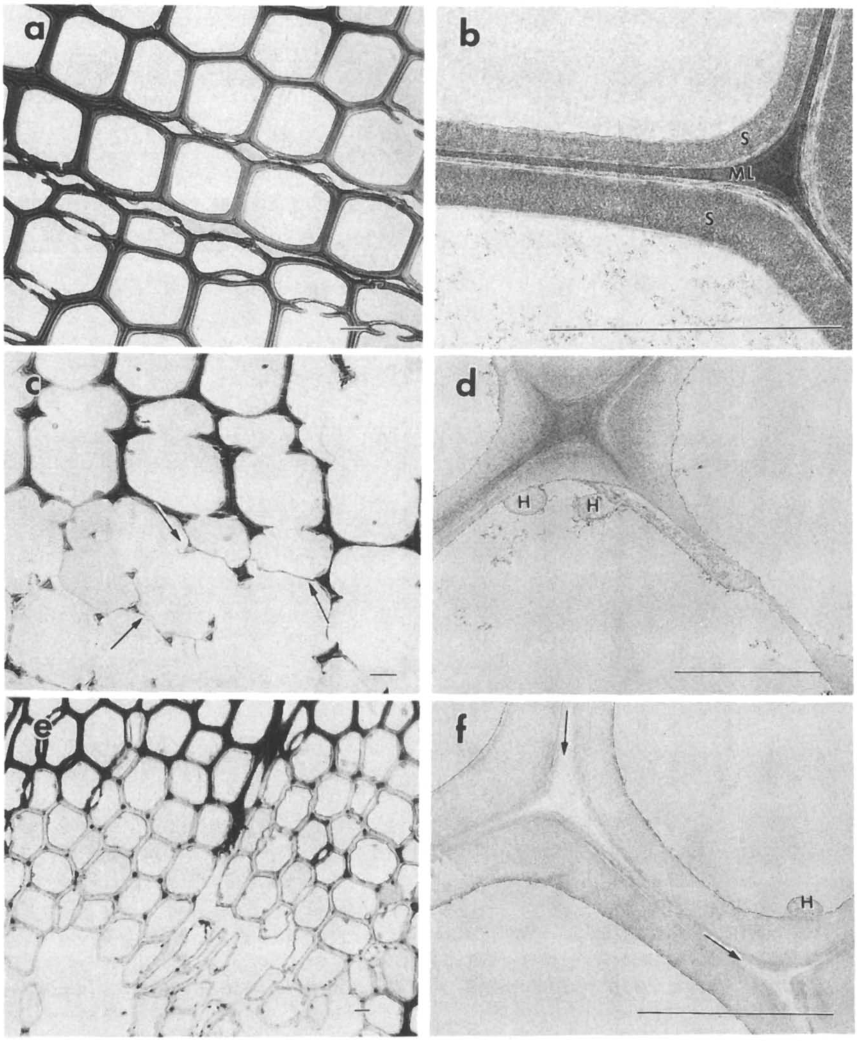


Figure 4. Morphology of sound and white-rotted coniferous wood, Picea mariana. *Key: ML, middle lamella; S, secondary wall; F, fiber; V, vessel; H, hypha. Bar: 10 μm. (a, b) Transverse section of tracheids showing arrangement of cells and various cell wall layers of sound wood (LM and TEM, respectively). (c, d) Extensive cell wall nonselective degradation by the white-rot fungus* Trametes versicolor. *Secondary walls and middle lamellae are severely eroded (arrows). Cell walls are progressively degraded, leaving only remnants of the middle lamella between cells and at cell corners (LM and TEM, respectively). (e, f) White rot showing a selective degradation of lignin in tracheid cell walls caused by* Phellinus pini. *Lignin is removed from throughout the secondary wall and middle lamella is completely degraded. The middle lamella is removed (arrows) from the wall without causing erosion or extensive degradation of the secondary wall layers (LM and TEM, respectively).*

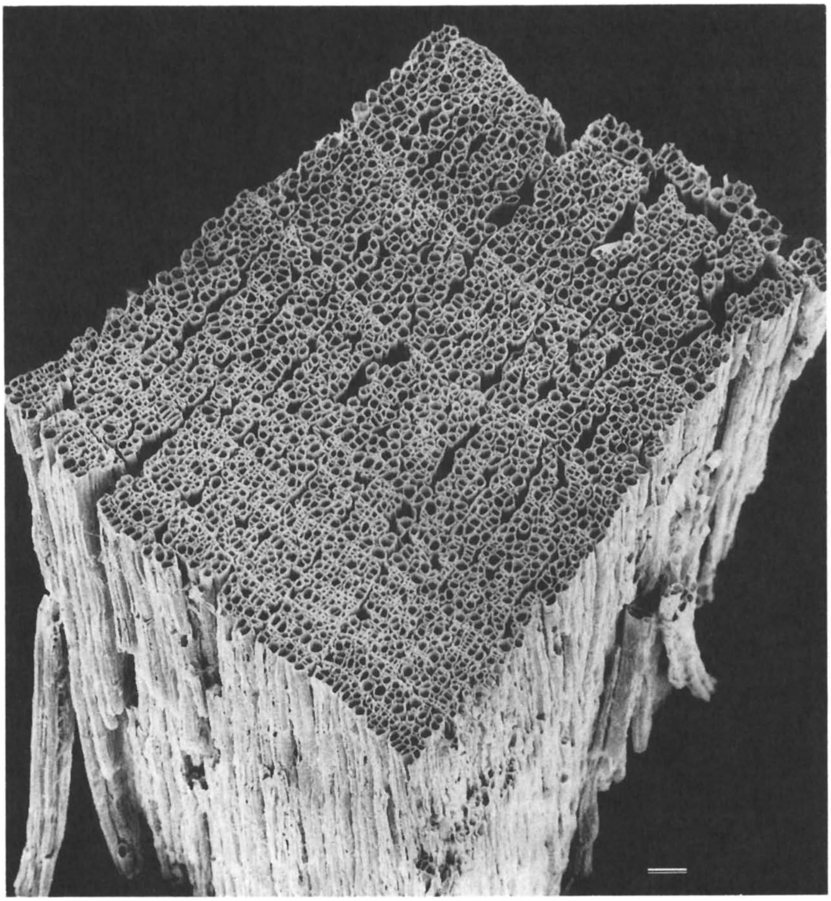


Figure 5. Advanced stage of a unique form of white rot in Acer *causing a white-stringy appearance to the decayed wood. In this type of white rot, a complete degradation of fibers and parenchyma cells occurs but vessels are not degraded. The resulting decayed wood consists of only a mass of vessel elements. (SEM) (Reproduced from ref. 31. Copyright 1988 National Research Council of Canada.) Bar: 500 μm.*

of the middle lamella. Figures 3f and 4f show cells where most, if not all, of the lignin had been removed. Although fungal hyphae are present only in cell lumena, extensive delignification occurred throughout the cell walls of many cells. Often, the selective lignin loss is not uniformly distributed in the wood, and "pockets" of delignification are apparent (Figures 3e and 4e). The extent of delignification that may occur in wood varies among species. Under certain conditions, the entire substrate (e.g., whole logs) may be delignified (*36*, *37*).

The fossil delignified wood referred to earlier (*24*) probably resulted from a white pocket rot type of decay in the heartwood of a tree. The delignified wood apparently was protected from subsequent microbial attack by the surrounding outer rings of sound wood. Because delignified wood is rich in polysaccharides, other organisms would normally attack the substrate, and thus cause a rapid disintegration. In the forest, delignified wood may be protected from invasion by other organisms when chemical and morphological barriers, such as pseudosclerotial plates, are produced by the white-rot fungus causing the decay (*38*). These biological defense mechanisms may be active for many years, but would not be sufficient for long-term protection.

Brown Rot

Brown-rot fungi are basidiomycetes that degrade polysaccharides by extensive depolymerization (*13*). In advanced stages of decay, cellulose and hemicellulose have been depleted and only limited degradation of lignin has occurred. The resulting wood, which has a very high lignin content (Table I), is brown, and when dry it may break apart into cubical pieces (Figure 6a). Brown-rot fungi impart a severe and rapid loss of wood strength early in the decay process (*39*).

The depolymerization of crystalline cellulose in wood has been observed with polarized light microscopy (*17*). A loss of birefringence was associated with early stages of brown rot. The attack on cellulose is rapid and diffuse throughout the wood. The cells appear to maintain their usual form, but will shatter and collapse because they lack the strength that cellulose provides the woody cell wall (Figure 6b).

During early stages of brown rot, some cells within wood may be more severely degraded than others (Figures 6c and 6e), but as decay progresses all cells within the substrate are uniformly attacked. The depolymerization of polysaccharides within the cell wall is accompanied by a modification of lignin by demethylation of both phenolic and nonphenolic units (*40*). Evidence also suggests that some lignin is metabolized by brown-rot fungi (*41–43*). Considering the large percentage of lignin that remains in brown-rotted wood, the amount of lignin metabolized by these fungi is relatively small.

As cellulose and hemicellulose within the cell walls are degraded and lignin is modified, microscopic and ultrastructural changes become evident. The loss of polysaccharides is first seen in the S_2 layer and progresses to the S_1 and S_3 layers of the secondary walls. The cell walls appear porous and do not readily absorb some histological stains (Figures 6c and 6e). The middle lamella also appears less distinct. Ultrastructural observations reveal that secondary wall layers are not discernible. Only a loose residual skeleton of lignin remains in the wall (Figures 6d and 6f). Cells no longer have a rigid wall structure, and the middle lamellae and secondary walls are extremely

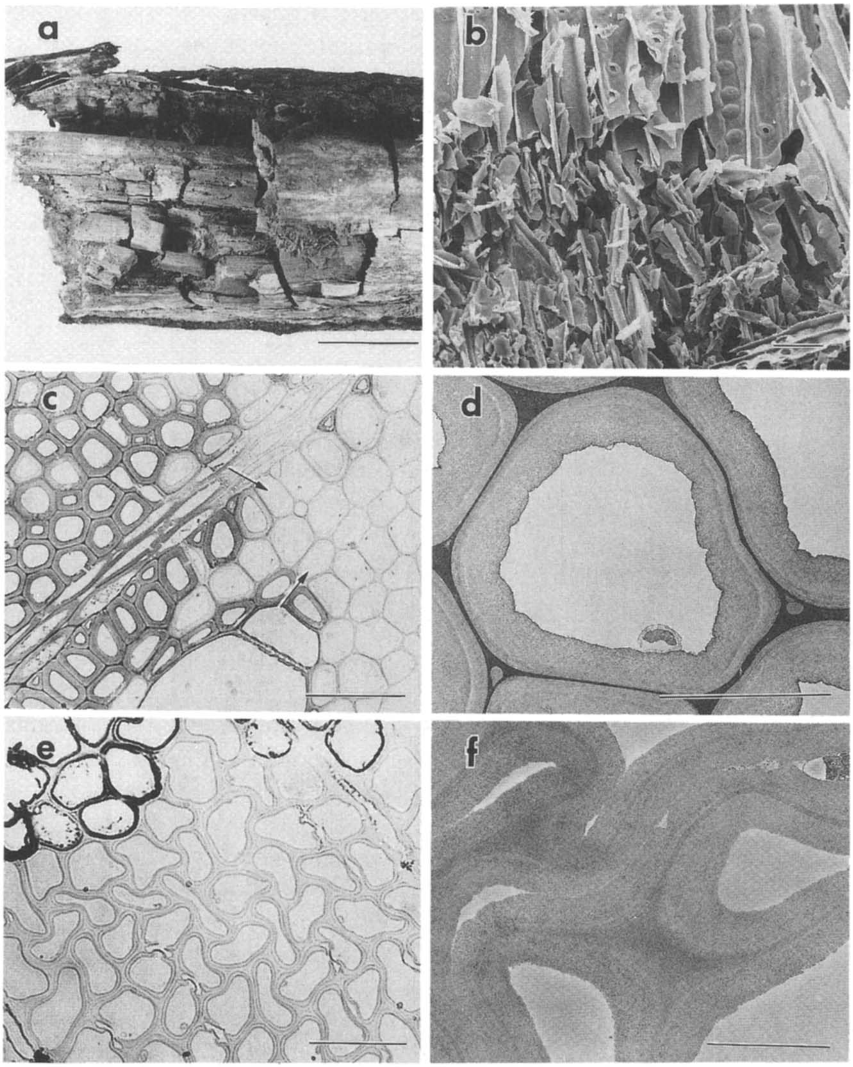


Figure 6. (a) Macroscopic appearance of brown rot. As the decayed wood dries, it cracks and checks into cubical pieces. Bar: 5 μm. (b) SEM showing that cell walls of wood with a brown rot are extensively brittle. The loss of wood integrity is evident because slight pressure applied to the wood results in breakage and collapse of cell walls. Bar: 50 μm. (c) LM view of cells of Betula *with extensive brown rot. These cells do not stain well with safranin stains and appear colorless (arrows). Bar: 50 μm. (d) TEM view of cells of* Betula *with extensive brown rot. The secondary wall layers have a porous appearance and are somewhat swollen. The middle lamella is intact, but is no longer rigid. Bar: 10 μm. (e) Tracheids showing an advanced stage of brown rot. The porous cell walls have lost their integrity and assumed distorted shapes. Bar: 50 μm. (f) Tracheids showing an advanced stage of brown rot. The electron-dense cell walls stained with $KMnO_4$ show secondary walls and middle lamella with a high lignin content and low concentrations of carbohydrates. Bar: 10 μm.*

pliable. If brown-rotted wood is dried, cracks and checks also may be evident throughout the cell wall (*44*).

Influence of Environment on Brown- and White-Rot Fungi

Environmental factors greatly influence decay by white- and brown-rot fungi (*45–47*). Adequate moisture is essential for decomposition to occur. A moisture content above fiber saturation (greater than 28%) but below total saturation of the wood (where cell lumena are filled with water) is needed for fungi to grow and cause decay. Usually when wood is saturated with water, the limiting factor for basidiomycete growth is the lack of adequate oxygen diffusion. Most brown- or white-rot fungi may tolerate very low oxygen concentrations (*48*, *49*), but they will not grow under anaerobic conditions. Optimum conditions for growth and cell wall degradation occur when oxygen concentrations are high and CO_2 concentrations are low (*45*, *50*). Increased partial pressures of oxygen stimulate cellulolytic and ligninolytic systems in white-rot fungi (*51*, *52*).

Temperature and pH also are important factors that influence decay. Most species of brown- and white-rot fungi, however, can tolerate a wide range of temperatures and pH. The optimum pH is 3.5 to 5.5, but growth may occur below a pH of 3.5 and well above 5.5 (*45*, *53*). In general, brown-rot fungi tolerate more acidic conditions than white-rot fungi, and they have a poor tolerance for high pH (*46*). Temperature optima of 25–30°C are most common among mesophyllic basidiomycetes (*45*). Some white-rot fungi, such as *Phanerochate chrysosporium*, grow best at 39–40°C. Other species of decay fungi may grow at temperatures above 40°C or below 20°C (*45*).

Soft Rot

Soft rot is a type of decay caused by ascomycetes and *Fungi Imperfecti*. The term "soft rot" was proposed by Savory (*54*) for a form of fungal decay where characteristic chains of cavities with conical ends were produced within wood cell walls. He recommended that the term soft rot should be used "for decay caused by cellulose-degrading microfungi to distinguish it from the brown and white rots caused by the wood-destroying basidiomycetes."

It was later discovered that some soft-rot fungi caused cell wall erosion, in addition to forming cavities (*55–57*). Today soft rot is commonly used to describe all forms of decay caused by ascomycetes and *Fungi Imperfecti*. Degradation of wood by ascomycetes such as species of *Daldinia*, *Hypoxylon*, and *Xylaria* is, however, often considered as white rot (*58–60*). A recent study on wood decay by several species of the mentioned genera show that they have characteristics of white rot as well as soft rot (*61*).

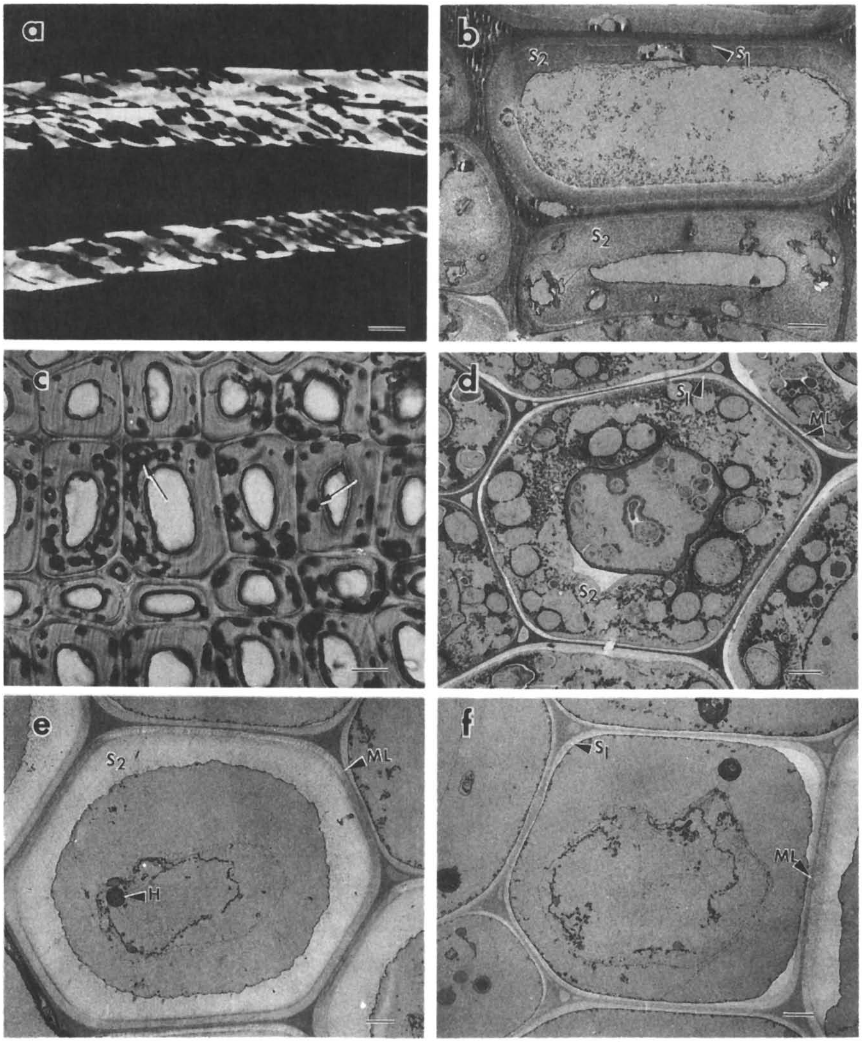
A large number of ascomycetes and *Fungi Imperfecti* are capable of causing soft rot. *Chaetomium globosum* is the most commonly studied species. Nilsson provided a list of 120 different species of soft-rot fungi (62). *Phialophora* species appear to be common in the terrestrial environment. In the marine environment, specific marine fungi adapted to saline conditions and cause soft rot in wood (63). Mouzouras (64) provided a list of several marine soft-rot fungi.

Cavity Formation. The most characteristic and well known form of degradation by soft-rot fungi is the cavities with conical ends that are produced through enzymatic activity of hyphae growing parallel to the cellulose microfibrils within wood cell walls. The cavities are best observed in longitudinal sections (Figure 7a). Cavities are usually formed along the length of the hyphae. A chainlike arrangement of the individual cavities is oriented helically or nearly parallel to the long axis of the wood cells, depending on the orientation of the cellulose microfibrils. The attack is mainly confined to the S_2 layer, but cavities may also be formed in the S_1 layer (65). In the S_1 layer the cavities are more or less transversely oriented with respect to the fiber axis.

The shape and size of the individual cavities are variable (55, 65). Some are very long and slender; others are broad and quite short to rhomboid. The cavities formed in hardwood fibers and in the thick-walled latewood tracheids of softwoods are usually larger than those formed in softwood earlywood tracheids. In transverse sections the cavities within the S_2 appear as rounded holes (Figures 7b and 7c). The size of the holes is related to the diameter of the cavities. Enlargement of cavities through continuous enzymatic activity and formation of additional cavities eventually leads to a complete destruction of the S_2 layer (Figure 7d). The middle lamella and the S_3 layer seem to vary in resistance to degradation by soft rot and will thus be the only layers that remain after a severe attack.

The degradation occurring in the S_2 layer is usually confined to the vicinity of the hyphae and expands through the enlargement of the cavities. Normally no degradation can be observed in areas of the cell wall surrounding the cavities. However, in several instances we observed a form of attack where the enzymes appear to have diffused out from the cavities and degraded all of the cellulose throughout the whole cell wall. Viewed in transverse sections, the holes of the cavities are seen to be surrounded by an amorphous structure that probably represents the remaining lignin. Zainal (66) observed and reported a similar form of attack.

Figure 7. (a) Polarized light micrograph of soft-rot cavities formed within a hardwood sample from an Egyptian mummy coffin (Code No. FP–F–S) dated 1000–2000 B.C. Chainlike arrangement is characteristic of cavities as seen in LS of macerated fibers. Bar: 50.0 µm. (b) TEM micrograph of soft-rot cavities formed within a hardwood sample from an Egyptian mummy coffin (Code No. FP–F–S) dated 1000–2000 B.C. Cavities appear in TS formed in both ray



(upper cell) and fiber S_2 *or* S_1 *cell wall layers. Bar: 2.0 μ. (c) LM photo of transverse section of* Pinus sylvestris *showing typical rounded appearance of soft-rot cavities (arrows) formed within the* S_2 *cell wall layer of latewood tracheids. Bar: 5.0 μm. (*See *Figure b also). (d) TEM micrograph of advanced soft-rot cavity formation in* Betula verrucosa *with only the middle lamella, parts of* S_1*, and isolated regions of* S_2 *remaining (arrows). The previous location of the fiber tertiary wall and soft-rot hyphae are represented by dense residues that form during cavity formation. Bar: 2.0 μm. (e) Early stage in soft-rot erosion decay of* Betula verrucosa *by* Daldinia concentrica*, with partial erosion of the* S_2 *layer by a lumenal hyphae (H). Bar: 2.0 μm. (f) Advanced stage in soft-rot erosion decay of* Betula verrucosa *by* Daldinia concentrica*. The* S_2 *is almost totally eroded, and only the* S_1 *and middle lamella regions remain. Bar: 2.0 μm.*

Soft-rot cavity formation is initiated by hyphae growing in the cell lumen. The first step in the attack sequence is penetration into the cell wall by a hypha that is considerably thinner than the parent hypha in the lumen. Some hyphae penetrate through the first and the adjacent cell walls to emerge in the next cell lumen. The damage will, in this case, be restricted to the small bore hole through the walls. Bore holes produced by soft-rot fungi never enlarge, as is the case with bore holes produced by certain white- and brown-rot basidiomycetes. Other penetration hyphae will, however, change their growth direction after having entered the cell wall to become aligned along the cellulose microfibrils. This change is done either through a simple bending of the hypha or through the formation of a T-branch (*67*). Further events leading to cavity formation have been covered in detail by Hale and Eaton (*67–69*).

Cell Wall Erosion. Cell wall erosion, resulting in thinning of the wood cell walls, occurs simultaneously with cavity formation in certain hardwood timbers (*62, 67, 70, 71*). This form of attack is rarely observed in softwoods and in hardwoods with exceptionally high levels of lignin (*61, 72*).

A typical example of soft-rot erosion is shown in Figures 7e and 7f. The attack proceeds until only the middle lamella and parts of the S_1 layer remain (*61, 62*). These layers appear to be resistant. Cell wall erosion is also a typical feature of attack by white-rot fungi (*73*). In contrast to soft-rot fungi, white-rotters usually cause erosion in softwood timbers, and most species will also degrade the middle lamella in the final stages of attack. Soft-rot erosion and white-rot erosion in hardwoods cannot be distinguished microscopically from each other.

Some soft-rot fungi lack the ability to form cavities within the S_2 layer of the wood cell walls (*62, 71*). Their activity is thus restricted to cell wall erosion. This restriction is typical for several cellulolytic microfungi and some of the higher ascomycetes such as *Daldinia* and *Hypoxylon* (*61*). A few soft-rot fungi cause no or very limited cell wall erosion (*62, 71*). Their main way of degrading wood is through cavity formation.

Wood that is severely degraded by soft rot (i.e., most of the S_2 layer is destroyed) is very soft when wet. This softness was the reason for proposing the term soft rot (*54*). On drying, soft-rotted wood cracks along and across the grain and is dark brown or nearly black (Figure 8a). Such extensive degradation is usually limited to the outer parts of the wood, varying from 1 mm to approximately 10 mm. However, wood that is substantially degraded may appear sound because the macrostructure is intact (Figure 8b) and the wood is quite hard. Only microscopic examination or strength tests will reveal the presence of soft rot. Although soft rot is often considered a surface phenomenon, quite extensive attack may occur throughout large timber dimensions (Figure 8b).

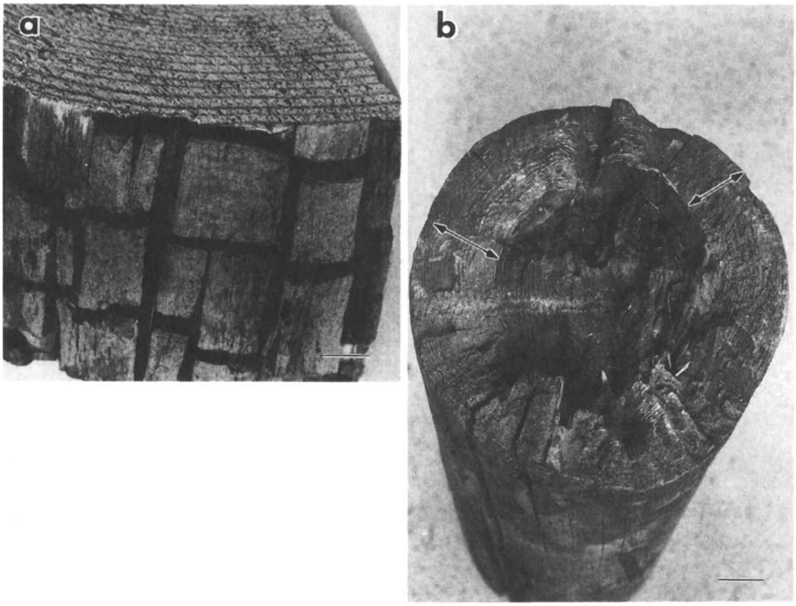


Figure 8. (a) Characteristic surface cracking both across and along the grain of a section from a soft-rotted pole after drying. Bar: 1.5 cm. (b) Typical appearance of an extensively soft-rot-degraded pine pole after fracture. Decay has occurred throughout the sapwood (arrows) of the pole, which can be distinguished from the inner nondegraded heartwood regions by the nature of the brash fracture. Bar: 2.6 cm.

Wood loses considerable strength during attack by soft rot when only a limited amount of the wood substance has been consumed. Liese and Ammer (*74*) reported a weight loss of 7.4% in beech stakes exposed in the laboratory to *Chaetomium globosum* for 3 weeks. The corresponding loss in impact bending strength was 61%. Zycha (*75*) also reported very extensive losses in strength at very low weight losses in beech stakes exposed to a number of different soft-rot fungi. A very characteristic brash fracture is obtained when soft-rotted timber is broken (Figure 8b). Early stages of soft rot may easily be detected by probing with the point of a knife. Poking of sound wood usually results in splinters, whereas soft-rotted wood breaks off in brash fractures.

Abrasive action by water and sand in aquatic environments may remove the outer softened layers of soft-rotted timber, and thus expose the underlying layers for further attack (*76*). This exposure will result in a more extensive attack at the water level, giving a characteristic appearance of the smooth rounded shapes common to driftwood. Wood-degrading bacteria may often also contribute to the surface softening in aquatic environments.

Chemistry of Soft Rot. Only a limited number of studies have been carried out on the chemistry of soft-rot attack, and most studies have focused on a single species, *Chaetomium globosum.* All studies indicate that wood carbohydrates are degraded in preference to lignin (*61*, *77–80*). Lignin degradation appears to be variable, depending on fungal species, culture conditions, and type of timber. Sulfuric acid lignin (Klason lignin) analyses have shown lignin losses up to 40%, a result indicating some ligninolytic activity (*61*).

Levi and Preston (*78*) reported an increase in the average degree of polymerization (DP) of the cellulose in beech wood attacked by *Chaetomium globosum.* This increase suggests a preferential degradation of the amorphous portions of the wood cellulose. Rapid depolymerization of the wood cellulose as observed with brown rot (*15*) has not been reported for soft rot.

Savory (*54*) observed that hardwoods were more susceptible to soft rot than softwoods. This observation was confirmed later in numerous reports. The obvious explanation is the difference in lignin content between softwoods and hardwoods from the temperate parts of the northern hemisphere. Butcher and Nilsson (*81*) demonstrated that soft-rot susceptibility was inversely correlated with the timber lignin content. Later Nilsson, Obst, and Daniel (*72*) provided further information about lignin content and also indicated that the type of lignin is important. They found that pine wood and certain tropical hardwoods with a high lignin content and a low syringyl:guaiacyl ratio were less susceptible to soft rot than many hardwoods with a lower lignin content and a high syringyl:guaiacyl ratio. This finding does not mean that high-lignin timbers are immune to soft rot, but that soft rot will progress more slowly in such timbers. Soft-rot fungi that lack the cavity-forming ability seem, however, to cause no or very limited attack in lignin-rich timbers.

Environmental Conditions. Savory (*82*) reported that superficial soft rot had been observed in very durable hardwoods, and Liese (*83*) found in an extensive study of European and tropical timbers that no species was completely resistant to soft rot. It thus seems that soft-rot fungi generally are more tolerant than basidiomycetes to heartwood extractives. A general tolerance is also evident from the soft-rot attack in preservative-treated wood in ground contact. The extreme longevity of certain timbers reported from field experiments where stakes have been buried in soil, an environment of high soft-rot hazard, suggests that although soft rot may occur, the progress of attack is very slow because of the effects of the heartwood extractives (*84*).

Soft-rot fungi are fully capable of attacking wood without any additional nutrients. However, the addition of nitrogen greatly increased the rate of attack (*54*). This finding may explain why soft rot is often observed in timber exposed in contact with soil from which nitrogen can be extracted. Several observations suggest that the rate of decay is faster in more fertile soils.

Most mesophyllic fungi are able to grow at temperatures close to or even below the freezing point (*85*). Although no studies appear to have been made of soft-rot attack, it is safe to assume that soft rot will occur, albeit slowly, at temperatures just above 0 °C. The upper temperature limit for growth of fungi is 60–62 °C (*86*). The fungi growing at such high temperatures are known as thermophiles. Several of the thermophilic species can cause soft rot (*62*). These facts suggest that soft-rot attack can occur from approximately 0 to 60 °C. The most thermotolerant wood-decaying basidiomycete, *Phanerochaete chyrsosporium*, stops growing at 50 °C (*87*).

No specific studies appear to have been carried out on the influence of O_2 and CO_2 on soft rot. The observations of soft rot in waterlogged wood suggest that the responsible fungi are able to attack wood at levels of oxygen that are too low for wood-degrading basidiomycetes. The absence of soft rot and presence of bacterial attack in samples from certain aquatic environments indicate that bacteria are even more tolerant of low oxygen concentrations.

Duncan (*88*) observed growth of several soft-rot fungi throughout the range of pH 3–9. Optimum pH varied, pH 6–8; pH 9 retarded growth of all isolates, but growth was not inhibited. Sharp and Eggins (*89*) noted that strength losses of beech wood veneers exposed to a mixed flora of soft-rot fungi did not differ much within the pH range of 3.7–8.6. The reports indicate that soft-rot fungi are more tolerant than wood-decaying basidiomycetes to alkaline conditions.

Savory (*82*) reported that soft-rot attack could occur at quite low moisture contents, as well as under waterlogged conditions. He stated that "the microfungi can attack wood which is too wet or too dry for Basidiomycete decay." He also reported severe soft rot in beech strips exposed at a constant relative humidity of 90%, corresponding to an equilibrium moisture content of 20–21%. Apparently it is a misconception that soft rot only occurs in very wet wood. Kirk and Cowling (*9*) state, for example, that only water-soaked timber is attacked by soft rot. In fact, soft rot may occur over a wide range of moisture conditions, from quite dry to fully waterlogged wood.

Soft-rot fungi also appear to be quite tolerant to great fluctuations in moisture content. Attack can thus be found in timber that remains dry for long periods and is only wet occasionally (*82*). Clearly, soft-rot fungi are able to attack wood in a broader range of diverse environmental conditions than the wood-decaying basidiomycetes. Soft-rot attack is, however, fairly slow compared with attack by basidiomycetes under conditions optimal for the latter. Competition for the substrate will often exclude soft-rot conditions that restrict basidiomycete activity. Such conditions are excessively dry or wet timber, restricted oxygen, high temperatures, or the presence of toxic heartwood extractives or synthetic preservatives.

Although soft rot occurs in above-ground situations, it is not so extensive, probably because of the low amounts of available nitrogen. Soft rot is thus mainly apparent in timber exposed in soil or in aquatic environments. The depth of penetration of decay in soil-exposed timber may be considerable. Large poles may be completely permeated with soft rot. The attack under waterlogged conditions, however, appears to be more of a surface phenomenon, not extending very far into the wood.

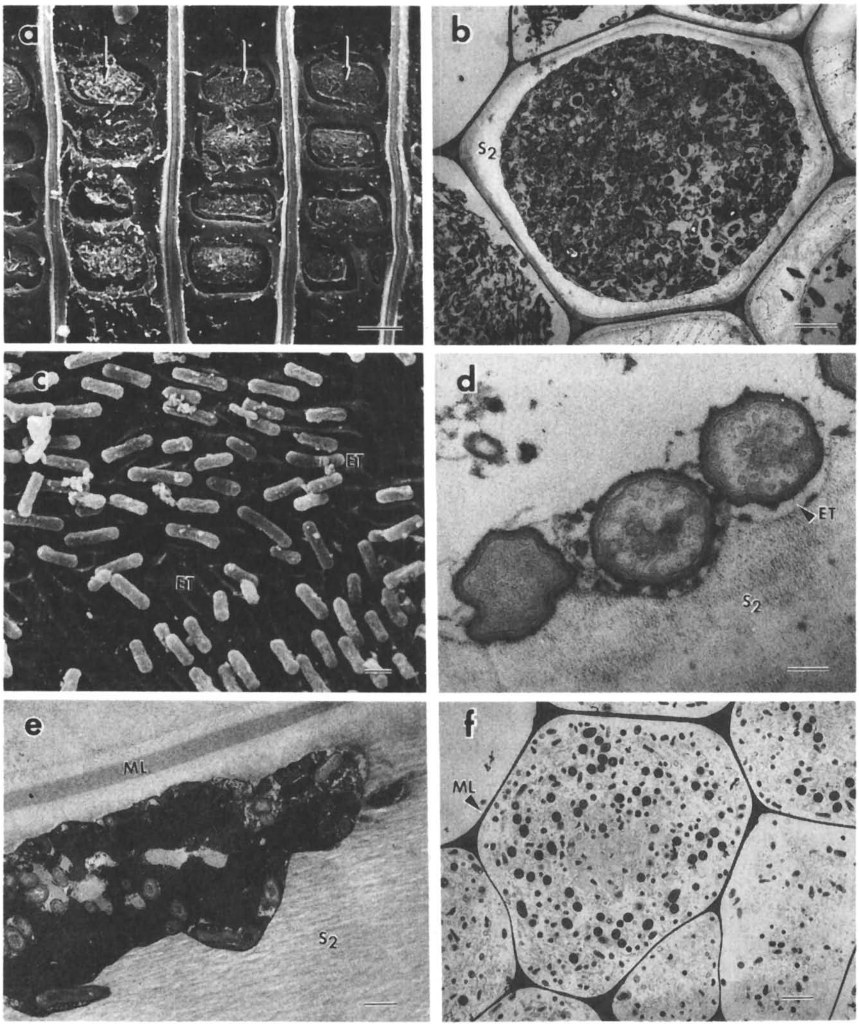
Bacteria

The best-known effect of bacteria in wood is the pronounced increase in permeability after storage under water or water sprinkling. The observed effects result from bacterial degradation of pit membranes. Wood degradation in the form of wood cell wall destruction is much less known. It has only recently been unequivocally shown that bacteria are capable of degrading the lignocellulose structure of wood (*90–95*). So far, no bacteria capable of degrading wood cell walls have been obtained in pure culture. Their taxonomic positions are thus unknown. All evidence from microscopic studies suggest that they are Gram-negative single-celled bacteria. Recent studies suggest that actinomycetes, which frequently are found colonizing wood, lack the ability to degrade wood (*96, 97*). Observations of bacterial attack relate to wood samples exposed under natural conditions, where accompanying attack by other decay microorganisms often occurs, or to wood exposed to bacterial consortia in the laboratory.

Bacteria are commonly found in timber exposed in very diverse environments. The bacteria may be divided into degrading and nondegrading species. The former may be further divided into two groups: bacteria that degrade only pit membranes and bacteria that actively attack the lignocellulose structure of the wood cell wall (i.e., true wood-degrading bacteria).

Bacteria That Degrade Pit Membranes. This form of attack is known mainly from softwoods submerged in water or from softwoods sprinkled with water. The bacteria direct their attack to the membranes of the pits in tracheids and ray parenchyma (Figure 9a). Pit membranes in the heartwood are much less affected than those in the sapwood. The thin walls of the ray cells in pine may also be degraded (*98–99*). The degradation of pit membranes results in a very pronounced increase in porosity, which is evident by a marked increase in the absorption of liquids. This phenomenon can be observed after only a few weeks of storage.

Figure 9. Characteristic features of bacterial decay of pit membranes and wood cell walls. Bar: a = 1.0 μm; b,f = 2.0 μm; c = 0.5 μm; d = 0.2 μm; e = 1.0 μm. (a) SEM shows bacterial attack of window pit membranes from the sapwood of Pinus sylvestris. *Decay is restricted to the membranes (arrows), with the bacteria unable to attack the lignified wood cell walls. Bar: 1.0 μm. (b) TEM shows intermediate stage in bacterial erosion decay, with a diverse population of bacteria present within the fiber lumena and erosion bacteria*



*forming a closely applied planar layer around the decaying S_2 layer. Bar: 2.0 μm. (c) SEM photo showing the characteristic erosion troughs (ET) that are formed during decay of the wood S_2 layer (*B. verrucosa*). The bacteria show considerable cell wall plasticity and are aligned with the underlying wood microfibrils during decay. Bar: 0.5 μm. (d) TEM photo showing the characteristic erosion troughs (ET) that are formed during decay of the wood S_2 layer (*B. verrucosa*). The bacteria show considerable cell wall plasticity and are aligned with the underlying wood microfibrils during decay. Bar: 0.2 μm. (e) TEM photo shows longitudinal penetration by erosion bacteria into the S_2 cell wall of* Pinus sylvestris *from exposed but adjacent regions, giving rise to a form of cavity formation. Bar: 1.0 μm. (f) TEM photo shows advanced bacterial attack of* B. verrucosa *with the tertiary wall, S_2, and S_1 layers degraded and only the middle lamella (ML) remaining. Large numbers of bacteria are still present within the fiber lumena. Bar: 2.0 μm.*

Cell-Wall-Degrading Bacteria. The classification of bacterial decay types is based on the micromorphology of attack. Three main types of bacterial attack have been described so far through microscopy: erosion, tunneling, and cavitation. They have been named after specific characteristics of the attack. Observations suggest that further forms of attack await description. Several other decay patterns of wood cells are suspected of being caused by bacteria, but no definite evidence is available.

Erosion. The degradation caused by erosion bacteria is somewhat similar to cell wall erosion by white-rot fungi. The bacteria grow in the lumen of wood cells and start by attacking the S_3 layer. The bacteria, which are Gram-negative rods, align themselves along the microfibrils where the individual bacteria erode the cell wall in a groove-like manner (Figures 9b–9d). The combined activity of numerous bacteria leads to a more or less uniform thinning of the cell walls. Large troughs extending to the middle lamella are also occasionally observed (*92, 100*). Longitudinal penetration by bacteria from areas of cell wall erosion into adjacent parts of the cell wall is commonly observed. This penetration results in cavities (Figure 9e) that, in thin transverse sections, could be attributed erroneously to soft rot or a form of cavitation. The middle lamella is not degraded even in late stages of attack (Figure 9f). In contrast to cell-wall-eroding soft-rot fungi, erosion bacteria actively degrade softwoods as well as hardwoods.

A very common form of bacterial attack in waterlogged timber is suspected to be caused by erosion bacteria when oxygen is restricted. In this case part (or all) of the S_2 is converted into an amorphous substance consisting of residual cell wall material and bacteria (Figures 10a–10d). Features of erosion attack can, however, be recognized along the border between degraded and undegraded cell walls. Light microscopic studies using polarized light indicate that the cellulose has been degraded (Figures 10a and 10b). The middle lamella is not degraded, and often large parts of the S_3 layer are still present. Earlier stages of attack in transverse sections appear as a hole in the cell wall containing an amorphous substance. Cavitylike structures can be observed in longitudinal sections (Figure 10c).

A characteristic feature of this form of attack is the nonhomogenous distribution of the decay (Figure 10b). Apparently sound fibers are found among heavily degraded ones. The degraded S_2 layer will irreversibly collapse upon drying. This collapse gives a very characteristic appearance in transverse sections (Figure 10d). The remaining middle lamella makes up a network in which the collapsed delaminated remains of S_2 can be observed. Severe attack by erosion bacteria may extend throughout the sapwood of large dimensions of timber (*101, 102*).

Tunneling. In this case the bacteria tunnel within the wood cell walls in a very peculiar manner (*94, 95*). They penetrate into the S_2 layer, where

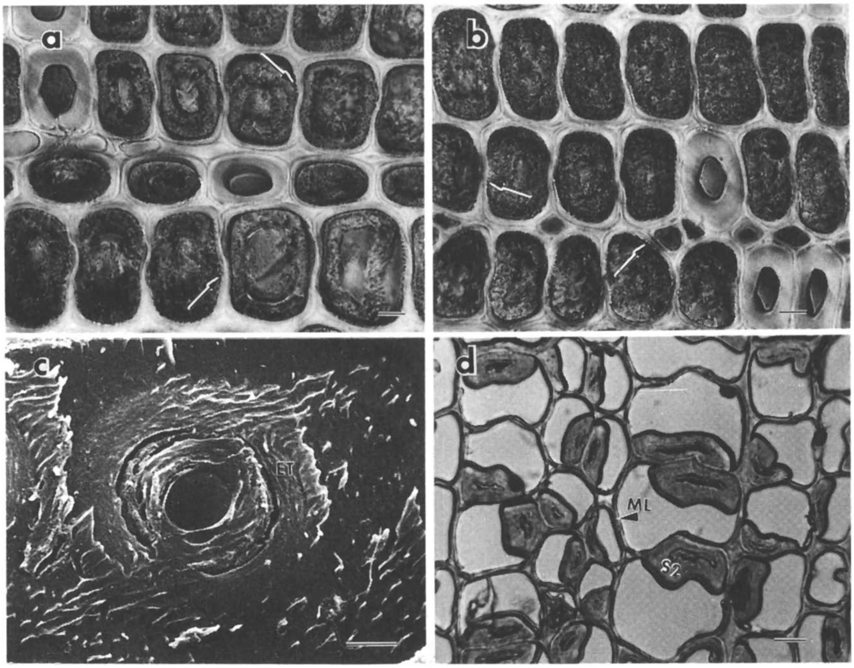


Figure 10. Bacterial decay of waterlogged timber. Bar: a, b, d, 5.0 μm; c, 1.0 μm. (a–c), Decay of Pinus sylvestris *wood samples from the wreck of the Swedish battleship* Kronan, *which sank in the Baltic sea in 1676; (a, b) advanced attack, with the tracheid S_2 cell walls being converted into an amorphous material consisting of residual wood cell wall materials, bacteria, and bacterial secretions. Decay is often nonhomogeneous, with undegraded cells recognized among those heavily degraded. Features of erosion trough formation are visible at the border between degraded and undegraded cell wall regions (arrows) (LM); (c) characteristic erosion troughs within undegraded remnants of the S_2 layer around a bordered pit (SEM); (d) transverse section of air-dried bacterial-degraded waterlogged timber (*P. sylvestris*) showing the characteristic appearance of the collapsed but degraded S_2 cell wall regions. The remaining undegraded middle lamella forms a network holding the wood structure together (LM).*

most of the degradation occurs. A single bacterium is found in the front of each tunnel (Figure 11a). A very characteristic feature is the concentric wall-like structures, probably consisting of polysaccharides, deposited behind the bacteria (Figures 11a–11c).

Division of the bacteria leads to an increased number of bacterial cells, some of which will initiate tunneling in new directions. This activity will

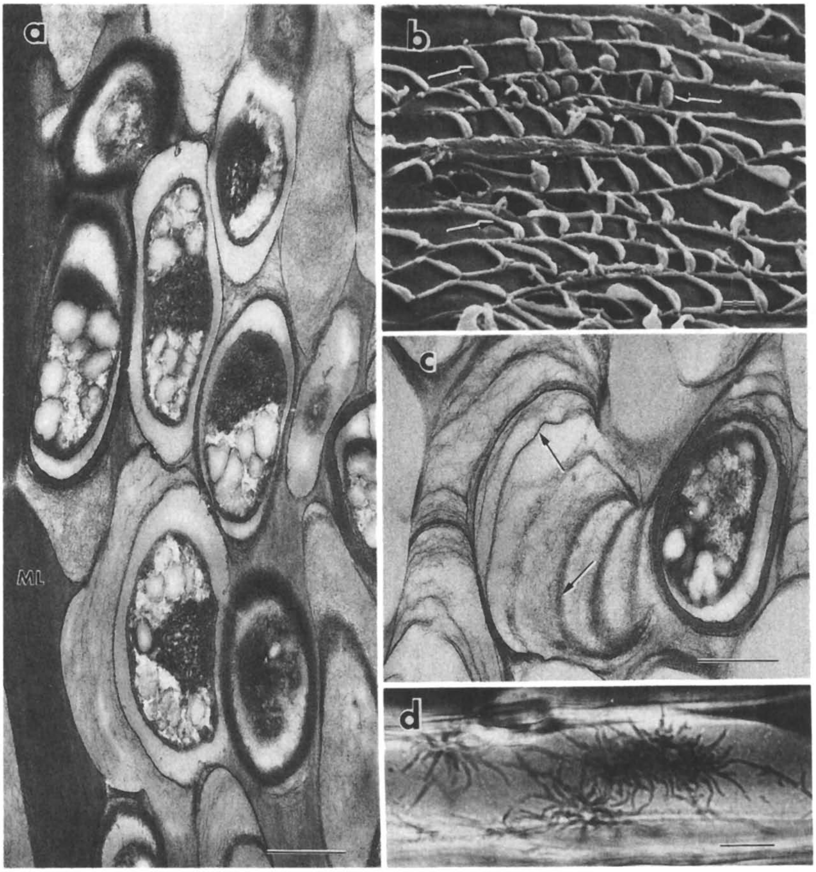


Figure 11. (a) TEM photo shows characteristic tunneling bacterial attack within the S_2 cell wall layer of a Pinus sylvestris *tracheid. Almost the entire S_2 has been degraded, and initial attack of the middle lamella region has also occurred. The several bacteria shown are localized at the ends of the tunnels where progressive decay occurs. Bar: 0.5 μm. (b) SEM showing the characteristic concentric wall-like materials (arrows) that are deposited in the tunnels behind the bacteria during the degradation process. Bar: 1.0 μm. (c) TEM showing the characteristic concentric walllike materials (arrows) that are deposited in the tunnels behind the bacteria during the degradation process. Bar: 0.5 μm. (d) Polarized LM photo showing the highly branched appearance of tunneling bacterial attack within the wood cell wall. Bar: 5.0 μm.*

result in a branched pattern of tunnels. Late stages of attack are characterized by a central heavily degraded area surrounded by a network of branched tunnels. A great variation in tunneling patterns has been observed, an observation that suggests that several different species of bacteria are involved (*103*). Figure 11d shows a typical form of tunneling caused by one species.

The tunnels are often observed to traverse the middle lamella, an indication that the lignin component is attacked. Tunneling through the middle lamella will facilitate the spread of bacteria throughout the wood structure. Tunneling may thus be regarded as a process that corresponds to the penetration through wood cell walls by fungal hyphae.

A considerable amount of severely degraded wood substance appears to remain, even after a very extensive attack. This wood substance, the bacteria, and the concentric layers make up an amorphous substance resembling that described earlier for erosion attack. Although the middle lamella and the S_3 layer will be extensively degraded in localized areas, large parts of these cell wall layers will remain. A quite distinct granular structure and absence of cavitylike attack differentiate decay by tunneling bacteria from that of erosion bacteria.

Cavitation. Like tunneling, cavitation is a process that takes place within the wood cell wall. Angular cavities of varying sizes are produced within the S_2 layer (*91*). The cavities appear to be initiated by one or a few bacteria that penetrate into the cell wall to form a minute cavity. This cavity will enlarge later, with a concomitant increase in the number of bacteria. The cavities are often somewhat elongated. In contrast to the cavities produced by soft-rot fungi, they are oriented more or less perpendicular to the long axis of the fibers. Cavities are often formed in or close to the pit border area (Figures 12a–12c). This position suggests that attack is initiated from the pit chambers.

In contrast to the two previously described forms of bacterial attack, cavitation has not been satisfactorily reproduced in the laboratory. The field material has been very limited, which makes it impossible to give details of advanced decay stages.

Considerably more research is required to obtain more detailed descriptions of the three forms discussed here, as well as of the many other forms that are likely to exist. The studies have been seriously hampered so far by the lack of pure cultures of wood-degrading bacteria. When such cultures become available, quick progress can be expected.

Macroscopic Appearance and Strength Characteristics. No difference in structural appearance can be seen in wood where only the pit membranes have been destroyed. Prolonged storage may, however, result in discoloration because of infiltration of substances from the water or chemical reactions. Strength losses, if any, are small.

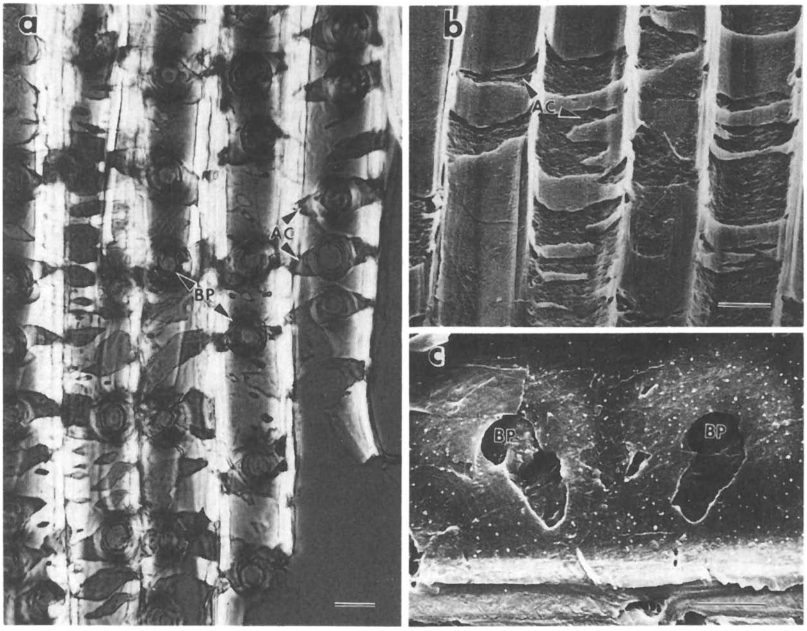


Figure 12. (a) LM photo of cavitation bacterial attack of Pinus radiata *wood cell walls. The cavities are generally oriented perpendicular to the long axis of the fibers and frequently develop from bordered pit (BP) areas. Bar: 5.0 μm. (b) LM photo showing appearance of the angular cavities (AC) of cavitation attack produced within the S_2 cell wall of tracheids. Bar: 5.0 μm. (c) SEM shows where the S_3 has collapsed during specimen preparation, giving the impression of surface attack. BP = bordered pit. Bar: 2.0 μm.*

Wood extensively degraded by erosion bacteria becomes very dark and shows extensive cracking of the surface layers in a manner resembling that of soft rot or brown rot (Figures 13a and 13b). Less degraded areas appear structurally intact, but show a grayish discoloration. Studies on foundation wood piles in Sweden (*101*) and Finland (*102*) suggest that wood, which apparently was attacked to a great extent by erosion bacteria, had suffered from severe losses in strength.

Very few examples of severe attack by tunneling bacteria have been available. The few observations mainly relate to driftwood, preservative-treated posts in ground contact, or material exposed in the laboratory. Wood with extensive attack by tunneling bacteria is only slightly discolored, usually to a light brown or light yellow. Areas of attacked wood that are surrounded by wood degraded by other decay forms usually have a slightly lighter color, suggesting a bleaching effect by the bacteria. Moist, extensively decayed wood is very soft and has a butterlike or sometimes granular consistency. Strength is obviously reduced, but no details are available.

Good examples of attack by cavitation bacteria have so far only been

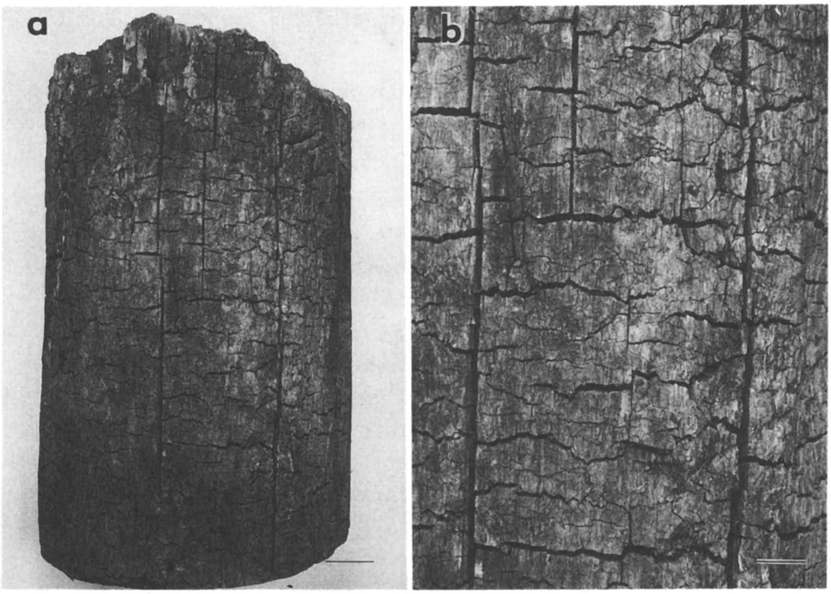


*Figure 13. (a) Pine (*Pinus sylvestris*) from an archeological excavation in Uppsala, Sweden, showing the macroscopic appearance of bacterial attack. Bar: 5 cm. (b) The surface regions of the* Pinus sylvestris *poles have been extensively degraded by erosion bacteria. After drying they have cracked characteristically, resembling soft- or brown-rot decay. Bar: 2.2 cm.*

found in a limited number of preservative-treated posts in New Zealand (*91*). The observed attack, which had not reached an extensive stage, was furthermore accompanied by soft rot. Thus, no details of macroscopic appearance and influence on strength can be given.

Chemical Changes. Very little is known about the chemical changes that follow attack by wood-degrading bacteria. Tunneling bacteria are also capable of degrading the lignin component in wood (*94*), but no detailed studies of wood degraded by these bacteria are available. Studies on foundation piles and river pilings with bacterial attack indicate that the carbohydrates are degraded preferentially, and this degradation results in an accumulation of lignin (*101, 104, 105*). The DP of cellulose was only slightly reduced in the foundation piles.

Timber Species. Bacterial attack has been observed in hardwoods and softwoods. Hardwoods like birch and beech have been found to be degraded faster than softwoods like pine and spruce, when fungal-free bacterial consortia have been used in laboratory experiments. Tunneling bacteria have been found capable of degrading a range of timbers that, for various reasons, are more or less resistant to fungal decay (*106*). This resistance could be caused by high lignin content, toxic heartwood extractives, preservative treatment, or chemical modification. Tunneling bacteria may thus be regarded as the "ultimate" degraders, able to destroy timber that is too resistant for fungal decay.

Environmental Factors. Very little is known about the influence of different environmental factors on bacterial decay. Boutelje and Goransson (*101*) reported that the degradation of foundation wood piles increased with increased nitrogen and phosphorus. Attack by tunneling bacteria in wood exposed in soil appears to be most frequently found in very fertile soils.

Findings of bacterial attack in wood exposed at the bottom of the Baltic Sea suggest that active degradation occurs at rather low temperatures. Tunneling bacteria in laboratory experiments have been found to attack wood at 40°C but not at 45°C. A different form of bacterial attack was observed at 70°C.

Bacterial degradation of wood under completely anaerobic conditions has not been unequivocally demonstrated. The occurrence of bacterial attack in situations that could be characterized as near-anaerobic suggests that some bacteria are capable of degrading wood in situations where fungi are completely excluded because of the limited oxygen. The responsible bacteria in such environments seem to be of the erosion type (*107*). Studies on wood exposed in aquatic environments or other waterlogged situations where oxygen may become limiting suggests that tunneling bacteria need more oxygen than erosion bacteria. Attack by tunneling bacteria is thus more prominent in driftwood or wood samples not exposed to great depths. Kohlmeyer (*108*) reports, however, an apparent attack by tunneling bacteria in wood exposed at depths of approximately 5000 m.

Attack by erosion bacteria and tunneling bacteria occurs in wood that is fully saturated with water. Although no details can be given, other observations from the terrestrial environment suggest that bacterial attack can also occur at lower moisture contents.

Occurrence. Bacterial degradation occurs at a slow rate compared with fungal decay. Bacteria cannot compete successfully with fungi if the substrate and the environmental conditions are suitable for fungal attack. Extensive bacterial attack will be limited to substrates or environments where fungal activity is restricted. Experiments in the laboratory have shown that hardwoods such as birch and beech, containing comparatively low levels of lignin, are quickly degraded by soft rot when exposed in unsterile soil. Impregnation of such timbers with an antifungal antibiotic that prevents fungal activity will, however, result in attack by wood-degrading bacteria. In contrast, exposing softwoods such as pine and spruce in unsterile soil normally results in a mixture of both soft rot and bacterial attack, because the higher lignin content of the timbers impedes soft-rot decay. A similar situation is also seen with lignin-rich hardwoods. The presence of toxic heartwood extractives or wood preservatives may also prevent or restrict fungal growth, and thereby permit bacterial attack.

Waterlogging will exclude white- and brown-rot basidiomycetes. Soft rot may still be active, although at limiting oxygen levels only bacteria are able to degrade wood.

Attack by wood-degrading bacteria has now been reported from all parts of the world. It is difficult when reporting on the occurrence to keep the bacterial decay types separate, because it is not always clear if the reported type falls into any of the three categories of attack. Thus, the attack type should only be reported when there is little doubt.

Bacterial attack has been observed in wood exposed in soil. The studies have mainly concerned posts treated with copper–chrome–arsenic preservatives. The reports show that erosion, tunneling, and cavitation forms of bacterial attack may occur (*91, 92, 109–112*). Extensive attack by bacteria in preservative-treated water-cooling slats was also reported by Greaves (*100*).

Advanced bacterial attack has been observed in wooden foundation piles below the water table (*101, 102, 113, 114*). Waterlogged timber extracted at archaeological excavations in Uppsala, Sweden, was extensively degraded by erosion bacteria.

Wood exposed in fresh water has also been reported to be attacked by bacteria (*103, 104, 115, 116*). The most commonly observed form of attack was erosion.

Attack by wood-degrading bacteria appears to be very common in the marine environment. Degradation by tunneling bacteria has been observed in driftwood samples from Sweden, New Zealand, and Ireland. Kohlmeyer (*108*) described attack similar to that of tunneling bacteria in driftwood samples from the Gulf of Panama. He also reported a similar type of attack in wood panels exposed at depths of up to 5000 m in the Pacific Ocean and Atlantic Ocean. Attack by tunneling bacteria has been found in preservative-treated wood samples exposed in the sea in England (*117*), Sweden, Australia, Papua New Guinea, and Italy. In addition, cell wall erosion has been found in wood exposed in the marine environment (*103*).

It has recently become evident that bacteria cause most of the microbial degradation of timber in sunken ships. Mouzouras et al. (*118*) describe various forms of bacterial attack that were observed in timber from the *Mary Rose*. The attack includes tunneling as well as erosion forms. Soft rot was also observed. Kim (*105*) reported that timber from a wrecked Chinese ship that had been submerged for over 700 years was degraded by soft rot and bacteria. Studies of timber from the Swedish battleship *Kronan*, which sank in the Baltic Sea in 1676, show that most of the microbial degradation of both oak and pine timber can be attributed to erosion bacteria. Soft rot and attack by tunneling bacteria occurred to a much lesser extent.

Wood degradation by bacteria is clearly of great importance in archaeology. Except for dry wood, most ancient wood that has survived until the present will have been exposed to the threats of microbial decomposition. Only wood that has been exposed to conditions restricting fungal decay, conditions that often favor bacterial attack, will survive for any length of time in a recognizable condition.

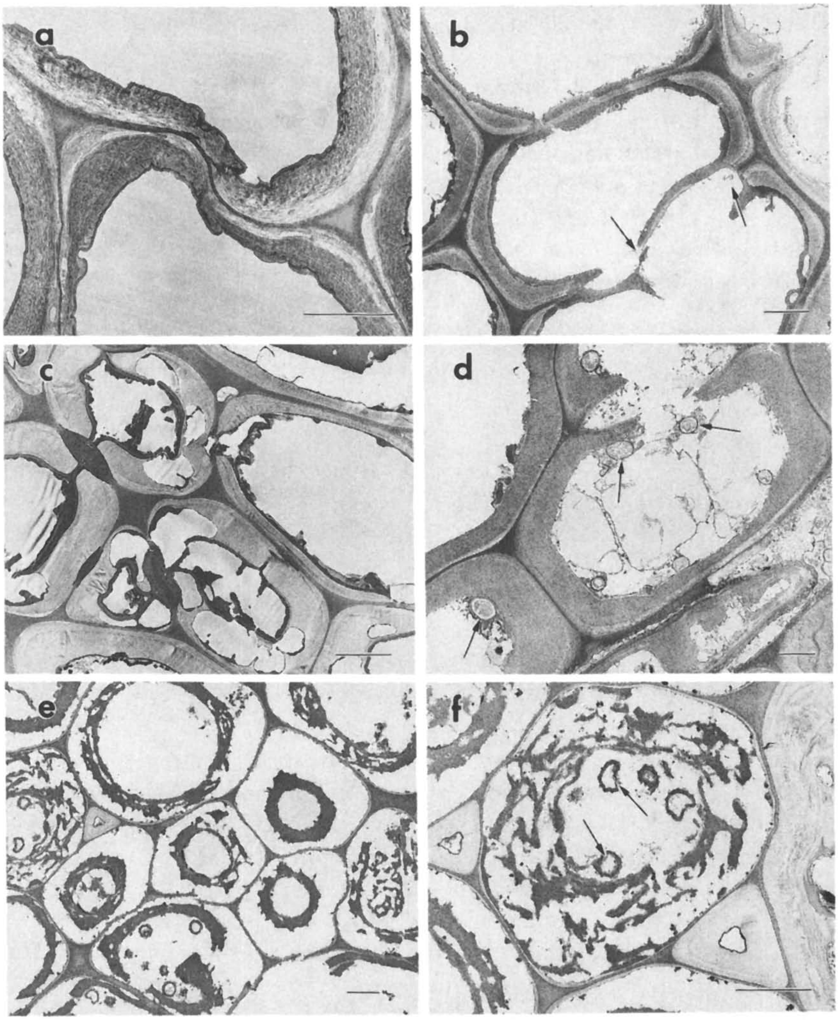


Figure 14. Examples of decomposition in archaeological woods. Bar = 5 μm. KMnO₄ fixation. (a) Conifer wood from northern Minnesota, Pillsbury site, buried by silt for more than 10,000 years. Cells do not have a rigid structure, and carbohydrates have been removed from the cell wall. The decay pattern is similar to advanced stages of brown rot. No evidence of fungi or other

Conclusion

The information in this review provides an overview of microbial degradation of wood. The patterns of degradation caused by different microorganisms are distinct and can be used to identify the type of degradation that may be present in archaeological wood. Figures 10 and 13 show bacterial degradation in waterlogged timber of a sunken ship and in foundation wood from an archaeological excavation in Uppsala, Sweden, respectively. Additional examples of decomposition by fungi in archaeological wood are presented in Figure 14. These samples demonstrate how decay characteristics can be used to elucidate the microorganisms responsible for degradation, as well as provide important insights concerning the condition of the wood. This type of information is crucial to conservators so that proper preservation methods can be determined.

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microorganisms, however, can be found within the specimen. Sample provided by H. Wright and L. Shane, Department of Geology and Geophysics, University of Minnesota. (b) Ponderosa pine wood from a cliff dwelling at 2440 m elevation, Sierra Ancha, Arizona. 1330 A.D. Cells of the sapwood had decay that was typical of a white rot. Cell walls were eroded in localized areas, and a simultaneous removal of all cell wall components occurred (arrows). (c) Quercus virginiana *wood removed from the historic ship* USS Constitution *during reconstruction in 1973. Wood is from original timbers felled in 1794. Cavity formation, typical of advanced stages of soft rot, is evident in the secondary wall layers of fibers. (d) Ponderosa pine wood from Chaco Canyon, New Mexico, 1525 m elevation, that had been buried in an open area. Approximately 1050 A.D. Fungal hyphae are evident within ray parenchyma cells and adjacent tracheids (arrows). Pit membranes are removed, but no cell wall erosion is present. The fungus most likely is a blue stain fungus that colonized the sapwood before the wood was buried. Extensive cell wall decomposition is not evident, and the fungus apparently utilized only the simple carbohydrates in the wood. (e, f).* Juglans nigra *wood from Carnegie Canyon, Caddo County, Oklahoma. 650–1250 B.C. Trees were buried in an area that had a fluctuating water table over the past 3000 years. Cavities in the* S_2 *layer of the fiber secondary walls are evident. The* S_3 *layer and compound middle lamella were not degraded. Fungal hyphae are present in lumena of some cells (arrows). The decay appears to be a combination of advanced stages of soft rot and tunneling bacteria. Samples for Figures b–f were provided by Cass Freedland, U.S.D.A. Forest Products Laboratory, Madison, Wisconsin.*

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7

Treatments for Waterlogged and Dry Archaeological Wood

R. James Barbour

**Forintek Canada Corporation, 800 Montreal Road, Ottawa,
Ontario K1G 3Z5, Canada**

Approaches to the evaluation of the condition of wooden objects and the selection of conservation methods for them are similar, regardless of whether the object is waterlogged, damp, or dry. Treatment methods for these three classes of materials are, however, quite different. Conservation processes for all of these classes of objects basically fall into the categories of arresting deterioration and repairing damage, whether biological, chemical, or mechanical; prevention of dimensional change; and restoration of the appearance of the object. With dry wood in museum collections, the conservator is generally faced with a situation in which restoration of the appearance and reinforcement of the structure of the object are the most pressing concerns. Biodeterioration is the greatest danger in damp material, and dimensional stabilization is most important in waterlogged wood.

CONSERVATION OF WOODEN OBJECTS RESIDES IN A REALM somewhere between a science and an art. This is as it should be, because some parts of the conservation process require the mastery of an artist and others demand the analytical abilities of a scientist. Both sets of expertise are necessary to successfully develop and apply conservation treatments.

The conservator must think like a scientist when developing new treatments, determining how and why they work and selecting the proper treatment(s) for a given object. Once treatments have been developed and selected, the conservator must use the skills of an artist to apply them. For example, it is not sufficient for the conservator to be able to prescribe a specific gap filler because it has a desirable set of chemical and physical

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characteristics. In most cases, the conservator must also be able to apply the gap-filling treatment in a way that is both aesthetically pleasing and functionally correct. After the void is filled, it may be necessary to paint or otherwise alter the surface. No matter how well the conservator understands pigment chemistry, a satisfactory result is unlikely if the conservator is not skilled as an artist. In practice, the selection and application of treatments may be carried out by different people, each with the appropriate set of skills, but a holistic analysis of the conservation process must recognize the importance of both sets of skills.

This chapter deals mainly with the scientific side of this balancing act. As with any scientific investigation, understanding of the mechanisms involved and the repeatability of the processes will be the central issues. Decisions about the types of treatments that will be used to conserve a particular object should be made on the basis of the condition of the object and the way it will be stored or displayed. The funding realities of the project will inevitably be a major concern, but they will not be considered in this chapter.

The bulk of the information in this book refers to the conservation of waterlogged and wet wood. In recent years, there has been a considerable amount of research in this area, although new research on the topic of dry wood has been relatively minor. This emphasis is not meant to imply that the conservation of dry wood is not important or of interest, but the procedures used in this field have changed only slightly over time, partly because dry wood is extremely stable. It may deteriorate as a result of biological attack (Chapters 1, 2, 3, and 6) or exposure to light or the elements (Chapter 11). In any case, the treatments used to conserve dry objects are much more firmly established than those for waterlogged wood. This chapter will present information on the evaluation and treatment of waterlogged, damp, and dry wood, but the information covered is admittedly slanted toward waterlogged and damp wood.

Regardless of whether the wood is wet or dry, the underlying goals and objectives of most conservation projects are quite similar. The treatments themselves may be very different. Obviously, the restoration of a historic building will not be undertaken in the same way as the conservation of a 14th century picture frame, but the route the conservator pursues in evaluating and restoring either object does not vary greatly. These steps can be outlined as follows:

1. Record the condition and appearance of the object.
2. Arrest biological and chemical deterioration.
3. Ensure physical integrity: prevent mechanical damage and excessive dimensional change.
4. Restore the original appearance of the object.

By approaching conservation in a systematic manner, it will be possible to keep track of what has been accomplished, what remains to be done, and how well the treatment works.

Steps in the Conservation Process

Throughout the conservation process, as well as during storage and display, care must be taken to ensure that no new damage occurs. A good way to prevent damage is to understand the properties of the wood, the characteristics of the treatment, and how the two will interact.

Recording of Condition and Appearance. As complete a record as possible should be gathered on the appearance, dimensions, and properties of the object at the time it is brought under the care of the conservator. Photographs, sketches, weights, measurements of dimensions, surface texture, and color are all useful pieces of information and should be noted as a first order of priority. The type and location of deterioration should be documented and recommendations made for the prevention of its progression. This record can be used to appraise the condition of the object at any future time, and its collection will provide a working plan for the conservation of the object.

When routine treatments are used, standardized data on the condition of the object can be collected. For example, at the Canadian Conservation Institute, all small pieces of waterlogged wood are now freeze-dried after impregnation with a mixture of polyethylene glycol (PEG) 400 and 3350 (*1*). Objects are weighed while suspended in water and again in air. Using this information, the species, and estimates of the original specific gravity for that species, a computer program determines the concentration of each grade of PEG to be used in the treating solution. If concentrations are to be changed, the program calculates the weight of each grade of PEG that should be added to the original solution to raise the concentration to the desired level. After a prescribed soaking period, the object is frozen and then freeze-dried. This method is based partly on theory and partly on empirical data. It works well for the types of objects that are generally encountered in Canada and requires very little investment in analytical techniques.

Techniques for Suppressing Deterioration. The methods that might be chosen to suppress deterioration depend on the type of deterioration that is taking place. The nature of biological deterioration has been amply covered in previous chapters.

Attack by microorganisms can generally be stopped by changing environmental conditions so that they are unfavorable to the microorganisms. Most microbiological attack can be suppressed by controlling the moisture content of the wood, but there are situations in which this control may not be possible. Storage of waterlogged wood creates special problems because the wood cannot be dried until dimensional stabilization treatments have been completed. Some conservators use biocides to control biodeterioration (*2*), but others prefer to avoid them (*3*). As a result, novel biological control methods have been suggested. Dawson et al. (*4*) proposed using snails to control slime growth on the surface of waterlogged wood in water storage. Jespersen (*3*) has suggested reburial of waterlogged wood rather than using chemicals to control microorganisms during long-term storage.

In damp wood, the greatest threat is posed by wood-rotting fungi. Small objects can simply be dried, and drying should alleviate the problem. In larger structures, such as buildings or ships, arresting fungal attack may be more difficult. Once fungal infections become established in large timbers, they can be difficult to inhibit because the breakdown of cellulose produces water, which is recycled by the fungi to continue growth. It may be impossible to arrest deterioration before so much damage has been done that the mechanical function of the member is lost. This situation can develop only in massive pieces with high moisture content, like large ship's timbers. In most situations it is possible to remove the moisture source and halt the decay.

Bianchini and Hastings (*5*) are presently in the process of conducting an interesting experiment on the suppression of decay in damp ship's timbers. In an attempt to arrest the activity of wood-rotting fungi, the hull of the steam schooner *Wapama* is being treated with boron compounds while it is slowly dried. This case is apparently the largest-scale application of this process yet attempted, and indications are that it is working. The success of the treatment will, however, not be known for several years.

In some situations (totem poles displayed out of doors, for example) the moisture source cannot be removed. Grading around the object and installation of drain tile at its base may help to slow the rate of decay. Groundline chemical treatments may also be used, as well as shielding the object by constructing a partial enclosure around it. Protection from weathering is the topic of Chapter 11. In many cases the chemical deterioration caused by weathering can be prevented by passive measures like shielding the object from the sun, wind, and precipitation. These types of techniques are considered passive methods because they do not require that the object be given any special chemical treatment.

Attack by insects presents a completely different set of problems. Insects can often be controlled by lowering the moisture content, but some wood-boring beetles and dry-wood termites can survive at moisture contents as low as 6–8%. Their control requires special techniques. These techniques are discussed in Chapter 12 and by Erickson (*6*) and therefore will not be covered in detail here.

Ensuring Physical Integrity. When objects become too weak to support their own weight, they must be mechanically supported. Some good examples of this support can be seen with ships, for example, in the figures presented by van der Heide (*7*, *8*) and Ginier-Gillet et al. (*9*). Support of objects in museum displays and in storage is an old practice, and few advances have been made in recent years. The most important aspect is to provide sufficient support so that the object is not damaged by the frames used to hold it. This aspect requires an understanding of the mechanical properties of the object. It is also important that sufficient records be kept on the appearance of the object so that deformations, which may take place over a period of years, can be recognized and corrected.

Moisture-related dimensional change is likely to be one of the more important threats to the physical integrity of wooden objects. When wood is moved inside after being used out of doors for many years, considerable distortion can take place during drying. Drying problems are inevitably encountered when ships are moved from water storage to indoor displays (*7*). Parts of the hull are above the fiber saturation point because they were in contact with liquid water, while other parts are at equilibrium with the outside air. Some pieces may have been put together while they were green and have never dried. If the saturated portions of the hull begin to dry too quickly, severe drying defects may occur. If they dry too slowly, attack by wood-rotting fungi may destroy large parts of the hull.

Several types of drying defects may arise. Checking and warping are the most likely, but honeycomb and collapse could also develop. Checks can be concentrated by cutting radially oriented saw kerfs. This method is used in the preservative-treating industry (*10*). Kerfing could be applied on round objects and large timbers with boxed heart to prevent deep uncontrolled checks from appearing. This suggestion may be distinctly unappealing to many conservators, because it involves damage to the object. It could, however, provide a method for preventing serious deformation of the object.

Restoration of Appearance. There is no agreement on whether the appearance of historic and archaeological objects should be altered after stabilization treatments are complete. Many methods are available for filling gaps and changing surface color or texture, but a description of their use and properties goes beyond the scope of this chapter.

Evaluation of the Condition of Objects

Conservation treatments should be chosen after the condition of the object has been evaluated, but unfortunately this sequence is often not followed. For waterlogged wood, polyethylene glycol (PEG) soak treatments are quite popular and are frequently applied without regard to the condition of the objects being treated. This treatment has sometimes proven to be a mistake. Some artifacts have been soaking in PEG for years or even decades but are not stable. Unfortunately, failures of conservation treatments are only infrequently reported in the literature; reports of successes can also be misleading. If the condition of an object is not evaluated and recorded before treatment begins, it will never be clear why a treatment worked, how it works, or when it is appropriate.

Restoration of an object may be as simple as regluing a broken piece. It could also require more difficult operations like fabricating missing pieces, filling voids, strengthening the wood structure, or returning the surface to its original color. When treatments are developed and tested, it is important to collect as much detailed information as is possible about the object. This information will allow better evaluation of the results and help in selecting the proper treatments in future work. When a conservator successfully treats an object, the question of why the method worked should always be asked. The function of each type of treatment is different, and it should be selected to suit the condition of the object. A tendency to neglect this fact is one of the primary reasons why so much confusion exists over why conservation techniques succeed or fail.

