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Chemical Technology in Antiquity

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Chemical Technology in Antiquity

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Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

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Preface

Chemistry is intimately involved in the development of the oldest known civilizations, resulting in a range of chemical technologies that not only continue to be part of modern civilized societies, but are so commonplace that it would be hard to imagine life without them. Such chemical technology has a very long and rich history, in some cases dating back to as early as 20,000 BCE. My own interest in the early history of these technologies began with a desire to understand the factors behind the late application of glass to chemical apparatus (i.e., chemical glassware), which did not become a mainstay of the chemical laboratory until nearly 4000 years after the initial synthetic production of glass (*1*, *2*). This of course soon led to a general interest in the history and chemistry of early glass (*2*). As the history of glass is deeply entwined with the corresponding histories of metallurgy, ceramics, and alcohol (*2*, *3*), I soon found that I had developed a deep, general interest in the broad range of early chemical technologies utilized throughout antiquity, as well as how these early technologies impacted later scientific pursuits.

A number of books are currently available that cover the history and chemistry of some of the individual topics included here, particularly that of glass (*2*, *4*), pottery and ceramics (*5*, *6*), metals and metallurgy (*7*), or various fermented beverages (*3*, *8*). However, sources presenting a broader scope of early chemical technology, especially those covering the number of topics contained in the current volume, are somewhat rare. The best of such works include Partington's *Origins and Development of Applied Chemistry* (*9*), Forbes' multi-volume series *Studies in Ancient Technology* (*10*), or the five-volume series, *A History of Technology,* edited by Singer et al. (*11*). All of these, however, are out-of-print and are no longer representative of our current knowledge of the history of these technologies. Although there are a couple more recent examples of this broad approach, including Joseph Lambert's *Traces of the Past: Unraveling the Secrets of Archaeology through Chemistry* (*12*), it was felt that a new volume presenting updated histories of a collection of early chemical technologies would be a welcome addition for chemists, historians, chemical archaeologists, and general educated readers interested in the development of some of mankind's earliest and most common technologies.

This current volume aims to present the discovery, development, and early history of a range of such chemical technologies and is based on the popular symposium, *Chemical Technology in Antiquity,* held March 23, 2015, at the 249th National Meeting of the American Chemical Society (ACS) in Denver, Colorado. The symposium was held as part of the programming of the ACS Division of the History of Chemistry (HIST) and was co-sponsored by the Multidisciplinary

Program Planning Group (MPPG) as part of the meeting's thematic program "Chemistry of Natural Resources," as well as by the ACS Divisions of Analytical Chemistry (ANYL), Chemical Education (CHED), Inorganic Chemistry (INOR), and Organic Chemistry (ORGN). During the organization of both the original symposium and the current volume, I had two primary goals. The first was to include a number of smaller subjects often ignored in the presentation of early chemical technology, while a secondary goal was to use this venue as a way to bring some younger members of the HIST division into active historical research roles. The outcome of this second goal was especially satisfying as the new authors included are all current or former students from North Dakota State University (NDSU) who were introduced to the history of chemistry via my own activities in the field. As a consequence, the resulting volume contains a core of the most significant and well-researched examples of early chemical technology written by established authorities on these topics, including chapters by Mary Virginia Orna on mineral pigments (Chapter 2), Nicholas Zumbulyadis on pottery (Chapter 3), Vera Mainz on metals and alloys (Chapter 5), and Zvi Koren on organic dyes (Chapter 7), as well as my own chapters on early fermented beverages and glass (Chapter 4 and Chapter 10). This core of traditional topics is then supplemented by less frequently covered topics by new authors, including chapters by Christopher Heth (NDSU Ph.D. 2010) on leather and tanning (Chapter 6), Narayanaganesh Balasubramanian (NDSU Ph.D. 2012) on oils and perfumes (Chapter 8), and my current graduate student Kristine Konkol doing the bulk of the work on a chapter on soap (Chapter 9).

While this volume is in no way a complete coverage of the full range of chemical technologies practiced during antiquity, I hope that it provides a feel and appreciation for both the deep history involved with these topics, as well as the complexity of the chemical processes that were being utilized at such a very early time period. In conclusion, I want to thank all of the authors involved, as well as everyone who contributed to this volume as reviewers. While the initial idea of this volume and the responsibility of its editing were mine, the quality and success of the final product is most certainly due to a collective group effort.

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Editor's Biography

Seth C. Rasmussen

Seth C. Rasmussen is a Professor of Chemistry at North Dakota State University (NDSU) in Fargo. He received his B.S in Chemistry from Washington State University in 1990 and his Ph.D. in Inorganic Chemistry from Clemson University in 1994, under the guidance of Prof. John D. Peterson. As a postdoctoral associate at the University of Oregon, he then studied conjugated organic polymers under Prof. James E. Hutchison. In 1997, he accepted a teaching position at the University of Oregon, before moving to join the faculty at NDSU in 1999.

Active in the fields of materials chemistry and the history of chemistry, his research interests include the design and synthesis of conjugated materials, photovoltaics (solar cells), organic light emitting diodes, the history of materials, chemical technology in antiquity, and the application of history to chemical education. As both author and editor, Prof. Rasmussen has contributed to books in both materials and history and has published more than 80 research papers and book chapters. He is a member of various international professional societies including the American Chemical Society, Materials Research Society, Alpha Chi Sigma, American Nano Society, Society for the History of Alchemy and Chemistry, History of Science Society, and the International History, Philosophy & Science Teaching Group.

Prof. Rasmussen currently serves as the Program Chair for the History of Chemistry division of the American Chemical Society and as the series editor for the *Springer Briefs in Molecular Science: History of Chemistry* book series. He also holds editorial positions for the journals *Fluorescent Materials* and *Topological and Supramolecular Polymer Science*.

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Chapter 1

Introduction − The Role of Chemical Technology in Early Civilizations

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The path to civilization can be traced from the end of the last Ice Age (ca. 20,000 BCE) to the formation of city-states in ca. 3500-1500 BCE. Chemistry is intimately involved in this process, resulting in a range of chemical technologies that are still part of modern civilized societies. It is this relationship between the chemical technologies of antiquity and the rise of civilization that is the focus of the presented discussion. An overview of the factors and timeline that led to the earliest civilizations is presented, followed by an examination of the role of chemical technologies in this progression. In the process, this discussion attempts to set the stage for the more detailed presentation of many of the chemical technologies that shaped this early period of human history.

Introduction

Chemistry is intimately involved in the development of the oldest known civilizations, resulting in a range of chemical technologies that are not only still part of modern civilized societies, but are so commonplace that it would be hard to imagine life without them - from material objects fabricated from metals, ceramics, or glass, to the paints and dyes that color everything around us, and so much more. Of course, such examples of everyday modern technologies are all representative of various primary chemical technologies from antiquity, many of which have very

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long histories dating back millennia. In fact, many such chemical technologies predate the formation of formal civilization.

Such civilization is typically designated as the development of a more complex way of life in comparison to the simple culture of the hunter-gatherer of the Paleolithic period. Thus civilization is often defined as a culture which has attained a degree of complexity usually characterized by urban life (*1*). Therefore, a diagnostic trait typically utilized in the identification of civilization is the presence of what we typically think of as cities. In other words, civilizations typically contain large settled urban centers with populations in the thousands, where persons divorced from subsistence carry out such specialized functions as administration, production, exchange, and religious ceremonies (*2*). Of course, a given culture is the sum total of all cultural traits possessed by a given people at a given time and thus there is really not one specific aspect that dictates the formation of civilization. This sum total of cultural traits includes such traits or items as any specific material objects, the political and social institutions of the people, and the associated habits, customs, and ideas of the specific culture. As such, what we think of as ‘modern civilization’ is an extremely complex culture consisting of thousands upon thousands of cultural traits (*1*).

The process describing the development of civilization started with the beginnings of farming and agriculture, ultimately leading to increasing populations that came together in villages, towns, and eventually cities. Here, the evolving populations developed architecture and commerce flourished. As a result, specialized occupations emerged and social divisions increased. Throughout all of this, new chemical technologies were being developed and older technologies were refined and advanced. As such, the development of civilization and chemical technologies were deeply intertwined. While development of advanced civilization provided a rich environment for chemical advances, the various chemical technologies in antiquity played a critical role in the growth of early civilization.

It is this relationship between the chemical technologies of antiquity and the rise of civilization that is the focus of this introductory chapter. The aim is to present an overview of the factors and timeline that led to the earliest civilizations, followed by an examination of the role of chemical technologies in this progression. In the process, the discussion here will attempt to set the stage for the following chapters detailing many of the chemical technologies that shaped this early period of human history.

Dawn of Civilization

During the last Ice Age (ca 20,000 BCE (*3*)), vast areas of the planet were covered with open woodlands and grasslands which supported large herds of bison (Figure 1) and reindeer, as well as large animals such as the mammoth and giant bears (*4*). Such herds were the primary source of food for the people of the Ice Age, who were nomadic and followed the natural migrations of the herds (*5*). This began to change in the period of 15,000-12,000 BCE, when the climate became warmer and wetter. Soon after 10,000 BCE, there was a more significant warming

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that formally brought the Ice Age to an end (*3*). In the process, forests started to spread and replaced open woodlands and grasslands (*4*). These climate changes also resulted in changes in the availability of familiar game (*4*, *6*). Some species, such as the mammoth, are believed to have become extinct at this point, while other species such as the reindeer slowly migrated northward (*6*).

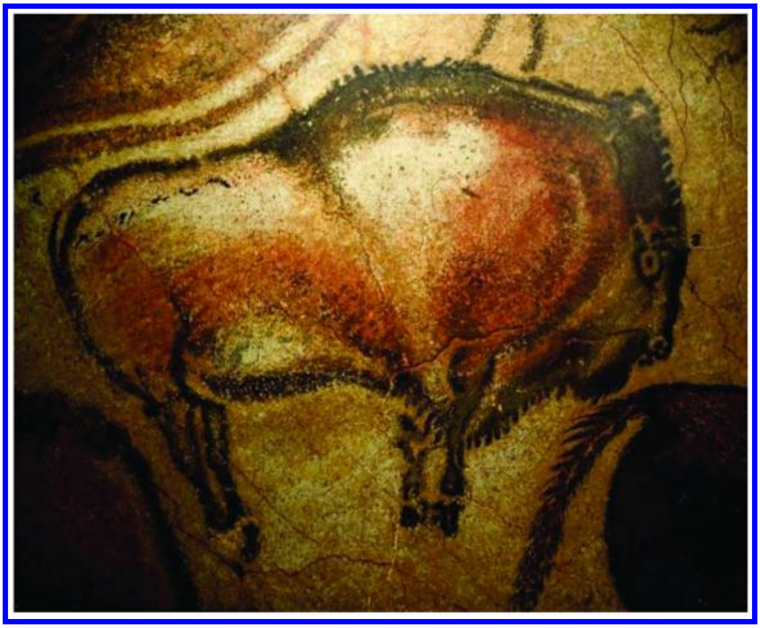

Figure 1. Reproduction of a Bison cave painting from Altamira, Spain (ca. 15,000-12,000 BCE). [photo by Ted, 2012].

While some people moved northward in order to continue to hunt the old game, in many places people were forced to adapt in order to find new sources of food, hunting smaller game such as deer or wild sheep, catching birds and fish, and gathering shellfish and edible plants (*4*, *6*). As a result, the people of Western Europe now consisted of small groups hunting largely red deer, wild cattle, and wild pigs, although it is also thought that they started to add smaller animals and birds to their diet. For the most part, however, they remained essentially hunters and their technology continued to be that of their Ice Age ancestors. In contrast, the regions of the Near East are thought to have not undergone a period of extreme cold as had Central and Western Europe. Instead, it is thought that the Near East probably had high rainfall with a forest cover of deciduous trees, which resulted in available wild game of cattle, pigs, and ancestors of sheep and goats (*6*). Although the people of this region continued to hunt wild animals, skeletal evidence suggests that their diet also comprised plant-based foods such as acorns, lentils, chickpeas, and various cereals. At this time period, these would have still been gathered in the wild, rather than deliberately cultivated (*7*). This new lifestyle of hunter-gatherers is exemplified by what is often referred to by archaeologists as the Natufian culture (*8*).

While the transition from nomad to village farmer is considered to be the largest single step in the ascent of mankind (*5*), it will most likely never be known how and why mankind took to the domestication of animals and to the deliberate growing of edible plants. However, it seems highly probable that, long before intentional agriculture, hunting communities had intentionally protected natural stands of wild plants that they found useful in their diet, perhaps even fencing them off against wild animals. Of course, the first domesticated herd animals, cattle and sheep, were precisely those species that would have been attracted by such patches of grain-growing plants (*6*). The transition to farming required a greater degree of control over the animals and plants contributing to the people's sustenance. Thus, the key to farming was domestication, which resulted in a mutually beneficial relationship. The domesticated livestock were protected from other natural predators, had their food supplemented by fodder when necessary, and were afforded shelter when conditions required. Plants were benefited by removing or at least reducing competition from weeds or grazing animals, as well as via cultivation of the soil, drainage, or irrigation (*9*). This ultimately led to the domestication of some plants and animals via planting or breeding specimens that would produce bigger fruit or seeds, or the best meat. Among the earliest food plants to be domesticated were the grain-bearing cereals. The Natufian people of Syria and Israel are thought to have begun to grow wild wheat and barley around 10,000 BCE and other grains such as oats, sorghum, millet, rice, and corn soon followed (*4*).

The first animal to be domesticated was the dog (*5*, *6*, *10*). This domestication is thought to have occurred sometime during the Ice Age via a form of symbiosis between canine and mankind, centered on the hunting activities of the two species (*6*). The domestication of wild sheep by people in the Zagros Mountains is thought to date to ca. 10,000 BCE (*4*, *5*, *10*). The domestication of goats quickly followed in the regions further to the east (*5*, *10*), with additional species ultimately domesticated. This included cattle and pigs by 7000 BCE (*11*), then camels, and finally horses and donkeys (*4*, *10*). Although it is generally agreed that the horse was domesticated at a later date than other livestock (*5*, *10*, *12*), it is still unknown when and where horse domestication first took place. A prime candidate for the site of this event is the Eurasian steppe, with domestication of the horse thought to have occurred as early as mid–4th millennium BCE (*12*).