The first stage in the evaluation process is to determine the state of deterioration of the object. In order to make this determination, it is important to understand the types of deterioration that can be expected. Mechanical damage often appears catastrophic, but it is relatively easy to repair in comparison to biological or chemical damage. If a chair has a broken leg, it can be doweled and glued; if a roof sags because of a broken beam, it can be reinforced. On the other hand, if the chair leg broke because the wood was riddled with beetle galleries, there may be nothing left to glue. If the beam broke because it was rotten, some remedial work may be necessary to solve a moisture problem before reinforcement of the structure will be effective.

Microscopic Examination. A description of the microscopic condition of the wood is commonly used (*11–14*). Microscopic examinations supply valuable information about the condition of the object (cf. Chapters 2, 3, and 6). They also help to predict how well proposed treatments will work on the basis of published data about the types of deterioration present in objects that have previously been treated successfully.

The most important use for microscopic examination is to document the effectiveness of treatments and to evaluate the success of new treatments. Organ (*15*), Watson (*13*), and others have used scanning electron microscopy to assess the treatment of objects with different types of consolidants. They have been able to demonstrate the parts of the wood in which the chemicals reside and how they function.

Microscopic examinations provide a record of the amount of cellular collapse that takes place during treatment. A preliminary examination of the wood can prevent confusion as to how well the treatment actually worked. In waterlogged wood and damp wood, cellular collapse is often present before treatment begins. If this fact is known, collapse observed after treatment will not be attributed to poor stabilization.

Barbour and Leney (*16*) combined microscopic observations and controlled drying to observe cellular collapse of highly deteriorated waterlogged wood. Such studies are useful in understanding how collapse takes place. Observations of this type help to explain results that had previously been reported for waterlogged wood. Muhlethaler (*17*), de Jong (*18*), Matsuda (*19*), and others have shown that the tangential dimensional change on drying of highly deteriorated waterlogged wood was much greater and more consistent than dimensional change in the radial direction. Barbour (*20*) demonstrated that tangential walls buckle early in the drying process, but radial walls do not begin to buckle until cellular collapse has almost completely closed the lumens. There simply is not sufficient space for a great deal of distortion to take place in the radial direction.

The tendency of waterlogged wood to collapse tangentially could account for the results reported for the Utrecht ship (*8*) that was soaked in creosote and linseed oil, a treatment that should have little effect on collapse, except in cells very close to the surface, and none on cell wall shrinkage. Jespersen (*3*) notes that the planking on ships of this type was split so that the wide face was a radial surface (i.e., equivalent to quarter sawn boards). Planks of this type could have collapsed considerably in the tangential direction and yet appear well stabilized. A second alternative is that the creosote and linseed oil may have acted as a moisture barrier that caused the wood to dry very slowly, thus reducing drying stresses and subsequent distortion. The results obtained with the Utrecht ship could also be a result of excellent preservation of the wood. Finally, the ship may actually have been damp and not waterlogged, which would have made drying much less difficult. Rather simple analysis of transverse microscopic sections makes it possible to determine which, if any, of these hypotheses are correct.

Chemical Analysis. Chemical analysis can be conducted either directly or indirectly (cf. Chapter 5). Barbour (*21*) demonstrated that in waterlogged woods, information about the chemical composition of deteriorated wood can be gathered from delignified samples. The carbohydrate skeletons of several samples were examined and their condition was shown to be directly related to the specific gravity of the wood. Matsuda (*19*) used similar delignification techniques to show that dry tightly collapsed waterlogged wood could be reswollen.

Matsuda developed this method to make identifications of species easier. Variations of this treatment could, however, have some utility in restoring small waterlogged artifacts that have been dried without treatment. Although this treatment creates a very fragile material, it might be combined with other treatments to save some objects that otherwise would be a complete loss. Even if this treatment is deemed impractical as a conservation method, it does demonstrate that dry waterlogged wood can be rehydrated. It shows that it may be worthwhile to attempt to develop lignin-softening techniques that would not remove lignin but cause it to swell, thus returning greatly distorted objects to something resembling their original shape.

Chemical composition makes certain cell types (e.g., ray parenchyma cells (*22*) and parts of cells such as pit membranes (*23*) more susceptible to biological attack. Hedges et al. (*24*) and Barbour and Leney (*25*) have shown that the degree of deterioration is often closely related to the topochemistry of individual cell types and parts of cells.

Information on the degree to which each cell type is deteriorated can be used to determine how impregnants will travel through the wood (*21*). If, for example, rays are more deteriorated than other elements, as is often the case with bacterial deterioration, treating chemicals can be expected to move relatively rapidly in the radial direction, but may not move quickly in the tangential direction. This disparity results in an uneven distribution of the chemicals (*22*). Rapid movement along rays and poor impregnation of fibers is especially noticeable in dense hardwoods with thick-walled fibers that may not be in direct contact with a ray. In other cases secondary walls are highly deteriorated, but the middle lamellas and pit membranes are mostly intact (*21*). In this situation, diffusion of high-molecular-weight impregnants may be quite slow, even though the wood is very deteriorated.

Hoffmann (*11*) published a set of chemical methods that can be used to determine the degree of deterioration of wood. He showed that the chemical composition of waterlogged wood was closely related to the maximum moisture content, which is in turn a function of specific gravity. Barbour (*21*) used the data provided by Hoffmann (*11*) to demonstrate that in waterlogged wood samples with low ash content, the existing specific gravity of the wood can be used to calculate its chemical composition. This method will work if an estimate of the original specific gravity and chemical composition of the wood is available.

After consideration of published chemical results, Grattan and Mathias (*26*) concluded that for routine conservation of small amounts of waterlogged wood, chemical analysis is unnecessary. They felt that the use of specific gravity to calculate loss of cell wall material was more economical and less time consuming to perform. This conclusion led to the development of the standard freeze-drying treatment method used at the Canadian Conservation Institute.

More traditional chemical analysis can be used to determine what type of treatment is appropriate. It can also provide information useful in devising new treatments. During experimental work to develop new treatments, chemical analysis is invaluable. Not only does it provide a more exact description of the wood, which is essential if reproducibility is to be ensured, but it allows treatments that affect certain chemical components more than others to be considered (*1*).

Physical Properties. For waterlogged wood, the most important consideration is whether the wood structure is sound enough to withstand capillary forces that will cause cellular collapse when the object is dried (cf. Chapter 4). Failure to address this question has been the bane of the PEG treatment, and several empirical methods have been developed to answer it. Almost all center around either the moisture content (*17*, *18*) or specific gravity of the wood (*26*). Wood is placed into various classes by its moisture content or specific gravity and, through trial and error, treatments are developed that will stabilize each class.

This method of evaluation is satisfactory when a large amount of wood of the same or similar species, which has been deteriorated under uniform conditions, is being treated. An appropriate use of this method would be in developing treatments for a ship's timbers. In some respects, experience gathered in this way can be transferred from one object to another. This type of classification system is less reliable when it is developed for one species but applied to another or when deterioration has occurred under different environmental conditions.

Waterlogged wood is, by definition, at or near its maximum moisture content. That is, every available void space is filled with water. The value of the maximum moisture content can be calculated as follows:

$$\mathrm{MC}_{\max} = \frac{1}{S_{\mathrm{o,g}}} - \frac{1}{S_{\mathrm{ws}}}$$

where $S_{\mathrm{o,g}}$ is the specific gravity on the oven-dry weight, green-volume basis; S_{ws} is the specific gravity of the wood substance or 1.53; and $\mathrm{MC}_{\max}$ is the maximum moisture content.

If we consider a piece of oak with an initial specific gravity of 0.55 and a piece of aspen with a specific gravity of 0.36, the $\mathrm{MC}_{\max}$ of the oak will be 116% and the $\mathrm{MC}_{\max}$ of the aspen will be 212%. If the oak loses 35% of its weight, it will have a specific gravity of 0.36 and an $\mathrm{MC}_{\max}$ of 212%. According to de Jong's classification system, the oak would be moderately to highly deteriorated at this point (*18*). The aspen, on the other hand, would not have been deteriorated at all, but would merely have a very high moisture content. Therefore, the original specific gravity of the piece of wood must be taken into account when using moisture content as a criterion for deterioration.

A second useful technique involves checking to see if the current moisture content matches the maximum moisture content. If the current moisture content is appreciably lower than the maximum moisture content, the wood is not truly waterlogged, and collapse during drying is not likely to be as great a problem.

Types of Treatments

Three types of chemical treatments can be applied to wood: coatings that cover the surface and do not penetrate the wood structure, bulking treatments that enter the cell wall and reduce cell wall shrinkage, and lumen-filling treatments that fill the lumens with a solid substance to prevent cellular collapse and improve mechanical properties.

Coatings. Coatings have more application in dry wood than in waterlogged wood. Numerous types of coatings and finishes are applied to wooden objects, but a description of their use, selection, and function is beyond the scope of this book. To the extent that they can be used to prevent weathering in the form of mechanical damage or deterioration by ultraviolet radiation, they are covered in Chapter 11.

Coatings are also used to improve the surface quality and integrity of very fragile dry artifacts. Coatings can be used to consolidate surfaces so that small pieces do not constantly fall off artifacts while they are in storage or on display. Polyvinyl acetate and microcrystalline wax are frequently used for this purpose.

When waterlogged wood is treated with PEG and stored or displayed in areas with high relative humidity, the low-molecular-weight fractions tend to bleed from the surface. A number of coatings have been used to arrest this accumulation of low-molecular-weight PEG on the surface of artifacts. The most common remedy is to apply a thin coat of molten high-molecular-weight PEG to the surface of the object.

Bulking Treatments. Bulking chemicals enter the cell wall. They are generally intended to prevent cell wall shrinkage, but almost universally change the mechanical properties of the cell walls. Some strengthen the walls and others weaken them. Bulking treatments can be divided into nonreactive and reactive treatments. Nonreactive treatments are those in which chemicals enter the molecular structure of the cell walls, replacing water and holding the walls in their swollen or semiswollen state. They are attracted to the cell walls by hydrogen bonding, but do not form covalent bonds with the cell wall substance. PEG, sugars, and salt treatments are examples of nonreactive bulking treatments. In these treatments the attraction between the bulking agent and the wood substance is weak and, at least in theory, reversible. These treatments tend to reduce the stiffness of the cell walls.

In reactive bulking treatments, a chemical is covalently bonded to the cell wall. Cross-linking of the cell wall material may also occur. Such treatments sometimes swell the wood and sometimes cause it to shrink. Examples of reactive bulking treatments include alkylene oxides and impregnation with thermosetting resins. These treatments are essentially nonreversible, but they often improve the stiffness of the cell walls. As a result of their nonreversibility, the conservation community is very cautious about adopting such treatments. It is, however, likely that these methods will find some utility with very deteriorated objects that cannot be satisfactorily stabilized by more traditional techniques.

Lumen-Filling Treatments. Lumen-filling treatments improve the mechanical properties of wood and prevent cellular collapse. In dry wood, improving mechanical properties is generally the objective; in waterlogged wood a combination of both functions is usually sought. The cell lumens, along with other permanent voids in the wood structure, are filled with a solid. The solid may be soluble or insoluble, but the intention is to improve the rigidity of the object, prevent cellular collapse, and in some cases to enhance surface characteristics. The treatment may be reversible if a soluble substance is used or nonreversible if an insoluble substance is chosen.

Depending on the final concentration of the treating solution, PEG can be either a lumen-filling treatment or a nonreactive bulking treatment. At low concentrations it will bulk only the cell walls, although at higher concentrations it will also fill lumens. Linseed oil, tung oil, and other drying oils fill the lumens near the surface. These treatments, which are normally thought of as coatings, actually change the refractive index and mechanical properties of the cells near the surface of the wood. In situ polymerization of hydrophobic monomers such as styrene and methyl methacrylate are nonreversible lumen-filling treatments (cf. Chapter 9).

Many in situ polymerization methods are also variations of solvent-drying treatments. In these treatments water is replaced by a carrier solvent that is replaced by a monomer (e.g., styrene, methyl methacrylate, or butyl methacrylate), which is then polymerized by either heat or γ radiation. The residual solvent is evaporated and the object is stable. When hydrophobic monomers are used in this process, it is a lumen-filling treatment and cannot control cell wall shrinkage. Variations of the in situ polymerization process that are now being developed use water-soluble monomers that, like soak treatments with high concentrations of PEG, would be a combination of bulking and lumen-filling techniques. The advantage would be the elimination of bleeding and better stabilization, but irreversibility would be a disadvantage. In situ polymerization treatments are covered in greater detail in Chapters 12, 13, and 16.

Drying Methods

The conservation of waterlogged wood involves removal of water, as well as improving mechanical properties. The simplest drying technique is to remove the object from water and allow it to dry. This technique will usually result in unacceptable amounts of dimensional change (i.e., a combination of cell wall shrinkage and cellular collapse). Some type of chemical pretreatment is usually applied before drying to improve the dimensional stability of the waterlogged wood. For damp woods, pretreatments may not be required.

The type of pretreatment depends on the moisture content of the wood and its degree of deterioration. For slightly deteriorated woods, no pretreatment may be called for, but in most cases a bulking treatment is used to prevent surface checking. For more deteriorated woods, some type of lumen-filling technique is used to reduce cellular collapse and improve mechanical properties.

Controlled Drying. Shrinkage-related defects such as checking, warp, and honeycomb (internal checking) can be controlled by limiting the development of moisture gradients within the wood. This technique is widely used in the forest products industry for drying lumber, but problems may be encountered when deteriorated wood is dried. Barbour (*20*) has shown that in deteriorated waterlogged wood the magnitude of cell wall shrinkage may differ from that expected for undeteriorated wood. Longitudinal shrinkage is significantly increased, and the ratio of radial to tangential shrinkage also changes. This result means that even if an object can be dried without serious degradation, it will not have the same shape as it did when it was manufactured.

Controlled drying is therefore more successful when combined with a bulking pretreatment. PEG is the most commonly applied pretreatment. Objects are either soaked or sprayed with aqueous solutions of PEG, and then moisture is removed under high relative humidity conditions. Controlled drying has been used with varying degrees of success (*27*, *28*). However, one of the most intriguing examples is the *Wasa*, in which controlled drying was not a specified part of the conservation process (cf. Chapter 8).

Several aspects of the treatment of this ship would serve to limit drying stress development. PEG was sprayed on the surface in aqueous solutions. It did not penetrate deeply, but dimensional stabilization of a thin outer layer helped to prevent the development of surface checks by keeping the surface partially swollen and relatively pliable. Adding liquid water to the surface would tend to decrease the steepness of the moisture gradient and in turn to reduce the likelihood of internal checking or honeycomb. Finally, the reduction of shrinkage of the outer layer of the wood could help to limit the amount of capillary tension type collapse. Stamm and Loughborough (*29*) suggested that this type of collapse is initiated by failures in the cell wall that occur as a result of compression of a fully swollen core by a dry shell. If compression failures in the cell walls do not occur, then the whole collapse process may be avoided. The combination of these factors could explain why the hull of the *Wasa* is well preserved, even though the PEG concentration is very low (*30*).

Conservators need to realize that controlled drying should be a part of any bulking treatment. Whether objects are large or small, moisture gradients and the stresses arising from them will develop if drying proceeds too quickly. The most common method for limiting drying rates is to wrap objects in polyethylene sheeting or to place smaller objects in controlled temperature and humidity cabinets.

Freeze-Drying. Freeze-drying is probably the second most commonly used drying method for waterlogged wood (cf. Chapter 10). The International Council of Museums (ICOM) Wood Working Group on Wet Organic Materials has conducted a comparative study in which 26 different treatment programs, including several freeze-drying methods, were compared on identical samples by 13 conservation laboratories around the world (*31*).

Three methods were used to characterize the woods being treated. (1) A microscopic record was made of each sample that included sections from each anatomical plane (i.e., transverse, radial, and tangential). Sections were made both before and after treatment. (2) Maximum moisture content was measured, and this was converted to specific gravity. (3) Finally, a detailed chemical analysis was conducted on each sample. Methods followed those developed by Hoffmann (*11*).

This was, by far, the most complete study of its kind ever conducted. It was designed in a way that will make it possible to compare results of treatments devised in the future to the treatments tested. Grattan (*32*) points out that the only satisfactory way to assess the different treatments is to actually view the samples. A repository housing all the samples and treatment records has been established at the University of Tronheim in Tronheim, Norway. A videotape has also been produced that shows each sample and describes its treatment and the results. This videotape will make it possible for those unable to visit Norway to determine which treatment is best suited for their artifacts.

Of the freeze-drying methods tested, pretreatment with PEG 200 and 400 worked well with undeteriorated wood. Very highly deteriorated hardwoods responded best to pretreatment with a combination of higher molecular weights of PEG or PEG dissolved in solvents such as *t*-butyl alcohol (*32*).

Solvent Drying. Solvent drying in its simplest form consists of a solvent exchange followed by controlled evaporation of the solvent from the object. This method was suggested when it was realized that capillary-tension collapse was responsible for most of the dimensional change that occurred during the drying of waterlogged wood. The used of solvent drying was recommended because solvents could be chosen that had a much lower surface tension than water. Drying from low-surface-tension solvents would, in theory, reduce the amount of capillary-tension collapse.

This method has not, however, worked well. Solvent drying does not stop all cellular collapse. In addition, it does nothing to reduce cell wall shrinkage. Even if it is successful, there is a real possibility that the shape of the object will not be representative of its original dimensions (*16*). Solvent drying alone has apparently never been applied successfully.

A second form of solvent drying is, however, used on waterlogged wood.

These methods involve solvent exchange of water for some carrier solvent, followed by exchange of the solvent for an impregnant. The acetone–rosin process is such a treatment, in which water is replaced by acetone and the acetone is replaced by rosin. The remaining acetone is then removed by evaporation, and stabilization is complete. Because rosin is hydrophobic, this method is classed as a lumen-filling treatment and does not work well on highly deteriorated objects where control of cell wall shrinkage is quite important. Fox (33) has, however, had considerable success with this treatment on slightly and moderately deteriorated wood, especially dead eyes and other ships' fittings.

Conclusions

Over the past 20 years the understanding of the influence of the types and severity of deterioration on the outcome of conservation treatments for wooden objects has greatly improved. The reasons that treatments succeed and fail is much more clearly understood, and new treatments are devised from a stronger base than was previously the case.

Analytical methods have evolved for the evaluation of the condition of objects. These have made possible comparisons of different treatments applied to wood in similar states of deterioration. Such comparative techniques are invaluable in selecting the best treatment for a particular object. Passive methods have been developed to suppress deterioration without the use of toxic chemicals. Considerable strides have also been made in the ethical aspects of when and how objects should be conserved. For example, reburial is now an accepted long-term storage technique for waterlogged wood when immediate conservation treatment is impractical.

There is still a need for further research into the properties of deteriorated wooden objects and improved methods for dimensionally stabilizing waterlogged wood, as well as techniques for improving the mechanical properties and appearance of both wet and dry wood. The field of conservation of wooden objects does, however, have a firm theoretical base. This work can now progress in a much more systematic fashion than was possible in the first half of this century.

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8

The Role of the *Wasa* in the Development of the Polyethylene Glycol Preservation Method

Birgitta Håfors

Statens Sjöhistoriska Museum, Museivägen 3, S–115 27 Stockholm, Sweden

The wreck of the Wasa, *a Swedish 17th-century man-of-war, was the first of the ancient ship hulls salvaged from the sea to be preserved with polyethylene glycol (PEG). The history of PEG use in wet archaeological wood is related as a background to the choice of PEG for the* Wasa. *The hull was preserved by spraying, and about 15,000 disconnected wooden pieces received tank treatment. The percentages of PEG in samples from different parts of the* Wasa *hull and from one of the batches of tank-treated material after preservation are presented. PEG distribution in the samples made a starting point for a discussion about the possible mechanism of PEG uptake in the wood.*

THE *WASA* IS A SWEDISH WARSHIP built between 1625 and 1628. She is a large ship with 64 guns. The hull is about 50 m long and nearly 12 m across its widest point. The sterncastle is 18 m high, and the height midships is about 10 m. The prow adds some extra 12 m to the length.

The *Wasa* met with catastrophe on her maiden voyage and sank in the Stockholm harbor. Immediate attempts to raise her failed. In the 1950s the private researcher Anders Franzén, after studying archival documents about the capsizing, dragged for the hull. Finally, on August 25, 1956, he got a sample of black oak with his special sampling device. Divers went down at the spot where the sample was taken and found a wooden hull on the seabed. The hull was later identified by one of the cannons, which was found in its original place on the lower gun deck, as the *Wasa* of 1628.

The salvage began in 1958. At the beginning of May 1961, the hull was

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raised and placed on a specially built pontoon. A housing was constructed around the hull, which became part of the *Wasa* dockyard museum.

Along with the excavation of the hull in the summer of 1961, divers at the *Wasa* wreck site between 1956 and 1967 recovered about 15,000 disconnected wooden pieces. Among these pieces are about 700 sculptures.

The hull underwent preservation treatment from 1962 until 1979 in its dockyard housing. The disconnected pieces have been preserved in tanks in a specially built conservation laboratory.

History of the Use of Polyethylene Glycol in Wet Wood

Synthesis. The first synthesis of polyethylene glycol (PEG) is attributed to the French chemist and Sorbonne professor Charles Adolph Wurtz. He derived ethylene oxide in 1859 by the action of caustic alkali on ethylene chlorohydrin. Then Wurtz reacted ethylene oxide with water to derive ethylene glycol. He obtained the lower-molecular-weight polyethylene glycols along with the ethylene glycol, and those polyethylene glycols first gained technical importance.

In the 1940s, however, the use and manufacture of the higher-molecular-weight PEGs grew in both variety of application and volume. By the beginning of the 1950s the PEGs, which later became important in the preservation of wet archaeological wood, were manufactured by 5–10 companies throughout the world.

The first step toward discovery of PEG's shrinkage-reducing effect on wood was probably the observation of its swelling effect on cellulose fibers when used in the manufacture of paper. This discovery was reported to the patent office of the Swedish company Mo och Domsjö in October 1946 by Rolf Morén, who was manager of the chemical applications and technical service department of the company. However, no report was published and no patent application was made at that time.

Alfred Stamm studied swelling of fibers at the Forest Products Research Laboratory in Madison, Wisconsin, during the 1940s. In 1956 Stamm published a paper (*1*) about dimension stabilization of wood with polyethylene glycol. The object of the research was discovery of a way to season green wood. The use of PEG for such seasoning was soon introduced on an industrial scale in the United States.

Museum Conservation of Wet Archaeological Wood. In 1951 the conservator at the National Museum of Denmark, Börje Brorson Christensen, published an article (2) about preservation of wooden objects found in peat bogs, in which he described the methods used to preserve that kind of material. By that time the drawbacks of the alum method, especially when glycerin was added, had began to show, and Christensen was working to find a suitable replacement for it. As PEG was not mentioned in his article, it should be safe to assume that conservators did not yet know of it as an agent capable of controlling the dimensions of wood during the drying process.

Something happened during the 1950s that changed this situation. Christensen (3) reported in 1970 that he had learned about the use of PEG for impregnation of waterlogged wood from Bertil Centerwall, who was conservator at the historical museum belonging to the University of Lund in Sweden. With that information, he started experimenting with PEG "some time about the end of 1957 or the beginning of 1958" (3).

Fishing Net. The finding of a 6000-year-old fishing net in a peat bog in summer 1951 probably started it all. The fishing net was part of a fish trap. Apart from the net, the trap consisted of some wooden pegs of around 25-mm diameter and varying lengths up to 60 cm. Centerwall was responsible for the conservation of the fish trap. The net, which was made of a cellulose fiber material, was the main object of concern.

In a speech at a Swedish chemists' society meeting in Örnsköldsvik in December 1959, Centerwall said that when considering treatment for the net he remembered that an archaeologist from the British Museum had once told him that a preparation called Bedacryl was used in England to preserve organic archaeological finds. To get a sample, Centerwall turned to Mo och Domsjö AB. The company provided him with poly(vinyl alcohol) and poly(vinyl acetate), which were the main constituents of Bedacryl. Together with those samples, he received some polyethylene glycol A4000, which was manufactured by Mo och Domsjö and had been sold by that company since 1946.

Centerwall tried poly(vinyl alcohol) on some peat that contained pieces of the net, but could not keep it in a swollen condition with that substance. Then he tried the PEG A4000. A very encouraging test dated October 23, 1951, resulted in only 3% shrinkage of a piece of peat containing some fragments of the net when PEG A4000 was substituted for the water. However, the net was still fragile after this treatment and could not be handled. Some of the wooden pegs that were treated along with it were very well preserved, with only 2% shrinkage of the diameter of the transverse section.

Method Development. This interesting result led Centerwall and engineer Rolf Morén into a prolific period of preservation method development. They worked with the PEG manufactured by Mo och Domsjö AB. Their goal was preservation of artifacts recovered from peat bogs and other wet areas within the field of operation of the historical museum of the University of Lund.

Preservation of artifacts with poly(alkylene glycol)s and their esters and ethers was first patented by Mo och Domsjö AB (*4*). The patent document, naming Morén and Centerwall as inventors of the method, was dated the September 30, 1953, "to be sealed as of the 10th of October 1952" (*4*).

During the 1950s Centerwall continued the systematic research work with PEG on preservation of archaeological wood. By special agreement, he got samples of wooden material from archaeological excavations. The wood was not of archaeological interest, but could be dated because it was found in archaeologically well-defined strata. Thus, he obtained different kinds of wood in varying states of chemical and biological decomposition. On this material he tested PEG (MW 200–20,000) that he obtained from several manufacturers.

The test results and preserved wooden objects caught the interest of visitors to the laboratory. In March 1957 the conservator of the archaeological institute of the University of Aarhus, Denmark, wrote to Morén and requested a sample of PEG. He had seen Centerwall's results and considered them excellent. Consequently, he would not hesitate to use the method on material that he had kept stored in water for a considerable time because of his doubts about the alum preservation method.

The PEG preservation method was presented by Morén and Centerwall (5) in an article in the publication series of the historical museum of the University of Lund.

In 1959 several articles (6–8) about PEG preservation of waterlogged archaeological wood appeared in *Studies in Conservation*. Some of the more delicate material from the Oseberg Viking ship had been kept in water with formaldehyde from its excavation in 1904 until 1954, waiting for a suitable preservation method (6). Treatment was then started by the conservator at the archaeological collection of the University in Oslo, Anna M. Rosenqvist. A number of methods were used on the material, including treatment with PEG (7). A group of wooden objects excavated by Desmond Clark in 1956 (Kalambo Falls, Southern Rhodesia) was dated by ^{14}C analysis as 53,000 years old. The objects were treated at the British Museum Research Laboratory with PEG 4000. The procedure was thoroughly described by R. M. Organ (8), head of the metals department at the research laboratory.

The *Wasa* and PEG. Because of storage and preservation problems, as much as possible of the disconnected wooden material from the *Wasa* wreck site was left on the seabed during the preliminary work to raise the hull. However, divers brought up some pieces, and in 1958 some small sculptures were treated with PEG. The salvage operation leader and head of the naval dockyard, Edward Clason, got written permission from the license holders Mo och Domsjö AB and Centerwall, dated February 9, 1959, to use the PEG method without license cost.

On February 21, 1959, an exhibition with 20–30 sculptures from the *Wasa* was opened at the maritime museum in Stockholm. Those sculptures were brushed with PEG solution before, during, and after the exhibition. Later in 1959, the lion figurehead and a few smaller sculptures were preserved with PEG by tank treatment.

Even though PEG had been introduced into the *Wasa* preservation work, it was not the only preservative considered. Even the technical and economic possibility of treating the hull and the coarser disconnected structural pieces was called into question.

Board of Specialists. In September 1960 a group of specialists was formed for the preservation of the *Wasa* material. Tore Boström was then in charge of the project. Other members were Bertil Thunell (specialist in wood technology), Lars Birkner, (specialist in preservation against rotting and fungi), and Morén. Morén presented information about PEG to the Board of the *Wasa*, which had been appointed by the Swedish government on September 30, 1959, to manage the technical and financial aspects of salvaging the *Wasa*.

The members of the Board of the *Wasa*, however, did not consider themselves competent to decide which preservative to use. To provide a broader competence on preservation matters, a board of specialists on the different kinds of materials involved was formed in April 1961. The specialists were Thunell (wood technology), Erik Björkman (wood deterioration and protection), Tore Boström (metals, glass, and ceramics), Hans Holmgren (wood protection), Hans Axelson (textiles and leather), Ernst Abramson (nutrients), and Arne Strömberg (iron, bone, etc.). All of these experts were attached to public scientific institutions. As such, they served on the specialists board with no charge to the Board of the *Wasa*. Other specialists were added later, as the need for further competence arose. The specialists board is still in operation, with the members Thunell, Bengt Rånby (who was appointed in 1964), and Claes Allander (ventilation specialist, appointed in 1981).

During 1961 a conservation laboratory was built to care for the disconnected *Wasa* finds. A staff was hired to do the preservation work; I joined the group as a chemist. The new head of the *Wasa* preservation effort, civil engineer Lars Barkman, became secretary to the board of specialists.

Treatments Considered. The board of specialists had to consider many products that were suggested for use as preservatives. PEG is not toxic to fungi. Therefore, if PEG was going to be used, either the archaeological material had to be treated with fungicide prior to the PEG treatment or fungicide should be dissolved along with PEG in the conservation solution. The latter treatment was recommended, and my first task at the conservation laboratory was to develop such a solution.

The fungicides suggested were pentachlorphenate, boron formulae, and fluorides. The chemical properties of PEG and the fire hazard connected with the organic solvents under consideration made water the only possible choice for solvent. First we used sodium carbonate as a pH-raising agent in an attempt to dissolve pentachlorphenate in PEG solutions. However, the combinations were not stable in contact with the acidic *Wasa* oak, and the sodium carbonate was abandoned. Instead we used the buffering capacity of the boric acid–borate system as a starting point.

Eleven mixtures of boric acid and borax (weight ratios 10:0, 9:1, . . . , 0:10) were prepared. A full series (1, 2, . . . % w/w) of these mixtures was dissolved in samples of distilled water and 10, 20, 30, 40, and 50% solutions of PEG 4000 and 1500. A mixture of 7 parts of boric acid and 3 parts of borax proved to be the most stable one. It was stable in concentrations of 1–8 wt % in water and in all of the PEG solutions except the ones with 50% PEG. The pH values of these solutions ranged from a little below 7 to nearly 9. This pH range promoted the solubility of pentachlorphenate.

The board of specialists was informed of the results. On April 9, 1962, spraying of the *Wasa* hull was started. The preservative was a combination of the boric acid–borax mixture with PEGs of various molecular weights.

Treatment of the Wasa

Although PEG was never explicitly chosen as the ultimate preservative for the hull, none of the other suggested agents could ever take its place, and the treatment with PEG continued. During the first 40 months the surfaces of the hull were treated by hand-spraying. The outside surfaces were sprayed once or twice, and the surfaces inside the hull were sprayed once, during each 24-h period. The aim was to keep all the surfaces constantly wet with preservation liquid so that the preservation situation would resemble the tank treatment as much as possible. Because the drying was faster on the outside, that side had to be sprayed more often. Hand-spraying was, however, expensive and not very efficient, so an automatic spray system was installed in March 1965.

PEG Purposes and Application. During the initial preservation period, several molecular weights of PEG were used, depending on the situation. On recommendation from Morén, the PEG 400 was used when the hull was first raised to protect the surfaces of the timbers from cracking. In the period before the actual preservation had been started, PEG 400 and 800 were added to solutions of pentachlorphenate in water. These solutions were sprayed onto the hull to augment the penetrability of the fungicide into the wood, in accordance with the Mo och Domsjö patent.

The preservation spraying was started on April 9, 1962. A pipeline air jet system had been constructed with nozzles to which sprays could be connected and handled within a certain area of the surface of the hull. PEG 1500 was used as a start, then followed by the PEG 4000 at the beginning of July 1962. Until January 1964, only the surfaces on the outsides of the outer and inner plankings were treated. Then the spraying activities were extended to the space around the ribs and thus, to some extent, to the hidden backsides of the outer and inner plankings. PEG 1500 was used for this additional spraying.

The advantage of being able to discriminate between areas and use different PEGs on each of them vanished when the fully automatic spray system was installed. In that system the PEG solution was pumped from a tank in the pontoon through the pipelines, and the surplus was drained back into the tank. In such a system the same PEG must be used on all the surfaces. PEG 1500 was chosen because this was the more soluble of the two types that were considered suitable. Higher solubility was expected to help the uptake of PEG in the wood at low temperatures.

Research by the *Wasa* museum laboratory during the 1960s had revealed that PEG 600 had an even better shrinkage-reducing effect on the *Wasa* oak wood than either the 1500 or the 4000. The effect of the increased hygroscopicity of the lower-molecular-weight PEGs apparently promoted the ability of the wood cell wall to keep a higher moisture ratio at a given relative humidity in the surrounding space. There were no drawbacks expected, so PEG 600 was added to the preservation solution in the tank starting on March 4, 1971.

Treatment Schedules. With spraying, the treatment schedule stipulates spray frequency, concentration of spray solution, and constancy of climate. If the spraying is continuous, climatic factors have little influence; however, they will have an effect if there are intermissions between sprayings. Thus, climate control in the surrounding atmosphere may also be considered a factor of the treatment schedule.

Spray Treatment. The capacity of the pumps in the spray system and the volume of preservation liquid in the tank were insufficient to permit continuous spraying. The spray system was split into five parts, or "stations", which were designed to work one at a time. The first schedule was 5 min of spraying and 40 min without spraying at each station. The previous climatizing plant, which could not be regulated by hygrostats, had been turned off when the automatic spray system was started. However, the surface of the outer planking dried faster than it should and the spraying had to be intensified. This was done by putting in another pump, which doubled the pumping capacity. The level of the preservation liquid in the tank was raised to be able to circulate a larger amount of preservation solution per unit time. The outer planking was then sprayed for 25-min periods separated by 20-min breaks. The original schedule was kept for the inside of the hull, where the climate was more stable and the surfaces did not dry so fast. This schedule was kept during the whole intensive spraying period, which lasted until November 1972.

At that time, the spray schedule for the outside was changed to 5-min spraying periods with 1-h breaks between sprayings. The periods between sprayings were made successively longer. In January 1974, about a year after reduction of the spray frequency had started, the periods without spraying lasted 2.5 h. The spray frequency was reduced further during the following 2 years. For the rest of the preservation period, a little more than 3 years, from October 1975 until January 1979, there were only one or two sprayings per 24-h period.

The concentration of PEG in the spray solution is the other important feature of the treatment schedule. During the first 2 years of automatic spraying, the concentration of PEG was kept at the rather low level of 10%. In March 1967 the concentration was raised by a 5% increment to 15%; it was kept at that level for the next 3 years. During the final part of the intensive spraying period, which lasted nearly 3 years, the PEG concentration was raised twice by 5% increments, once in February 1970 at the beginning of the period and the next after 5 months. These increases created a 5-month period with 20% PEG in the solution and a concluding intensive-spraying period of 2.5 years with 25% PEG in the preservation solution.

In January 1973, when the spray periods were made shorter and less frequent, the PEG concentration was raised by another 5%. The resulting 30% level was kept for 9 months before the next 5% increment was made. This 35% level was kept for 11 months until September 1974, when a last 10% increment was added to the concentration to create an ultimate 45% solution. The spraying was continued at that concentration for about 4 years, until the automatic spray system was turned off in January 1979.

Tank Treatment. Tank treatment followed the schedule recommended by Morén and Centerwall (5), which prescribed a 10% PEG concentration and a temperature of 30 °C as the starting point. The concentration was successively raised by adding a 10% PEG solution to replace evaporated water. The temperature was raised according to a preset schedule as the PEG concentration went higher until it reached 70 °C. The PEG concentration was brought to 100%; thus most of the water was removed from the wood.

This schedule worked very well with some small oak sculptures from the *Wasa*. To test it on a broader scale, conservator Bo Lundvall at the *Wasa* preservation laboratory chose some objects of different wood species and of varying sizes and shapes. The tank used had about 5-m^3 capacity, with thermostat and circulation pump. The 7-month process was modified slightly. For the first 3 months the concentration level was 30%. During the next 2 months, the concentration was raised by 10% increments to 90%. Then it took another 2 months to reach the final 100%. The temperature was kept at 18 °C for the first 2 months and was brought to 70 °C by steps of 10 °C in the next 2.5 months.

PEG 4000, considered to have better qualities as a preservative than the other molecular weights of PEG, was used for the test and for most of the tank-treated batches of material. Our preliminary research on the effects of various PEGs made it obvious that the molecular weight of PEG to be used ought to be chosen in accordance with wood species and grade of deterioration of the material to be preserved. Therefore, some batches were preserved with PEG 1500.

Samples were taken from all the pieces in the test batch before starting and after finishing the preservation procedure. Some pieces were also sampled after 4.5 months of treatment to test the water and PEG contents of the wood. As a measure of the contents of water and PEG, the ratios between the analytically determined weights of these substances and the weight of the wood fibers in the test samples have been calculated.

The pine samples had moisture ratios of 112–170% before and 18–72% after preservation treatment and PEG ratios after treatment of 39–92%. Thus, the amount of PEG in the pine pieces could be rather high. One of the objects even cracked under the strain of too much PEG.

The oak samples had about the same moisture ratios before preservation treatment as the pine samples. One oak sample, though, had a moisture ratio of 290%. This moisture ratio indicated a higher degree of degradation of the particular oak piece than of the other oak pieces in the test batch. After preservation it had a moisture ratio of only 12%, which fits in well with the rest of the oak pieces (3.5–40%). The PEG ratios after the preservation treatment were 0–47%, except for the piece with 290% before-preservation moisture ratio. That piece acquired a PEG ratio of 118%, half of that amount during the latter part of the 2.5-month preservation period, when the PEG concentration in the conservation solution was raised from 70 to 100%. The effect on the PEG ratios during that part of the preservation schedule was less obvious in the rest of the oak samples.

However, the increase in PEG concentration to 100% had a marked effect on shrinkage. The average tangential shrinkage of the oak pieces was 9.9% at 100% PEG, about four times as large as at 70% PEG concentration in the preservation solution.

As a result of this test preservation, we decided not to treat oak and pine together in the same preservation bath, not to proceed to 100% PEG in the bath, and to keep a slower pace when raising the PEG concentration of the preservation solution.

In the first regular tank-treated batch of *Wasa* material, the PEG concentration of the preservation solution was brought to 80% with a temperature schedule of 30–60 °C. Further improvements on the preservation schedule for tank treatment of oak were made after evaluating laboratory test preservations. One conclusion drawn from those tests was that the temperature ought to be rather high and kept at a constant level during the process. The level chosen for the *Wasa* material was 60 °C. The starting concentration, the pace at which it was raised, and the PEG molecular weight all had a great influence on the preservation process.

After the laboratory tests, all the tank treatments were started by heating the material in water with only the boric acid–borax mixture, before adding any PEG at all. An individual schedule was adopted for each batch of material that was to be tank-treated. These schedules specified the end-point concentration of PEG and the daily increments during various parts of the preservation process, depending on the status of the material and the status of knowledge.

The treatment of the *Wasa* material, both pine and oak, was performed at 60 °C. PEG 4000 was used for the tank treatment. The schedule for the pine had a higher end-point concentration of PEG in the solution and a faster pace of raising the PEG concentration than that used for the oak material.

Evaluation of Treatment. When will it be feasible to evaluate the treatment? What criteria are relevant for evaluation? The answer to the first question must be when the result of the treatment has manifested itself. Thus, in the case of a wooden object, treatment can be evaluated when the moisture content of every part of the wood is in equilibrium with the climate in which it is going to be kept. The answer to the second question depends on the aims of the PEG treatment. These aims could be expressed as preventing cracks, distortions, and unwanted dimensional changes. This outcome would require complete control of the shrinkage that naturally occurs during the process of drying the wood.

Is it possible with PEG to have no shrinkage at all? Test preservations on *Wasa* oak have shown that it is possible to get no shrinkage with PEG 600 if the relative humidity (RH) stays at 85% with a temperature of 20 °C and if the PEG ratio in the wood is at least 40%. PEG 1500 might produce the same result at over 90% RH and with about 50% PEG ratio in the wood. With PEG 4000, on the contrary, it is not possible at any RH level or any PEG ratio in the wood to keep the dimensions unchanged, according to the laboratory tests described.

For the preservation of the hull, PEG 600 was used during the period of high PEG uptake into the wood. The PEG ratios in some parts of the wood, however, are not high enough to keep the wood from shrinking, even at high RH levels (Figures 2–4). Furthermore, the *Wasa* cannot be kept in an atmosphere with a very high RH level for practical reasons. The RH level chosen for the permanent *Wasa* museum will be 60% at 20 °C. Thus, the effect of different PEG ratios in the wood at 60% RH will be of interest. The antishrink efficiency (ASE) is used as a measure of this effect. The ASE, in this case corresponding to a certain PEG ratio, is calculated as follows:

$$S = \frac{V_{\text{wet}} - V_{\text{dry}}}{V_{\text{wet}}}$$

where S is shrinkage, V_{wet} is wet volume, and V_{dry} is volume at the chosen RH.

$$ASE = \frac{S_0 - S_{\text{PEG}}}{S_0}$$

where S_0 is shrinkage without PEG and S_{PEG} is shrinkage with a PEG ratio in the wood.

The ASE of some lower ratios of PEG 600 can be deduced from the laboratory test preservations. For example, for PEG ratios of 10, 20, and 25%, the ASE at 60% RH would be 20, 39, and 49%, respectively. Thus, there is an antishrink effect even with moderate PEG ratios in the wood. In addition, PEG treatment and PEG in the surface layer of the wood regulate the rate of drying of the wood, and this regulation by itself reduces cracks and distortions as a result.

With an artifact like the *Wasa*, the criterion of a successful preservation is how well the object serves its function as a museum piece. The outer and inner plankings, the wales, and the sculptures might be considered the most important parts of the *Wasa* as a museum object. Those parts today, in 1988, are visibly in good condition and in equilibrium with a climate of about 65% RH and 20 °C. According to the laboratory test preservation, only a slight shrinkage occurs when the RH is lowered from 65 to 60%. Thus, the parts mentioned will change very little when the *Wasa* is moved into her permanent museum.

Location of PEG in the Wood

Core Sampling. After the automatic spray system had been turned off, there was a period with no treatment of the hull. After about 3 years, however, in order to protect the deteriorated surface layer of the wood, an ultimate treatment with PEG 4000 was done.

Core samples were taken at time intervals to check on the status of preservation and drying. To describe the result of the preservation process in various parts of the hull, samples were chosen from the outer and inner plankings and the wales (Figure 1). The situation before the automatic spray system was turned off will be represented by samples 31 and 32, which showed identical results. Samples 33 and 34 will represent the situation after that part of the preservation treatment was completed. Finally, the situation after surface treatment with PEG 4000 is represented by samples 35 and 36.

To obtain a picture of the distribution of PEG in the wood, each core was cut into a number of pieces, which were analyzed separately. The mean values of the PEG ratios of each layer and each sample (Table I) indicate

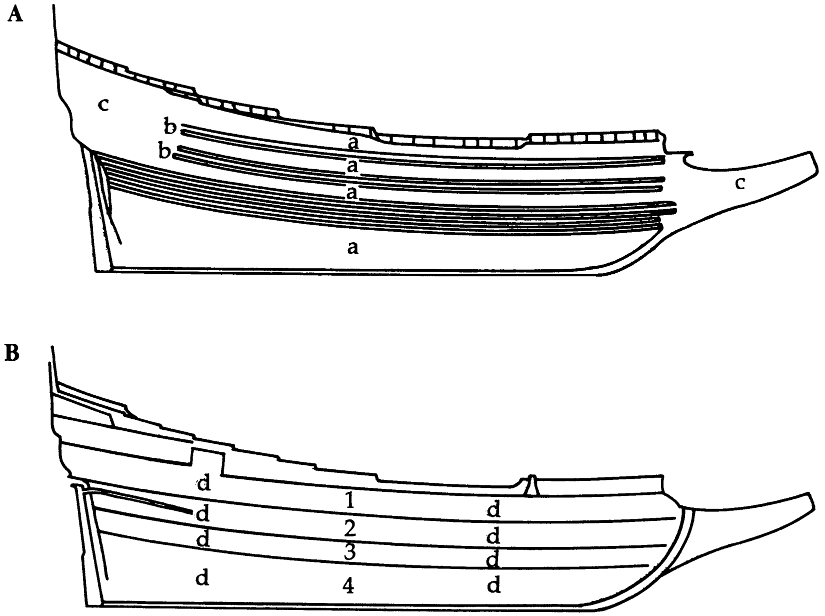

Figure 1. Identification of Wasa *ship parts. (A), outer view; (B), longitudinal section. Key: a, outer planking; b, wales; c, main areas of sculptural adornment; d, inner planking; 1, upper gun deck; 2, lower gun deck; 3, orlop deck; 4, hold.*

Table I. Mean Percentage Values of PEG Ratios in the *Wasa* Hull for Samples 31–36

Layer	*31*	*32*	*33*	*34*	*35*	*36*
Outer planking						
1	65	63	62	63	76	72
2	10	11	21	16	17	14
3	5.7	8.7	20	15	15	13
4	36	31	49	42	55	44
Inner planking						
1	71	78	74	76	80	78
2	26	23	22	19	38	31
3	22	24	19	15	33	31
4	42	45	49	40	59	56
Wales of the outer planking						
1	43	56	60	59	60	65
2	7.1	8.1	18	13	9.2	21
3	7.2	3.0	7.7	3.5	5.3	18
4	6.3	2.2	13	0.1	7.2	20
5	30	28	35	25	25	41

that the PEG had penetrated all through the wood before the automatic spray system was turned off. Samples 31 and 32 were taken 16 and 6 months, respectively, before the automatic spray system was turned off. The mean values of the PEG ratios give the impression that there was no change with respect to PEG in the wood during the time period represented by these two samples. In the same way, samples 33 and 34, which were taken 8 and 20 months, respectively, after the automatic spraying was stopped, resemble each other. Samples 35 and 36 were taken after the surface treatment with PEG 4000 and thus represent the same status of PEG preservation. They show a markedly higher PEG ratio in layer 1 (*see* the following section) than the previous samples, especially where the outer planking is concerned.

Each sample consists of 20 cores from each of the outer and inner plankings, but only 10 cores from the wales. There is no reason to object to considering each of the pairs of samples (31 and 32, 33 and 34, and 35 and 36) as one single sample where the distribution of PEG ratios in each layer is concerned. The operation raises the number of cores of each sample from each structural part to at least 20.

PEG Ratios in Different Layers. The individual pieces into which each core was cut represent successively deeper levels of the structural part from which the core was taken. Layer I, the surface layer, is represented by the outer 10 mm of each core. After the surface layer was cut from the cores, the rest of the cores taken in the outer and inner plankings were cut into three equal parts, each with a length of 10–30 mm. The rest of the cores, taken in the wales, were cut into five to nine pieces, each about 20 mm long. The pieces into which the cores from the outer and inner plankings were originally cut represent layers 1–4 of those structures. Where the wales were concerned, the two outermost and the two innermost pieces of each core represented layers 1, 2, 4, and 5. Layer 3 was an internal layer consisting of all the pieces between those mentioned.

Each piece was analyzed for its PEG contents, and the amounts of this substance were calculated as percentages of the corresponding dry fiber weights. To create a picture of the distribution of PEG in each layer, the percentages of PEG ratios were grouped into the categories <1.0%, 1.0–9.9%, 10–19%, 20–29%, 30–39%, and ≥40%. These categories are represented by the outer and inner plankings and the wales in the black bars of Figures 2–4. To simplify the survey, the categories <10%, 10–29%, and ≥30% are represented in the white bars of the figures.

Surface Layer. Figures 2–4 indicate that layer 1 is characterized by a majority of PEG ratios in the ≥40% category. Between 70 and 98% of the PEG ratios from the structural parts chosen belong here. In the samples taken after the automatic spraying was stopped, the amount of PEG ratios in the ≥40% category was 7–10% higher in the cores from the outer and

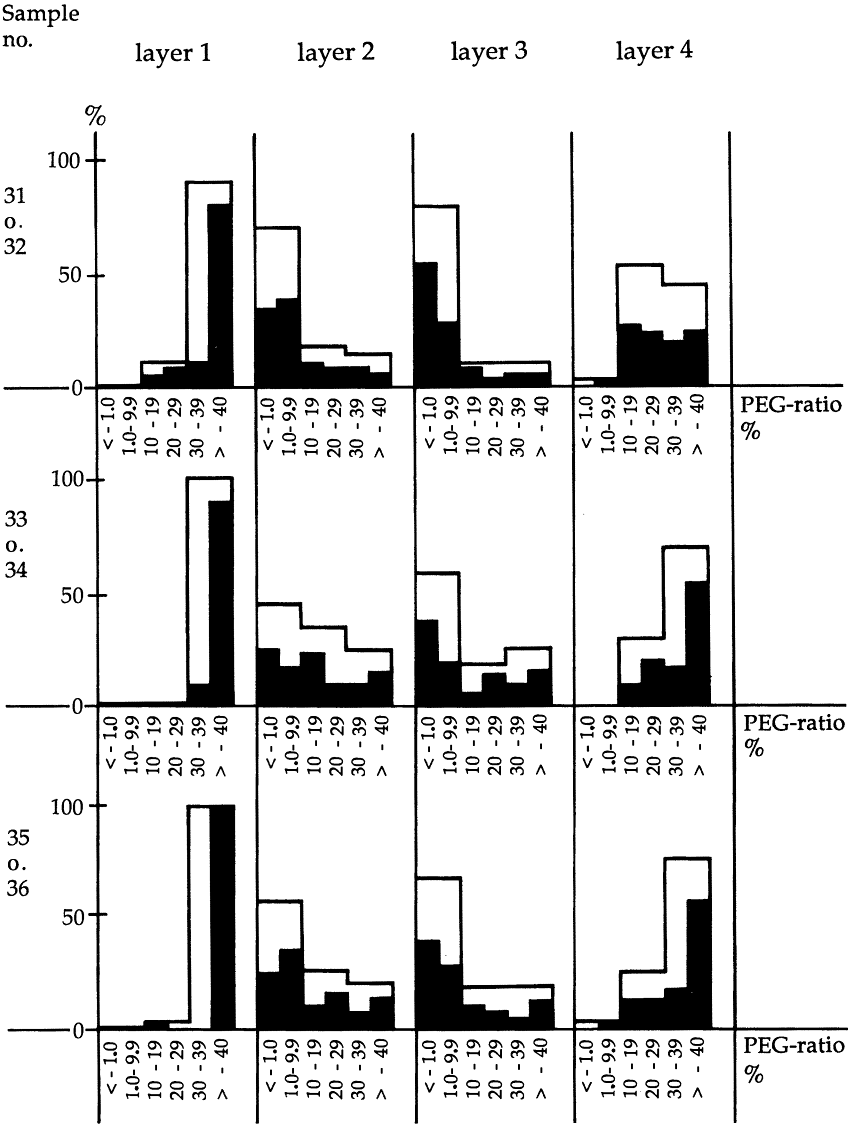

Figure 2. Distribution of PEG in the outer planking of the Wasa *hull.*

inner plankings. However, the ratios in this category were unchanged in the cores from the wales, as compared to the corresponding samples representing the situation before the treatment was stopped. The final surface treatment naturally raised the amount of higher PEG ratios in the outermost layer.

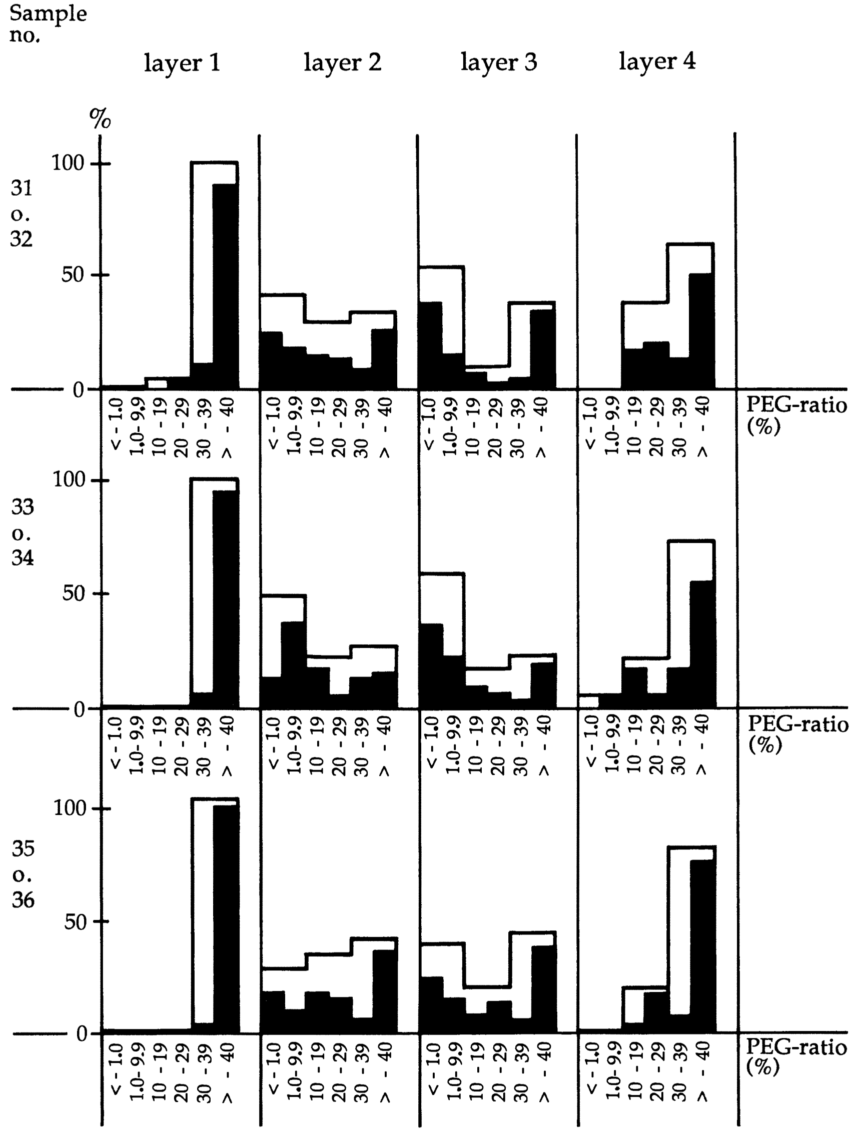

Figure 3. Distribution of PEG in the inner planking of the Wasa *hull.*

Inner Layers. Layers 2 and 3 of the outer and inner plankings have rather high amounts of very low PEG ratios. According to combined samples 31 and 32, 33% of the PEG ratios of layer 2 of the outer planking and 23% of the ratios from layer 2 of the inner planking belonged to the <1.0% category when the spraying stopped. In layer 3 the corresponding amounts

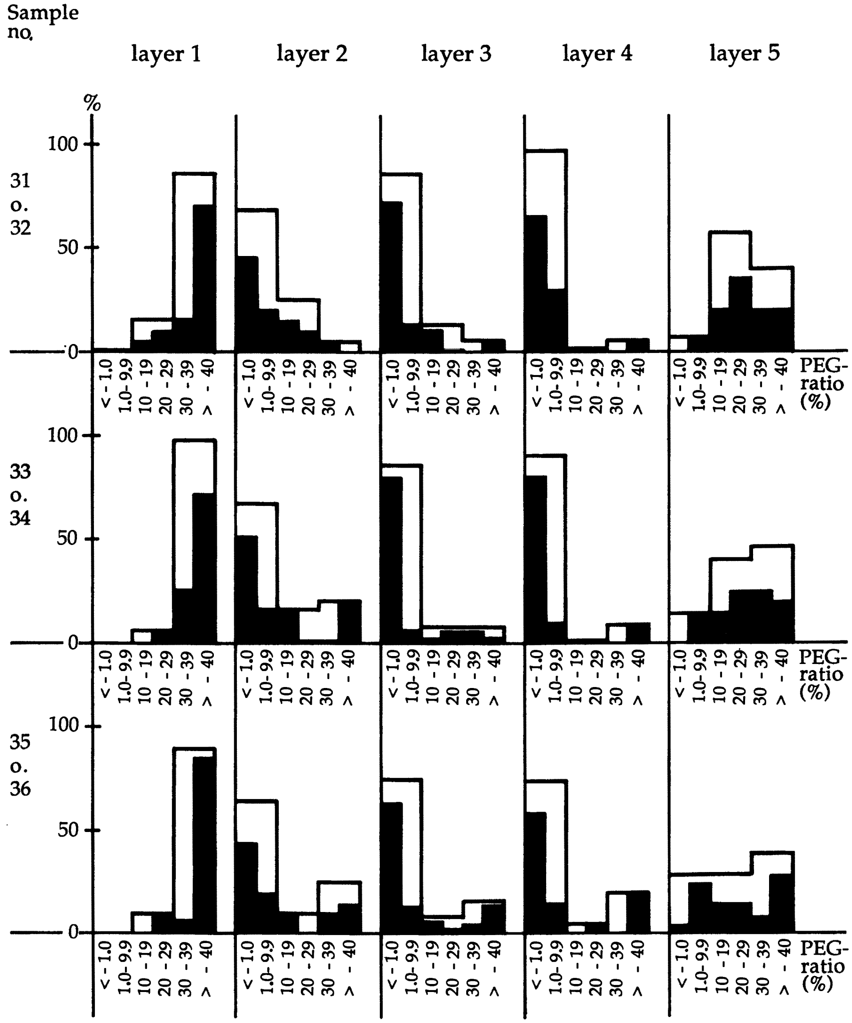

Figure 4. Distribution of PEG in the wales of the Wasa.

were 53 and 38% After the spraying stopped, the relative amounts of the PEG ratios below 1.0% were 25, 13, 38, and 38%. These values point toward a movement of PEG from the surface layer into the layer below and to some extent even deeper into the wood.

The surface treatment, on the other hand, seems not to have had any influence an the deeper layers of the outer planking. In the inner planking, the relative amounts of PEG ratios below 10% are at least one-third fewer and those above 30% one-fourth more numerous after surface treatment than before it. These relationships can be deduced by comparing combined samples 35 and 36 with combined samples 33 and 34 (Figures 2 and 3).

Likewise, the second and deeper interior layers of the wales are characterized by high percentages of low PEG ratios. Here the patterns are about the same before and after the automatic spraying was stopped. The second layer also seems to be unaffected by the surface treatment. However, the third and fourth layers show lower percentages of low PEG ratios and doubling of the percentages of ratios belonging to the ≥40% category after surface treatment was performed (Figure 4).

Surface of the Back. The fourth layers of the outer and inner plankings and the fifth layer of the wales are the surface layers of the backsides. The planking structures have rather high percentages of PEG ratios of the ≥40% category in that layer. The fifth layer of the wales shows a practically even distribution of PEG ratios among all of the categories except the lowest.

Oak and Pine Batch. The first batch that was preserved has been chosen as representative of the tank-treated material. This batch contains both oak and pine. PEG 4000 was used for its treatment. The preservation schedule was performed for 16 months until the preset end concentration of 80 wt % PEG in the solution ought to have been reached. The actual concentration obtained, a little less than 60%, was steady for the 3-month final stage of the preservation. As a check, core samples were taken several times during the preservation process. The sample taken after the preservation schedule was completed consisted of eight cores taken from eight different oak pieces and four cores taken from four pine pieces. Although the cores of the oak sample were of varying lengths, they can be made to represent five different levels in the oak material in accordance with the discussion about the wales of the hull of the *Wasa*.

For tank-treated material, layer 1 is the top surface layer of the wooden object in the tank during treatment. Figure 5 shows that only 50% of the PEG ratios in layer 1 of the oak material are of the ≥40% category. In layer 5, which is the surface layer opposite to layer 1, none of the PEG ratios exceeds the 20–29% category. The same applies to layers 2–4.

The pine material of the same batch shows that all the PEG ratios are ≥40%. The pattern (Figure 6) looks practically the same for all of the layers, with a more or less even distribution of PEG ratios between 40 and 100%.

The mean values of PEG ratios for the tank-treated oak material resemble those from the cores taken in the wales (Tables I and II). Comparison among the PEG ratio distributions after preservation (the wales, samples 33 and 34) shows that, apart from the somewhat lower percentage of high PEG ratios in the outer layer of the tank-treated material, the pictures from the inner layers resemble each other. The two categories of low PEG ratios show percentages about equal to each other for the two methods of treatment.

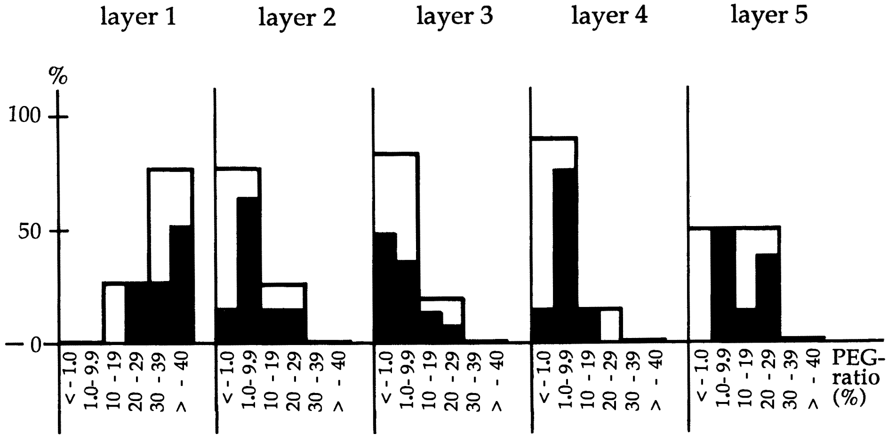

Figure 5. Distribution of PEG in the oak material of the first batch of disconnected pieces preserved.

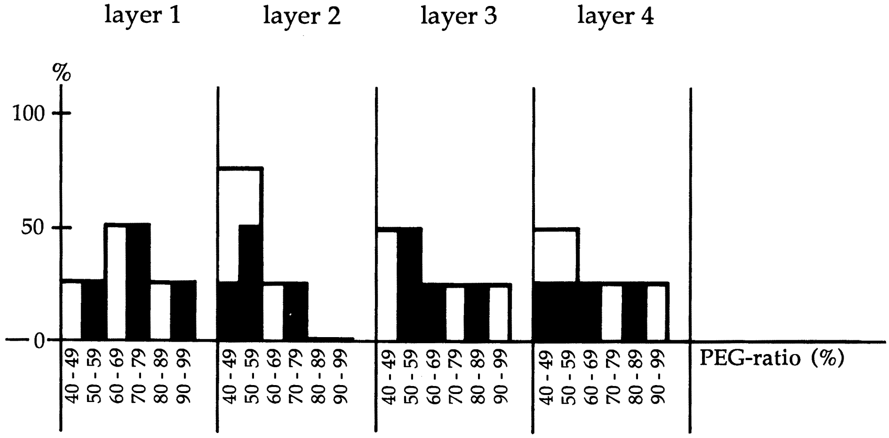

Figure 6. Distribution of PEG in the pine material of the first batch of disconnected pieces preserved.

Table II. Mean Percentage Values of PEG Ratios of the First Batch of Tank-Treated Material After Preservation

Layer	*Oak*	*Pine*
1	43	73
2	7.0	59
3	4.5	64
4	3.3	63
5	14	—

However, the lowest category, <1.0%, includes the overwhelming percentage of the spray-treated material. The 1.0–9.9% category outnumbers it by 3 or 4 times for layers 2 and 4 or about equals it for layer 3 of the tank-treated material (Figures 4 and 5).

PEG Treatment and Wood Species

The pine material of the first batch of disconnected pieces to be preserved had far better PEG penetration than the oak material of the same batch. This result may be attributed to size, as the pine pieces were usually smaller, at least as regards thickness, than the oak pieces. To see if this explanation would be valid, the PEG ratios of a core of the one oak plank of minor thickness in the sample were compared to those of a core of a pine plank of equal dimensions.

Table III shows that the PEG ratios of the oak core, apart from the surface layer, are about 10% of the corresponding values of the pine core.

Table III. PEG and Water Ratios in Oak and Pine Specimens

	PEG Ratio, %		*H_2O Ratio, %*	
Layer	*Oak*[a]	*Pine*[b]	*Oak*	*Pine*
1	39	51	92	100
2	4.4	45	38	80
3	3.0	50	39	81
4	2.8	49	42	82

[a] Thickness = 41 mm.
[b] Thickness = 42 mm.

Moisture ratios of the pine core after preservation are much higher than those of the oak core. This contrast may point to differences in wood qualities of the oak and pine pieces. The maximum water contents of the two pieces of wood are deduced from the core samples taken at the beginning of the preservation. This investigation revealed that the maximum water contents of the surface layers of the oak and pine pieces are 200 and 240%, respectively. The layers beneath the surface layers have 150% maximum water ratios in both cases. The next question to be considered is whether the differences in preservation results depend upon the method of treatment used. To get some spray-treated material for comparison, the orlop deck of the *Wasa* was chosen because the sternmost third of that deck is made of oak and the other two thirds are made of pine planks. The PEG and H_2O ratios of the cores from the two different parts of that deck after the automatic spray treatment was stopped (samples 33 and 34) were compared.

Table IV shows that the PEG ratios of the pine cores are 10-fold those of the corresponding layers of the oak cores, apart from the surface layers

Table IV. PEG and Water Ratios in Oak and Pine from Different Parts of the Orlop Deck

	PEG Ratio, %		*H_2O Ratio, %*	
Layer	*Oak*	*Pine*	*Oak*	*Pine*
1	51	130	27	50
2	11	110	20	55
3	2.1	88	20	53
4	7.9	81	20	43
5	61	110	31	49

(layers 1 and 5). The H_2O ratios at the same time were about twice as high in the pine cores as in the oak cores. Both results are in accordance with the situation found in tank-treated material.

There may be some difficulty in investigating quality differences between the oak and pine material with the aid of maximum H_2O ratios because no cores were taken in the deck planks immediately after the hull was raised. However, the earliest samples taken, from 1965 and 1968, give no evidence of pronounced quality differences between the oak and the pine parts of the orlop deck.

Mechanisms of PEG Uptake in Wet Wood

The effect of PEG on shrinkage is achieved by the molecules of PEG inside the secondary wall of the wood cell. Discussions are going on about how deep into the secondary wall the PEG molecules of different sizes may penetrate. However, before the PEG molecule will be in a position to penetrate the secondary wall, it must enter the wood structure.

There are two ways to accomplish this entrance. One way is molecular diffusion of PEG from a surrounding PEG solution of higher concentration into the water medium or more dilute PEG solution in the wood structure. This is the only way if the wood is completely filled with water, and it can best be accomplished by soaking treatment. The other way is liquid flow of PEG solution as such into the wood structure. For this to happen, the wood must not be completely filled with water. The process can be effected by soaking or by vacuum–pressure treatment.

Diffusion processes are encouraged when a PEG solution in water is brought into contact with pure water or with a PEG solution of a different concentration. The obvious diffusion situation is tank treatment. The almost continuous spraying of the *Wasa* hull was an attempt to create a similar situation without a tank.

The preservation solutions used for the spraying of the *Wasa* hull and the tank treatments of disconnected material have consisted of solutions in water of PEG, boric acid, and borax. The concentration of PEG of each solution has been brought from a low level at the beginning of the process to a fairly high level at the end of it. The concentrations of the boric acid–borax mixtures in the solutions have been kept between 1 and 4 wt % during the whole of the processes. The PEG distribution in the treated wood is uneven. In contrast, the distribution of borate is fairly even. According to the analyses of boric acid in the core samples, complete penetration into every part of the wood has been obtained. Penetration of borate takes place at an early stage in the preservation processes.

The observed differences in diffusion rates between borates and PEG are expected. The slowness, size, and chemical characteristics of the PEG molecule may lead to PEG uptake by liquid flow instead of by diffusion of PEG molecules into the wood structure.

Core samples taken in the hull during the spraying period suggest that the PEG uptake occurs mainly outside the intensive spraying period. Apart from PEG uptake, this period is characterized by drying of the wood. The mechanism of PEG uptake during that part of the preservation ought to have been liquid flow of PEG solution, rather than diffusion of PEG molecules into the wood structure.

In the case of tank treatments, the submerged wooden objects nearly always lose weight during the preservation process. The only possible explanation for this is that H_2O molecules, being more easily movable than the PEG molecules, diffuse from the wood into the surrounding solution. This diffusion might lower the pressure inside the wood and create a liquid flow of PEG solution into the wood resembling vacuum-pressure treatment. The substantial PEG uptake at later stages of the preservation process may be explained by the vacuum–pressure mechanism. There should be diffusion of PEG molecules at the earlier stages, when the PEG concentration of the surrounding preservation solution is low.

Limitations in the Use of PEG

Is PEG always a suitable preservative? In my opinion, there are very few situations in which PEG is not suitable as a preservative for wet wood. One, however, is obvious: when the object is going to be kept outdoors. The solubility of the PEGs in water makes them leach when it rains. Even with a sheltering roof, the hygroscopicity of the PEGs makes them leach at relative humidities above 80%. A coating of lacquer can protect the object in an outdoor situation and delay the effect of the PEG hygroscopicity, but it cannot be prevented.

Painted waterlogged wooden objects present a problem because the paint layer or patches of paint are prone to come off during tank treatment with PEG. This has occurred with the very insignificant paint residues on the *Wasa* sculptures. If, on the other hand, the wood is not treated with a dimension-stabilizing agent, the paint layer normally comes off because of the shrinkage of the wood.

PEGs have a plasticizing effect on lacquers and some paint-binding media. This effect makes it inadvisable to brush or spray PEG solutions on a painted surface. Even treatment with PEG of unpainted surfaces of the object may endanger paint layers because the PEG may move inside the wood structure and eventually reach the painted surface. Such a one-sided treatment may not be totally satisfactory as dimensional stabilization. Thus, painted objects need another type of dimension-stabilizing agent.

Recommendations

More than 25 years of experience with the *Wasa* project has provided data for evaluating PEG as a preservative for dimension-stabilizing treatment of waterlogged wood. The PEGs have shown themselves to be stable substances under the circumstances to which they have been subjected during the preservations in tanks and by spray treatment. No unexpected and unwanted characteristics of PEGs have come forward. Therefore, PEG is recommended as a suitable preservative for waterlogged wood and wood with a high water content. The choice of PEG molecular weight should be made in accordance with wood species and grade of deterioration of the wood. It is necessary to consider the future climatic conditions in which the object is going to be kept in order to make the best choice.

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9

Impregnation with Radiation-Curing Monomers and Resins

Quôc-Khôi Trân, Régis Ramière, and André Ginier-Gillet

Laboratoire ORIS–SAR–Nucléart, Centre d'Etudes Nucléaires
de Grenoble, 85X, 38041 Grenoble Cedex, France

Gamma rays emitted by a ^{60}Co source are used for in situ polymerization of vinyl monomers or resins impregnating waterlogged wood. Two types of chemicals are considered: water-soluble (such as N-*vinylpyrrolidone and methacrylamide) and non-water-soluble (such as* n-*butyl methacrylate monomer or unsaturated polyester resins). The corresponding impregnation processes are presented: direct water–monomer exchange for the water-soluble chemicals and two successive steps required for the non-water-soluble chemicals, water–solvent and solvent–resin exchanges. Research results on treatment of waterlogged oak and beech samples are assessed on the basis of their dimensional changes and surface appearance. Some significant treatments of waterlogged wooden objects by this method are described.*

IMPREGNATION OF SOFT SOUND WOOD WITH MONOMERS, which are then polymerized in situ by γ radiation, was a method used in many laboratories during the 1960s in an effort to obtain wood–plastic composites. The process was attractive in two respects; there was a large choice of consolidants, and radiation-induced polymerization had many advantages. Various vinyl monomers are cured by γ rays. By proper selection of the polymer or copolymer, materials can be "tailor made" for specific applications. The radiation process presents several advantages over the chemically catalyzed polymerization of monomers in wood.

- The process can be carried out at room temperature and atmospheric pressure.

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- The absence of chemical catalysts enables the impregnation time to be modulated. Nonconsumed resin can be recycled and safely stored if appropriate conditions are applied.
- Because of the penetrating power of γ rays, impregnated wood is more rapidly and uniformly treated.
- It is possible to control the exothermic reaction within the wood by varying the irradiation dose rate (i.e., the distance between the γ source and the wooden object).
- The irradiation dose for complete polymerization of most common monomers does not affect the wood.

As an alternative to the conventional polyethylene glycol (PEG) treatment of waterlogged wood (*see* Chapter 8), attempts were made in 1966–1967 to apply a radiation-curing process (*1*, *2*). The aim was to reduce treatment time and achieve more stability for treated objects subjected to interior climatic changes. The impregnation of waterlogged wood by immersion involves a liquid–liquid exchange process. Dry wood was directly bulked by monomers by a vacuum-pressure process.

Monomers with low molecular weights will diffuse into the wood more rapidly than polymers such as PEG. In a second phase, their in situ radiation curing will form wood consolidants that are much stronger than PEG. However, this method requires very heavy irradiation equipment, which is usually available only in nuclear research centers. The irradiation cell dimensions and the γ-source geometry limit the size of the artifacts. For mainly these reasons, the radiation process was applied in very few institutions and in most cases only at the experimental level. The "Nucléart" Laboratory, which routinely conserves waterlogged wood by this technique, is located in the Grenoble Nuclear Research Center of the French Atomic Energy Commission.

Radiation conservation of waterlogged wood has been practiced in cooperation with the Grenoble Archaeological Center since 1976. It began with artifacts excavated from a medieval site (11th century) in Paladru Lake near Grenoble. The principles of the process will be described in detail. Its features will be emphasized in the experimental section, which shows how wood samples are tested with selected monomers and resins. Two significant treatments are described that relate to artifacts of various sizes from several parts of France. An overview of research work involving different consolidant systems used in other laboratories will be presented.

Radiation-Catalyzed Polymerization

Monomers and Resins. Radiations such as γ rays, ultraviolet light, and electron beams can initiate free-radical polymerization of vinyl monomers or unsaturated resins. Styrene, vinyl acetate, acrylonitrile, acrylates, and methacrylates are among the most-studied monomers in radiation chemistry. The most widely used of these monomers is methyl methacrylate. Water-soluble monomers are more limited in number; the main ones are *N*-vinylpyrrolidone, acrylamide, hydroxylated acrylates, and hydroxylated methacrylates. Upon curing, they form linear macromolecules (the so-called thermoplastic polymers) that can be dissolved in suitable solvents. Copolymerization of various monomers is carried out to satisfy specific applications.

Unsaturated resins are usually mixtures of vinyl monomers and prepolymers, such as unsaturated polyesters, polyurethane acrylates, and acrylated epoxides of the bisphenol A type. Polymerization of styrene-based resins involves the formation of a three-dimensional network via the cross-linking of prepolymer chains by styrene radicals. These standard thermoset resins are therefore characterized by great hardness (Shore D over 80, DIN 53505, arbitrary scale 0–100 based on the penetration of a needle point in the tested material), do not melt, and are not soluble in organic solvents.

The first products tested for waterlogged wood treatment were the usual monomers that impregnate the wood easily because of their low molecular weight. However, they present some disadvantages: high volumetric shrinkage (up to 20% for methyl methacrylate); high vapor pressure, resulting in possible loss of consolidant on the wood superficial layer; and large oxygen inhibition when acrylates and methacrylates are cured in air, which produces a tacky surface. On the other hand, acrylic functions are among the most readily polymerized under radiation with doses that should not alter the wood itself (i.e., less than 100 kGy or 10 Mrad) (*2*). The use of styrene alone for wood impregnation requires a very high irradiation dose and therefore is to be avoided.

Some of the problems inherent in radiation curing of acrylics in air could be solved by using conventional styrene–unsaturated polyester resins that have been used for over 30 years in the plastics and composite industry. These resins are characterized by volumetric shrinkage of 6–9% on curing (depending on the styrene content) and in most cases by a hard nontacky surface after radiation curing. Their initially high viscosities can be reduced by adding more styrene up to a 1:1 styrene:polyester ratio without drastic changes in their mechanical properties. This relatively high viscosity nevertheless constitutes a disadvantage in wood impregnation by a liquid–liquid exchange process.