The general practice of farming and agriculture developed independently at different times in a number of different places around the world between 13,000 and 10,000 BCE (*4*, *11*). Thus, by 9000-6000 BCE, a number of scattered communities throughout the Near East can be found that had made the change from hunter-gatherer to at least part-time agriculturalist and stock rearer (*4*, *6*, *11*, *13*). Some of the earliest farming communities are found in the area of the Middle East called the Fertile Crescent (Figure 2). This region of rich soil stretches from the Nile Delta of northeast Egypt, up the Mediterranean coast to along the mountains of Anatolia, and then down again to encompass the land in and around the Tigris and Euphrates rivers (*4*, *5*, *14*). The name stems from a happy accident of geography that provided a rich supply of native plants such as wheat and barley that were suitable for domestication, as well as ideal upland environments for wild sheep, goats, cattle, and pigs (*4*, *5*, *7*). As such, the Fertile Crescent provided

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch001

an ideal environment for the initial development of permanent, year-round settlements and it is not surprising that farming developed so early in this region (*4*, *7*, *14*, *15*). Although such plant cultivation may have first occurred in the Near East, evidence suggests that people in other regions also began to cultivate and domesticate local plants as early as 9,000-8,000 BCE. Such examples include squash in Ecuador and rice along the banks of the Yangtze river in China (*11*, *16*).

One consequence of the shift to farming was that human society began to change. Hunter-gatherers lived in small family groups and typically had to travel distances to obtain enough food to survive. It has been estimated that ten square miles of forest was required to provide enough food to support just one hunter-gatherer (*4*). In contrast, it is thought that even the most primitive kind of farming would be able to support a population much greater than that able to exist from hunting and foraging alone (*1*). Thus, it is postulated that the ten square miles referenced above could now support roughly 800 people via farming (*4*). Therefore the adoption of farming boosted and solidified the food supply, which allowed an increase in population (*1*). In addition, this now made it possible to obtain all that was needed within close proximity of a permanent community, which freed people from the need to range over vast regions and made it possible to occupy the same settlement year round. This in turn made it possible to significantly increase both the population density and potential size of groups able to live together, giving such communities distinct advantages in the competition for land and resources (*9*).

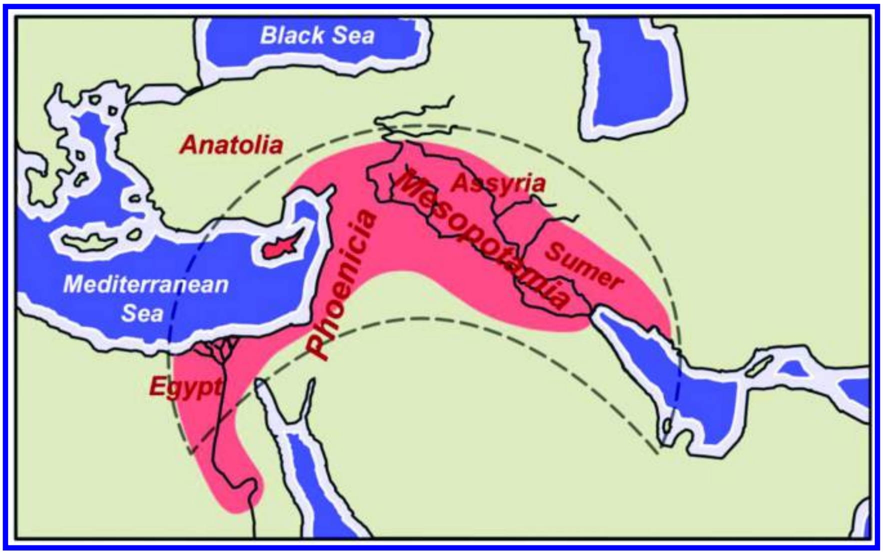

Figure 2. The Fertile Crescent (ca. 4th-2nd millennia BCE).

As a result, it is thought that people transitioned through a sequence of transitory cave sites, to semi-permanent open-air settlements, to fully agricultural permanent villages (*4*, *17*). The earliest such villages are thought to have typically consisted of approximately 50 simple, round huts, which supported a community of 200-300 people (*7*). As populations increased, family groups developed into

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larger tribes consisting of up to 1000 people. The tribal leaders would meet to make collective decisions or to settle disputes, but overall there were very few distinctions between individuals in terms of wealth and status (*4*).

In regions where conditions were especially favorable for agriculture, some farmers would have been able to produce a surplus of food which could then be used to barter for other goods or exert power over their neighbors. Through this process, inequalities of wealth and power gradually developed between tribal members, leading to the development of chiefdoms - ranking societies of ~5000 or more people. It is believed that these chiefdoms were probably divided into extended family groups called clans. The ruler of a chiefdom was the head of the most important clan within the chiefdom population, while the leading men of the clans formed a ruling aristocracy (*4*).

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Such chiefdoms resulted in a second transition from small farming villages to urban towns. This includes sites such as Jericho, dated ca. 8350-7350 BCE, which had an estimated population of 2000-3000 people and was believed to be served by subsidiary settlements throughout the Jordan valley (*5*, *6*, *17*). Jericho started as a Neolithic village and was thought to consist of a population of over 500 in ca. 9600 BCE. Within a few hundred years, however, it had grown to more than 70 dwellings and a proposed population of 1000 people (*18*). An even earlier site was Tell Abu Hureyra, which was originally a village dated to 13,000 BCE and populated by hunter-gatherers transitioning to farming. By ca. 9500 BCE, however, this site is believed to have achieved urban status, with a population of several thousand people (*17*). A somewhat later site is the settlement at Mehrgarh, which is thought to date to the 8th millennium BCE (*19*). Located in the northwestern part of the Kachi-Bolan plain, a great alluvial expanse that merges with the Indus Valley, this site includes 46 buildings and provides the first evidence a farming economy in the northwestern part of the Indo-Pakistani subcontinent (*19*). Early sites have also been found in China (*20*), with the most archaeologically significant of these being Banpo (or Pan-p'o) (*21*), dated to ca. 4000 BCE (*16*). Situated on the eastern bank of a tributary of the Yellow River, Banpo covered approximately two and a half acres and consisted of several houses of two distinct types, grouped around a large rectangular building thought to be a clan building or a communal lodge. In addition to the town, the site includes a cemetery and six pottery kilns of various forms (*21*).

One of the largest of such investigated sites is the southern Anatolia settlement of Çatal Hüyük, dated 6300-5400 BCE. This site is roughly four times the size of Jericho with a population that has been conservatively estimated at 5000-7000 people, quite possibly more. The enlarged size of such settlements now permitted an increase in the subdivision of labor which in turn favored advances in technology (*9*). This is supported by the quantity, quality, and variety of material found at such sites, strongly suggesting specialization of craftsmen, probably full-time (*17*).

In the period ca. 3500-1500 BCE, some chiefdoms developed into larger, more complex civilizations based on significantly sized cities. The populations of these cities were as large as tens of thousands of people and most were ruled by kings. Civilizations based on such cities developed where there were rich natural resources for farming. This is aptly illustrated by the fact that the earliest civilizations developed in the fertile flood plains of various great rivers: between the Tigris and Euphrates rivers in Mesopotamia (~3400 BCE, Figure 3) (*4*, *17*); in the Nile valley of Egypt (~3000 BCE); in the Indus valley of Pakistan (~2600 BCE); and in the Yellow River basin region of China (~1700 BCE) (*4*). Here, food surpluses were brought by farmers as taxes to the city, where they were stored and then reissued to the people of the city (*4*). As the first two of these examples occur within the Fertile Crescent, this region is also often called the Cradle of Civilization.

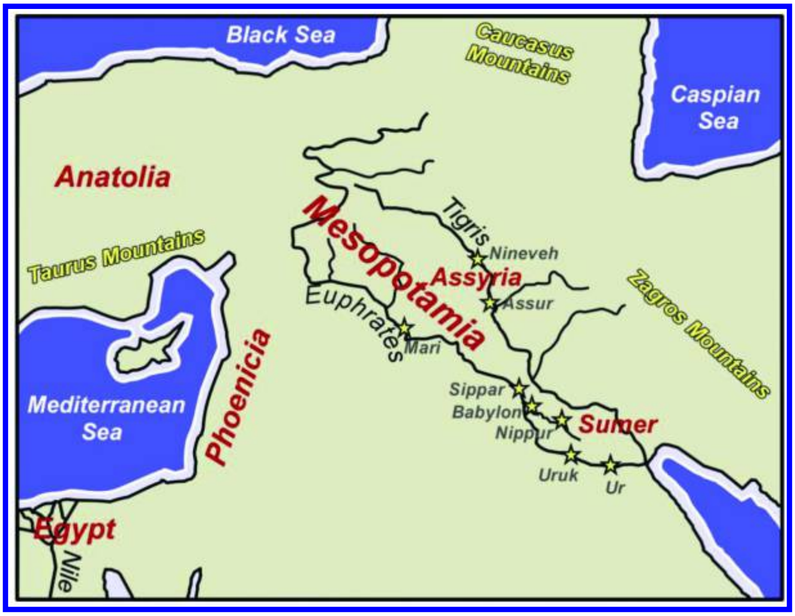

Figure 3. Early City States of Mesopotamia.

Chemical Technology in Antiquity

The use of chemical processes to manipulate matter dates deep into prehistory. The taming of fire was one of the first major milestones in human history (*22*) and evidence of campfires date back to at least 500,000 BCE (*23*). The earliest habitual use of fire, however, occurs ca. 400,000-300,000 BCE and becomes more common and well established in sites younger than 100,000 BCE (*24*). Of course, it should be stressed that it is generally believed that only the ability to sustain fire was known at this time, rather than the ability to purposely start fires. While the earliest use of fire was most likely as a source of heat and light (*22*), fire was eventually utilized to cook sources of food thus leading to the earliest form of chemical technology (Table 1). Cooking meat made it more tender and possibly tastier, but more importantly it made it safer by destroying bacteria and parasites (*22*, *23*, *25*). As diets became more diverse, cooking made food easier to digest by breaking down larger chemical species such as proteins and carbohydrates (*25*).

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Archeological evidence suggests that cooking fires began in earnest only about 300,000 BCE (*24*).

Another significant use of chemical species was the crushing and grinding of colored minerals to produce powdered pigments (*31*). These pigments were used either dry or dispersed in water or oil and darker colors could be lightened by mixing them with chalk. Early uses were for cave paintings as illustrated in Figure 1, but were also used as cosmetics to color the body and face (*22*).

Table 1. Chronological List of Common Chemical Technologies in Antiquity

Technology	*Time period of origin*	*Volume chapters including topic*	*References*
cooking	ca. 300,000 BCE	4	(*24*, *25*)
mineral pigments	pre-30,000 BCE	2	(*22*, *26*)
pottery	ca. 18,000 BCE	3	(*27*)
fermented beverages	10,000-8000 BCE	4	(*28*)
smelting and metalworking	ca. 6000 BCE	5, 10	(*22*, *29–31*)
cloth and fabrics	ca. 6000 BCE		(*32*)
tanning hides and leather	4500-2000 BCE	6	(*33*)
organic dyes	ca. 3000 BCE	7	(*31*)
scented oils and perfumes	ca. 3000 BCE	8	(*34*)
soap	ca. 3000 BCE	9	(*35*)
synthetic glass	3000-2500 BCE	10	(*22*, *30*)

By 30,000 BCE, early mankind was well-versed in the use of fire (*5*) and it was some point after this that fire started being applied to various pyrotechnology beyond simple cooking. The earliest of these technologies was the development of pottery and ceramics from the firing of clays and other alumina-silicates. Such pottery dates back to ca. 18,000 BCE (*27*) and became the pre-dominate structural material for the next 15-20 millennia. Such pottery was particularly important for a variety of foodstuffs which could be stored, cooked, and transported in these vessels (*22*).

With reliable vessels now available, it was only a matter of time before it was discovered that sugar-rich solutions stored too long in such containers underwent fermentation to produce alcoholic beverages. Upon consumption of these transformed solutions, early cultures found they liked the taste and the aftereffects, resulting in efforts to reproduce and refine the production of these drinks. These efforts are thought to have begun in the period of 10,000-8000 BCE and resulted in the production of a variety of drinks from mead (fermented honey), to date and palm wine, and finally beer and grape wine (*22*, *28*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch001

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By 6000 BCE, the ability to extract metals from their ores resulted in a second major pyrotechnology (*22*, *30*). These efforts began with the smelting of copper to generate a new material that could be molded, drawn, hammered, and ultimately cast. This versatility of material processing resulted in a wide new range of tools, ornaments, or vessels. Copper only had one shortcoming - it was soft. This changed, however, when it was discovered that the addition of tin or zinc resulted in the harder and more durable alloys bronze and brass (*22*, *29*).

The time period characterized by the introduction of metals also began the development of a number of new chemical technologies based on organic species. These included the processing of plants to produce linen and other fabrics (*32*), the tanning of hides to produce leather (*32*, *33*), the isolation of organic dyes to color fabrics (*31*), the production of scented oils and perfumes, and ultimately soap (*35*). Examples within these technologies include some of the most complex chemical processes yet known to early cultures.

This period of developing organic chemistry was then bookended with the last of the major forms of pyrotechnology - synthetic glass. While natural glasses such of obsidian had been used well into prehistory, the intentional production of glass from silica sources dates to no later than 3000 BCE (*30*). Such glass was unlike any other material of this time period and its closest modern material analogues are the organic plastics utilized extensively today. Glass in its molten state can be poured into almost any shape and retains that shape upon cooling, making it an extremely versatile material and a good compliment to the previous structural materials of pottery and metal.

The Role of Technology in Evolving Civilizations

It is a widely held belief that technology is a major determining factor in the evolution of a culture (*2*, *36*). In fact, it is believed by some that the technological aspect of culture is fundamental, and the nature of cultural institutions derive from the way a group works together to support itself. This leads to the view-point that societal evolution is the direct result of advances in technology. In fact, in reviewing the various chemical technologies outlined above, it is hard to imagine how early cultures could have developed without many of the basic chemical technologies essentially taken for granted in the modern era (i.e. pottery, metals, etc.). As such, it is not surprising that emphasis has been placed on the concept of technological "stages" in discussions of social evolution (Stone Age, Copper Age, Iron Age, Plastic Age, etc.) (*26*, *37*). Of course, these commonly quoted historical eras all reference technologies based on chemical processes.