Irradiation Facility. The swimming pool type irradiator includes an irradiation chamber (4 × 4 × 2.3 m) connected to a 4-m-deep pool where the ^{60}Co panel source is stored (Figure 1). The source activity at present is 7.4×10^{14} Bq (2×10^4 Ci), with a permissible maximum of 3.7×10^{15} Bq (10^5 Ci) for this facility. ^{60}Co gives a very simple γ-ray spectrum, two sharp lines of equal intensity at 1.17 and 1.33 MeV.

The penetrating power of γ rays is quite considerable. Its intensity is

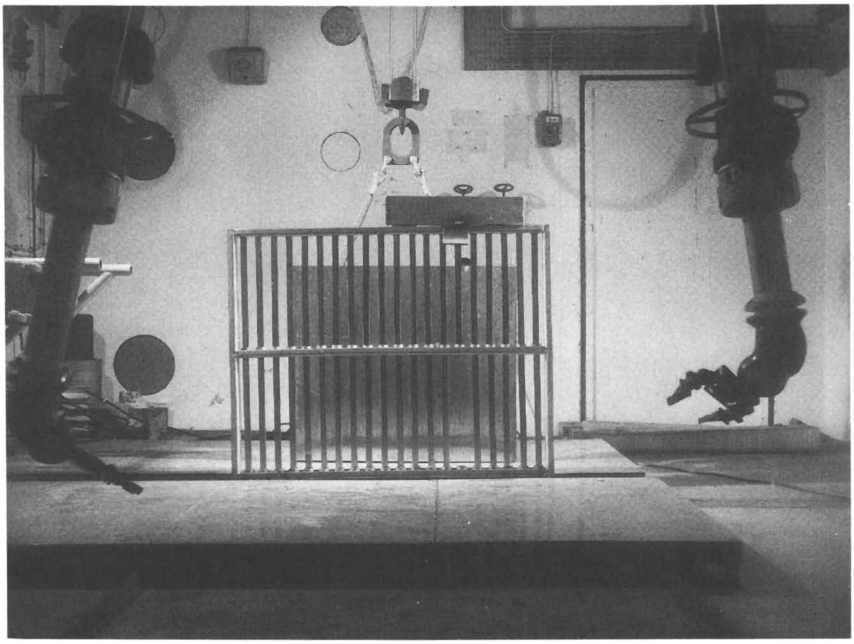

Figure 1. Irradiation cell with the ^{60}Co panel source in the center.

reduced to 10% of its initial value by passing through 43.2 cm of water or 4.1 cm of lead. No radioactivity can be induced in the irradiated materials because the threshold energies of photonuclear processes for common elements such as ^{12}C, ^{16}O, and ^{14}N are 18.7, 15.6, and 10.5 MeV, respectively. The half-life of ^{60}Co is 5.3 years.

The usual initiating dose rate for in situ polymerization is about 1 kGy/h (10^5 rad/h) at 15 cm from the source. The dose rate decreases greatly as the source-to-artifact distance increases; it is reduced to 0.5 kGy/h at 55 cm. Periodically turning the artifacts ensures homogeneity of the absorbed dose. Artifact size is limited by the irradiation cell dimensions and the central position of the panel source. The maximum length of the object is 3 m, and its thickness may not exceed 0.30 m.

Radiation Polymerization of Monomers and Resins. Following the classical kinetics scheme of free-radical polymerization, the reaction rate *R* of pure monomers or resins is generally proportional to the square root of the initiation rate of radicals or the radiation dose rate *I* (*3*, *4*):

$$R = k \times I^{1/2}$$

This square-root law is essential in radiation processing and especially in our application. The in situ exothermic reaction can be controlled by varying the dose rate, and overheating of the wooden object can therefore be avoided. The effect of the radiation dose rate on polymerization temperatures of selected monomers and resins is illustrated in Figures 2–5. The products were placed in 100-mL glass vessels and irradiated at room temperature.

The polymerization kinetics were studied via time-conversion relationships at different dose rates (Figures 6–9). The radiation curing was carried out at room temperature in closed aluminum capsules. Percent monomer conversion was determined gravimetrically for *N*-vinylpyrrolidone. Evaporation was accomplished under vacuum in a ventilated oven at 50 °C until the weight was constant. For butyl methacrylate and polyester resins, the residual monomer content was determined by gas chromatographic analysis after immersion of the cured products in acetone.

Impregnation of Waterlogged Wood by Monomers and Resins

Impregnation involves liquid–liquid exchanges by immersion in successive baths at room temperature and atmospheric pressure. Waterlogged wood was first dehydrated by a solvent such as acetone or ethanol. In a second phase, the solvent within the wood was substituted by monomer or resin. For water-soluble monomers, the use of solvents is not necessary because direct water–monomer exchange can take place.

To moderate the diffusion flows at the beginning of the process, diluted solvent or monomer solutions were preferred to pure ones. With a pure solution, water could diffuse out of the wood more rapidly than solvent or

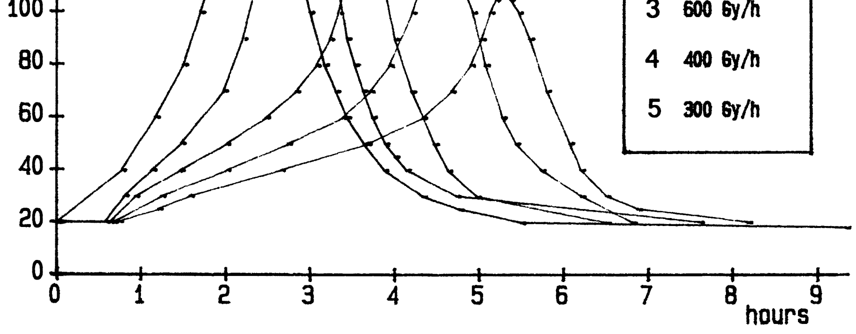

Figure 2. Effect of dose rate on polymerization temperature of N-*vinylpyrrolidone.*

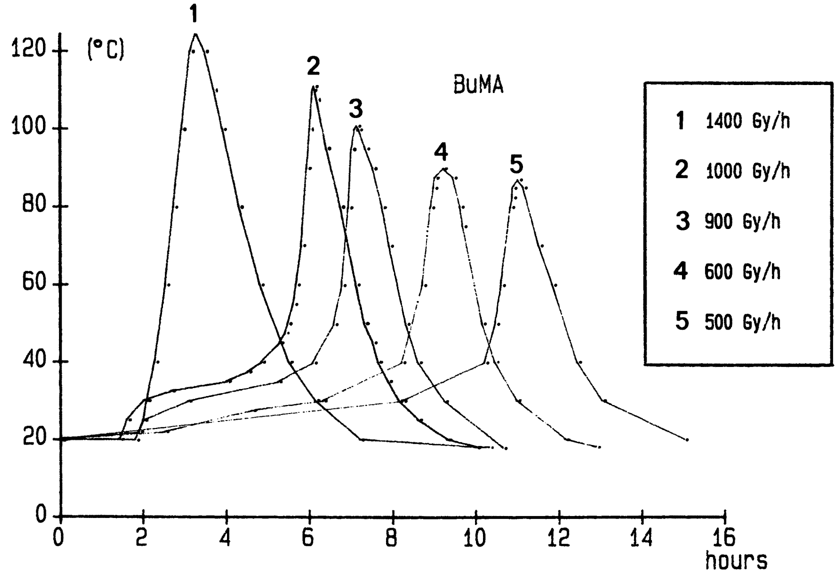

Figure 3. Effect of dose rate on polymerization temperature of n-*butyl methacrylate.*

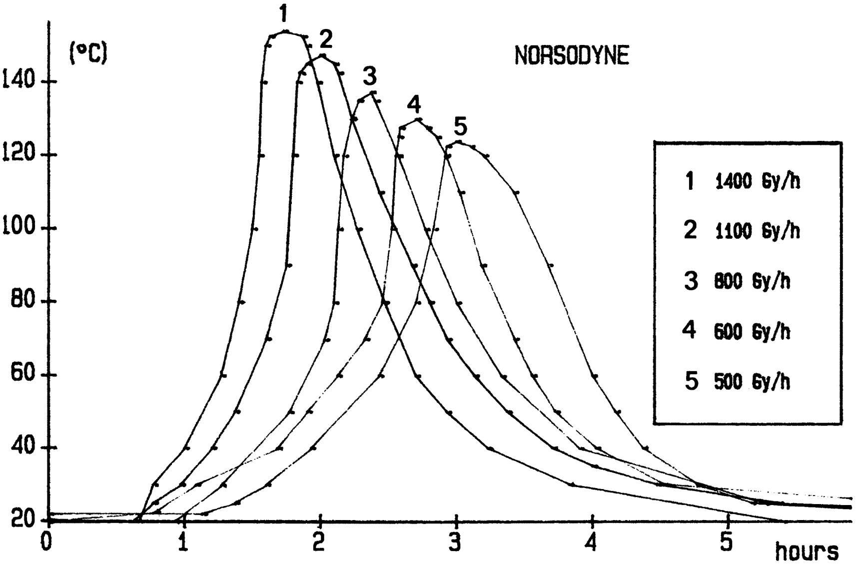

Figure 4. Effect of dose rate on polymerization temperature of Norsodyne styrene–unsaturated polyester resin.

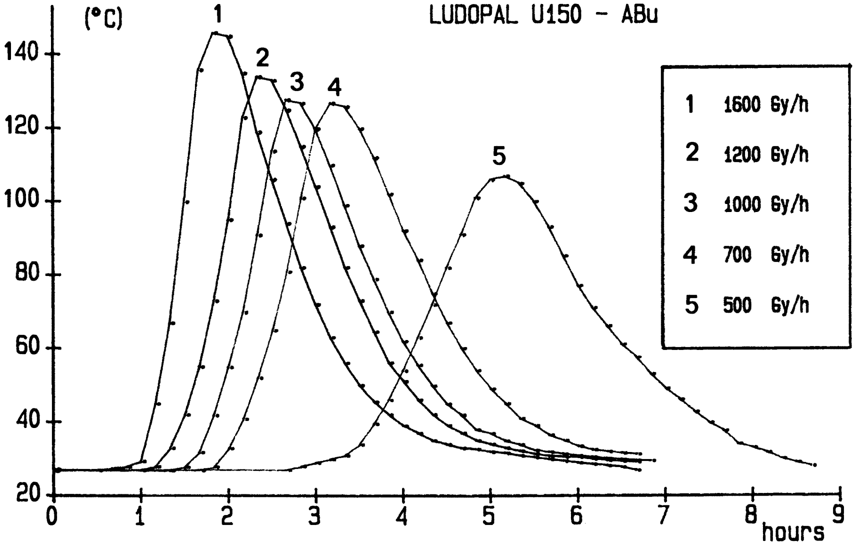

Figure 5. Effect of dose rate on polymerization temperature of Ludopal U150–butyl acrylate formulation.

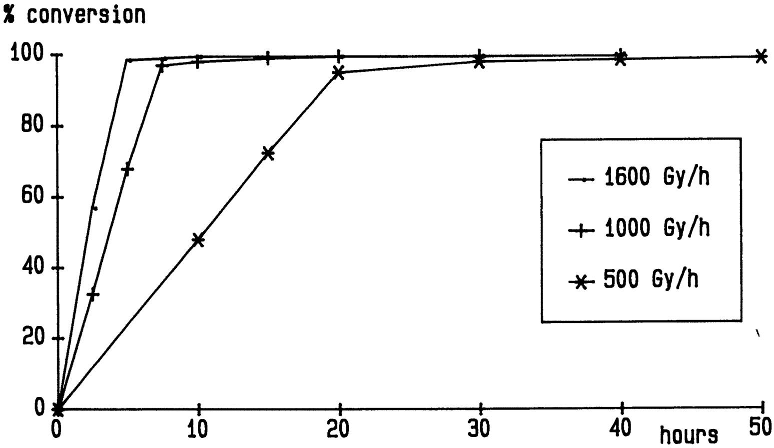

Figure 6. Radiation polymerization of N*-vinylpyrrolidone at different dose rates.*

monomer moves in the opposite direction. This rate difference could cause wood shrinkage. After equilibrium has been reached for the first baths, pure solutions can be used for the following steps up to full dehydration or monomer impregnation. The wood-to-solution volume ratio is variable, ranging from 1:5 to 1:10 or more for individual cases.

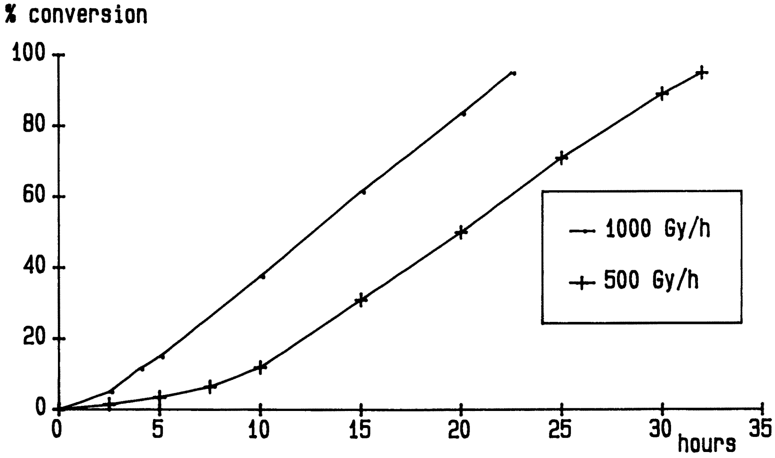

Figure 7. Radiation polymerization of n-*butyl methacrylate at different dose rates.*

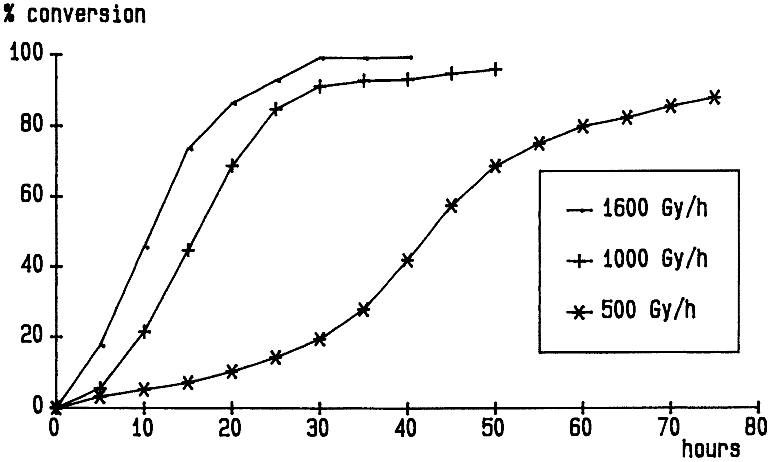

Figure 8. Radiation polymerization of Norsodyne resin at different dose rates.

Water-soluble monomers tested in this work were *N*-vinylpyrrolidone and methacrylamide. *N*-vinylpyrrolidone is water-soluble in all proportions, whereas methacrylamide is partially soluble up to 20 wt %. The water–monomer exchange was monitored by specific-gravity determination of the solutions.

The waterlogged wood impregnation by *n*-butyl methacrylate monomer and unsaturated polyester resins requires a solvent-exchange process. Two solvents, acetone and ethanol, were tested with butyl methacrylate, whereas

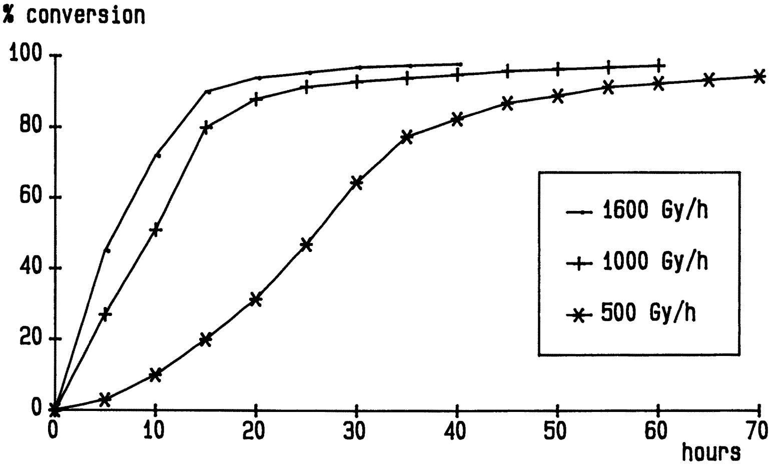

Figure 9. Radiation polymerization of Ludopal formulation at different dose rates.

only acetone is miscible with the resins. Specific-gravity measurements and gas chromatographic analysis monitor the dehydration and impregnation steps, which can be considered complete when the residual product concentration is less than 0.5 wt %.

Experimental Work

The aim of this section is to emphasize the specific features of the radiation-curing method. Waterlogged wood samples were treated with the monomers and resins described previously. A quite sound wood and a very degraded one were tested. Assessment of the results was based on their behavior during irradiation, their surface appearance, and their dimensional changes.

Materials. The waterlogged wood tested was a still-sound oak (water content, 120%) from a 19th-century site in Grenoble, France, and a highly deteriorated beech (water content, 600–900%) excavated from the 11th-century site in Paladru Lake near Grenoble. Block samples for each species were cut to 4 × 2 × 2 cm and 20 × 7 × 1 cm. Measurements were made in the fiber, radial, and tangential directions by using a caliper square that is accurate to 0.1 mm.

Monomers and resins were used as received from the manufacturers. *N*-Vinylpyrrolidone was chosen for its low vapor pressure (0.1 mbar at 24°C) and its relatively low toxicity. Methacrylamide was used as 15 wt % aqueous solution (maximum water solubility up to 20%) with the aim of partial wood impregnation. *n*-Butyl methacrylate was preferred to methyl methacrylate for giving a more flexible polymer with a lower glass-transition temperature, t_g (20 °C instead of 105 °C for poly(methyl methacrylate) (PMMA)) (5) and much lower vapor pressure [2.7 mbar at 20 °C, compared to 38.7 mbar for methyl methacrylate (MMA)].

Two different styrene-unsaturated polyester resins were involved in this study: (1) Norsodyne resin (Norsolor, France) and (2) a research flexible formulation based on Ludopal U150 resin (BASF, West Germany) diluted by butyl acrylate in a mass ratio of 80:20. The main characteristics of these two unsaturated polyester resins are as follows.

Norsodyne Resin. Isophthalic type (high resistance to hydrolysis and organic solvents); acid index, 13; styrene content, 50 wt %; viscosity (Brookfield-type rotational viscometer) at 25 °C, 160 mPa • s (cP); and volumetric shrinkage, 9%.

Ludopal–Butyl Acrylate Formulation. The Ludopal U150 resin is recommended for wood varnishes. It forms films with elasticity and surface hardness. It contains 34% styrene; the butyl acrylate–styrene–polyester ratio is 20:27:53, and the formulation viscosity is 150 mPa · s at 25 °C.

Impregnation. Three samples of each species were used for each monomer or resin bath. The wood-to-bath volume ratio was at least 1:10. Samples were soaked in a 10% water-diluted *N*-vinylpyrrolidone (NVP) solution that was later replaced three times by pure NVP. The baths were darkly stained by wood tannins. Impregnation time was about 4 weeks.

Partial wood impregnation by 15% aqueous solution of methacrylamide (MAID) started directly with this solution. It also had to be changed because of darkening, especially with oak samples. The soaking time was the same as previously described.

Dehydration in acetone and ethanol was carried out by four successive baths, for 1 week each. The solvent–butyl methacrylate exchange followed the same pattern. In each case the first bath was diluted by 10% of water or solvent. A slightly faster dehydration rate was observed with ethanol on deteriorated beech samples, although solvent–monomer exchanges behaved practically the same for acetone and ethanol.

No significant volumetric change was observed on oak samples after dehydration. On the other hand, deteriorated beech samples showed a mean volumetric shrinkage of 3% in both solvents. Acetone-impregnated samples were immersed for 2 weeks in Norsodyne and Ludopal resins diluted by 15% acetone in each first bath. The solutions were then changed three times by pure resins at 2-week intervals, totaling an impregnation time of 8 weeks for this final phase.

Irradiation. To reduce the loss by monomer evaporation during irradiation, impregnated samples were wrapped in different materials according to the products involved. With unsaturated polyester resins, samples were wrapped in textile, then covered by plastic film (usual procedure for artifact treatment). The textile can thus easily absorb any excess resin on the wood surface. Three different wrappings were tested with monomers: aluminum foil, plastic film, and textile covered by plastic film.

Resin-impregnated samples were irradiated for 40 h at a dose rate of 1 kGy/h (total dose, 40 kGy). Monomer-impregnated samples were cured in two batches, one at a dose rate of 0.6 kGy/h and the other at 1 kGy/h, also for 40 h (total doses of 24 kGy and 40 kGy, respectively). Dosimetry was carried out by using a Red Perspex dosimeter, based on the radiation coloration of commercial red-dyed Perspex type Red 4034 and a calibration curve relating the induced absorption coefficient to dose.

Results

Very poor results were obtained with water-soluble monomers. All the samples impregnated with NVP presented brown polymer gel on the surface during and even after radiation curing. This phenomenon led to important cracking and splitting of beech samples and radial cracks on oak samples. Such gel formation could be explained only by the fact that even traces of water remaining within the wood were enough to swell the NVP polymer dispersed throughout the wooden structure. The dark coloring of the polymer is another disadvantage of this method.

Samples partially impregnated with MAID were air-dried after irradiation. Cracks had already appeared on both oak and beech samples during the radiation curing. After drying, warping was observed on the oak samples; beech samples showed severe shrinkage and cell collapse. The principle of wood impregnation by water-soluble monomers was attractive, but their in situ radiation curing has not given satisfactory results so far.

Important polymerization inhibition by oxygen was observed on samples impregnated with butyl methacrylate, in spite of different wrappings. Radial and tangential cracks appeared on some oak and beech samples. The wood surface was still wet after irradiation, and important weight losses were determined on beech samples after monomer evaporation (40–70%) without collapse of the wood structure. The extent of impregnation was therefore very low, and it resulted in very fragile treated wood, especially in the case of degraded wood.

The best results in this study were obtained with the Norsodyne resin, which is currently used for artifact treatment. No cracks were observed on treated samples that presented a hard surface. However, radial cracking occurred with cylindrical forms. The mean shrinkages in the longitudinal (l), radial (r), and tangential (t) directions were, respectively: for beech samples, 0.9% (l), 2.3 % (r), and 4.6% (t); for oak samples, 0% (l), 0.9% (r), and 1.2% (t). As far as highly deteriorated wood is concerned, some warping can be expected.

Impregnation with the Ludopal formulation gave the following results: For beech samples, the mean shrinkages were 0.1% (l), 0.9% (r), and 3.5% (t); Some radial cracks were present because the wood has a relatively soft surface. The softness can be explained by the presence of butyl acrylate in the formulation, which gave a more flexible resin than the Norsodyne formulation, but was more sensitive to oxygen inhibition. For oak samples, the mean shrinkages were 0.4% (l), 1.2% (r), and 0.9% (t). No cracks were observed.

More investigations are necessary to formulate flexible polyester resins that produce a nontacky surface after air irradiation. Flexibility is important in order to reduce the radial and tangential shrinkages. No air inhibition is important in obtaining a good surface consolidation.

Case Studies of the Impregnation–γ-Irradiation Process

For conservation of waterlogged wood, as well as for other materials, no method is optimal for all of the widely varying cases encountered. The two treatments described in this part as illustrations of the radiation process concern artifacts that differ by their age, size, and degree of deterioration. The reasons for the choice of the radiation-curing method rather than the other method also applied in our center (freeze-drying) will be given.

Artifacts Collection from Montpellier (Department of Hérault, France). This collection includes 97 small household artifacts: dishes, bowls, spoons, combs, spinning wheels, toys, etc., many of which are turned. They date from the end of the Middle Ages and were excavated in 1985 from an unused well. The species are essentially *Buxus* (box), *Acer* (maple), and *Fagus* (beech).

The wood was generally well preserved, although some pieces were fragile because of their small thickness. Moreover, the place where the artifacts are to be exhibited (Montpellier Archaeological Society Museum) has unstable climatic conditions (temperature and relative humidity). The radiation-curing method was adopted instead of freeze-drying to preserve the strength and stability of the treated objects when subjected to environmental changes.

The wood-to-bath volume ratio was about 1:5. The dehydration phase in acetone necessitated four successive baths for 3.5 months. The acetone–resin exchange was then performed by four baths lasting 4 months. The irradiation dose absorbed by the items was 45 kGy, with dose rates ranging between 0.5 and 1 kGy/h. Although the treatment result was satisfactory for most of the artifacts, the very thin plates warped during polymerization, a phenomenon caused by volumetric shrinkage of the cured resin (Figures 10 and 11).

Bourg–Charente Canoe. This canoe was discovered in 1979 in the Charente River (Department of Charente, France) under 4.5 m of water and partially embedded in the sediment. It has the following dimensions: length, 5.65 m; width, between 0.4 and 0.6 m; mean thickness between 3 and 5 cm, and a maximum thickness of 35 cm at one end. The wood weight is 260 kg. It was carved out of a half-trunk of an oak tree and has been dated by ^{14}C to 2560 B.C ± 110 years. The water content ranges from 220 to 375% except in a sapwood zone, where it reaches 980%.

It was taken out of the water almost intact by nonprofessionals and left in the open air without any special precautions. A few weeks later it was split into more than 50 fragments and presented a large number of longitudinal cracks. This canoe could be of museographical interest only if these fragments, some of which weighed over 50 kg, could be reassembled. A well-consolidated dry wood had to be obtained to achieve efficient adhesion, so the radiation process was selected to treat this item. This operation required four 900-L acetone baths (dehydration time, 12 months) and four resin baths (12 months). During the radiation curing, the mechanical stresses generated by the resin shrinkage brought about widening of some cracks

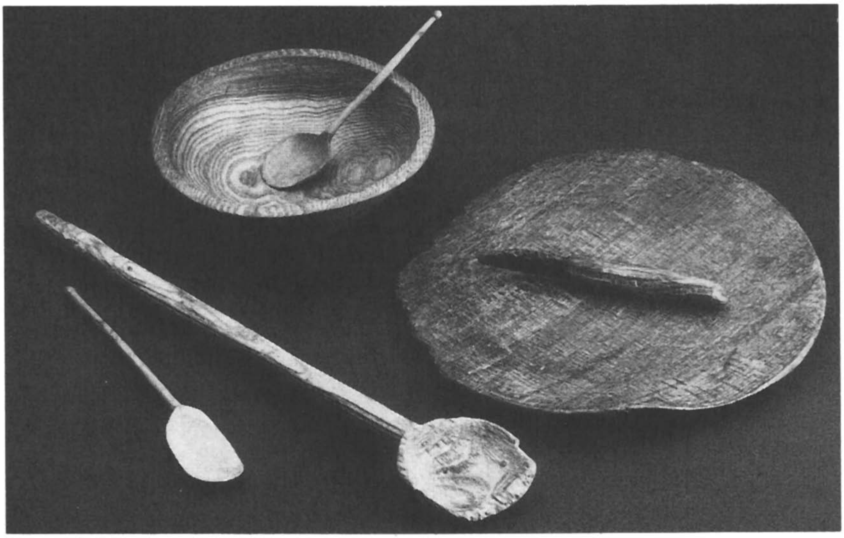

Figure 10. Treated artifacts from Montpellier excavation (late Middle Ages).

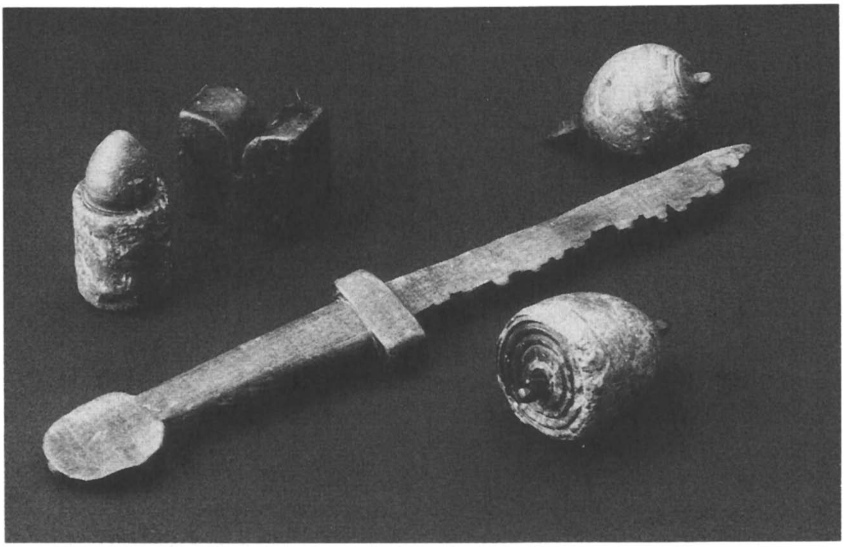

Figure 11. Treated artifacts from Montpellier excavation (late Middle Ages).

caused by the previous drying. The strength of the treated wood enabled the fragments to be stuck easily with an epoxy glue, but wooden pegs had to be fitted for the larger pieces to be assembled. When the treatment was completed, the canoe was restored to its overall shape, but none of the cracks had been filled. Although this very ancient item could be saved by this treatment, it still bears the traces of the disastrous drying it was subjected to just after it was discovered. It is at present exhibited in the Cognac Museum (Department of Charente, France) (Figures 12 and 13).

Other Waterlogged Wood Treatments by Radiation Polymerization

Few institutions have been involved in this conservation method. In most cases, the work is limited to laboratory research studying monomer impregnation with more or less satisfactory results. Up to now, radiation treatment of waterlogged wooden artifacts on a large scale was performed by impregnation with unsaturated polyester resins only. The different processes studied since the late 1960s are summarized as follows.

- Direct waterlogged wood impregnation by aqueous emulsion of styrene, methyl acrylate, and methyl methacrylate. Of these methods, only styrene emulsion was stable. Ash samples were immersed in styrene emulsion, and in situ radiation curing was then performed at a dose rate of 6 kGy/h (0.6 Mrad/h) for 30 h. Treated samples presented severe shrinkage and cell collapse because of a very low extent of impregnation (*1*). Another water–monomer exchange obtained with the 2-hydroxyethyl methacrylate monomer did not give satisfactory results (*2*).

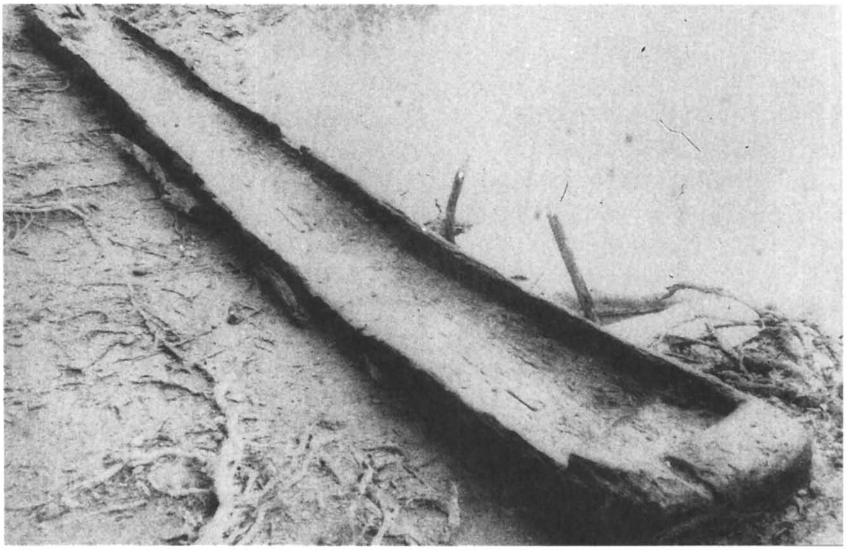

Figure 12. Bourg–Charente canoe (2600 B.C.) after excavation.

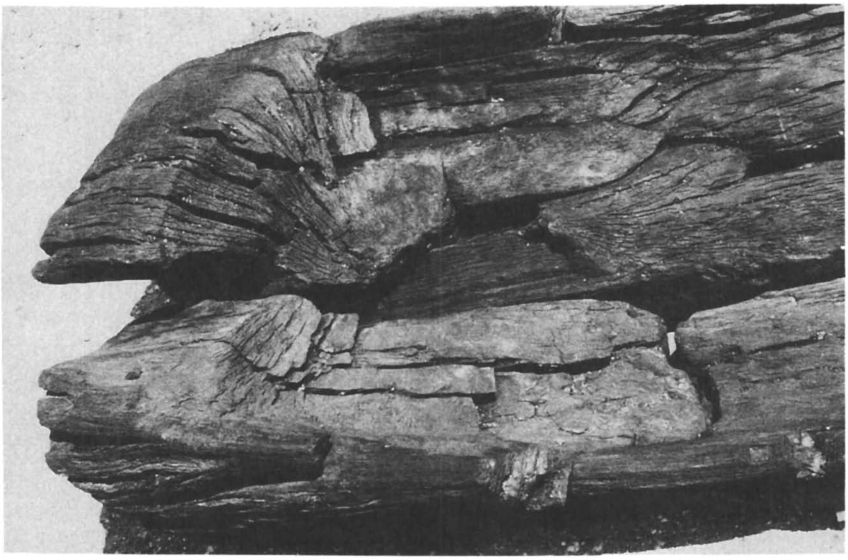

Figure 13. Bourg–Charente canoe after treatment (splitting is due to air-drying before treatment).

- Treatment by the solvent-exchange process was tested on ash and spruce samples by using solvents such as methanol and ethanol for dehydration, followed respectively by styrene and methyl methacrylate (or methyl acrylate) impregnations. The most satisfactory results were obtained with the styrene–carbon tetrachloride mixture, but the irradiation dose was excessively high (210 kGy or 21 Mrad). Cracking was observed on methyl methacrylate and acrylate-impregnated samples (*1*). The same process was applied for the treatment of oak samples that were still well preserved (water content, 160%). They were dehydrated by methanol and then impregnated with methyl methacrylate. The irradiation dose was 50 kGy (or 5 Mrad), with a dose rate of 1 kGy/h. After irradiation, the treated samples were dried at 60 °C for 8 h and overnight at 103 °C (*2*). Vinyl acetate was tested for wood impregnation after dehydration with methanol. The irradiation dose was 20 kGy (*6*).
- An interesting method that was developed some years ago combines two processes for waterlogged wood treatment. The first step is freeze-drying in order to obtain dried wood with maximum dimensional stability, and the second step is impregnation of this dried wood by an unsaturated polyester resin. The conservation of a pole used as a ladder excavated from a

medieval mine was described. The whole conservation process took 1 year (7).

Conclusion

The tests carried out with monomers (either water-soluble or not water-soluble) have not given satisfactory results. Various reasons are suggested, such as loss of product because of very low viscosity and high vapor pressure, large volumetric shrinkage, and above all the oxygen inhibition effect on hardening of most monomers. Irradiation in a nitrogen atmosphere could be a solution to the last-mentioned problem, but it is not realistic because frequent handling operations are necessary in the course of polymerization to achieve a good surface appearance.

Standard styrene–unsaturated polyester resins, which have a much higher viscosity than monomers, present two main features of interest for our application. Resin shrinkage is approximately half that of monomers, and nontacky hard surfaces are obtained after polymerization in the presence of air. We therefore now use these resins to impregnate the wood by a liquid–liquid exchange process. The treatment takes longer and the quantity of raw materials is greater. The process implemented in our laboratory for over 10 years uses acetone as solvent and an isophthalic polyester resin characterized by a high resistance to hydrolysis and organic solvents.

Although the resin shrinkage, reduced to 9%, still induces stresses that give rise to cracks under certain conditions, the treated wood is strong throughout. Furthermore, when solvent extraction is correctly performed, the wood remains stable under the variable temperature and humidity conditions encountered in museums without proper environmental control. Research is being carried out to formulate more flexible resins to attempt to solve this problem of cracking (notably on cylindrical shapes) while providing a good superficial consolidation.

The bulky equipment required to implement this method is costly, and the large quantities of raw materials involved make it difficult to apply to large items such as wrecks. Among the existing treatment methods, in spite of the comments often made on the γ irradiation process (in particular its irreversibility), the latter is appreciated when strength and stability of the wood are predominant factors for its restoration and preservation.

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10

Application of Freeze-Drying to Archaeological Wood

W. R. Ambrose

Department of Prehistory, Research School of Pacific Studies, Australian National University, Canberra, ACT 2601, Australia

Vacuum freeze-drying is routinely used at several conservation laboratories to dry fragile wet wooden archaeological finds. Pretreatment by solution impregnation with a range of polyethylene glycol is commonly adapted to take account of the variability in condition and properties of individual timbers. Satisfactory results have been achieved through vacuum freeze-drying small wooden artifacts, although there has been less success in treating larger timbers. Large composite artifacts have been successfully freeze-dried at normal air pressure in engineered environmental enclosures and in naturally occurring frozen environments. Meteorological records for parts of Antarctica show that it could be climatically well suited for naturally freeze-drying large decayed timber constructions.

THE USE OF SUBLIMATION DRYING TO REMOVE WATER from saturated archaeological wood appears to be an ideal method of great simplicity. All that is required is a frozen object and an environment that has a water vapor pressure less than that of the vapor pressure of the ice in the object. But although freeze-drying (or its synonyms, lyophilization and ice sublimation) remains an ideal method in theory, in practice it has encountered certain difficulties. Wood is an intrinsically complex material, to which the complications of its degradation have been added. The theoretical basis for freeze-drying is relatively well developed. However, its application to removing bound or entrained water from frozen solutions in a diverse range of media requires a large body of empirical and experimental data (*1*).

The theoretical and practical questions raised by sublimation cryotech-

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nology in the food industry and biomedical research include those related to primary freezing damage, efficient water vapor transfer, efficient heat transfer, overall drying rates, cell and product distortion, chemical degradation, loss of physical qualities, and postdrying storage. These factors and the basic engineering requirements for apparatus to achieve a desired end product at the least financial cost have all been the subject of consideration in treating wet archaeological wood. In these respects, archaeological applications research applies strategies similar to those used for freeze-drying in the food, pharmaceutical, and biomedical fields. There are, however, rather major additional problems in archaeological freeze-drying.

Challenges in Freeze-Drying

The obvious differences are those of scale, with wooden items ranging from spoons to ships. The most pressing difficulties reside in the inherent variability of woods and their water-transformed condition. Unlike peas, orange juice, and other commercially dried products, where the dried material is intended to be restored by the addition of water at some later stage, archaeological wood should be in a near-perfect end state when freeze-drying is complete. This means that any dimensional distortions caused by cell wall shrinkage and cell wall collapse during drying are unacceptable. The history of the application of freeze-drying to archaeological materials is dominated by efforts to deal with damage arising in treatment and to scale up the process to accommodate large structures weighing many tons.

The futility of expecting any single conservation procedure always to be successful in drying water-degraded wood is apparent when the nature of the deterioration and its products are considered. Cellulose is the main component in sound wood and imparts most of its useful qualities in obvious ways. As a result, conservation treatments have concentrated on this structurally ordered fraction, whether it remains dominant over time or not. Chemical analysis of archaeological wood (*2*, *3*) (*See* Chapter 5) shows a general decrease of the holocellulose–lignin ratio as a measure of increasing degradation, with increasing porosity and lower density of woody matter (*4*). These general effects of biodeterioration have been described in greater detail by wood chemists, for the major cellulose and lignin components, as well as the lesser fractions and extractives (*5*).

Basic differences in the degradative pathways of cellulose, lignin, and their end products greatly affect the response of saturated wood to drying. Cellulose decomposes to soluble liquid and gaseous products that can be leached or diffused away from degrading wood. In contrast, lignin converts to intermediate products through a number of steps (*6*), some of which remain in the degraded wood as relocated aggregations (*7*). Therefore, although lignin is generally regarded as long-lasting, it is not structurally inert in degrading wood. Under anaerobic conditions, cellulose loss invariably precedes loss of lignin. Indeed, there is some doubt about whether lignin can be metabolized at all by biodeterioration organisms in the absence of oxygen (*8*).

Conservators have not generally attempted to treat the major holocellulose and lignin components as separate problems, or to devise chemical treatments according to their relative proportion in degraded wood. This disregard of chemical differences has been possible because for many years the standard procedure for wood treatment involved total water replacement and impregnation with waxy, crystalline, or polymer solids. More recent work aimed at defining the chemical properties of water-degraded wood (*3*, *9*, *10*) for conservation purposes will inevitably lead to greater attention to the treatment of lignin, as well as depleted cellulose. The growing application of freeze-drying techniques to archaeological wood, from which water can be removed without its total replacement by solids, makes attention to the residual physical and chemical properties of the degraded dried wood much more important.

In sound wood, the equilibrium moisture content and swelling at different relative humidities differs according to whether it is measured during an adsorption or desorption cycle. The hysteresis effect in such wood can be explained in terms of wood chemical component hydroxyl groups bonding during drying and then being unavailable as sorption sites when humidity increases. The relative contribution to total wood adsorption of separated fractions of the Australian hardwood *Eucalyptus regnans* indicates the dominant role of cellulose and hemicellulose by their accounting for 47 and 37%, respectively. In contrast, lignin manages only 16% of total water adsorption (*11*), even though it accounts for 25–30% of the wood substance.

Although these figures refer to separated fractions rather than sound wood, they do indicate the relatively smaller contribution lignin makes to the hygroscopic behavior of wood. The decreased total cellulose–lignin ratio in degraded wood is consistent with wood's diminished swelling response and hygroscopicity once its contained water has dried. The change reflects both the poorer affinity of lignin for water and the increased random hydroxyl bonding in degraded cellulose. Freeze-drying appears to be well suited to dehydrating such wood because it avoids the irreversible surface tension strains and subsequent cellular collapse that inevitably accompany drying directly from the liquid phase.

Freeze-Drying of Archaeological Materials

Reports of the first wooden object treated by freeze-drying in the mid-1950s refer to a 3-m-long 8000-year-old oak canoe from the Netherlands (*12*, *13*), research in the Soviet Union around the same time (*14*), and European trials at other centers (*15*). Similar work was done in London (*16*). All of these projects used a simple system of freezing without pretreatment, followed by sublimation drying under vacuum. The process was not widely adopted because of damage to the wet wood, manifested as deep or random surface cracking and distortion from shrinkage.

Attempts by Organ (*16*) to apply freeze-drying to wet archaeological wood failed, and the experience led him to draw attention to deficiencies in various stages of the freeze-drying process. For example, attempts at evaporative cooling of wood under vacuum produced damage as vapor escaped rapidly from the interior of the wood. Similar damage was found when wood was prefrozen with CO_2 (−79 °C). Better results were reported for some specimens after rapid freezing in liquid oxygen (−183 °C), but other specimens were shattered. After drying was complete, the desiccated wooden objects tended to warp and suffer both radial and longitudinal shrinkage. As a result, confidence in the use of freeze-drying for water-saturated wood was lost.

There were divisible stages in the progress of damage, first by cracking and shattering when the object was frozen, second by shrinkage while drying under vacuum, and third by warping and delaminating when the dried object was exposed to normal air humidity.

Freezing-Related Damage. Wood can be mechanically typified as a material with an anisotropic pore structure and a large specific surface (square meters per gram). As the wood substrate is an active adsorption site, the contained pore water can be divided between surface-adsorbed water and unbound free water. With a large surface-to-volume ratio, a significant amount of the total water will be adsorbed.

Action of Water. As wood freezes, adsorbed water and unbound free water will behave differently. Adsorbed water may supercool below 0 °C and expand in volume until around −38 °C at normal air pressure, when it will freeze. The ability of the wood substrate to accommodate the increased volume of supercooled water will be impeded by two factors. First, the viscosity of water increases rapidly from 1.8 mPa s^{-1} at 0 °C to around 10 mPa s^{-1} at −30 °C (Figure 1). Second, its surface tension increases slightly from 7.56×10^{-6} N at 0 °C to around 7.75×10^{-6} N at −10 °C. These two effects increase the rigidity of saturated wood. The wood itself is not passive to temperature change. When dry wood is cooled it undergoes nonuniform shrinkage, following the pattern tangential > radial > longitudinal (*11*), which is also the familiar order of drying shrinkage. Wood substrate stress with lowering temperature is aggravated by its tendency to shrink while the supercooled water expands.

The most deleterious effects, however, occur when free water undergoes its phase change to ice. A rapid volume increase of up to 13% (*17*) is accompanied by enormous pressure increases. Ice pressure in confined pores can reach 12.1 MPa for each degree Celsius of temperature reduction below the

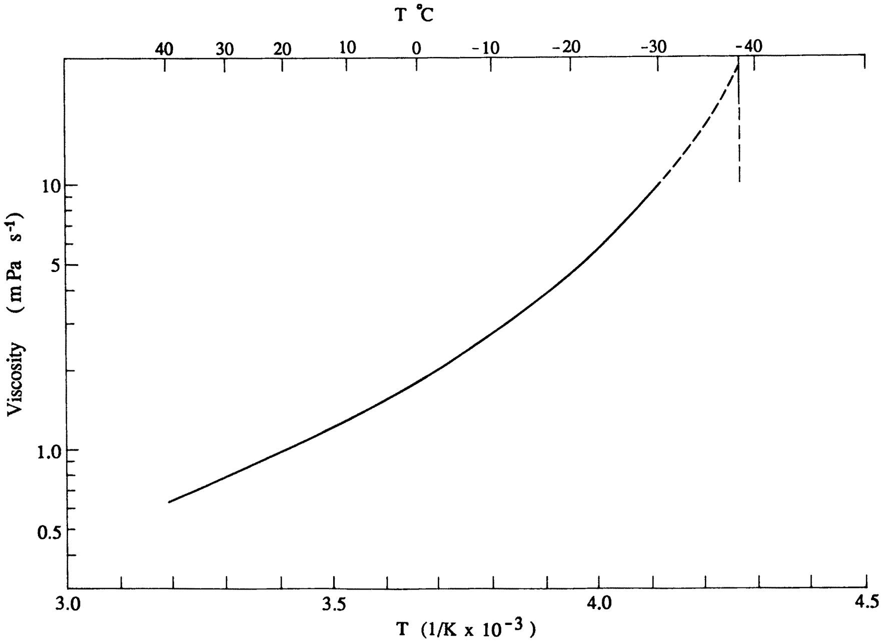

Figure 1. Viscosity of supercooled water, extrapolated (dotted line) to −38 °C.

freezing point. In another context, this pressure is sufficient to disrupt rocks (*18*). The considerable potential damage of hydraulic pressure at an advancing ice front into saturated wood will be aggravated by the increasing viscosity of supercooled water, its increasing surface tension, and shrinkage of the main wood components, cellulose and lignin. The ultimate damage will be affected by a number of variables, including porosity, the internal specific surface area, and the structural coherence of the wood (that is, its relative deterioration).

Chemistry of Wood Cells. Other factors that will affect the ultimate freezing damage are related to the chemistry of the wood cells and their contained solutes. Even sound living trees may be damaged by large temperature gradients between frozen and unfrozen sections of the trunk (*19*), despite the presence in living cells of solutes that could act as cryoprotectors by lowering the freezing point of aqueous solutions. As wood degrades and extractives and carbohydrates are removed, the composition of aqueous solutions in the wood will change with the addition of degradation products. These, too, could affect the formation of ice and the final eutectic temperature at which the whole system solidifies.

Franks (*20*) has summarized at a chemical level the different consequences of low temperature and freezing on organic systems. Although his observations are not specifically directed toward degraded woody plants, they are nevertheless relevant to them. These consequences include changes in chemical equilibria, changes in diffusion rates of molecules, changes in solute concentration from phase separation, the possible irreversible aggregation or separation of macromolecules, complications from supercooling of the aqueous phase, and the expulsion of dissolved gases. The weak hydrogen bonding between water and other polar molecules in an organic substrate such as wood is very sensitive to changes in temperature and does not cease at the freezing point of water.

Vapor Pressure Deficit. The water-holding capacity of saturated wood changes when it cools below the freezing point, with lowering of the fiber-saturation point (*11*). When saturated wood is frozen, the vapor pressure of ice, e_i, is lower at the same temperature than the vapor pressure of supercooled water, e_w, bound to internal surfaces. The resulting saturated vapor pressure difference between the ice and the supercooled water is given by $e_w - e_i$ and may be referred to as a vapor pressure deficit (VPD).

VPD can be defined as the difference between the actual vapor pressure, *e*, and the maximum vapor pressure possible at the temperature of the sample (*21*). The difference in vapor pressure between supercooled water and ice is not a constant. As Figure 2 shows, the VPD (measured in pascals) increases from 0 to a maximum of 27 Pa at around −11 °C before falling to 26 Pa at −15 °C.

The VPD will drive water vapor away from the supercooled surfaces to condense on the nearest ice contained in cell lumens or voids. Long-term storage of waterlogged wood at temperatures around the maximum VPD may cause some drying of microscopic structures in cell components. It could be useful to examine this possibly damaging process in the case of highly degraded wood, where the structural resilience imparted by ordered cellulose has been lost and replaced by the dominant disordered lignin.

Temperature Gradient. Organ's experimental work in the 1950s included rapid freezing of very degraded wood by immersing it in liquid oxygen (*16*). This procedure would produce a very steep temperature gradient of around 200 °C, from −183 °C at the surface in contact with liquid oxygen to ~20 °C at the core. The accompanying rapid phase change from water to ice in the surface zone caused sufficient stress to produce an audible cracking as cooling proceeded. Similar severe damage, with destructive shattering of a sample from freezing degraded waterlogged wood in liquid nitrogen (−195 °C), has been reported by Till (22). Less severe damage was caused by prefreezing in solid CO_2 (−76 °C), followed by cooling in liquid nitrogen. Even less damage resulted from freezing in CO_2 alone. In this case the damage was comparable to that caused by simply freezing in a domestic freezing cabinet at −20 °C.

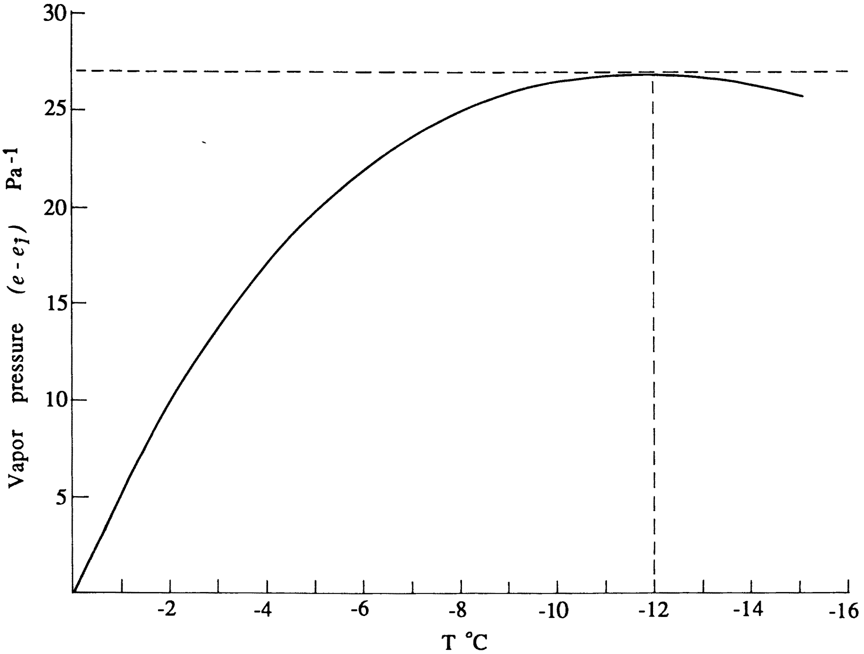

Figure 2. Vapor pressure deficit (VPD) between supercooled water and ice at the same temperature.

The evidence presented by Till's study indicates a strong correlation between the surface-to-core temperature gradient and damage to degraded wood on freezing. The gradient can be reduced by reducing the cooling rate and by precooling the entire object to around 0 °C before slowly reducing the temperature below the freezing point. As a low temperature gradient necessitates a slow cooling rate, the evidence presented by Till (*22*) is contrary to the view that a fast "shock freezing" cooling rate should be adopted after precooling to around 0 °C (*23*). Saeterhaug achieved a maximum cooling rate of around 0.6 °C min^{-1} in archaeological wood (*24*), but this rate is very slow in terms of freezing biological tissue.

In biological applications, much discussion of the need for fast cooling rates and steep temperature gradients is based on preserving the viability of membranes in tissues or cells at a microscopic level, where small items are involved. The rapid cooling rates of between 10 and 400 °C min^{-1} (*25*) for biological specimens are not achievable for degraded saturated timbers of the size normally encountered in archaeological conservation, and the evidence indicates that they are not desirable. Rapid freezing may be suited to histological specimens where volumes are small or samples are thin. However, for relatively large-volume wooden items, the cumulative dimensional changes extending from the frozen surface to the unfrozen core can combine to produce high-velocity release of stress, with characteristic splitting and rupture. The superficial freezing of large samples, arising from attempts at rapid cooling with a steep temperature gradient, should be avoided, as was suggested by Rey (*26*) some time ago.

Alleviating Freezing Damage. In the early archaeological application of vacuum freeze-drying, the two problems of ice expansion damage and extreme desiccation damage of dried wood under vacuum were recognized by Christensen (*15*), Rosenqvist (*13*), and Organ (*16*). In order to avoid the ice expansion problem, Christensen introduced a modified histological drying technique linked to a secondary vacuum removal of the dewatering fluid, in this case *t*-butyl alcohol $(CH_3)_3COH$. Water removal took place necessarily between 25.5 and 82 °C, the freezing and boiling points of *t*-butyl alcohol. When water was finally replaced by 100% *t*-butyl alcohol in a series of graduated solution changes, the whole object was cooled to below 25.5 °C to allow the frozen liquid to be removed by sublimation, under vacuum or at normal air pressure.

This method still produced desiccation damage in the finished product (*15*), but the damage was circumvented by the addition of waxy polyethylene glycol, PEG 4000 (later renamed by the manufacturer as 3350), to the final soaking solution of *t*-butyl alcohol. The removal of the solvent by sublimation left a porous waxy support that imparted a good surface finish, a substantial increase in strength and compressibility over the wet original wood, and a very small-dimensional change.

The success of the Christensen system is evident in its continued use over the last 30 years and in the development of large installations to carry it out. The large-scale plant at Brede in the Danish National Museum has a vacuum chamber capacity of nearly 9 m^3, a pumping capacity of 2100 L min^{-1}, and a condenser capacity of 300 kg at −50 °C (*27*). An even larger plant is operating on thousands of wooden items at the Nara Palace site in Japan, where a 19-m^3-capacity installation based on the system established in Denmark is in operation (*28, 29*).

The *t*-butyl alcohol–PEG 3350 system was recognized by its originator as being complicated and somewhat hazardous, but this disadvantage was outweighed by the quality of the finished wooden artifacts (*15*). PEG 3350, a solid at room temperature, must be heated to around 50 °C in solution with *t*-butyl alcohol in order to diffuse into wood. The relative impenetrability of sound wood to relatively high-molecular-weight PEG (*30*) means that total impregnation is unlikely to occur. The removal of moisture and *t*-butyl alcohol, with cooling of the wood mass at the end of the impregnation cycle, without diffusion back by PEG 3350, could cause low-vapor-pressure core collapse in timber, although Christensen did not observe this in his Danish oak artifacts. Strictly speaking, this system is not a freeze-drying process, as the free water content has been removed long before the *t*-butyl alcohol is removed under vacuum.

The damaging effects of freeze-drying in other biological contexts have been dealt with in a different way by the protection afforded by certain chemical additives. One of the earliest was inadvertently discovered by Smith (*31*) and Polge (*32*) in 1948. They showed that the addition of 5–20% glycerol to serum, with slow freezing to −79 °C, dramatically increased the thawed survival rate of protozoa. Although none survived direct freezing and thawing, the addition of an aqueous 10% solution of glycerol resulted in a 50% survival rate. The complex reactions of living organisms to freezing and the role of glycerol and other cryoprotectants have been the subject of much research; Morris and Clarke (*33*) published a bibliography of nearly 1000 references. The application of PEG 400 as a protectant in the freeze-drying of degraded wet wood was first used on a collection of wooden digging implements, parts of fence lines, and other items from excavations in Papua New Guinea in the 1960s (*34, 35*).

Polyethylene Glycol in Freeze-Drying

The evidence of Morén (*36*) and other Swedish wood technologists indicated that polyethylene glycols were very effective in reducing drying shrinkage and increasing the dimensional stabilization of green wood. At the same time this finding was confirmed and extended in a systematic way by Stamm (*37*). With hardwoods, the lower-molecular-weight grades of PEG produce the most effective dimensional stabilization and reduce the overall hygroscopicity of the impregnated wood below that of either the liquid PEG or the untreated wood (*38*). This effect indicates the presence of some hydrogen bonding between elements in the wood and PEG. Because the average hydroxyl content is greater in lower-molecular-weight PEG, it is more effective in neutralizing potential moisture adsorption sites within the wood structure.

This difference is confirmed in the case of water-degraded wood by Rosenqvist (*39*), who showed that the adsorption–desorption isotherms of oak treated with PEG 400 were less responsive below 60% relative humidity to moisture-affected dimensional change than untreated oak. Her comparative X-ray diffraction analysis, between PEG-treated and untreated wood fiber, seemed to show the growth of more crystallinity with slightly increased intensity and sharpness of the diffraction image in the PEG 400-treated sample. Rosenqvist's results are based on a low concentration of PEG 400 in the wood and are certainly not comparable to the total replacement of water by heavier-molecular-weight PEG 3350.

An equally effective reduction in hygroscopicity and increased dimensional stability from the use of low concentrations of PEG 400 is reported by Grattan (*40*) and Cook and Grattan (*41*). For undiluted PEG there is nevertheless an overriding increased hygroscopicity with decreasing molecular weight. Any excess PEG in wood above that needed to satisfy the surface sorption requirements of the sample would have the same hygroscopicity as undiluted PEG. For PEG 400 there is a logarithmic relationship of total water absorption to relative humidity. At room temperature and at 55% relative humidity (RH), PEG 400 may contain up to 15% absorbed water (*42*).

Hoffman (9) has shown that in air-drying degraded wood, poor antishrink efficiency is found with PEG 400 or PEG 200 at 50% concentration in soaking baths. This result is understandable because the retained concentration of liquid PEG is well above the sorption capacity of the dried wood, so that free PEG liquid will exert surface tension effects in voids and on capillary surfaces in a manner similar to that of water.

Moisture Content. Most water-degraded woods in archaeological collections have a moisture content of 100–500% on a dry-weight basis. It would therefore be counterproductive to simply replace the water with an equal volume of low-molecular-weight liquid PEG because this volume would be greatly in excess of the dry wood's sorption capacity and would produce a rather soggy product with poor dimensional stability.

The distinction between fiber saturation point (the maximum water content of swollen cell walls) and the maximum possible moisture content has a diminishing value for degraded wood, which may eventually have no effective fiber saturation point at all. The ordered and disordered cellulose in sound wood are the main sites for water adsorption (*11*). As they diminish over time, their relative role in determining fiber saturation also diminishes. Nevertheless, the measurement of relative water adsorption will have some value in determining the relative degradation in a wood sample.

Wood becomes less hygroscopic in a progression from sound to very degraded, until eventually any drying cycle below saturation produces irreversible shrinkage. In drying such material, residual PEG left after the loss of water should only be sufficient to account for surface and solution adsorption in the swollen sample. Unfortunately, the measurement of specific surface in swollen degraded wood is problematic; it needs to be dried before it can be measured, but drying may destructively alter the volume and therefore its specific surface. It is possible to empirically evaluate the optimum residual concentration of PEG 400 that produces the most satisfactory product, in terms of minimum shrinkage and surface appearance. This was the approach used in the development of freeze-drying of the archaeological collection of wood from the Papua New Guinea Highlands swamps in the late 1960s and early 1970s.

These wooden artifacts, such as digging implements and parts of old pig fences or house timbers, were recovered from the Papua New Guinea Highlands swamps in an excellent condition, with clear surface marks of their means of fabrication by stone axes. The choice of freeze-drying for this material in preference to the indifferent results expected from stewing the artifacts in cauldrons of hot water-soluble wax seemed reasonable at the time. The now-familiar response in wood to attempts at direct vacuum freeze-drying, ice rupture and postdrying shrinkage cracks, prompted a consideration of pretreatment with low-molecular-weight PEG as a way to avoid these two deleterious effects.

PEG 400. The main propositions behind the modified freeze-drying system for this archaeological wood were that PEG 400 could diffuse into the wood better than heavier-molecular-weight grades, that the freezing range of PEG 400 encompassed the freezing point of water, that these water-soluble PEGs would shrink near the freezing point of water (Figure 3) and reduce ice expansion damage in the cell cavities, that upon freezing the water could be preferentially removed by sublimation under vacuum, and that the residual PEG 400 would displace surface-bound water and alleviate postdrying shrinkage. Other benefits imparted by the PEG 400 were reduced hygroscopicity and dimensional change in the wood and improved resistance to biodeterioration.

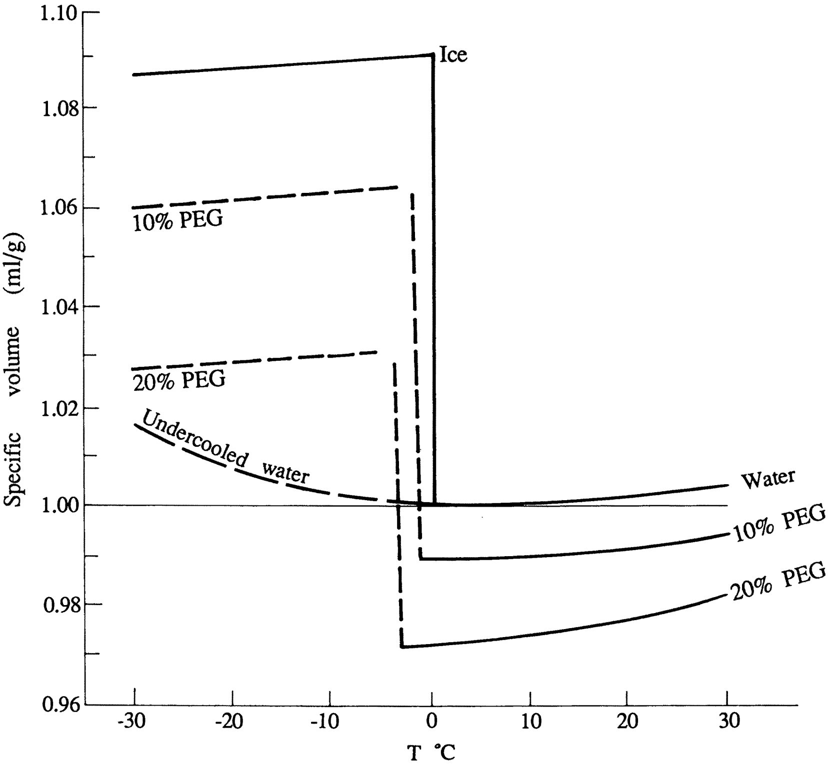

Figure 3. Change in specific volume (mL g^{-1}) of PEG 400 solutions with temperature.

Materials cost for 5–15% PEG 400 solutions was lower than for heavy impregnation in 100% solutions, and there were minimal hazards from the nontoxic PEG itself. The time necessary to counterdiffuse PEG with water in wood is, among other factors, dependent on the molecular size of the diffusing liquid. In this case, PEG 400 has distinct advantages over higher-molecular-weight water-soluble waxes. The development of a workable system and its modifications have been described previously (*35, 43–46*). Wood sections retained from work done in 1968 show no obvious deterioration to the present. Although the cautionary suggestion of Brownstein (*47*) on thermal oxidative degradation of PEG should be considered, the inherent antioxidant properties of lignin may contribute to stability in the cellulose–lignin–PEG complex (*48*).

One of the main difficulties of the PEG 400 freeze-drying system is in determining the amount of residual PEG to produce dimensional stability in wood without leaving excess liquid in pores or voids. An important contribution to understanding the diffusion of PEG in cell walls is provided by Young and Wainwright (*10*). They adopted microscopic staining techniques that use cobalt thiocyanate for determining the location of PEG 400 after freeze-drying from a 35% solution. Because cobalt thiocyanate preferentially stains PEG with inhibited fluorescence, the lack of fluorescence in treated wood compared to its presence in untreated control samples indicates the depth of diffusion of PEG into cell walls.

The results from fluorescence microscopy of stained freeze-dried sections indicated the presence of PEG 400 within the cell wall capillary matrix. This result contrasts with the demonstrated lack of penetration of heavier-molecular-weight PEG 3350. In terms of dimensional stabilization tests on the antishrink efficiency of various PEG solutions, the greatest stability was achieved when the amount taken up by wood was at the lower limit of the fiber saturation point, around 30%. Fiber saturation point is a dynamic concept related to water and holocellulose, and as such it has reduced value in degraded wood. In view of this, and when the treatment process for freeze-drying wood with residual nonevaporating PEG is involved, the notion of specific surface is better.

The approach of Young and Wainwright (*10*) and Hoffman (*9*), with microscopic staining of selected wood sections, could provide a semiquantitative means for determining the optimum residual PEG levels for freeze-drying purposes. This determination could be done by using stained sections coupled with quantitative computer imaging systems, which would allow a better assessment of relative ratios of cell surface areas to volume in sound and degraded wood. This approach would be more thorough than the simple weight-loss ratios for determining appropriate aqueous PEG solution strengths for pretreating wood prior to freeze-drying, such as that proposed as a rough guide in earlier work (*43, 45*).

A recent study (*49*) at the British Colombia Provincial Museum attempted to predict the response of structurally complex wood to variations in PEG pretreatment on wood from the Ozette site in Washington State. Although the response of the wood to treatment was within predictions according to its deterioration, grain complexity, and species, the heavier-molecular-weight PEG 600 was used and difficulties with the vacuum equipment marred the result. No tests for optimum PEG concentration were made.

Two-Stage Treatment. Knowledge of the optimum concentration of low-molecular-weight PEG for a particular small sample may not always provide the optimum concentration for an entire piece of wood. This condition follows from the diverse properties of wood itself, from dense heartwood rich in polyphenols to relatively porous sapwood, and from the relative deterioration that may extend from sound wood to almost total destruction in a single block. Piles or stakes may be so degraded as to be hollow. It is more usual for exposed ends of artifacts, or their outer surfaces, to be preferentially degraded.

One approach to such objects has been to adopt a double-stage impregnation of both liquid and solid-grade PEG in solution before freeze-drying. Watson (*50–52*) has developed a procedure using a preliminary impregnation with 10% PEG 400, followed by a longer period of immersion in increasing concentrations of PEG 3350. The greater diffusion rate and penetrability of PEG 400 produces its dimensional stabilization on cell components, while the larger-molecular-weight PEG 3350 supports voids and lumens in a more mechanical fashion without diffusing into cell walls. The net effect for extensively degraded wood with over 400% water content on a dry weight basis is a better result than the use of PEG 400 alone.

Grattan has provided an improvement in applying the two-stage PEG 400–3350 pretreatment with a mathematical model for determining the ideal proportions and concentration of the two PEGs. The solution is balanced according to the relative loss of dry cell matter in the wood to be treated. A computer program has been developed to calculate the ideal relative proportions of PEG400–PEG3350 and the optimum solution strength according to the percent loss of dry cell matter, compared with sound wood of the same species (*53*).

In Norway, Saeterhaug found that freeze-drying with low-concentration PEG 400 (less than 16% soaking solutions) did not provide the necessary physical strength for degraded wood to retain its form after drying. Although PEG 400 provided the best dimensional stabilization for lesser degraded samples, those with a water loss of 378–483% on a dry weight basis, and very degraded, suffered collapse and splitting in radial and tangential directions. PEG 3350 was therefore adopted at saturation concentration of 50–60% as a pretreatment for freeze-drying. The results from this were better. Saeterhaug's work (*24*) further examined the question of appropriate residual PEG after treatment. He concluded that relative deterioration, found from measurement of water loss on a dry weight basis, was the best indicator.

Freeze-Drying Installations

There has been an increasing acceptance over the last 20 years of low-concentration PEG pretreatment freeze-drying, particularly for small wooden artifacts where surface marks from manufacture or use are present. Small areas of burnishing, pigmentation, residues, and charring may show clearly on small freeze-dried objects because of the light tone and fine texture preserved on surfaces treated by this method. Vacuum technology has predominantly been used in archaeological freeze-drying applications because of its advantages of speed and the ready availability of engineering expertise and design specifications. In fact, many smaller freeze-drying installations are modified commercially available systems designed primarily for biological or pharmaceutical purposes; the small unit at the *Wasa* in Stockholm (*54*) and the Swiss Archaeological Museum laboratory (*55*) are examples of this type of system.

At the large-capacity end of the range there is a vacuum freeze-drying installation at Moesgaard in Denmark, with a capacity of 2.7 m^3 and vacuum pumps designed to remove water vapor without the conventional intervening cold trap (L. M. Anderson, Moesgaard, personal communication). The facility at the English Heritage Laboratory in London has a capacity of 2.0 m^3, a cold trap of −50 °C, and a working vacuum of 27 Pa. Since it was commissioned, around 40 m^3 of archaeological wood has been processed there (J. Watson, English Heritage, personal communication). Another relatively large custom-built machine in Dunedin, New Zealand, has a capacity of 4.6 m^3, a cold trap temperature of −80 °C, and optimum vacuum of 13 Pa (*22*). In the United States, the very large vacuum freeze-drying facilities of a 65-m^3-capacity environmental testing chamber were employed to handle ship parts. However, the equipment had difficulty in removing the high water vapor yield of the objects, and the best achievable working vacuum was only about 10 kPa (*56*).

Large-Scale Freeze-Drying. The scale of operation in vacuum freeze-drying, although very satisfactory for objects up to a few kilograms, rapidly becomes difficult as the mass of the wood increases. This difficulty is a function of rapidly increasing energy and plant size needed for operating vacuum chambers above a few cubic meters, but it also arises from the diminishing yield of water vapor from wooden items as their thickness increases. Therefore, simply increasing vacuum chamber capacity cannot yield a commensurate gain in drying capacity for larger cross-sectional dimension timbers. The sublimation of ice in vacuum requires that heat be transferred to the ice surface through an ever-thickening dried layer. Sublimation can be accelerated to some extent by transferring heat to the ice surface by cyclical changes of dry air pressure gas, followed by removal of vapor from the heated ice under vacuum (*1*). The advantage in sublimation time is of the order of 30–40%, which could be significant for a long running time on large timbers.

Other methods of heat transfer rely on creating a large thermal gradient across the dry outer shell to transfer sufficient heat flux at the point of ice sublimation. The exponential relationship of vapor pressure to temperature creates extremely desiccating conditions at the outer heated dry surface when this is under vacuum. The temperature used on the heating coil in early work on freeze-drying wood was up to 40 °C, which could contribute to the displacement of bound water by PEG. The same conditions could also thermally swell wood components to some extent. Whether this temperature gradient has damaging or beneficial effects is not clear, although Watson (*52*) recommends that the entire process should take place at a temperature of no more than −15 °C so that PEG does not migrate preferentially to the surface.

Atmospheric Pressure Freeze-Drying. Some of the difficulties in multiplying the capacity of freeze-drying vacuum equipment can be overcome by converting to freeze-drying at normal air pressure. The basic principle of providing an environment with a lower water vapor pressure than the frozen item exposed within it applies to both vacuum and air pressure ice sublimation. The major difference at atmospheric pressure is that the transport of water vapor through the dried surface is by a slower diffusion process at a low temperature, at which the temperature gradient from the dry surface to the ice surface is very small. This diffusion is to be compared with a faster mass vapor transfer process through a dried layer in vacuum with a large temperature gradient in the wood. Such a process gives rise to expansion of the released vapor and a large reduction in the vapor pressure at the dry surface.

There is also a difference in the achievable vapor pressure gradient between the dry surface and the ice surface in the two systems. Air pressure drying has the advantage of avoiding the extreme desiccation of vacuum methods. Basically, the air pressure freeze-drying system is limited by the maximum rate of water vapor transfer to the dry surface. For vacuum freeze-drying, the main factor limiting the sublimation rate is the transfer of heat from the dry surface to the sublimating ice surface. In both systems the rate will be moderated by variable permeability and heat-conducting properties in the wood.

Engineered Environment. A simple arrangement for air pressure freeze-drying of archaeological wood was described in 1973 (*45*). The system consisted of an insulated chamber in which the frozen sample was supported to allow unimpeded air circulation. Air was blown across the surface to an ice trap, where it was dried by cooling to –40 °C. After being heated to around –5 °C, the air was recirculated across the wood to continue the cycle. Provided that the air vapor pressure remains less than the saturation, or ice point, vapor pressure of the ice surface at –5 °C, sublimation will continue. Ideally, the specific humidity (q), defined by Oke (*21*) as the ratio of the mass of water vapor to the mass of air in kilograms per kilogram, will be less on the warmed inlet side of the chamber than at the cooled exit side of the condenser. Oke shows that the specific humidity (q) of air, but expressed in grams per kilogram, can be given by equation 1.

$$q = \frac{0.622e_i}{P - 0.378e_i} \tag{1}$$

where e_i is the ice point vapor pressure and P is the total air pressure in kilopascals (*21*). For the conditions in the enclosure at –5 °C, the condenser at –40 °C, and P around 100 kPa, the air has a potential specific humidity or drying capacity, from q(–5 °C) minus q(–40°C), of around 2.4 g kg^{-1}, or in other terms 3.2 g m^{-3} [air has a density at sea level of about 1.32 kg m^{-3} at –5 °C (*21*)].

In practice, considerably less than 3.2 g m^{-3} in drying potential can be achieved. Apart from the diminishing rate of water vapor transport with increasing dry wood thickness, there is a need to remove the water vapor from the air immediately above the dry surface. In still air this would be by slow eddy diffusion, but the rate of evaporative removal will increase as a square root of the air speed across the surface (*19*). Removal will reach a limiting value governed by diffusion through the dry layer from the ice beneath. The limiting value for air speed efficiency has been given as 0.5 m s^{-1} (*1*).

A further limiting factor is the presence of PEG in unfrozen solution at –5 °C. The wide molecular range of PEG 400 in the published data (*42*) indicates that about 9% has a molecular weight of 300 or less, including about 1% < 200. The presence of these light-weight fractions would lower the freezing range of the solution and also contribute to a reduction in potential evaporation according to Raoult's law of vapor pressure lowering by a dissolved solute. This effect would increase with enrichment of PEG by the preferential loss of water as drying proceeds.

Clearly, the additional time required for air pressure freeze-drying of water-saturated wood will be an important factor in utilizing this system in preference to vacuum treatment. Some measure of the extra time required is available for wood (*44*, *57*) and other organic materials (*1*, *58*). The time required for atmospheric pressure drying appears to have a multiple of 1.5–8 times that necessary for vacuum drying. For large structures, the time element will be less important than cost of plant installation and running costs. At the Canadian Conservation Institute, work was carried out on a comparative study of financial and time budgets between the two freeze-drying systems. The study concluded that air pressure freeze-drying cost less than 10% of the cost of the vacuum method (*57*), although drying time increased by a factor of about 6–8.

Large Structures. In recent years the atmospheric freeze-drying system has been applied to some remarkably large structures. The most notable of these has been the large Roman boat with plan dimensions of 19 × 8 m and a wet weight of about 20 tons. The wreck, which was uncovered during construction work in Marseille (*59, 60*), was not complete. The superstructure was missing from an earlier salvage attempt. The hull was better preserved, but biologically degraded on its upper section. During its excavation and later storage, some damage to the waterlogged timbers occurred from workmen's treadage and premature drying before it was stored for 5 years in a water bath.

The freeze-drying was carried out, without the use of cryoprotectants such as PEG 400, in a 500-m^3 enclosure integrated with equipment for refrigeration, dehumidification, and air circulation that was housed outside. The boat remains within were frozen to a core temperature of around −25 °C by the use of 5000 L of liquid nitrogen. This temperature was reached after around 15 h. When the wood was frozen, the turbine began its circulation of air, cooled to a dewpoint of −50 °C from the refrigeration unit, at 10,000 m^3 h^{-1} through the chamber with an effective velocity of 0.1 m s^{-1}. The air containing the sublimed water vapor from the timbers was returned to the condenser, where it yielded up to 3 kg of water per hour. The circulation was continued while the weight of the timber was monitored until it reached an equilibrium weight loss after 18 months. Some equipment problems were encountered, and there was leakage of moist exterior air into the system.

The appearance of the timber in the dried wooden vessel is not perfect, and some longitudinal and transverse cracking has appeared. This result raises the question of the need for pretreatment to alleviate the considerable stresses involved in direct freeze-drying of degraded wet wood. The system used to treat the Marseille wreck was nevertheless conceived on an imaginative scale and deserves further research and development, particularly with respect to appropriate pretreatment.