The importance of technology has not only been acknowledged with regard to the general evolution of culture, but also specifically in terms of the origin of civilization (*2*). Developments in technology made it possible for early cultures to provide for greater populations, thus allowing their culture to grow and expand. Of course, the best example of such a discovery was agriculture, which enabled mankind to increase enormously in number (*38*). This resulting shift from hunter-gatherer to early settlements was accompanied by a series of technological advances, at least some of which may be seen as a direct result of the changed

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch001

economy (*6*). As such, the origin of civilization itself was made possible by the development of agriculture. This single technological advance allowed the support of a greater number of people, resulting in an increase in the subdivision of labor and allowing classes of specialized function to develop, which led to yet further advances in technology (*2*, *9*, *17*, *38*). These advances included additional critical technologies in the development of civilization, such as the discovery of pottery as a method to store and transport the products of agriculture, thus leading to further stability and avenues for further population growth. Also of significance was the development of methods of working metals and ultimately the isolation of metals via the smelting of ores, which allowed for the production of better tools. In turn, such tools serviced both growing agricultural efforts as well as the further development of new technologies. As such advancements allowed people to live together in increasingly larger numbers, it also became important that methods of documentation should be available, thus leading to the intellectual inventions of writing (Figure 4), numbers, and the beginning of calculation (*38*). As such, technological advances ultimately resulted in changes in the way that mankind both communicated and expressed themselves, but also how they viewed the world around them. Some have even gone so far as to claim that technology controls civilization, such that the details and variations in social organizations are relatively unimportant, except where the social organization affects technology itself (*38*).

Others, however, have suggested that the origin of civilization can be better understood as an organizational response to certain ecological problems than as any result of technological advances (*2*). Even with such a view, however, it would be hard to argue that technology did not contribute to such an organizational response, particularly as important chemical technologies (pigments, pottery, leather, etc.) predate even the development of urban towns, much less formal civilization itself. If nothing else, technology can be viewed as a catalyst for the formation of civilization; that is, increasing the rate of development that may have occurred anyway (*2*).

It has also been stressed that the relationship between technology and society is much more complex than a simple linear relationship in which new technology results in advances in society. Thus, technology charts the course of societal development, but technology itself is also a social construction and is thus influenced by the society in which it is developed (*39*). As such, it goes without saying that civilization has also played a role in the development of technology. In the simplest sense, it is possible to postulate that the greater the variety of raw materials and the greater the ease of transportation, the greater the potential for technological development. As such, one would expect that the more advanced a society became, the more its rate of technological advances theoretically increased. However, this was not necessarily the reality in practice.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch001

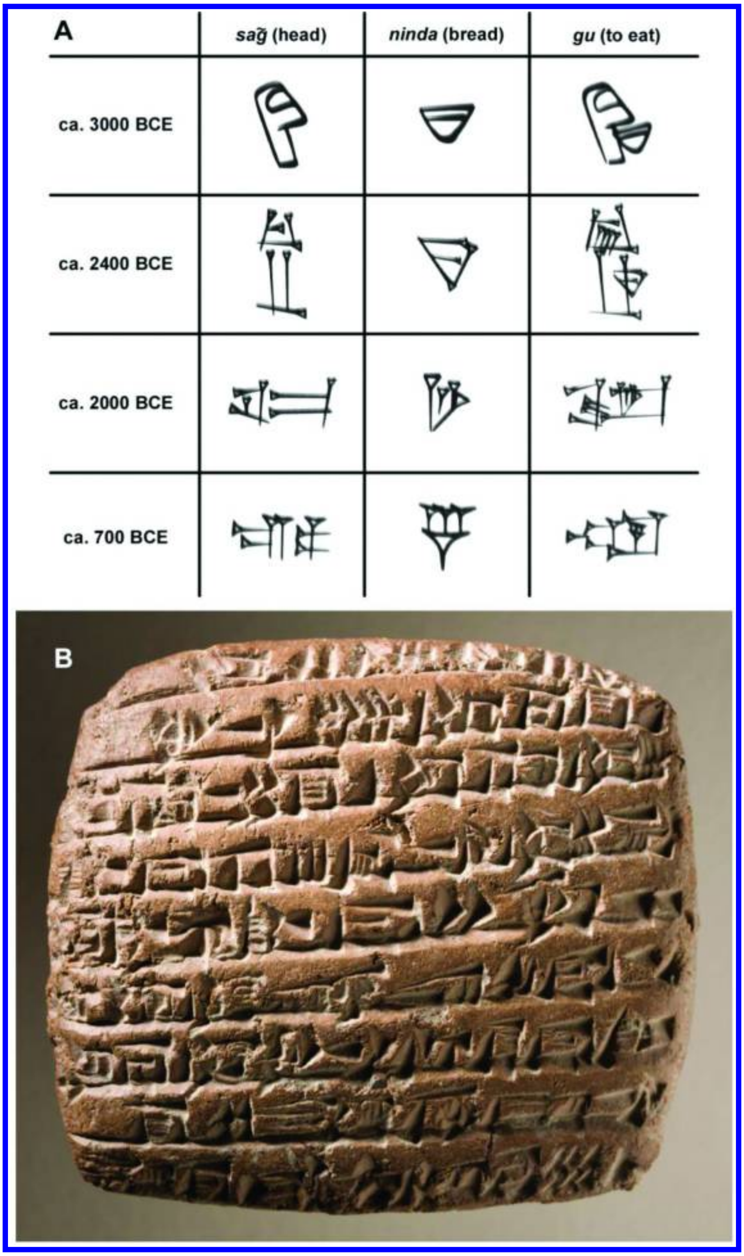

Figure 4. Evolution of Sumerian language from pictographs to cuneiform (A) and a cuneiform clay tablet representing the earliest form of writing, 1875-1840 BCE (B). [M.79.106.2; Courtesy of the Los Angeles County Museum of Art].

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch001

Some have gone so far as to give technology a wider meaning that embraces both a cultural and organizational aspect beyond the underlying technical principles and see innovation as the outcome of mutual adjustments between social, cultural, and technical factors (*39*). This can be seen in that one of the limitations to technological evolution in antiquity seems to have been imposed by mankind itself; for certain social conditions were apparently unfavorable to further technological innovation. For example, authoritarian regimes aiming at stable social conditions appear to have been those under which there was the least technological advance (*40*). In contrast, history has shown that periods of sudden technological evolution are often seen at a time shortly after a stable society had suffered a setback at the hands of one of its less technologically advanced neighbors. In such events, new technologies were invariably initiated via the intrusive population, which ultimately strengthened society providing at least the core of the older society was left more or less intact. In addition, the introduction of new people into a society (either as conqueror, immigrant, or slave) brought with them technologies of their own and by cross-fertilization, they were able to introduce new concepts. Ultimately, for a technology to continue to advance and develop, it required an influx of inspiration. This could often result from the presence of quite unrelated technologies from which ideas could be loaned, borrowed, or adapted (*40*). All in all, however, history testifies to the extreme adaptability of technological development to both societal constraints and needs (*39*).

In the end, it is quite clear that technology and civilization are intimately intertwined, leading to the mutual evolution of both technology and society (*39*). No matter the conflicting views on which of the two dictate the other, we can view the relationship between technology and civilization as a continuous feedback loop. That is to say, new technology allows advances in civilization, while advances in civilization provide optimal conditions for the development of new technologies.

Conclusion

Over a period of some 17,000 years, early mankind progressed from simple hunters to the formation of the world's earliest civilizations. In the process, mankind developed a wide range of technologies, many of the most important of which utilized chemical processes, particularly in the development of new materials. While not all can agree if such technologies are responsible for the development of civilization, it cannot be argued that they most certainly played a critical role in early societies. As the region of the Fertile Crescent saw the development of many of the earliest human civilizations, it is perhaps not surprising that many of the earliest examples of chemical technology also originated within the same region.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch001

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Chapter 2

Historic Mineral Pigments: Colorful Benchmarks of Ancient Civilizations

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Our ancient forebears certainly made use of pigments to color virtually everything they used or had: bodies, caves, pottery, sculpture, stone structures, clothing and other textiles. This paper will document their usage with an emphasis on mineral pigments, natural and synthetic. Modern investigations on their preparation and uses have gradually increased our awareness, and in some cases, awe, of the degree of sophistication possessed by these early civilizations.

Introduction

Color usage in antiquity naturally revolves around the identification of colored materials in the various artifacts dating back to ancient times, as well as to how they were prepared and applied. Perhaps the first person to recognize the need for actual chemical analysis of ancient colors was Sir Humphry Davy (1778-1829) who, in 1815, published a paper (*1*) outlining his sampling, chemical analysis, and comparisons of his results with information provided by ancient Greek and Roman sources. Davy had a unique opportunity: he spent a prolonged time in Italy and was able to visit ruins in Rome, Pompeii, and Herculaneum, among other sites where colored works of art were available. He also had a good friend in the sculptor Antonio Canova (1757-1822) who was charged with the care of the works connected with ancient art in Rome. It seems that, through Canova's good offices, Davy (Figure 1) had the freedom to sample whatever colors he wished. He then subjected the samples to chemical tests that he describes in enough detail to make the modern chemist realize how skilled he was in analysis despite the fact that he lacked any sort of the instrumentation that we heavily rely on today.

In Chemical Technology in Antiquity; Rasmussen;
ACS Symposium Series; American Chemical Society: Washington, DC, 2015.

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Figure 1. Sir Humphry Davy, 1830. Engraving on wove paper (21.5 x 14.25 in.) by G. R. Newton, after a painting by Thomas Lawrence, London. Gift of Fisher Scientific International. Chemical Heritage Foundation Collections. Photograph by Gregory Tobias.

In this paper, we will follow in Davy's footsteps by examining the colors one by one, just as Davy did, but not in his exact order. We will also utilize in the process the modern instrumental means that are now at our disposal. But first, we must look at how we think about, describe, name, and classify color, how it was used in the prehistoric past, and then enter the historic past via the literature sources cited by Davy.

Color Naming and Classification

De Coloribus (or *On Colors*), a work far ahead of its time, is a treatise attributed to Aristotle (384-322 BCE) but sometimes ascribed to Theophrastus (371-287 BCE) or Strato of Lampsacus (ca. 335-269 BCE). It is remarkable that the author was able to distinguish between what he observed as "primary" colors and various mixtures of color, that he could speak about various "strengths" and "saturations" of color, that he could observe that we never see a color in absolute purity, that objects assume different colors under different viewing conditions, and that anything that has a color of its own may transfer that color to other things (*2*).

The work outlines the theory that there exist primary, secondary and tertiary colors. The primary colors, or simple colors, are not mixed with any other color and consist of black, white, and "fire yellow." Furthermore, black is the proper color of elements (i.e., air, fire, earth and water) in the process of transmutation, and that the "remaining colors" arise from blending by mixture of these primary colors. The author goes on to say that there are many arguments to prove that darkness is not a color, but merely privation of light. Since the author lacked a precise color vocabulary, as well as any kind of experimental evidence, but relied strictly on limited observations of phenomena, his conclusions were in many cases erroneous.

The totality of subjects discussed in *De Coloribus* were (1) the simple colors, including black; (2) secondary and tertiary colors, and observations on methods; (3) causes of variety of colors; (4) coloration by tincture; (5) colors of plants; (6) colors of animals. The reason why *De Coloribus* had a pronounced impact on subsequent color theories and remained influential until Isaac Newton's experiments with light refraction was the fact that it pointed to the need for a science of color, a systematic color naming protocol, and method for color classification. That same need certainly became more evident following the explosion of synthetic colors that hit the market in the late 19th century.

Color Names

Color, at least on the visual level, is the most obvious property an object can have. Hardly a day goes by that one does not have recourse to naming a color, and we must presume that this need goes back to the first societies and the first use of human language. The origins of the names of the colors, therefore, are shrouded in antiquity, and many of the names evolved due to other considerations. In fact, color terminology is the second most frequently studied word-field after kinship terms (*3*). Even awareness of the various colors differs among cultures, as Zollinger (*4*) has pointed out in his study of how we name colors. Berlin and Kay (*5*) proposed a model of color theory that, though highly criticized because the test subjects all lived in an English-speaking environment, suggests an evolution from a color awareness of only two basic color terms (black and white) to a second stage (addition of the term red) to third and fourth stages (addition of the color terms green and yellow, but sometimes in reverse order) to a fifth stage (addition of the color term blue) and beyond to brown, orange, pink, purple, and gray. This modern test is quite remarkable in that it underlines the fact that the three basic colors in all ancient cultures were indeed black, white and red! Even more remarkable is the place of blue in the study. Many people and color systems consider blue a primary color, and yet, as pointed out by Pastoureau (*6*), "*the modest role played by blue in ancient societies and the difficulties many ancient languages have in even naming it caused many nineteenth-century researchers to wonder if the men and women of antiquity could see the color blue, or at least see it as we do [today].*" Blue seemed not to have had any symbolic value nor did it seem to have played any

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role in ancient rituals. Only in the mid-12th to mid-13th centuries did blue take its place with yellow and green as a tripartite system in replacing the black-white-red system of antiquity. Table 1 is an outline of the origin of the names of the spectral colors.

As the need developed in art, commerce, and in many other areas, other color names were invented so that today, there are over 8,000 color names. The need to translate among color vocabularies so that their meaning is clear (*7*) is a daunting task since some of them are completely unintelligible to persons working in a different field. For example, for the color shade called "moderate pink," Maerz and Paul's general *Dictionary of Color* (*8*) lists the names almond blossom, almond, aurore, blossom, Corinthian pink, dawn, débutante pink, hermosa pink, hydrangea pink, la France pink, lilac, lilaceous, lilas, nymph pink, orient, peach blossom, pink pearl, récamier, rose Hermosa, roseleaf, sea pink, and Venetian pink, whereas the Plochere system (*9*) for interior decoration would describe the same color as dignity, evening haze, light mauve, mountain haze, orchid pink, rose cloud, and vesta. Given the enormous variety of descriptive terms that seem to have no relationship to the color being described, it is no wonder that modern disciplines that deal with color have resorted to other systems. Today these areas include chemistry, biology, botany, horticulture, mass market, textiles, paint and dye industries, plastics and other polymers, geology, philately, soil colors, agriculture, and medicine. Once we realize that a basic color vocabulary has to be established, we can then actually name objects on the basis of their color.