Research into the efficiency of atmospheric freeze-drying in Canada (*57*) and France (*60*) confirms its cost benefit and practicability for large structures. However, there is no diminution in the perceived importance of pretreatment. Although the engineering difficulties inherent in drying large structures can be overcome, the cost and time involved in diffusing PEG 400 cryoprotectants or bulking agents such as the heavier PEG 3350 increases as the size of the wood increases, regardless of whether vacuum or atmospheric drying occurs.

Natural Environment. Atmospheric freeze-drying with engineered environments of low vapor pressure and temperature has a direct corollary in natural environments where natural freeze-drying occurs. The potential for freeze-drying in such places as Antarctica or the high Andes has been recognized for some time. However, the pioneering work at the Canadian Conservation Institute was the first to seriously address the research necessary to evaluate the use of natural environments for freeze-drying archaeological timbers.

Grattan and others (*61*) experimented with enclosures aimed at maximizing sublimation rates at five locations across Canada. Before the samples were exposed to field conditions, they were pretreated with 15% v/v PEG 400. The exercise was hampered by the short cold period available during the Canadian winter; freeze-drying had to be discontinued when temperatures rose above the freezing point. Despite the short exposure of 2.5 months, up to 50% of the water was removed before the wood was brought indoors to dry completely by simple evaporation at 20 °C at a relative humidity of 38–55%. It was determined that the drying rate was a function of the square root of object mass over time, $M^{1/2}/t$. Refinements in enclosure design to allow greater ventilation and exclude precipitation improved the results.

More recently, in 1984–1985, excavations in Quebec uncovered several lightweight boats and two heavier and larger sailing craft (*62*). Pretreatment differed between the two types of boat. The lightweight type was impregnated for 1 year with up to 35% PEG 400. One of the two heavier sailing boats was treated with both PEG 400 and PEG 540 for a total of 5 months. Over 2.5 months of winter in 1987, the two boats had lost 20 and 34% of their weight, respectively. When the temperature rose in the spring, the boats were removed to a microclimate chamber to achieve a lower stable relative humidity.

Climate Restrictions. The major obstacle to successful freeze-drying in both the earlier work of Grattan (*61*) and that of Bergeron (*62*) is the short period of usable climate and the need to house half-dried wood in normal indoor conditions between winter seasons. An inspection of the climate data provided in Grattan's published work (*61*) allows a comparison of natural environmental conditions. The five Canadian sites vary in average temperature T, between −11 and −30 °C for the period of Grattan's experimental freeze-drying program. The relative humidity (RH) was uniformly high, with averages of 75–88% RH.

From the relationship of RH and the air saturation vapor pressure e (in

Pa) at T, the ice point vapor pressure, e_i, can be found by equation 2.

$$e_i = e \frac{\mathrm{RH}}{100} \qquad (2)$$

and therefore the vapor pressure deficit, VPD, can be found from $e - e_i$.

The Canadian vapor pressure data for the five short-term experimental locations are included in Table I with the artificial laboratory conditions of McCawley and others (*57*), as well as equivalent data from the dry natural conditions at Davis Base, Antarctica, for comparison. The data in Table I show that the potential drying efficiency of the natural air, as indicated by VPD, is low compared with the experimental laboratory situation. None of the Canadian sites appear to be particularly good freeze-drying locations, even during the optimum conditions of a short 2–3 months per year.

Nevertheless, a 3- × 0.6-m canoe freeze-dried in atmosphere in the Canadian winter of 1979 lost 34% of its wet weight in 66 days, before it was returned indoors to complete the drying process. The 15% pretreatment with PEG 400 ensured that the craft suffered no cracking, checking, or shrinkage. The finished canoe had a pleasant light color and a dry weight of 23.7 kg, compared with its initial wet weight of 54.3 kg. McCawley and Grattan (*63*) point out that the entire treatment took only 1/3 the time of conventional 100% bulking with heavier-molecular-weight PEG. The fact that useful sublimation rates have been achieved in the short term confirms the validity of atmospheric pressure freeze-drying under natural conditions. Other natural locations, particularly selected locations in Antarctica, present better prospects.

The Antarctic as a Freeze-Drying Location for Large Timbers

Antarctica (Figure 4) is the world's driest continent. Davis is one of the driest bases, with the least number of days of blowing snow of all the record stations (*64*).

Meteorological data are available as readings taken every three hours at the Davis base in Antarctica covering 1981–1985, with less-detailed records for the previous 22 years. Computer reduction of the raw meteorological records has been applied to produce statistics on temperature, wind direction, wind velocity, vapor pressure, and the vapor pressure deficit. The mean monthly air temperature records (Figure 5) indicate that conditions are generally below the freezing point, but do not reach extremely low levels.

The difference between the air temperature and the ice point (dew point) temperature is an indicator of humidity and the drying capacity of the air. The mean monthly air temperature and ice point temperature for a 22-year

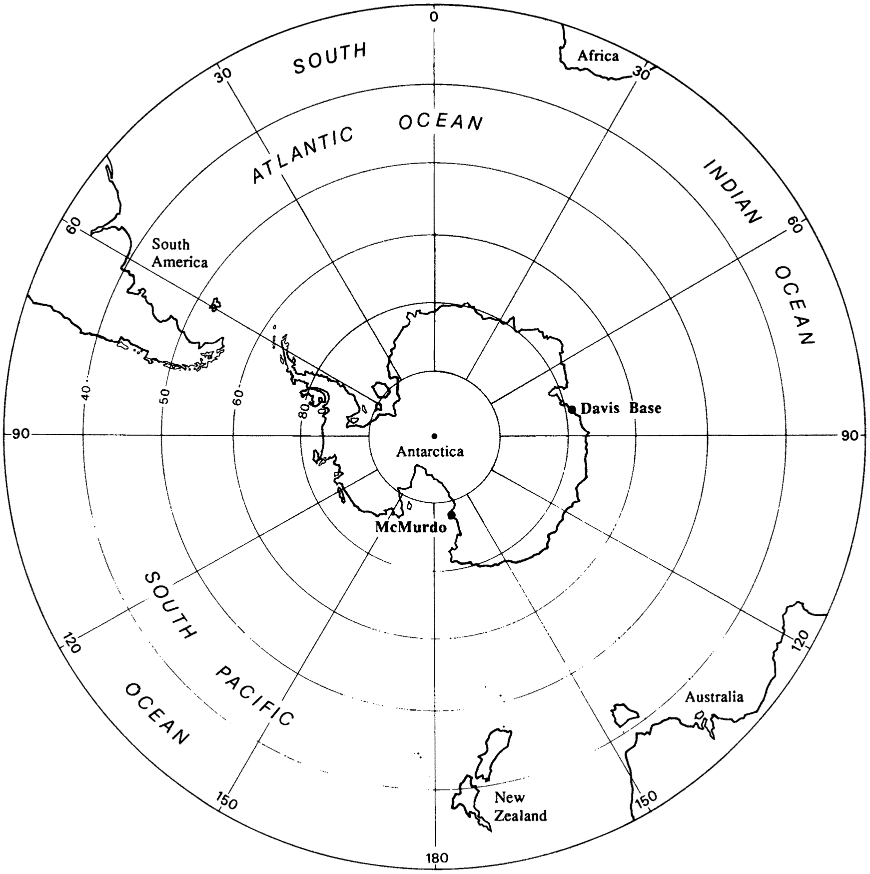

Figure 4. Map of Antarctica, showing the position of Davis Base.

record is presented in Figure 6, based on daily readings at 0900 h and 1500 h. Relative humidity is not a particularly good measure of potential sublimation rate, because it does not reflect the critical dependence of vapor pressure on temperature. For this reason, the calculated value of the VPD is also given in Figure 7 and Table II. For the 5-year period the grand mean VPD is 154 ± 127 Pa, which is about 1/3 as effective as that achieved in the experimental equipment designed by McCawley and others (57) (Table I). The VPD for the 6 winter months in most years at Davis Base is below 100 Pa, but only for 1 month in 10 did the value fall below 60 Pa. This result compares with the optimum VPD in the 2-month winter data from the Canadian outdoor sublimation experiments, where Ottawa had an average VPD of 58 Pa and Yellowknife the very small average VPD of 7 Pa and a correspondingly poor potential sublimation rate.

Table I. Canadian, Antarctic, and Laboratory Climate Data for Air Pressure Freeze-Drying

Parameter	*Ottawa*	*Wakefield*	*Kirkland Lk.*	*Winnipeg*	*Yellowknife*	*Laboratory*	*Antarctic*
T, °C	–11	–14	–16	–22	–30	–6	–11
e, Pa	238	181	151	85	38	368	310
RH, %	75.5	88	74	80	81	3.5	50
e_i, Pa	180	160	112	68	31	13	156
VPD, Pa	58	22	39	17	7	355	154

NOTE: Canadian data are expressed as average values. Antarctic values are means for a 5-year period based on a 3-h recording interval.

Table II. Davis Base Meteorological Data, 1983–1985

	1983			*1984*			*1985*		
Month	T, °C	*RH, %*	*VPD, Pa*	T, °C	*RH, %*	*VPD, Pa*	T, °C	*RH, %*	*VPD, Pa*
Jan	1.7	42	420	2.2	47	395	1.4	53	331
Feb	–2.0	44	294	–2.6	48	265	–3.7	44	263
Mar	–8.4	47	164	–8.0	53	151	–7.6	52	166
Apr	–10.5	50	137	–10.9	59	98	–11.4	52	116
May	–13.2	44	124	–14.2	51	98	–15.1	54	76
June	–15.0	55	88	–17.5	48	75	–13.6	50	108
July	–20.6	51	54	–18.6	59	65	–25.2	55	33
Aug	–16.3	49	93	–15.9	56	76	–18.1	46	74
Sept	–13.2	46	108	–14.8	51	81	–17.4	44	80
Oct	–13.6	49	105	–15.5	54	80	–12.8	53	98
Nov	–7.7	54	161	–5.5	47	210	–6.1	53	182
Dec	–1.3	52	274	1.2	50	356	–1.3	52	267

NOTE: Monthly means for temperature, relative humidity, and vapor pressure deficit (VPD) in pascals.

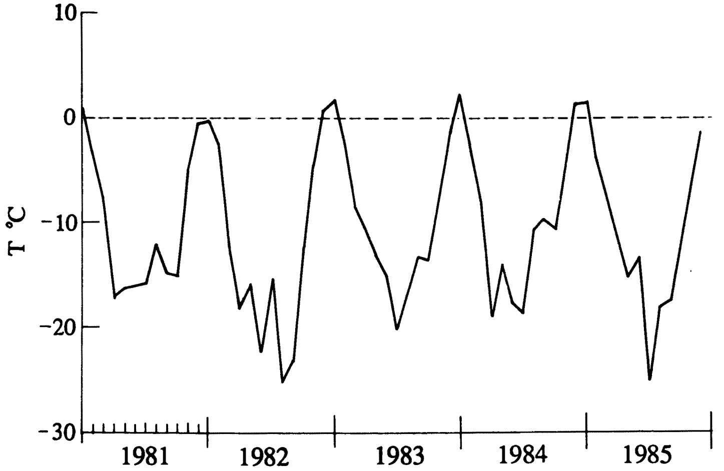

Figure 5. Monthly mean air temperatures for 1981–1985 for the Davis Base, Antarctica.

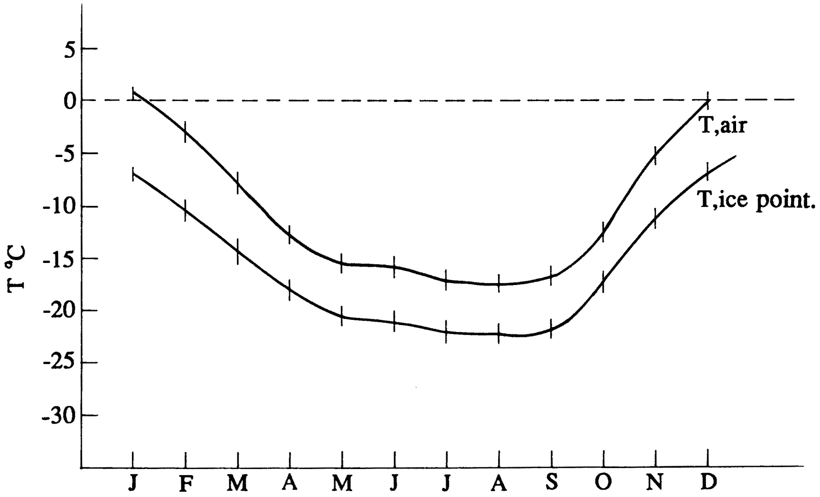

Figure 6. Mean monthly temperature for air and ice points, based on records for 22 years from Davis Base, Antarctica.

Air flow across the dried wood surface is essential to remove the escaping water vapor, a factor that was emphasized by Meryman (58), who was able with his equipment to achieve sublimation drying for his standard specimen in 8 h, as opposed to 6 h in an efficiently designed vacuum apparatus. The Davis Base wind is predominantly from an easterly sector, with little seasonal variation, and has a mean velocity of 5 ± 4.4 m s^{-1}.

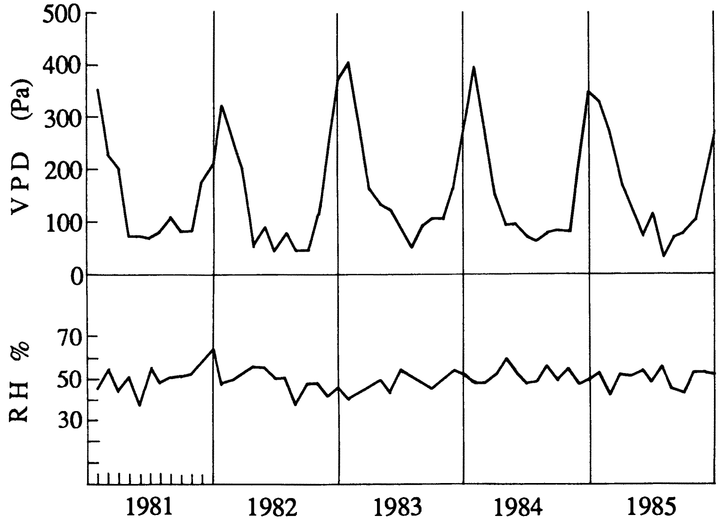

Figure 7. Vapor pressure deficit (VPD) and relative humidity (RH), based on monthly mean records for 1981–1985 for the Davis Base, Antarctica.

Advantages. The Vestfold Hills area of the Davis Base is clear of snow and is a desert in the strict sense. It could be an excellent location to site an experimental conservation facility to test the feasibility of freeze-drying some of the large ships and timbers that are so difficult, expensive, and time-consuming to handle with conventional equipment and methods. Anyone who has seen the black oily appearance of heavy timbers from shipwrecks that have been treated with massive impregnation of PEG waxes would recognize some advantage in the lighter-colored surfaces of objects now being freeze-dried by vacuum air pressure methods at low PEG concentrations.

Apart from the question of aesthetics, there are other distinct advantages in atmospheric freeze-drying of large timbers, pretreated with appropriate additives. In a longer drying program, lower stress can be expected because of lower temperature gradients from the outer surface to the frozen interior of a slab of wood. As a corollary to the low temperature gradient, atmospheric drying does not produce the extreme desiccation gradient in the dried surface of the sample that is inevitable in vacuum freeze-drying. The use of pretreatment solution concentrations, 10–20% for PEG, produces a lighter-weight product and a considerable saving in chemical costs. The other obvious cost savings are energy and capital-related, in the absence of plant and machinery to drive the process. Because atmospheric freeze-drying is relatively slow, it also gives an opportunity for more careful monitoring of the progress of any collection of degraded wood. Conditions are dry and cold in the Antarctic deserts, so the need to provide special storage facilities after drying is complete is not so pressing.

Disadvantages. There are, of course, disadvantages. These problems mainly lie in administrative and transport difficulties. Whether these are offset by the perceived advantages could be examined. Another major cost in using an Antarctic desert would be in providing a suitable housing for large timbers. It must be constructed to withstand the occasional cyclonic winds, and preferably would be semisubterranean to buffer short-term thermal changes and provide a small positive natural heat increment during the winter months while avoiding the warmth of the short summer. The orientation of such a building would be governed by the predominant wind direction; variable ventilation could optimize air flow through a drying collection. If a source of low-grade heat could be supplied during the coldest 6 months, the sublimation rates could be greatly enhanced from the exponentially raised ice vapor pressure in the frozen wood.

Conclusions

The potential of the Antarctic for drying large timbers, at a site such as Davis Base or other locations in the dry valleys where katabatic winds scavenge moisture from stony fields, has been neglected. The work carried out in Canada has indicated that atmospheric freeze-drying is a workable process for difficult wooden objects. Successful freeze-drying of degraded wet wood has progressed in sophistication while the scale of operation has grown enormously. Perhaps the next time a Wasa, a Bremen Cog, an Amsterdam, or Viking ship is found, serious consideration should be given to using the natural climate of Antarctica to achieve its return to dry land. In the meantime, experimental work on likely locations should be undertaken.

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11

Outdoor Wood Weathering and Protection

William C. Feist

U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI 53705–2398

The natural weathering process subjects exposed wood to discoloration and degradation by light, moisture, and staining microorganisms. Physical deterioration consists of surface roughening, checking, and cracking. Chemical deterioration involves a complex sequence of free-radical reactions. However, because light does not penetrate wood past 200 μm, degradation reactions are a surface phenomenon. Consequently, wood can be protected by paints, stains, and similar materials. The influence of outdoor weathering on the performance of wood is discussed here in detail. The chemical and physical changes of wood exposed outdoors are described, and the mechanisms of weathering and methods for protecting exposed wood surfaces are summarized. The studies described here have implications for the preservation of historic structures.

WOOD IS A NATURALLY DURABLE MATERIAL that has long been recognized for its versatile and attractive engineering and structural properties. Wood has immense archaeological importance. Contrary to the misconception that old wood is not sound, wood in a favorable environment can last for centuries (*1*, *2*). The tomb of the Egyptian pharaoh Tutankhamen, who ruled in the 14th century B.C., contained wood objects that were in perfect condition when recovered in the 20th century. Some Japanese temples constructed with wood date back 13 centuries. In Lucerne, Switzerland, a covered bridge built in 1440 is still in service, and in the United States, some 950 covered bridges built during the 19th century still remain. Many wood dwellings in the United States are centuries old (Figures 1 and 2).

Figure 1. Old Fairbanks house at Dedham, MA, built in 1637. Most of the white pine clapboard siding was replaced in 1903, and it has withstood 85 years without paint.

However, like other biological materials, wood is susceptible to environmental degradation. When wood is exposed outdoors above ground, a complex combination of chemical, mechanical, and light energy factors contribute to what is described as weathering (*1–3*). Weathering can be detrimental to the surfaces and appearance of historic structures. Thus, weathering must be taken into account in a discussion of the preservation and protection of outdoor wood. Weathering of wood is not to be confused with wood decay (rot), which results from organisms (fungi) acting in the presence of excess moisture and air for an extended period (*4*). Under conditions suitable for decay, wood can deteriorate rapidly, and the result is far different from that observed for natural outdoor weathering.

Figure 2. White oak log cabin near Middleton, WI, constructed around 1845 and never painted or finished.

The degradation of wood by any biological or physical agent modifies some of the organic components of wood (2). These components are primarily polysaccharides (cellulose, hemicelluloses) and polyphenolics (lignin) (Figure 3). Extractives are also present in relatively small quantities, and their concentration determines color, odor, and other nonmechanical properties of a wood species. A change in the organic components may be caused by an enzyme, a chemical, or electromagnetic radiation, but invariably the net result is a change in molecular structure through some chemical reaction. Stalker (5) conveniently divided the environmental agents that bring about wood degradation into categories; all agents other than fungi, insects, or animals are categorized as physical forms of energy. The relative effects of various energy forms on wood, indoors and outdoors, are compared in Table I. The most serious threat to wood indoors comes from thermal energy, and outdoors, from weathering—the combination of chemical, mechanical, and light energies.

Although the degradative effect of the environment on wood has undoubtedly been recognized for centuries, Berzelius (6) first reported the

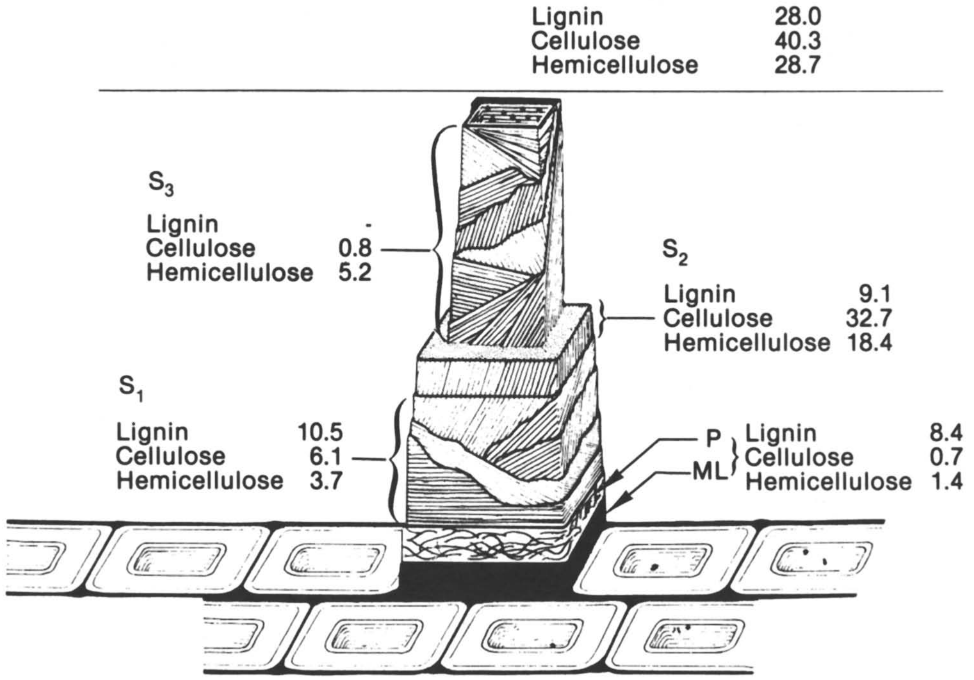

Figure 3. Chemical components in a typical softwood cell wall. Values are given as percentages.

Table I. Relative Effect of Various Energy Forms on Wood

	Indoors		*Outdoors*	
Form of Energy	*Result*	*Degree of Effect*	*Result*	*Degree of Effect*
Thermal				
Intense	Fire	Severe	Fire	Severe
Slight	Darkening of color	Slight	Darkening of color	Slight
Light[a]	Color change	Slight	Extensive color changes	Severe
			Chemical degradation (especially lignin)	Severe
Mechanical	Wear and tear	Slight	Wear and tear	Slight
			Wind erosion	Slight
			Surface roughening	Severe
			Defiberization	Severe
Chemical	Staining	Slight	Surface roughening	Severe
	Discoloration	Slight	Defiberization	Severe
	Color change	Slight	Selective leaching	Severe
			Color change	Severe
			Strength loss	Severe

NOTE: Based on data from ref. 5.
[a] Both visible and ultraviolet light.

chemical phenomenon of wood weathering in 1827, followed by Wiesner (7) in 1864, and Schramm (8) in 1906. Systematic studies on weathering reactions in wood did not begin until the 1950s (*1*).

General Aspects of Wood Weathering

In outdoor weathering of smooth wood, original surfaces become rough as the grain raises. The wood checks, and the checks grow into large cracks (Figure 4). Other changes may also occur. The grain loosens; boards cup, warp, and pull away from fasteners; the roughened surface changes color, gathers dirt and mildew, and becomes unsightly; the wood loses its surface coherence and becomes friable; and splinters and fragments break off the surface. All these effects, which are brought about by a combination of light, water, and heat, are encompassed in weathering.

Surface chemical changes occur very rapidly when wood is exposed to the natural weathering process. Studies on the effect of short periods of weathering before finishing (9, *10*) showed that adhesion of both an acrylic latex and an alkyd–oil primer to wood was significantly reduced after the wood substrate had weathered for 4 or more weeks before painting. Reduced paint adhesion and increased failure of the wood–paint interface will inevitably result in poor long-term paint and finish performance. These studies conclude that wood should be protected with a finish that will prevent

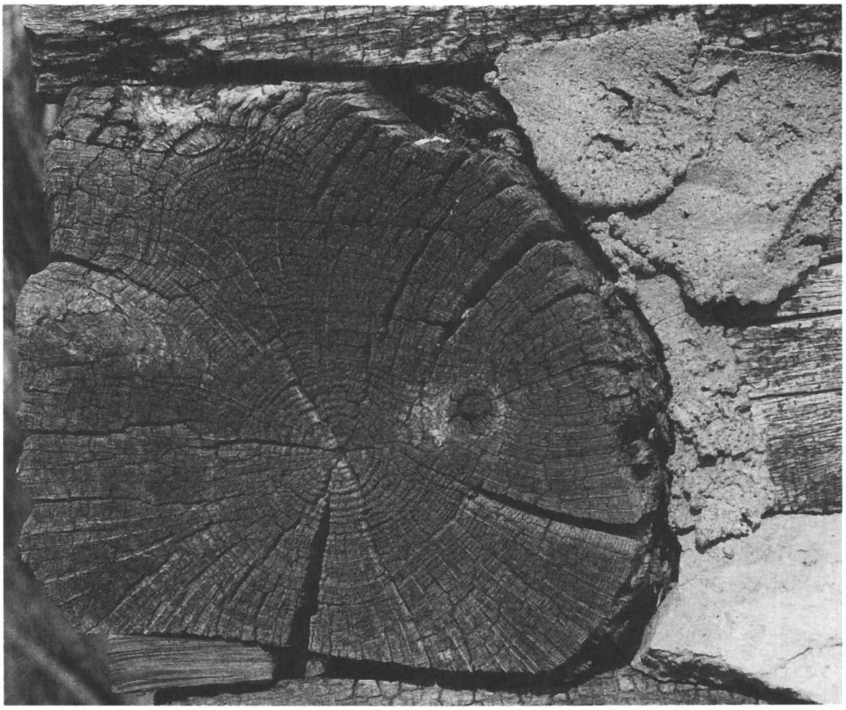

Figure 4. Close-up view of 140-year-old weathered white oak logs of house shown in Figure 2.

photodegradation and water damage if the wood remains outdoors for more than 2 weeks.

Kleive (*11*) and Underhaug et al. (*12*) also conducted studies on how the weathering of unpainted wood affects the durability of exterior coatings. These authors demonstrated that the surfaces of spruce and pine wood degraded rapidly when exposed to the weather. After 1 month of outside exposure, the paint-holding properties of the wood were adversely affected. The wood continued to deteriorate throughout the next 6–10 months. Kleive and Underhaug et al. also demonstrated that a good finish performance on weathered wood could be obtained by planing the top layer to at least 1 mm to expose the unweathered wood. Moreover, wood that is porous because of the action of microorganisms should be primed with a very-low-viscosity penetrating primer to ensure saturation of the wood.

Weathering Factors. The deleterious effect of wood weathering has been ascribed to a complex set of reactions induced by a number of factors (*2*). The weathering factors responsible for changes in the wood surface are as follows: moisture (dew, rain, snow, and humidity), solar radiation (ultraviolet (UV), visible, and infrared light), temperature, and oxygen. Of these factors, the photon energy in solar radiation is the most damaging, initiating a wide variety of chemical changes at wood surfaces. Moreover, in recent years, an additional weathering factor has arisen because of atmospheric pollutants such as sulfur dioxide, nitrogen dioxide, and ozone in the presence or absence of UV light (*13*). The following section describes the weathering factors of moisture, light, and acid deposition, as well as other factors such as temperature.

Moisture. One principal cause of weathering is frequent exposure of the wood surface to rapid changes in moisture content (*1*, *2*). Rain or dew falling on unprotected wood is quickly absorbed by the surface layer through capillary action, followed by adsorption within the wood cell walls. Water vapor is taken up directly by the wood by adsorption under increased relative humidities, and the wood swells. Stresses are set up in the wood as it swells and shrinks because of moisture gradients between the surface and the interior. The steeper the gradient, the greater the stress. Stresses are usually the greatest near the surface of the wood. Unbalanced stresses may result in warping and face checking (*14–21*).

The importance of the effect of water on wood exposed outdoors was demonstrated by Banks and Evans (*22*), who exposed thin radial sections of scotch pine and lime to deionized water over the temperature range 25–65 °C. Losses in wet tensile strength and toughness occurred rapidly at temperatures ≥50 °C. After about 2 months of exposure, the pine lost 10–30% tensile strength and 20–60% toughness. For lime, the losses were somewhat greater: about 20–60% tensile strength and up to 80% toughness. Further exposure for about 18 months led to about 60% tensile strength loss in pine and 80% in lime. Both species lost approximately 90% toughness after this period of exposure. Banks and Evans believe that these phenomena were due purely to physicochemical processes and that the losses in strength may contribute significantly to detachment of paints and other finishes from wood surfaces.

Light. The photochemical degradation of the exposed wood surface from sunlight occurs fairly rapidly (*1*, *2*, *23*, *24*). The initial color change of wood exposed to sunlight is a yellowing or browning that proceeds to an eventual graying (Figure 5). These color changes can be related to the decomposition of lignin in the surface wood cells. The changes are strictly a surface phenomenon (*2*, *24–27*) and occur to a depth of only 0.05–2.5 mm (*see* section on penetration of light). Photodegradation by sunlight, particularly UV light, induces changes in chemical composition, especially in lignin, and subsequent color changes (*23*, *28–34*).

Miller and Derbyshire (*35–37*) showed that visible light may also contribute to the breakdown of wood during weathering. A loss in strength was

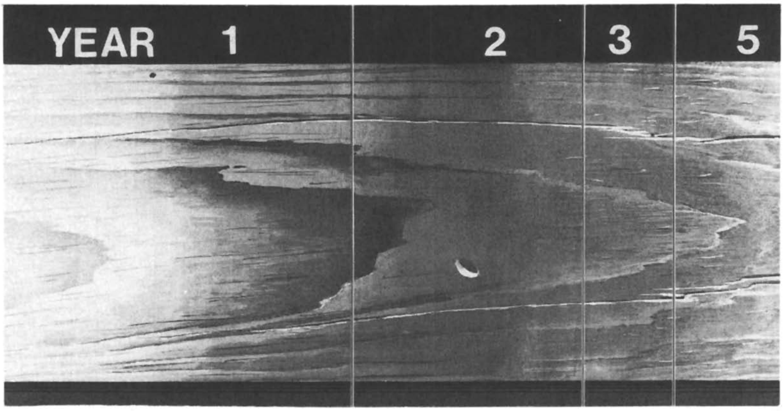

Figure 5. Artist's rendition of surface color changes during the outdoor weathering process of a typical softwood. Wood initially darkens (yellows or browns) and eventually lightens (grays).

associated with light-induced depolymerization of lignin and cell wall constituents and with the subsequent breakdown of wood microstructure.

The two most important factors of weathering—sunlight and water—tend to operate at different times. The time of wetting is important in relating climatic conditions to exterior degradation of wood. For example, exposed wood may be irradiated while it is wet from rain, dew, or other conditions of high humidity. The action of the combined elements can follow different degradation paths, with irradiation accelerating the effect of water or the converse. The role of water and free-radical generation is discussed in a later section.

Acid Deposition. The attention given to acid deposition (acid rain) during the last decade has prompted interest in the effect of acids on wood weathering (*9*). Raczkowski (*38*) showed that in the summer, the decisive factor in wood weathering is the intensity of solar radiation, whereas in the winter, it is the increased amount of sulfur dioxide in the surrounding air (central Europe exposure). Williams (*39*) measured the effect of acid treatment on the erosion rate of western redcedar by using xenon arc accelerated weathering techniques. Test specimens were periodically soaked in nitric and sulfuric acids at different pH levels during accelerated weathering. Compared with the unsoaked controls, specimens treated with acids at pH 3.0 experienced a 10% increase in erosion rate; at pH 3.5, a 4% increase; and at pH 4.0, no increase. The pH levels used in this study were felt to be somewhat conservative because naturally occurring atmospheric acid concentrations have been reported in the range of pH 2.0.

The effects of acid rain on painted materials can be seen in the degradation of the coating and substrate. The type of pigment and extenders used in paint formulations has a direct bearing on paint performance in an acid environment (*9*). The degradation of the substrate also has a direct bearing on coating performance. Because substrate degradation may induce different coating-failure mechanisms, future research should include the reaction of the substrate–coating interface to acid rain.

Other Factors. Although heat may not be as critical a weathering factor as UV light or water, as the temperature increases, the rate of photochemical and oxidative reactions increases (*1*, *2*). Freezing and thawing of absorbed water can also contribute to wood checking. Abrasion or mechanical action caused by such elements as wind, sand, and dirt can significantly affect the rate of surface degradation and removal of wood. Small particles such as sand can become lodged in surface checks, and the swelling and shrinking of the wood can weaken fibers in contact with these particles. Solid particles in combination with wind can have a sandblasting effect (*1*, *2*, *23*).

Penetration of Light and Wood Surface Deterioration. Although the weathering of wood materials depends on many environmental factors, there is mounting evidence that only a relatively narrow band of the electromagnetic spectrum (the UV light portion of sunlight) is responsible for the primary photooxidative degradation of wood.

Because light must be absorbed before a photochemical reaction can occur, the concentration, location, and nature of chromophores are highly significant in determining the rate of photooxidation of wood (*40*, *41*). Essentially, wood is an excellent light absorber. Cellulose absorbs light strongly below 200 nm, some absorption occurs between 200 and 300 nm, and a tail of absorption extends to 400 nm (*42*, *43*). Because hemicellulose is structurally similar to cellulose, its UV light absorption characteristics are also similar. Lignin and polyphenols absorb light strongly below 200 nm and have a strong peak at 280 nm, with absorption down through the visible region (*43*). Extractives usually have the ability to absorb light between 300 and 400 nm (*43*, *44*). In summary, most components in wood are capable of absorbing enough visible and UV light to undergo photochemical reactions that ultimately lead to discoloration and degradation.

Because a wide range of chromophoric groups is associated with the surface components of wood, wood cannot easily be penetrated by light. The discoloration of wood by light is essentially a surface phenomenon. The dark brown surface layer of ponderosa pine and redwood affected by light has been reported to reach only 0.5–2.5 mm into the wood (*1*, *2*, *24*, *43*). As weathering progresses, most woods change to a grayish color, but only to a depth of about 0.10–0.25 mm. Browne and Simonsen (*45*) reported that visible (400–750 nm) light, as measured spectrophotometrically, can penetrate into wood as far as 2540 μm. They mentioned that the gray layer of the wood surface was 125 μm thick, and a brown layer beneath the gray layer ranged from 508 to 2540 μm thick. These color changes are a result of photochemical reactions, which always involve free radicals.

Hon and Ifju (*46*) reported the use of UV light transmission techniques to measure penetration of light through radial and tangential surfaces of different woods as a function of thickness. By using electron spin resonance (ESR) techniques to monitor free radicals generated in different layers of wood, these authors found that UV light cannot penetrate deeper than 75 μm; visible light, on the other hand, penetrates as far as 200 μm into wood surfaces. Hon and Ifju claimed that visible light of 400–700 nm is insufficient to cleave chemical bonds in any wood constituents. The light energy is less than 70 kcal/mol (*43*, *47*). The brown color formed beneath a depth of 508–2540 μm in wood cannot be caused by light, as claimed by Browne and Simonsen (*45*). Hon and Ifju suggested that the aromatic moieties of wood components at wood surfaces initially absorb UV light, followed by an energy-transfer process from molecule to molecule to dissipate the excess energy.

The energy-transfer processes between electronically excited groups at the outer layer of the wood surface and groups beneath the wood surface presumably account for the photoinduced discoloration of wood underneath the surface, where practically no UV light penetrates. Furthermore, free radicals generated by light are high in energy and tend to undergo chain reactions to more stable radicals. Consequently, new free radicals formed in this way may migrate deeper into wood to cause discoloration reactions.

Property Changes During Weathering

Chemical Changes. Over a century ago, Wiesner (*7*) reported that weathering causes loss of the intercellular substance of wood. He concluded that the remaining gray layer consists of "cells that, leached by atmospheric precipitation, have been robbed entirely or in large part of their infiltrated products so much that the remaining membranes consist of chemically pure or nearly chemically pure cellulose." Schramm (*8*), Wislicenus (*48*), and Mobius (*49*) reported similar observations.

The increase in cellulose content of the weathered wood surface was shown by Browne (*50*) in work reported by Kalnins (*26*). Browne compiled analytical data on white pine wood that had been weathered outdoors for 20 years. Results showed that weathering degraded and solubilized lignin. Cellulose appeared to be considerably less affected, except in the top surface layer of the wood. Similar results were obtained with various kinds of wood exposed on a test fence for 30 years. The outer gray layer consistently exhibited very low lignin content (Table II). The lignin content of the brown layer immediately below this layer varied from 40 to 60% of that normally found for fresh nonexposed wood. The composition of inner wood layers only a few millimeters under the outer gray surface was similar to that of

Table II. Cellulose and Lignin Content of Wood Weathered for 30 Years Outdoors

		Wood Component in Different Cell Layers, %					
		Cellulose			*Lignin*		
Sample Type	*Wood Type and Species*	*Inner*	*Middle*[a]	*Outer*[b]	*Inner*	*Middle*	*Outer*
Extracted	Softwood						
	Western redcedar	48	48	44	42	28	7
	Douglas-fir	50	46	47	36	30	7
	Southern pine	51	52	51	50	21	4
	Hardwood						
	Yellow-poplar	51	59	62	27	15	2
	Birch	55	57	60	28	21	6
Unextracted	Softwood						
	Western redcedar	54	47	44	33	27	10
	Douglas-fir	49	50	53	34	29	6
	Southern Pine	52	51	49	31	20	7
	Hardwood						
	Yellow-poplar	50	64	64	22	16	2
	Birch	47	56	70	21	17	4

NOTE: Data from ref. 50.
[a] Middle brown layer.
[b] Outer gray layer.

normal unweathered wood. Analysis of wood sugars from hydrolysis of a water extract of the weathered wood showed that xylan and araban were solubilized more rapidly than glucosan. In addition, glucose did not predominate in the hydrolyzed water extract, although glucose units do predominate in unaltered wood polysaccharides.

Lignin degradation after weathering was demonstrated by analyzing aspen wood samples exposed to accelerated weathering. The 2400 h of artificial weathering was equivalent to approximately 5 years of outdoor exposure. The composition of the exposed wood compared to unexposed wood is described in Table III. The outer weathered layer was scraped away for analysis. Reduced lignin content and a corresponding increase in cellulose content (as shown by an increase in glucose content) was found in the wood surfaces exposed to controlled accelerated weathering (UV light and water). There was an accompanying decrease in xylose and mannose.

Table III. Chemical Composition of Aspen Wood Before and After Accelerated Weathering

Component	*Exposed Wood, %*	*Unexposed Wood, %*
Klason lignin	1.9	20.5
Acid-soluble lignin	3.1	5.6
Glucose	82.2	49.8
Xylose	10.1	23.3
Mannose	1.6	4.2

Free radicals, which are generated in wood by UV light during the weathering process, play an essential role in surface deterioration and discoloration. Kalnins et al. (*51*) investigated the formation of free radicals in wood after exposure to light by the use of ESR. The free radical concentration of wood kept in the dark was very low; it increased when the wood was exposed to daylight, especially UV light. In a vacuum or inert atmosphere, the free radicals were stable, and in the presence of oxygen, they rapidly decomposed.

Wood apparently does not contain any intrinsic free radicals (*26*, *51*, *52*). However, free radicals were generated by irradiation of wood with fluorescent light at ambient temperatures (*52*, *53*). Rate of free-radical formation was enhanced when moisture content increased from 0 to 6.3%. The ESR and UV absorption studies on the behavior of generated free radicals and their interaction with oxygen molecules to form hydroperoxides revealed that free radicals and singlet oxygen play important roles in the discoloration and deterioration of wood surfaces. The chemistry of weathering and protection was summarized in a technical publication (*2*).

The degradation process in wood caused by UV light is initiated by the formation of free radicals and begins presumably with oxidation of phenolic hydroxyl (*23*, *26*, *28*, *32*, *54*). The degradation process results in a decrease in methoxyl and lignin content and an increase in acidity and carboxyl concentration of wood substance (*see also 32*, *33*). These photochemical changes are enhanced more by moisture than by heat (*54*). The products of decomposition of weathered wood, in addition to gases and water, are mainly organic acids, vanillin, syringaldehyde, and high-molecular-weight compounds, which are all leachable (*26*, *32*). Chemical changes following artificial-light irradiation of wood have also been reported (*26*, *29–31*, *33*, *34*, *55–58*).

Some characteristics of the photochemical reactions in wood (*2*, *3*) are as follows:

1. Lignin is easily degraded by light with a wavelength <350 nm. Significant color buildup or formation of chromophoric groups occurs.
2. Lignin is not significantly degraded by light with a wavelength >350 nm, but photobleaching or whitening of lignin occurs when it is exposed to light >400 nm.
3. Methoxyl content of lignin is reduced.
4. Phenoxy radicals are readily produced from phenolic hydroxy groups.
5. Carbon–carbon bonds adjacent to α-carbonyl groups are photodissociated.
6. Compounds bearing benzoyl alcohol groups are not suscep-

tible to photodissociation except when photosensitizers are present.

7. α-Carbonyl groups function as photosensitizers in the photodegradation of lignin (*28*).

Work on the chemical changes of weathered wood has indicated that absorption of UV light by lignin on the wood surface results in preferential lignin degradation. Most solubilized lignin degradation products are washed out by rain. Fibers high in cellulose content and whitish-to-gray in color remain on the wood surface and are resistant to UV light degradation.

Free radicals rapidly interact with oxygen to produce hydroperoxide impurities, which in turn are easily decomposed to produce chromophoric groups, such as conjugated carbonyl and carboxyl groups (*2*, *59*, *60*). A preliminary study of the surface of wood exposed to outdoor weathering and UV irradiation (*59*) showed that electron spectroscopy for chemical analysis (ESCA) provides valuable information and insight into the manifestation of weathering and photooxidation. From the ESCA spectra, the increase in signal intensities of carbon–oxygen bonds and oxygen–carbon–oxygen bonds (or unsaturated carbon–oxygen bonds) and oxygen-to-carbon ratio, and the decrease in carbon–carbon and carbon–hydrogen bonds of weathered and UV-irradiated wood surfaces demonstrated that the wood surface was oxidized. Only slow oxidation was observed at 100 μm under the exposed wood surface. Oxygen-to-carbon ratio data showed that the weathered wood surface was rich in cellulose but poor in lignin. The leached degradation products from the weathered wood surface accounted for the discrepancy between the ESCA shapes of UV-irradiated and weathered wood surfaces.

Surface characteristics of UV-irradiated wood were analyzed by infrared and UV spectroscopy (*60*). Analyses of infrared spectra revealed that the UV-irradiated wood is rich in conjugated carboxylic and carbonyl chromophoric groups and poor in aromatic functional groups. Ultraviolet spectral studies suggested that water-soluble low-molecular-weight fractions of degraded products from the wood surface were mainly derived from lignin. These degradation products contained carbonyl conjugated phenolic hydroxyl groups and had a weight-average molecular weight of about 900, as confirmed by gel permeation chromatography.

The use of singlet oxygen generators, as well as singlet oxygen quenchers, suggests that singlet oxygen participates as an effective intermediate in photooxidation reactions at the wood surface (*61*). The presence of water in wood also influences the rate of free-radical formation. When moisture content in wood is increased from 0 to 6.3%, more free radicals are formed (*53*); beyond this stage, the rate of free-radical decay increases. Infrared studies revealed that carbonyl groups are generated in cellulose and lignin (*62*) during weathering. Water-soluble fractions of degraded wood exhibit characteristics of phenolic absorptions caused by the loss of lignin. The ESCA studies showed that oxidized wood surfaces contain higher oxygen contents than unexposed wood surfaces.

Color Changes. ***Light-Induced Changes.*** Wood exposed outdoors changes color very rapidly. Generally, the color of wood changes to yellow or brown because of the chemical breakdown (photooxidation) of lignin and wood extractives (*1*, *2*, *7*, *24*, *28*, *63*; Figure 5). This discoloration occurs after several months of exposure in sunny, warm climates. Woods rich in extractives may become bleached before browning is visible. In the early stages of weathering, dark woods tend to become light and light woods, dark. Eventually, all woods become gray if fully exposed to sun and rain.

Changes in brightness and color were readily observed in wood exposed outdoors or to artificial UV light for a relatively short period (*2*, *60*). Some wood species, such as redwood, southern yellow pine, and Douglas-fir, lost significant brightness in the first month of exposure. These wood species, however, regained brightness after 6 months of outdoor exposure. After an additional 6 months, the brightness decreased again. Western red cedar gained in brightness for the first 6 months of outdoor exposure, then decreased in brightness after another 6 months of exposure. Besides the change in brightness, all wood species exposed outdoors changed in color from pale yellow to brown to gray after 6 months of exposure. Significant discoloration took place between 3 and 4 months of exposure.

Hon and Feist (*64*) exposed four hardwoods (red oak, white oak, yellow poplar, and sweet gum) to outdoor weathering and artificial UV light. Discoloration and loss of brightness were observed for all species, regardless of their exposure conditions. White oak and sweet gum changed color at a slower rate than red oak and yellow poplar.

Changes in wood color reveal chemical changes in wood during weathering. Only those parts of the wood close to the exposed surface are affected (*see* Penetration of Light and Wood Surface Deterioration). As rain leaches the brown decomposition products of lignin, a silver-gray layer consisting of a disorderly arrangement of loosely matted fibers develops over the brown layer (Figure 6). The silver-gray layer is chiefly composed of the more leach-resistant parts of the partially degraded wood cellulose. This change to gray is observed when the wood is exposed to the sun in climates with little precipitation. However, another mechanism of surface graying of weathered wood—fungal action—usually predominates, particularly in the presence of moisture.

Biologically Induced Changes. All modern studies on the weathering of wood conclude that the final discoloration (graying) of wood in the presence of moisture is practically always due to growth of fungi on the wood surface (*1*, *2*, *54*, *65–69*). The most frequently observed species is *Aureobasidium*

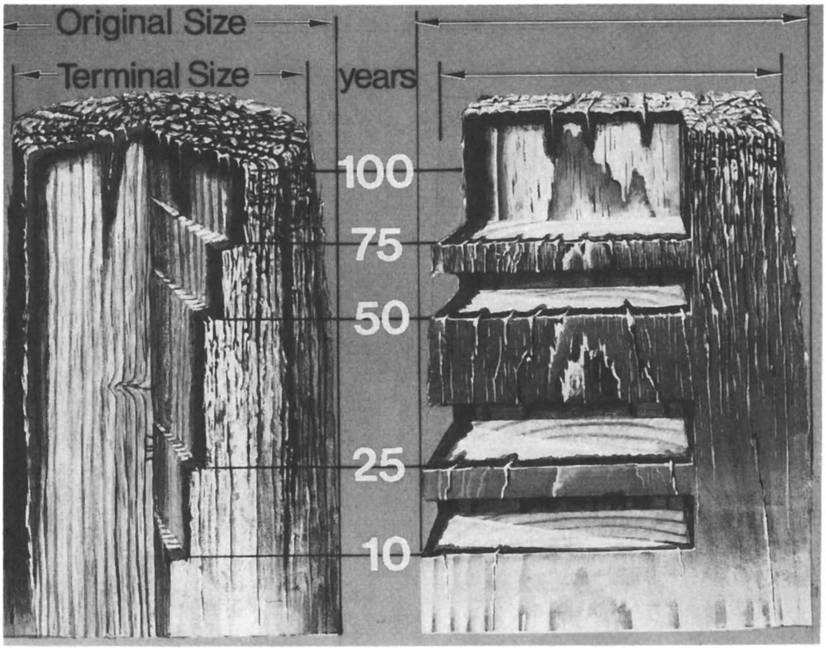

Figure 6. Artist's rendition of the weathering process of round and square timbers. Cutaway shows how wood just below the surface is relatively unchanged.

pullulans (*Pullularia pullulans*), which under favorable conditions grows not only on wood surfaces but also on the surface of coatings and various organic and inorganic materials (*70*). This fungus is commonly referred to as mildew. The ecological requirements of *A. pullulans* and related fungi are modest; the most important condition for its growth is the sporadic supply of water. The fungus is otherwise relatively resistant and adaptable.

Sell (*16*) found that *A. pullulans* grew on finished as well as unfinished or untreated softwood and hardwood surfaces. Fungal infection resulted from wetting the wood surface with water. Sell concluded that discoloration of wood by mildew is more general than commonly believed. Sell and Leukens (*54*) subjected 20 European and non-European softwood and hardwood species to unprotected outdoor weathering in Switzerland; samples faced south and were inclined at 45°. Although the density and mechanical strength properties of each species were very different at the beginning of the study, these differences lessened with photochemical and mechanical deterioration, as well as attack by blue-stain fungi (mildew). After only 1 year of weathering, all wood surfaces had a uniformly weathered and gray appearance.

Physical Changes. Weathering of wood surface caused by the combined action of light and water results in surface darkening and leads to formation of macroscopic-to-microscopic intercellular and intracellular cracks or checks. Cell wall bonds near the wood surface lose their strength. As weathering continues, rainwater washes out degraded portions of the wood and further erosion takes place (Figures 4 and 7). Thus, a cyclical sequence

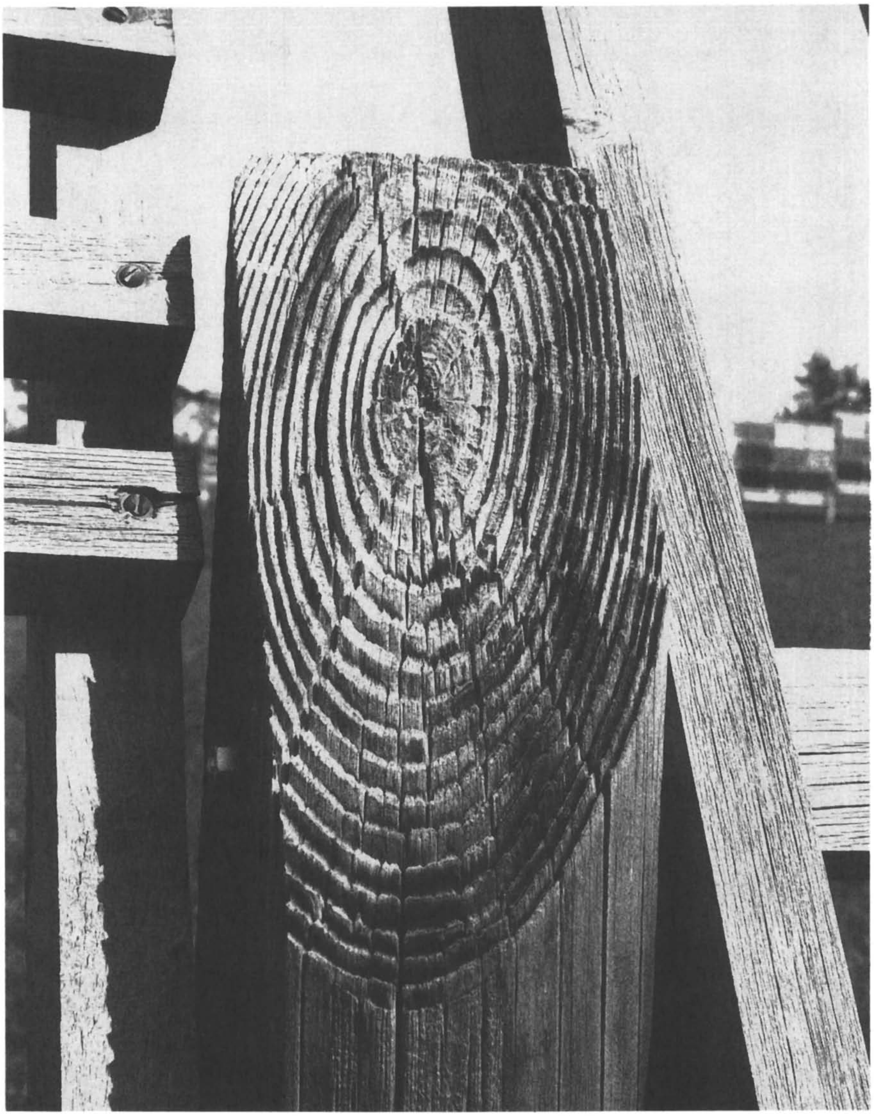

Figure 7. Weathered surface of softwood after 15 years of exposure in Madison, WI.

of events occurs during the natural weathering process (Figure 8). Erosion and checking differ in intensity because of different types of wood tissue on the surface, and the wood surface becomes increasingly uneven (Figure 6).

Loss of surface wood fibers caused by weathering varies according to climate and species. Browne (*71*) reported that the weathering process is so slow that "only 0.25 inch (6.4 mm) of thickness is lost in a century." This would represent thickness loss for a "typical" softwood like southern pine

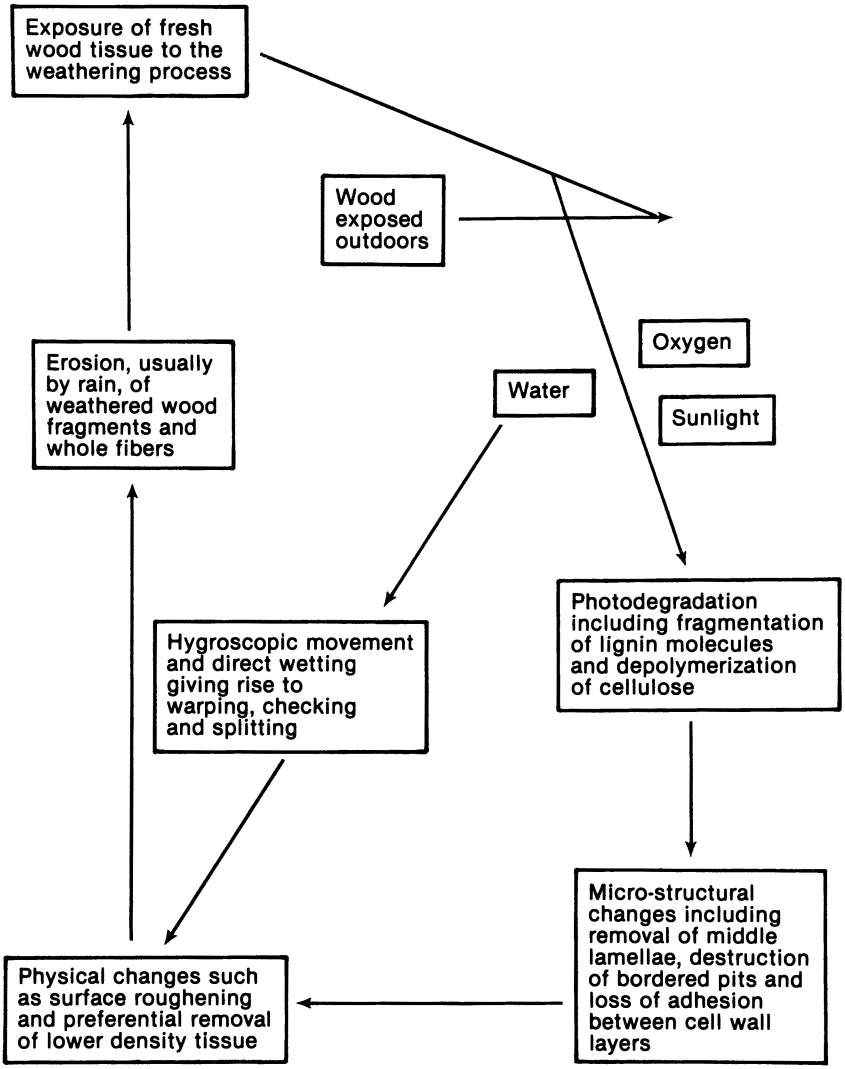

Figure 8. Cyclical sequence of events during natural weathering (Reproduced with permission from ref. 88. Copyright 1986).

or Douglas-fir. Loss of surface fibers of only 1 mm per century has been reported for wood exposed in northern climates (*68*). In contrast, Feist and Mraz (*72*) reported an erosion value of 13 mm per century for western redcedar. This value was based on exposure data for 8 years of outdoor weathering at 90° facing south. Erosion data obtained from controlled accelerated weathering of redwood, Douglas-fir, Engelmann spruce, and ponderosa pine, which were used to estimate outdoor weathering, showed that these species would erode at a rate of approximately 6 mm per 100 years, a rate similar to Browne's (*71*). In Norway, the 10-mm-thick cladding (siding) on stave churches was estimated to have been reduced by half over a few hundred years of weathering (*73*). Jemison (*74*) found that ponderosa pine dowels of 5-mm diameter lost 7.8% of their weight after 10 years of exposure in full sunlight, while dowels of 13-mm diameter lost 16.4%. In another study, heartwood samples of western redcedar, redwood, iroko, and teak, weathered for 3 years, lost up to 10% of their weight (*75*). Boettcher (*76*) found that the surface profile had an insignificant effect on the erosion of wood.

In some recent work at Forest Products Laboratory, the erosion rate of wood exposed outdoors was estimated from data obtained by controlled accelerated weathering of several woods, by using techniques described elsewhere (*72*). Specimens were exposed to a high-density xenon arc light in an accelerated weathering chamber. Exposure consisted of cycles of 24 h of light, including 4 h of distilled water spray. Erosion was measured microscopically. The results showed that the hard, dense hardwoods erode at a rate similar to that observed for the latewood of softwood species (estimated at 3 mm per century, compared to 6 mm for earlywood of softwoods). Generally, the higher the density, the slower the erosion rate. Lower-density woods such as basswood erode at a faster rate than woods such as oaks, but at a slower rate than the earlywood of softwoods. The results of these studies and several others are summarized in Table IV.

In related work on the relationship of wood density to weathering rate, Sell and Feist (*77*) investigated the artificial weathering of 12 hardwoods and 6 softwoods. The surface erosion rate was measured with a light microscope at exposure intervals of 600 h. The results showed that the erosion rate per unit time depended predominantly on the wood density and thus on the wood cell wall thickness. The relationship was approximately linear within a wood density range of 0.3–1.0 g/cm^3.

Thus, the physical changes that occur in weathering can have a pronounced effect on the appearance of wood. From a historic viewpoint, unfinished (unprotected) wood could survive many centuries. However, the wood surface slowly wears away (erodes), and this can necessitate eventual replacement. The more severe the exposure, the faster the weathering process. The weathering process can be greatly reduced or stopped by using suitable treatments and finishes (*see* Protection Against Weathering). Many

Table IV. Oven-Dried Density and Erosion Rates for Different Wood Species

Wood Species	*Wood Density,[a] g/cm³*	*Erosion Rate,[b] µm/h*
	Softwoods[c]	
Douglas-fir		
Heartwood	0.53	
Earlywood	0.30	0.163
Latewood	0.95	0.040
Sapwood	0.39	
Earlywood	–	0.192
Latewood	–	0.056
Redwood		
Heartwood	0.35	
Earlywood	0.30	0.217
Latewood	0.95	0.040
Sapwood	0.32	
Earlywood	–	0.271
Latewood	–	0.063
Southern Pine		
Sapwood	0.65	
Earlywood	0.30	0.204
Latewood	0.95	0.046
Spruce, European		
Heartwood	0.41	
Earlywood	0.30	0.181
Latewood	0.95	0.042
Western redcedar		
Heartwood	0.33	
Earlywood	(0.25)	0.263
Latewood	(0.95)	0.063
Sapwood	0.27	
Earlywood	–	0.273
Latewood	–	0.139
	Hardwoods[c]	
Alder, red	0.44	0.135
Ash, white	0.76	0.083
Basswood	0.41	0.160
Beech, European	0.74	0.067
Birch, yellow	0.65	0.125
Elm, American	0.53	0.090
Cherry, black	0.60	0.083
Hickory	0.81	0.060
Maple, hard	0.59	0.102
Maple, soft	0.45	0.104
Oak, red	0.67	0.083
Oak, white	0.78	0.075
Yellow-poplar	0.52	0.129

[a] Earlywood and latewood densities for softwood are from the literature. Values for western redcedar are estimates.

[b] Erosion rate after 2400 h of accelerated weathering.

[c] Because of fairly small differences in the erosion of earlywood and latewood of the hardwoods, only one average value was measured.

treatments and finishes currently available for wood are acceptable from a historic viewpoint and will not change the general appearance of the wood.

Microscopic Changes. Microscopic changes accompany the gross physical change of wood during weathering. In a series of papers, Miniutti (*78–82*) reported changes in softwood surfaces after outdoor exposure. The first sign of deterioration was enlargement of apertures of bordered pits in radial walls of earlywood tracheids. Next, microchecks occurred. Miniutti showed that these microchecks enlarge principally as a result of contraction in cell walls. During weathering, the leaching and plasticizing effects of water apparently facilitate enlargement of the microchecks. Changes were more rapid for redwood than for Douglas-fir.

Borgin (*73, 83, 84*) and Borgin et al. (*85*) used the scanning electron microscope (SEM) to study the breakdown of wood structure caused by weathering. Old wood surfaces, both protected and exposed, were investigated. These studies revealed the slow deterioration and ultimate destruction of the middle lamella, the various layers of the cell wall, and the cohesive strength of wood tissue. Single individual fibers were found to be remarkably stable and durable. The most stable part of the whole fiber seemed to be the microfibril. Various layers of the cell wall failed because of loss of cohesive structure between microfibrils and loss of adhesion between layers. All apertures or voids were enlarged, weakening the whole fiber structure. The destructive weathering process was limited to a thin surface layer of 2–3 mm. In very old, protected wood, there was only a slight breakdown of certain elements at the ultrastructural level, and samples retained their normal macroscopic appearance and properties (*85*). Thus, as long as the main reinforcing structural elements, the microfibrils, remain intact, the major properties of wood do not undergo drastic changes.

Several publications (*58, 79, 81*) describe microscopic changes caused by artificial weathering (UV irradiation) of wood surfaces that resemble the changes caused by natural weathering. Coupe and Watson (*14*) observed longitudinal checks between adjacent walls of neighboring elements, which apparently occurred in or close to the middle lamella; longitudinal checks in element walls; and diagonal checks through pits, which probably followed the fibril angle of the S_2 layer. The SEM studies by Chang et al. (*62*) showed that most cell walls on exposed transverse surfaces are separated at the middle lamella region, apparently because of the degradation of lignin. However, tangential surfaces were quite resistant to UV light, compared to transverse and radial surfaces. Only microchecks were observed at the tangential cell walls.

Bamber (*86*) and Bamber and Summerville (*87*) studied the pattern of breakdown of surface wood cells and cells adjacent to the surface in radiata pine sapwood exposed outdoors for 4.5 years. The pattern was characterized by a progressive decrease in deterioration of wood cells away from the exposed surface. Deterioration was found only 10–12 cells away from the surface. The nature of the deterioration was twofold: initial loss of histochemical staining properties of lignin, followed by progressive thinning of the cell walls. The thinning of the tracheid walls occurred centrifugally; the inner secondary wall appeared to be lost first.

Using SEM, Groves and Banana (*88*) investigated the effect of natural weathering on the microstructure of radiata pine. The study suggested that under the weather conditions prevailing in Canberra, Australia, deterioration of the exposed surfaces was readily apparent after only 4 months. Complete surface degradation and erosion of some tissue were observed after only 6 months. One of the more conspicuous effects of exposure was destruction of the bordered pits. The observed changes included the following:

1. Degradation of the pit membranes.
2. Gradual enlargement of the pit aperture to the approximate limit of the pit chamber.
3. Development of microchecks in the pit borders.
4. Initial destruction of pit borders on the weather side, leaving a half-bordered structure.

The bordered pits in earlywood tracheids were completely destroyed in about 6 months. After 6 months of exposure, virtually all ray tissue had disappeared from the surfaces of weathered wood and only cavities remained.

Kucera and Sell (*89*) studied the erosion of the large rays in European beech in tangential surfaces exposed to natural weathering. The authors observed a differential shrinkage of the ray compared to normal wood tissue, partially combined with the photochemical degradation of the wood substance. Kucera and Sell concluded that surface finishes for woods like beech would be particularly stressed around the ray area. Thus, finishes for hardwoods (with low dimensional stability and large rays) must protect the wood surface against photochemical degradation and intense moisture changes by means of adequate pigmentation and sufficient coating thickness. Consequently, finishing considerations for hardwoods are more important than those considered necessary for most softwoods.

Hon and Feist (*64*) investigated the erosion of several hardwood surfaces. The SEM studies showed that all wood species exhibited surface deterioration after only 30 days exposure to sunlight or 500 h to UV light. Loss of the middle lamella, separation of procumbent cells, and damage of pit structures were observed on transverse sections for all species. The ESCA studies revealed high oxygen content at the wood surfaces, indicating severe oxidation of wood exposed either outdoors or to artificial UV light. The generation of new chromophoric groups, such as conjugated carbonyls, carboxylic acids, and quinones, and the loss of lignin at the oxidized surfaces were demonstrated by infrared spectroscopy.

Many aspects of wood weathering are not completely understood. A complete understanding of the mechanisms involved in outdoor weathering would aid in developing new pretreatments and finishes to enhance wood durability. The ever-changing commercial wood supply and the introduction of previously unused species at increasing frequency pose particular challenges to the use of modern wood finishes. A detailed study of the various interactions that affect the performance of wood materials is needed to protect wood products when they are used outdoors.

Protection Against Weathering

Paint and other coatings (finishes) for wood used indoors can protect the wood for many decades and can obviate refinishing (*4*, *90*, *91*). Indoor finishes are relatively unaffected by wood properties. Outdoors, some wood finishes may last only 1–2 years because of degradation from UV light and water. The durability of outdoor finishes primarily depends on the wood itself. Wood properties that are important in finishing are moisture content, density and texture, resin and oil content, width and orientation of growth rings, and defects such as knots, reaction wood, and diseased wood (*92*). Other contributing factors are the nature and quality of the finish used, application techniques, pretreatments, time between refinishings, extent to which the surfaces are sheltered from the weather, and climatic and local weather conditions (*93–99*). The stressing factors, which influence factors and weathering effects that contribute to wood-finish performance, are summarized in Figure 9.

The primary function of any outdoor wood finish is to protect the wood surface from weathering elements (sunlight and water) and help maintain appearance (*2*, *4*). Where appearance does not matter, wood can be left unfinished to weather naturally, and such wood will often protect the structure for an extended time (Figures 1 and 2) (*1*, *2*, *4*, *70*). Different finishes give varying degrees of protection from the weather (*4*, *93*, *94*). Generally, the greater the pigment concentration (that is, the greater the opacity), the greater the protection; paints give the most protection, transparent varnishes the least.

Any protection that surface treatments provide against light and water will be affected by the weather resistance of the bonding agents of the finish (such as drying oils, synthetic resins, and latexes) (*99*). These bonding agents are subject to photodegradation to some degree. The mechanism of failure of paints and other finishes has been described (*90*, *91*, *100*), and it will not be discussed further here. Wood exposed outdoors is protected from the effects of weather by various finishes, construction practices, and design factors, which have all been addressed in detail (*4*, *16*, *93*, *94*, *101–104*).

Two basic types of finishes (or treatments) are used to protect wood surfaces during outdoor weathering: (1) those that form a film, layer, or

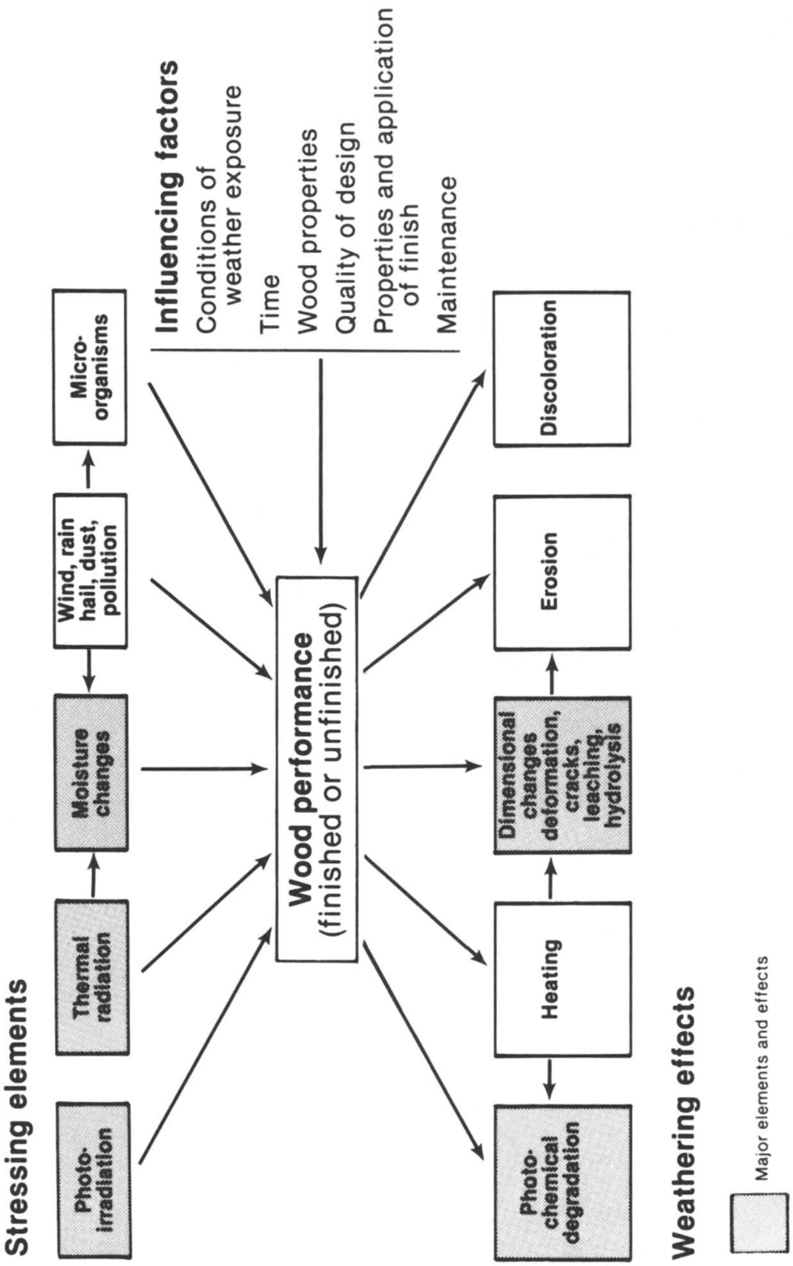

Figure 9. Stressing factors, influencing factors, and weathering effects that contribute to wood-finish performance.

coating on the wood surface (film-forming), and (2) those that penetrate the wood surface and leave no distinct layer or coating (non-film-forming).

Film-Forming Finishes. Film-forming finishes include paints of all description, varnishes, and solid-color stains, as well as overlays bonded to the wood surface.

Paints. Film-forming finishes such as paint have long been used to protect wood surfaces. Of all the finishes, paints offer the greatest degree of protection against erosion by weathering and the widest selection of colors. A nonporous paint film retards penetration of moisture and thereby reduces paint discoloration by wood extractives, paint peeling and checking, and warping of the wood (*4*, *98*, *99*). Proper pigments will essentially eliminate photodegradation of the wood surface. However, paint is *not* a preservative; it will not prevent decay if conditions are favorable for fungal growth. The durability of paint coatings on exterior wood is affected by variables in the wood surface, moisture, and type of paint.

Paints are commonly divided into oil-based or solventborne systems and latex or waterborne systems (*90*, *105*). Oil-based (or alkyd) paints are essentially a suspension of inorganic pigments in an oleoresinous vehicle that binds the pigment particles and the bonding agent to the wood surface. Latex paints are suspensions of inorganic pigments and various latex resins in water. Acrylic latex resins are particularly durable, versatile materials for finishing wood and wood-related materials.

Varnishes. The most natural appearance for wood is obtained by using clear varnishes, lacquers, or shellac. Other treatments either change wood color or completely cover the wood. Unfortunately, clear varnish finishes used on wood exposed to sun and rain require frequent maintenance to retain a satisfactory appearance. Durability of varnish on exposed wood is limited, and many coats are necessary for reasonable performance. Moreover, the varnish surface must be refinished as soon as signs of breakdown occur. In severe exposures, this may be as soon as 1 year after application. Lacquers and shellacs are usually not suitable as exterior clear finishes for wood because they are sensitive to water and crack or check easily.

The addition of colorless UV light absorbers to clear finishes sometimes helps to retain the natural color and original surface structure of wood (*1*, *2*, *25*, *106–110*). Opaque pigments in paints and stains generally provide the most effective and long-lasting protection against light (*55*, *111–113*). Even when relatively durable, clear, synthetic resin varnishes are used, the weatherproof qualities of the wood–varnish system are still limited because UV light penetrates the transparent varnish film and gradually degrades the wood underneath (*29*, *114*, *115*). Eventually, the varnish begins to flake and crack off, taking with it fibers of the wood that have been degraded photochemically (*68*, *79*, *116*).

Ashton (*117*, *118*) reported on studies for predicting the durability of clear finishes for wood from the basic properties of the finishes. He reviewed the relationships between composition, water absorption, water vapor permeability, tensile strength, and elongation. Single and multiple regressions were used to establish the relative importance of the different properties in determining the durability of the finishes on wood exposed outdoors. The durability of clear phenolics and alkyds could be predicted from water absorption and permeability properties. Tensile strength and mechanical properties were of less importance.

Solid-Color Stains. Solid-color stains are opaque finishes (also called hiding, heavy-bodied, and opaque stains) that come in a wide range of colors and are made with a much higher concentration of pigment than the semitransparent penetrating stains. As a result, solid-color stains totally obscure the natural wood color and grain. Oil-based or alkyd solid-color stains form a film much like paint, and consequently they can peel from the substrate. Latex-based solid-color stains are also available and likewise form a film. Both oil-based and latex-based solid-color stains are similar to thinned paints and can usually be applied over old paint or semitransparent stains.

Penetrating Finishes. Penetrating finishes, which do not form a film over the wood, include oils, water repellents, stains, preservatives, and surface treatments.

Oils. A number of oils (linseed, tung, oiticica) and modified oils have traditionally been used as penetrating wood finishes. These oils do not leave a film, and they do not last longer than 1–1.5 years because of their low resistance to UV light and water. Therefore, penetrating oils find limited use as outdoor finishes, but they are widely used as interior furniture finishes.

Water Repellents. A large proportion of the damage of exterior woodwork (such as paint defects, deformations, decay, and leakage) is a direct result of moisture changes in the wood and subsequent dimensional instability (*4*, *16*, *99*, *119–125*). Water generally enters wood through open cracks, unprotected end-grain surfaces, and defects in treated surfaces. Although such problems can be avoided or at least reduced by proper design and correct choice of materials, it is extremely difficult to eliminate checks or cracks when woodwork is subjected to harsh long-term exposure. Even a high-quality coating often loses its protective ability because the coating cannot tolerate the stresses and strains of wood shrinkage and swelling, especially around joints. Eventually, the coating gives way.

Because of these problems, researchers have often suggested that woodwork exposed outdoors be protected with a coating that is both water repellent and resistant to decay fungi. Such treatment could be used as the finish itself or prior to the final finish. Materials developed for such purposes are termed water-repellent preservatives (WRP). They generally comprise a resin (10–20%), solvent, wax (as the water repellent), and preservative (fungicide or mildewcide) (*4*, *16*, *99*, *120–122*, *126*).

A great store of information has been accumulated on the effectiveness of WRPs in protecting exterior wood (*1*, *2*, *4*, *112*, *119–123*, *127–131*). The treatments can be applied by immersion (which is preferred), by brush, or by spray application. They improve the performance of many finishes and greatly add to the durability of exposed wood. Even chipboard or particleboard, which is very susceptible to moisture, can be protected against the effects of outdoor exposure by using a WRP pretreatment followed by a diffusion-resistant coating (*128*, *132–135*).

The WRP treatments give wood the ability to repel water, thus denying stain and decay fungi the moisture they need to live. Wood surfaces that remain free of mildew fungi retain an attractive "natural" appearance. The WRP reduces water damage to the wood and helps protect applied paint from the blistering, peeling, and cracking that often occur when excessive water penetrates wood.

The preservative in a WRP helps control decay and acts as a mildewcide—it kills any surface mildew living on the wood. Some research studies indicate that in many situations where there is a medium-to-low risk of decay, the preservative may not be needed for successful performance of the water repellent (*124*, *126*). These studies support the general concept that protecting exposed wood from water is of prime importance in improving the durability of the wood (*119*).