Table 1. Origin of Names of the Spectral Colors

Color Name	*Origin*	*Language*	*Extended Meaning/Names*	*Comment*
Red	eruthros	Greek	Erythrocyte (red blood cell)	Russet, ruby, ruddy, rust are some derivatives; words for "red" are similar both north and south of the Alps
Orange	narangah	Sanskrit	Orange (the fruit)	Evolution of word to Persian, Arabic, and French
Yellow	ghel or gohl	Proto-Indo-European	Denotes both yellow and green	Evolved via many terms such as *galbus* (Latin). "Ghel" means "to shine or glitter" and is the origin of both the modern words "glass" and "gold"
Green	gronja, groen	West Germanic, Dutch	To grow	Emerged almost unchanged into Northern European modern languages

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Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Table 1. (Continued). Origin of Names of the Spectral Colors

Color Name	*Origin*	*Language*	*Extended Meaning/Names*	*Comment*
Blue	bhlewos	Proto-Indo-European	Yellow to pale to color of bruised skin	The word, while remaining unchanged, evolved through various meanings; "blue" as such was unknown in the ancient world
Violet	viola	Latin	From the color of the flower	Violet is a spectral color, whereas purple, often used synonymously, is a mixture of colors

Color Naming

Until quite late in the 20th century, the beginning student of chemistry was encouraged to explore the physical properties of substances, chief among which were color, odor, and taste. Other properties, that required measurement rather than sensory perception, were density, crystallinity, hardness, and so forth. Color was by far the most important property perceived by the senses, and the other two sensory properties declined in importance as safety considerations came into play such that, by about 1980, absolutely no one would think of actually tasting an unknown chemical substance in order to describe it! However, we must recall that lead acetate was once called *sugar of lead* (because of its sugar-like appearance) and magnesium sulfate was once called *bitter salt*, presumably because of its taste. The ancient Romans actually used lead acetate to sweeten their fruit.

The earliest "written" color terminology for objects are Egyptian hieroglyphics since copper, gold, and iron ore were certainly known by about 4000 BCE. Although the origins of many names in the languages of the ancient world are still in dispute, it is safe to say that we can deduce the Egyptian name for gold in the hieroglyphic *nub*, which is also the term meaning "to smelt." The Egyptian word for silver is *hetch*, meaning "white," and the term for malachite is *vatch*, which means "to be green (*10*)." Figure 2 illustrates the use of the words for gold and silver to describe a different reality, silver-gilt.

Similar tendencies at colorful descriptions can be found in the Babylonian and Assyrian cultures. Sumerian cuneiform (about 700 BCE) was particularly well-suited for the identification, classification, and naming of minerals. For example, the descriptor for sapphire was "very hard blue stone," or ^{a}ZA. GÌN. AŠ. AŠ. Crosland (*11*) remarks that this excellent systematic nomenclature was not carried into any other language and it had no parallel until the development of the nomenclature of organic compounds in the 19th century of our own era.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

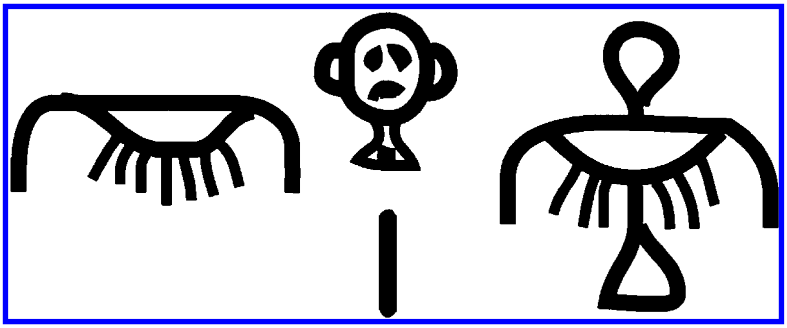


Figure 2. Hieroglyph for Gold on Silver (nub ḥer ḥetch)*, i.e., Silver Gilt.*

Over the centuries, color continued to be of primary importance in distinguishing various substances on the basis of shades such as light blue and pale blue, although for lack of a systematic nomenclature, as well as lack of knowledge of the nature of the substances, confusion reigned. Table 2 is a partial list of commonly known substances originally named for their color.

Table 2. Common Chemical Substances Originally Named for Their Color

Ancient Name	*Significance*	*Chemical Identity*
Hematite	Bloodlike stone	Iron(III) oxide (Fe_2O_3)
Magnesia alba	White substance from Magnesia	Magnesium carbonate ($MgCO_3$)
Magnesia nigra	Black substance from Magnesia	Manganese dioxide (MnO_2)
Orpiment	Gold pigment	Arsenic(III) sulfide (As_2S_3)
Plumbum candidum	White lead	Tin (Sn)
Plumbum nigrum	Black lead	Lead (Pb)
Plumbum cinereum	Ash-colored lead	Bismuth (Bi)
Verdigris	Green of Greece	Dibasic copper(II) acetate ($(Cu(C_2H_3O_2)_2 \cdot 2Cu(OH)_2$)
Vermilion	Worm-colored	Red mercury(II) sulfide (HgS)

A fine overview of the use of colored substances from the Paleolithic era to the advent of synthetic organic colors is the chapter on color in Joseph B. Lambert's "Traces of the Past (*12*)." For a concise yet thorough review of the physics and chemistry of color, please see "The Chemical History of Color (*13*)."

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Pigments in Antiquity

What Are Pigments?

All materials used for coloring other objects may be classified as either pigments or dyes, depending upon the method of application. Typically dyes are dissolved in a medium into which the object to be dyed is then immersed. A physical or chemical interaction between the dye and a substrate is necessary for the dye to become "anchored" in place. Pigments, on the other hand, do not react with the substrate and must be applied by first being suspended in a medium, called the vehicle, which allows the pigment to adhere to the surface. The more general term for both dyes and pigments is "colorant."

The colorants under consideration in this chapter are largely mineral colors derived from either naturally occurring rocks or other geological substances, such as ores, found in the earth, or synthesized from their appropriate starting materials. All, however, are substances generally termed "inorganic" by chemists, an adjective that applies to materials made from any element except carbon. Since none of these substances is soluble in ordinary solvents, all of them require a vehicle, sometimes called a binder or medium, in order to adhere to the surface of the object being colored. Some organic compounds are also often used as pigments, and some will be included in this discussion if they were important in antiquity.

How Is "Antiquity" Defined?

It is difficult to apply the criterion of chronology to the term "antiquity." Every civilization has undergone an evolutionary trajectory from its perceived beginnings to its status as viewed from the present moment. Some civilizations are virtually contemporaneous, such as the Roman and Etruscan civilizations; others may pre-date them by many centuries, such as the Chinese and Egyptian cultures, and others may be far-removed in time such as the pre-Columbian civilizations of the Mayas and the Aztecs. What we might term "antiquity" for one, on an objective time scale, may be a period from 5,000-2,500 BCE whereas "antiquity" for another may be from 1,400-1,700 CE. Hence, the civilizations discussed in this paper may be far-removed in objective time from one another, and at the same time their technologies may be deemed to arise in "antiquity."

Use of Color in Antiquity

Obviously, human activity through countless millennia was concentrated on survival. Hostile elements from weather and seismic conditions, predatory animals, other human and perhaps subhuman groups, illness, disease, accidents, lack of nutrition, food, clothing, shelter and the basic necessities of life all took their toll. It has been estimated that the average life span (discounting infant mortality) for a prehistoric human being was less than thirty years, and those who survived beyond that magic number did so minus teeth. And the magic number did not change very much even up to the time of the Roman Empire. So how do we account for the fact that puny little human beings continued in the ascendancy seemingly against all odds? Of course, the answer is brain power, and in particular, inventiveness and adaptability with respect to the use of material objects so that virtually every material substance could contribute in some way to survival.

Survival depends in large part on how well an individual or a group can control and adapt to its environment. Groups that lived in caves had a better chance than those who lived out on the open steppes. People who had fire managed better than those who did not. Those who had plentiful combustible material were more likely to survive than those who did not. In fact, archaeological evidence points to a key factor in the growth of a civilization: the hearth. The hearth was a source of warmth and protection from the elements. It was the place where food could be cooked or tools fashioned. Casting a look far into the future, we can see that the hearth was the birthplace of chemical thermodynamics, fuel chemistry, tribology, food chemistry, color chemistry, and so much more. With respect to color, Philip Ball remarks that "the chemical technology that existed for color-making in ancient times was not developed specifically for that purpose…pigment manufacture in antiquity was an offshoot of a large and thriving chemical industry that transformed raw materials into the substances needed for daily life (*14*)."

However, observing what artifacts remain from many an ancient civilization may suggest that we take exception to Ball's statement. Granted that color chemistry was not necessarily a "survival" technology, at least in terms of gaining more food, adequate clothing, and better shelter, then we might ask why it was so highly developed even among the ancient cave painters of tens of millennia ago. Perhaps the answer lies in a perceived mysterious world where survival depended not only on practical necessities but also on having the favor of certain spirits whose images, painted on cave walls, would allow a tribe to control the outcome of the hunt that would assure survival for another winter. See Figure 3 for an example of how Paleolithic artists worked their chemistry on the walls of Grotte Chauvet 32,000 years ago.

While we cannot second-guess the motives of ancient peoples, we can certainly infer a belief structure that was a powerful force in human activity, including belief in an afterlife. Conflicting opinions on the motivations of Paleolithic artists continue to stir our imaginations (*15*). Our knowledge of ancient civilizations depends in large part upon what archaeologists have managed to excavate from gravesites, some of which, as everyone knows, were elaborate tombs far larger and more imposing than many a modern building. And in these tombs we have found not only the tools designed to aid the deceased in the afterlife, but images of the afterlife itself in, for example, elaborate wall paintings from the famous Etruscan tombs at Tarquinia.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Figure 3. This horse study from Grotte Chauvet, France (32,000 years BP) by Thomas T. (Flickr; Creative Commons) is indicative of the ability of ancient humans to transform abstract and symbolic thinking into concrete forms.

Why Analyze Paleolithic Pigments?

Human expression, no matter what the form, is intimately related to our cultural heritage. Knowledge of the identities of materials used for this expression and how they were prepared can be valuable markers of the sociological context in which they were created. The artifacts, both wall paintings and other objects found in the Paleolithic caves, can be valuable, and indeed unique, witnesses to a culture that existed long before other modes of cultural transmission, such as writing, sculpture, or architecture, were developed. The subject matter of the paintings is also a window that opens onto a long-disappeared world where extinct species such as the aurochs and mammoths roamed the plains of what we now call Europe. It is no wonder that their discovery mesmerized the world in 1900; a century later, scientists continue to be mesmerized by the unexpected discoveries they are making as they probe their composition.

The Oldest Known "Color Works" – The Painted Caves of Europe

The dawn of the Upper Paleolithic era can be dated to roughly 100,000 years BP when anatomically modern humans came on the scene in Europe. Sometime around 60,000 years BP, archaeologists mark what they call the Upper Paleolithic transition when new and more sophisticated stone and bone tools began to appear along with artistic expression by way of sculpture, painting, and even body painting as evidenced by the appearance of what seem to be tattoo kits. Cave and rock art began to appear at this time, the most famous of which are the painted caves of Europe.

Figure 4 is a map showing the major sites of the Paleolithic caves that cluster in three areas of France: the Ardèche valley north of Marseilles, the Dordogne and Lot valleys due east of Bordeaux, and the Ariège area in the central Pyrenees around Grotte Niaux, south of Toulouse. It is in these areas, seemingly culturally connected to one another by their color-making tradition, that this astounding art form flourished for tens of thousands of years from the Aurignacian culture through the Magdalenian culture (See Table 3 for a summary of these time periods) (*16*). In Europe, some 200 other caves and rock shelters are known to contain art, the majority of which are in France and Spain, with other scattered sites in Italy, Romania, Portugal, Germany, Ukraine and Russia.

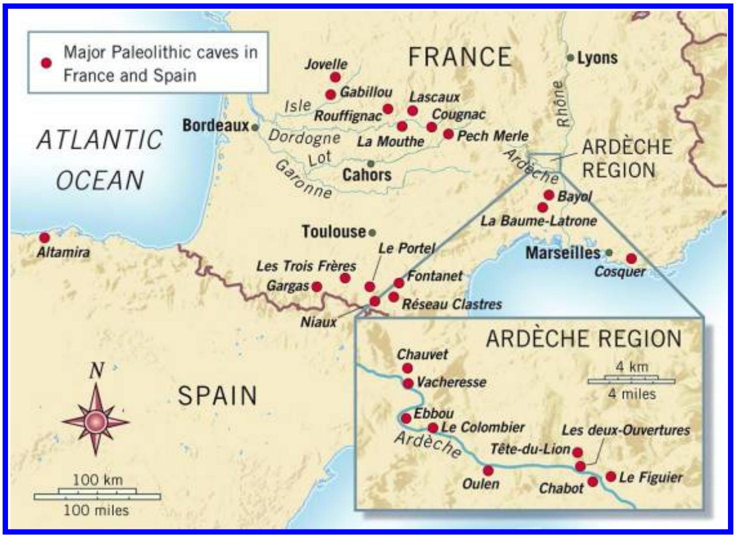


Figure 4. Sites of the Major Paleolithic Caves in France and Spain. Sayre, Henry M., Discovering the HumanitieS, 2nd, ©2013. Printed and electronically reproduced by permission of Pearson Education, Inc., New York, NY.

Table 3. Evolution of Cultures Following the Upper Paleolithic Transition

Culture	*Time Period (BP)*	*Span*
Aurignacian	34,000 – 23,000	11,000
Gravettian	28,000 – 22,000	6,000
Solutrean	19,000 – 15,000	4,000
Magdalenian	18,000 – 10,000	8,000

Discovery of the Caves

1879 was the year that an amateur archaeologist and his 8-year old daughter stumbled upon the polychrome paintings hidden for 13,000 years in the cave of Altamira, Spain. Once their antiquity was verified (at first dated to the Magdalenian period), our perception of early human beings immediately emancipated them from their "cave man" status and conferred on them the capacities that we once considered qualities of "modern" humans: the ability to do representational art, to express creativity, to develop a sophisticated color technology, to engage in the collaborative effort necessary to carry out such tasks, and to respond to the evolutionary nature of developing technology over generations. However no one could imagine how many generations until just a few years ago: application of uranium-thorium dating techniques showed that the paintings were executed over a 20,000 year period, and furthermore, that some of them could be dated back to the Aurignacian period (*17*) time spans that have never been achieved by any other culture. Such figures therefore also changed our definition of "civilization."