Stains. When pigments are added to water-repellent or WRP solutions or to similar penetrating transparent wood finishes, the mixture is classified as a pigmented, semitransparent, penetrating stain (*1*, *2*, *4*, *112*, *136*). The pigment provides color and greatly increases the durability of the finish because UV light is partially blocked. These semitransparent stains permit much wood grain to show through; they penetrate the wood to some extent without forming a discrete, continuous layer. Therefore, they will not blister or peel, even if excessive moisture enters the wood. The durability of any stain system is a function of pigment content, resin content, preservative, water repellent, and quantity of material applied to the wood surface. The performance of stains during outdoor exposure has received a great deal of attention (*137–143*).

Penetrating stains are suitable for both smooth and rough surfaces. However, their performance is markedly improved if applied to roughsawn, weathered, or rough-textured wood (*4*, *96*, *99*, *112*, *136*, *137*, *141–144*) because more material can be applied to such surfaces. They are especially effective on lumber and plywood that does not hold paint well, such as flat-grained and weathered surfaces, or dense species. Penetrating stains can be used effectively to finish such exterior surfaces as siding, trim, exposed decking, and fences. Stains can be prepared from both solventborne resin systems and latex systems; however, waterborne (latex) systems do not penetrate the wood surface. Commercial finishes known as heavy-bodied, solid-color, or opaque stains are also available, but these products are essentially similar to paint because of their film-forming characteristics. Such "stains" do find wide success when applied on textured surfaces and panel products such as hardboard. They can be oil based or latex based.

Preservatives. Although not generally classified as wood finishes, preservatives do protect wood against weathering and decay, and much preservative-treated wood is exposed without any additional finish (*4*). The following are the three main types of preservative (an example of each is given in parentheses) (*4*): preservative oils (coal-tar creosote), organic solvent solutions (pentachlorophenol), and waterborne salts (chromated copper arsenate).

Although these preservatives can be applied to wood in several ways, pressure treatment provides the greatest protection against decay. In general, the greater the preservative content of pressure-treated wood, the greater resistance to weathering and the greater surface durability. The chromium-containing preservatives also protect against UV light degradation (*1*, *2*, *144*, *145*).

Surface Treatments. Recent trends in the use of wood for exterior siding have emphasized natural-type finishes that enhance the texture, grain, and inherent beauty of the wood. While several approaches have been used for developing an acceptable natural finish, inorganic surface treatments have been extensively studied (*145*) to improve the service life of clear exterior finishes. The studies on natural wood finishes have also involved measuring the erosion of treated and untreated wood surfaces caused by leaching and by UV irradiation in accelerated weathering. A procedure was developed for quantitatively measuring the effect of erosion, as well as the effects of wood species and composition of treating solutions on resistance of the finish to leaching and UV irradiation (*145*). A promising method for improving the fungal resistance, color, and permanence of acid–copper chromate treatments with resorcinol was also reported.

More recent work at the Forest Products Laboratory (*138*, *140*, *144*, *146*, *147*) showed that certain inorganic chemicals (especially hexavalent chromium compounds), when applied as dilute aqueous solutions to wood surfaces, provide the following benefits:

1. Retard degradation of wood surfaces by UV irradiation.
2. Improve durability of UV-light-transparent polymer coatings.
3. Improve durability of paints and stains.

4. Provide a degree of dimensional stability to wood surfaces.
5. Provide fungal resistance to wood surfaces and to coatings on the surface.
6. Serve as natural finishes for wood and obviate further treatment.
7. Fix water-soluble extractives in woods such as redwood and redcedar, and thereby minimize subsequent staining of applied latex paints.

The most successful treatments investigated were those containing chromium trioxide (chromic acid, chromic anhydride), copper chromate (mixtures of soluble copper salts and soluble chromates), or ammoniacal solutions of these chemicals. The most spectacular result—an exterior natural finish with a service life of approximately 15 years—was achieved by treating the wood surface with an inorganic UV-light absorber and coating it with a clear polymer transparent to UV light. Effective inorganic treatments were ammonium chromate, ammonium copper chromate, ammonium copper–chrome–arsenate, cupriethylene diamine, copper molybdate, and copper ferricyanide. In addition, chromate treatment improved performance of oil and latex stains, linseed oil-based paint, clear latex coatings, and oil-based varnishes. Chromium treatments were found effective on both softwoods and hardwoods (*103*). Additional studies showed the value of using simple chromium compounds like chromium trioxide (*144*) and trivalent chromium compounds (*148*) as treatments and natural finishes.

Desai and Clarke (*149*) reported successful results using zinc-containing compounds. Sell et al. (*150*, *151*) described surface treatment with chromium–copper–boron salts. Field weathering tests, leaching tests, and electron-probe microanalysis showed that this treatment was resistant to leaching and weathering. Water-soluble extractives in redwood and redcedar were fixed by treating the wood surface with dilute solutions of copper and chromium salts. This treatment permits direct application of latex paints to these woods (*146*).

A serious disadvantage of the chromium treatments is the toxicity of the chemicals. However, the Cr^{6+} valence state is apparently the hazardous form of chromium-containing compounds; reduction of Cr^{6+} to the lower, less hazardous trivalent state (Cr^{3+}) might make these compounds attractive as treatments for wood surfaces. Investigations (*144*, *147*) were conducted on the fixation and interaction on wood surfaces of compounds containing hexavalent chromium. Almost total fixation of Cr^{6+} was achieved by heating wood surfaces, treated with chromium trioxide (CrO_3) solutions, for 10 min at 135 °C. Only traces of chromium of any valence state were detected in water extracts. These studies also showed that the degree of protection provided to the wood surface by CrO_3 solutions (chromic acid) is directly related to Cr^{6+} concentration. Solution pH was important; a 4.8% CrO_3 solution was most effective at its original pH of 0.5. Surface treatment with CrO_3 reduced dimensional changes in wood exposed to water.

Liquid water uptake of CrO_3-treated wood was decreased to that observed after treatment of wood with a water repellent. This decrease in liquid water uptake was found for treated flat-grained and vertical-grained surfaces, but not for end-grain wood, a result indicating that capillary uptake could still occur. Water repellency was observed in both water-immersion and water-spray experiments. Preliminary studies on CrO_3-treated wood surfaces using ESCA showed that Cr^{6+} was reduced to Cr^{3+} at concentrations of 1.25% chromium. The reduction undoubtedly plays a role in the fixation of Cr^{6+} on the wood surface.

Chang et al. (*62*) showed that when wood was treated with 0.1% CrO_3 solution, protective effects could be recognized on transverse surfaces even after 500 h of UV irradiation. Although some longitudinal microditches in the middle lamella zone were observed, cell walls were less deteriorated and microditches were narrower than those of untreated wood. The degree of protection was directly proportional to the concentration of CrO_3 used in the treatment. When woods were treated with 5 and 10% CrO_3 solution, most cell walls were protected. The cell walls appeared to be very resistant to photodeterioration; only small voids created at the cell corners were observed after 1000 h of exposure. The middle lamella region was mostly preserved.

The SEM studies by Chang et al. (*62*) revealed that both CrO_3 and ferric chloride treatments are capable of protecting wood surfaces against UV light degradation. The exact mechanism of the protection is not clearly understood. The authors speculated that the incorporation of inorganic cations at the wood surface results in the formation of a wood–cation complex that could interfere with the photochemical reaction by either emitting effective light energy or shifting the absorbing zone to a short wavelength zone to minimize light absorption. It is possible that inorganic salts would decompose peroxide intermediates, and thus prevent oxidative chain reactions at wood surfaces.

In related work, Williams and Feist (*148*) showed that a trivalent chromium compound was capable of adhering to wood to produce nearly the same weathering protection and water repellency as hexavalent chromium compounds. The critical factor was the ability of the chromium to fix or become unleachable, not the oxidative action of the hexavalent chromium ion on the wood. A further study by Williams and Feist (*152*) proved that CrO_3 fixes to both wood and pure cellulose. With both materials, complete fixation of chromium resulted in a highly water-repellent surface. The similarity between treated wood and treated cellulose indicated that chromium–cellulose interactions should be included in defining the mechanism for wood surfaces stabilized with Cr^{6+} and that previously proposed chromium–wood mechanisms based solely on extractives, lignin, or hemicellulose were too limited. The authors used ESCA to evaluate wood and cellulose surfaces that had been modified by aqueous CrO_3 treatment. The data showed that Cr^{6+} was reduced to Cr^{3+} on all substrates by at least 80%. Leaching experiments confirmed this reduction to a highly water-insoluble or "fixed" chromium complex on both wood and filter paper (cellulose). Similar oxidation products were observed with wood and filter paper. These experiments indicate that chromium–cellulose and chromium–lignin interactions are involved in the mechanism of Cr^{6+} stabilization of wood surfaces described earlier.

The coating durability of organo–lead-treated southern pine in exterior exposure was reported by Barnes (*153*). The durability of a vinyl–acrylic latex and an alkyd paint on treated wood significantly improved. This result appeared to be independent of the type or concentration of the organo–lead-treating compounds.

Pizzi and coworkers (*154–156*) described in detail the role of chromium in the treatment of wood, including wood waterproofing, lignin cross-linking, kinetics of reaction, and kinetic behavior.

Hon et al. (*158*) showed that wood surfaces could be protected against photoinduced oxidative degradation by using effective coating agents. Several penetrating chemical agents, such as triol-G 400, polyethylene glycol (PEG-400), and 1-octadecanol, provided good protection for wood surfaces against discoloration during UV irradiation. In addition, wood surfaces coated with clear film-forming finishes, such as homo- and copolymers of 2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone, were extremely successful in inhibiting discoloration and surface deterioration. The infrared and UV light absorption spectra and SEM studies revealed that the clear polymeric coatings containing an internal UV-light absorber were very stable and resistant to photooxidation.

Overview of Weathering and Implications for Preserving Historic Structures

Wood exposed outdoors without protection undergoes photodegradation by UV light; leaching, hydrolysis, and swelling by water; and discoloration by staining microorganisms. Unfinished wood surfaces exposed to weather change color quickly, are roughened by photodegradation and surface checking, and erode. Although weathering causes physical as well as chemical changes, these changes affect only the surface of the exposed wood. Ultraviolet light cannot penetrate wood surfaces deeper than 75 μm, and visible light no deeper than 200 μm. This means weathering is a true surface phenomenon. Scanning electron microscopy studies show that most cell walls on exposed transverse surfaces are separated at the middle lamella region.

Half-bordered and bordered pits on exposed radial surfaces are severely degraded by UV light.

Free radicals are generated at the wood surface during irradiation. The rate of free-radical formation is enhanced when moisture content increases from 0 to 6.3%. Electron spin resonance and UV light absorption studies on the behavior of generated free radicals and their interactions with oxygen molecules to form hydroperoxides have revealed that free radicals and singlet oxygen play important roles in discoloration and deterioration reactions of wood surfaces.

Fortunately, wood exposed to the weather can be protected by paints, stains, and similar materials. Paints provide the most protection because they are generally opaque to the degradative effects of UV light and protect wood to varying degrees against water. Paint performance may vary greatly on different woods. Pigmented stains also provide durable finishes. Treatments applied to the wood before finishing, such as water-repellent preservatives and certain inorganic chemicals (chromium compounds), can significantly improve the performance of the finishes.

Many aspects of wood weathering are not completely understood. A complete understanding of the mechanisms involved in outdoor weathering would allow the development of new treatments and finishes that would greatly enhance wood durability and provide greater protection against degradation. New techniques and tools for the study of wood surfaces, such as Fourier transform infrared spectroscopy, electron spectroscopy for chemical analysis, and electron spin resonance spectroscopy, can provide a great deal of insight into the weathering process for both finished and unfinished wood. These techniques allow in-depth study of treatment and wood surface interactions and the importance of these interactions in the ultimate performance of the wood. Understanding the role of new techniques in controlling the outdoor weathering process is significant to the future use and protection of both new and historic wood exposed outdoors.

From a historic perspective, it is very important to recognize the effects of weathering. Weathering may be so severe that the wood may need to be replaced. Different finishes and treatments protect outdoor wood surfaces to varying degrees. Generally, the more the pigment, the greater the degree of protection; transparent finishes give the least protection and opaque paints the most; the effectiveness of semitransparent finishes falls in between these. Probably the most difficult aspect of wood protection is to retain the original color of the wood. This aspect may be desirable from the perspective of historic authenticity. However, constant care will be needed to protect the wood surface from the weathering elements and prevent unwanted color change. Lastly, historic authenticity requires the use of traditional finishes, even though they may not provide the most protection for the wood. The shortcomings of some traditional finishes must be taken into account when the finishes are specified for use on historic wood structures.

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12

Simple and Integrated Consolidation Systems for Degraded Wood

James A. Wermuth

Conservation Technology Group, 32 Green Street, Newport, RI 02840

This chapter presents a current assessment of consolidation treatments for degraded archaeological wood. It suggests ways of refining the use of consolidation materials and technology through the discipline of conservation. Because consolidation tends to controvert conservation ethics, however, this work necessarily discusses the character of the consolidation process relative to the field of conservation. Emphasis is placed on conservation principles and types of material diminution as they relate to consolidation, as well as on practical application advice. Because of the diversity of the consolidation process, there are no formulas or patent solutions. Evaluation and application guidelines for developing appropriate consolidation technologies are offered instead, along with two case studies to illustrate the application of theory.

CONSERVATION IS AN ATTEMPT TO STAY the natural progression of aging and to achieve enduring stability through temporal and reversible processes. Conservation is a highly developed and rational integration of art, science, and mental discipline directed toward the stabilization of cultural and natural history artifacts for anthropological interpretation by future generations. Conservation, as a professional discipline, engenders many creative and ingenious solutions to the problems of preservation.

Wooden artifacts pose many unique problems by their substance alone. Wood is a common provider in the ecosystem, and artifacts constructed from wood are isolated from the food chain only by contrivance. The conservator must understand the wide range of deleterious conditions and predators that affect wood.

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Complex degradation processes generally occur to some degree, even in controlled environments. In the case of wood, such processes terminate in reversion to topsoil in the natural environment. The conservation of archaeological wood might best be defined as any effort directed toward the retention of desirable intrinsic characteristics. In other words, conservation attempts to slow down or reverse the process that turns a fauteuil into fertilizer. Consolidation is one of a number of treatments available to conservation. Before approaching the technical aspects of consolidation, it is useful to have an overview of the process and to relate its role to the field of conservation.

Consolidation as a Component of Conservation

Consolidation can be considered as a form of restoration; treatments or procedures are used to correct or restore deficient mechanical or physical properties. Conservation-oriented restoration limits the degree of restoration to a point where the effects of deleterious degradation are corrected. Popular restoration is not similarly restricted.

The science of conservation depends on objective knowledge of an artifact's condition. The degree and status of retained properties are essential criteria for determining the necessity, type, and degree of treatment. Specifically, the conservator needs to determine the ability of an artifact to withstand the stress of an anticipated function or environment. Establishing the condition of wood is difficult, however, as wood does not lend itself to evaluation.

Wood, a multifarious and complex material, is difficult to evaluate when sound. A glance at the Mechanical Properties Chart of the U.S. Forest Products Laboratory (U.S. FPL) *Wood Handbook* (*1*) illustrates the variety in even a single species. As various components of the macro- and microstructure become assimilated, altered, or disintegrated, wood becomes an even more diverse material. Because evaluation processes are generally destructive by design, there are few, if any, usable test options. As a result, appearance is often the criteria for soundness. The need for treatment is generally recognized when an artifact is visibly disintegrating and residual strength is dangerously low. Consequently, most treatments are referenced to a level of gross failure, although less ambitious, more refined intervention would provide a better solution.

Consolidation tends to be a gross treatment. It is often considered as the treatment of choice for visibly degraded wooden artifacts, particularly for artifacts that have been subject to attack by microorganisms or insects. It is an attractive solution, in that treated artifacts are made perceptibly stronger, but the treatment is compromised by ethical and technical problems.

Whereas popular restoration may not be particularly concerned with the degree of replacement or adulteration of original materials, the conservator is ethically bound to control intervention. The success of a conservation treatment could rightly be measured as an inverse relationship between the degree of restoration and the quantity of replaced or added materials: As more materials are introduced into the artifact, it becomes less authentic.

Because consolidation functions through the addition of relatively large quantities of materials, it is always performed, to some degree, at the expense of the artifact. Consolidation is a very effective treatment, however; in some cases, it may be the only treatment.

Consolidation. A certain degree of understanding can be gained by observing how the term "consolidation" is used in conservation. Perhaps because conservation is in the process of evolving into a highly technological profession, no firm definition of consolidation has evolved. Instead, it refers to a generic group of treatments, including surface consolidation, mechanical consolidation, impregnation, and chemical stabilization. An important distinction can be made, however, between its common use and its use in conservation with respect to process and purpose.

In common use, consolidation is defined as a process of solidification or joining into a single unit. Emphasis tends to be placed on process more than purpose. Business concerns are consolidated for strength, estates are consolidated for simplicity of handling, and funds are consolidated to a single holding for strength of bargaining.

In conservation, consolidation refers to processes that increase an artifact's stability through any one of a number of processes that integrate dissociated tissue and restore mechanical properties. Encapsulation, infilling, cell wall loading, bracing, bulking, impregnation, and occlusion of porosity are all processes associated with consolidation. Its singular purpose, however, is the achievement of stability.

Stabilization. Stabilization, a fundamental concept to determine conditions under which consolidation is considered for treatment, can be defined as the reduction or elimination of potential for adverse change. As fiduciaries, conservators are particularly concerned with diminution of cultural information intrinsic to the artifact, loss of any information-bearing material.

Stability is a relative material qualification. It can be achieved by either deductive treatment (reducing interactive forms of energy, forces capable of physically, chemically, or mechanically altering the artifact) or inductive treatment (increasing the resistance of the artifact). Consolidation is an inductive process.

Although consolidation embraces a large range of processes, it is generally considered to be a chemical process: the introduction of a liquid substance that solidifies around disintegrated intrinsic materials. Technically, it has been defined as the introduction of a monomer that polymerizes or precipitates in situ, or as the introduction of a thermoplastic substance that sets in gross voids.

Ethics of Consolidation. An ethical dilemma is inherent to the process of consolidation. Extrinsic material (consolidant) becomes bound to the original material and, for practical purposes, becomes inextricable from that fabric. Any extrinsic substance incorporated into a historic artifact adulterates the original fabric. Factual interpretation becomes more difficult as the fabric is obscured or altered.

Loss, obscuring, or physical alteration of original fabric is particularly relevant in light of modern analytical practice. Information about authenticity, use, and associations can be teased from seemingly insignificant particles. Information-bearing materials, such as pollen and spores, are usually obliterated by the consolidation process. The degree of adulteration can be related directly to the degree of primary consolidation that takes place. (Primary consolidation will be discussed in the next section of this chapter.)

The consolidation process, therefore, constitutes an indelible adulteration of historic fabric, although it imparts positive properties. Deductive treatments should always be considered before consolidation.

Deductive treatment achieves stability by reducing potentially damaging forces instead of by increasing the artifact's resistance. It is a very attractive alternative, as fabric integrity and access are not altered. Environmental conditions and artifact use often dictate the use of inductive treatments, however.

If consolidation is necessary, all efforts should be taken to minimize the adulteration of intrinsic material. Treatment should be directly related to the artifact's mechanical or physical ability to withstand the anticipated environment or function. Careful analysis supports minimum intervention so that the least amount of intrinsic fabric is altered.

Consolidation Methodology

Consolidation techniques can be divided into two systems categorized by the number of different materials used in the process: simple and integrated consolidation.

Simple consolidation, the most common form, uses a single active chemical substance with generic properties to compensate for the artifact's dysfunction. Material interfaces are reduced and treatment time is often less than that required for integrated consolidation. However, a single chemical substance rarely has mechanical and physical characteristics capable of matching the artifact's dysfunction. The results are usually a compromise between necessary intervention and ethics.

Integrated consolidation relies on a system of materials selected for properties that correlate with the artifact's dysfunction. The precise agents permit discrete application and less adulteration of the artifact. Often the system can be more easily adjusted after consolidation. Disadvantages are the increase in material interfaces and in design and application time.

The consolidation process develops stability through three planned phases and a fourth unknown phase.

Penetration or Distribution and Bonding. Liquid consolidant is introduced into the degraded tissue. In this phase, called primary consolidation, an intimate bond should form with the intrinsic material. The integration prepares the degraded macro- or microstructure for interfacing with strength-enhancement materials. Attachment can occur through both mechanical interlocking and chemical bonding.

The effectiveness of both simple and integrated consolidation systems depends on successful *cis* penetration of the disintegrated fabric. The methods of simple consolidation are similar to those of integrated consolidation at this phase. Similar materials are often used to make the initial bond with the artifact.

This first critical phase may initiate the most permanent alteration of the artifact's tissue, as its field often involves the microstructure of the wood cell. Attachment through adhesive bonding tends to engage the most widespread interaction with the intrinsic tissue. Mechanical interlocking devices, such as threaded rods and pins held in place by friction, function by crushing the substrate to increase its solidity.

Matrix Formation. During this phase, a continuous matrix is formed as the consolidant solidifies. Properties of that matrix, such as elasticity, ability to recover from distortion, and stability, are critical as they are imparted to the consolidated section of the artifact. In simple consolidation, the matrix consists of homogeneous regions of consolidant. In integrated consolidation, a primary matrix is formed by the primary consolidant. In addition, an ancillary matrix is usually made from other materials selected for properties relative to the artifact's dysfunction.

The set characteristics of a resin affect the stability of the artifact during this phase. General considerations concerning the solidification of liquid consolidants will be discussed more thoroughly later in this chapter.

Load Transfer. The third phase of consolidation is the final or working phase. A consolidated artifact generally has mechanical properties very different from those it had before being degraded. Consolidation works by reintegrating dissociated tissue and by imparting properties of the consolidant to the artifact. Stresses should be transferred harmoniously through the treated tissue and consolidation matrix. In most consolidations, load is conducted primarily through the consolidation matrix. The substrate is generally too degraded to contribute any useful resistance. A functional interface, the product of adhesion, must exist between the substrate and the consolidation matrix for the artifact to successfully withstand mechanical and physical forces, such as static or dynamic loading and hygroscopicity. In complex consolidation, one or more interfacing consolidation components transfer load from the artifact substrate to the consolidation matrix.

Posttreatment. Three planned phases are associated with consolidation, and somewhere in the future there will most likely be a fourth, unplanned, phase: decomposition of the consolidant or further decomposition of the substrate. Because conservation is concerned with extending the stability of an artifact, theoretically into perpetuity, some pathway to future preservation should become part of every treatment.

Characteristics of Consolidated Wood. Consolidation introduces new materials to the artifact profile, materials that have their own stability characteristics. Thus, a consolidated artifact often acquires complex behavioral alterations. Subtle and gross alterations imbue characteristics that must be anticipated.

Axial differentials are significant alterations that occur particularly in wooden artifacts treated with simple consolidation. The normative mechanical characteristics of wood are highly axial, primarily because of the alignment of the S_2 helix in concert with S_1 and S_3. (S_1, S_2, and S_3 are the outer, inner, and terminal wood cell wall layers, respectively.) These layers, composed of linear cellulose chains, are assimilated by brown rot, one of the most common microorganic predators affecting wooden artifacts. Loss of the cellulose component alters wood to a homogeneous mechanical state. As consolidating resins have homogeneous mechanical characteristics, assimilated axial tissue is replaced by a nonlinear material. The resultant product is a reinforced homogeneous material with little resemblance to the original material. Simple consolidation is generally effective only under compressive loads. An integrated consolidation system is generally required if a consolidated component is to withstand tensile load.

Numerous subtle alterations occur in consolidated wood. The perpetual exertion of microforces can gradually impair mechanical characteristics. The introduction of materials with different thermal coefficients might allow heat conduction into previously insulated regions. Incorporated resins may increase an object's thermoplastic response to infrared (IR) light, or they may depolymerize on exposure to ultraviolet (UV) light. There is potential for chemical interaction between the consolidant, chemicals naturally present in wood, and chemicals that have been introduced by biological agents. Conservation science is just beginning to understand the nature and behavior of wood extractives. I am not aware of any study evaluating long-term chemical interactions between consolidating resins and extractives or any study that has examined the effect of enzymes and pH-altering chemicals on those resins.

Most importantly, the behavioral complexity of a consolidated artifact is subject to increase, not decrease, as resins and other materials used in consolidation become degraded. Consolidation, therefore, incurs a treatment continuum and should be considered as part of an ongoing stabilization process; it is not an end.

Analysis

The analytical process begins with a gross characterization of material fields that have been deleteriously altered and the relationship of those components to the artifact. The following arbitrary categories are offered to assist in classifying the material fields (Figure 1):

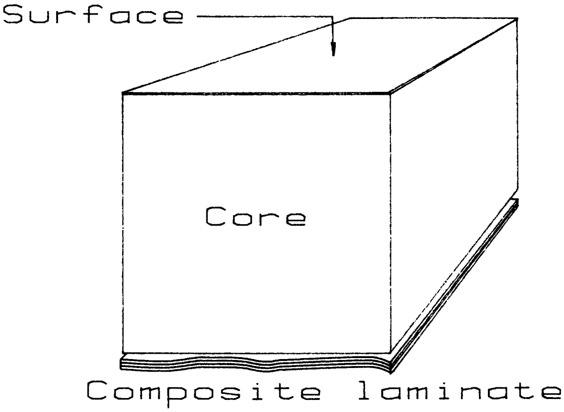

Figure 1. Material fields.

1. On the surface or the superficial structure of the artifact, disintegration is restricted to a simple, applied surface film and the outer surface of the intrinsic fabric. The value of surface materials is generally characterized as surface quality, configuration, color, reflective and refractive qualities, and density. The primary concern for these degraded artifacts is the loss of aesthetic qualities and potential for loss or alteration of surface material.

   Surface films and the surface of wood can be degraded in several ways: photochemically, particularly by near-IR and UV light; by hygroscopic differentials, particularly between wood and nonelastic surface coatings; by microorganisms, particularly by surface-staining mold; by exfoliating salts, particularly in maritime artifacts; chemically, particularly by cleaning agents and by inherent instabilities; by erosion of chemical components and breakdown of microstructural bonds caused by prolonged immersion in water; and by wind and particle erosion.

2. In composite artifacts, disintegration is restricted to the interface between or within discrete layers or laminants (primary stratum, secondary stratum, and ancillary material substrate) and to the contact surfaces of interlocking or frayed fabric. The value of materials in the second field is generally characterized as structure and stabilization. The primary concern for these degraded artifacts is loss of configuration or support as components become dissociated.

   Materials in this film are typically degraded by hygroscopic forces that result from differentials in grain orientation, where movement often exceeds the elasticity of adhesives and splitting may occur as wood is placed in tension along its axis; biological agents that use organic adhesives as nutrition; and excessive surface temperature that releases thermosetting adhesives.

3. In the secondary, ancillary, or core structure, disintegration is restricted to intrinsic subsurface or core material.

Minimum Effective Consolidation

Serious physical and ethical problems inherent to the consolidation process are apparent. A relationship exists between those problems and the extent of consolidation: As more consolidant is introduced into the artifact, adulteration of cultural significance also increases. Therefore, only the minimum *effective* consolidation (MEC) should be applied. A thorough evaluation of the object and its anticipated environment is essential to determine what is effective.

This determination is a particularly singular task, considering the individual characteristics of an artifact and the reaction of those properties to an environmental range. Because of the complex range of wooden artifacts, the evaluation must always be conscientious and creative. An attempt to establish routine procedures would be detrimental. It is better to understand the objectives of the evaluation than to learn one or two methods.

An evaluation should quantify the object's ability to resist energy forms likely to interact with it. The desired goal of stability can be stated as:

$$\text{resistance} > \text{anticipated (potential) load}$$

Load is a product of the environment. It is, in this case, defined as any form of energy within the classical physical spectrum (compressive to electromagnetic waves) capable of making a change in the intrinsic material. The full physical spectrum should be evaluated for interaction with the artifact. In theory, the artifact is stable when it is able to reflect, deflect, absorb, transmit, or otherwise tolerate load without deleterious alteration.

Degraded wood, and in particular biologically degraded wood, is subject to a wide range of energy forms. It easily becomes unstable as it loses the ability to resist alteration under normal load conditions:

$$\text{resistance} < \text{potential load}$$

The first stage of evaluation is the determination of whether the artifact is stable in its ambient, potential environment(s).

A System of Evaluation for Consolidation Projects

The term "system" is used with caution, as systems tend to be limited to predictable circumstances, and predictability is rare in conservation. At best, systems provide perspective and discipline. Any profession, however, requires awareness of an appropriate system's limitations and the need to modify the system to fit individual projects.

One essential aspect of testing any artifact is the impact of the test on the artifact's materials. Most testing procedures were developed by or for industry; complex configurations are rarely addressed outside of construction testing, and the inherent value of the material is nil. Consequently, most engineering tests are destructive by nature and are designed to analyze homogeneous unjoined sections of wood. Thus, standard testing methods are not generally applicable to conservation.

Despite substantial efforts, conservationists have been unable to develop reliable, usable, nondestructive test procedures. Much of the evaluation procedure relies on the judgment of the conservator, with assistance from consultants. Because conservation analysis often requires knowledge of an extensive range of materials, conditions, and physical laws, an optimum approach often includes a team effort. A polymer chemist, mechanical engineer, wood pathologist, supervising conservator, and technicians should all be considered for complex projects.

As this procedural system is a guideline to developing an individual approach and not a standard, the process begins with generic analysis and evaluation. Suggestions for specific test procedures are offered, however. Three primary components are analyzed:

1. Normative characteristics; normative material properties of the artifact relative to inherent design characteristics.

2. Dysfunction characteristics; residual strength of the degraded artifact.
3. Potential (anticipated) load to be resisted; the composite energy capable of interacting with the artifact.

Normative Characteristics

Normative characteristics are a function of materials and design. The practitioner should work toward establishing both a material and an environmental profile that will be interpreted through physical and mechanical laws. The greater the accuracy and scope of the data base, the more predictable the outcome of the treatment will be. Evaluation includes the following areas.

Material Strength or Mechanical Properties. The U.S. FPL *Wood Handbook* (*1*) provides a starting point to determine the generic range of properties. Actual properties inherent to the artifact's fabric should be analyzed whenever possible, however, to establish a more accurate data base. In particular, determination of density, or specific gravity (essentially a factor of the S_2 layer thickness), is important; it relates directly to the homogeneous material's mechanical and physical properties.

Even though the largest variations in specific gravity occur across species (0.11 for balsa to 1.05 for lignum vitae), a significant range variation can occur within a tree or even within a section. The *Wood Handbook* (*1*) contains data that establish the relationship between mechanical properties and density. Naturally occurring anomalies and specific grain characteristics are more difficult to evaluate, but are important factors that seriously alter the characteristics of otherwise homogeneous grain structure.

Hygroscopic Forces. Hygroscopic forces can be significant factors, particularly in high-density wood. They are directly related to specific gravity. There is no indication that hygroscopicity diminishes as wood disintegrates until the point of total loss.

Hygroscopic characteristics are important in anticipating the effect that environmental fluctuations will have on the artifact. They are important criteria when selecting a consolidant. Most dry-wood consolidants are not hygroscopic; when introduced to a highly hygroscopic environment, they may become dissociated because of the differential.

Consideration should also be given to interfaces between consolidated (less hygroscopic) wood and nonconsolidated (normally hygroscopic) wood. Stresses at the interface can be and often are deleterious to the artifact.

Design Characteristics. Design characteristics are determined by the configuration and orientation of member elements, object function, mechanical interaction between elements, and differential interfacing materials. The more complex the artifact, the more difficult its evaluation becomes.

In this evaluation, the conservator must understand how the object works as a unit, how load is transferred through the unit, and how the design load is applied (compression, tension, shear). A basic understanding of mechanical engineering or the assistance of a qualified engineer is often useful.

Joinery often imposes serious stresses as grain orientation and capture become factors. Normative design characteristics are often sufficient to split and destruct otherwise sound artifacts. A typical example is the common split found in the sides of chests of drawers that have 90° drawer runs affixed to the side plank. As normal relative humidity cycles occur, the anisotropic differential stresses the case to the point of splitting (Figures 2 and 3).

Lamination and surface finishes can further aggravate the evaluation

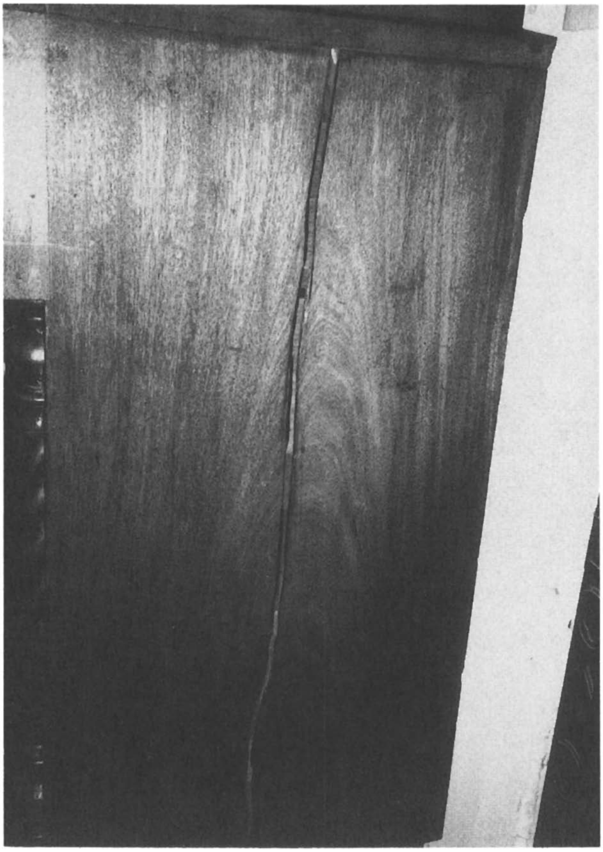

Figure 2. Exterior split on the side of an early 19th-century New York chest of drawers. This split demonstrates a normative design failure.

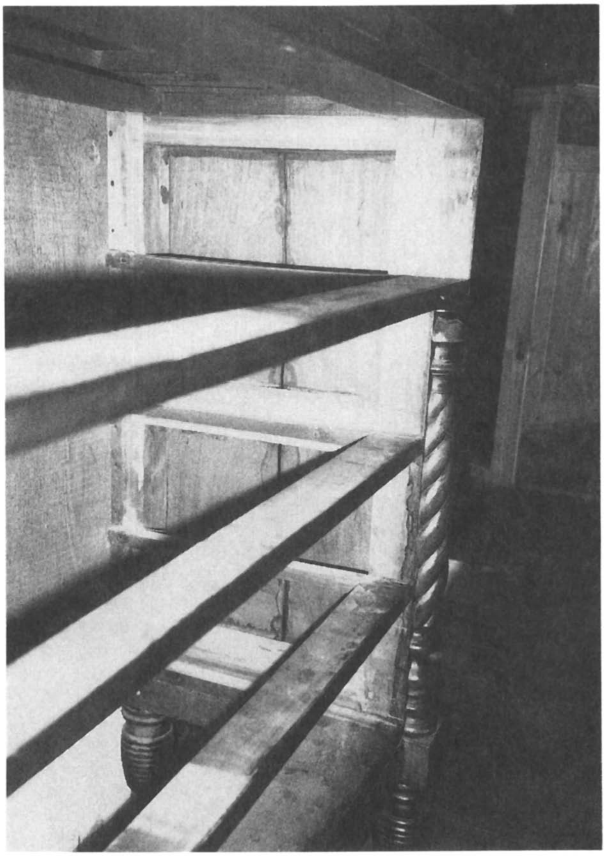

Figure 3. Interior joinery on an early 19th-century New York chest of drawers.

process. Grain orientation is often obscured and rheologic differentials occur as porosity is altered.

Dysfunction Characteristics

The second major component of the evaluation equation is the dysfunction characteristics. Properties of a degraded artifact are the product of the artifact's normative characteristics and the particular type of diminution it has sustained. Dysfunction characteristics are properties of the degraded structure.

Wood strength is derived from a cellulose–hemicellulose skeletal structure held in a matrix through cell configuration and lignin. Tightly bound microfibrils are integrated by lignin, a large, three-dimensional polymer that can be thought of as an amorphic packing material. Each component of the ultrastructure contributes an individual mechanical characteristic to the structure.

As the structure is assimilated or altered by deleterious agents, resistance is diminished relative to the component that has been lost or altered. Loss or alteration of wood components can occur on either the microstructural level (as precipitated by microorganisms) or on the macrostructural level (as precipitated by insects). Dysfunction properties are qualitatively and quantitatively related to degradation. A knowledge of wood anatomy and the relationship between its components is essential to understanding what occurs when a particular component or section of the matrix has been degraded. Some appropriate publications are Core et al. (*2*), Jane (*3*) and Panshin and de Zeeuw (*4*).

Because the function of consolidation is stabilization, the quantification and qualification of dysfunction properties are important criteria in developing a consolidation system. The MEC system should only compensate for reduced or lost properties enough to withstand ambient load. Stabilization does not mean restoring an artifact to its original resistance. Excessive restoration can be harmful, particularly when the restoration is in contact with untreated degraded surfaces.

It is also prudent to restore only those characteristics that have been reduced. For example, if compressive strength has not been lost, there is little need to consider a gap-filling system that works primarily in compression. It is important, then, to begin the process of relating a consolidant property to a particular type of dysfunction.

The particular mechanism of a deleterious agent provides a starting place for evaluating dysfunction. Deleterious agents can be classified into four groups:

- Biological: microorganisms, insects, bacteria, and animals.
- Chemical: photochemical and hydrolytic agents.
- Mechanical: physical load, abrasion, and internal stresses.
- Physical: hygroscopic (thermal–moisture) changes.

Biological predators are one of the most common and important causes of dysfunction. Wood, as a component of the natural ecosystem, is predisposed to reversion processes once it is cut. Conservation provides artificial isolation from this natural occurrence, a process that often begins with assimilation and nesting by animals and insects and ends in total reversion to topsoil by the action of simple bacteria. The term "biological predator" or "biopredator" is used throughout this chapter to identify the consumer of wood.

Wood degraded by biopredators warrants special attention when consolidation is being considered as a treatment. Identification of actively participating biological organisms is important. Every biopredator has relatively predictable habits of assimilation or destruction. For example, fungi release enzymes that are often polymer-specific. Diminution caused by fungi typically occurs more extensively in one of the major components of wood, while other components may remain relatively untouched. Insects bore chambers with more or less predictable dimensions, and they typically have bore-pattern peculiarities. Symbiotic relationships between insect and fungi create even more distinct disintegration patterns.

The following discussion of fungal and insect predators is intended to provide an overview of particular problems associated with individual species. Conservators should be prepared to secure the consultation of a wood pathologist for projects that involve extensive or unusual biodegradation.

Fungal Diminution of Archaeological Wood. Fungi present a particular problem in wood because of the covert nature of assimilation and effectiveness of migration. Loss of impact resistance often exceeds 50% at the first overt sign of fungal infection, weight loss. Because of the covert nature of diminution and its rapid rate of growth, fungal disintegration is often not detected before some degree of serious failure has occurred. Abrupt failures are commonly associated with fungal diminution.

The following arbitrary organization of dysfunction levels is useful in discussing decay characteristics (Figure 4).

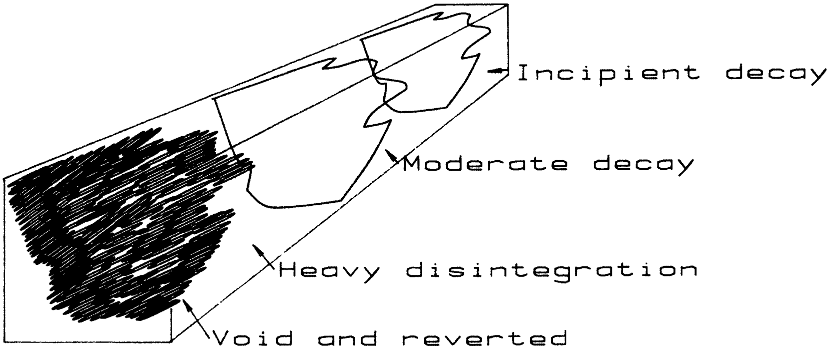

Figure 4. Arbitrary dysfunction levels associated with microorganic degradation.

- Incipient decay of exterior surfaces. The external surface of the artifact has been diminished. The inner structure remains solid and retains normative characteristics. A simple field test can be made by measuring the resistance or depth of penetration while probing with a narrow-gauge needle along the grain axis. The region of decay can be subjectively defined for depth and scope.

- Incipient decay at the interface of moderate decay. This level can be anticipated as frontier hyphae send bore holes through cell walls and release the initial assault of enzymes. Although actual measurement technology has not been developed, it can be assumed that incipient decay always physically precedes moderate decay. Its range is dependent on conditions and organism.
- Moderate disintegration or decay. This level of decay can be identified when significant portions of the macro- or microstructure have been altered or assimilated. Strength characteristics are reduced in excess of 50%. Diminution is apparent at this level through evidence of weight loss or visible alterations such as fatigue, exit holes, and discoloration.
- Heavy disintegration. This level of decay can be identified when whole areas of the structure have been assimilated, and only dissociated portions are left. The physical matrix has been seriously violated so that it no longer works as a unit. Degradation is apparent through the loss of mechanical properties, as well as through evidence from byproducts (frass, macerated cells, surface hyphae) and often audible sounds as dissociated sections rattle or rub together.
- Extensive void volume and reversion. This final stage of decomposition occurs when gross areas have been assimilated, converted to soil, or lost. This level of diminution is completed by final bacterial decomposition or by void volumes of 90–100% (normal void volume in wood is 40–60%).

Moderate decay is bordered by incipient decay and heavy decay by moderate decay. If a treatment must establish full-strength restoration, the consolidation must function at the incipient level, as well as at the region of heavier decay.

Rot, a particular type of fungus, is classified into three categories for evaluation of dysfunction.

Brown Rot. Brown rots can assimilate only carbohydrates. Decay generally begins in the S_2 layer of the cell wall, which provides the greatest concentration of cellulose without lignin. Assimilation of the S_1 and S_3 layers follows. The loss of cellulose reduces or eliminates axial properties. Wood becomes brittle and subject to mechanical failure across the grain (Figure 5).

Brown rots may be extremely covert because of the nature of assimilation. Pocket and dry rot typically exist in core material or adjacent to protective surfaces. In pocket rots, an elevated moisture content (the product

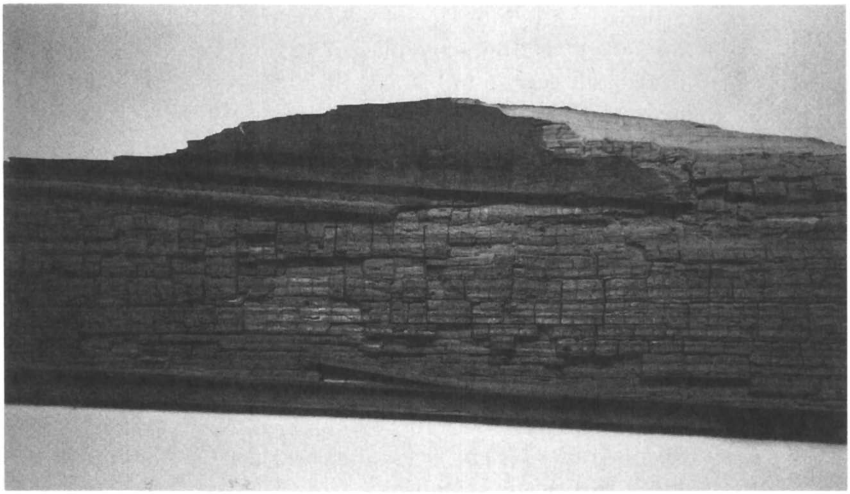

Figure 5. Section of yellow pine degraded by brown rot. Anobidae *exit holes are associated with rot.*

of moisture produced by metabolism) can most easily be maintained in internal portions. As fungi move to the surface, desiccation occurs and stops growth. In other forms of dry rot, such as *Serpula lacrymans*, moisture is carried via rhizomorphs.

Assimilation generally varies considerably from section to section and even between adjacent cells. The alterations of mechanical properties that occur with brown rot, loss of elasticity and axial strength, suggest that the best consolidation treatment should incorporate axial and elastic augmentation.

White Rot. White-rot fungi assimilate both lignin and cellulose; the degree and rate of component assimilation depend on the particular species. White rots generally move through cell lumens and decay from the lumen surface outward. Often, some degree of cell integrity is retained until advanced stages of decay. Separation of cells occurs early, however, as portions of lignin are assimilated (Figure 6). This pattern produces the antithesis of brown rot. Elasticity is greatly increased as cells lose their matrix configuration.

Consolidation treatment of wood degraded by white rot should restore rigidity while reintegrating dissociated cells.

Soft Rot. Soft rot decomposes cellulose and, to a lesser degree, lignin. Because soft-rot enzymes function only within close proximity to their hyphae, total decay tends to occur in the proximity of the infection, which moves as a concentrated colony with little extension.

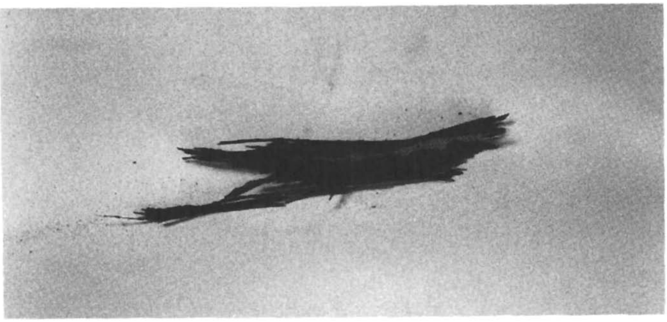

Figure 6. Section of white pine degraded by white rot. Note dissociation of cell clusters.

Because loss of material and reduction of compressive resistance occur, the best consolidation might be very gap filling and nonelastic.

Insect Predators of Cultural Property. Insect predators can often alter the mechanical properties of a sizable wooden structure or artifact within a short period of time. Like biopredators of the low plant orders, insect predators assimilate nutrition from wood. They may also attack wood to make a nesting site.

Conservators should be able to recognize infestations by type, even if they are not typically found in a specific area of the country. Because of the mobility of modern society, and particularly the buying and selling of European objects for sale in the United States, there has been a considerable increase in both the number and types of wood-degrading insects found in many regions. Many species of insects that degrade cultural properties have been identified as recent additions to previously clear geographic areas.

Symbiotic relationships frequently occur between insects and fungi. By identifying the type of insect and its stage of development, the conservator can gather clues as to the nature of degradation and decay that can be anticipated. The young larvae of the deathwatch beetle, *Xestobium rufovillosum*, are dependent on fungi that develop in their chambers, although they become less dependent as they mature. Old house borers, *Hylotrupes bajulus*, become more dependent on fungi with every molt. Some anobiids are so dependent on fungi that they will stop feeding where decay ceases.

Fungi are also believed to provide vitamins and nitrogen to termites. Several varieties of fungi are associated with termites, but brown rot is thought to be the most common symbiotic fungus, in that it increases the growth rate more rapidly than other forms.

Other less common insects have strong symbiotic relationships. *Ambrosia* beetles cultivate mold in their brood chambers and can survive for only one generation without a supply of the ergosterol that is produced by the mold growth. The woodwasp, *Sirex*, carries spores at the base of its ovipositor. During oviposition, the wasp deposits eggs and spores that send *Mycelium* into the surrounding wood. This fungus produces an enzyme that is present in the adult beetle's alimentary canal for digestive functions.

The following arbitrary organization of dysfunction levels is useful in discussing destructive insect characteristics.

Termites. Termites are socializing wood predators believed to have descended from the cockroach family. Of all of the wood-destroying insects, termites account for the greatest amount of damage to cultural property. Often securely hidden in the soil beneath a structure or artifact, termites have developed ingenious methods of migration and survival in hostile environments. Four types should be known to the conservator:

1. Subterranean termites have their colony beneath the soil, where they must return to replenish body moisture. They construct an elaborate network of hydration and bridging tubes through masonry, on top of masonry, and between wood members to be able to move undetected between sites. They can infect decorative arts that are located on soil and infected floors (Figure 7).
2. Dry-wood termites thrive in dry wood and do not require contact with the soil. They have been found in furniture, where they may seal off their entrance holes with a "seal off" paste.
3. Powder-post termites are the most common termite that attacks furniture. Thought to be introduced through Hawaii, they are predators only of manufactured objects and do not fare well in the natural environment. Damage from powder-post termites can be severe in furniture and small wooden artifacts.
4. Damp-wood termites do not require contact with the soil. Their infestation is even more devastating than the damage created by subterranean termites. This species derives moisture from numerous sources and has been found on the upper floors of masonry structures where there were plumbing or structural leaks.

Termites have discrete tunneling patterns. Subterranean termites typically assimilate wood, leaving only shells of the hardest wood when they are finished. These latewood sections are often cleaned as neatly as if they were polished. Because of the great variation that occurs with termite excavation, each species must be considered individually when evaluating for

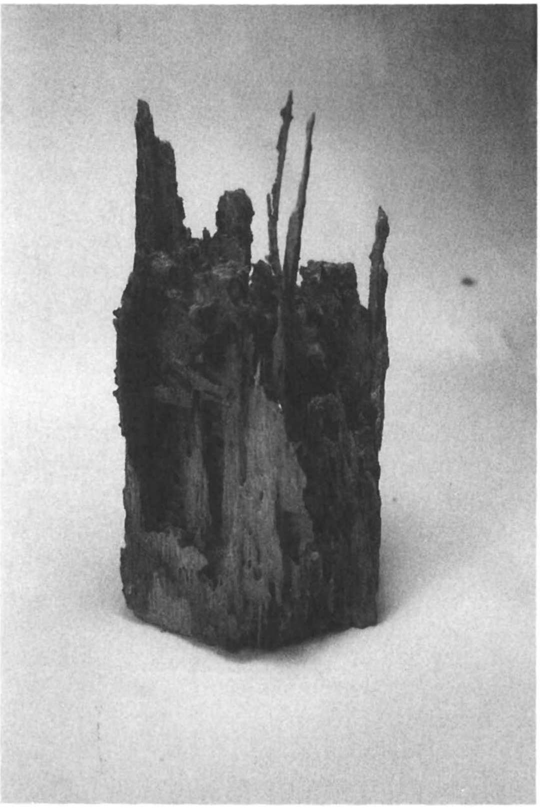

Figure 7. Section of red oak degraded by subterranean termites. Note reduction of earlywood, leaving bands of latewood.

the nature of dysfunction. Void volume, earlywood–latewood ratio, and grain orientation must all be considered. For example, subterranean termites often cause extensive excavation of earlywood. In a species where latewood dominates, such as oak, there may well be sufficient restoration of strength through reintegration of the annual rings. A gap-filling, highly adhesive consolidant might be considered.

Powder-Post Beetles. Powder-post, false powder-post, and deathwatch beetles are three common predators of relatively dry wood. Although they progress at a much slower rate than termites, they are capable of serious and often devastating damage to wooden objects. Powder-post beetles (*Lyctidae*) fill their chambers with a very fine powder that is similar in consistency to talcum powder. They attack hardwoods.

The beetles, 2–7.5 mm long, are reddish to various shades of brown or black. Their predominant head is not covered by a prothorax, and they have short 11-segmented antennae with a two-segmented terminal club.

There are 66 known species, 6 of which are important as predators of cultural property. They will infest furniture, houses, laminated wood products, and almost any wooden artifact when provided with a suitable source of nutrition and environment. They are difficult to detect until they have exited from their chambers.

Adult beetles mate quickly after exiting from their chambers. Oviposition begins within 2–3 days. The female oviposits into the pores, cracks, and crevices of hardwood. Eggs incubate for 2–3 weeks before hatching.

Mature larvae are usually under 5 mm long, curved, and enlarged at the thorax. Their antennae are three-segmented. Their abdomen has eight spiracles; the posterior spiracle is generally 6 times larger than the others. In a heated room, the larvae will develop with no seasonal period of inactivity. In unheated northern environments, the larvae will purge and become dormant in the fall and winter.

Pupation lasts for 12 days, following which the adult will exit from a 2–3-mm hole it chews to the exterior. Adults can easily bore through asbestos, plaster, and heartwood.

Time from oviposition to emergence of the adult is as low as 6 months in high-starch-content wood at warm temperatures, and 12 months under less adequate conditions. Under very adverse conditions, the life cycle may be prolonged for as long as 4 years.

Infestation is usually promoted by a warm climate and an adequate supply of high-starch-content sapwood of hardwood. Larvae cannot digest lignin, hemicellulose, or cellulose. Females tend to oviposit in wood with a starch content of at least 3%. Larvae can survive in moisture contents (MC) between 8% and 32%. Dehydration is a primary threat to the beetle.

False Powder-Post Beetles. False powder-post beetles (*Bostrychidae*) fill their chambers with a coarse boring dust that contains small wood fragments. They will attack both hardwood and softwood.

These insects, primarily tropical predators, feed on both hardwood and softwood. The head is deflected and not visible from above, being hidden beneath a large thorax that gives the beetle a humpback appearance. Antennae are short, with three or four enlarged sawtooth segments.

Adult beetles bore into selected wood and prepare egg tunnels instead of ovipositing into cracks. They will continue to tunnel in a section, and reinfest it, until they have depleted its food supply. The female bores the egg tunnel, making use of existing crevices for leverage. After the gallery reaches a depth of 8 mm, it turns sharply and runs parallel to the surface for another 6 mm or so.

Eggs hatch in 3 weeks, and the larvae tunnel parallel to the grain of the wood. Larvae mature after 9 months. By that time each has tunneled 50–60 mm. Pupation takes 14 days, after which the adult will remain in the wood for another 1–6 weeks, until its case is hardened. They exit from holes 2–7 mm wide and mate on the surface of the wood.

Furniture Beetles. *Anobiidae*, an insect family important to the conservator, contains six genera that attack wood. Of the six, *Anobium punctatum* and *Xestobium rufovillosum* are of particular interest, as they commonly attack cultural property. Both beetles excavate randomly, ignoring anatomical variations, within confined regions that generally are defined by higher MC and lower extractives.

The *Anobium punctatum* or furniture beetle is a particularly severe pest in the United Kingdom and along the American eastern seaboard. Known also as "woodworm", these pests attack flooring, furniture, wooden artifacts, structural timbers, and interior architecture (Figure 8).

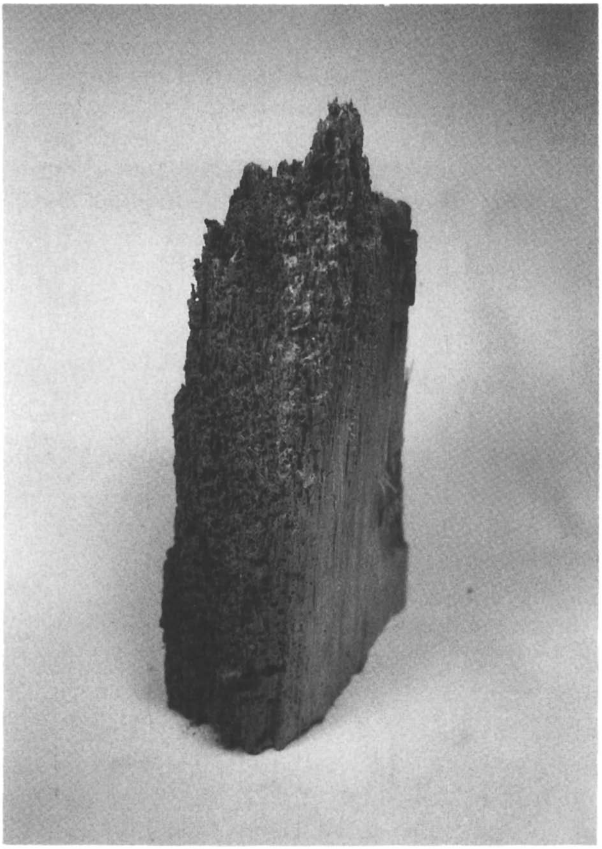

Figure 8. Section of white pine post from a 17th-century stable, degraded by Anobium punctatum *(furniture beetle). Note chamber concentration proximity to relatively sound wood.*

Furniture beetles attack well-seasoned wood, but require openings or fissures in the surface for oviposition of eggs. Finished surfaces, even sandpapered surfaces, discourage oviposition. Transverse surfaces, such as the feet of legs and drawer backs, offer excellent ovipositional sites, however.

The beetle is reddish to dark brown, 4–6 mm long, with longitudinal rows of pits on its elytra or wings. The antennae have 11 segments, the last three being longer than the first eight. Larvae are 6 mm long with seven segments. Frass is elongated, with small segments of chewed wood mixed in. Adults emerge in the spring, and the life cycles are staggered between 2 and 4 years; all stages of development may be present at one time. The insect develops more slowly indoors because of the reduced moisture content.

Deathwatch Beetles. Deathwatch beetles (*Xestobium rufovillosum*) fill their galleries with small pellets. They are one of the most important insects degrading decorative arts. Deathwatch beetles infest both hardwood and softwood and are widely distributed geographically. They are 1.1–8 mm long and have a characteristic "bell-shaped" pronotum concealing the head. The last three segments of the antennae are lengthened and broadened.

The deathwatch beetle is peculiar because of the clicking sound it makes as it bangs its head against the surface it is standing on. Females often will return a click when they are stimulated by the sound of tapping on a wood surface with a fingernail or pencil.

The adult beetle is darkish gray-brown and approximately 7 mm long. The pronotum and elytra have a pattern of yellow hair, but no pitting. Antennae have 11 segments but are much shorter than *A. punctatum*. *X. rufovillosum* larva is the largest of the *Anobiid* sp. *Anobiidae* larvae, growing up to 11 mm long. It has a yellow head, with two black spots (false eyes) and black mandibles.

Their tapping can be heard when the adults emerge in April and May. They may remain in a pupal stage for a full year before this emergence. Adults mate quickly, followed by oviposition of eggs. The life cycle takes 3–7 years and often is staggered.

Other *Anobiidae* are not as important to the degradation of cultural property, if only because they are less abundant as predators. All varieties will attack the decorative arts and have similar lifestyles and habits.

Roundheaded Borers. Roundheaded borers (*Cerambycidae*) are common pests to architectural properties, although they have been known to damage decorative arts in passing. An entomologist acquaintance once related a story of placing a bowl, turned from native wood, on his desk before going on vacation. On his return, a *Cerambycidae* larva had bored its way from the bowl through the desk and into the floor.

Old House Borers. Old house borer (*Hylotrupes bajulus*) is prevalent in Northern Europe and is becoming common in the United States. The old house borer can be present in both new and old houses, and can reinfest sections from which it has exited. Examination of structures excavated by this species suggests that they avoid only the hottest and driest of environments, conditions such as might be found under a tin roof.

The female is typically 2.5 cm; the male is half that size. Adults are grayish black to dark brown, with yellowish gray hairs. About one third of the way down the elytra, there are two grayish transverse marks.

Larvae are gray to white, 2–4 cm long, heavily segmented, and with dark jaws. Larvae feed on sapwood for 2–10 years, until it is completely destroyed. Their chambers are filled with small compressed pellets that are larger than the chamber. This condition causes the chamber walls to bulge and gives them a rippled appearance on the exterior surface (Figures 9 and 10). The larvae make an audible rhythmic rasping noise as they chew through the wood. The noise is loudest as they tunnel next to the surface of the wood. A crackling noise can often be heard as tunnel walls are stressed.

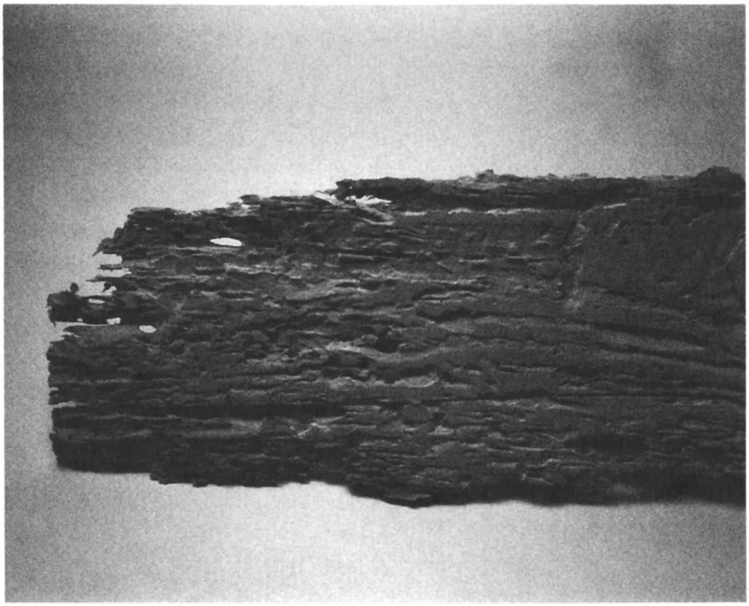

Figure 9. Section of white pine from an 18th-century church, degraded by Hylotrupes bajulus *(old house borer). Note chamber concentration and random pattern.*

Methods of Controlling Infestation. As with any conservation treatment, stopping the destructive agent is imperative; the disease must be treated along with the symptom. Biological agents, in particular, have a

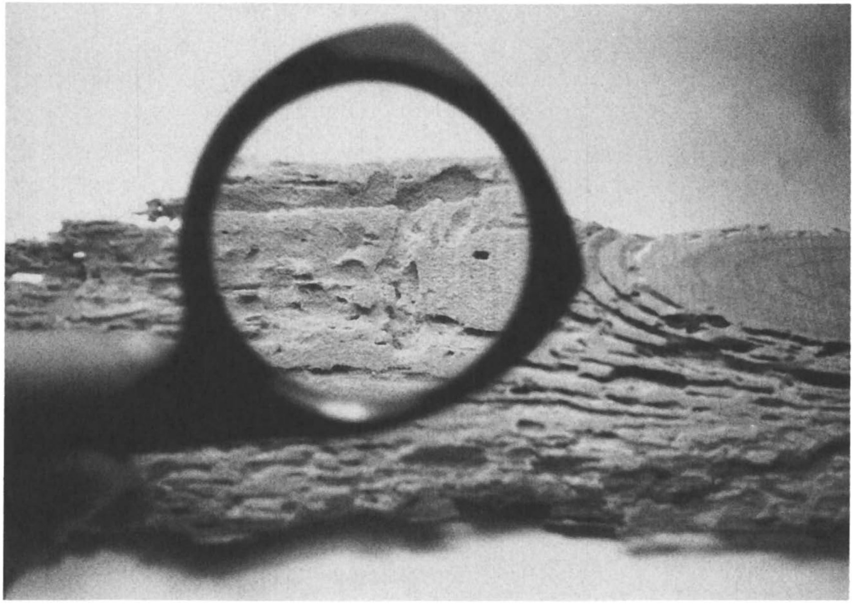

Figure 10. Hand-lens magnification of sample shown in Figure 9. Note chamber proximity to top surface of beam.

propensity to reactivate if the environment is not corrected. For this reason, the consolidation practitioner is encouraged to undertake ancillary maintenance.

An extremely important preventive measure is sanitation, the removal of all diseased and decayed wood. Firewood, old construction timber, and cuttings from shrubbery should all be removed as potential breeding grounds for these insects.

Finishes and wax are two methods of controlling and preventing infestations. Because neither powder-post nor anobiid beetles can oviposit on finished surfaces, this method is very effective. Care should be given to ensure that all surfaces, including secondaries and the bottoms of feet, are coated.

Although the consolidation treatment will often exterminate living organisms, there can be no assumed assurance. Brown-rot hyphae growth has been observed following consolidation by methyl methacrylate in a laboratory specimen. Again, specific forms of extermination should be matched to the predator organism. The advice of a pathologist, mycologist, or entomologist is useful. The conservator might look to some standard solutions, however.

Heat is a very effective method for an "all-stage" kill of most wood-boring beetles. Detailed lethal temperature and exposure time has been determined for powder-post beetles. Wood-boring insects will dehydrate above 44 °C

(110 °F). Kill time is a factor of temperature, MC, thickness and mass of the object, and species. Great care should be taken with this method, however, because of the possibility of causing physical and mechanical damage to the object being treated.

The use of toxins in the control of insect populations should be approached with great care. Chemical interactions, mammalian toxicity, and nonreversibility are important considerations before involving any toxic treatment. Zycherman and Schrock (5) provide a greater understanding of deleterious biological agents, toxins, and methods of treatment.

With insects, two forms of chemical treatment can be used: chemical solutions that are either diffused into the surface or impregnated into the wood structure, and fumigants that are vapors.

Structural wood and new wood insecticides that have proven to be effective are solutions of Toxaphene, Dieldrin, Lindane, and Dursban. Most are controlled toxins and should be used only with the advice of a professional applicator.

Fumigants can be very effective but costly methods of pest control. Objects can be brought to a commercial or museum chamber (such as a "Vacudyne" chamber, which draws a negative pressure for increased permeation) or they can be tented and treated at ambient pressures.

Fumigants can be as reactive as surface treatments and should be investigated with great caution. Some fumigants that should be avoided because of reactivity are methyl bromide and Vapona. Sulfuryl fluoride (marketed under the name of Vikane) is currently being tested for application to cultural artifacts. The concentration of 10 lb/1000 ft^3 (4.5 kg/2830 m^3) is thought to kill larvae and pupal forms, but there is some question of efficacy as an egg-kill toxin. Hydrogen cyanide, perhaps the most effective "all-stage" fumigant, is extremely toxic to mammals. It should be used only under drastic circumstances and with considerable caution. Ingestion of salts or moderate breathing of fumes will result in rapid death to humans.

Fungi, with the exception of dry rots, can most easily be controlled through the environment by deductive treatment. Fungi have the ability to lie dormant for long periods of time, however. On reintroduction of moisture, they often will reactivate and continue growth. Unfortunately, most effective chemicals contain metal salts or fluorides, both of which must be evaluated for physical and chemical interaction with consolidants.

Design Characteristics vs. Dysfunction

The design characteristics of an artifact should be evaluated for relationship to degraded areas. Bearing surfaces, load-transfer points, and areas expected to withstand the highest load are often subject to the highest degree of degradation because of their physical location and the amount of protein introduced into the wood structure by the organic adhesives.

Figure 11 demonstrates that minimal reserve strength can occur as a design weakness in some artifacts. The example is an 18th-century English looking glass frame (Figure 12) with rococo line and ornamentation. Load (the weight of the mirror) is carried across narrow sections that contain transverse grain and joinery; loading occurs in the weakest direction (Figure 13). This particular artifact was infested by the common furniture beetle.

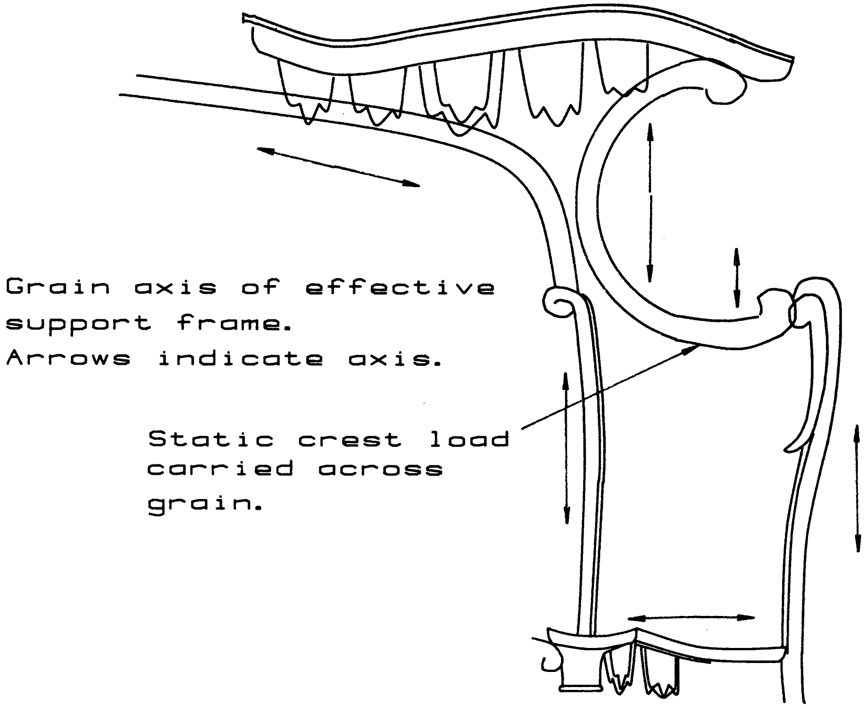

Figure 11. Grain orientation analysis of an 18th-century English looking-glass frame. Grain axis of effective support frame is indicated by arrows.

Diminution occurred consistently as 1.35–2.1-mm chambers throughout the ancillary structure. Although loss of materials was reasonably uniform in all members, the relative importance of the loss varied significantly as the larval holes crossed areas with low design resistance. At these minimal areas, resistance became equal to static load. Failure occurred as vibrations from a passing helicopter were transmitted through the wall to increase the load beyond resistance.

Although degradation was relatively consistent throughout the structure, the design weakness was the point of failure. If this artifact had been evaluated for consolidation, the treatment should have been limited to the region of design failure. Residual strength of the longitudinal sections remained far in excess of potential load.

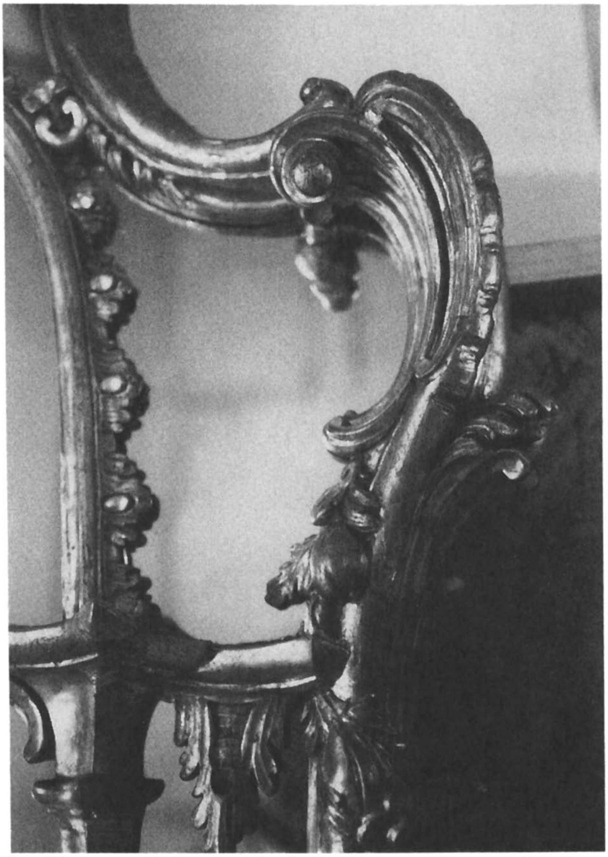

Figure 12. Upper right quadrant of an 18th-century English looking-glass frame.

Anticipated Load

The anticipated load is the composite of energy that might interact with the object. Both the artifact's fabric and the potential consolidant need to be evaluated for interaction with potential energy forms. Once again, the more comprehensive the evaluation, the more accurate the consolidation will be. The evaluation should include

1. Mechanical forces: use stress, wind load, static load, reasonable potential trauma load, and abrasion. An engineer is useful in anticipating loads.
2. Physical forces: photo energy (particularly IR and UV), subsonic, sonic, and ultrasonic vibrations and moisture changes. IR energy interacts with moisture to determine availability

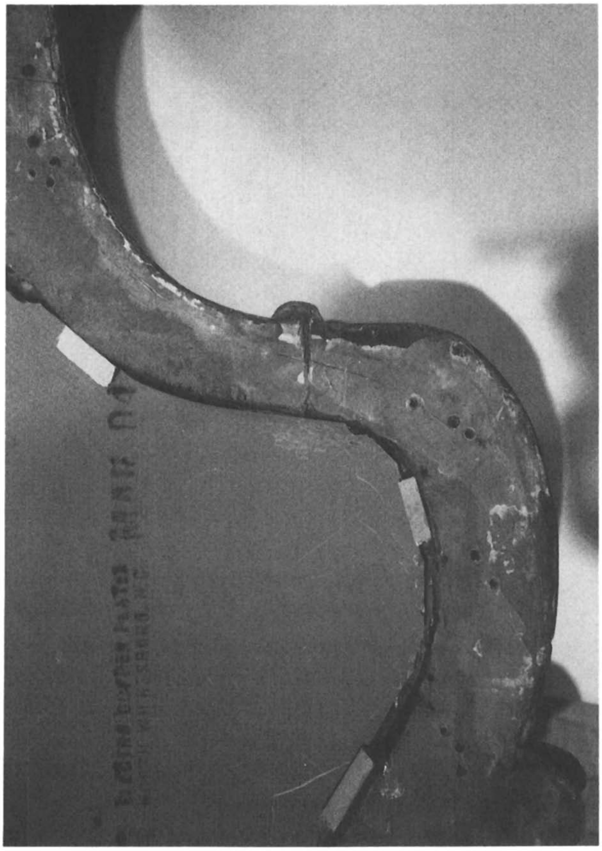

Figure 13. Reverse and opposed section of the 18th-century looking-glass frame shown in Figure 11. Grain orientation is apparent at break near top of section.

and rate of chemical exchange. UV radiation is an effective depolymerizing agent for surface consolidants. Subsonic, supersonic, and sonic vibrations can set groupings of molecules in motion to generate heat and create fatigue at weakened sections. Some cross-linking consolidants might have the effect of increasing interaction with sonic energy.

3. Biological forces: fungal, insect, and human interaction with the materials. The potential for recurring biological predation or new involvement should be taken into account so as not to retain or create a suitable environment for the organism.

Evaluation Procedure

Anticipated load is a major reference for MEC. Any treatment must restore resistance characteristics to the object with a predetermined safety margin.

The treatment method must be considered for its compatibility with the subject material and for its ability to augment the residual strength of the object beyond the level of competency.

$$\text{margin} + \text{dysfunction } (-\text{ value}) = \text{resistance}$$

$$\text{resistance} / \text{load} \times 100 = \%\text{ competency}$$

$$\text{safety factor} = \%\text{ competency} - 100$$

Safety margin is the normative amount of strength in excess of that required for stability. Acceptable safety margin (above 100% competency) is a factor of application.

Consolidants

Consolidants have been found in many forms; many elastic and transformable materials have useful characteristics. Adhesives, in particular, have effective properties that stem from their ability to reintegrate dissociated tissue. Chapter 14 presents a more thorough explanation of the principles and mechanisms of adhesion and cohesion.

Consolidants must achieve *cis* penetration and provide a functional interface and a strength-enhancing matrix. Depending on the consolidation system, materials may either be introduced into the artifact or function externally. Achievement of MEC is further refined if the conservator is able to provide most consolidation external to the artifact, as less material becomes involved with the intrinsic structure.

Internal Consolidants. The following is a list of substances that have been used traditionally as internal consolidants. These substances are neither approved nor recommended for artifact consolidation.

1. Water-soluble adhesives, such as animal byproducts (hide, fish, blood albumin, gelatin, and bone), starches, mineral composites (clays), and casein.
2. Organic resins in evaporative solution, such as shellacs and rosins.
3. Organic and mineral waxes, such as beeswax and ceracin applied with solvents and in a molten state.
4. Seed oils, such as linseed and tung oils applied in solution.
5. Soluble resins, such as nitrocellulose, caseins with caustic solvents, poly(vinyl acetate)s, soluble nylons, and polyacrylates.
6. Exothermal resins, such as epoxides, isocyanates, and polyester resins.

Evaluation. Consolidants should be evaluated for their properties relative to the artifact material profile. In general, the consolidant should have an appropriate degree of surface tension to adequately wet and penetrate the disintegrated fabric. It should also possess sufficient flexibility of polymerization or set time to allow for full penetration of the degraded area.

Appropriate adhesive and cohesive qualities are needed to effectively reattach degraded sections within the degraded structure. The consolidant must be dimensionally stable as it sets. Expansion and shrinkage of the consolidant can induce considerable deformation of the shape of a degraded object. Anti-shrink-effect (ASE) properties are highly useful in determining the effect the primary consolidant will have on the dissociated tissue.

Properties of the consolidant should be similar to those of the wood structure. The optimal consolidant has hygroscopic and mechanical properties that coincide with the material it is replacing. A consolidant should have approximately the same tensile and compressive strength as wood. A consolidated field enhanced to the point of being too strong is likely to destroy surrounding nonconsolidated materials.

A consolidant should be as reversible as possible. In the event that the treatment is not a success or if the consolidant begins to deteriorate after a period of time, removal of the consolidant is essential.

Treatment must allow for interim treatment of the artifact. The consolidant must not eliminate the possibility of treating the section if an infection or infestation should occur.

The consolidant should be toxic to biodegrading organisms. Arresting the deleterious organism is essential to ensure that it will not continue activity in the consolidated artifact. If the consolidant is not considered to be toxic, it should not react with fumigant or residual toxins that may be required.

A good consolidant is reversible and manageable during application treatment. Application control is essential in the event that the consolidant begins to leave its intended confines.

Relative heat stability during setting is important. Exothermal conditions may elevate the temperature of the surrounding tissue, and thereby alter the moisture content and material properties. It should also be reasonably creep resistant after setting.

Whether the conservator is performing a simple or complex consolidation, an intimate bond must be established with the disintegrated material. Penetration or introduction of the consolidant into the disintegrated fabric should theoretically occur to a predetermined level of decomposition (incipient, moderate, heavy). The conservator is concerned with three sets of properties: liquid phase, transitional phase, and solid phase. Table I indicates the particular concerns for the three phases.

Liquid-phase properties should allow reasonable control during application and should facilitate the degree of introduction into the disintegrated tissue with minimal alteration of the original structure. Viscosity, temperature, and chemical interaction are important conventions to measure.

Table I. Mechanical, Chemical, Physical, and Biological Properties of Concern During Consolidant Liquid, Transition, and Solid Phases

Phase	*Type of Interaction*	*Properties of Concern*
Liquid	Mechanical	Congealed or particulate matter obstructions Application distortion
	Chemical	Exothermal reaction Interaction with wood components Discoloration
	Physical	Refractive index may be altered Reflective index may be altered Spurious flow out of confines
	Biological	Should be toxic to biopredators
Transition	Mechanical	Swell distortion Volumetric loss
	Chemical	Exothermal reaction
	Physical	Spurious flow out of confines Swelling of consolidant Continued dispersion into other materials Refractive index may be altered Reflective index may be altered
Solid	Mechanical	Strength differential Hardness differentials Elasticity differentials
	Chemical	Discoloration of primary surfaces Should be reasonably reversible Should allow further treatment
	Physical	Hygroscopic differential Thermal stability Cold flow or creep distortion Refractive index may be altered Reflective index may be altered
	Biological	Should be resistant to enzymatic action May reduce desorptive index, creating a favorable isolated environment

Predictable transition-phase properties are critical, particularly in simple consolidation and during the initial stages of complex consolidation. Exothermal reactions, swelling, and shrinking are common physical occurrences during the polymerization process. Permanent hidden and overt alterations that can occur during the set time may further diminish the cultural significance of an artifact.

Predictable set characteristics are also important to process control. Predictability of set is often a factor of application environment (humidity, temperature) and material purity. The prevalence of unstable and contaminated monomers in conservation laboratories (possibly a result of the infrequency of consolidation treatments) can be a significant problem, as incomplete polymerization and retarded transition can occur.

Solid-phase properties should be compatible with the material evaluation profile. Materials that violate the envelope of normative properties may be too weak or too strong for a given section. Adverse effects often occur as a result of mechanical and physical differentials.

The incipient decay region should not be overlooked as a primary factor in determining the effect of the solidified region on the artifact unit (Figure 14). This field, as the most occluded and restrictive, is often not engaged by the consolidant. As it provides the interface between sound fabric and consolidated fabric, its diminished resistance if often further reduced by hygroscopic and mechanical forces. Failure commonly occurs at the perimeter of the consolidation in an incipient decay field.

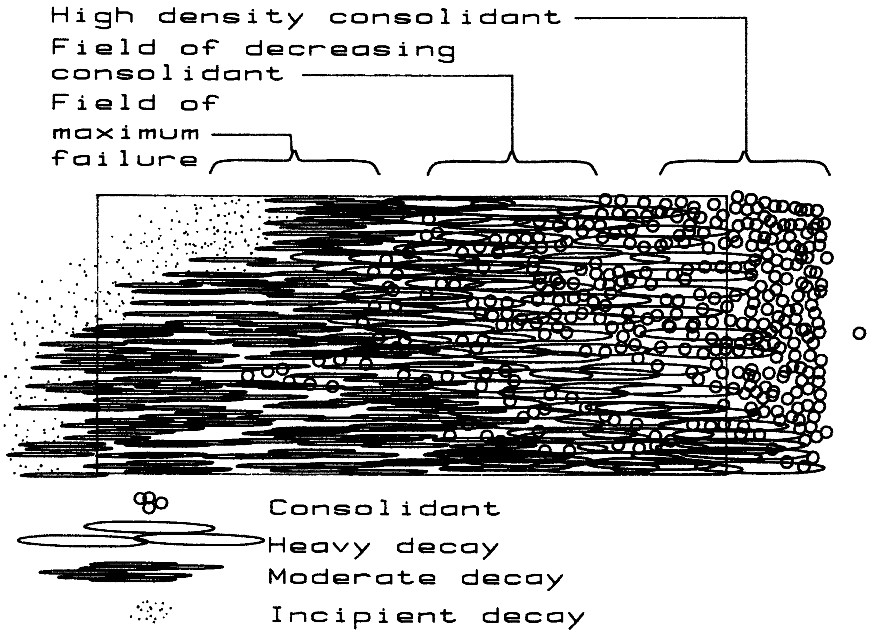

Figure 14. Consolidant concentration in decayed wood.

To be effective, the treatment must ensure adequate engagement with sound materials or sufficient elasticity to compensate for load differentials. Further, it must fail before the failure of sound fabric, as the consolidated field should remain the weak component to preserve unadulterated fabric.

Integrated Consolidation Systems. An integrated consolidation system can be defined as any consolidation system that uses two or more materials to achieve stabilization. Although multiple materials may be introduced into the artifact, many advantages are realized in systems where the consolidant system is transferred to an external system. Three components make up the system: initial fabric engagement, interfacing or transition, and strength matrix.

The most critical component is the artifact interface. The initial bonding process or penetration of the disintegrated fabric is selected relative to the characteristics of the degraded field. The following categories are presented with suggestions for the type of consolidant that might be used.

Level 1. Artifacts that require restoration of surface integrity or consistency more than strength enhancement or reintegration of loose elements. For example, loss of surface components caused by incipient surface decay or chemical decomposition.

- Surface consolidation, where little strain is placed on the object, other than handling, may provide ample stabilization. These conditions might best be managed by the use of reversible surface resins such as the acryloids or not dewaxed shellac resins in reduced concentrations of ethanol.
- Layer void impregnation, application of discrete isolated sections of consolidant where laminants have lost adhesion. Lacquerware surfaces separated from their ground or dissociated laminates can often be stabilized with this method. Judicious use of molten waxes or thermosetting adhesives is generally successful because of their unique physical and mechanical properties.

Level 2. Artifacts that require restoration of mechanical properties as well as reintegration. In simple consolidation, the consolidant provides strength enhancement, as well as the bond with the original fabric. Integrated consolidation relies on one substance to consolidate the boundary of the disintegrated fabric; a second or series of materials is then used to transfer mechanical load to an internal or external brace system for strength enhancement.

- Partial loading. Fixing of isolated clusters of material or coating cell walls may be desirable over total impregnation as a favorable ratio of consolidant to original fabric is maintained. The reintegrated fabric then provides attachment for materials that ultimately restore strength characteristics to the artifact. Acrylic and vinyl resin precipitations should be considered for the degree of adjustments that can be made with various solvents, inhibitors, initiators, and percentage of solids.
- Total impregnation. The infusion of consolidant becomes necessary when the original fabric is degraded to the point of being dissociated to an amorphic substance. While acrylic and vinyl resins are preferable for their solvency after polymerization, cross-linking epoxides and polyesters may be necessary for their cohesive and gap-filling properties.

Practical Introduction of Consolidants into Wood Structure. The term "practical" is used to stress the point that attempted technology must be within the reach of the conservator. The most appropriate technology is that which can be adapted to a wide range of applications. Sophistication does not equal complexity.

The process of introducing consolidants into degraded wood meets less resistance as degradation increases. Even the minute bore holes found in incipient decay tend to facilitate infusion. Problems often occur, in fact, because the artifact integrity is too poor to confine the consolidant.

Selection of a consolidant and engineering its properties (viscosity, temperature, and polymerization time) are based on analysis of the artifact, the level of degradation, and the materials that will provide transition and strength-reinforcement properties.

Because of the opacity and complexity of most wooden artifacts, disintegration and loss are difficult to measure. Consequently, the amount and distribution of consolidant required for MEC often have to be approximated.

Dimensional evaluation and testing can give reasonably accurate quantitative data; nondestructive measurement is especially important with cultural artifacts, however. The conservator may be able to determine volume on the basis of weight, intact cross section, fluoroscopy, or through judicious use of probes.

Time evaluation is essential. Factors such as application, infusion, solidification, polymerization, and full cure time balance penetration against unavoidable risks. As application time increases, so does penetration. However, the risks of occlusion, spurious flow, and loss of critical temperature and environmental control also increase. Application should be accomplished in the fastest and most predictable manner.

The following is a review of methods to introduce liquids into the wood structure. The type of degradation that has occurred must be known to determine what method will best match the state of the artifact.

1. Capillary action or absorption depends on the takeup of the consolidant through the gross cell structure and voids as a result of surface-tension forces. Absorption is a factor of time, surface tension, capillary dimension and exposure, and viscosity.

2. Diffusion or the introduction of the consolidant can be a result of a concentration gradient. Flow occurs from the area of high concentration to the area of lowest concentration. Diffusion is increased by time, concentration, and porosity. It is reduced by viscosity and distance. Diffusion generally is integral to and a minor part of absorption.

3. Impregnation or permeation is the infusion of a consolidant

> through a differential pressure gradient. Permeation increases with lower viscosity consolidants, time, void volume, and a higher pressure gradient. Impregnation can occur through the use of an impregnation tank in a vacuum chamber or by introducing the consolidant by injection. Pressure used in treating degraded timbers should not exceed 150 psi, and pressures should be reduced when elevated temperatures are used to reduce the potential of collapsing cell walls.

Selection of the primary consolidant is based on the materials it will interact with and the method of introduction. It may be selected for high reversibility, or to isolate a less reversible secondary consolidant selected for strength enhancement, or it may be selected for its ability to integrate extremely disintegrated fabric.

Equipment necessary for consolidation depends on the consolidant and the method of application. Typically, apparatus includes a reservoir for retaining the consolidant, a well-ventilated and lighted working facility, environmental control for humidity- and temperature-sensitive resins, a source of heat, a measurement device such as a load cell, and application equipment that may be as simple as a brush or syringe or as complex as a vacuum impregnation tank.

The practitioner should carefully review methods of incorporating substances into wood. Bulk systems, such as impregnation tanks, are useful only when attempting to treat an entire artifact. It tends to be a restrictive method, as control over the region of treatment is reduced. An alternative, based on the same pressure differential principle, is the use of injection devices such as a syringe or injector probe.

Interfacing Components

Consolidation necessarily creates a more complex artifact, as new materials must interface with old. Integrated consolidation requires engagement between the disintegrated fabric and a strength-enhancing matrix. This second component provides a transition material between less stable solidified fabric and a more homogeneous mechanical matrix. Discrete consolidation materials have an advantage over simple consolidation materials, in that they are required to do less. Penetration for tissue solidification is not required, only bonding to the interfaces in a created and more predictable environment.

Selection of a secondary consolidant or interfacing material is based on the properties that are to be imparted. The secondary consolidant may be the final consolidant, or it may provide an interface to a tertiary component. In the case of an external reinforcement matrix, load is transferred to external components, and adulteration of the intrinsic fabric is thereby reduced.

Some examples of the use of secondary components follow, with examples of materials that might be considered.

- To fill voids with semirigid material (isocyanate foams)
- As an interface between rigid nonhygroscopic materials and the consolidated fabric (ethafoams)
- To fill voids with a short, rigid material (latex or vinyl with a microsphere suspension)
- To fill voids with an interlocking matrix (epoxides–polyesters)
- As a direct load to a skeletal matrix (poly(vinyl chloride), stainless steel, aluminum tubing)

The Reinforcement Matrix Concept

Tertiary components typically impart mechanical properties to the artifact through an internal or external skeletal structure. The structure may be designed to impart predetermined rigidity to resist static and dynamic load.

Access and adjustability are significant advantages of external reinforcement. Because the system is not concealed by the artifact, it can be monitored visually, by strain gauges, or by other devices to determine the degree of load it is assuming. Its performance can be judged, and the matrix can be reinforced or adjusted. Adjustability can be engineered into the matrix by using tensioning devices, mechanical locks, compression devices, or weighting devices.

Isolation from the artifact fabric provides a further advantage in integrated systems. Impregnated materials can be chosen for nonreactivity with extractives and other catalytic chemicals intrinsic to wood. As the matrix is external or isolated, a greater range of materials becomes available to the practitioner, materials that can be chosen for mechanical properties with less concern over chemical interaction.

Case Studies

The following case studies detail integrated consolidation in two very different artifacts. The studies are extracted from actual working documentation; notes have been interjected for clarity.

First, the sternpost from James Cook's H.M. Barkentine, *Endeavor*, which was consolidated with an external removable skeletal support. Second, the 12-ft-long figurehead "Scotsman" from H.M. Clipper *Glasgow*, which was treated with an integrated internal and external skeletal matrix.

Case I: The *Endeavor* Sternpost. The 2- × 0.3-m, 59-kg sternpost, once part of James Cook's barkentine *Endeavor*, sailed on the expedition that confirmed the existence of *Terra Australis Incognita* (Figures 15 and 16). The highly successful scientific voyage landed at Botany Bay, later to be the establishment of the first British penal colony and mark the founding of Australia.

Following the *Endeavor*'s 1768–1771 voyage, she was declared unseaworthy, converted into a store ship, a whaler, and finally a merchant vessel. In the later 1790s, she was damaged while leaving a New England port and grounded in New Bedford, where treasure hunters, legitimate cannibalism, and insects took their toll. The sternpost was moved, untreated, to a museum in the early 20th century. Finally, it was donated to symbolize the opening of the Australian National Maritime Museum, Sidney, Australia, as part of their bicentennial celebration.

Figure 15. Sternpost from H.M. Barkentine Endeavor.

The artifact was evaluated with particular concern for the transport to Australia and for a planned tour across Australia. Because of the radical difference between the anticipated transport load and exhibition load, the primary objective was to design a consolidation system that would be almost entirely reversible, yet replaceable when the artifact was to be moved.

As the artifact was not seen during the actual transport between stations, the system could obscure the artifact, as long as it was reversible.

The design evolved into a high-tech case that would consolidate the artifact during transportation, yet be removable when the artifact was to be

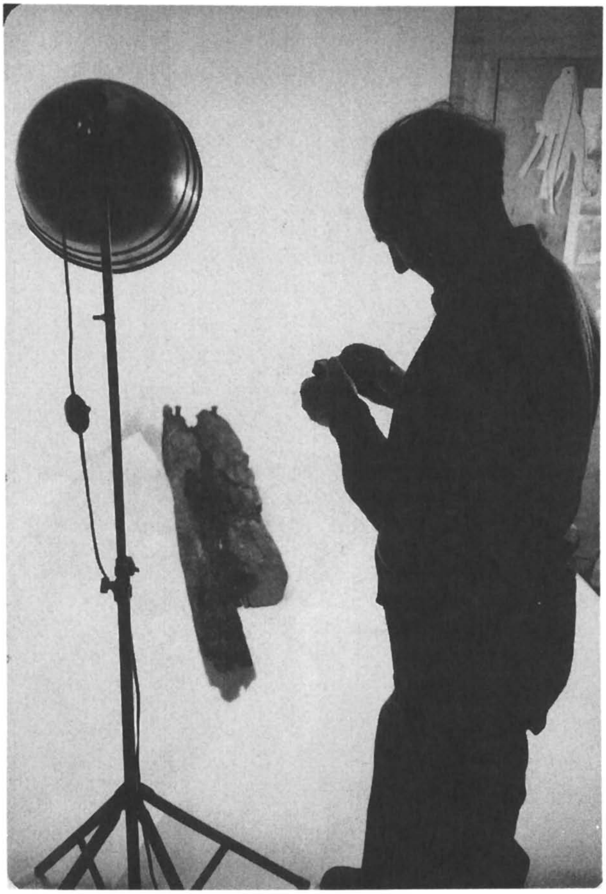

Figure 16. Preparing for photographic and CAD documentation of the sternpost.

placed on exhibit. Minimal internal consolidation was required to ensure adhesion of fragment masses. The primary method of load transfer and absorption was through physical contact, not chemical bonding. The following is the report on the original condition of the sternpost.

Physical Description. The sternpost is an 87- × 11- × 11-in. (221- × 28- × 28-cm) irregular single section of wood with two parallel 1-in.-diameter (2.54-cm) iron drift pins driven in 16 in. (40.6 cm) from the base of the post. No mount or other device is attached.

Material(s). The sternpost is a quarter section of top-growth white oak with knots and irregular grain orientation at one end.

Condition. The post weighs 124.5 lb (56.6 kg) and has been seriously diminished by larval and fungal activity. There are extensive insect chambers, surface mycelium, and cross checking concentrated in the lower section of the artifact (Figure 17).

There appears to be no active infestation. Frass and exposed chambers are well oxidized and covered with a layer of dust.

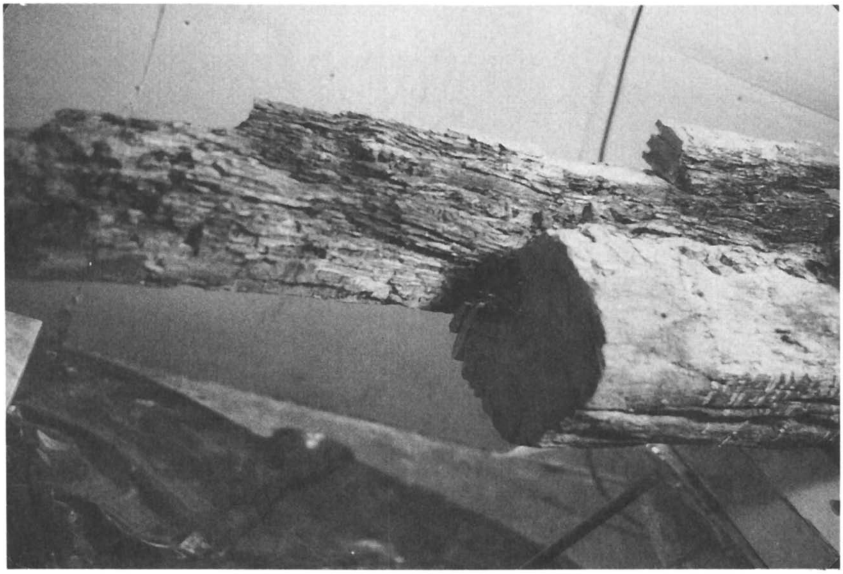

Figure 17. Upper section of post illustrating insect and fungal degradation. Large cut section resulted from section being removed for sample taken aboard spacecraft Endeavor.

Brown rot is dormant because of the low moisture content. The presence of fragile mycelium suggests that the infection was recent.

The surface has a fine white semiopaque coating that smells like thymol. There are late cut sections marked by removal of sections for *Endeavor*, the space craft, and *Endeavor*, the America's Cup challenger.

The iron drift pins are lightly oxidized, but are retained securely in sound wood. Apparently, the iron salts acted as a local biocide. A brown composite material has been used to fill isolated cavities in the structure. The substance has no integration function and falls out with touch.

Proposed Analysis. The first step is to evaluate normative properties to establish a baseline for treatment design, then to evaluate dysfunction characteristics, scope, and extent of disintegration. Most deterioration appears to have occurred close enough to the surface for evaluation and treatment. Subjective compression resistance using a 22-gauge probe and mechanical loading of sections to measure deflection will be used to determine the extent and scope of disintegration. Results will be mapped on a computer-assisted design system for graphic analysis.

The final step is to evaluate anticipated interactive energy forms. Particular attention will be given to anticipated mechanical loading during transportation. Finally, essential treatments will be recommended for evaluation and approval.

Potential Load. The artifact will travel to Australia via truck and air, travel through Australia, and then be placed on permanent exhibit in a controlled environment. It will not function as a sternpost and will be mounted flat, with its weight distributed across the exhibition table.

The largest single energy form that will interact deleteriously with the artifact will be the constant vibration and shock during the transportation process. Extreme mechanical shock could occur if the artifact is dropped, struck, or collides with something.

Because the artifact is simple, not joined, and for all purposes fabricated from a single material, hygroscopic alteration is a consideration only with respect to the materials of consolidation.

Normative Properties. The artifact was fabricated from white oak, a dense strong wood with a porous structure. Design and anomalies are negligible factors. The normative reserve strength of the artifact is, beyond doubt, very high for the potential load.

Dysfunction Properties. The following breakdown defines the level of dysfunction at 6-in. (15.2-cm) increments (Figure 18). V defines the vertical field in inches; V 0–6 is the material field from the base to 6 in. Trilateral analysis was used to identify regions of dysfunction for classification.

V 0–6:	Isolated masses affixed by friable sections. Little elasticity, and sections deflect with less than 0.33 psi load.
V 6–12:	Isolated masses affixed by friable sections. Little elasticity, and sections deflect with less than 0.33 psi load. Sound section reinforces disintegrated section.
V 12–18:	Main mass divided into two sections. Isolated masses affixed by friable sections. Little elasticity, and sections deflect with less than 0.33 psi load. Sound section reinforces disintegrated section.

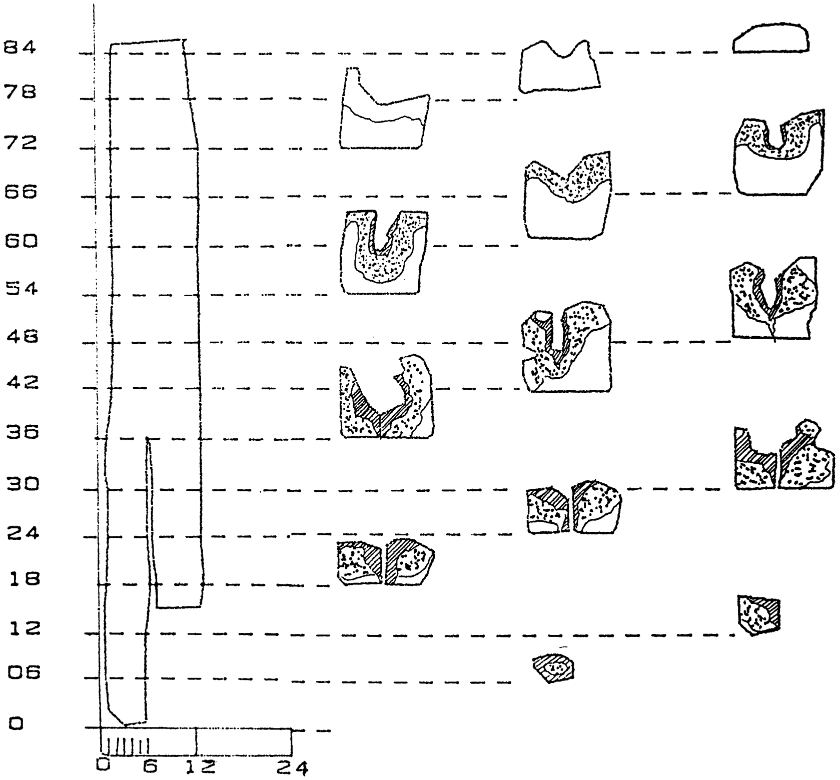

Figure 18. Vertical CAD analysis of sternpost, illustrating regions of severe and moderate decomposition.

V 18–24:	Main mass divided into two sections. Isolated masses affixed by friable sections. Little elasticity, and sections deflect with less than 0.33 psi load. Sound section reinforces disintegrated section.
V 24–30:	Main mass divided into two sections. Isolated masses affixed by friable sections. Little elasticity, and sections deflect with less than 0.33 psi load. Sound section reinforces disintegrated section. Heavy losses apparent in split cavity.
V 30–36:	Main mass divided into two sections. Isolated masses affixed by friable sections. Little elasticity, and sections deflect with less than 0.33 psi load. Sound section reinforces disintegrated section.

V 36–42: Main mass divided into two sections. Sound section reinforces disintegrated section. Cavity diminishing, disintegration associated with surface infestation and infection.

V 42–48: Irregular configuration with strong supportive core. Disintegration associated with surface infestation and infection.

V 48–54: Irregular configuration with strong supportive core. Disintegration associated with surface infestation and infection.

V 54–60: Irregular configuration with strong supportive core. Disintegration associated with surface infestation and infection.

V 60–66: Irregular configuration with strong supportive core. Disintegration associated with surface infestation and infection.

V 66–72: Irregular configuration with strong supportive core. Disintegration associated with surface infestation and infection.

V 72–78: Irregular configuration with strong supportive core. Disintegration associated with surface infestation and infection.

V 78–84: Irregular configuration with strong supportive core. Disintegration associated with surface infestation and infection.

Indication. Isolated and friable sections located at the base section of the artifact will disintegrate further with loading normally associated with transport: turbine-generated vibration and mechanical impact.

Recommendations. The recommendation is to reintegrate the friable sections with a semireversible consolidant. Because the artifact will not always be subjected to energy associated with transport, a highly reversible structure should be used to reinforce strength during transport.

Action. Methyl methacrylate inhibited by the phenol quinone was introduced to level 3 (V 12–18) disintegration up to V 48 with initiator. The consolidant was chosen for reversibility, ease of infusion, and reliability of polymerization. The method of application was through probe holes with a 22-gauge syringe (Figures 19 and 20). The total volume was determined to be in the proximity of 2.75 L.

A double, reversible, external skeleton (case) was designed to counteract travel-associated energy forms (Figures 21 and 22). The inner case functioned to secure the artifact physically while providing more substantial support to weakened masses. The inner case was designed to absorb higher vibration and sonic frequencies, but would not provide insurance against the potential for impact from being dropped or crashed into other objects. The second, outer case added impact resistance and a second layer of absorbent material to isolate vibration transmission.

Figure 19. Conservator injecting friable surface with 22-gauge syringe.

Polyurethane-coated plywood was prepared as the working base. Isolated poured foam was used to form an interlocking, conforming surface that was intimate to the shape of the artifact. The walls of the case were individually formed in a similar manner, with protrusions to support masses with a high dysfunction level.

The artifact was captured by an adjustable, tensioned system. Load was transferred through a system of closed-cell foam selected for density. The closed-cell foam was captured by a spring-loaded rigid system that transferred load to the inner case.

Figure 20. Consolidated field of sternpost.

The very rigid inner case transferred load to the less strong outer case (designed to fail before damage would occur to the inner case) through isolated pads of high-density polyethylene foam. Film layers of polystyrene provided a hermetic seal in the inner case. The environment was buffered by silicone gel to adjust for environmental changes that occur at high altitudes.

Because the artifact was to be moved throughout Australia, the case was designed for deconstruction and reconstruction. Consolidation was achieved with very little impregnated consolidant in isolated regions, only where it was essential. The remaining consolidation was ultimately as reversible and adjustable as the case.

Case II: Figurehead "Scotsman". The large, 12-ft figurehead "Scotsman" from the clipper ship *Glasgow* was appropriated in the late 19th or early 20th century. An early photograph (Figure 23) suggests that it sat

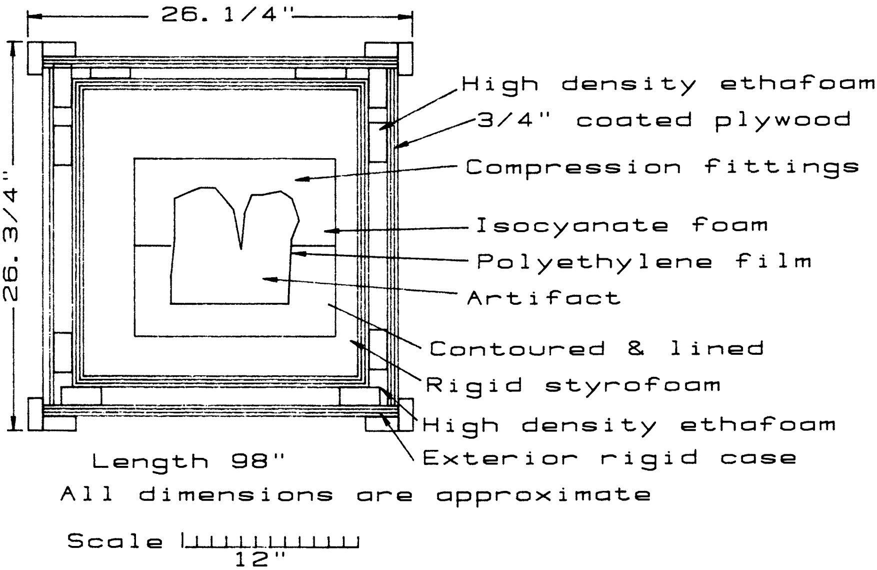

Figure 21. Consolidation case design, illustrating range of materials used.

on the ground in a shipyard for a period of time before a documented move to serve as a figurehead for an Albemarle Street, London, shop. It was privately purchased in the 1950s and moved to America, where it was mounted on a concrete block. The artifact was vandalized and disintegrated by dry rot and multiple insect colonies before being donated to the Fall River Marine Museum.

During its years as a decorative artifact, it suffered major losses of the right arm (facing position), fox head purse, sash, hair, nose, and other lesser elements. These losses were restored by area handymen with lumber stock, linseed putty, and house paint.

In the Fall River Maritime Museum, the artifact was laid on its back and buttressed by the curator in an effort to support its sagging structure. Diminution continued as a poria infection continued to revert the interior tissues to topsoil. As losses occurred, they were, unfortunately, filled with a range of materials from concrete to epoxy lagged with nails. Further decay occurred as the infection moved to decompose the restoration lumber stock.

Structural cracks, sagging, and compression loss were evident on initial observation. As analysis began, the considerable loss and degradation of materials became apparent. The project is currently in its final stages: an internal "skeletal matrix" has been installed, and an external brace is soon to be engaged.

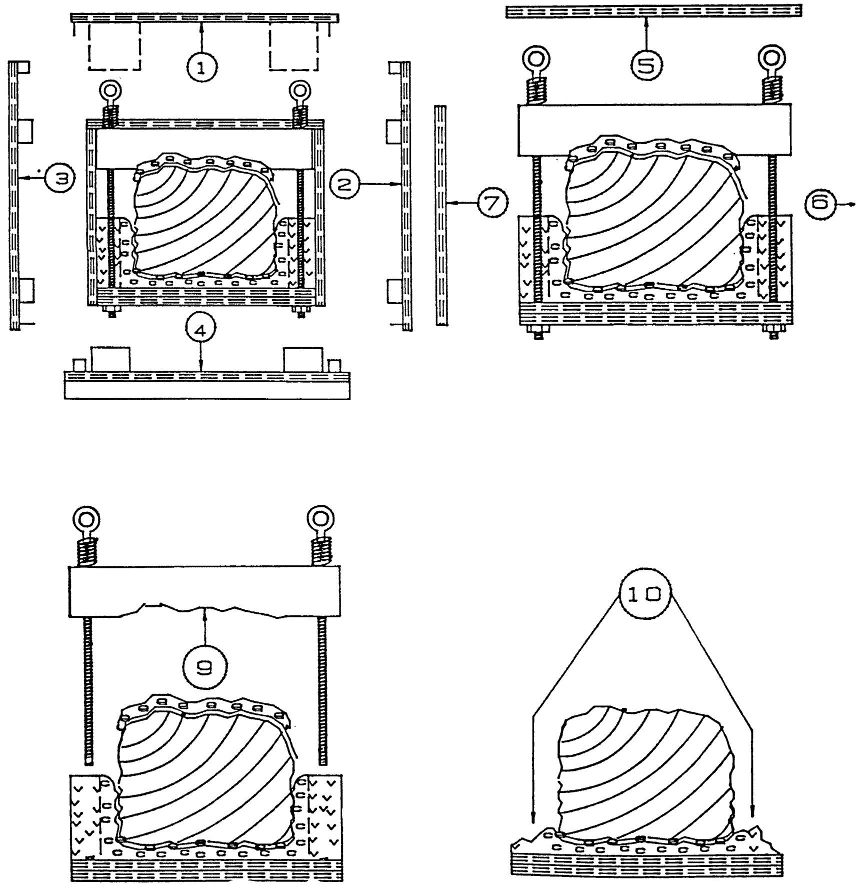

Figure 22. Case illustrating deconstructive and reconstructive design.

The overall objective is to arrest the decay, stabilize the artifact, and return it to a standing or "near original" mount position. The material project was to remove deleterious spurious materials, fill voids with appropriate materials, and to enhance the strength of the intrinsic artifact. Because of the serious state of diminution and the extreme exhibition load, a complex system of consolidation was designed to transfer the total load to a rigid heli-arced aluminum brace.

The following is the report on the initial condition of the figurehead.

Physical Description. The figurehead is an approximately 144- × 50- × 39-in. (366- × 127- × 99-cm) figure carved from joined blocks (Figure 24).

Origin. H.M.S. *Glasgow*, ca. 1828.

Figure 23. Early 20th-century photograph of the figurehead from the H.M.S. Glasgow.

Material(s). The primary and secondary material is *Pinus strobus* (American white pine). Spurious materials are also present: Cement, plaster, unknown composite fill, house paint, and iron and brass original and modern ties. The surface is polychromed.

Initial Location. The figurehead is in a sunken (subgrade) level exhibition chamber, which is exposed to the ground-floor exhibition room through a well-ventilated opening.

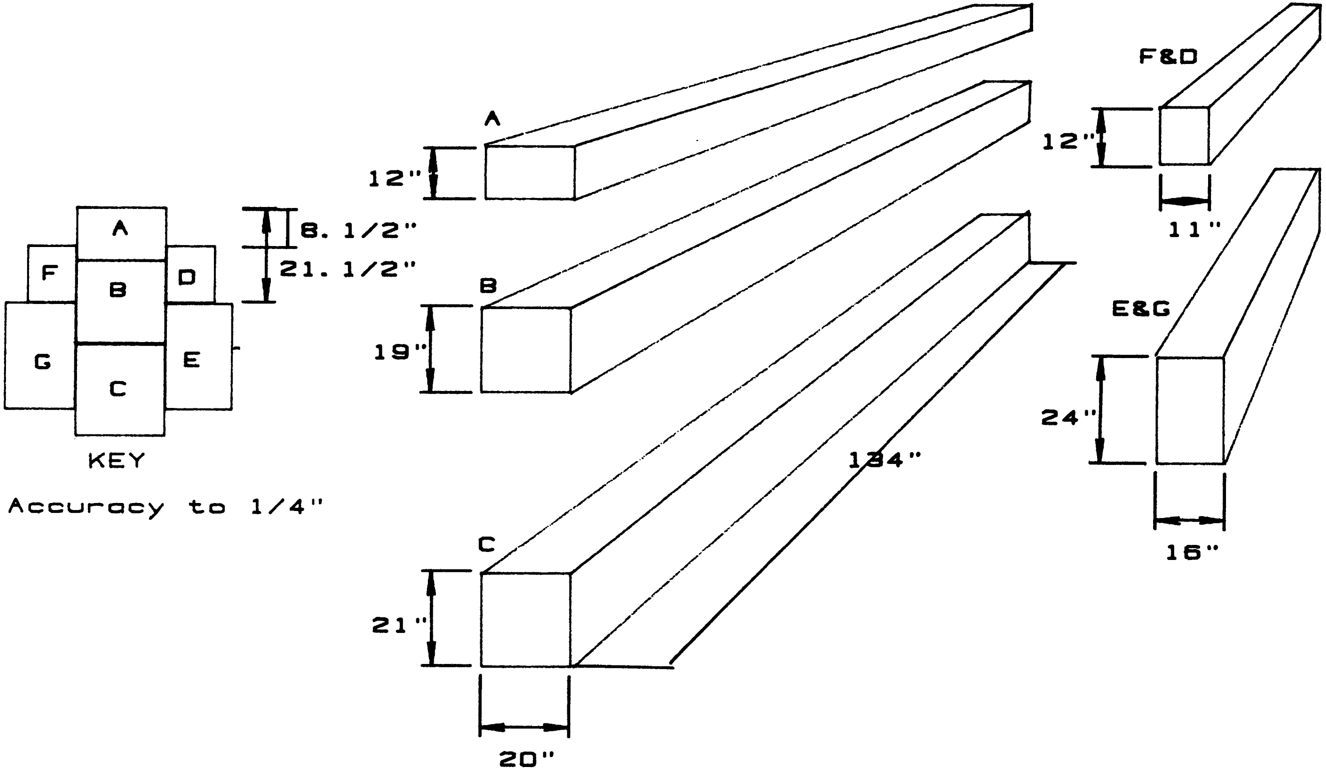

Figure 24. Carving block configuration used to determine normative characteristics of the figurehead artifact.

Condition History. The softwood figurehead spent a considerable time in a marine environment, where it was subject to hydraulic and wind stresses. At the decommissioning of the H.M.S. *Glasgow*, the figurehead was cut from the ship's structure and mounted for exhibition.

The figurehead was repainted many times during its exhibition period; little if any structural preservation action was taken; the object was permitted to degrade internally while external appearances were maintained.

Structural degradation became apparent in the late 20th century, when it began to lose significant portions of its structure. These heavily degraded broken sections were replaced with cement, plaster, and an unknown composite filling material. Later, iron rods were introduced into the structure in an attempt to retain rigidity.

Summary. The figurehead has been allowed to disintegrate for an excessive period of time and is in danger of total structural failure. The present location of the object is environmentally unstable and unacceptable as an exhibition chamber.

Analysis. The approach was to evaluate the condition and properties to establish a method of conservation. Analysis of the object included

1. Void-volume measurement to determine the location and degree of degraded materials. Sonic, X-ray, and probe methods were evaluated for practicality. Because of the extensive decay and numerous access cavities, probing was selected as the most suitable measurement procedure.
2. Stress analysis was considered to determine residual strength characteristics. After initial evaluation, it became apparent that the degree of residual strength was excessively below stability and that stress analysis was not warranted.
3. Because of the complexity and scope of the problem, trilateral graphic analysis was selected as a method to document the artifact and to evaluate potential consolidations. Three-dimensional mapping was digitized for hard copy and electronic manipulation (Figure 25).
4. Biological analysis, particularly of fungal predators, will be undertaken to determine safe exhibition parameters or to determine the most effective neutralization treatment.

Other conservation-related procedures not involving consolidation treatment were intentionally omitted from this report.

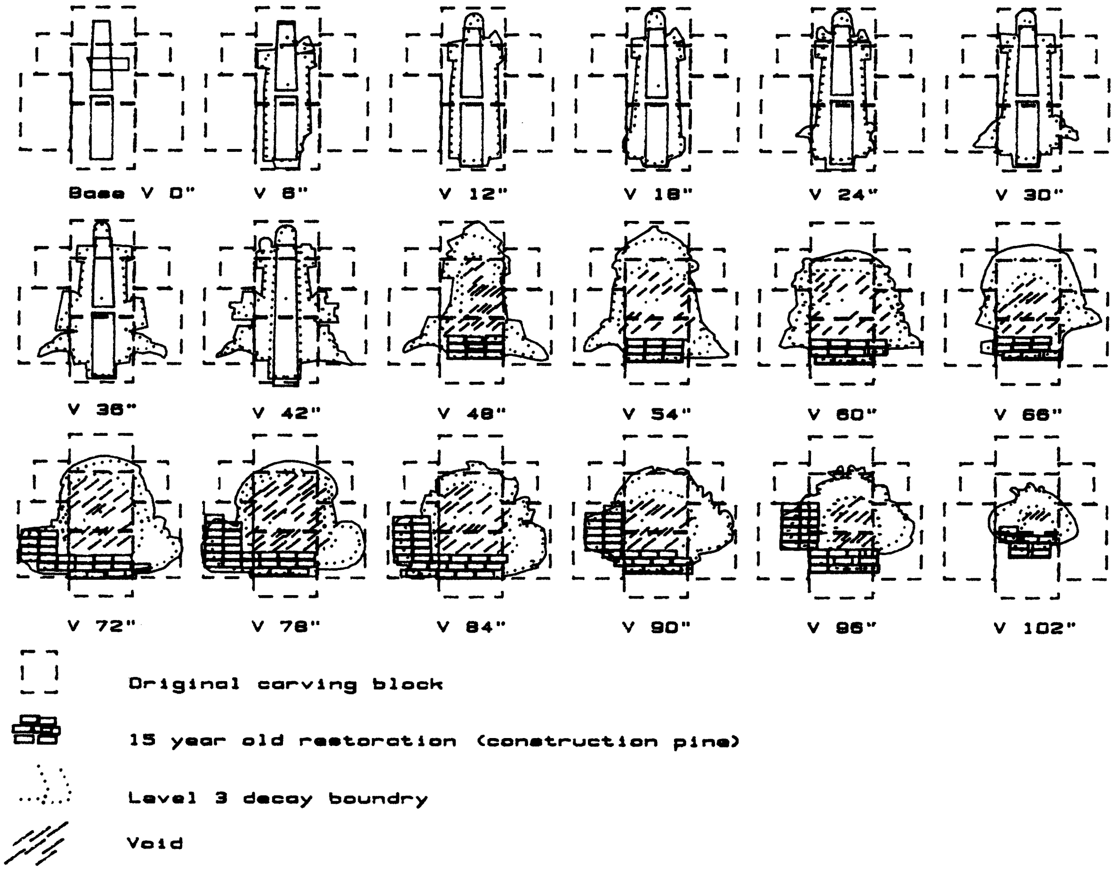

Figure 25. Overlay of section scans onto block configuration for normative property evaluation.

***Method*(*s*).** The following steps should be taken:

1. Visual, hand lens, microscopy should be used.
2. 0.25- × 18-in. (0.6- × 46-cm) core samples should be taken.
3. Conductivity moisture content readings should be taken.
4. Mechanical penetration resistance should be measured.
5. Pitch and resonance response should be measured.
6. An engineering consultant should be called.

Potential Load. The artifact will be mounted in a permanent exhibition room in a diagonal position that reflects its original orientation. The room will have moderate environmental controls. The artifact will be lagged to a secure metal stanchion. Interactive energy will most likely consist of static and hygroscopic load; the primary concern is material collapse or fatigue and the interface between the consolidation system and intrinsic fabric.

Normative Properties. The artifact was fabricated from joined white pine carving blocks (Figure 8). The blocks were joined by irregularly spaced wooden dowels and brass pins. The joints are a design weakness, as the extremity details are poorly supported. The joint block relationship to dysfunction will be a major factor in the residual strength determination (Figure 9).

Dysfunction Properties. Initial examination and analysis of the figurehead structure indicates that the structure is very close to total failure. Failure is already apparent in collapsed sections and through dissociation of peripheral details at the site of block joints and where the heavy decay has broken the surface. Continued failure will most likely occur as continued collapse of the main section and breaking of the figure across its axes. The interior structure has little useful integrity and cannot be expected to support any mechanical stress; parting of the head and other structural portions during relocation to the exhibition chamber provide graphic evidence that disintegration has been an ongoing occurrence at a very serious level.

The artifact is degraded with extensive void volume, and massive sections of level-2 and -3 heavy decay. Vertical analysis is revealed by profile sections taken at 6-in. (15.2-cm) intervals (Figure 26).

Loss of axial orientation properties (cellulose and hemicellulose components in the ancillary structure) have seriously diminished structural properties. Amorphic friable material appears to lie 0.5–3 in. (1.27–7.6 cm) under the polychromed surface.

Hand lens analysis of the sample has revealed frass from several larval predators. Termite, ant, and beetle populations appear to have been active at different times.

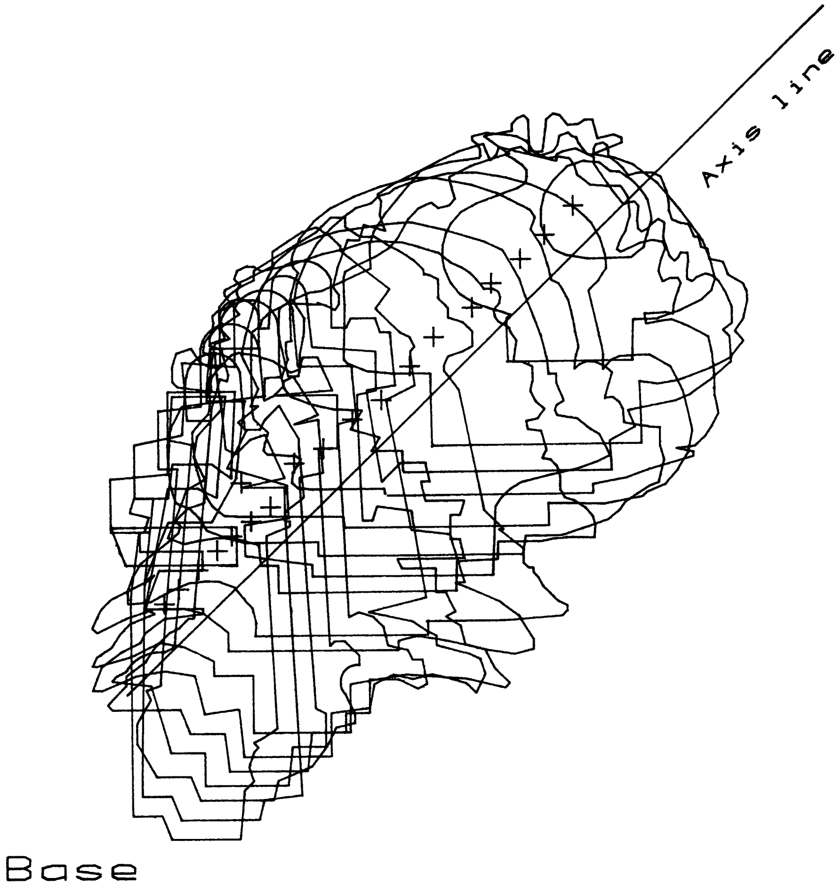

Figure 26. Three-dimensional CAD analytical drawing, illustrating the distribution of weight across the axis of the figurehead.

Spurious restoration materials, cement, plaster, and an unknown composite fill are not hygroscopic and will create physical differentials as moisture content alters. These materials pose a further threat from collapse attributable to weight. Tissues surrounding the fills are compressed, impregnated with oxidation salts, and are not capable of maintaining adhesion when in tension.

Successive paintings of the artifact have served to preserve much of the surface wood through the toxicity of the lead paint. The successive layers have also provided a mechanical layer that may or may not have preserved much of the carving detail. Evidence of original surface may be preserved by these layers and irregular pockets of linseed putty.

Mechanical penetration resistance and pitch–resonance response have revealed extensive degradation of the ancillary structure. There appears to be an extensive area of disintegration, with areas of collapse and loss voids. Several locations were tested, with similar results; the heavily repainted surface is often the primary form-retention material.

Moisture-content readings are not consistent with the ambient environment of the artifact, and thus indicate the potential for active dry rot.

Indication. The extent and degree of disintegration is severe. Residual strength is not adequate to support the artifact's own weight; it is collapsing in on itself.

Recommendations. Considerable strength restoration must occur before a return to an exhibition mount is possible. Treatment should include reintegration of internal, friable sections with a moderately gap-filling consolidant with a high strength coefficient. This interior solidification will help to retain configuration during treatment and serve as an interface for a semirigid internal matrix.

Internal materials that have reverted to soil and no longer contain any significant cultural information will be removed and replaced with an internal integrated system that will transfer load to an external frame.

Because of the mass of the artifact, the consolidated layer will be limited to a layer capable of retaining and supporting configuration. Total simple consolidation impregnation will be too heavy for any one material to support the intended mount.

Action. A thorough analysis of the structure was undertaken to determine the exact extent of decay. Particular attention was devoted to the relationship of the carving block (inherent design weakness) joints to the dysfunction.

Because of the extensive treatment to be performed, the object was moved to a suitable work location. Temporary strength-enhancement jigs and a suitable foam moving carriage were constructed to ensure integrity during the interim move.

Photographic and written documentation of the existing condition and all changes were made. Spurious materials (cement, plaster, and Fiberglas that could be nondestructively removed) were removed. This removal reduced weight and kinetic load induced by the masses and opened the interior cavity for access.

The interior reverted materials were scooped out (by hand). Any intact sections were stored for later examination. The interior cavity was opened to between 1 and 6 in. (2.5 and 15.2 cm) of the exterior.

The open cavity allowed exceptional access to analyze the interior of the artifact. Strength readings of the interior were taken and charted on the section scan (Figure 27). The detail shown in Figure 28 illustrates the value

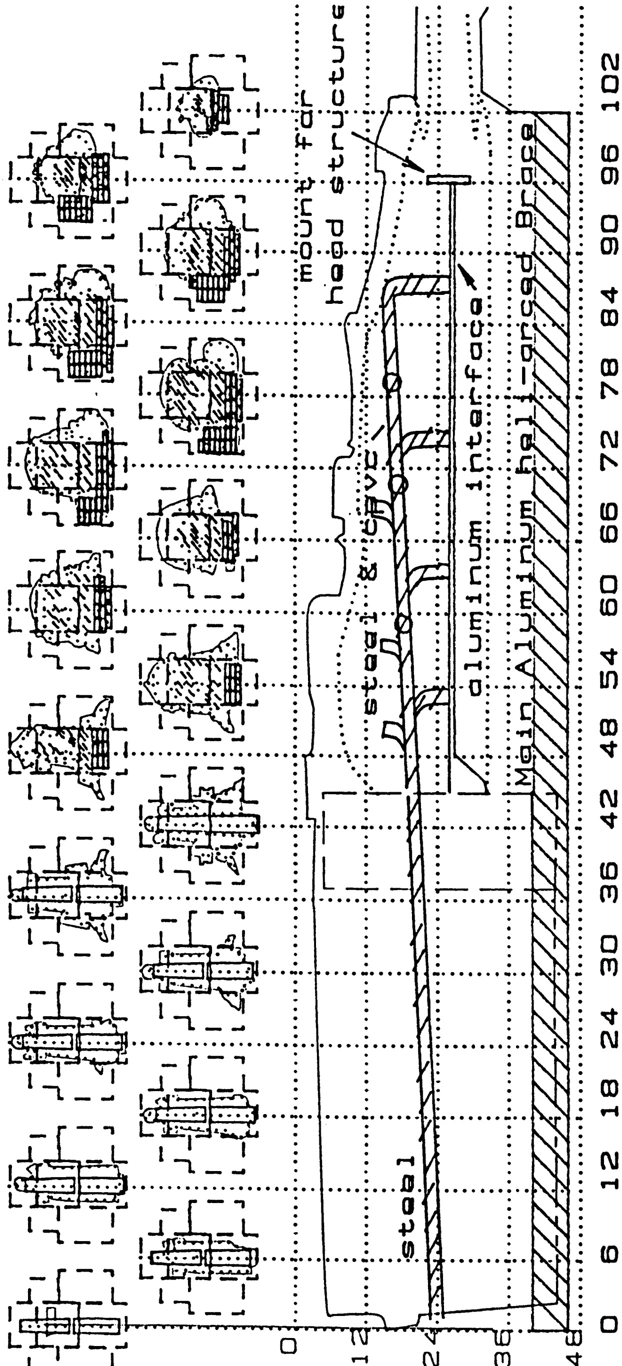

Figure 27. Section layout illustrating levels of degradation and void volume. Initial transition brace design is indicated in center of profile cavity.

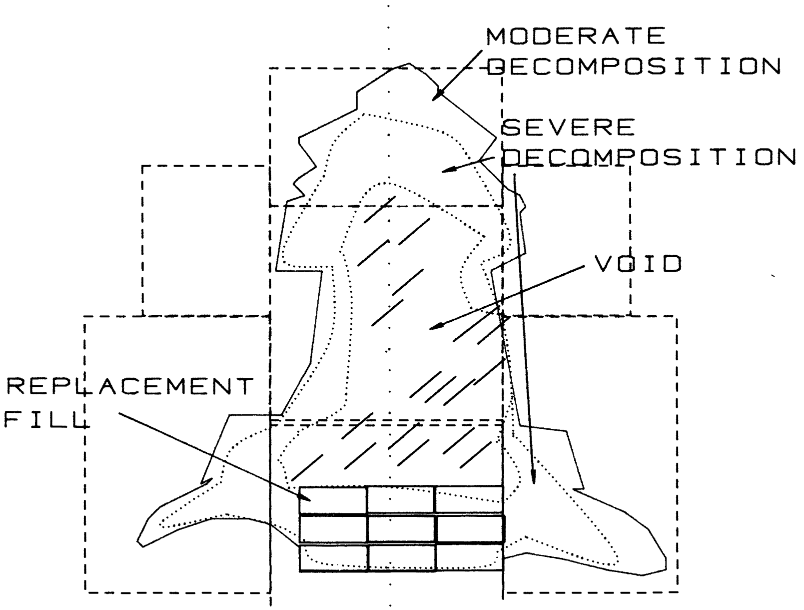

Figure 28. Close-up of section at V 48 illustrating void (cross-hatched) surrounded by severe and heavy disintegration.

of section analysis. Degradation levels are graphically indicated relative to mass and joinery.

The outer surface was reintegrated by incremental impregnations of thinned epoxy. The thickness of the impregnation was between 1 and 2 in. (2.5 and 5 cm) on average, with some critical fields being impregnated to a greater depth.

Construction of the internal skeletal brace began with the insertion of a 0.75-in. (1.9-cm) steel rod through the center of the artifact (Figure 27). The upper body cavity section of rod was surrounded by 1.5-in. (3.8-cm) poly(vinyl chloride) (PVC) pipe, which was affixed to the rod with epoxy putty. The integrated steel, epoxy, and PVC pipe formed a semiflexible internal skeleton. The skeleton was enlarged through T and Y connections into an internal matrix. This enlargement allowed the dissociated block sections to be lagged together with particular attention to the inherent design weakness of the artifact, supporting sections with low normative and dysfunction properties.

Polyurethane, a semirigid foam, was selected to transfer load from the artifact inner surface to the internal skeleton, which is to be linked directly to the rigid external brace.

The foam, mixed in small, workable batches, was injected into loosely confined cavities. The small quantities allowed a safety margin to ensure that the bonding to the artifact fabric was satisfactory and that cure was consistent. Polyethylene sheets were used to contain and isolate batches.

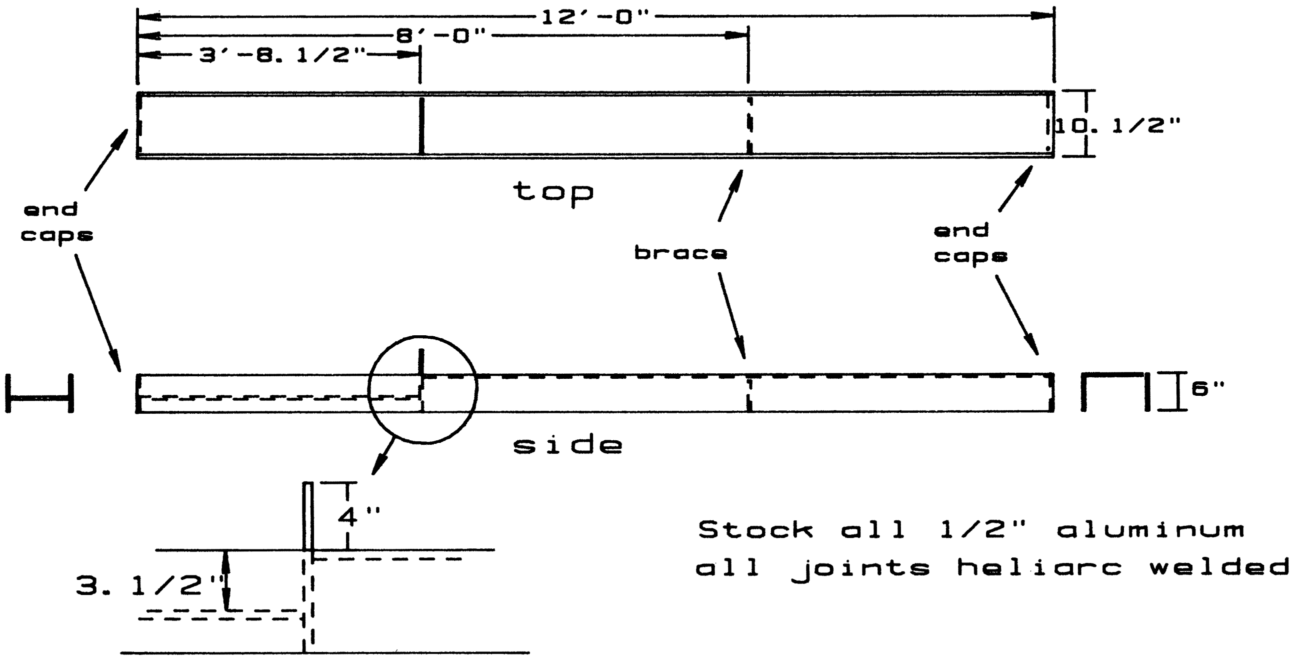

Figure 29. Heli-arc aluminum back brace to provide final restoration of rigidity.

The internal skeleton was terminated into three extension posts that projected from the back of the figure at the site of the mast's mount. The posts transfer the load to a rigid internal transition brace, which is mounted to the key block of the figurehead. The transition brace will be affixed to the external brace fabricated of heli-arced aluminum (Figure 29). The brace was designed to impart adequate rigidity to the artifact in its exhibition posture. To ensure accuracy, a mechanical engineer was consulted for all material and design configuration.

Current Status. The reinforcement brace is currently ready for mounting. It will be adjusted to the CAD profile to ensure that the original configuration is conserved.

Once the artifact has been consolidated and stabilized, the foam transition component will be extended to replace missing surface configuration. The foam can be carved and coated with a latex microballoon emulsion to

Figure 30. Head of figurehead, illustrating degree of spurious materials: right eye, nose, and left cheek were composed of cement, Fiberglas, and plaster composite.

"pull in" visually with the existing surface texture. The insets, based on early photographs for accuracy, will retain the cultural integrity of the artifact. Although the insets are not apparent to the naked eye, they are apparent on close examination, by surface density, and by pitch response.

The final consolidation will be surface impregnation with ethyl methacrylate. The simple consolidant will be brushed over decayed surface por-

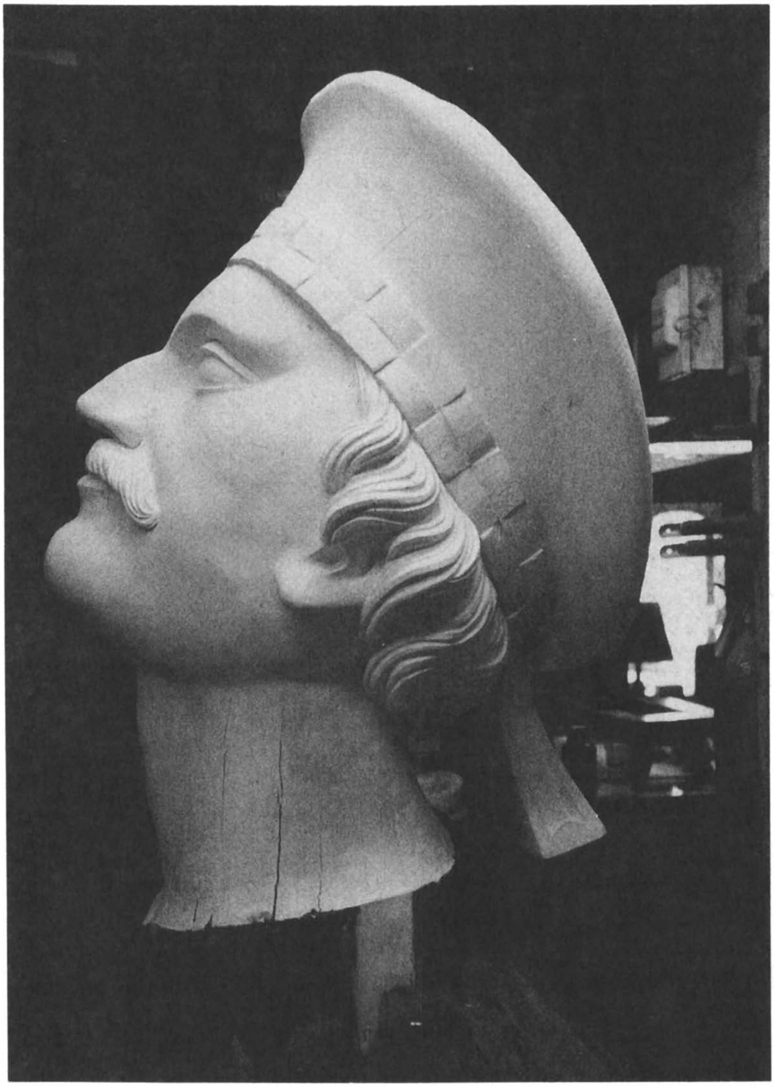

Figure 31. Head of figurehead consolidated with epoxy, metal armature, and foam.

tions to act as a skin. The selection of the consolidant is based on its reversibility, predictability, and compatibility with wood and the primary consolidation material, epoxy.

Head of the Figurehead

The head of the figurehead has been completed. Like the main body of the figurehead, it contained large quantities of cement lagged by nails and Fiberglas (Figure 30). Following careful trilateral documentation, spurious materials and the internal reverted tissue were removed. At this time, the head was in large sections.

The dissociated tissue was, as in the main body, reintegrated with a thin solution of epoxy. A 22-gauge syringe was used to impregnate the inner 0.5–1.5 in. (1.27–3.8 cm) of tissue, depending on its condition. A skeletal armature was affixed to the frontal section and, through cavities, carefully lagged to the other sections.

Small batches of polyurethane foam were used to set the matrix by filling the voids. The foam was allowed to flow out through surface cavities. This foam formed the base material for cutting in the missing configuration. (Photodocumentation of the original configuration was available as a guide.)

When all components of the head were reintegrated and the surface configuration was completed, the head was coated with a heavy latex–microsphere suspension (Figure 31). This coating provided a UV-radiation-stable surface, protected the not-UV-stable foam, and permitted further contouring.

Foam has several advantages as a structural and surface material. It is light, has excellent mechanical and physical properties, and can easily be detected as an unoriginal material, a feature that helps prevent confusion.

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13

Consolidation of Dry Archaeological Wood by Impregnation with Thermoplastic Resins

Arno P. Schniewind

Forest Products Laboratory, University of California, Berkeley, CA 94720

Soluble resins have advantages as well as disadvantages over other consolidants, such as thermosetting resins, for deteriorated wood. Methods of application and choice of solvents are discussed. The effectiveness of soluble resins depends on the degree of deterioration, ranging from little or no effect on the properties of sound wood to substantial strengthening of severely degraded wood. Retained solvents can act as plasticizers and thus influence consolidant effectiveness. The adhesive qualities of consolidants were also investigated. Consolidation with soluble resins, like all real systems, was found to be irreversible in the strict sense, but some of the commonly used consolidants could be removed almost completely, depending on the solvents used.

PROBLEMS ASSOCIATED WITH DRYING of severely deteriorated and weakened material are not evident when dealing with dry archaeological wood, as distinct from waterlogged wood. Nevertheless, dry wood may have undergone deterioration that makes it weak and friable. If the state of preservation is such that the intended use and exposure would threaten the safety of the object, a consolidation treatment may be indicated. The purposes of such treatment would be to arrest further deterioration, to reattach loose particles, and to provide a general strengthening that enables the object to withstand the stresses of its intended use (*1*). The use referred to here may be identical with the original use of the object, or it may be simply the use entailed by occasional removal from storage to exhibition areas and vice versa. The nature

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of the consolidation treatment must be tailored to the requirements of the intended use.

Materials used as consolidants may be classified as either natural or synthetic in origin. Natural consolidants include water-soluble glues such as hide glues, solutions of natural resins such as shellac, molten waxes such as beeswax, and drying oils such as linseed oil (*2*). These natural materials have their advantages and limitations, and are still used as consolidants, but will not be discussed further here.

Synthetic resins may be either thermoplastic or thermosetting. Thermoplastic resins are sensitive to temperature (i.e., they will melt and flow at elevated temperatures and are generally soluble in a variety of neutral organic solvents). Thermosetting resins, on the other hand, will decompose before they will melt and are not truly soluble. Treatments with thermosetting resins are therefore completely irreversible, but sometimes their use cannot be avoided. Epoxy resins are the best examples of thermosetting resins used in conservation, particularly in architectural preservation, where their excellent strength properties are required for the repair of fully functional structural elements.

Thermoplastic resins can be introduced into wood either in solution or as liquid monomers, which are then polymerized in situ (*2, 3*). Cross-linking agents can be included with the monomer to produce a thermosetting resin upon polymerization, initiated by heat, catalyst, or γ irradiation (*4*). Even if there is no cross-linking, the prospects for reversibility are not very good for such systems (*3*). Surface residuals of poly(methyl methacrylate), polystyrene, and polyester mixtures could only be removed with some difficulty with solvents (*5*). The present discussion will be limited to thermoplastic resins that can be introduced into wood in solution.

Soluble Resins as Consolidants

Materials used as consolidants should (1) have long-term stability, including resistance to cross-linking; (2) not change the appearance of the treated object; (3) not create significant internal stresses during solidification within the object; (4) be effective in fulfilling their purpose of strengthening; (5) achieve good penetration and consolidant loading (consolidant retention, i.e., weight gain after consolidation); and (6) have the characteristics required for a reversible treatment. Soluble resins have the potential of meeting or approaching all of these criteria.

Most soluble resins that are being used as consolidants in conservation today are also used in picture varnish. Thus these resins have a history of satisfactory use that, in the case of poly(vinyl acetate), extends over almost 60 years (*6*). Consolidants can cause some darkening of wood surfaces much in the way wetting them with water deepens their color, but with proper technique they will not leave a shiny surface film (*7*). Because excessive shrinkage leading to internal stresses would be objectionable in a picture varnish as well, we may presume that this shrinkage does not become a problem in wood consolidation. Effectiveness, a relative matter involving both adhesion to wood and cohesion within the resin, will be addressed in more detail later. Substantial penetration is possible, but polymer loading is limited by resin concentration and the void volume in the wood. Finally, some evidence suggests that these treatments are reversible, at least to a first approximation (*8*).

The particular advantages of soluble resins as consolidants are that they are easy to apply by a variety of methods and that they offer the potential of reversibility, at least in the short term. The main disadvantage is that their effectiveness in strengthening deteriorated wood is somewhat limited. This is not to say that they are ineffective. However, they are introduced in the form of solutions, typically with a solids content of 20% or less. Therefore, the maximum polymer loading that can be achieved is limited to 20% or less of the total void volume. In addition, the resin itself may not be nearly as strong as sound (undeteriorated) wood parallel to grain, so that the achievable amount of strengthening is also limited. The greatest potential for effective strengthening is therefore found with the most severely deteriorated material.

According to Grattan (9), the most common polymers used in solvent–resin consolidant systems are acrylics, poly(vinyl acetates), poly(vinyl butyrals), and soluble nylon. Of these, soluble nylon has since been shown to be unsuitable because it inevitably cross-links and embrittles within as little time as a few weeks (*10*). The others are known to have excellent long-term stability (9). Most likely the stability of polymers placed inside the wood may be even better, because they would be protected from light-catalyzed degradation reactions. Possible wood–polymer interactions, however, are unknown at this time.

Methods of Application

Although commonly used resins are sometimes sold as solutions, they are usually obtained in powder or pellet form. No single solvent is suitable for all types of resin, so that the choice of solvent must be tailored to the particular resin used. For wood, the first choice might be between polar and nonpolar solvents. The latter would allow resin solutions to penetrate wood better because polar solvents tend to get adsorbed on cell walls, and adsorption reduces their mobility (*11*). Additionally, solvents with low boiling points are preferable because they minimize problems with residual vapors. Another consideration is the viscosity of a given solution. Low viscosity is necessary if good penetration is desired. Some commonly used solvents are ethanol, methanol, acetone, and toluene.

Solution concentration needs to be decided by balancing the requirements of good penetration and adequate polymer loading. Given complete saturation and a constant fraction of void volume, loading will be in direct relation to polymer concentration in solution, but at high concentrations penetration may be incomplete because of high viscosity (*12*).

If consolidation is required only for surface layers of an object, application by brushing may be sufficient. Consolidant may be applied in several coats, but eventually a saturation of surface layers will lead to formation of undesirable glossy films. More resin can be introduced by application of many coats of low-concentration solutions than by use of solutions in high concentration, because the latter lead to early gloss formation (*9*). Barclay (*7*), for example, used a 5% solution of poly(vinyl butyral) resin (Butvar B90) in ethanol for brush treatment of parts of an English fire engine.

Better penetration and loading can be obtained either by soaking in consolidant solution or by continuous (or intermittent) spraying of solution within a closed system (*13*). Spraying is advantageous for large objects where it would be neither practical nor desirable from a safety viewpoint to prepare the quantity of solution required for soaking. Consolidation of a dugout canoe 5 m long was accomplished by spraying with a 13% solution (weight basis) of a poly(vinyl acetate) resin (AYAF) in methanol within a temporary enclosure (*14*). Another variation is to apply consolidant dropwise over a period of time (*15*).

Soaking or spraying may achieve complete penetration, but this will take time. The best chance of getting maximum penetration and maximum loading as well is to use vacuum impregnation. For small objects this method would not require elaborate equipment, but it may not be practical for large objects. Objects need to be evacuated while submerged in consolidant solution. After the air is removed from the wood, the vacuum is released and consolidant solution is pushed into the wood by atmospheric pressure. Vacuum impregnation was used for detachable parts of the fire engine mentioned previously. In that case the concentration of consolidant was raised to 20%, as it leads to greater loading and the restrictions that apply to brushing are of no concern (*7*).

Effectiveness of Soluble Resin Consolidants

The effectiveness of consolidation treatments depends on the depth of penetration and the loading of consolidants, on the type of consolidant and the type of solvent used, and on the extent of wood deterioration. For small objects where the only concern might be stabilizing the surface against abrasion during handling, a surface treatment with shallow penetration may be quite sufficient. If, on the other hand, some overall strengthening is required, it will be advantageous to obtain full or nearly full penetration. Given full penetration, effectiveness as measured by improvements in strength of the wood after consolidation would be expected to increase in some proportion to polymer loading. This increase was found to be true to some extent for deteriorated wood treated with poly(vinyl butyral) and acrylics, but in some cases little or no difference was found between loading of about 20 versus 30% (*12*).

When sound ponderosa pine wood was treated with poly(vinyl acetate) (AYAF) in methanol at either 5.67 or 13.2% concentration (weight basis), no measurable increase in strength could be observed (*14*). However, significant increases in strength have been found for deteriorated Douglas-fir taken from bacterially degraded foundation piles. Figure 1 shows some data taken from several studies that indicate a functional relationship between the degree of deterioration and the improvement that could be achieved by treatment with poly(vinyl butyral) resin (Butvar B98) as 12.5 or 15% solutions (weight basis) to give approximately 20% polymer loading (*12, 14, 16*). Samples with the lowest residual bending strength (highest degree of deterioration) show the greatest improvements in strength following consolidation.

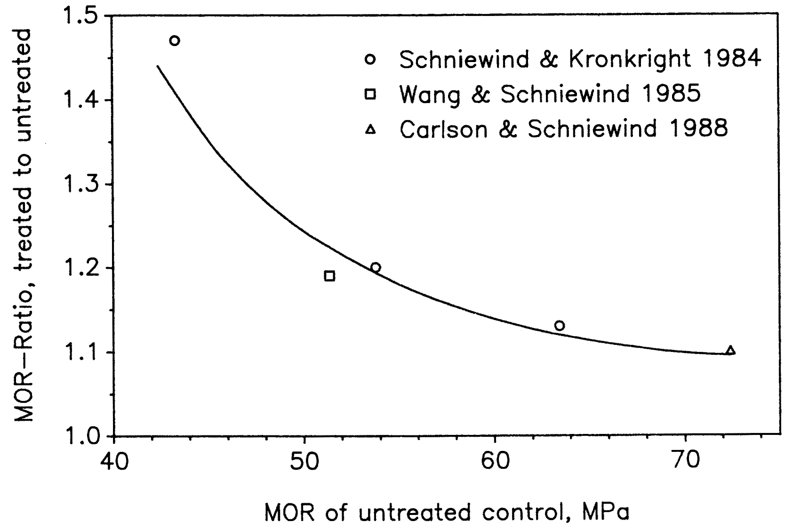

Figure 1. Improvement factor; ratio of modulus of rupture (MOR) (bending strength) values of wood treated with Butvar B98 and untreated wood for deteriorated Douglas-fir at various levels of residual bending strength (degrees of deterioration).

Table I shows some physical data for several commonly used consolidants. The improvement factors of the first four resins—i.e., the poly(vinyl butyrals) (Butvar B90 and B98), the acrylic (Acryloid B72), and the first poly(vinyl acetate) (AYAT), which has the highest molecular weight—were shown statistically to be significantly different from 1.0 (1.0 implies no im-

Table I. Properties of Resins and Their Strengthening Capability

Resin	*Molecular Weight*	*Tensile Strength, MPa*	T_g, °C	*Improvement Factor*[a]	*Ref.*
Butvar B90	45,000	46	68	1.14	12
Butvar B98	34,000	46	68	1.19	12
Butvar B98	34,000	46	68	1.20	14
Acryloid B72	–	–	40	1.16	14
AYAT	167,000	29	28	1.13	14
AYAF	113,000	18	24	1.10	14
AYAA	83,000	10	21	1.03	14
AYAC	12,800	[b]	16	1.11	14

[a] Improvement factor is the ratio of bending strength (MOR) values of treated wood vs. untreated controls.

[b] Listed as "not practical to measure."

provement); the others were not significant. The explanation for the lack of improvement with the other poly(vinyl acetates) lies with their relatively low tensile strengths—sound Douglas-fir wood has a tensile strength of about 125 MPa—and their low glass-transition temperatures, T_g, which are near or even below room temperature.

A rough estimate of the properties of a composite can be obtained from a volume-weighted average of the properties of the components, which makes the properties of the resin so important (*12*). Polymers near or above their glass-transition temperature lose stiffness and become rubbery, in which state they can contribute little to improving the strength of a much stiffer component. The best improvement factors were obtained for Butvar B98, followed by Acryloid B72 (trade name for an acrylic resin), and Butvar B90. Similar conclusions were reached by other investigators (*9*, *15*). The major disadvantage of poly(vinyl butyrals) is the relatively high viscosity of their solutions (*9*), which appears to make them somewhat more difficult to remove again (*15*).

Retained Solvents as Plasticizers

Retained solvents may act as plasticizers (i.e., unless the solvent evaporates completely, the deposited resin may not have the same properties as the original solid in its pure state). Retained solvent lowers the glass-transition temperature. If the T_g of the mixture is at or below room temperature, rubbery behavior will result, and consolidant effectiveness will be reduced. Acryloid B72 seemed to retain solvent in films cast from acetone and toluene solutions and then air-dried (*12*). Further study showed that Acryloid B72 may retain measurable amounts of solvent even after 30 days at room temperature (*16*, *17*). Results are shown in Table II.

After 1 day of air-drying, substantial amounts of solvent were retained and T_g values were too low to measure. After 30 days, only traces of acetone

Table II. Glass-Transition Temperatures and Retained Solvent Concentrations of Cast Films

	Solvent		Drying Condition					
			1 Day, 20 °C		*30 Days, 20 °C*		*30 Days, 50 °C*	
Polymer	*Type*	*B.P., °C*	T_g, °C	*Residual Solvent, %*	T_g, °C	*Residual Solvent, %*	T_g, °C	*Residual Solvent, %*
B72	Acetone	56	–	5.8	39	0.3	40	0.0
B72	Ethyl acetate	77	–	6.3	–	2.2	40	0.2
B98	Methanol	65	–	19.7	54	3.2	75	0.3
B98	Toluene–ethanol	74[a]	–	12.3	49	4.8	66	1.5

SOURCE: Adapted from ref. 16.

[a] Azeotrope boiling point of toluene–ethanol–water.

remained in Acryloid B72, and T_g values approached those of the original resins. The fact that some of the T_g values in Table II exceed those for the same resins given in Table I probably reflects the method (differential scanning calorimetry, DSC) used for the resins in Table II. DSC tends to give values 5–8°C greater than the method known to have been used for the Butvar data in Table I. The remaining resin–solvent combinations show more substantial residual solvents, and T_g for the Acryloid B72–ethyl acetate combination was still too low to measure.

Films dried for 30 days at 50°C showed normal values of T_g for Acryloid B72 and only a trace of retained solvent. For Butvar B98 the solvent removal was not as complete. The data also show that the solvents with higher boiling points (i.e., ethyl acetate and the ethanol–toluene mixture) are more difficult to remove than acetone or methanol. When the same process of drying at 50°C was applied to wood specimens treated with consolidants, the Butvar B98 specimens dried at the elevated temperature had greater improvement factors than those dried at room temperature, whereas for Acryloid B72 the opposite was true (*16*). The data of Table II would have indicated improvements connected to drying at elevated temperature for both resins.