In the early 20th century, more caves were discovered, including the spectacular Lascaux cave in 1940. Many of the caves, including Altamira and Lascaux, were open to the public for decades but now have been closed due to the alarming rate of biogenetic deterioration, rendering the caves objects of intense conservation efforts (*18*). It was generally agreed that several factors allowed the caves to survive intact over the centuries, viz., stable temperatures and atmospheres, but that the impact of human presence upset this balance by introducing changes to the internal climate (*19*). Happily, the Grotte Chauvet, discovered in 1994 after 22,000 years of concealment, stands now as a model of what can and should be done to preserve this cultural heritage. Due to its late discovery, it was never subjected to the factors that placed many of the other caves at risk. It was never opened to the public and plans right now are to keep it fully intact where all types of future research will still be possible. Conservationists are struggling to determine how to transmit and share knowledge fundamental to this site which is unique in the history of development of modern human thought (*20*). Over the same time period, the caves have been subjected to archaeological examination and the pigments used have been analyzed by some of the most sophisticated modern means of analysis such as Scanning Electron Microscopy (SEM), and Infrared and Raman Spectroscopy, with some very surprising results.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Scientific Examination of the Caves

Archaeological examinations of the caves have taken place over a period of about a century, but modern analytical techniques have only been applied in the past several decades, and those only on samples taken from the wall paintings and from the moveable artifacts found scattered throughout many of the caves. Some groups have begun to plan, and several have already carried out, *in situ* investigations.

Early research was carried out without benefit of the methods now at the disposal of the modern chemist. Henri Moissan, 1906 Nobel laureate in chemistry for the isolation of fluorine, was among the first to carry out analyses on the paints found in the caves of Font-de-Gaume and La Mouthe in the Dordogne valley (*21*). He reported the presence of hematite and manganese oxide mixed together with calcite and small grains of quartz. A few years later, the Abbé Breuil and E. Cartailhac described, without experimental justification, a black pigment from the Salon Noir of Grotte de Niaux as carbon, manganese oxide, and animal fat (*22*).

Less selective work consisted in determining the nature of the pigments found in the well-known caves of Altamira and Lascaux, where excavations have provided in sufficient quantity the tools and materials used by the artists. Beginning in 1880, the Altamira paintings were subjected to numerous optical observations in order to characterize their pigments. But the actual physico-chemical determinations did not begin until 1977 with the work of Marti and Cabrera-Garrido (*23*). Analyses on samples from Lascaux in 1979 by Couraud (*24*) and Ballet (*25*) revealed the nature of the colorants' constituents (hematite, ochres, manganese oxide, and carbon), the techniques of their manufacture, and their mode of application. The systematic combination of minerals, usually quartz, has been interpreted as a deliberate action on the part of the artists to prepare the painting and the presence of an inorganic filler added to the binder for the pigment seems to have been well considered. Some samples from other cave paintings have been studied by Vandiver (*26*) who compared them with the material found at the base of the walls and with geological samples and found evidence of prolonged grinding of a mixture of minerals to control the color and fluidity of the paint. All of the later studies done in the 1980s demonstrate the use of different types of pigments and sometimes deliberate association with certain minerals. It seems therefore that one has to deal with paintings realized with different materials, each providing specific desired properties such as color, texture, and luster.

Groups working under the auspices of the *Société préhistorique française* and publishing in their journal have carried out the major portion of investigations in several caves of the Ariège area during the latter part of the last century. Their work has given us a great deal of information not only about the nature and identification of the pigments used in the caves, but also of the sources of their raw materials and the technology underlying their use (*27*, *28*). This approach led to the identification of ateliers, i.e., of socially organized groups in order to make a definite artistic product. Later researchers realized that a better understanding of the function of these groups would be helpful in clarifying the artists' motives. Hence, they began to carry out their analyses of the colors represented in their geographical context.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

These are some of their observations:

- The intimate mixing of the mineral fillers and the grains of pigments testify to a long period of grinding to bring about a homogeneous mixture;
- The fillers were intentionally associated with different pigments with the aim of obtaining good surface adhesion and hiding power, and perhaps, in certain cases, to economize on the use of precious pigments;
- The mixture of pigment, finely ground charcoal, and mineral filler was absolutely never found in nature;
- While it is clear that this association of minerals cannot be found in nature, it is equally clear that the mixture was not a fortuitous result in the grinding stage of the pigment;
- The research identified three different recipes for the mineral fillers: F (feldspar), B (biotite and feldspar), and T (talc) in use in 8 of the caverns;
- The multiplicity of pigment recipes on the one hand, and of the fragility of some of the pigments used on the other, cannot explain the different proportions of the paint constituents;
- Analysis of trace minerals was able to differentiate the provenances of the raw materials: some of the materials with the same geologic nature had very different provenances.

Some Conclusions from These Examinations

- The deliberate choice of the same mineral filler but taken from different sources introduces the notion of pots of paints made up from recipes scrupulously followed;
- The introduction of biotite brings specific improvements to a liquid paint and may point to an evolution in the method in which a paint was applied;
- For the Magdalenians, the passage from recipe F to recipe B can be interpreted from this model of evolution in manufacturing techniques.

As for the identities of the pigments themselves, analysis by SEM yielded the following results for five of the caves examined, as summarized in Table 4.

Continuation of the work will be for the purpose of better estimating the geographic extension of a given workshop, the culture that gave rise to it, and furthermore, on the same site where several groups have been able to work, a better understanding of the evolution of their techniques could create chronological benchmarks.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Table 4. Identities of Red and Black Pigments from Five Paleolithic Caves

Cave	*Location*	*Red Pigment*	*Black Pigment*
Niaux	Ariège		Charcoal
Lascaux	Dordogne	Hematite Goethite	Oxides of Manganese Carbon
Altamira	Spain	Oxides of Iron	Oxides of Managnese Charcoal or Mineral
Quercy	Dordogne		Oxides of Manganese (+ Ba) Charcoal
La Vache	Ariège	Oxides of Iron + Biotite	Oxides of Manganese + Biotite

Further Work

For the entire span of the 20th century – from 1902 until 1999 – examination of the materials taken from the Paleolithic caves concentrated on samples that were removed from the caves for analysis. Early techniques reported in the literature were principally X-ray and grating infrared spectroscopy, while Fourier transform infrared spectroscopy and X-ray fluorescence spectroscopy became more widely used later in the century However, since these techniques require samples of a certain size, some of them are intrinsically destructive and very few of them can be employed *in situ* so as to leave the original artifact intact.

Cultural heritage analysis has long felt the need for techniques, particularly analytical instrumentation, which are sensitive, reliable, and non-destructive, and preferably able to be carried into the field to do *in situ* work, thus obviating the need for the extraction of samples from sites and artifacts. There is a body of literature building up that illustrates that one particular form of analysis – Raman microscopy – is ideal for these examinations (*29*, *30*). Pioneered by Robin J. H. Clark, more and more archaeological scientists are using this method to obtain information on organic and inorganic compounds, but they are finding that the requirements for *in situ* Raman spectroscopy applied to rock art are extremely stringent: uneven surfaces, sometimes inaccessible art high up on a wall, possible instability of the instrument under difficult conditions. Nevertheless, instrument design is improving rapidly; portable models equipped with fiber optic probes are getting not only more powerful but also smaller. Figure 5 shows an example of such an instrument (*31*, *32*). In the words of one group of researchers: "The usefulness of portable spectroscopic equipment to analyze immovable and non-easily accessible artworks have been demonstrated after characterising the valuable rock paintings of La Peña de Candamo Cave. The combined use of hand-held EDXRF and Raman has allowed (us) not only to identify the colour palette employed by the prehistoric artists but also to distinguish between different painting techniques through chemometric analyses (*33*)."

It is not surprising then that Raman, which has been used for general purpose analysis since the 1980s, is being applied in virtually all the literature on cave art analysis that has appeared since 1999 when the first application was done collaboratively by individuals from the Museum of Natural History (Paris) and the University of Toulouse (*34*). The group reported that in addition to the identification of ordinary hematite in red microsamples from each cave (located in the Lot and Dordogne valleys; see Figure 4), they were also able to distinguish a rare orange-red phase which they thought was a disordered form of goethite. They confirmed the presence of carbon in some black microsamples and recognized the presence of manganese oxide/hydroxide in some other black samples. Their work showed that Raman microscopy was powerful enough to distinguish between different red and black pigments without the use of additional complementary techniques. They also envisioned the day, which is now here, when micro fibers and remote sensors would allow for analysis to take place within the caves, thus avoiding damaging the fragile Paleolithic art.

Figure 5. A Portable Raman Spectrometer Measuring 9.1 X 7.1 X 3.8 cm. Courtesy Ocean Optics.

The adaptability of portable equipment as well as the feasibility of *in situ* micro-Raman analyses in a cave environment was tested and reported on in a paper describing the first *in situ* micro-Raman spectroscopic analysis of Paleolithic art (*35*). The results obtained were compared with *in situ* XRF, and X-ray diffraction microanalyses which were performed at the same time in the cave. The authors demonstrated that a portable Raman instrument is very useful to analyze non-destructively drawings in such difficult conditions as high humidity, various wall geometries, and small amounts of material available. Their results showed that the black manganese oxides romanechite and pyrolusite were used as pigments by the Paleolithic artists. Just a few months later, another group reported on successful *in situ* analyses of rock art from the lower Paleolithic era in the central India Bhimbetka site (*36*).

In another report, researchers tested and compared 3 different portable analytical systems that can be used in cave environments for detecting carbon in prehistoric paintings: (1) a very compact X-ray fluorescence (XRF) system in Villars Cave (Dordogne, France); (2) a portable micro-Raman spectrometer in Rouffignac Cave (Dordogne, France); and (3) an infrared reflectography camera

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

in both caves. They chose these techniques for their non-destructive capabilities: no sample had to be taken from the rock surface and no contact was made between the probes and the paintings or drawings. The object of the research was to identify the presence of carbon-based material *in situ* in order to do direct dating of the prehistoric paintings later on. This was accomplished by verifying the identities of the black pigments first, which were found to be manganese-based. By eliminating carbon's presence on the images; the dating research could be centered on samples of the torch marks, enabling protection of the visual integrity of the paintings and drawings (*37*).

We conclude this section with words from Guthrie (*38*):

> Paleolithic art is a silent touch from distant ancestors, their marks a reminder of our own vitality and mortality, prompter to savor our present in this ancient arena of life. Despite our sometimes muddy and bloody way of arriving, we are sisters and brothers in time and space.

Literature Sources on Pigment Usage in Antiquity

While our only knowledge of pigment usage in Paleolithic art is drawn from experimental examination of the works themselves, in later times, principally in the era of the Greeks and Romans, a considerable body of literature on this subject developed. There are about a half-dozen primary sources from which we can extract our knowledge of the geographical locations of pigment raw materials, and the preparation and uses of pigments in antiquity. Theophrastus and Dioscorides represent the Greek tradition; Vitruvius and Pliny the Elder give us an insight into painting and decorative materials of ancient Rome; The Leyden X and Stockholm Papyri take us up to the third century CE in terms of chemical usage, including the use of colored materials. These sources are summarized in Table 5.

Table 5. Summary of Literature Sources on Pigment Usage in Antiquity

Work	*Author*	*Date*	*Origin*
De Lapidibus	Theophrastus	315-314 BCE	Greece
De Architectura	Vitruvius	After 27 BCE	Rome
De Materia Medica	Dioscorides	64-77 CE	Greece/Rome
Historia Naturalis	Pliny the Elder	77-79 CE	Rome
Leyden X Papyrus	Unknown	3rd Century CE	Egypt
Stockholm Papyrus	Unknown	3rd Century CE	Egypt

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Theophrastus (371 – 287 BCE)

Theophrastus was born in Lesbos, Greece. As successor to Aristotle (384 – 322 BCE), he led the Athens Lyceum for 35 years, greatly expanding the number of students. Although he was a prolific writer on a variety of subjects, most of his works have been lost. His two-volume work "On Plants" has earned him the title of the "Father of Botany." No less important, at least to chemists, is his treatise *De Lapidibus*, "On Stones (*39*)," a 69-section systematic discussion of what we would now call inorganic substances, including rocks, minerals, gems, and metals, along with substances like pearl and ivory. Pliny the Elder drew upon this source for much of his *Historia Naturalis*, and it continued to influence natural historians up until the time of the Renaissance.

Vitruvius (b. 80-70 BCE; d. after 15 BCE)

Vitruvius (full name: Marcus Vitruvius Pollio) was a Roman architect and engineer. Little is known of his life. His major work, *De Architectura* (*40*), consists of ten books on all aspects of architecture including city planning. Although Book II contains some information on brick, sand, lime, and stone, it is Book VII that contains most of the material of interest to chemists regarding colored materials. In it he discusses substances such as cinnabar, quicksilver, natural and artificial colors, burnt ochre, blue, white lead, verdigris, purple, and color substitutes.

Dioscorides (40-90 CE)

Dioscorides (full name: Pedanius Dioscorides) lived at the time of the Emperors Nero and Vespasian. He was born near Tarsus, in Asia Minor, at that time part of the Roman Empire, and now in present-day Turkey. A learned physician, he practiced medicine as an army doctor, and saw service with the Roman legions in Greece, Italy, Asia Minor, and Provence in modern-day France. His military years provided opportunities for studying diseases, collecting and identifying medicinal plants, and discovering other healing materials. His vast experience led to the composition of *De Materia Medica* (*41*) sometime between 64 and 77 CE. Book Five, on vines and wines, contains most of the descriptions of inorganic materials that may be applied as medicinal substances.

Pliny the Elder (23-79 CE)

Gaius Plinius Secundus, known almost universally as Pliny the Elder, composed his monumental treatise *Historia naturalis* (*42*) late in life, and fortunately, it survived, a fate not granted to many of his other works. He was a busy Roman official who found the time to transcribe much of what was known in the ancient world in accurate and precise detail. Books XXXIII through XXXVII describe the natural history of metals, stones, precious stones, paintings and colors.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

The Leyden X and Stockholm Papyri

These two complementary documents, thought to be written by the same author, taken together give us an excellent view of the beginnings of chemical technology and operations during the early centuries of the Christian Era. Their great value for the history of chemistry is that they are the only original laboratory "manuals" from that period. Part of a collection of papyri purchased by a Swedish vice-consul to Egypt, they lay unnoticed until the late 19th century. The *Leyden X Papyrus* (*43*) was translated from the Greek into English in 1926, and in the following year, *The Stockholm Papyrus* (*44*) was translated as well. The Leyden document consists of 111 recipes, the last 10 of which were extracted almost verbatim from Dioscorides' *De Materia Medica*. In one of its recipes (no. 90), gold and silver are designated by special characters, giving the earliest evidence of the use of symbolism in chemistry. The Stockholm document consists of 154 recipes, only 9 of which treat of metals. About 70 recipes deal with precious stones: how to imitate them or to improve the appearance of genuine ones. The remaining recipes describe the mordanting and dyeing of cloth. This document contains some code words, such as "garlic," which is used to denote human excrement. Curiously, recipes 25 and 60 deal with the cleansing of pearls that have become dirty with use: a pearl fed to a rooster or cock [*sic*] will be whitened in the crop of the bird. While neither of these documents augments our knowledge of the sources, preparation and uses of inorganic pigments, they are helpful in understanding the arts of metallurgy and metals, the elemental sources of the pigments.

Some Useful Secondary Sources

Gettens and Stout's *Painting Materials: A Short Encyclopedia* (*45*), originally published in 1942, is a classic in the varied activities of painting and conservation, cultural research, chemistry, physics, and paint technology. The book contains over 100 entries on pigments and inert materials arranged in alphabetical order from alizarin to zinnober green, complete with references to primary sources when available. Another source, though more restricted in scope, is Alfred Lucas's *Ancient Egyptian Materials and Industries* (*46*). Pertinent chapters in the 4th edition are IX (Glazed Ware), X (Glass), XI (Metals and Alloys) and XIV (Painting Materials).

Pigments that have played a major role in the history of painting are dealt with in the four-volume handbook on artists' pigments published by the National Gallery of Art as a continuation of a series of monographs originally published in *Studies in Conservation* between 1966 and 1974. Each monograph begins with an extensive history of the pigment including terminology, properties, chemical composition, sources, preparation, characterization, identification, and notable occurrences from ancient to recent times. The pigments chosen for inclusion are those that have played a major role in the history of painting and much of the information that the authors supply is based on original laboratory work and bibliographic research. Volume 1 (*47*) contains monographs on yellows (Indian, cobalt, cadmium, chrome, lead antimonite), whites (barium sulfate and zinc white), reds (red lead, minium, and carmine), and green earth. Volume 2 (*48*) treats blues and greens (azurite, blue verditer, natural and artificial ultramarine, smalt, verdigris, copper resinate, malachite green, and green verditer), as well as lead white, lead tin-yellow, vermilion and cinnabar, and calcium carbonate whites. Volume 3 (*49*) covers more blues and greens (Egyptian blue, indigo, woad, Prussian blue, emerald green, Scheele's green, and chromium oxide greens), yellows and browns (orpiment, realgar, gamboge, Vandyke brown), as well as madder, alizarin, and titanium dioxide whites. Volume 4 (*50*) contains valuable chapters on carbon-based pigments (Winter, J.; FitzHugh, E. W.), natural and synthetic iron oxide pigments (Helwig, K.), and asphalt (Bothe, C. I.). While many of the pigments discussed in these volumes are of more recent origin, there are many that date back to the period of our interest, so this handbook is very useful indeed.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Palette Expansion in the Ancient World

In examining the cave paintings of the Paleolithic era, we recognize a limited palette of black, as well as the reds, yellows, and oranges of various hydration states of iron oxide. While some attempts at production of synthetic pigments were evident from the analytical data, they were largely brought about by the application of heat. This state of affairs persisted for tens of thousands of years until the advent of naturally occurring yellow and red pigments such as orpiment and cinnabar, the result of the development of mining. Blue and green were notably absent from the very ancient palette since they are not earth colors. However, as early as the IV Dynasty (c. 2,500 BCE), Egyptian "synthetic chemists" invented a stable blue frit, Egyptian blue, that became a staple of the Mediterranean palette until the secret of its manufacture was lost some time in the 7th century CE (*51*). Blue in the form of lapis lazuli (natural ultramarine) also became available through mining, although the only known source in antiquity were the caves of the remote Afghanistan province of Badakhshan. The blue and green compounds of copper afforded a major expansion of the palette as well, an occurrence that developed in the Mediterranean basin. Hence, in Table 6 we summarize the ancient literary sources of Vitruvius and Pliny for each of the major colors and add actual analyses of artifacts (wall paintings, paint pots, frescos, etc.) from some representative sites in the ancient Greco/Roman/Etruscan/Egyptian world over the course of almost two centuries. The names of the pigments given in the table are those used by the authors; in the discussion of each of the pigment color groups that follows, their nature and synonyms will be elucidated. While organic colorants were undoubtedly used in the ancient world, they will be discussed in a different chapter of this volume; moreover, their absence from the analytical list is an indication of their chemical instability over the course of centuries. In the case of Humphry Davy, the analyses were done by heating, blowpipe redox reactions, and observation of changes upon addition of acids and bases; the other two more recent sets of analyses were carried out using the usual battery of spectroscopic and chromatographic tests.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Table 6. Pigments Used in the Mediterranean and Middle Eastern Worlds from the Fourth Century BCE to the First Century CE

	Vitruvius (40) (ca 27 BCE)	*Pliny (42) (77-79 CE)*	*H. Davy (1) (1815)*	*Béarat (52) (1997)*	*Kakoulli (53) (2009)*
Black/ Brown	Carbon black Charcoal Vine black	Atramentum Ivory black Fossil black Sepia (cuttlefish)	Ochres Manganese oxide Carbon black	Charcoal Bone-black Lamp-black	Charcoal Carbon black
White	Alum White clay Lead white Magnesium hydrosilicate or calcium carbonate	Alum White clay Lead white Magnesium hydrosilicate or calcium carbonate	White clay Fine chalk (calcium carbonate)	Chalk Lead white Limestone Dolomite Aragonite Diatomite	Calcium carbonate (bianco di San Giovanni)
Red/ Orange	Red ochre Burnt ceruse (minium)	Red ochre Burnt ceruse (minium) Red ochre of Sinope	Minium Red ochre Cinnabar	Minium Red ochre Burnt yellow & brown ochre	Red ochre Realgar Cinnabar
Yellow	Yellow ochre Orpiment	Yellow ochre Orpiment	Yellow ochre Orpiment Massicot?	Yellow ochre Brown ochre	Yellow ochre (goethite, jarosite, limonite mixes) Orpiment Sulfur
Green	Terre verte Malachite Verdigris	Terre verte Malachite Verdigris	Copper carbonates	Malachite Verdigris Celadonite Glauconite Chlorite	Malachite* Verdigris Celadonite Terre verte
Blue	Azurite Indigo	Azurite Indigo	Indigo Blue frit (Egyptian) Azurite?	Egyptian blue	Egyptian blue
Violet	Burnt ochres Tyrian purple	Burnt ochres Tyrian purple	Mixtures of reds and blues	Hematite	Tyrian purple Mixtures of red and blue

* Found in other studies but not in the one cited here.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Black and Brown Pigments

Carbon Black Pigments

Carbon black pigments may be defined as any pigment containing predominantly elemental carbon (*54*). Boneblack, lampblack, and charcoal black are the common forms of carbon black pigments used in antiquity. In fact, charcoal may be the first synthetic material ever produced – a possibility accomplished by Cro-Magnon people 38,000 years ago and verified by modern thermochemical equilibrium calculations: carbon is a preferred product of biomass pyrolysis at moderate temperatures (*55*). Pliny the Elder (Book XXXV, Chapter 25), Vitruvius (Book VII.10), and Dioscorides (Book V, 183) describe burning pitch pine or rosin to obtain a charcoal which is then ground to form a carbon black suitable as a pigment. Pliny calls this material "atramentum" when it is mixed with glue; it is resistant to smoke from fire and soot from lamps. Recent results using a variety of analytical tools such as SEM coupled with energy dispersive spectroscopy (EDS), indicate the use of carbon black pigments as writing inks at Pompeii (*56*) lampblack in a Pompeiian wall painting (*57*), wood charcoal in an Etruscan tomb (*58*), coal black in Roman Era wall paintings in northern Italy (*59*), and carbon black in a Theban necropolis in Egypt (*60*). Figure 6 is a photograph of a room with walls decorated almost entirely with atramentum. This was a strategy recommended by Vitruvius: a dark background will absorb the heat and make the room warmer in cold weather.

Figure 6. Triclinium (Dining Room) of the Villa of Livia, Rome, 40 BCE –3rd Century CE. National Museum of Rome – Palazzo Massimo alle Terme. Photograph by Mary Virginia Orna.

The use of crystalline graphite and other carbonaceous black pigments in prehistoric Ethiopian rock paintings were reported for the first time in 2012 (*61*) whereas in neighboring Eritrea, it was determined that the black pigments were derived from manganese oxides (*62*). Examination of rock art in the Oxtotitlán Cave, Mexico (c. 800-400 BCE) revealed exclusive use of pyrogenic carbon, specifically a mixture of charcoal and soot (*63*). Obviously, much more work needs to be done to discern a regional pattern in pigment usage.

Manganese Oxide Pigments

Manganese oxides have been identified on wall paintings in Paleolithic caves (27, 28 Buisson, Clottes) and more recently as dark, globlular inclusions mixed with fibrous wood charcoal (*58*) in Etruscan tomb paintings. Remarkably, manganese oxides have also been identified in Hopi pottery of the Pueblo area of the American Southwest dating to Neolithic times, although some time later than the European Neolithic age (*64*). The only stoichiometric form is that of β-MnO_2, pyrolusite, with a rutile structure, but identity of the oxide or oxides in nature is confused and uncertain because nonstoichiometry is prevalent. In addition, MnO_2 is not the most stable form since it decomposes to Mn_2O_3 at temperatures about 560 °C (*65*). Given the fact that the ancient artists collected the pyrolusite in nature, one might assume that the predominant form in the paintings is MnO_2, but if some "hearthwork" were done, it is not unlikely that some of it could have been transformed into other oxides of manganese.

Mineralogists have identified about 20 different naturally occurring manganese oxides. Two of the main families are oxides without any associated other cation, such as manganite (MnOOH), pyrolusite (MnO_2), bixbyite (Mn_2O_3) and hausmannite (Mn_3O_4). A second family consists of manganese oxides enriched by other cations such as barium: romanechite ($Ba_2Mn_5O_{10}\cdot xH_2O$), hollandite ($BaMn_8O_{16}\cdot xH_2O$) and todorokite [(Ba, Ca, K, Na)$Mn_6O_{12}\cdot xH_2O$)] are typical examples. A study of samples from Lascaux and Ekain caves by Emilie Chalmin and co-workers (*66*) identified a great variety of manganese oxides used singly or in mixtures, like pyrolusite, romanechite, hollandite, and todorokite. Their observations did not reveal any trace of heat treatment such as dehydration pores and/or evidence from examining characteristic crystal structure. Furthermore, two adjacent figures were not made of the same paint since the manganese oxides used had different crystal sizes and mixtures. They concluded that the figures were created from different "paint pots" coming perhaps from different deposits and executed at different times. They also concluded that in the case of Ekain, since manganese oxide use was limited to uncommon figures, that the pigment was precious or symbolic.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Brown Pigments

Apart from some ochres, which will be discussed later, the common lists of brown pigments mentioned in various pigment handbooks are few and the pigments described are of dubious origin and quality. A bituminous earth that might be a mixture of asphalt with lignite, or simply the syrupy petroleum-like excrescence noted in areas of the earth with seismic activity, is called "asphaltum" by Dioscorides (Book I, 99-101) and bitumen or "pissasphaltos" by Pliny (Book XXXV, 51). Gettens and Stout tell us that it would make a poor painting medium because it never dries; the dreadful state of some works by Joshua Reynolds and Albert Pinkham Ryder can attest to this property. However, this same source traces the later history of these bituminous substances in such pigments as "mummy" and Van Dyke brown, both of which were used by artists many centuries after the time period of classical antiquity. "Mummy" is precisely what it says it is. Gruesome as it may be, it consists of the ground up parts of Egyptian mummies and seemed to have been a favorite brown pigment of European artists from the late 16th century on. Van Dyke brown, also of bituminous origin, was its more benign successor. To be prescise in its definition, however, we must have recourse to the definitive description by C. I. Bothe (*67*), which states that it is neither a pigment nor a dye, but a color preparation containing a mixture of inorganic and organic materials, the latter being the binding medium, bitumen.

Finally we come to sepia, both the name of the pigment and of its source, the cuttlefish (*Sepia officinalis*), called sepia (σέπια) in Greek. Dioscorides mentions both the animal and its ink (Book II, 23) but is mainly concerned with its (dubious) medicinal powers. Pliny (Book IX, 44) erroneously claims that it is an animal that has ink in its body in place of blood. Although some sources, without documentation, say that this ink was used as a writing medium from time immemorial, we cannot seem to trace it to Egypt. The oldest extant specimen of papyrus upon which there is clearly some writing dates to 2,500 BCE according to a *British Museum Guide* of 1896, p. 312, but the basis of the black ink was animal or vegetable charcoal mixed with gum or oil to enable spreading using a reed pen. However, there are sources from the 1st century CE that speak of the use of sepia for writing, notably the writer/poet/satirist Persius (full name: Aulus Persius Flaccus, 34-62 CE) who claims use of the "blood" of the cuttlefish (Figure 7) for ink (*68*) which, in dilute form, is really the brown we dub as sepia. The ink itself has a very high tinting strength: the ink from a single cuttlefish is capable of rendering a 1,000 gallon tank of water opaque in a matter of minutes.