The difference in behavior probably results from the fact that the heat treatment was carried out above T_g for Acryloid B72 and below T_g for Butvar B98. Such a heat treatment or annealing can lead to improved properties if it is carried out below T_g (*18*). Similar effects take place at room temperature (if the T_g is above it), but at a lower rate. Of course, prolonged heating at temperatures as high as 50°C could rarely, if ever, be justified for dry archaeological artifacts.

Adhesive Qualities of Consolidants

An effective consolidant must adhere well to the material to be treated (*2*, *9*, *19*) and must act as an adhesive to reattach loose fragments (*7*, *15*). An acrylic (Paraloid B72, the European designation for Acryloid B72) was tested for use as a conservation adhesive in the form of a 50% (weight basis) solution and performed satisfactorily (*20*). In another study, the adhesive qualities of Acryloid B72, AYAT, and Butvar B98 in the form of 15% solutions (weight basis) (i.e., a concentration suitable for consolidation) were investigated. At this concentration the viscosity of the consolidant solution is much lower than that of most adhesive formulations. Tests were made with polar solvents (acetone for Acryloid B72 and ethanol for AYAT and Butvar B98) and also with nonpolar solvents (toluene for Acryloid B72 and AYAT and a 60:40 mixture of toluene and ethanol for Butvar B98, for which a suitable nonpolar solvent in its pure form could not be found). Some of the results are summarized in Figure 2.

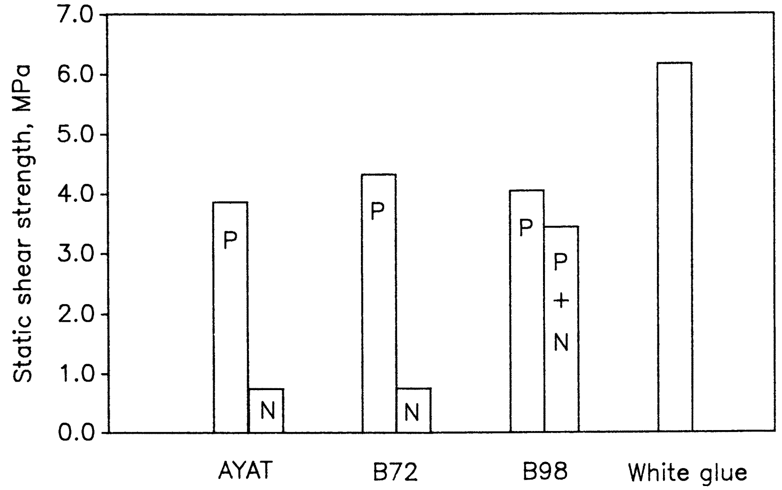

Figure 2. Static shear strength values for adhesive joints in deteriorated Douglas-fir made with AYAT, Acryloid B72, Butvar B98, and PVA emulsion "white glue". Key: P, polar solvent; N, nonpolar solvent. (Adapted from ref. 21).

Figure 2 shows average static shear strength properties for deteriorated Douglas-fir (*21*). When polar solvents are used, the shear strength of joints made with the three consolidants is about the same. By comparison, the shear strength obtained with consolidant solutions was only about two-thirds of the value of joints made with a commercial PVA "white glue". The difference is hardly surprising because the white glue is specifically formulated as an adhesive, which implies a high enough viscosity to prevent excessive penetration. The consolidant solutions, on the other hand, are formulated to penetrate well. The solution tends to do just that, leaving what is commonly termed a "starved joint". On the basis of these considerations, the adhesive qualities of all three consolidants can be termed excellent.

The conclusion of excellence, however, is reserved for consolidants dissolved in polar solvents. When toluene was used as the solvent, very little adhesive quality remained for AYAT and Acryloid B72. The use of toluene–ethanol as solvent reduced the shear strength for Butvar B98 by a relatively small amount, compared to ethanol alone as the solvent. These results agree with previous consolidation tests, in which the improvement factor tended to be larger for polar solvents than for nonpolar solvents (*12*). The poor adhesion of systems with nonpolar solvents may in part result from the superior penetration of nonpolar solvents, leaving little or no "adhesive" on the surfaces to be bonded.

Reversibility of Consolidation Treatments

Consolidation treatments with soluble resins can be considered reversible in principle, but it has been questioned (*1*, *9*) whether this reversibility would ever be practically feasible. Experiments with an acrylic and a poly(vinyl butyral) consolidant showed that most of the resin could be removed from treated wood, and that the acrylic could be removed more readily than the poly(vinyl butyral) (*15*). In another study, a consolidation treatment of archaeological wood with Acryloid B72 in toluene could be substantially but not completely extracted again, as evidenced by scanning electron microscopic examination (*22*).

Several processes take place when wood is treated with solvents. Solvents may swell wood, depending on their nature; they may extract some of the adsorbed moisture; some of them may be retained in wood by tenacious adsorption within; and most importantly, the solvents may remove wood extractives (*8*). Thus, some of the extractives may be removed or redistributed within the wood during consolidation treatment, and more may be removed along with the consolidant when attempts are made at treatment reversal. It is therefore not possible to return the wood to exactly the same state as before the initial consolidation treatment.

Loss of extractives implies loss of potential diagnostic features, but otherwise does not necessarily have any practical significance for archaeological wood because the amount is usually small. It is therefore desirable to investigate how closely reversibility can be approached, even if it cannot be reached in the strict sense. Results of experiments to explore this question (*23*) are summarized in Table III. The experiments were made with deteriorated Douglas-fir. Specimens measuring 0.25 × 1 × 2 in. were first conditioned to a constant moisture content of nominally 12%, treated by vacuum impregnation with a 15% solution (weight basis) to a polymer loading of 21–28%, reconditioned, extracted, and reconditioned again for final weight determination. Extractive content was determined on parallel control specimens. Extraction was accomplished by Soxhlet extraction or by soaking, with or without agitation and several changes of fresh solvent (*23*).

Table III. Reversibility of Consolidation Treatments as Indicated by Residual Resin Content

Polymer	*Solvent*	*Extraction Method*	*Residual Resin, %* *Uncorrected*	 *Corrected*
Butvar B98	Methanol	Soxhlet	-0.3	0.8
	Toluene–ethanol	Soak and agitate	2.7	2.9
	Toluene–ethanol	Soak only	6.0	5.7
AYAT	Acetone	Soxhlet	-1.0	-0.3
	Toluene	Soxhlet	1.2	1.9
Acryloid B72	Toluene	Soxhlet	0.2	0.9
	Acetone	Soxhlet	-0.1	0.6
	Acetone	Soak and agitate	-0.3	0.4
	Acetone	Soak only	0.7	1.3

SOURCE: Adapted from ref. 23.

Residual resin percentages in Table III are given both before and after correction for the amount of extractives, which are presumed to have been extracted along with the consolidant. In several cases the uncorrected values are negative, which would be expected if all consolidant and some extractives had been removed. After the correction, the only negative value is for the AYAT–acetone system, which must therefore be considered the most reversible. The least reversible treatment was the Butvar B98–toluene–ethanol system, especially when removal was attempted by soaking only, which left corrected residual resin of 5.7%. For AYAT and Acryloid B72, the polar acetone was much more effective than the nonpolar toluene in removing consolidant.

When the extraction method was by soaking, agitation using a magnetic stirrer was very beneficial. For Acryloid B72 and acetone, soaking with agitation was just as effective as Soxhlet extraction. This finding is important because Soxhlet extraction would not be a practical method in all but the most exceptional cases and with very small objects. The data of Table III show, however, that with proper choice of solvent and extraction method, residual resin content can be held to less than 1%.

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14

Gluing of Archaeological Wood

James T. Rice

School of Forest Resources, University of Georgia, Athens, GA 30602

The gluing of archaeological wood can variously involve problems of dealing with wood that has aged or fragile surfaces, possibly with reduced wettability and poor resistance to glue film shrinkage during hardening; poorly fitting and unmachinable surfaces that necessitate the use of gap-filling glues; wood stabilized with polyethylene glycol, with possible weak boundary layers or chemical interference with a glue's bonding; or wood consolidated with other polymers (e.g., acrylics), that might present problems with reduced hygroscopicity and require special care in bonding with water-based glues. Furthermore, the conservation constraint of reversibility often limits glue choices to those that can be softened or redissolved by some combination of aqueous or organic solvents and heat. The limited published information on these problems and their solutions is reviewed, and general suggestions are made for glues and procedures in common situations.

GLUING CHARACTERISTICS OF ARCHAEOLOGICAL WOOD have received relatively little attention in the literature of archaeology, conservation, and wood technology. This chapter will deal with the problem of gluing archaeological wood by reviewing basic wood-gluing theory and the principles of good gluing practice that have evolved in the wood products field; noting how archaeological wood may differ from the wood routinely glued in industry and the theory of how one might deal with those differences; and summarizing some of the relevant research findings and experiences from industrial wood gluing and conservation literature and practice.

In this chapter, archaeological wood is defined as wood that, as a result of time, exposure, and possibly conservation-related treatments (e.g., consolidation or stabilization), may have gluing properties or limitations signif-

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icantly different from those of the freshly prepared and unmodified wood commonly used in industrial or modern craft wood-gluing operations. In addition, gluing limitations are often imposed by an artifact's configuration and condition, especially by the presence of irregular and poorly fitting joints and the difficulties of properly clamping irregular shapes. Finally, the conservation-ethic recommendation of using reversible glues (i.e., glues that can, in the future, be nondestructively debonded) can impose severe limitations on the choice of glues used.

One might expect to encounter several types of archaeological wood gluing. For instance:

1. The regluing of artifacts where breaks have developed in the wood (perhaps ages before). Regluing may involve the gluing of aged surfaces, irregular or poorly fitting joints, deteriorated wood (e.g., wood with decay and insect damage), and the difficulties of not being able to clamp joints properly in irregularly shaped artifacts.
2. The regluing of original (or earlier repair) glue joints in an artifact where they have opened up or come apart, to expose surfaces that are now aged and also contaminated with old glue. Difficulties would be similar to those described in example 1, but with the added problem of dealing with the old glue residue.
3. The gluing or regluing of artifacts that have been exposed to prolonged water immersion (and possibly decay) and that will probably require treatment to minimize shrinkage and collapse when dried—usually treatment with polyethylene glycol (PEG). The PEG treatment will alter the absorbency and gluing characteristics of the wood and may also leave a surface coating that can be a potential weak boundary layer problem if not removed.
4. The gluing of artifacts that, as a result of decay, insect attack, or possibly mechanical damage and wear, may require polymer reinforcement (consolidation) to be useful or serviceable. Gluing differences and difficulties, although similar in principle to those in example 3, may be more intense and difficult to deal with.

Each of these types of archaeological wood will have gluing characteristics somewhat different from those of the fresh unmodified wood normally encountered in an industrial or modern craft wood gluing situation. As a result, they will require some degree of special consideration and care in gluing. These differences and the question of how to deal with them can best be approached from an understanding of accepted theory and practice related to successful wood gluing. Much of the following theory is based on the early papers of Marra (*1*, *2*).

The Properly Formed Wood–Glue Joint

Anatomy and Development. Marra (*1*) likened the "anatomy" of a glued wood joint to that of a chain, where the joint can be no stronger than its weakest link. Figure 1 shows a five-link joint anatomy diagram. Links 1

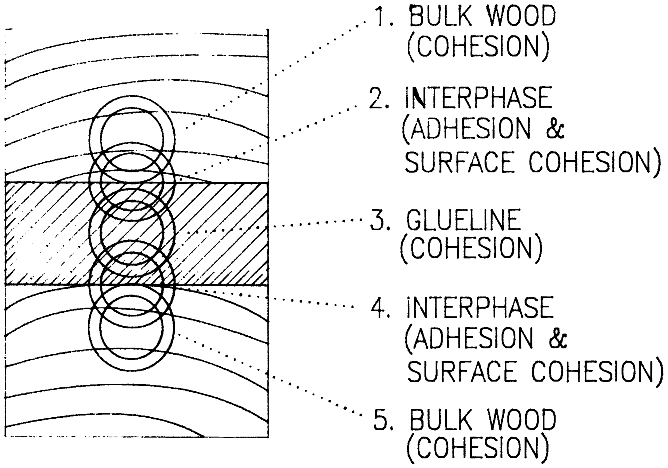

Figure 1. Chain-link diagram of well-formed (proper) wood–glue joint. The materials and conditions that were used have led to a joint with good bulk wood strength, a strong interphase with good adhesion, and a strong glue film. (Reproduced with permission from ref. 1. Copyright 1950 American Furniture Manufacturers Association.)

and 5 represent the cohesive strength of the bulk wood (the adherends), links 2 and 4 represent adhesion at the boundary interface regions involving both the wood's surface and the glue that has penetrated it (with porous surfaces, it is probably better to call them interphases rather than interfaces), and link 3 represents the cohesive strength of the glue film itself. In a proper joint, all five links are well formed.

Strength of the bulk wood will depend, first, on the wood's density, grain pattern, grain direction, and moisture content. Second, it will depend on any damage or deterioration the wood may have suffered. Deterioration will normally be quite significant with archaeological wood, and considerably more attention will be given to it later.

The strength of the interface (or interphase) links will depend on a host of factors, particularly the amount of glue applied, the glue's viscosity and wetting power, and the wettability, permeability, and absorbency of the wood. Later sections address the viscosity behavior of various common glues and the related wood properties affecting glue penetration, especially as those properties may be affected by archaeological time and conditions.

The bulk strength of the glue will depend on the existence of a thin but measurable and continuous film of properly hardened glue in the bondline. This film, in turn, is the net result of the amount of glue initially applied (less the amounts that have penetrated into the substrate or been squeezed out of the joint edges before hardening occurred) and the thoroughness of the glue's hardening. Although there may be some small differences in the basic strength of cured films of various glues, they probably will not be reflected as noticeable differences in the strength of common glued wood joints. This is especially true if, as is often the case, the wood is the weaker link in the joint.

Steps in Preparation. The physical process of forming a good wood–glue joint generally involves several considerations. Careful storage and preparation of the glue are needed, including accurate measuring and mixing of components when multicomponent systems are involved. The wood must be properly prepared, including drying and machining so as to produce a dry, clean, flat surface wherever possible. An appropriate amount of glue must be applied uniformly to the wood surfaces. Assembly time requirements or limitations should let the glue's viscosity increase as needed to avoid starved joints, which might result from excess penetration or squeeze-out during bonding, but avoid excessive increases in glue viscosity that might lead to dried-out or precured joints.

The joint must be clamped with pressure adequate to bring the mating parts into close-fitting contact, if possible. For routine wood gluing, adequate glueline pressures are on the order of 50–150 psi, depending on the type of wood and glue involved. However, joints can be formed at much lower pressures as long as the substrates can be brought into close-fitting contact. A continuous glueline with a thickness of less than about 0.010 in. (0.25 mm) is ideal. Heat, moisture, and time will bring about thorough hardening of the glue.

The Bonding Process

The formation of a proper wood–glue joint is the net result of several fluid actions. Marra (*1*, *2*) outlined them as follows.

Flow. In industry, adhesives are frequently applied to the wood by means of roll or spray applicators. Often the result is, initially, discrete strips or droplets of glue on the wood. These discrete areas of glue should flow or merge to form a continuous film. Some forms of application (e.g., curtain coating and hand brushing) produce a continuous film from the outset. Flow, as a separate step, would not be involved in this case.

Transfer. In industrial wood-gluing practice, glue is applied usually to only one of the two surfaces being joined. In these cases, a critical step in bond development is for some of the glue to transfer from the spread to the unspread surface. Where glue is applied to both surfaces of a joint (called double spreading), transfer is not involved. The requirement now becomes a fusing or flowing together of the two half-films. Inadequate transfer will lead to an unanchored joint (Figure 2).

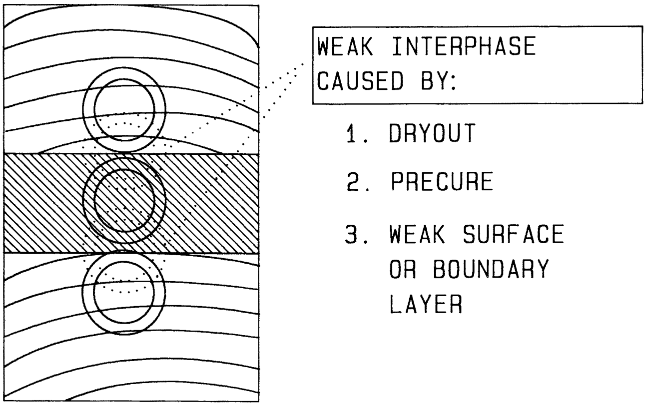

Figure 2. Chain-link diagram of a weak interphase joint. This "unanchored" joint often results from premature hardening (dryout or precure) of the glue, which leads to inadequate transfer and penetration, especially with respect to the unspread surface. The glue film is not adequately attached to at least the one surface. However, a weak interphase can also arise when the wood has a damaged or deteriorated surface. This situation might very well occur with archaeological wood. (Reproduced with permission from ref. 1. Copyright 1950 American Furniture Manufacturers Association.)

Penetration. The glue should ideally penetrate slightly into the wood's porous structure. Such penetration will establish full contact with the surface's anatomical and machining irregularities and reinforce any damaged or loose surface material that might otherwise lead to the formation of a weak boundary layer. This reinforcement is a form of surface consolidation. However, excess penetration is undesirable, because it can lead to a glue-deficient or "starved" joint (*see* Figure 3).

Wetting. Wetting is closely related to penetration. The liquid glue film must "wet" the substrate that it has been spread onto or has penetrated into (i.e., the glue must establish extensive and intimate molecular scale association with the surfaces of the wood fibers). Figure 4 depicts how a liquid might, in a poor wetting situation, be spread onto a surface but not make intimate contact with the microroughness of surface. In contrast, Figure 5 depicts a fully wetted surface, where the liquid has established extensive and intimate contact with the substrate, including association at the molecular level.

Wetting is often illustrated by diagrams that show a droplet of liquid attached to a solid's surface. The contact angle that the leading edge of the droplet makes with the solid's surface is then analyzed with regard to whether a wetting or nonwetting relationship exists.

Generally speaking, when the surface tension of a liquid is high relative

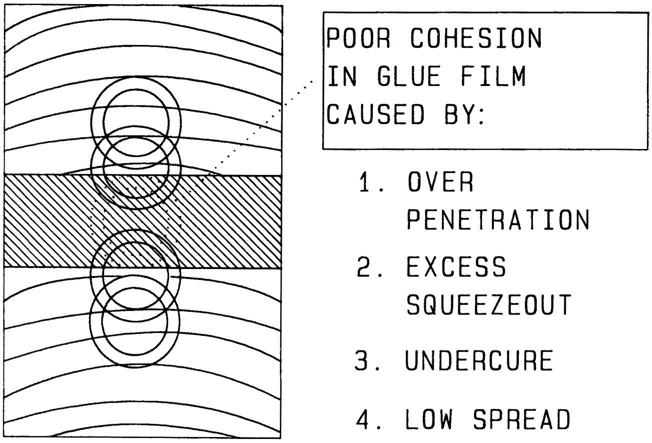

Figure 3. Chain-link diagram of a joint with weak glueline cohesion. This is frequently called a "starved" joint, in which insufficient glue is left to form the thin but continuous film necessary for good joint strength. It often results from inadequate initial glue spread or from excessive loss via penetration or squeeze-out. In the case of double spreading (where half the glue is applied to each of the surfaces being joined), dryout or precure would lead to a weak central link as shown here, but probably not to real joint starvation. (Reproduced with permission from ref. 1. Copyright 1950 American Furniture Manufacturers Association.)

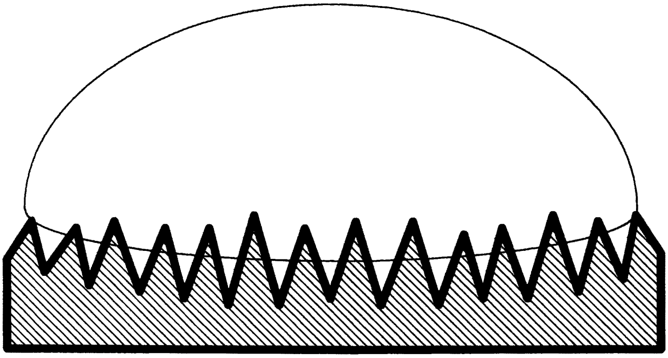

Figure 4. Depiction of a poor wetting situation. The liquid is resting on the high points of the substrate, but not making extensive contact with it at the microroughness and molecular level.

to the surface energy of the solid it is contacting (such as with water on a paraffinic wax), the contact angle will be well over 90° (*see* Figure 6). This angle size indicates poor wetting, and the liquid, after being spread on the solid, will often contract and puddle or bead. Poor adhesion usually results.

If the surface tension of the liquid is moderately lower than the surface

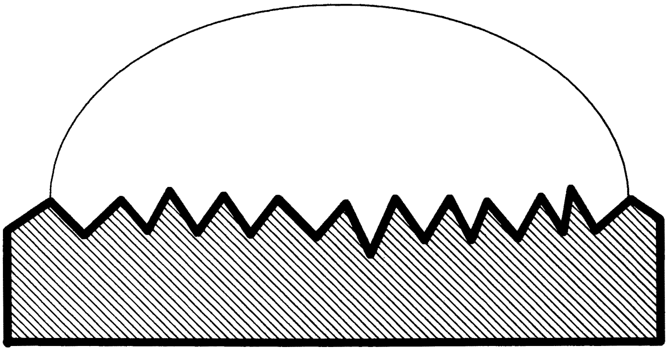

Figure 5. Depiction of a good wetting situation. The liquid has established extensive and intimate contact with the substrate, including contact at the molecular level.

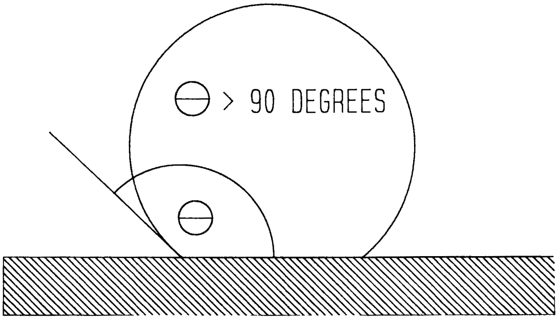

Figure 6. Droplet of liquid on a solid where wetting is not good. The contact angle is greater than 90°, and a film of this liquid, if spread on this solid, would tend to contract and puddle or bead. If the liquid were an adhesive, the potential for adhesion would be poor.

energy of the solid, the contact angle will usually be in the range of 0–90° (*see* Figure 7), indicating a better wetting situation. This level of wetting is common and is usually adequate for good adhesion.

If the surface tension of the liquid is significantly lower than that of the solid, the contact angle may go to 0°. Viscosity permitting, such a liquid will spontaneously spread over the surface of the solid. This level of wetting offers good adhesion potential.

Hardening. Once the glue has properly undergone the preceding fluid functions and has formed a thin but continuous liquid film that has wet the substrates, it must harden so as to develop adequate joint strength and durability. However, archaeological wood gluing will normally be subject to the conservation ethic of reversibility. This ethic suggests that, wherever

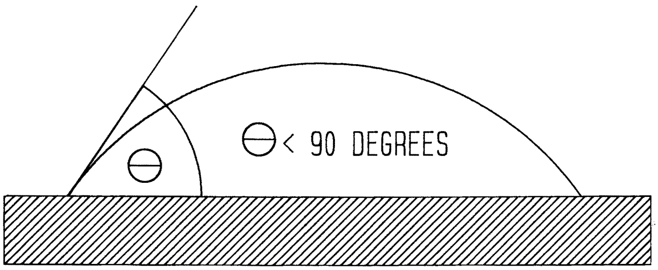

Figure 7. Droplet of liquid on a solid where wetting is good. The contact angle is less than 90°. If the liquid were an adhesive, adhesion should be good.

possible, glued joints should be capable of nondestructive disassembly well into the future.

Thus, adhesives used in the gluing of archaeological wood will generally be limited to those that can, even in the long term, be "unhardened" (i.e., dissolved, softened, or weakened), and permit the joint to be disassembled. This limitation normally means adhesives that remain soluble in water, are organic solvents, or can be heat-softened at moderate temperatures. Further comments on specific adhesives are given later.

Viscosity Behavior During Gluing

The gluing process generally involves wood preparation, glue preparation, glue application, possibly some assembly time attention, and adequate clamp or press time and conditions. To understand differences in the use characteristics of common wood glues, it is helpful to consider their patterns of viscosity behavior at various stages during the bonding process. Troubleshooting in wood gluing is basically a matter of making proper adjustments in the material and process variables that control the glue's viscosity and flow behavior during the various stages in bond development.

Hardening Mechanisms. Differences in the viscosity response of various glues during bonding are largely associated with differences in their hardening mechanisms. The major hardening mechanisms are as follows.

Many glues, especially those commonly used in conservation work, harden primarily by an increase in concentration of the glue's polymer solids as the carrier (water or solvent) is lost into the substrates and surrounding air. Glues based on water-soluble or dispersible polymers (e.g., starch, casein, animal hide gelatin, and cellulose esters and ethers) would be in this category.

Emulsion glues (e.g., the poly(vinyl acetate) based "white" and "yellow" or "carpenter's" glues) harden by a variation on drying that involves coalescence. After the loss of some water, emulsified particles of polymer begin to touch and coalesce to form a hardened film of polymer that possesses sufficient molecular weight to provide quick initial bond strength. Continued drying produces further strength increases.

Other glues (some are solutions, some are 100% reactive material) harden predominantly by chemical action. If these cure at room temperature, they begin to increase in viscosity as soon as they are mixed and continue to do so until fully hardened. Hot-setting glues will require certain minimum temperature and time combinations for proper hardening.

Lastly, some glues harden, at least in part, by congealing or freezing as they cool. Such glues are often called "hot melts". Older examples of hot melts include the hot applied resins and waxes and, to some extent, the hot animal glues. Synthetic polymer hot-melt glues have recently become widely used in industry and may have conservation applications as well.

Changes During Use. Glues may experience various viscosity changes during use (3). Some glues, especially those supplied as reactive liquids, can undergo undesirable viscosity increases during storage. Multicomponent glues will very often show an abrupt increase in viscosity when the components are mixed. Some glues may undergo significant viscosity increases while in the "pot" awaiting use. This period may be spoken of as pot time or, in terms of limits, as pot life.

The time period between application of glue to the wood and the bringing to bear of final bonding pressure is known as assembly time. This period may be subdivided into open and closed assembly times, depending on whether the glueline surfaces are directly open to air or closed upon one another. Major increases in the glue's viscosity can occur as a result of varying combinations of drying, cooling, and chemical action during assembly time.

The application of final closing pressure to the joint initiates the clamping or pressing period. During this period the glue's viscosity, with very few exceptions, must increase dramatically for the initially liquid glue to become rigid.

Figures 8, 9, and 10 give somewhat idealized but helpful representations of the viscosity behavior of three common industrial wood glues (3). As depicted in Figure 8, a high-temperature-setting, chemically curing, phenol–formaldehyde, resin-based glue would experience some viscosity increase during storage, an abrupt and significant increase on mixing, additional increases during pot time and assembly time, a brief viscosity drop when first warmed, and then a dramatic final increase when heat accelerates polymerization and resultant hardening during press time.

Figure 9 depicts the somewhat similar behavior for a room-temperature-setting, urea–formaldehyde or phenol–resorcinol–formaldehyde resin-based glue. However, no initial heat-related drop in viscosity occurs during clamping, and the final polymerization hardening proceeds at a slower rate because it occurs at room temperature.

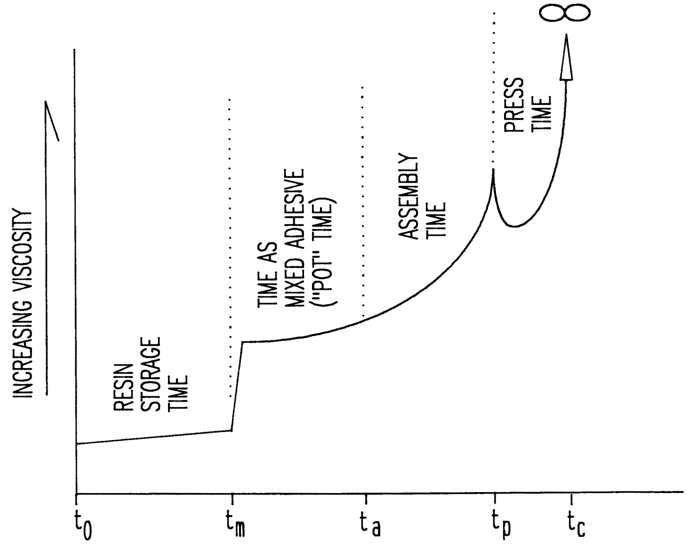

Figure 8. General pattern of viscosity change during bonding with hot-press, resin-based glues, such as phenolics and certain ureas. (Reproduced with permission from ref. 3. Copyright 1983 Pennsylvania State University.)

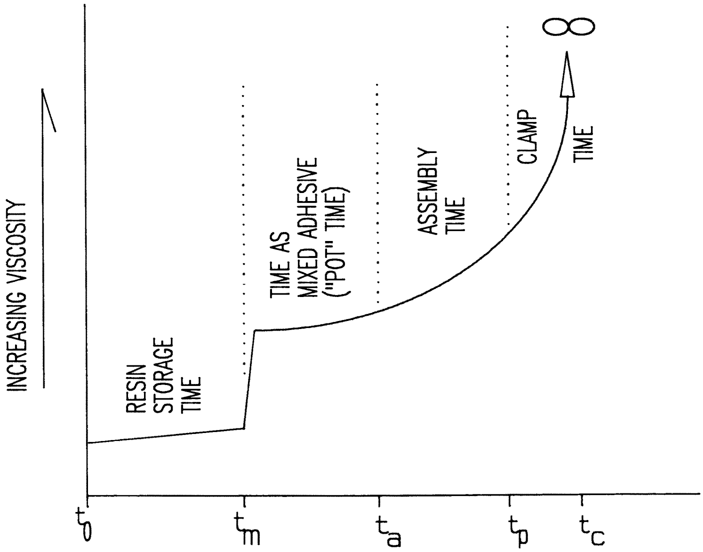

Figure 9. General pattern of viscosity change during bonding with cold-press, thermosetting glues, such as phenol–resorcinols, certain ureas, and epoxies. (Reproduced with permission from ref. 3. Copyright 1983 Pennsylvania State University.)

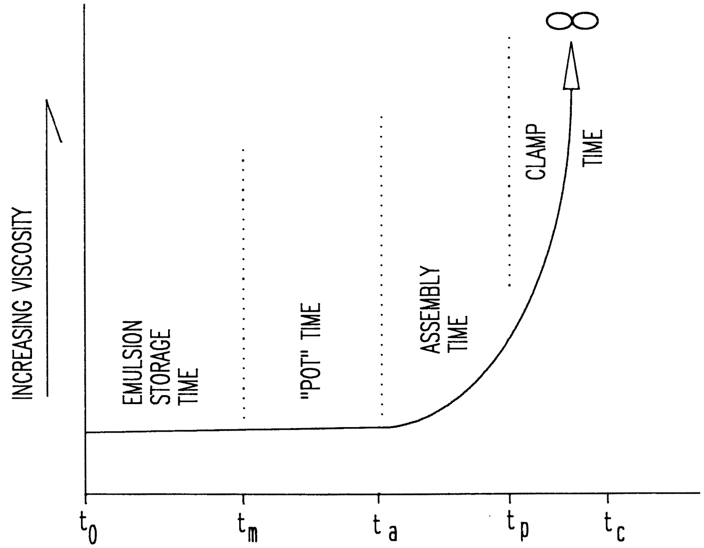

Figure 10. General pattern of viscosity change during bonding with cold-press glues such as the polyvinyl acetate-based, emulsion-type "white" and "yellow" glues and the animal glues. (Reproduced with permission from ref. 3. Copyright 1983 Pennsylvania State University.)

Figure 10 depicts the behavior of a room-temperature-setting, polyvinyl acetate-based emulsion glue. Little viscosity increase occurs during storage or pot time. However, because of the nature of coalescence, a rapid increase occurs during assembly time and clamp time. With emulsion glues, assembly time limits must be strictly observed to avoid dryout and poor transfer. By the same token, clamp times for emulsion glues can be relatively short, as room-temperature-curing glues go.

Chain-Link Concept

Joint Strength Problems. Where glued wood joints have been properly formed, they are frequently (but not always) stronger than the wood itself. When ruptured, such joints will yield a high percentage of failure in the wood rather than in the glue film or in the interphase region. This failure would be depicted, as in Figure 1, by a chain-link diagram where all links are strong, especially those representing the interphase and bulk glue.

If adequate transfer, penetration, and wetting have not occurred, a joint can be unanchored in varying degrees. Such bonds will show low strength and wood failure when tested. Figure 2 depicts such a bond with its weak interphase link, a condition that often reflects poor transfer arising from the glue's being either precured or dried out before the application of bonding pressure.

Several combinations of conditions can lead to joints that have discontinuous and weak gluelines (poor film cohesion). These joints are said to be starved. If the amount of glue initially applied is inadequate or if the glue is initially too fluid or remains fluid too long during assembly and clamping–pressing time, excessive penetration into the wood or squeeze-out from the joint's edges can occur and lead to some degree of joint starvation. Deficiency of glue in the glueline region will often lead to bonds that have poor strength and will show low wood failure if tested. Figure 3 depicts a starved joint, with its weakness in the link representing the cohesive strength of the glue film itself.

Joint Durability Problems. Durability commonly means resistance to weathering, especially to the effects of heat and moisture. In glued wood joints, the problem is twofold. Shrinking and swelling of the wood can stress and damage the joint's integrity, and heat and moisture can lead to softening or decomposition and weakening of the glue itself. Joints with weak glue film cohesion or with poorly developed interphases (poor adhesion) will have reduced durability, even if the glue is nominally of a durable type. The reduced cohesion or adhesion could result from the previously mentioned conditions that lead to either poorly anchored or starved joints (Figures 2 and 3).

Adhesives: General Considerations

The key requirements for an adhesive suitable for use in conservation wood gluing are as follows.

Reversibility. The code of ethics generally followed by conservators (*4*) says that, wherever practical, any work done on an artifact should be reversible. Succeeding generations of conservators should be able to undo that work to correct mistakes, make new or improved repairs, etc. In the case of adhesives, reversibility means being able to unglue the joint with a minimum of damage to the artifact.

Nonstaining and Nondiscoloring. Although conservators specifically avoid any attempts to hide the fact that repairs have been made, they also do not want them to be or become unsightly or degrading to the artifact. In particular, this goal means the absence of staining and discoloration, even over long periods of time.

Evidence of Repair. Conservation repairs should be evident as such to future conservators working on the artifact. In the case of adhesives, some difference in appearance of the joint or in the composition of the glue should be discernible, as contrasted to the original work or earlier repairs.

Reasonable Joint Strength and Durability. The artifact and its glued joints must have the strength at least to remain intact for exhibition or storage, and may need sufficient strength for some degree of use and handling. However, the high levels of joint strength called for in common industrial and modern craft joints should rarely be needed. Likewise, normal museum exposure and storage should not create a durability problem for any historical or modern adhesive likely to be used in conservation work. However, should exposure ever include conditions conducive to microbiological attack, modern synthetic resin glues would have an advantage over the more traditional natural-origin glues, such as starches, hide glues, and some caseins.

Adhesives: Specific Considerations

Collectively, a good deal of conservation wood gluing work has been done, but concerted opinion or experience as to the best choices of adhesives is not apparent. Currently, the Canadian Conservation Institute has a large study underway, with emphasis on staining and discoloration problems (*5*, *6*). However, the results of that work are not quite available yet. Several publications have dealt with specific aspects of conservation gluing, using mainly the older, natural-origin glues (e.g., *7–11*). However, current interest seems to run more toward finding modern glues that will fit well into conservation gluing applications. The following discussion attempts to outline choices of both historical and modern glues that should be acceptable in conservation and archaeological wood-gluing work.

Reflecting on the chain-link concept of a glued wood joint, we can see that debonding with minimum damage to the substrates will basically mean disrupting the joint by reversing the cohesion of the glue film. By reexamining the mechanisms by which glues harden to develop that cohesion, we can begin to think about means of reversing it.

Cure-by-Drying Category. When glues have hardened primarily by loss of carrier (water or organic solvent used to dissolve or disperse the adhesive component), it may be possible to soften or redissolve them by the effects of water, moisture, or appropriate organic solvents. Many of the historical wood glues have this hardening mechanism, and it has been reported that, with care, they can be so reversed (*10*, *11*). However, adhesives that are soluble or dispersible in nonpolar solvents (assuming they have little or no chemical cure) may be more easily reversible than the water-borne type. Examples of generally reversible adhesives in this cure-by-drying category are as follows.

Animal-Hide Glues. This category includes hot and liquid animal-hide glues, as well as other water-soluble animal gelatins (e.g., fish and rabbit-skin glues).

Water-Soluble Starches, Gums, Cellulose Derivatives, and Synthetic Polymers. Water-soluble plant starches and gums have historically been used as glues and should be reversible. Some of the modern water-soluble polymers (e.g., cellulose ethers and esters and soluble nylon) should also be reversible.

Water-Soluble Proteins. Historically, several water-soluble plant and animal proteins have been used as adhesives, both industrially and in conservation work. Currently, only the milk-based casein products are in significant industrial use. Casein glues have also been used in conservation work, but formulations designed for high water resistance could be difficult to reverse. Plant proteins, especially those from legumes such as soybeans and peanuts, have been used industrially, some until fairly recently. Presumably at least some forms of plant protein glues would be reversible enough to be of interest to conservators.

Aqueous Polymer Emulsions. Emulsion-polymerized dispersions, most of which are based on poly(vinyl acetate), are widely used in industrial wood gluing and are attracting a lot of attention in conservation work as well (*6*). The two most common categories are known as "white glues" and "yellow glues" (also known as "carpenter's glue"). They are sold under numerous trade names. Although these glues are initially dispersed in water, once they coalesce, their hardened films are not as easily reversed as might be thought. However, they do soften in the presence of moisture, especially when coupled with heat. Certain formulations, known generally as "kids' glues", have been designed to wash out of clothes, even when the glue has been allowed to dry before laundering. From the standpoint of reversibility, these may be desirable for conservation work. However, they will also probably have somewhat reduced strength and durability.

Solvent-Soluble Natural Polymers. The exudate of the lac insect is dissolved in alcohol to yield shellac. This solution has adhesive properties and should be reversible by treatment with the appropriate alcohol or similar solvent, although it may present problems in other performance areas (*8*). Solvent-soluble plant gums, especially coniferous resins (e.g., from firs or pines) can be dissolved in organic solvents and used as adhesives. Solvent solutions of some plant waxes may also have limited utility in gluing. All such glues should be reversible by treatment with solvents similar to those they were dissolved in when applied.

Solvent-Soluble Synthetic Polymers. Nominally linear polymers of several chemical types can be dissolved in appropriate organic solvents and used as adhesives. They should be reversible by subsequent treatment with similar solvents. In addition to the older cellulose nitrate solutions, several types of polyacrylics are now attracting much interest (*6*, *12*, *13*). Various esters (methyl, ethyl, propyl, butyl, etc.) of acrylic and methacrylic acid have been used for adhesive purposes, both alone and in various copolymer and terpolymer forms. They are dissolved in appropriate organic solvents, harden by the loss of that solvent, and should generally be reversible by solvent action as well. This family of adhesives is currently receiving considerable attention in conservation gluing work.

Hot Melts. Glues that harden primarily by congealing (also referred to as freezing) as they cool in the joint should also be reversible with heat. Although hot animal glues harden, in part, by a congealing mechanism and can probably be reversed more easily with a combination of both moisture and heat, the main glues in this category are those natural and synthetic polymer-based glues known collectively as hot melts.

Plant Resin Formulations. Sometimes compounded with shellac, as in DeKhotinsky cement, these compounds have long been used as hot-melt glues. Likewise, waxes of plant and animal origin have also been used as hot-melt adhesives (*12*). They all should be reversible by application of heat, possibly in conjunction with solvent action in the more difficult cases.

Polyolefins and Polyamides. Modern hot-melt adhesive compounds are commonly based on polymers of the polyolefin or polyamide type. The polyolefin-based ones are usually modified with other natural and synthetic polymer resins and waxes. The melt temperatures of hot melts vary rather widely. Some begin to melt just above 100°C, whereas others may require temperatures in the range of 200°C to melt. The high-temperature ones might very well damage the artifacts being bonded. Hot melts may be of considerable interest in conservation gluing, but additional research is needed on the most appropriate formulations and forms of application.

Chemically Curing Systems. For glues that harden significantly by chemical reaction, true reversibility will usually be difficult, if not impossible. Some chemically curing systems, especially epoxies, have apparently been used in conservation gluing and are said to be reversible, although only with the use of rather strong solvents (*13*). However, further evaluation of epoxies might be productive, because specific hardeners (e.g., polyamides) can render the cured epoxy somewhat meltable and perhaps more solvent reversible. Epoxy hardener–resin combinations, not normally of interest in structural gluing, might be of value in conservation work.

In other cases, chemically curing glues may have been used with the realization that the opportunity for reversal may sometimes have to be sacrificed in deference to other bonding needs or objectives. This situation might be particularly true when the artifact must bear significant loads or manifest real durability.

Pressure-Sensitive Adhesives. Some glues do not fully harden in the short term. They remain tacky enough, for very long periods of time, to permit effective bonding under pressure, but they are also sufficiently viscous to provide significant bond strength. These are referred to as pressure-sensitive adhesives. Although their most common usage is in pressure-sensitive tapes, they could be applied and used separately and might be useful in some conservation work. Reversibility would, at least initially, simply be a matter of applying debonding peel or cleavage force. Some heat and solvent action might be needed after significant aging.

Contact-Bond Adhesives. Another group of glues, referred to collectively as contact cements or contact-bond adhesives, bear some similarities to the pressure-sensitive adhesives in that they do not rapidly achieve full hardening. Until a few years ago, contact-bond formulations were mainly organic solvent solutions of elastomers, compounded with tackifying resins and antioxidants. However, with recent concerns over energy, environmental, and fire safety questions, interest has turned to water-based systems.

Contact-bond adhesives are applied to both of the surfaces to be bonded, allowed to dry until approximately nontacky to the touch, and then pressed together to form a bond. The elastomers in these adhesives have the property known as autohesion. This means that when the dried adhesive-coated surfaces are brought together under some pressure, the films join by a process of molecular diffusion and form a completed bond.

Although the strength of such bonds is not as high as those of other adhesives, the load-bearing ability is adequate for many applications, especially for simply attaching decorative surface materials to a structural substrate. As an example, most of the high-pressure decorative laminates used as coverings for kitchen counters are bonded to their substrate (usually particleboard) with contact-bond adhesives. Contact-bond adhesives can be softened and redissolved by combinations of heat and solvent. Thus, they should be at least nominally reversible and of possible interest in conservation bonding applications.

Staining and Discoloration. This area of adhesive performance is probably the one in which we have the least experience and confidence, especially considering the lengths of time involved (i.e., decades and centuries). The Canadian Conservation Institute's program focuses sharply on these questions and includes extensive measurement of staining and discoloration, both with and without exposure to light (*6*). Although we know something of the behavior of certain polymers, especially the good resistance of acrylics to ultraviolet light degradation (*14*), we must await the results of tests like those underway at the Canadian Conservation Institute for further guidance in these areas. Laboratory tests have shown that polymers such as poly(vinyl butyral) (which are generally thought to be acceptable) can, under severe conditions, show considerable discoloration, imbrittlement, and reduced solubility with time (*9*).

Evidence of Repair. As mentioned earlier, conservation ethics call for repairs to be evident to future conservators who might work with an artifact (*4*). In the case of gluing, this condition raises the question as to how dissimilar the adhesive used should be from other adhesives used in the artifact or from the adhesives in use during the time period when the artifact was made. At times this need might militate against the use of the historical animal-hide, casein, or starch glues. However, it is always possible to color or load the new adhesive with detectable components, that would differentiate it from original usage or earlier repairs. Modern adhesives, such as the emulsion and hot-melt glues, should be identifiably different and present few problems in this area.

Potential Problems

A definition for archaeological wood was given earlier and examples were listed. The following discussion considers each of the types of wood that might be encountered in an archaeological context. They might differ in gluing characteristics and responses from fresh unmodified wood. These potential differences in archaeological wood are analyzed, according to the theory that has been outlined, for their probable effects on gluing results.

Significant Decay. Wood decay organisms produce enzymes that break down the chemical structure of the wood and provide food for the decay's growth. This breakdown results in a progressive loss of the wood substance. The process is reflected in reduced density and strength, increased fluid permeability, and altered color and texture.

Decay spores are almost universally present. Given the presence of wood, sufficient moisture and air, a tolerable temperature, enough time, and the absence of substances toxic to the decay organism, decay will surely begin and proceed to the total destruction of the wood available. Therefore, there are few truly ancient or "archaeological" wooden artifacts, and the problems involved in gluing them may often be as much academic as real.

However, some archaeological wooden artifacts have survived, at least in part. Before discovery, most of these objects have either been in a relatively dry environment, frozen, or continuously immersed in water. These conditions limit the moisture, air, or temperature needed for the growth of decay, and thus they prolong the life of the wood.

Moderate Decay. The following comments address gluing problems that might arise with artifacts showing only moderate decay.

Loss of Strength. Loss of strength may not directly affect the wood's basic gluability. However, even joints properly formed from moderately decayed wood will be limited in strength and strength-related serviceability (*see* Figure 11). Unless the wood is first subjected to consolidation treatment, the strength of even well-formed glue joints will be limited by the wood's reduced bulk strength. Thus, joints could be produced that, if tested to destruction, would most likely yield the normally desirable result of high wood failure, but would also have very low load-bearing ability. Artifacts with such joints could require great care in exhibition and the avoidance of real usage.

Increased Permeability and Absorbency. Decay organisms will digest away the anatomical structures that normally somewhat impede the movement of liquids in and through the wood. Specifically, they may consume intracellular deposits (e.g., heartwood deposits or tyloses in hardwood vessels) and perforate or remove the structures that commonly limit intercellular communication (especially bordered pits). During gluing, this damage could lead to increases in glue penetration and could possibly result in starved joints if there is no offsetting action. Increased amounts of glue or longer assembly times (to allow some drying before clamping) might be in order as corrective actions.

Insect Attack. Insect attack may be accompanied by decay or may occur separately and in widely varying degrees of severity. Extreme infestations, such as can occur with termites, may leave little more than a fragile lace of residual wood and nothing much to glue at all, unless it is first subjected to extreme consolidation treatment. On the other hand, minor infestations should have little effect on gluing. The differences in properties of insect-attacked wood, as with decayed wood, would primarily be in its reduced density and strength and its increased permeability. However, with minor insect infestation and little or no decay, the effects on gluing should not be noticeable.

Consolidated Wood. Wood that has suffered significant damage from decay, insects, or mechanical action must often be reinforced via impregnation with polymers that can be hardened in situ to form a strengthening matrix. If the polymer loading is high, this consolidation process produces wood with rather special gluing characteristics. The consolidated wood's reduced absorbency and permeability will be most noticeably different. On the basis of the gluing theory already outlined, one would expect problems in using high-water-content glues (e.g., hot or liquid animal, casein, poly(vinyl acetate) emulsion, and amino or phenolic resin-based glues). Similarly, one would expect glues with less water carrier or the use of longer assembly times (especially open assembly time) to be more successful because they let water dissipate. Further, one would expect at least some nonaqueous glues (e.g., solvent solutions of acrylic and related polymers, and possibly contact cements and hot-melt adhesives) to be useful. Cross-linking nonaqueous systems (e.g., epoxies, urethanes, silicones) would also be likely candidates. However, with their normally very low reversibility, they might not be acceptable in conservation work.

Dimensionally Stabilized Wood. Wood that has been saturated by immersion in water for long periods of time and subjected to related biological deterioration will often require a dimensional stabilization treatment before drying can be permitted safely. This treatment is usually done with "bulking" compounds such as polyethylene glycol (PEG).

However, the PEG treatment may also alter the wood's gluing properties. First, the treatment might leave a surface coating of PEG polymer that could act as a weak boundary layer if not removed. Second, PEG-treated wood may have reduced absorbency, which would cause it to have a gluing response similar in part to that of consolidated wood, and yet to react differently, especially with traditional water-based wood glues. Higher-solids aqueous glues or solvent-based glues may be advantageous.

With heavy loadings, it would certainly be desirable to clean off any surface PEG build-up. Wiping with solvents such as toluene has been suggested (*15*). More detail on this cleaning is given later.

Irregular and Poorly Fitting Joints. The formation of good wood–glue joints depends on the wood surfaces being flat and capable of fitting closely to form joints with thin but continuous glue films. Problems can arise when joints are irregular and poorly fitting. Stresses are imposed by high shrinkage in thick areas of the glue film, and stress concentrations can develop at irregularities along the film.

In order for a glue to function effectively in such a situation, it must be of the "gap-filling" type. In general, these glues exhibit minimum film shrinkage on hardening, and their hardened films are characterized by a degree of toughness rather than brittleness. Glues with minimum carrier content (water or solvent) are likely to shrink the least. Toughness will vary with the polymer structure but could be enhanced by the use of plasticizers, preferably of the internal (reacted-in) type.

Theory and Experiences

The literature of archaeology and conservation seems to yield little in the way of systematic studies, information, recommendations, or experiences related to the gluing of archaeological wood. Individual experiences are referenced (e.g., *7*, *9*) and fundamental adhesion theory is presented in several conservation articles and book chapters (*12*, *16*), but little is to be found in the way of recommendations, guidelines, or in-depth problem analyses. The following comments are based mostly on industrial wood-gluing theory and experience in problem areas similar to those that might arise in gluing archaeological wood.

Aged and Contaminated Wood Surfaces. Where artifacts have been broken and the surfaces are to be reglued without remachining, the problems of gluing aged surfaces will have to be handled. Further, if the breakage involves surfaces that have been glued previously, the problems of gluing over old glue must be dealt with, too.

Although the question of aged surfaces has often been brought up in industrial wood-gluing circles, there is little actual data on its effect. In industry, the general assumption is that the strongest possible joint is desired and that freshly machined surfaces are necessary to achieve such a joint. For example, the rule of thumb in structural wood laminating is to glue surfaces that have been properly machined (flat and with sharp cutter heads) within the preceding 24 h.

However, in conservation gluing, the highest possible joint strength is generally not as necessary. In many (if not most) instances, it may not be possible to machine the surfaces at all. Machining may lead to poorly fitting and gappy joints, and those problems will be addressed shortly. As for the general question of aged surfaces and their effects on gluing, the following situations seem to be more important and likely to occur. Some specific gluing recommendations are given:

1. Loose or oxidized surface material can lead to a weak boundary layer (i.e., a weak interphase link, as depicted in Figure 2). Such material should be removed by machining, sanding, or vigorous brushing wherever possible. Light brushing or the vacuuming away of surface dust, dirt, and debris (including loose old glue) would be a minimum. Where adequate cleaning and preparation of the surface cannot be done, efforts should be made to see that the glue penetrates into and preferably through any weak outer layers to make contact with stronger underlying material. This step, in essence, consolidates the surface. Solvent-based glues (e.g., acrylic or cellulose), if low enough in viscosity, might, by virtue of their lower surface tension and better wetting power (as opposed to water-based glues), penetrate better into such surfaces, including those contaminated by old glue. In addition, they should be reversible.

2. Aged surfaces, perhaps with reduced wettability and absorbency, may present problems, especially when combined with water-based glues. The glue should not be too viscous initially. It should be applied vigorously, so as to be worked into the surface, including the anatomical irregularities. Solvent-based glues, especially those with low surface tensions and low viscosity, would be worth a try. They might do a better job of wetting and should be easier to reverse as well.

Decayed and Insect-Attacked Wood. The problem of gluing wood that has experienced extensive decay or insect attack may often be compounded by the presence of consolidants, but that problem is covered separately. Assuming that loose surface material can be removed, moderately decayed or insect-attacked wood can be joined without difficulty by using any of several glues that are nominally reversible. Hot animal and poly(vinyl acetate) glues should work well, although the increased permeability and absorbency, especially with decayed wood, may call for greater care in controlling penetration. In some cases, heavier spreads of more viscous glues or longer assembly times could be required. In any event, the strength of the glued joint will be weakened to the same extent that decay or insect attack has weakened the bulk wood (*see* Figure 11). Exposure of such joints to loads should be approached with care.

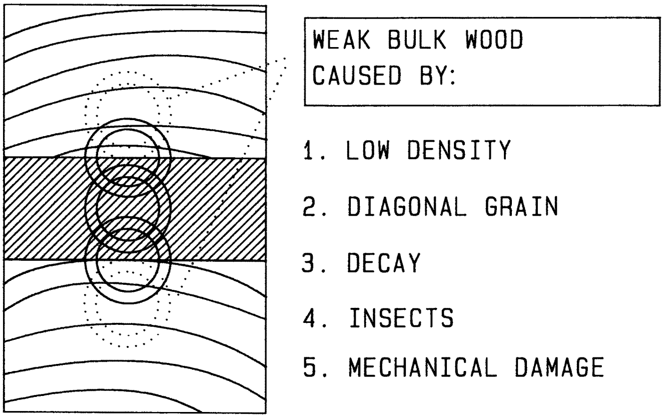

Figure 11. Chain-link diagram of a joint involving weakened wood. The ultimate strength of even a well-formed wood–glue joint is usually limited by the strength of the wood. In the case of wood that has been weakened by decay or insect attack, joint strength is likely to be severely limited.

Consolidated Wood. Consolidation generally means impregnation with an in situ polymerizable material. It results in wood that will have noticeably reduced permeability and absorbency and will probably have a surface coating of plastic. Although the surface coating might be strong enough not to create a weak boundary layer problem, it would generally be better to remove it flush with the wood surface before gluing.

Glues chosen for use in bonding material with low absorbency and permeability should not have high carrier (especially water) content. High-carrier glues require sufficient assembly time (preferably open assembly) to allow for dissipation of most of their carrier. A better option would probably be to use solvent solutions of polymer compatible with the consolidant.

With heavy loadings of acrylic consolidant, it might be possible to achieve gluing by the use of solvent only. The application of an appropriate solvent would soften the surface plastic, which would then function as an adhesive (similar to the way acrylic sheets are bonded with methyl ethyl ketone).

Currently, the nearest industrial counterpart to consolidated wood is a product called "acrylic flooring". Wood flooring (usually oak or maple) is impregnated with acrylic monomer and polymerized in situ to yield a long-wearing, permanent-finish flooring for heavy-traffic areas such as in stores and malls. Sometimes it is necessary to laminate pieces of this material. As might be expected, traditional high-water-content wood glues must be used with considerable care if any degree of success is to be achieved (*17*). One of the better choices of adhesive seems to be the phenol–resorcinol wood glue, but this is one of the most permanent and nonreversible of all wood glues. Recently, emulsion polymer isocyanate (EPI) glues have been used in some applications with acrylic flooring, but mostly where one substrate was untreated wood. EPIs are nominally waterproof glues and are not thought of as reversible at all.

In early work on plastic-impregnated wood, it was found that traditional water-based wood glues could be used, especially the hot-setting ones (*18, 19*). However, longer assembly times, which allowed reductions in glue-film water content before clamping, led to improved results.

PEG-Treated Wood. Wood treated with PEG will also have modified gluing properties, although, if properly redried, not as much so as heavily consolidated wood. The use of PEG as a dimensional stabilization treatment was developed in the 1950s (*20*) and it has been used on a limited scale since then. The utility of PEG treatment for waterlogged archaeological wood is now widely recognized, and it is quite possible that some of the wood so treated has been or will need to be glued.

Wood technology research has shown that, even with high loadings (up to 33% by weight), PEG-treated wood can be glued successfully (as measured either by strength or by percentage wood failure). The glues first recommended for industrial use were casein, cold-setting urea, and hot-setting phenolic (*20*). Although not as good, the poly(vinyl acetate) emulsion and hot animal glues tested worked moderately well and would probably be preferable in conservation applications. Secondary tests confirmed the poorer results with poly(vinyl acetate) glues on PEG-treated wood. Epoxies were also recommended, in addition to the phenol–resorcinol glues. Just before gluing, the wood surfaces should be given a solvent cleaning (e.g., with toluene) to remove any excess PEG.

Theory and related experience predict that it should be possible to use selected solventborne glues successfully on PEG-treated wood. Specifically, non-cross-linking polymer glues dissolved in solvents that could also dissolve the surface PEG might work well and also be reversible.

Poorly Fitting Joints. As stated earlier, poorly fitting joints call for gap-filling glues. Such glues shrink relatively little on hardening and yield glue films with good residual toughness and crack propagation resistance. High-solids, chemically hardening glues can best fill these requirements, but they will normally be poorly reversible at best. Epoxies are good gap fillers, and the formulations that have been found reversible (*13*) might be good choices for conservation gluing of PEG-treated wood.

Another possibility might be to use solutions of acrylic polymer dissolved in acrylic monomer and to harden the glue in situ by heat-activated, free-radical-initiated polymerization. Such a glue should have acceptable shrinkage properties and, if the components are properly chosen, could remain fairly tough. Further, if non-cross-linking components are used, it should be a reversible system.

Summary

Wood that has survived archaeological time and conditions will undoubtedly have gluing properties that are, in varying degrees, different from those of fresh unmodified wood. Bulk strength may have been reduced and fluid permeability and absorbency increased. Surfaces, in particular, may have strength and wettability that have been altered by aging. Treatment with consolidants and dimensional stabilizers may have been necessary, and this will often leave surface residues and reduce permeability and absorbency.

Surfaces to be glued will often be irregular and poorly fitting. Because proper machining and surface preparation may not be possible or permissible, the resultant joints will be gappy and difficult to glue properly. The shape of artifacts will often preclude normal clamping and joint closure, a situation further exacerbating the problem of gappiness.

Last, but by no means least, is the matter of the conservation ethic. All bonding, wherever possible, should be reversible over indefinite time. If rigorously adhered to, this constraint severely limits the types of adhesives that can be used.

In wood-gluing theory, a joint is often viewed as a chain that is no stronger than its weakest link. Joint strength may variously be limited by cohesion in the bulk wood, adhesion at the wood–glue interface (or interphase), or cohesion in the hardened glue film. We find that an ideal joint is the result of a series of properly controlled fluid movements. The glue contacts, lightly penetrates, and fully wets both wood surfaces, and then hardens, leaving a thin but continuous film of glue to maintain the bond and transmit loads. The various effects of archaeological wood's specific characteristics on the formation of each of these elements of a joint's anatomy are considered, and general suggestions are given for good gluing results in various situations.

Glues are suggested that should work satisfactorily within these constraints and be reversible by means of water or solvent action, perhaps with heat, and with moderate joint separation force. However, the question of how resistant some of these glues (especially the modern ones) will be to staining and discoloration over long periods of time is just now being researched, and the answers are not yet in.

Candidates in the water-based group include the hot and liquid animal-hide glues, poly(vinyl acetate) emulsions (including the more reversible "kids' glue") and other water-soluble natural or synthetic polymers (e.g., starches, natural gums, cellulose esters and ethers, soluble nylon).

The solvent-based candidates include various solvent-soluble natural and synthetic polymers (e.g., shellac, coniferous resins, cellulose nitrate, acrylics, contact-bond glues).

Reactive glues suggested are the reversible epoxies (and possibly special ones in the polyester, polyurethane, or silicone classes) and solutions of acrylic polymer in monomer, which can be reacted in situ to form linear polymers that should also be reversible with solvents and moderate heat.

Further consideration of pressure-sensitive adhesives, especially those that could be solvent- or hot-melt-applied and then be reversed by the application of peel or cleavage stresses, possibly with the use of some heat or solvent action, is also suggested.

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15

Exhibition and Storage of Archaeological Wood

Ronald Harvey[1] and Cassia Freedland[2]

[1]Conservation Section, Milwaukee Public Museum, Milwaukee, WI 53233
[2]U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI 53705

Prolonging the life of archaeological wood in the museum setting can be a complicated task. The interaction of delicate wooden artifacts with the museum environment requires a new level of sophistication, incorporating many areas of scientific inquiry. This review will delineate past and present accepted practices for the proper exhibition and storage of old wood. A brief overview of the chemistry of wood degradation will serve as a foundation for the problems associated with exhibition and storage of archaeological wood. Problems addressed include the effects of light, temperature and relative humidity, mounting, infestation, and the chemical interaction of materials associated with exhibition and storage.

MUSEUMS COLLECT, EXHIBIT, AND STORE MATERIALS that reflect a single culture, many cultures, or the "natural" world. As early as 290 B.C., Ptolemy created an institution for learning called a museum, which housed both biological and cultural objects (*1*). Wooden artifacts represent a significant component of past cultures. Historically, wood was particularly suited for the needs of various cultures, because it could either be used with little alteration or be manipulated with heat, tools, or water.

Wood introduces a unique set of concerns for the museum conservator. As an organic material, wood is susceptible to the forces of its environment. Organic materials continually undergo biological and chemical degradation in their natural settings. When a wooden artifact is displaced from its native setting, further degradation is not suspended. When the artifact is suddenly

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introduced into the new environment of a museum, the artificial environment of its adopted home can further influence the integrity of the wooden piece.

Herein lies the paradox. As a cultural representative, wooden artifacts provide the visitor and the scholar with insight into past cultures. However, public display of delicate artifacts can cause further degradation. This delicate balance between visitor needs and conservation considerations must be attended to by the museum staff. A stable environment (control of temperature, light, pests, and atmospheric pollution) must be provided for such artifacts, while still remaining true to the educational function of a museum.

This chapter will address many of the problems associated with the exhibition and storage of wooden artifacts. Wooden artifacts enter the museum in many states—wet or dry, fragile or sound, raw or worked, pigmented or gilded, associated with composite materials, or even fossilized. Ideally, this cultural artifact should be treated in a sympathetic manner, so that it will be assured a lengthy future of exhibition, storage, study, and institutional loaning. The demand for environmentally stabilized display cases and mounting techniques, as well as proper storage systems and cabinetry, is of paramount importance.

Chemistry of Wood Degradation

A number of unanswered questions exist in the field of wood conservation. Previously, the conservation literature addressed empirical descriptions of old wood structure and preservation. However, the complex chemical and physical state of the wood was not explored. Without a fundamental understanding of how wood reacts with its environment, it is impossible to accurately assess the best system of exhibition and storage.

Structure. Wood is considered a composite material because it is a mixture of many chemically and structurally different parts, the three most important parts being cellulose, hemicelluloses, and lignin. Because of their fundamental differences, these parts can be expected to react dissimilarly under identical environmental conditions. Therefore, the strengths and weaknesses of wood as a whole can only be related to the relative strengths and weaknesses of the parts.

When we address the changes that could affect the wooden artifacts during museum storage and exhibition, we must look at the chemistry and structure of the individual artifact (Chapter 5). Strengths and weaknesses must be assessed, and a three-dimensional picture of the wood system should be envisioned. Once we gain a better understanding of this complex organic object, we can measure the effects of light, pollution, and relative humidity on that system.

Cellulose. Cellulose is the most abundant component of wood, comprising 40–45% of the dry weight of wood. Classified as a polysaccharide, cellulose is composed exclusively of D-glucose sugar units, which are joined in a pyranose ring structure by acetal linkage to form β-D-glycopyranose segments. These segments are, in turn, bonded together by (1 → 4) glycosidic bonds, forming high-molecular-weight linear chains. These individual polymer chains can pack very closely together and form hydrogen bonds with adjacent chains. Bundles of such hydrogen-bonded chains, referred to as microfibrils, serve as structural support for the cell wall.

The structure of a microfibril is quite complex. It is believed to contain ordered crystalline regions, as well as disordered amorphous regions. In the crystalline areas, the glucan chains are tightly packed and hydrogen bonded to one another. The resulting rigid crystalline structure is quite resistant to liquid penetration, and so the rate of swelling is greatly reduced in these regions.

The amorphous areas, on the other hand, are structurally disorganized. Naturally occurring chain defects and loose polymer chain ends prevail, giving the region a loosely packed character. Therefore, hydrogen bonding between glucan chains can occur only when the chains randomly come into close contact with one another. Where no such bonding occurs, internal space results. These voids facilitate the movement of liquids into the amorphous region. As the liquid reacts chemically with the free hydroxyl groups, swelling and contortion of the polymer system results. Such disordered areas prove to be the weak link of microfibrillar structure. Degradation and depolymerization of cellulose could occur from the cleavage of hydrogen and glucosidic bonds, the breakage of acetal linkages, or by end-group reactions at the ends of polymer chains.

Cellulose, because of its highly crystalline nature, is a fairly resistant polymer. In alkaline condition, the cellulose structure will swell and "peeling" of sugar units off the chain ends can result if the pH is high enough (*2*). However, the cellulose chain will not undergo extensive depolymerization. If ozone is added to this cellulose–alkaline system, glycosidic bonds will be cleaved and reactive carbonyl groups will be introduced to the newly cleaved chain ends (*3*). Ozone is a stronger oxidant than atmospheric oxygen, and it attacks unsaturated double bonds (*4*).

In acidic conditions, glycosidic bonds are cleaved in the cellulose structure. The rate of this reaction is controlled by the crystallinity of the cellulose and the temperature of the system (*3*, *5*, *6*). The resultant hydrolyzed cellulose has a shorter chain length than the original polymer, which greatly decreases the strength of the wood (*7*). Hackney (*8*) noted embrittlement and discoloration of sulfur dioxide exposed cellulose fibers. Such acid hydrolysis experiments have been conducted in aqueous systems, with the degradation rate dependent on the diffusion characteristics of the acidic solution into the wood structure. Because museum artifacts will not normally have to withstand such extreme conditions, these results serve as a worst-case scenario.

Archaeological wood is often found in association with metals. In this mixed-media situation, the presence of ferrous ions will catalyze cellulose oxidation and hydrolysis by forming free peroxide radicals (2, 3).

Hemicelluloses. Hemicelluloses are low-molecular-weight polysaccharides composed of a heterogeneous mixture of nine sugar monomers (D-glucose, D-mannose, D-xylose, L-arabinose, L-rhamnose, D-glucuronic acid, 4-*O*-methyl-D-glucuronic acid, D-galactose, and D-galacturonic acid). These sugars combine in a variety of ways, forming three groups of hemicellulose polymers: xylans, mannans, and galactans. The solubility characteristics of these hemicellulose groups differ as a result of differences in their structure and degree of polymerization.

Xylans, the principle components of hardwood cellulose, are found to a lesser degree in softwoods. Two representatives of the xylans are glucuronoxylan, a major constituent of hardwoods, and arabinoglucuronoxylan, a lesser component of softwoods. Xylan structure is characterized by a backbone of D-xylose monomers linked by (1 → 4) linkages. From this xylose backbone branch 4-*O*-methyl-α-D-glucopyranose and arabinose side chains, as well as acetyl groups.

Glucomannans, the principle component of softwood hemicellulose, occur in very small quantities in hardwoods. Unlike the chemically homogeneous backbone of the xylans, the glucomannan backbone is formed from varying ratios of D-mannose and D-glucose sugar units. From this heterogeneous chain branch side chains of acetyl and D-galactose units. A special group, the galactans, are constructed from D-galactose units linked by 1 → 3-β-D linkages. Side chains of D-galactose, L-arabinose, and D-glucose extend from the galactosidic backbone. This water-soluble hemicellulose group is found primarily in larches.

The hemicellulose polymer chains contain side groups that protrude from the polymer backbone. Because these chain projections obstruct orderly chain alignment, the resulting polymer system will not pack as tightly as the crystalline portion of the cellulose microfibril. For this reason, hemicelluloses are more susceptible to chemical degradation than cellulose.

In the cell wall, hemicelluloses are thought to surround and sheath microfibrils, forming a chemically bonded cellulose–hemicellulose network. Whereas the composition of cellulose is consistent for softwoods and hardwoods, the chemistry and structure of softwood and hardwood hemicelluloses differ. Even within a single tree, different parts will contain varying amounts of certain hemicellulose species (9). Given this variability, hemicellulose contents for hardwoods and softwoods are generally reported as ratios, rather than as exact quantitative measurements.

Hemicelluloses have a lower crystallinity than cellulose, and so they will be more susceptible to degradative forces. Under alkaline and acid conditions, the acetyl groups of xylans and glucomannans are hydrolyzed to acetic acid (9). When exposed to acidic conditions, the chemistry of hemicellulose degradation becomes more complex because the different sugar monomers show varying levels of resistance to acid treatment (6). (The rank order of resistance to acid treatment, from least to most resistant, is xylose, arabinose, mannose, and glucose–galactose.) Glycosidic bonds between the D-xylose units of xylans are readily hydrolyzed. The glucomannan backbone is also depolymerized, and the L-arabinose and D-galactose side branches are cleaved from the main chain (9). Seifert (*10*) found that pinewood pentosan chains were cleaved after only 5 months in a weakly acidic environment. Therefore, acid hydrolysis of hemicelluloses cause structural change, the product of which is a mixture of sugar monomers and their degradation derivatives (6).

Lignin. The third important component of wood is lignin, a complex polyphenolic polymer whose extensively branched structure is still not well understood. Lignin is composed of basic phenylpropane units joined into different structural configurations via ether linkages or carbon–carbon bonds. The resultant lignin is a high-molecular-weight amorphous substance, apparently organized into discrete units rather than polymer chains. Phenolic and benzylic hydroxyl groups, as well as reactive carbonyl groups, allow lignin to bond with hemicelluloses via hydrogen bonding. Lignin is distributed in domains throughout the secondary cell wall and in the middle lamella, where it acts as an intracellular glue or encrusting material.

Lignin is much more stable under acid conditions than carbohydrate polymers. However, chemical deterioration of lignin can occur, and such deterioration causes cleavage of ether bonds. This reaction may occur during the prehydrolysis of hemicelluloses, when the lignin–polysaccharide bond is broken, and it may affect the chemical structure of lignin (6). Lignin is greatly affected by UV light (Chapter 11), and so improper lighting might serve as the initial degradative catalyst.

Exhibition and Storage Environment

The degradation mechanisms active during long-term exhibition and storage of collections have only recently been subjected to scientific scrutiny. Such factors as display case construction, temperature and moisture regulation, and lighting effects have proven to be important considerations for fragile wooden pieces. The stabilization of the museum environment will, in the long run, benefit the structural integrity of archeological wood, in both storage and exhibition.

Moisture and Temperature. Water exists in wood as liquid and vapor. Within the wood structure, water fills cell lumens and chemically bonds with hydroxyl groups in the cell walls. To obtain a measure of how much free and bound water is in the wood system at any one time, the moisture content can be calculated. If the wood is subsequently dried, with the free water liberated and only the cell walls saturated, the fiber saturation point (FSP) has been reached. Any drying below this FSP will cause the chemical bonds between the cell wall and water to be broken. The force of pulling the water from the cell wall hydroxyl groups causes damage in the form of cell wall distortion and collapse.

Wood structure can respond to environmental changes in many ways. For instance, it can equilibrate with its environment, provided that the surrounding environmental conditions are constant. This equilibrium moisture content (EMC) is characterized by an unchanging wood moisture content. If, however, the environment is constantly changing, wood will react to the abundance or absence of moisture in the air. In general, moist or humid air will cause wood to swell, as well as provide a favorable environment for fungal attack. Conversely, if the air is too dry, wood will shrink and become brittle. The combination of humid and dry fluctuations can eventually lead to cracking, checking, and warping of the wooden artifact (*11*, *12*). Complicating this picture is the fact that wood is anisotropic, which means that it will shrink unevenly along its tangential, radial, and longitudinal directions.

The moisture content of the air is not a discrete system in itself. The amount of water vapor in the air is intricately linked to the temperature of the environment. Therefore, in order to get a proper perspective on the water–wood interaction, it is important to understand the relationship between temperature and relative humidity (RH). RH is a measure of how much water vapor is in the environment relative to the maximum amount of water vapor that the air could possibly hold (saturation) at a certain temperature.

Air temperature plays a very important role in the relationship of RH and the stability of the environment. In general, cool air cannot hold as much water as warm air can. If a pocket of cool, humid air (RH = 100%) were heated, the newly warmed air would be able to hold more moisture. If none were supplied, the relative humidity would steadily decrease as the temperature rose. In this situation, the initially water-saturated pocket of cold air would be a warm, dry air pocket.

This illustration can be translated into real-life situations by examining the heating–cooling systems found in museums. The process of heating and cooling the museum environment without proper humidity control can result in large seasonal shifts of relative humidity. In this system, it is easy to envision the structural movement that wooden artifacts must undergo. Each RH fluctuation would result in specimen reequilibration to the new environmental condition. As the wood absorbs or emits moisture, its structure undergoes stress. If severe drying occurs, cell walls will collapse and structural distortion results. Painted wooden panels are especially sensitive to frequent environmental changes. One side of the panel is covered with a hydrophobic layer of paint and perhaps a layer of gesso, although the support structure is unfinished. The unfinished wooden surface will expand and shrink with changes in RH. These changes cause the paint-covered portion of the panel to pucker and peel (*13*).

Climate Control. What guidelines can a conservator follow to ensure structural stability for a wooden artifact? An ideal environment has been achieved when no cyclic variations occur around the organic artifact. Slight seasonal shifts are permitted, as long as the change is slow (*14*). Thomson (*15*) recommended 19–24 °C and 45–55% RH as ideal conditions for the museum environment housing unpainted wooden objects. At lower RH values, wood cracks and undergoes dimensional changes; above 65% RH, mold growth is promoted (*16*).

These values may be economically feasible for the climates found in Great Britain, Holland, Belgium, France, Germany, and Scandinavia. However, they are unrealistic for temperate climates that experience seasonal climatic extremes (*17*). Providing the proper humidity values year-round, while fighting low outside winter temperatures, would be an infeasible standard for most buildings. Condensation would form on or within the exterior walls, thus negating the effects of a proper vapor barrier (*18*).

Rather than an effort to precisely regulate the entire museum environment, a much more economically practical solution has been proposed. Michalski (*19*) recommends the use of separate climate controls for each display case, creating a series of microenvironments. Many problems can be overcome if the cases are climatically controlled as individual microenvironments. These self-contained units facilitate the maintenance of specialized conditions, rather than relying upon the museum's heating, ventilation, and air conditioning (HVAC) system for control (*20*). Aside from saving energy, the microenvironments can be altered as the exhibits change.

The important consideration is the equilibration of the artifact to its surroundings. The damage caused by dramatic climate shifts may not be readily visible at first, and so equilibration is essential. Johnson and Cairns (*16*) note that an artifact can become acclimated to previous nonideal environmental conditions. When subsequently placed in an ideal situation, it will undergo warping. Therefore, even if the necessary RH level is lower than the ideal of 45–55%, it should be maintained at this value (*18*). The ideal environment for each wooden artifact must be individually assessed. Stolow (*17*) suggests that ". . . an account must be taken of the object's past environmental exposure (and corrective treatments, if any), its present condition and fragility, geographic location and climate, the building environment, public comfort, and whether the object will travel and be exhibited elsewhere."

Consideration should also be given to poorly designed or operated HVAC systems. Proper operation and regular maintenance is necessary to keep the system efficient and effective. This emphasis on the proper stabilization of the museum environment with properly operated HVAC systems is a relatively new effort. Historically, artifacts have been housed in buildings with nonregulated environments. It is often through chance that some wooden objects have withstood the test of time.

Display Cases. In the past, the ideal display case was solidly constructed of wood. Gasketed doors and access panels provided a tight fit, so that air exchange into and out of the case was restricted. Such a construction buffered the wide temperature and RH fluctuations that befell museums. However, the tightness of the display case did not stop fluctuations in RH, as heat emitted from light fixtures gradually increased internal case temperatures. Thus, a more reliable system of internal climate control was needed. Even though the wooden components of the display case could react with RH changes, wood can absorb only 9–11% moisture by weight (*13*). A new system should be able to regulate RH shifts while maintaining a specified RH value. In this way, the wooden artifact could equilibrate with its surroundings.

Silica Gel. Toishi (*21*) found that internal case humidity values could be controlled chemically with preconditioned silica gel, which can absorb over 30% moisture by weight (*13*). When preconditioned to 55% RH and placed inside a display case, the gel not only reduced humidity variations, but also buffered the small changes in RH (*21*, *22*). In fact, not only was silica gel a good reusable buffer, but it also allowed for a specific RH to be set within the case. However, its use can be financially prohibitive. Large quantities are needed to properly regulate display case conditions, and reconditioning this bulk can be labor-intensive.