Although earlier reports on the composition of the ink described it as mainly melanin and mucus, an early 20th century analysis gives a composition of melanin (78%), calcium carbonate (10.4%), alkali metal sulfates and chlorides (2.16%), and mucins, a group of high molecular weight heavily glycosylated proteins (0.84%) (*69*). The impurities are normally removed in modern preparations. Although sepia is organic in nature, it is discussed here because of its appearance in Table 6.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

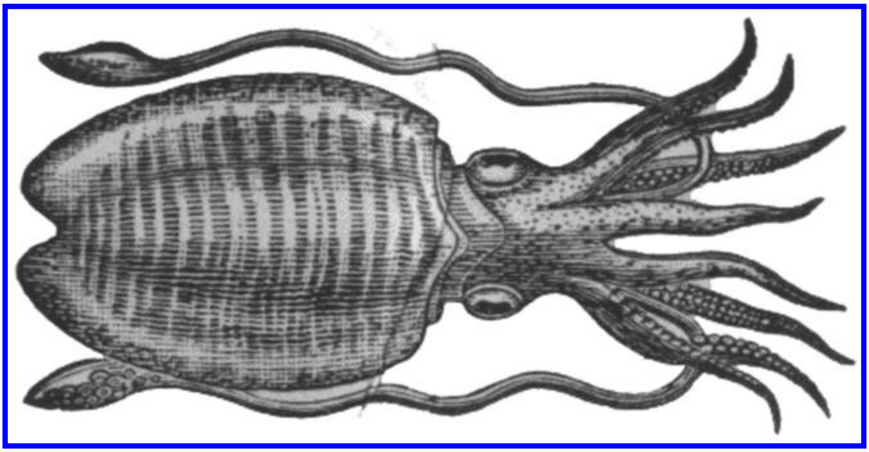


Figure 7. Line Drawing of the Cuttlefish, Sepia officinalis. The ink ejaculatory duct is at the posterior of the animal.

White Pigments

Later Stone Age rock art of Southern Africa has been extensively studied and is one of the best understood prehistoric painting traditions in the world. These people seemed to prefer gypsum and calcite as their white pigments (*70*), whereas the palette of the Mediterranean world was slightly expanded to include other forms of calcium carbonate, white lead, and some naturally occurring white minerals.

Calcium Carbonate Whites

Calcium carbonate ($CaCO_3$) occurs naturally in a variety of forms, the most common of which is called calcite, a trigonal-rhombohedral birefringent crystalline material. It is the primary mineral in marble, and a common constituent of chalk, limestone, and other sedimentary rocks. Aragonite is one of its less stable polymorphs. Diatomite is the fossilized remains of single-celled aquatic algae of the phylum *Chrysophyta*, and is synonymous with chalk. Chalk deposits were laid down in various geological ages from the lower Jurassic (200 million BP) to the Cenozoic (65 million BP). From the medieval period onward, chalk has been referred to as whiting, lime white, and occasionally as *bianco di san Giovanni*, the slaked lime form that went into Italian frescos. Dolomite, a close relative, is calcium magnesium carbonate ($CaMg(CO_3)_2$). All varieties of calcium carbonate are lightfast, making for a very permanent pigment, stable down through the centuries until the advent of acid rain in our own time (*71*). In addition to the occurrences noted by the analyses in Table 6, its presence has been noted in Egyptian Fayum portraits (*72*) and in the Bersheh sarcophagus (*73*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

White Clay

Clay was formed by the action of wind and water upon the earth's surface long before human beings appeared on this earth. Clay minerals are mainly composed of three of the most abundant elements in the earth's crust, oxygen, silicon, and aluminum. They have a sheet-like structure of mainly tetrahedrally arranged silicate and octahedrally arranged aluminate groups. The ideal clay mineral is kaolinite, $Al_2Si_2O_3(OH)_4$: it is pure white, very stable, and has a plasticity that is easily workable. Although it may have been used to some extent as a pigment in antiquity, it is presently much sought-after as a ceramic material (*74*). Figure 8 shows a schematic structure of kaolinite, which consists of a silicate layer and an aluminate layer separated by water, the ionic layer. The two outer layers can slide by one another lubricated by the water layer, much as playing cards can slip by one another. This allows the pigment to be easily applied to any surface.

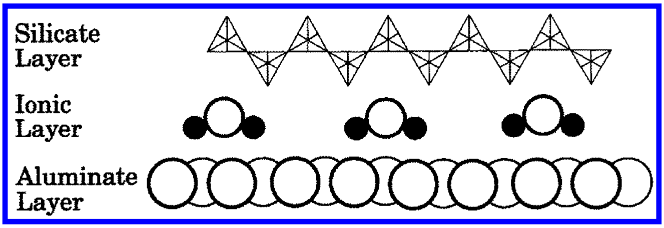


Figure 8. Layers of Kaolinite.

Lead White

Lead white (sometimes called white lead) is the most important of the lead-based pigments and one of the first to be synthesized artificially. It is a basic lead carbonate with the formula $2PbCO_3{\cdot}Pb(OH)_2$. Its naturally occurring form is lead carbonate, $PbCO_3$, corresponding to the mineral cerussite, which has rarely been used as a pigment.

Lead white has been prepared for centuries according to methods described in Pliny, Vitruvius, and Theophrastus. Essentially, lead sheets or plates are exposed to vinegar in a moist atmosphere of fermenting manure or tanbark (which provides the CO_2) for a period of about three months. Historically, it is the most important of all the white pigments and has been mentioned in catalogs of pigments from ancient times up to the present day. In addition to the instances noted in Table 6, it has been found in 1st century CE Egyptian mummy portraits (*75*), in the ground layer of a Chinese polychrome terra cotta figure from the Tang dynasty (618-907 CE) (*76*), and in 11th century CE Chinese Buddhist polychrome sculptures (*77*). Numerous other notable occurrences can be found by a cursory examination of the literature.

Lead white has two serious drawbacks: it is highly toxic, and it darkens to form black lead sulfide, PbS, upon exposure to sulfur-containing compounds.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Iron Oxide Pigments (Ochres, Siennas, Umbers)

While it would be ideal to discuss each pigment group in terms of the color it exhibits, the iron oxide pigments are a special case – they cover the entire gamut of the earth color shades. Their colors depend on three factors: the oxidation state of the iron, the degree of hydration of the compound, and structural type (*78*).

The iron oxides and iron oxide-hydroxides are widespread in nature and have been used from ancient times as both ores and as pigments. There are three oxides of iron. Iron(II) oxide, FeO, occurs in nature as the mineral wūstite. Iron(III) oxide, Fe_2O_3, occurs in nature in its most stable form as hematite; it is also a polymorph in that it can exhibit several structural types, the most common and most stable of which is α-Fe_2O_3, with a corundum structure. Its anhydrous form is a dark purple-red or maroon; its hydrated forms, $Fe_2O_3 \cdot nH_2O$, have a range of colors from red through yellow. Iron(II) iron(III) oxide, Fe_3O_4, is called magnetite. Both wūstite and magnetite are black; they do not have any history as pigments and are only mentioned here for completeness.

The term ochre is sometimes confusing because of the variety of types: red ochre, yellow ochre, brown ochre, golden ochre, burnt ochre, etc. They are all natural earth pigments that owe their color to iron(III) oxide in either its anhydrous form or one of its hydrated forms mixed with varying amounts of silica, clay, and other impurities like magnesium carbonate, gypsum, or aluminum oxide. Their wide variations in content give rise to similarly wide variations in quality, which is why pigment deposits in the ancient world acquired local names to designate not only source, but also, in most instances, the quality of the colorant to be expected. For example, there were different kinds of red ochres from different locations around the Mediterranean: the Cappadocian, the Egyptian, the Spanish, and Lemnian. All were red iron oxides, but the Lemnian, from the isle of Lemnos, and the Cappadocian, called by the Romans *rubrica Sinopica*, from Sinope on the Black Sea, were the most sought-after.

Yellow ochre has goethite, α-FeO(OH), as its primary component. It is the second most abundant ochre in the earth's crust, after hematite. The siennas, raw and burnt, are varieties of yellow ochre, named after the city of Siena where one the best grades was mined from antiquity. Also consisting mainly of goethite, the raw type has a deeper tint than yellow ochre. Burnt sienna is calcined raw sienna and has a much deeper, reddish-brown hue.

Brown ochre is the name given to what we now call limonite, which is another principal iron ore. Its generic formula is $FeO(OH) \cdot nH_2O$ although the ratio of oxide to hydroxide is variable. Colors range from shades of brown through yellow.

The umbers, raw and burnt, are also hydrated iron(III) oxides but contain a large proportion of manganese oxides as well, which accounts for their darker color.

Some notable occurrences and variations:

Not surprisingly and as previously noted, hematite was the most common pigment identified in prehistoric red paintings. For the most part, an elaborate, multi-step series of washings and grindings were used to prepare the pigment, indicating a knowledge of preparatory techniques to improve pigment quality before application (*79*).

In a study of originally polychrome Phoenician ivories dating from 2,800 BP using an innovative Color X-Ray Camera, traces of elements from no longer visible pigments led the researchers to postulate the use of original red (hematite, α-Fe2O3), yellow (goethite, FeOOH or maghemite, γ-Fe2O3), or black (magnetite, Fe_3O_4) coloration or, on the other hand, deposits of sediment (iron oxide-containing clays or ferric iron complexes). Referring to similar ivories from Assyria shown to have been colored by natural hematite allowed the authors to postulate a similar palette used by the Phoenicians (*80*).

A rare opportunity to examine lump raw pigments from a pigment shop dating to the 2nd-4th centuries CE excavated in Rome's Forum Boarium area allowed the researchers to gather data from the entire color spectrum of pigments used in Imperial Rome. They identified all of the red pigments from the collection as red ochre, but their diversity with respect to appearance, texture, hue, and trace element content led to the conclusion that they originated from a variety of sources (*81*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Other Red, Orange, and Yellow Pigments

Red Lead and Minium

This colorant has been known from ancient times in both its synthetic and naturally occurring forms. Minium is the mineral that Pliny and Vitruvius call "burnt ceruse," although Pliny also confused the name minium for cinnabar. Red lead and minium both have identical chemical formulas and crystal structure, Pb_3O_4, or lead tetroxide ($PbO_2 \cdot 2PbO$). The synthetic variety, red lead, is produced by roasting litharge, PbO, at temperatures above 480 °C for a few hours. Vitruvius seems to have been the first to record this process (*82*). There is evidence that it was produced in China and Japan; it was certainly used in China in the Han dynasty since it has been identified as an orange pigment on the 2nd century BCE Terracotta Army (*83*). As noted in Table 6, it was also identified by Humphry Davy on an object taken from the Baths of Titus, Rome. Another notable occurrence is on a 3rd-4th century CE Egyptian figure of a woman (*84*). Red lead's use became much more widespread in the Middle Ages and the Renaissance.

Vermilion and Cinnabar

Since the names of this priceless red pigment from antiquity have often caused confusion, it is well to define them at the beginning. Both are mercury(II) sulfide, HgS. The term vermilion is the standard name for the synthetic variety, prepared for use as an artists' pigment from the 8th century CE on. The term cinnabar, which is reserved for the natural mineral and its specific crystal structure, is used by mineralogists and crystallographers (*85*). The origins of these names deserve some explanation (*86*):

> *Vermilion was formerly known as* vermiculus, cinnabaris, cenobrium *and* minium*; the last name is now appropriated to red lead. Vermilion and vermiculus are derived from the Latin* vermes*, a name originally designating the* kermes *insect found in the ilex or evergreen oak and used for the preparation of a red dye. From kermes, in its turn, the words crimson and carmine are derived. The name cinnabar is supposed to be of Indian origin, and was sometimes used to designate dragon's blood, a red resin. Theophrastus informs us that two kinds of cinnabar were known to the Greeks. One of these was undoubtedly real cinnabar (chiefly from Spain), the other was red lead. Pliny's* cinnabar *or* minium *was true vermilion; so was the* minium *of Vitruvius.*

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Obviously it is the natural material that was used in ancient times. It is the principal ore of mercury and was well-known to the Greeks prior to the 6th century BCE and to the Romans by technology transfer. Pliny states that almost the entire Roman supply came from Sisapu in Spain; the reference is probably to the famous mines at Almaden which is the most important source of mercury in the world even today. However, the slaves condemned to work there faced a slow and nasty death from heavy metal poisoning. Cinnabar's toxic nature was well-known in antiquity.

According to Vitruvius, cinnabar was prepared by crushing lumps of dry ore in a mortar and the powder was then repeatedly washed and heated to remove impurities. It is well-known that cinnabar darkens when exposed to the wavelengths of the high energy end of the visible spectrum. We now know that the cause of the darkening is the transformation from the red α-HgS to the black metacinnabar, α'-HgS, though the process is reversible if the cinnabar is left in the dark. For this reason, Vitruvius recommends that it be used to paint the walls of interior rooms, as indeed, was done in the case of the Roman Villa of Livia (Figure 9).

The Romans just loved raw cinnabar. They painted their gladiatorial heroes with it and women made their lips more luscious by using a cinnabar-based lipstick. It was a luxury pigment (*87*) and only the wealthiest could afford to have entire rooms decorated with it, as is the case with the room in Figure 9, where the background color for the entire room is raw cinnabar. People of more modest means would normally use it mixed with less expensive red pigments. It has never been identified in Egyptian or Minoan paintings, but it was used extensively Etruscan tombs, the marbles of the Parthenon, and in other mural paintings and marble decorations of the Late Classical and Hellenistic period ((*53*), p. 51).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

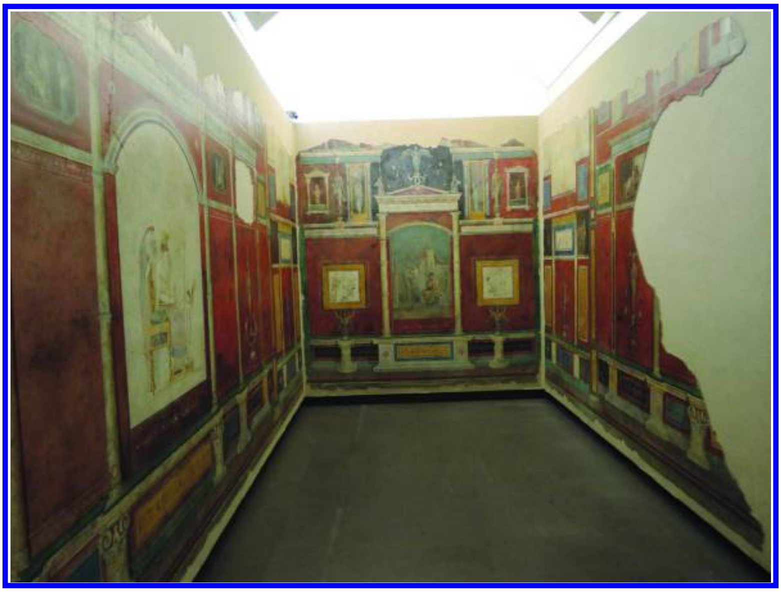


Figure 9. Cubiculum (Bedroom) of the Villa of Livia, Rome, 40 BCE –3rd Century CE. National Museum of Rome – Palazzo Massimo alle Terme. Photograph by Mary Virginia Orna

Orpiment and Realgar

The two sulfides of arsenic, yellow orpiment, As_2S_3, and red-orange realgar, AsS or As_4S_4, have a common origin and a common history. The natural minerals occur intimately mixed with one another such that, if an object is painted with realgar, yellow flecks of orpiment can often be seen throughout. Pliny called the yellow pigment *auripigmentum*, literally 'gold paint,' and this has come down to us as orpiment. Pliny called realgar *sandarach*, but its modern name is derived from the Arabic Rahj al ghār, or "powder of the mines."