To solve the problems of bulk, Nikka pellets and Artsorb were introduced. Although a large quantity of these sorbents is still required, they are more responsive absorbing agents than silica gel, and so less is needed.

Air Exchange. Mechanical control of display case conditions has been developed. Such systems condition the ambient museum air outside the case to a specific RH, and then introduce this conditioned air into the cases under low pressure. This system allows for several air changes per day within the case. A daily exchange of air within the case frequently removes pollutants that have been released from display case construction materials or from the artifact itself.

In an effort to better understand the air exchange between the display case and the air outside the case, Thomson (*23*) introduced the concept of hygrometric half-time (*23*). If vapor exchange can be predicted, then display case microclimates can be regulated reliably. Brimblecombe and Ramer (*24*) used the guidelines prescribed by Thomson and calculated that, with air exchange, the amount of silica gel required to stabilize a case would be 20 kg/m^3. Stolow (*17*) noted that the vapor exchange in larger display cases is more difficult to control. He advised the use of both chemical buffers and mechanical buffers, such as fans, pumps, and ducts.

Of course, consideration of case design is essential in the effort to achieve proper climate control. If the cases are tightly sealed, then temperature and RH shifts that occur outside the case are buffered within the case. If cases are not sealed, air movement into and out of the case is facilitated, and so environmental fluctuations are more pronounced. In this situation, the proper installation of lights is important. Internal case lighting will cause large RH shifts.

Temperature. An interesting interplay between temperature and RH has been seen in closed display cases housing moisture-containing material (*22*). Normally, as the temperature in the display case rises, the local RH would correspondingly decrease. With moisture-containing material, however, the RH actually increases with increasing case temperature. At elevated temperatures, water evaporates from the wood structure. This liberated water vapor enters warmed air, which has a greater potential to retain moisture. Thus, RH within the case increases.

Light. Light, divided into three fundamental components of radiation (infrared, visible, and ultraviolet), emits a range of wavelengths. All three of these components are found in daylight. Wood that has been exposed to the visible and ultraviolet wavelengths of daylight will undergo a color change. Because light penetrates wood superficially, the degradation by rays will only affect the outer few millimeters of the surface. The absorption of light by chromophoric groups in wood will result in chemical bond breakage, free radical formation, and subsequent depolymerization of wood polymers. The chromophoric groups within the polysaccharide polymers (hydroxyl, carbonyl, carboxyl, and acetyl groups) and lignin polymers (i.e., phenolic hydroxyl groups, double bonds) will strongly absorb light at slightly different frequencies (*25*). Feist and Hon (*26*) note that cellulose and hemicelluloses absorb strongly below 200 nm, and also have various levels of absorption to 400 nm. Lignin strongly absorbs below 200 nm, and peaks again at 280 nm.

Sunlight appears to degrade lignin more rapidly than the polysaccharides. Chemical analyses of outer, weathered surfaces of wood reveal large losses in the lignin fraction. This loss is the result of light initiating the oxidation of lignin phenolic hydroxyl groups. As the degradation progresses, the methoxyl content of lignin decreases, and the carboxyl content increases. Thus, the wood becomes more acidic in nature. Cellulosic and hemicellulosic alcohol groups will also be oxidized in sunlight, to form carboxyl groups (*26*). Xylose and arabinose are more susceptible to hydrolysis than is glucose.

Illumination poses a hazard to museum collections. Bromelle (*27*) cites the bleaching, yellowing, and darkening effects in wood caused by exposure to light. Historically, museums have relied upon the use of natural light to illuminate galleries. Windows and skylights provided a bright environment, allowing the visitor to see the collections. However, natural light is both difficult to regulate and meteorologically unpredictable. A greater amount of environmental control became possible with the introduction of artificial light and different types of lighting sources.

Today, we know that visible light and the shorter wavelengths of ultraviolet (UV) radiation are damaging to wooden artifacts. Therefore, lighting options that selectively delete those aspects should be chosen. Daylight, fluorescent lights, halogen lights, and some incandescent lights emit UV radiation. Each of these light sources falls within a particular color–temperature range and will therefore affect the viewer's perception of the object on display. In addition, each of these light sources has inherent limitations for use in exhibit and display. Fluorescent lighting is energy-efficient and has a long service life. If the light is reflected off a wall painted white with titanium dioxide before it reaches the artifact, the UV element can be greatly diminished (*18*). Quartz halogen lights emit UV in the 310–400-nm range and produce heat. Incandescent lights (tungsten filament) release less UV radiation, but also emit heat (*17*).

Lighting Requirements. Brommelle (*27*) notes that a delicate balance exists between visibility for visitors and conservation lighting concerns. It is easier to control incandescent lighting than fluorescent lighting at low light levels (i.e., 50 lux). The reason for this is three-fold: incandescent systems accept a wide range of bulb wattage; existing incandescent fixtures can accept a rheostat; and the light from incandescents is perceived by the viewer as a warmer light. Spot lamps should not be installed inside display cases without barriers, as they produce IR radiation in the form of heat. Lighting, when sequestered in cabinetry separated from the exhibit case, should be vented to allow air circulation to dissipate heat buildup (*28*). Spot lamps, which focus highly localized heat on a specific object, cause thermal fluctuations in the object's surface temperature. Overall, the choice of any lighting system determines a balance between light generated, viewer perception, and heat released (*29*).

Published lighting requirements (*20*) note a 300-lux maximum–50-lux minimum as appropriate light levels for use in display cases. Staniforth (*28*) and Thomson (*15*) recommend a maximum of 150 lux for wooden objects; they discourage direct lighting on any object. Light monitoring is essential (*28*). The total cumulative light exposure is the critical value, with monitoring expressed in kilolux-hours (*15, 30*). Display lights can be turned off when museums close, and sensitive materials can be rotated out of display (*20*). Ideally, the storerooms should remain darkened (*28*).

Interaction with Temperature. A complicated interaction between light emission and object temperature also exists. This combined heat–energy system can affect all organic materials. If an object is illuminated with an incandescent light bulb, part of the heat produced by the filament will be transferred to that object.

Thomson (*15*) states that "most of the electricity which passes through an ordinary tungsten lamp is converted to heat (98% for a 100 watt lamp) not light". Because chemical reactions are accelerated in the presence of increased heat, the conditions are prime for chemical and physical deterioration of the artifact. If a fluorescent bulb were substituted for an incandescent bulb, the heat emission would be diminished, provided that the element were separated from the display case. However, extremely energetic UV radiation would be introduced (*15*).

Filters. UV emissions can be controlled through the use of a polycarbonate filter or an acrylic sheet with UV-absorbing capabilities (*31*). Flexible polyester sleeves with UV-filtering capacities have been popular in museums since the 1970s. These sleeves slide over the standard fluorescent bulb, and the UV-absorber component has a working life of approximately 10 years (*32*). However, the use of flexible sleeves presents several problems: They must be removed and repositioned onto a new bulb during bulb replacement, and these sleeves have a tendency to become brittle and lose effectiveness with age. The cathodes of the fluorescent tube produce heat and can cause embrittlement of the polyester sleeve. The sleeve then shrinks away and exposes the cathode ends of the bulb. This area of the bulb generates more UV emissions, so these filters must be checked regularly (*18*).

The use of rigid polycarbonate sleeves serves as an alternative. According to manufacturer specifications, these UV-absorbing sleeves reduce the majority of UV emissions from fluorescent bulbs. These rigid filters do not shrink from the cathode ends of the bulb, and they reduce the potential for bulb damage. The sleeves may last up to 10 years, with a slight yellowing of the material (*32*).

Even with the use of these filters, there is now evidence that blue light in the visible range (400+ nm) will also cause photodegradation (*30, 33*). The filtration systems presently available do not effectively eliminate this less-active region of the spectrum.

Mounting. The purpose of proper mounting is to provide sympathetic support for the collections. Museum collections, while on exhibit, serve the needs of several masters: the curator, the educator, the designer, and the conservator. At no time should the act of exhibition endanger the collections. The fine balance between proper exhibition technique and effective, sympathetic mounting demands the interaction of the designer, mount maker, and conservator. Of paramount importance is the use of chemically inert, stable materials for mount making and exhibition installation.

Degraded materials are weak and prone to damage from improper movement and handling. The effects of gravity also play a role in reducing the longevity of collections. If pieces are not adequately supported, they will be subject to tension and stress. Conservators must work against gravity, because many objects were never intended to be self-supporting (*34*). For example, wooden boats and long wooden objects need to be properly supported along their length to prevent distortions of shape over time. The goal of proper mounting is to prevent distortion of shape, to be unobtrusive to the integrity of the piece, and to make mounting materials conform to the object, rather than vice versa. By taking into account the structural components of the artifact as well as its material makeup, the conservator should be able to anticipate future changes the object may undergo. Ward (*34*) recommends a two-part support system, composed of one part that fits the artifact exactly and a second independent part that can be used to display the supported artifact in many ways.

Materials used in mount-making should not adversely affect the object. They should not be hygroscopic in nature. This requirement reduces the possibility of supporting biological degradation and of chemical interaction. Hodges (35) cites several mounting aids that may cause problems. For instance, animal glues can support mold in humid environments. Polymer adhesives, on the other hand, can contain plasticizers that volatilize, migrate, and become unstable over time. Metal pins and fasteners can corrode in high humidities and cause staining where they are in contact with the artifact. Therefore, the watchword is sympathetic mounting, geared to eliminate any deleterious elements within the exhibition parameters.

Storage Areas. Artifacts in storage can be subjected to a number of destructive environmental effects. These effects are influenced by building design, storage design, and the placement of storage areas within the museum complex. Wooden objects in storage can be influenced by the proximity of the storage area to an exterior wall, inadequate vapor barriers and insulation, or an improperly balanced environmental control system. Also of importance is the proximity of artifacts to heating outlets, air conditioning ducts, radiators, plumbing, and windows.

The requirements for proper storage of archaeological wood are as follows:

- There must be protection from extremes in temperature and RH fluctuations, airborne dust–dirt, and pollutants.
- The object must be properly supported; areas of undue stress must be eliminated.

- There must be control of handling, excess light, and biodegradation.
- There must be the ability to protect collections from newly introduced artifacts that may harbor infestation.
- There must be the ability to access the collections and observe the distinguishing characteristics of the object.
- The storage facility should offer long-term protection to the collections, including the need for security and monitoring for fire and water damage.

The selection of any storage system should take into account the stability of the building materials, the nature and size of the collections, access to the collections, and the individual needs of the material that is to be stored. Frequently, museums have designed and constructed storage units with readily available materials such as wood. These systems were often duplications of previously existing storage facilities at other museums. Therefore, inherent design problems were carried from museum to museum. For years, wood acted as the skeletal structure for museum storage. Problems developed from this type of construction, such as the introduction of infested building materials and the further support of infestation. Collections have been directly affected in storage by volatile substances emitted by plywood and particleboard, as well as from paints and finishes used as vapor barriers (*36*).

Materials. Other materials, such as industrial shelving and cabinetry, have been adapted for museum use. Because the manufacturers of these units did not have the same concerns as conservators, the museum community has encountered difficulties in trying to adapt storage systems from commercially available products. Eventually, companies began to design and advertise cabinetry that would fit the particular needs of the museum community. The burgeoning area of museum storage case production has had to overcome quality control problems such as improper paint curing and door gasket failure (*37, 38*). Therefore, all materials used in storage and within the proximity of the collection should be tested for compatibility with the collection.

A barrier that would protect an artifact from RH shifts, dust–dirt, and pollutants would be of great use in storage areas. The introduction of a polytetrafluorethylene (PTFE) membrane, which can be manufactured into bags, offers the potential for long-term inert storage. Although the opaque nature of PTFE limits visual contact with the object, it could function as a barrier for open storage. A more cost-efficient alternative is the use of virgin polyethylene and polypropylene bags or sheeting. This system buffers environmental shifts, as well as protects against infestation, water leakage, and airborne particulate matter. Both polyethylene and polypropylene bags provide visual access to the objects, but several potential problems have been noted. Polypropylene may develop a static charge, and the release of dioctyl phthalate plasticizers used in the production of polyethylene may influence the results of organic analysis (39). These bags should not be considered as support mechanisms for the objects, and so caution should be exercised when lifting objects.

Containerized Storage. Containerization for collections has been advocated as a long-term storage technique. It is important to assess the type of container to be used. For instance, corrugated wood pulp paper supports infestation, both as a food source (glues) and as an environment for insect habitation (corrugations). Compounding these problems is the hygroscopic and acidic nature of the material. An alternative to the use of paper products is the corrugated polypropylene box. By nature hydrophobic, these boxes are chemically stable and will therefore provide long-term stability. An inherent vice of opaque material, however, is the lack of visual contact with the collections. Once a collection is boxed and removed from sight, museum staff must periodically check it for signs of destructive elements.

Cotton and paper products should be avoided for long-term storage. These materials will hold moisture, which encourages collection deterioration by mold, as well as providing nesting material for insects and rodents. An alternative is polyester batting, a thermoplastic material that has low water absorption properties and is stable as a storage material. Polyester sheeting has been found to be an effective vapor barrier when used between the objects and the storage shelving. Expanded polyethylene foam has been used extensively as a cushioning and support material for fragile artifacts, and as a barrier between collections and shelving. The compatibility of storage and exhibition materials to be used in conjunction with artifacts should be tested via a procedure similar to that proposed by Oddy (*40*). Formulations may change and materials may fall in and out of favor, but the final choice of storage materials must be compatible with the collections.

Drawer Storage. The drawer system for storage was embraced for its flexibility, compartmentalization, and universality. The drawer offered overall support, the potential for individual compartmentalization, expansion within areas as collections increase, and limited visual access. Some problems associated with the drawer system include the lack of dust–dirt control, the problem of insect and rodent infestation throughout the open system. The temptation to overload the drawers and stack collections represents negative aspects of the system.

Compacted Storage. Because of space constraints in buildings and the need to better utilize storage space, movable compacted storage systems have appeared in many museums in North America. These systems, either motorized or manual, can be customized to fit existing storage areas. Compacted storage systems provide more storage space and easy access to the artifacts. Customized gasketing can eliminate light and particulate matter when the unit is in the compacted position. However, pollutants are also trapped by this gasketing. Because all of the collections are encompassed in one unit, rampant infestation is possible. In addition, vibrations caused by the movement of the shelving units could damage fragile objects. An important consideration is the weight-load parameters of the building itself. Because a great deal of concentrated weight is being installed in a small area, building load capabilities may be violated.

Choice of System. The selection of a closed cabinetry system requires the scrutiny of available systems (commercial or customized) to attend to the overall collection storage needs. Can the units be vented, and can these vents be filtered to eliminate the entrance of pollution, dirt, dust, and infestation? If metal cabinetry is chosen, will the units provide a tight seal to both stop the entrance of infestation and isolate infested cabinets? Are the construction materials and their surface treatment inert and nonthreatening to collections? Is the metal cabinetry compatible with the museum environment, or does the museum have climatic fluctuations that could result in condensation on metal surfaces? Does the storage system allow for flexibility as the collections grow?

An object may only need to be placed in a polyethylene bag and rested on a padded shelf or cabinet. Small pieces of archaeological wood, if deemed stable, can be boxed in acid-free cardboard or containerized in open boxes and then placed in storage drawers. When structural support is needed, a cradle can be fashioned from a nonabsorbant material, such as expanded polyethylene foam. Larger-scale supports can be constructed from acrylic sheeting, brass rods cushioned with inert tubing, or wooden cradles equipped with pallets for easy movement and handling. Large objects that do not fit into existing storage space can be placed on pallets for safety and ease of mobility (*41*).

Environmental Destroyers

Infestation. Historically, the approach to infestation control in museums has been chemical intervention (*42*). The chemical approach has resulted in physical changes of the artifacts, surface deposition of chemicals on collections, and health and human safety policies within the field. Chemical pest control does not guarantee the elimination of all stages of insect infestation; thus, consistent protection requires the continued application of chemicals. As Environmental Protection Agency (EPA) standards constrict the use of fumigants and as the list of available pesticides has been reduced, the museum community is embracing the concept of integrated pest management (IPM) (*43*).

The holistic concept of an IPM system involves the integration of all museum personnel and activities. These activities include the monitoring of museum exhibition and storage areas with adhesive insect traps; placing collections in polyethylene bags; establishing nonchemical procedures to combat active infestation; and maintaining comprehensive record-keeping. The scope of infestation control includes the design and types of materials in the construction of a new building, exhibition and storage areas, and the selection and maintenance of an HVAC system. It is only through understanding the life cycles of the insects and the organic material prone to infestation that we can formulate policies and procedures to eradicate infestation and provide long-term safety for the collections.

Florian (*44*) tested and reported a nonchemical approach to the control of infestation within collections. The focal point of this technique is freezing at a prescribed temperature for a prescribed amount of time. This freezing technique eradicates all stages of insect life (egg, larva, and adult). No structural changes within the material result, and there are no negative health and safety aspects. Notable exclusions from this procedure are wet and waterlogged materials; some wooden artifacts with finishes, coatings, and adhesives; and objects with fragile surfaces.

Pollution. Gaseous and particulate air pollution is a fact of life. Although it may be invisible to the human eye, its detrimental effects on a fragile wooden object may be very visible. Aided by an uncontrolled warm, humid microclimate in the display case, pollution chemically degrades wood and can diminish the aesthetics of an artifact by discoloration or decay.

External Pollution. Air pollution can come from sources outside of and inside the museum. Externally produced pollutants include carbon particles from fires, salt particles from sea spray, carbon monoxide and carbon dioxide, nitrogen, sulfur dioxide, and ozone (*11*). The extent of the wooden object's chemical and structural damage caused by these gases and particles is not fully understood. However, the interaction of these pollutants with the surrounding environment can be elucidated. Sulfur dioxide, the product of fuel combustion and carried in water droplets, readily oxidizes to sulfuric acid. This acidic product can enter the museum environment through the ventilation system and be deposited on the wooden artifacts (*45*). On particularly foggy days, the sulfur dioxide content of the air can be 10 times higher than usual (*46*). Salt crystals, another harmful pollutant, are carried inland by fog and wind. By nature hygroscopic, the salt could create a moist microclimate on the surface of a wooden object and thereby promote localized fungal growth (*20*). Finally, carbon particles that come to rest on organic surfaces can cause staining (*27*).

Outside air, containing many of these harmful agents, can be purified before it enters the museum environment. The proper ventilation system should be able to combat both particulate and gaseous forms of pollution. Such a system requires a water–air particulate washer or a separate, chemically active gaseous filter (*18*). However, the museum will still have to deal with internally produced pollution from light fixtures and assorted materials used in the construction of display cases and storage units. This in-house pollution is more insidious in nature, because harmful vapors can be emitted from surfaces in direct contact with artifacts. The damage caused by these degrading materials, previously thought to be inert, might go unnoticed for some time.

Museum-Generated Pollution. The sources of museum-generated pollution are diverse. For instance, sulfur compounds are released from wood adhesives used in case construction (*35*), as well as from the rubber gaskets that seal display case gaps (*36*). The use of polyvinyl chloride (PVC) materials in storage areas can create indoor pollution, as they release vapors that can cause the formation of small amounts of hydrochloric acid (HCl) in the atmosphere (*47*). Ozone is produced by neon light transformers and the ionizing wires of electrostatic filter systems (*48*). Electrostatically charged particles and water drops, released by improper humidification systems, will cling to gallery walls and exposed artifacts (*48*). In addition, curing cement will create an alkaline atmosphere, while linseed oil and paper will gradually acidify its surrounding environment (*35*).

The greatest internal pollution offender, by virtue of its prominent use in display and storage situations, is wood. In its natural state, wood can release acetic acid (*49–51*). The exact amount of acetic acid that is liberated varies with species, tree age, and the season in which the tree was felled (*51*). In the presence of moisture (high RH or EMC) and elevated temperatures, these acidic vapors will corrode metal (*52*, *53*). This acidity is the result of the hydrolysis of acetyl groups in the hemicellulose fraction, forming volatile acetic acid vapor. Oak, valued for its strength and durability, should not be used as a building material in museums because of its highly corrosive nature (*53*). The process of kiln-drying wood appears to inhibit losses of volatile acetic acid. A great release of acidic vapor follows kiln-drying. On the other hand, air-dried wood is thought to steadily release volatile acetic acid, and so gradual dissipation of the destructive vapor is facilitated.

Plywood and particleboard, affordable building materials, have been used in many facets of exhibition case design and storage. Unfortunately, these wood products are often bonded together with formaldehyde resins. As the resin cures over time, it will release formaldehyde vapors into the environment. In the presence of moisture, atmospheric formaldehyde will be converted to corrosive formic acid (*36*). In an attempt to diminish the acidifying effects of wood, coating and varnishes have been applied on the wood surface that is in contact with the artifact. Instead of sealing the wood, these coatings have themselves been found to emit pollutants (*54*). Therefore, materials to be used in case construction must be chosen carefully. All the elements included in exhibition and storage design should be inert (*35, 36*). This is particularly important for composite artifacts, because many types of deterioration are possible. Oddy (*40*) recommends the testing of any wood, display textile, paint, or adhesive that is to be in the vicinity of an exhibited or stored object.

Once the types and sources of pollution have been identified, it is necessary to explore possible pollutant–artifact degradation scenarios. The fundamental chemistry of wood, presented earlier in the chapter, provides the interactive backdrop. In reality, archaeological wood will be subjected to a host of atmospheric pollutants and varying climatic conditions at one time. However, to understand the entire complex system, it is important to study the interaction of its individual parts.

Future Directions

In recent years, the focus has been on preventive conservation rather than treatment and restoration. This holistic approach emphasizes aspects of proper management, storage, and exhibition of museum collections. Nonchemical control of infestation and long-term conservation planning are important considerations. The focus of curatorial, exhibition, and conservation concerns should converge on the overall well-being of the collections. It is only through understanding all aspects of a museum environment that we can successfully extend the existence of organic artifacts. Through exploration we will gain an understanding of the mechanics of degradation, chemical interaction, and human intervention, so that future generations may study and view existing museum collections.

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16

Chemical Modification of Cell Wall Polymers as Potential Treatments of Archaeological Wood

Roger M. Rowell

U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI 53705

The properties of wood are a result of the chemical and physical properties of the cell wall polymers. During the aging process of wood, the chemical and physical properties of the cell wall polymers change. Degradation of the cell wall matrix and depolymerization of the cellulose molecule result in losses in strength and integrity. This loss of integrity in waterlogged wood results in shrinking, severe checking, and cracking upon drying. Traditional approaches to the restoration of archaeological wood have been either to consolidate the degraded wood to restore strength by encasement with a polymer or polymerizing system or to maintain it in its swollen state with bulking chemicals to avoid shrinking when it is dried. Theoretically, another approach to restoration would be to chemically restore the cell wall matrix and cell wall polymers to a condition simulating their original state. This chapter will focus on ways to react the remaining cell wall polymers with simple reactive chemicals, cross-linking agents, or polymerizable systems.

THE CHEMICAL AND PHYSICAL PROPERTIES OF CELL WALL POLYMERS and their matrix determine the properties of wood. During the aging process, chemical, biological, and physical reactions take place that degrade the cell wall polymers and alter the matrix. Loss of properties such as strength, integrity, and general aesthetics can be directly attributed to changes either in the cellulose, hemicelluloses, and lignin molecules or in the micro- and macrostructure of the cell wall. In most cases, if the wood has survived "nature's degradation system", the resulting material has little resemblance to the original composite. In one sense, we should appreciate nature's degradation system for lignocellulosic material. Without this system, the world would be covered with undegraded wood.

The loss of wood strength and integrity and the dimensional changes that occur with changes in moisture content (which are worsened as a result of the aging process) are the most serious problems facing conservators. Before I discuss treatments intended to restore strength and integrity properties or to reduce the tendency to sorb moisture, I will describe what is meant by strength, integrity, and moisture sorption.

Strength

The chemical components responsible for the strength properties of wood can theoretically be viewed from three distinct levels: the macroscopic (cellular) level, the microscopic (cell wall) level, and the molecular (polymeric) level (*1*).

Macroscopic. Wood, with its inherent strength, is a product of growing trees. Wood exists as concentric bands of cells oriented for specific functions. Thin-walled earlywood cells act as conductive tissue; thick-walled latewood cells provide support. Each of these cells is a single fiber. Softwood fibers average about 3.5 mm long and 0.035 mm in diameter. Hardwood fibers are generally shorter (1–1.5 mm) and smaller in diameter (0.015 mm). The fibers constitute a large mat, bonded together by a lignin phenolic adhesive. The mat is anisotropic in character, but is reinforced in two of the three axial directions by longitudinal parenchyma and ray parenchyma cells. These parenchyma cells function as a means of providing lateral support by increased stress distribution.

The macroscopic level of consideration takes into account fiber length and differences in cell growth, such as earlywood, latewood, reaction wood, sapwood, heartwood, mineral content, resin content, and density. Differences in growth chemistry can cause significant differences in the strength of wood.

Microscopic. At the microscopic level, wood has been compared to multipart systems such as filament-wound fiber products. Each component complements the other in such a manner that, when considering the overall range of physical performance, the components together outperform the components separately.

Within the cell wall, each distinct region (*see* Figure 3, Chapter 11) has a distinct composition and attributes. For a typical softwood, the middle lamella and primary wall are mostly lignin (8.4% of the total weight) and hemicellulose (1.4%), with very little cellulose (0.7%). The S_1 (outer) layer consists of cellulose (6.1%), hemicellulose (3.7%), and lignin (10.5%). The S_2 (inner) layer is the thickest layer and has the highest carbohydrate content; it is mostly cellulose (32.7%), with smaller amounts of hemicelluloses (18.4%) and lignin (9.1%). The S_3 layer, the innermost or terminal layer, consists of cellulose (0.8%), hemicelluloses (5.2%), and very little lignin.

The large number of hydrogen bonds existing between cellulose molecules results in such strong lateral associations that certain areas of the cellulose chains are considered crystalline. More than 60% of the cellulose (*2*) exists in this crystalline form, which is stiffer and stronger than the less crystalline or amorphous regions. The crystalline areas are approximately 60 nm long and are distributed throughout the cell wall.

Microfibrils are highly ordered groupings of cellulose that may also contain small quantities of hemicellulose and lignin. The exact composition of the microfibril and its relative niche between the polymeric chain and the layered cell wall are subjects of discussion (*3*). The microfibril orientation (fibril angle) is different and distinct for each cell wall layer. The entire microfibril system is a grouping of rigid cellulosic chains analogous to the steel reinforcing bars in reinforced concrete or to the glass or graphite fibers in filament-wound reinforced plastics. Most composite materials use an adhesive of some type to bond the entire material into a system. In wood, lignin fulfills the function of matrix material, although it is not truly or solely an adhesive and by itself adds little to strength.

Molecular. At the molecular level, the relationship of strength and chemical composition determines the individual polymeric components that make up the cell wall. The physical and chemical properties of cellulose, hemicelluloses, and lignin play a major role in the chemistry of strength. These three polymers are distributed throughout the wood cell wall, and each layer of the cell wall varies in content of these three polymers (*see* Figure 3, Chapter 11). Our perceptions of wood polymeric properties are based on isolated polymers that have been removed from the wood system and, therefore, possibly altered. The individual polymeric components may be far more closely associated with one another than has heretofore been believed.

Cellulose is an unbranched, rigid-chain, linear polymer composed of anhydro-D-glucopyranose ring units covalently bonded to each other by β-1-4-glycosidic linkages. The greater the length of the polymeric chain, the higher the degree of polymerization, the greater the strength of the unit cell (*3*), and thus, the greater the strength of the wood. The cellulose chain may be 5000–10,000 glucose units long. Cellulose is extremely resistant to tensile stress because of the covalent bonding within the pyranose ring and between the individual units. Hydrogen bonds between the cellulose chains provide rigidity to cellulose via stress transfer and allow the molecule to absorb shock.

The hemicelluloses are carbohydrate molecules that consist of various elementary sugar units (primarily the six-carbon sugars, (D-glucose, D-galactose, and D-mannose) and the five-carbon sugars (L-arabinose and D-xylose). Hemicelluloses have a linear chain backbone with branched side chains and have a lower degree of polymerization than cellulose. The sugars in the hemicellulose structure exhibit hydrogen bonding both within the hemicellulose chain and between other hemicellulose and cellulose chains. Most hemicelluloses are found in the amorphous regions of the cellulose chains and in close association with the lignin. Hemicelluloses may be the connecting material between fibrous cellulose and amorphous lignin. They may also act as a matrix for the cellulose and increase the packing density of the cell wall.

Lignin is the least understood and most chemically complex polymer of the wood-structure triad. Its composition is based on highly organized three-dimensional phenolic polymers rather than linear or branched carbohydrate chains. Lignin is more hydrophobic (water-repelling) than the carbohydrate polymers of the wood cell. Its ability to act as an encrusting agent on and around the carbohydrate fraction, and thereby to limit water's influence on that carbohydrate fraction, is the cornerstone of the ability of wood to retain its strength and stiffness as moisture is introduced to the system. Dry delignified wood has nearly the same strength as normal dry wood, but wet delignified wood has only approximately 10% of the strength of wet normal wood (*4*). Thus, wood strength is due in part to lignin's ability to limit the access of water to the carbohydrate moiety and thereby to lessen the influence of water on the hydrogen-bonded structure of wood.

In conclusion, wood strength results from contributions due to growth (macroscopic level), the make-up of the cell wall (microscopic level), and the properties of the polymers in the cell wall (molecular level). Losses in strength at the macroscopic level result from cracks, splits, delaminations, and extraction of resins and minerals. Losses in strength at the microscopic level result from breakdown of the fiber and the cell wall matrix, extraction of lignin, biological degradation of a cell wall layer, and degradation of the microfibrils. Losses in strength at the molecular level result from depolymerization of the cellulose molecule, degradation of the lignin molecule, and changes in the degree of hydrogen bonding between cell wall polymers.

Integrity

Webster defines integrity as "completeness, wholeness or unimpaired condition". Integrity and strength are somewhat related. Strength of an object is measured in terms of mechanical properties, but integrity is measured in terms of its completeness, mainly visual. A wooden object can undergo considerable hydrolysis resulting in loss of the degree of polymerization (DP) of cellulose (which results in significant strength loss) and still look undamaged.

It is somewhat difficult to describe the properties of integrity. A wooden object has obviously lost both strength and integrity when it falls apart in your hands. However, many wooden artifacts look "original" or "normal" or can still be said to have integrity when, in fact, they possess only a fraction of their original modulus of rupture, fiber stress at proportional limit, modulus of elasticity, work to proportional limit, work to maximum load, compression and tension strength, hardness, and toughness (i.e., their strength properties).

Losses in integrity are mainly a result of losses in strength at the macroscopic and, to some extent, the microscopic levels. For example, after many years of outdoor weathering, wood becomes gray, with a very rough surface, and may develop deep splits and surface checking (*see* Chapter 11). Surface carvings in such wood may also be lost, but very little loss in strength has occurred. In many small wooden objects, losses in integrity may be more important than losses in strength.

Moisture Sorption

Wood changes dimensions with changing moisture content because the cell wall polymers contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding. Moisture occupying space within the polymers swells the cell wall, and the wood expands in direct proportion to the moisture sorbed until the cell wall is saturated with water (fiber saturation point). Water beyond this point is free water in the void structure and does not contribute to further expansion. This process is reversible, and wood shrinks as it loses moisture below the fiber saturation point.

Cellulose, the hemicelluloses, and lignin sorb moisture to different extents (Figure 1). The hemicelluloses are more hygroscopic than cellulose, which is more hygroscopic than lignin (5). This means that lignin (noncrystalline and probably totally accessible), the hemicelluloses (all noncrystalline and nearly totally accessible), the noncrystalline portion of cellulose, and the surfaces of the cellulose crystallites are responsible for moisture uptake by the wood cell wall.

Much more swelling would occur in wood were it not for the matrix the cell wall polymers reside in. Cellulose and varying amounts of hemicellulose and lignin constitute the microfibrils, which are oriented in different directions in each cell wall layer (*see* Figure 3, Chapter 11). Microfibrils in the S_2 layer are nearly parallel to the cell axis and swell mainly in the transverse direction as moisture increases. Microfibrils in the S_1 and S_3 layers are oriented more perpendicular to the cell axis and tend to restrain transverse swelling of the cell wall in much the same way as cross-laminated veneers do in plywood. These restraining forces originating in the matrix of the cell wall polymers control the maximum swelling the cell wall can undergo.

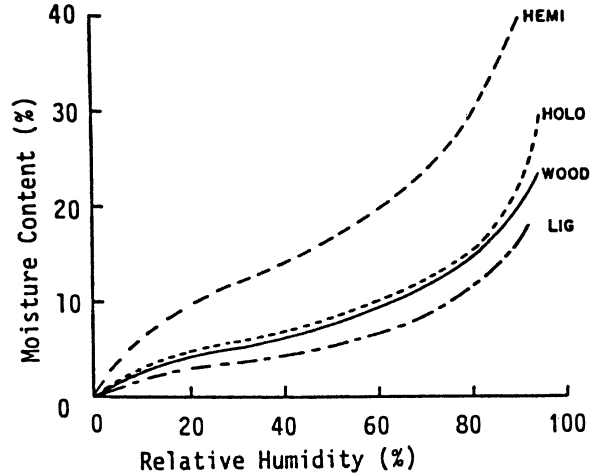


Figure 1. Sorption isotherms for wood hemicelluloses (HEMI), holocellulose (HOLO), Klason lignin (LIG), and wood (WOOD).

The amount of swelling that occurs because of the hygroscopic expansion of the three major cell wall polymers and the wall matrix is dependent on the density of the cell wall (i.e., the amount of sorbing material). Latewood cell walls have a higher density than earlywood walls and therefore swell more. In southern pine, latewood has a density of 0.70 g/cm^3, and earlywood has a density of 0.33 g/cm^3. Latewood cell walls will swell about twice as much as springwood cell walls. Because the tangential cell wall is thicker than the radial wall, more tangential swelling occurs than radial swelling. In most species radial changes are about 40–70% of tangential.

Aged wood can swell more than new wood. Most (60%) of the crystalline cellulose is not accessible to moisture in new wood. However, as degradation caused by chemicals and microorganisms begins, more of the cellulose becomes available for moisture sorption. Along with this degradation comes more surface area and space for additional moisture to penetrate into the wood.

Degradation of the cell wall matrix with aging can lead to the loss of the restraining forces offered by the matrix. This loss allows the cell wall polymers to swell beyond their green volume restrained state.

Treatments for Strength and Integrity Losses and To Reduce Swelling from Moisture Sorption

This topic will be covered from two aspects: traditional methods and theoretical methods. Traditional methods have been covered more extensively in Chapters 12 and 13 and will only be briefly reviewed here.

Traditional Methods. Traditional approaches to strength and integrity restoration center around consolidation systems. These consist of natural or synthetic resins that are impregnated into the wood. The natural resins are usually waxes or oils. Synthetic resins are either thermosetting (based on epoxys, polystyrene, or a polymethyl methacrylate) or thermoplastic (such as poly(vinyl acetate)s, poly(vinyl butyral)s, or acrylics). In general, all of these consolidation systems do not penetrate the cell wall because they are not polar enough or because their molecular size is too large.

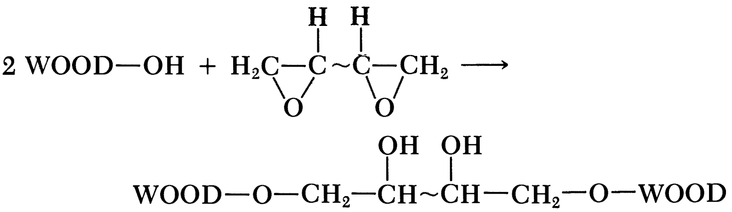
The main function of consolidation systems is to encapsulate the remaining wood structure. Strength and integrity are restored through the properties of the resin system. Strength is restored on the basis of the high molecular weight and cross-linking of the synthetic resins; integrity derives from the filling capacity of the natural or synthetic resins. Additional materials are sometimes added to the synthetic resins for additional strength, space-filling capacity, or color (e.g., fibers, powder fillers, stains).

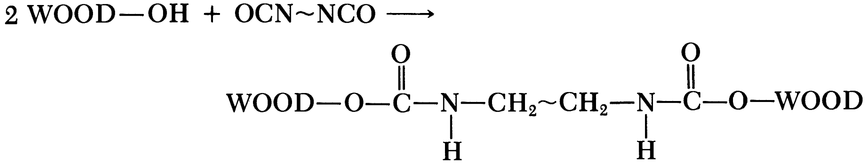
Traditional approaches to reducing wood swelling caused by moisture sorption are based on cell wall bulking with polar, water-soluble, and low-molecular-weight chemicals. The most commonly used chemical is polyethylene glycol (PEG) (*See* Chapter 8). The molecular weight of the PEG is controlled to allow cell wall penetration. After treatment, PEG bulks the cell wall to its green volume. PEG is hygroscopic and water-soluble, so PEG-treated wood must be coated with a moisture barrier and not be allowed to come in contact with liquid water. Other bulking chemicals have been used, including simple sugars, salt solutions, and other organic chemicals, but none is as widely used as PEG.

Theoretical Methods. For the most part, traditional approaches to preserving archaeological wood do not rely or depend on the cell wall polymers still remaining. This section will deal with theoretical approaches based on using what is left of the cell wall polymers as part of the restoration system.

Strength. Because cellulose is an integral part of wood strength, one approach to restoring strength is to attempt to put the pieces of the remaining cellulose back together through chemical reactions. This step can be approached from two reaction types: cross-linking and bonding–grafting combined with copolymerization.

In the cross-linking approach, a difunctional chemical is used that can react with hydroxyl groups on cellulose, the hemicelluloses, or the lignin. Difunctional epoxides and isocyanates have been shown to react with wood cell wall polymers (*6*, *7*).





$$2\,\text{WOOD—OH} + \text{OCN}\sim\text{NCO} \longrightarrow \text{WOOD—O—}\overset{O}{\overset{\|}{C}}\text{—}\underset{H}{\underset{|}{N}}\text{—CH}_2\sim\text{CH}_2\text{—}\underset{H}{\underset{|}{N}}\text{—}\overset{O}{\overset{\|}{C}}\text{—O—WOOD}$$

The remaining cell wall polymers are recombined through these cross-linking reactions; thus some of the strength properties that were lost to aging degradation are restored.

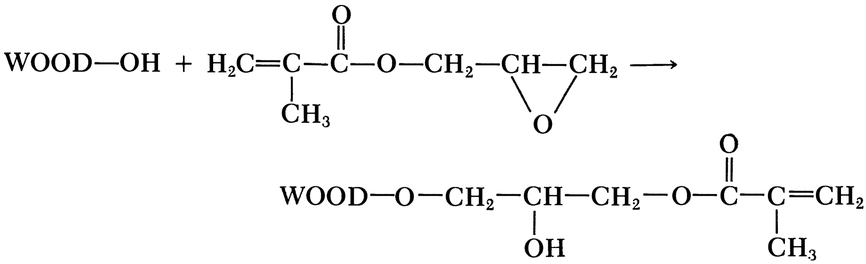
One problem associated with this approach, or with any treatment requiring the penetration of chemicals into wood, is the difficulty in getting the chemical into the cell wall. Either polar chemicals or nonpolar chemicals in polar solvents could be used to greatly improve penetration (*8*). Penetration is made easier in degraded wood by the opening up of the cell wall structure that results from the aging process.

Many difunctional epoxides, isocyanates, anhydrides, or aldehydes are available for reaction. In general, the shorter the carbon chain is between the two functional reactive groups, the faster the reaction will occur. In many cases, once one functional group has reacted, the reactivity of the second is reduced.

Other problems are associated with this approach, such as removal of excess chemicals after cross-linking, reactions with large wood cross sections, and drying the wood before reaction. It is, however, an interesting approach that has had very little research effort.

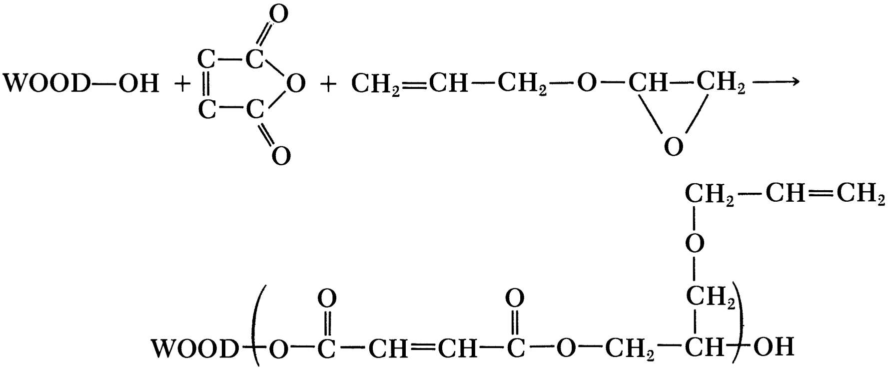
A second chemical system that can be applied to strength restoration is first to react a chemical with a hydroxyl group on one of the cell wall polymers and then to copolymerize this graft into a large cross-linked polymer network.

An example of this method is the reaction of glycidyl methacrylate with wood (*9*, *10*).



The epoxide reacts with a hydroxyl group on one of the remaining cell wall hydroxyl groups, giving an ether-bonded methacrylate nucleus ready for polymerization with an acrylate or methacrylate monomer (*11*). The addition of a cross-linking agent in the acrylate polymerization, such as a glycol di- or trimethacrylate, produces a highly cross-linked, strong, nonleachable polymer.

Another chemical system that has been investigated is the reaction of wood with maleic anhydride and allyl glycidyl ether (*12*).



The introduction of a vinyl group on the graft again allows copolymerization with nitrile, acrylates, styrene, or other vinyl monomers following the initial reactions with a fragment of a remaining cell wall polymer.

As with the difunctional cross-linking reactions, very little research has been done with grafting–polymerization reactions. None of the research done was directed toward archaeological wood restoration.

Integrity. The chemical reactions described in the last section also restore integrity, but go beyond what is needed for integrity restoration alone. In situ polymerization without first cross-linking or grafting can be used to establish integrity in archaeological wood. Traditional methods generally deal with preformed polymers that are impregnated into degraded wood. In contrast, in situ polymerization builds the polymers within the wood cell wall.

Many monomers have been studied, including acrylonitrile, acrylates, methacrylates, styrene, and *t*-butylstyrene (*11*). Most of the research done with these monomers has shown that the formed polymer is in the lumen rather than in the cell wall. Swelling, cell-wall-penetrating solvents can be used to achieve cell wall penetration, so that the polymers that form are in both the cell wall and the lumen.

In this case, a new strength–integrity matrix is formed that is independent of the existing cell wall polymers but in contact with them. Bioactive monomers can also be incorporated into the monomer blend before polymerization; thus biological resistance is given to the treated specimen. Tri-*n*-butyltin methacrylate (*9*, *13*) and pentachloro- and pentabromophenyl acrylate and methacrylate (*13*) have been copolymerized in wood, and the result was resistance to both fungi and marine organisms.

Water-soluble phenol–formaldehyde solutions can also be impregnated into degraded wood and polymerized (*14*). Although this resin system greatly improves strength and integrity, the color of the treated wood is always reddish-brown. This color may not be a problem for darker wood, but it is a serious drawback for many potential applications.

Moisture Sorption. Sorption of moisture and resulting changes in wood volume can be reduced by several methods that take advantage of the remaining cell wall polymers. The cross-linking, bonding–grafting, and cell-wall-filling systems all result in a reduction in moisture sorption and an increase in dimensional stability. The chemicals added to the cell wall occupy space that water would occupy if the wood sorbed moisture. Very little additional swelling can take place unless the cell matrix is so degraded as to allow unrestrained swelling.

Another chemical approach to dimensional stability and a reduction in moisture sorption is to bond simple reactive chemicals to the remaining hydroxyl groups. Anhydrides, isocyanates, epoxides, aldehydes, methylating chemicals, and alkyl chlorides have been studied (*8*). Some of these chemicals are single-site additions (i.e., react with a single hydroxyl group) and some are polymerizing additions (i.e., react with a single hydroxyl group and then polymerize). Either way, the cell wall ends up bulked and expanded to its green volume.

If the chemical used is hygrophobic, it will not only bulk the cell wall, but increase the hygrophobicity of the wood at the same time. In this way a lower amount of bonded chemical is need to achieve the end effect. The modified wood is both water repellent and dimensionally stable.

It is also possible first to react the polymers that still remain in the cell wall with a simple reactive chemical and then to follow this with impregnation of a polymerizable monomer (*15*). The simple bonded bulking chemical provides dimensional stability, and the polymerized monomer provides strength (*16*).

It is also possible to build into the chemical systems other properties that are desired in the treated wood. Fire retardancy, chemical resistance, or resistance to ultraviolet radiation can be built into the bonding or polymerizing systems. Thus, serious problems can be solved while stability, strength, and integrity are improved.

Summary

Strength, integrity, and dimensional stability can be greatly improved through chemical modification of the remaining cell wall polymers left in a partially degraded piece of archaeological wood. Very little research has been conducted in this field. New reactive monomers, cross-linking agents, and polymerizable systems will be found to expand the approaches to the preservation of archaeological wood.

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New Directions in the Conservation of Archaeological Wood

Curtiss E. Peterson

National Center for Maritime Preservation Technology, 21 State Circle, Annapolis, MD 21401

Archaeological wood, often the only surviving example of a society's use of organic materials, can contribute a significant portion of what we understand about the society and its physical and cultural environment. Success in its preservation requires blending archaeological expectations with chemical and physical preservation of its remaining degraded structure. This chapter explores the history and context of archaeological wood and the nature of its value to generators and consumers of archaeological wood, and defines some problems for wood scientists.

ARCHAEOLOGY IS THE STUDY OF HUMAN CULTURES through examination of things left behind. In order for an event to be recognized as existing, it must produce an effect. Effects take many forms. The significant form in the study of mankind is the pattern. Human behavior is patterned. We act in ways that have meaning to us and to others. Patterned behavior includes language, manners, town plans, universities, and chemistry departments; all the things that we do and the ways we do them.

In the attempt to study the human past objectively, archaeologists examine the only available evidence of the peoples of interest: things that they themselves had created, used, altered, moved, eaten, or otherwise changed physically or chemically. The changes reveal the presence and sometimes the purposes of people in the fugitive past. The evidences found and studied by archaeologists consist chiefly of chemically and physically altered soils and, of course, artifacts.

The term artifact has quite different connotations in archaeology and the

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physical sciences. The artifacts of concern to chemists are usually unwelcome phenomena of their own making. Those of concern to archaeologists constitute the objects of their investigations. Archaeological artifacts are cultural products that reflect cultural patterns.

Value of Artifacts

Artifacts are very valuable bearers of information from the past to the present. Their information transcends their intrinsic value and, in combination with other evidences from an archaeological site, their collective value as objects.

Tools are among the most archaeologically valuable artifacts. Their intrinsic value seldom approaches the expense of excavating and conserving them. However, as bearers of information, tools contain and convey information about the nature of the problems they were made to solve. Just as important, tools provide evidences of the definition of those problems and the choice of solutions. The choices we make of methods to accomplish goals and solve problems reflect our society's methods of problem identification and solving, and its attitudes toward materials and the proper ways to deal with them. Tools are excellent reflectors of patterning.

The difference between a sickle and a scythe, tools that solve the same problem, can reflect both the types of crops grown and harvested and the attitudes of the society toward the crop and harvesting. The differences between the saws of Japanese and European carpenters reflect different traditions of woodworking and attitudes about the use of wood in the two societies. Early English settlers in North America built frame houses that required the establishment and operation of saw pits that were very laborious. Frame houses were thriftier with trees than were the log houses built by Scandinavian settlers. The buildings reflected different attitudes about the value of labor and timber, attitudes that probably reflected differential access to trees in England and Scandinavia.

The basic problems of maintaining organization and providing for human needs have been faced by societies throughout human history. Solutions that have been found for these problems vary widely and reveal the ways various cultures have defined the world in different places and at different times. This information, as well as information about religion, status, seasonality of occupation, and practically the entire lexicon of a culture, is recorded in its artifacts. Things made by human beings to control both the natural and the cultural world often constitute the only information available to us about entire past societies.

Wood is and has been the best "workable" material available. It is light, strong, readily shaped, and easily obtained and transported. Wood has always been ubiquitous in human society. Most structures, tools, boats, weapons—the range of human paraphernalia—have always had wooden components. Our assumptions of the proper form and range of function of the things we make and use revolve around the characteristics of the wood chosen for the task. Most of the materials even of modern societies are designed with characteristics of wood in mind. Wood metaphors permeate our languages. "Strong as an oak" or "supple as a willow" imply that an understanding of the characteristics of wood is so common in the society as to obviate explanation. Yet in archaeological contexts, wood is rare. In the examination and excavation of archaeological sites of societies in which the use of wood was widespread, the remains of wood and wooden artifacts are conspicuous by their scarcity. One can get the impression by investigating past cultures archaeologically that the widespread use of wood is a recent phenomenon.

The primary value of archaeological wood lies in its representative value as a bearer of information about people through time, and not in any intrinsic value it might have as an artifact or art object. Because of the workability of wood and its widespread use in human societies, archaeological wood has a very high data content. As a result, archaeological sites that contain wood and other organic materials are avidly sought for excavation and study.

Preservation in Archaeological Sites

Conditions that lead to the preservation of wood are exceptional in archaeological sites. Wood is best preserved in very wet soils (where the rate of oxygen transport into the soil is extremely low, producing conditions inhospitable to wood-metabolizing microbes) and in very dry soils (where conditions are also inhospitable to degradative organisms). Very wet and very dry conditions are inhospitable to human beings, as well as to degradative organisms. As a result, archaeological sites tend not to occur in the locations best suited to preserve archaeological wood.

The recently famous Windover site near Melbourne, Florida, contained wooden tools from over 12,000 years ago in a small boggy pond that apparently had been used as an ancient cemetery. The pond also preserved human brains so well that attempts are being made to extract and study DNA from the brain tissue. Warm Mineral Springs near Sarasota, Florida, contained tools made of wood, bone, and shell in association with extinct Pleistocene megafauna. The Ozette Site in the Makah Indian Reservation on Washington's Olympic Peninsula contains an entire Indian village over 500 years old that had been destroyed by a mud slide. In a sort of wet Pompeii (*1*), the mud preserved an incredibly elaborate and complex array of wooden houses, tools, and religious paraphernalia. Archaeologists are rapidly recognizing that wet sites are likely caches of wooden artifacts and are actively seeking them out for excavation.

Dry sites, too, are rich sources of organic artifacts. Burial sites in the Egyptian desert are famous for the condition of wood, viable seeds, and human and animal mummies that have been protected from degradation by very dry conditions. Sites in the deserts of the American southwest have yielded wooden artifacts, clothing, and building materials that are thousands of years old.

Archaeological sites are usually found in soil, with artifacts and other cultural material that have with the passage of time become constituents of the soil. Because of the tendency of cultural situations to move toward thermodynamic equilibrium in becoming sites, higher energy materials tend to be lost during the process. Organic materials are not usually found in archaeological situations nearly as frequently as they existed in the cultural situation in which they were made and used. Entire prehistoric cultures have been defined exclusively on the basis of artifacts made of stone and ceramic because these were the only materials that withstood the process of becoming part of the soil. Wooden artifacts, the archaeological wood of our interest, are both precious and rare.

Climate

One of the ongoing problems in the investigation of past peoples is discovering evidences of the physical world in which they lived. The way the past climate of an area is interpreted is predicated on the length of the human observation span. In the absence of evidence to the contrary, investigators usually assume that present climatic conditions were prevalent during the time of the peoples under investigation. Plant materials recovered from archaeological sites can be compared with data on the ecological situations in which the identified species are known to occur. Thus, assumptions can be made about the climate of the site at the time it was occupied. Such information provides insight into the world of the people being studied.

One of the areas of uncertainty in the study of the earth's climate involves placing observed variations and trends in an appropriate temporal context. The developing concern over whether the earth is entering a period of global warming, with associated rises in sea level and consequent inundation of land masses, has added a sense of urgency. International concern centers on the possibility that a significant portion of the observed climatic phenomena is an artifact of human activity, rather than normal climatic variation. Information on the climate hundreds and thousands of years in the past, derived from dated archaeological contexts, is giving a new significance to archaeological investigations. In particular, the examination of recovered plant materials can yield climatological information.

Preservation of Archaeological Wood

Archaeological wood is of considerable value for the information it contains about both the people who used it and the conditions under which it grew. It is not commonly found in archaeological sites of any antiquity. When it is found, wood can represent a considerable research and interpretive opportunity, but only if it can be protected from further deterioration.

Wood deteriorates as the result of physical, chemical, and biological agents acting selectively on its chemical and physical structures. After surviving in an archaeological context, wood's structure and composition can be quite different from the original substance. The process of cheating Mother Nature, of arresting deterioration and preserving what remains of the wood, is not without its price. In order to preserve what remains of archaeological wood, a value hierarchy of attributes must be constructed. The attributes remaining in the excavated deteriorated wood must be ranked within the hierarchy. Conservation methods can be planned to preserve these attributes in descending order of value.

Hierarchy of Values. The conservation of archaeological materials is an exercise in controls. Decisions are made and processes are selected to achieve the ends desired. In selecting ends to be accomplished and defining the product of conservation, the material and condition of the artifact and the expectations of the end consumers of the process must both be considered. Consumer expectations are a major component of the process of developing and assigning values to attributes possessed by the artifact.

Objects possess attributes whose value is related to the value of the object. Retention of some attributes in the conservation process is essential to maintaining the value of the object. Other attributes are of considerably less consequence in value preservation.

I suggest that attributes that impart value to a wooden archaeological object can be arranged as shown in List I. The list implies that the attributes that impart the most value can be visually discerned; those that impart the least value require other methods of examination to discover. This evaluation is related to the function of archaeological artifacts in our society. We are interested in the use and function these artifacts once had in the societies that produced them. However, upon being transferred into our society, they have no function other than as objects of study and appreciation. Therefore, those attributes that affect the appearance of the object are very important. If such attributes conform to the expectations of the end user, they impart a positive value.

List I. Attributes That Impart Value to Archaeological Wood

Most Value	*Moderate Value*	*Least Value*
Form	Color[a]	Composition
Size	Texture	Mass
Dimension		Function
Surface detail[b]		
Proportion		

[a] There are a limited number of acceptable colors for conserved archaeological wood; most of them are dark.

[b] Carvings, use marks, and other details are extremely important in imparting value to archaeological wood.

Unfortunately, the art, science, and technology of preserving wooden artifacts from archaeological sites has not kept pace with their rate of discovery and excavation. Public attention was recently focused on archaeological wood by the publicity generated by the recovery of historical shipwrecks. Previously the conservation of degraded materials was relegated to museums and a few universities with well-developed programs in archaeology.

Development of Methods. Traditionally the preservation of antiquities was the province of the museum workshop. Early practitioners, trained to repair paintings and reassemble pottery, fell heir to the preservation of wood as well. In spite of this inauspicious beginning, the conservators were resourceful people and good technologists who began researching the problem, as well as preserving wood. The entry of physical scientists into the field has been gradual, beginning with a few dedicated chemists, physicists, and biologists. These scientists are generally driven by interest or a spotty job market into consulting with or actually working in museums and government historical and archaeological programs.

The knowledge that wood decays in contact with soil and water has probably always been with humanity. An understanding of the mechanisms and processes of decay, however, remains elusive. Early archaeological teams generally did not treat excavated wood much differently than more durable finds; they treated degraded wood by methods appropriate to nondegraded wood. Treatments of archaeological wood have improved as much by the time-honored trial-and-error method, intuitively applied, as by an understanding of the composition and structure of wood, the processes involved in its decay, and the principles involved in its preservation.

The value of archaeological wood is, like all values, relative. Value, like beauty, lies in the eye of the beholder and consists as much of the expectations of the beholders as of the characteristics of the object under scrutiny. Who then, are the beholders, the ultimate arbiters, of the value of archaeological wood? What are the distinguishing criteria of its value?

Users of Archaeological Wood

Traditional users of archaeological wood have been members of the temporal professions, archaeologists, historians, and others; those who use archaeological wood and other evidences of past humanity as grist for their professional mills, who produce and classify it, who assign the measure of "scientific and historic value". These professions have been the principal packagers and consumers of archaeological products, and their definitions of value and proper usage of this material are predominant in current use. Other traditional users of archaeological wood are museums. Museums, which traditionally store and display items of artistic and historic value, serve as resource repositories for archaeologists and historians. These institutions preserve and display items of historic value and association that collectively form a data base of past human activity. Art museums concentrate on items that have a current aesthetic appeal by applying a modern critical filter to the objects they collect and display. As a result, objects of past religious, ritual, and decorative function serve as contemporary art objects. This aesthetic filtering is of considerable importance in museum acquisition policies that select certain archaeological objects to be conserved and afforded the protection of museums. In addition, by imparting a tangible value to archaeological finds, aesthetic filtering increases the demand for conservation methods and services. Identification of archaeological objects as art significantly influences the selection of methods for the preservation of archaeological wooden objects.

As a result of the concentration of archaeological objects in museums, conservation has become defined in a museum context. Almost all of the major efforts to conserve archaeological wood have been concentrated in or sponsored by museums. Traditionally, museums have been administered and staffed by persons trained in the arts and social sciences. Conservators, who tend to come from archaeology and arts backgrounds, are drawn to the profession by archaeological and artistic interest in the material. Artistic and social science definitions have a very strong influence on conservation definitions. These definitions and the museum situation have a very important effect on the way conservation is conceived and performed. Collectors of archaeological artifacts form another traditional receiving public for archaeological wood. Though a relatively small group, they have a great impact on the market for archaeological items that supports a world-wide trade in archaeological materials. The demand for antiquities for the collectors market has led to widespread commercial looting of archaeological sites, which has become a matter of international concern. Most collectors' standards for utility and appearance are very similar to those of museums.

Historic Ships

The public's knowledge of and appreciation for wooden archaeological objects has expanded considerably in the last three decades. The discovery, recovery, conservation, and exhibition of several historic wooden ships has received international attention, capturing the interest of both the public and the scientific community. This publicity has elevated problems of and necessity for conserving the vessels to the status of "proper scientific concerns" worthy of scientific attention and of governmental and institutional funding.

Recovery. The most famous of these historic ships is the *Wasa*, flagship of King Gustavus Adolphus of Sweden (2). The *Wasa* sank in Stockholm in 1628. Upon her rediscovery and recovery over 300 years later, she became an excellent symbol of the glory and might of Sweden at the height of its military and cultural expansion. As a result, the ship and its conservation and interpretation became a national priority. A considerable research effort was undertaken into methods and materials for its conservation. (Conservation of the *Wasa* was described by Birgitta Håfors in Chapter 8.)

Other conserved vessels include Danish Viking ships, which were conserved and are on display at the Viking Ship Museum in Roskilde, Denmark (*3*), and the *Gokstadt* and *Osberg* Viking burial ships in Norway. The *Ship of Cheops*, a funerary barge excavated near the pyramid of the same name in Egypt after being buried for over 4500 years, was sound enough to be reconstructed with practically no treatment in an Egyptian museum (*4*). In England, Henry VIII's flagship, *Mary Rose*, which sank in 1545, was excavated and recovered between 1979 and 1982 with the active participation of Prince Charles in an effort largely supported by public subscription. The *Mary Rose* was discovered to be a trove of hitherto unseen Tudor artifacts, most of them made of wood, representing a treasure of material from the time of one of England's most famous monarchs (*5*). The 8th-century *Utrecht Ship* (*6*) and the 14th-century *Bremen Cog* (*7*) are almost the sole representatives of major commercial and military artifacts of those centuries.

The United States has seen no major recoveries of historic ships. The 47-foot-long *Brown's Ferry Vessel*, an 18th-century coasting vessel recovered from South Carolina waters, is currently undergoing conservation by immersion in polyethylene glycol (PEG) (*8*). The USS *Monitor*, the Civil War Ironclad, has its own National Marine Sanctuary off the Atlantic Coast. The *Monitor* has become the focus of international attention both for her role in the American Civil War and for the conservation problems presented by her construction of both iron and wooden components.

Conservation. The excavation of major wooden vessels, with the immense conservation problems they present, marks a watershed in the conservation of archaeological wood. The development of public awareness of the value of the recovered vessels has led to public demands for the development of materials and technologies to ensure their preservation. These demands are largely responsible for erasing the public and governmental prejudice that preserving rotten wood is not progressive. This change of attitude has been reflected in the funding and academic prestige accorded the study of degraded materials. The prejudice against studying degraded materials extends to metals as well. As with wood, there are entire industries devoted to preventing degradation and corrosion, but very little attention is given to preserving corroded material. Early efforts to stabilize archaeological wood were not systematic. Rather, they were extensions of methods that had been used successfully in the treatment of wood that had not been buried. The conservation efforts were carried out by archaeologists and museum technicians. These workers were usually armed with very little knowledge of wood chemistry or anatomy, but they had an interest in the objects and a desire to prevent their deterioration. Museum laboratories used a variety of approaches to deal with wooden objects, often of considerable importance, from archaeological contexts.

Their success is attested by the presence of preserved wooden objects in museum collections, although they were hampered by a lack of understanding of the variability of wood and the mechanisms and effects of wood deterioration processes. The development of a systematic scientific approach was complicated by conservation successes that produced both preserved artifacts and a body of preservation myth. Comparable myths exist in agriculture, medicine, science, and other areas of human concern in which causes are inferred from observed effects without understanding the phenomena under observation.

Almost every conservator has encountered objects—in my case, small boats and log canoes—that, according to their finders, were simply removed from an archaeological context ideal for producing waterlogged wood and allowed to dry. Similar artifacts were treated topically with a commercial wood fungicide, or linseed oil, or creosote, or "something Uncle Hiram had in the barn". The results of these treatments can appear to be as good as many conventionally conserved objects from similar contexts. Like physicians dealing with spontaneous remissions, the conservator can only rejoice with the developer of the unorthodox treatment. However, there is a high degree of certainty that this and other comparable episodes will resurface when requests for funds for archaeological wood research and treatment must be defended. The first generally successful treatment for waterlogged archaeological wood was the alum method introduced in the 1850s. This treatment consisted of exchanging the water in the wood with a preservative, potassium aluminum sulfate. The alum mixes with water, will solidify, and has a sufficiently low vapor pressure to remain in the wood under ordinary conditions.

As reported by B. Brorson Christensen of the National Museum of Denmark, the preservative formula used in his museum consisted of 4 parts by weight of alum, 1 part by weight of glycerol, and 1 part by weight of water. The ingredients were heated to about 92 °C in a vat large enough to contain the materials to be preserved until the alum was melted and the wood was preserved. The process, according to Christensen, was as follows:

> *After loading, the tank was covered up and left for 24 hours. The unloading was an experience never to be forgotten: Alongside the conservation tank stood a similar tank containing two tons of water only slightly below the boiling point. The whole personnel of the department, numbering at the time 4–6 persons, assembled and took part in the operation. Simultaneously, the lids of the two tanks were removed and a few seconds later the atmosphere of the dismal cellar was a dense fog. Persons wearing*

> *glasses could see almost nothing at all, hot packets were removed from the conservation tank, dipped for a few moments in hot-water tank and opened with great haste. The contents were then, as speedily and carefully as the situation permitted, rubbed down with soft brushes to remove a sediment of grayish mud which had always settled upon all upper surfaces. If allowed to cool, this sediment (consisting of undissolved alum, calcium sulfate, calcium carbonate and—presumably—some lead carbonate) would solidify and be nearly impossible to remove later on. When the contents of one packet had been thus treated (lead numbers had to be taken care of also) they were removed to a neighboring room for cooling.*
>
> *To see these persons working with incredible speed in this dense fog, trying to avoid bumping into each other, swearing copiously because of inevitable burns and scalding, was like a nightmarish mixture of a grotesque ballet in a London fog during rush-hour.* (Reproduced with permission from ref. 9. Copyright 1970 The National Museum of Denmark.)

My own experiences with alum, while on a considerably smaller scale, were quite similar to Christensen's. The addition of glycerol to the mixture was an attempt to control dimensional changes in the wood caused by the treatment. Unfortunately, the alum–glycerol mixture had a tendency to become hygroscopic with time. Hygroscopicity causes the mixture to liquefy and recrystallize within the wood as atmospheric humidity increases and decreases, and thus ultimately destroys the wood. It is possible to remove the alum mixture and reconserve the wood by different methods, but not without cost both in additional resources and in damage to the artifact. The alum method was successful in that it saved generations of material that would otherwise have been lost shortly after excavation. Except for the unexpectedly short life span of some treated objects, it worked very well. The period after the end of the war brought an end to treatment regimens like the alum method. This period witnessed a development of the scientific attitude and a systematic approach to the study of archaeological wood. One of the early results of this change was the introduction of polyethylene glycol (PEG) to conservation. It was introduced as a dimensional stabilizer for sound wood and is still used for that purpose. The ability of PEG to penetrate and stabilize wood led to its use as a preservative for archaeological wood. The first major research into the use of PEG for this purpose was the *Wasa* project in Sweden (Chapter 8) and projects in Denmark. Since then PEG has proven to be the best material developed to date for general wood conservation.

PEG is used in many molecular weights between 200 and 4000. Lower molecular weights are better able to penetrate into and bond with the microstructure of wood. However, they are liquids at ordinary temperatures and impart very little physical reinforcing or bulking to wood. Higher molecular weights provide more support, but they do not penetrate or bond as well (*10*). Recently, projects have begun using different weights of PEG in the same objects. Lower weights impart penetration and initial bonding, while the higher molecular weights provide hygroscopic stability, physical bulking, and a higher melting point of the preservative.

Several methods have been developed for getting PEG into artifacts. Most small artifacts and a few whole ships are being treated by immersion in appropriately sized and configured tanks in which a controlled sequence of concentrations and, recently, molecular weights of PEG are added to an aqueous solution. The PEG enters the wood by diffusion. When a desired concentration is reached, the objects are removed and dried slowly while maintaining a low moisture gradient within the artifacts to control dimensional changes.

The expense of constructing and maintaining tanks large enough to immerse a vessel and the large quantities of PEG required to reach desired end concentrations in a large tank must be taken into account. Therefore, with large objects PEG is sometimes sprayed in a program of gradual increases in concentration that resemble immersion. The Swedish ship *Wasa* was conserved by a PEG spraying regimen.

PEG is also used as a consolidant in freeze-drying wood, as discussed by Ambrose in Chapter 10. Another method of using PEG in freeze-drying, which uses *tert*-butyl alcohol as a solvent, was developed and is in use in Denmark, with excellent results (*11*).

PEG works very well, but it has some significant drawbacks that limit both its effectiveness and the prospects for long-term storage of treated items:

- It is comparatively expensive. The cost of the chemicals and the facilities necessary to use them place conservation of large wooden items out of the reach of most projects.
- It requires a long time to apply. The wood structure forms barriers to diffusion of PEG into wood. Application requires long-term treatment, tying up facilities and limiting the numbers of items that can be treated by a facility.
- Perhaps most significantly, PEG-treated wood can become unstable under temperature and humidity conditions frequently encountered in temperate-zone summers. This instability requires that treated items be curated in climate-controlled facilities.

Another technology used in the conservation of archaeological wood is the use of sucrose applied by aqueous diffusion as a preservative. Sucrose has the advantages of not being as temperature- and humidity-sensitive as PEG, is less expensive, penetrates well (*12*), and it is commonly available in Third World countries without requiring the expenditure of precious foreign exchange (*13*). The development of technologies to use sucrose in the conservation of archaeological wood is extremely promising in terms of bringing the ability to conserve wood to the areas where the need is great and resources available for conservation are scarce. The widely used acetone–resin or acetone–ether–resin technique involves exchanging the free water in an artifact for a solvent and then diffusing pine resin into the artifact via the solvent (*14*). This method can give excellent results but it involves heating volatile flammable liquids, often in quantities measuring in the tens of gallons; is difficult to control; and can result in the loss of soluble wood extractives.

Other conservation techniques involving extraction of free water from artifacts with solvents include

- The use of radiation-curing resins, as described by Trân in Chapter 9, adds the most strength and stability to the artifact of any processes currently in use. The difficulty of access to γ-ray sources and the lack of reversibility of the process have limited its use among conservators.
- The use of oxysilanes to precipitate silicates within the remaining structure of degraded wood gives them added strength and dimensional stability (*15*). Conservators have had difficulty obtaining consistent results using oxysilanes, and the technique is not in common use (*16*).

New Directions

In the planning of this chapter, I was charged with presenting new directions in the conservation of archaeological wood. After a great deal of searching for new directions, all I could find were old directions. Therefore, I am going to offer new problems, or old problems restated, in the hope and the expectation that the identification of new problems will lead to new solutions.

The conservation of organic materials from archaeological contexts is in crisis. More material is being recovered than can be conserved with existing facilities and technologies. Existing collections of conserved archaeological wood are in need of reevaluation and, too often, retreatment. In an era of rising energy costs, much of the treated material currently in museum collections is dependent upon costly temperature and humidity control for its continued existence.

Archaeological wood is generated by archaeological projects run by archaeologists pursuing archaeological goals in archaeological contexts. In order to be successful, the conservation of archaeological wood must address these goals in these contexts. The problems of the preservation of archaeological wood begin in the field upon excavation. The wood is removed from the microenvironment that had both nurtured and attacked it and within which it had survived, in some recognizable form, to be found. Once it is excavated, the adaptation that the object had made to its surroundings is no longer appropriate and its rate of degradation increases. Because of field considerations, conservation treatment is usually not begun immediately, and the unstable wood must be stored. Depending on the duration of the field project, its budget, and the completeness of planning, storage can last for months or even years while arrangements are made for conservation.

The challenge is to devise a system for storage of archaeological wood that can be applied immediately upon excavation. Such a system must either provide protection from chemical and biological degradation for a wide range of wood species and burial conditions, or incorporate a method for field analysis of wood type and condition as a guide to selecting storage conditions. The system should also be compatible with as wide a range as possible of subsequent preservation processes. It would be very desirable to incorporate the storage system as part of a preservation process so that preservation could begin immediately, leaving out the intermediate step. The ability to store excavated archaeological wood unpreserved for long periods of time without deterioration or loss of value would allow decisions on what to preserve and how to preserve it to be made away from the immediate pressures of the field situation. This flexibility would allow for more efficient operation of conservation facilities.

Time Frame. Archaeological projects tend to be relatively short term, rarely lasting for more than 5 years from inception to conclusion. Archaeologists ply their trade by excavating a site; analyzing the data, including artifacts, gathered in the excavation; and writing a report detailing what was done, what was discovered and its relevance to the science. Processes to preserve materials recovered, if they are to be successful, should produce their results within the time frame of the project. If an entire project from excavation through final report requires 3 years to complete and the preservation of wood from the project takes 15 years, unless it is an unusual project of immense popular and scientific interest like the *Wasa* or the *Bremen Cog*, interest in and funding for the preservation of material from the site will suffer significantly. The challenge then is to devise preservation systems for archaeological wood that can operate in a time frame appropriate to that of the rest of the project.

Costs. Archaeology is largely dependent upon public sector support. In this it is in competition with education, roads, hospitals, public safety, defense, and the myriad other feeders at the public trough. The nature of support for archaeology is episodic, supporting excavation to answer research questions or to mitigate damage to sites caused by construction or other land-altering activity. Support for conservation is dependent upon support for archaeology. Capital-intensive facilities, such as conservation laboratories, cannot usually be supported by projects, but have to be developed and funded separately. The cost of conserving artifacts from a site rich in organic material can easily be the most expensive part of a project. The high cost of the conservation of archaeological wood is a serious limiting factor on the amount of recovered wood that can be conserved and on the choice of processes to preserve it. The challenge then is to devise preservation systems and methods that can be funded from resources available for the conservation of archaeological materials.

The conservation and curation of archaeological wood is caught in a loop of diminishing returns. The level of resources available for the conservation and curation of items of historical and cultural significance is, and undoubtably will continue to be, less than what is required to maintain existing collections adequately. The products of most preservation processes in use today are dependent for their continued existence upon their being kept within narrow ranges of temperature and humidity. In order to be kept in our public and private collections, the value of preserved artifacts must continue to exceed the cost of keeping them. Any reasonable estimate of future conditions indicates that the expense of maintaining temperature and humidity controls in museums and other storage facilities will continue to increase. As long as "preserved" archaeological wood must be curated under conditions of increasing expense, its affordability will continue to decrease and the selection processes that determine what is to be preserved and kept will become increasingly stringent. A decreasing amount of archaeological wood will exist, while the cost of curating that wood increases.

Stability. Perhaps most important to the long-term survival of conserved wood, which is the only real indicator of success in preserving archaeological wood, is the requirement that the product be stable under normal conditions. The problem then is to develop preservation systems and methods that produce a product that does not require high-energy storage conditions to continue to exist. This is the most pressing problem in the conservation of archaeological wood. Continued dependence on high-energy increasing-cost systems for access to conserved archaeological wood will price our efforts out of our reach and make the rest of the endeavor futile.

Professional Collaboration

The existence of the Archaeological Wood Symposium at the 196th meeting of the American Chemical Society in Los Angeles, California, in September 1988 reflects a significant increase in the involvement of wood scientists in the study and preservation of archaeological wood. The wood sciences have become, along with archaeologists, conservators, museums, and many others, consumers of archaeological wood. Their expectations are having a revolutionary effect on the way the conservation of archaeological wood is conceived and practiced.

Discussions at the symposium among conservators, archaeologists, and wood scientists emphasized their different approaches and emphases to their common ground and created bridges over areas of miscommunication and misunderstanding. The concerns voiced by conservators tended to be object- and application-oriented; those voiced by wood scientists tended to be analytically and process-oriented.

Varying Concerns. Conservators' concerns tend to lie in preservation of objects of value, rather than in analysis of wood or a better understanding of the process of wood deterioration. Conservators often deal with one-of-a-kind objects that require immediate attention in order to continue to exist as objects of interest. Therefore, conservators feel that they need to have highly reliable preservation methods available to them. The situational dynamic of conservation emphasizes the use of low-risk established techniques in the production of preserved objects rather than research into degradation processes or methods of preservation, a situation that tends to inhibit basic research in conservation laboratories.

Wood scientists see wood as highly variable material that degrades in a variety of ways for a variety of reasons, with a variety of mechanisms. Wood scientists also conceive of wood as material; conservators conceive of it as fabric. Wood scientists conceive of wood as having a finite and predictable period of existence, which is capable of being extended by environmental manipulation; conservators conceive of it as having an infinite period of existence that can be interrupted by unfortunate conditions. Wood scientists are interested in the chemical, physical, and biological processes of wood degradation; conservators are concerned with the effects of degradation on wooden objects. The catalog of differing viewpoints could be considerably longer, but the point is that conservators and wood scientists have quite different points of view in their approaches to their common ground, degraded wood.

Mutual Understanding. If we are to successfully encourage wood scientists to research areas that have application to conservation problems, scientists must be able to understand, if not appreciate, what constitutes both conservation problems and conservation solutions. On the other hand, if they are to become familiar with wood science literature and to apply wood science experimental results to conservation problems, conservators must be able to understand and appreciate the variability of wood, the results of degradation processes, and how these conditions affect the types of questions that can be answered, as well as the types of answers that the wood sciences can supply to conservation questions.

A frustration voiced by conservators and archaeologists is that scientists do not answer their questions, or that the answers they get are not answers they can use. Perhaps the problem lies as much in the questions asked as in the answers given. Many of the questions posed cannot be answered satisfactorily because the questions do not take into account the reality of wood and wood deterioration. Questions like "What is the best method to preserve wooden shoes?" cannot be answered satisfactorily because information essential to the formulation of the answer (such as the species of wood of which the shoes are made, the cause and state of their deterioration, the desired appearance, and the intended use of the preserved shoes) are not provided by the questioner. Implicit, too, in the question is the unproven assumption that all wooden shoes are related so that there is a best preservation method for the category, wooden shoe.

Conservators need to know how to preserve a particular object or set of objects in a situation that, to them, possesses an immediacy comparable to medical situations. The objects in question have an intrinsic individual value and are not interchangeable with other similar objects.

The common solution posed for problems of communication between disciplines is better dialogue and more education. This remedy is quite easy to pose, but quite difficult to implement. The education that is called for is intended for practitioners of the discipline to which the poser does not belong. Of course, this requires "them" to make the effort to understand "our" problems. Because this approach requires no effort by anyone, it has proven to be quite popular.

This volume and the symposium on which it is based provide an excellent example of breaking this communication deadlock. This dialog among conservators, archaeologists, and wood scientists, if continued, can become a most significant event in the conservation of archaeological wood. It represents, perhaps, a true "new direction in the conservation of archaeological wood."

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