Both compounds have been known from earliest antiquity, but seems that not much use was made of them for pigments. They were important as both medicines and as poisons. They have been found in lumps and cakes in tombs and remains of palaces in Mesopotamia (*88*). Kakoulli ((*53*), p. 51) reports that realgar is rarely found in paintings in the Mediterranean area. It has only been identified in some of the Egyptian paintings of the Dynastic period and on the marble throne of the tomb of Eurydice in Vergina. On the other hand, orpiment was a common pigment used in Egyptian Dynastic painting, suggesting a local influence on Hellenistic paintings in Egypt ((*53*), p. 54)

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Massicot

Massicot and litharge are names that have been used for the yellow lead monoxide, PbO. The differ in crystal structure: litharge is tetragonal while massicot is orthorhombic. Therefore, they are not synonymous; they are derived from different sources and have slightly different properties. As a powder, massicot has a soft yellow color which is not intense, but it has good hiding power. It finds use as a pigment, but litharge does not. Davy ((*1*), p. 105) identified it mixed with minium on a piece of stucco in the ruins near the pyramidal tomb of Caius Cestius, Rome.

Other Yellow Pigments

Two yellow pigments worth noting that were never mentioned in our ancient sources are hydroniumjarosite, $Fe_3[SO_4]_2[OH]_5 \cdot 2H_2O$, and lead antimonate yellow (or Naples yellow), $Pb_2Sb_2O_7$.

Hydroniumjarosite, a naturally occurring mineral, seems to be associated in nature with goethite. It was identified by Siddall (*89*) as the main coloring component of an earth pigment from Pompeii in 2006.

Lead antimonate yellow has a long history, especially regarding its use as a glaze colorant and opacifier in Egypt and Mesopotamia in the 2nd millennium BCE (*90*). One of the earliest artificial pigments, it also found use as a colorant and opacifier in the Roman world (*91*).

Green Pigments

Terre Verte (including Glauconite, Celadonite, and Chlorite)

Terre verte, *terra verde*, or green earth is the term given to several closely related siliceous minerals with greenish hues. Glauconite, also called greensand, has the formula $(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$. It is of sedimentary origin and has varyingly green, blue green, and yellow green hues. Celadonite, with the formula $K(Mg,Fe^{2+})(Fe^{3+},Al)[Si_4O_{10}](OH)_2$, is so named from the French *celadon*, meaning sea green. It is of altered volcanic origin that occurs in gray green to bluish green masses. The chlorites are a group of about a dozen minerals, the most common of which is chamosite with the formula $(Fe_5Al)(AlSi_3)O_{10}(OH)_8$. All three are phyllosilicate (micaceous sandwich-like parallel silicate sheets) minerals. The ancient use of green earths is well documented (*92*), particularly with respect to the use of celadonite and glauconite, as also noted in Table 6. An analytic study of 80 samples of green pigment coming from various Roman sites in Switzerland and from Pompeii identified celadonite, glauconite, chlorite (as chamosite), along with malachite and verdigris (*93*). The study found that celadonite was the most common green pigment and that all three green earths were often applied as mixtures.

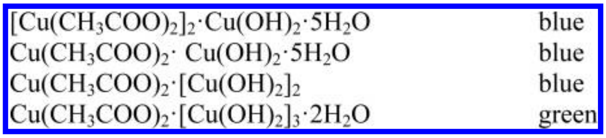
Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Malachite

Malachite, the green basic copper carbonate, $CuCO_3 \cdot Cu(OH)_2$, sometimes called chrysocolla, is usually associated in nature with azurite, the blue basic copper carbonate with the formula $2CuCO_3 \cdot Cu(OH)_2$, though malachite is more abundant (*94*). It has been identified in paintings of Egyptian Middle and New Kingdoms ((*46*), p. 345), pigment pots from Pompeii (*95*), as well as in Greek tombs, Etruscan wall paintings, and in numerous other instances ((*53*), p. 46).

Verdigris

Verdigris, as its name implies, is a green colorant, although some of its forms are blue. While currently the term designates copper salts of acetic acid exclusively, it has been used since antiquity to indicate any corrosion product of copper, and so may have been a mixture of other salts such as chlorides or carbonates. Neutral verdigris, with the formula $Cu(CH_3COO)_2 \cdot H_2O$, is a blue-green compound that readily dissolves in water to yield a green solution. Four forms of basic verdigris have been identified:



$[Cu(CH_3COO)_2]_2 \cdot Cu(OH)_2 \cdot 5H_2O$	blue
$Cu(CH_3COO)_2 \cdot Cu(OH)_2 \cdot 5H_2O$	blue
$Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_2$	blue
$Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3 \cdot 2H_2O$	green

Verdigris can contain one or some of all of these forms as well as the neutral verdigris (*96*). While Pliny, Vitruvius, Dioscorides, and Theophrastus all discuss verdigris, what they describe is the variety of blue-green copper salts known in antiquity, including the acetates. However, it seems to have been used rarely since extensive studies of a “blanket” nature on pigments from the Greek/Roman Imperial era have not found it ((*53*), p. 44). However it has been identified in the painted decorations on the marbles from the Parthenon (*97*) and the later Roman paintings from Pompeii (*98*). However, the chemist, Earle R. Caley, justifies its absence on account of its unstable nature: it can spontaneously decompose over time to basic copper carbonate, a far more stable compound (*99*).

Egyptian Green

Egyptian blue (to be discussed below) and Egyptian green seem to differ in two respects: the firing temperature range for producing the blue frit is 100 degrees less than that of the green product, and the ratio of CuO to CaO is > 1 in the blue frit, and the reverse in the green frit (*100*). This conclusion is confirmed by Pagès-Camagna (*101*), who set the presence also of parawollastonite ($CaSiO_3$) as a marker for Egyptian green.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Blue Pigments

Nature has made it very hard to come by bright and stable blue pigments. Each civilization has had to struggle to produce satisfactory blues and, in some instances, to rediscover ancient technologies. Part of the problem has been alluded to earlier in this chapter. Blue is not an earth color, so one has to dig deep in order to find blue in the mountain: this is the story of lapis lazuli. Blues can be made from copper as various copper salts, many of which are fugitive and unsuitable for painting (*102*, *103*). Or blues can be discovered as "gold" in the furnace and their synthesis can be perfected over the course of many centuries by trial and error: this is the story of Egyptian blue, and to a certain extent, of Han blue and purple. The story of this struggle to produce satisfactory blues is as much a demonstration of human ingenuity as any other groundbreaking discovery of the past. A recent work tells this intriguing story from the points of view of history, art, geography, chemical research, technological innovation and commercial necessity (*104*).

Egyptian Blue

Recipes for the production of Egyptian blue were found on Babylonian clay tablets that can be dated to the 17th century BCE; these are the oldest technical recipes known. However, its presence was determined on artifacts that were manufactured 8 centuries earlier from the Old Kingdom (2,575-2,134 BCE) (*105*). Other analytical evidence shows clearly that Egyptian Blue was the staple blue pigment, and indeed in many instances the only blue pigment, of the ancient world for many thousands of years. Its stability on wall paintings was excellent, but its tinting strength was not very great. An example of its use in ancient Egypt is shown in Queen Nefertiti's headdress (Figure 10).

Egyptian blue was the subject of virtually the earliest ever archaeometric analysis, first by Jean-Antoine Chaptal (1756-1832), comte de Chanteloup, a renowned chemist, in 1809, and a few years later by Sir Humphry Davy. Chaptal, at the behest of the Empress Josephine, was given access to the treasured collection of wall paintings excavated from Pompeii (discovered in 1739) residing in the Villa Reale in Portici. He demonstrated that the blue pigment consisted of silicon dioxide, copper oxide, lime and alumina (*106*). He observed that the blue "seemed to be the result, not of a precipitation, but the effect of a beginning of vitrification, or rather a veritable frit (*107*)". Davy ((*1*), pp. 106-107) describes his treatment of some large lumps of a deep blue frit found in the baths of Titus: upon applying chemical tests, he found "sulphate of soda….coloured with oxide of copper."

Egyptian blue was subjected to many further chemical tests, notably by French geologist Ferdinand André Fouqué (1828-1904) in 1889 and much later by Mike Tite and co-workers at the British Museum and Laboratory, London (*108*), and by Heinz Berke at the University of Zurich (*109*). Stoichiometrically, Egyptian blue is identical to the relatively rare blue mineral cuprorivaite, $CaCuSi_4O_{10}$. A mixture of lime ($CaCO_3$), sand (SiO_2) and copper in the form of a copper mineral, metallic copper, or a copper alloy, together with a flux such as K_2CO_3, NaCl, or Na_2SO_4

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

heated under oxidizing conditions to temperatures held between 800-900 °C for quite a few hours can produce this coveted and rather pricey material. However, the "devil is in the details:" the quantities of the reactants, the rather specialized furnaces needed to maintain the proper temperature for the proper time, and the means for the addition of oxygen had to be passed down either orally or in technical manuals from workman to workman (sometimes father to oldest son). It is no wonder that there were very few places in the ancient world where Egyptian blue manufactories were established, and that most of the rest of the world relied upon importing it.((*104*), pp. 8-21).

Figure 10. Bust of Queen Nefertiti (c. 1,370-1,330 BCE). Ägyptisches Museum Berlin. Photograph courtesy of Gunnar Bach Pedersen (Wikimedia Commons).

Several sources discuss the impurities found in Egyptian blue: percentages of tin, lead, iron and other metals. This indicates that perhaps the copper used was in the form of alloys, particularly bronze. Some samples from a painter's hoard in Delos contained a markedly high concentration of lead, which raises some questions. Was the lead accidentally or deliberately added? How does a high lead concentration influence the production of the pigment? Would the lead be helpful in the manufacture of the pigment either as a flux or a catalyst as is the case with Egyptian green? These questions demand further investigation ((*53*), p. 41).

Notable occurrences of the use of Egyptian blue abound in the Mediterranean world. In addition to its already noted use in Egyptian objects from 2,500 BCE ((*46*), pp. 340-44), and in Greek and Roman artifacts and paint pots, some other examples are specimens from Etruscan terracotta panels (*110*) and tombs (*111*). Figures 11 and 12 are from the Etruscan tomb sites of Cerveteri and Tarquinia, near Rome.

Figure 11. One of the thousands of tombs sculpted from volcanic tufa. Cerveteri Banditaccia Necropolis, Italy. Photograph by Mary Virginia Orna.

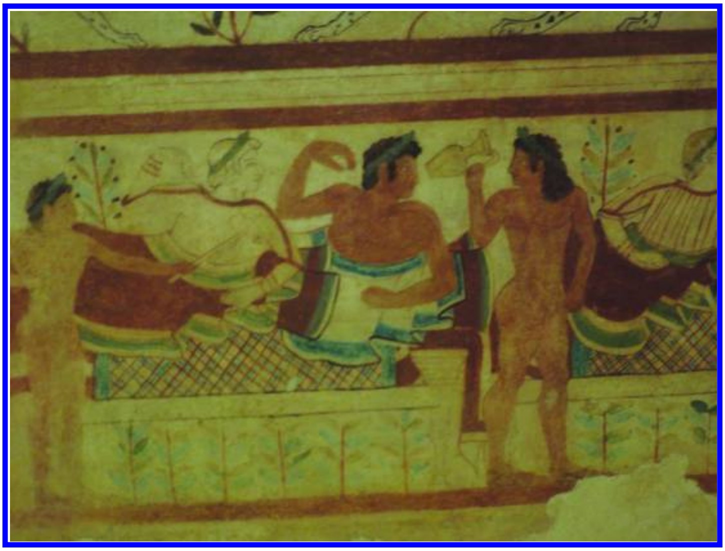


Figure 12. This banqueting scene in the Etruscan Tomb of the Leopard, Monterozzi Necropolis, Tarquinia, Italy (470 BCE) shows the central figure being served by a naked serving girl. The dark border of his robe is painted with Egyptian blue. Photograph by Mary Virginia Orna.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Interest in the synthesis and degradation of Egyptian blue continues to this day and has become the subject of laboratory exercises in contemporary college and university classes. Students in Marseilles, France synthesize it as part of their first-year university chemistry course (*112*) and chemical engineering students at the Universitat Politècnica de Catalunya, Barcelona, study its degradation pattern with a view to possible remediation (*113*).

Han Blue

Han blue is an analog of Egyptian blue in which the counterion Ba^{2+} substitutes for Ca^{2+}, yielding a compound with the formula $BaCuSi_4O_{10}$. It occurs as paint on ceramic and metal artifacts from the Han dynasty (208 BCE – 220 CE). It has also been identified in stick form from the Warring States period (475-221 BCE) (*114*). It can be synthesized using a starting material of barite ($BaSO_4$) or witherite ($BaCO_3$) and a lead supplement (as the carbonate or oxide), found to be essential, and at a firing temperature maintained within 50 °C of 900-1,000 °C for some 20 hours.

For both Egyptian blue and Han blue, copper ions (in the form of CuO_4^{6-}) have been identified as the chromophore. Both compounds have the same basic structure and very similar properties. They both have a stable silicate matrix in which the copper ions are tightly bound in a square planar complex, which is the key to the high stability of both pigments ((*109*), p. 20). Recent work suggests that the introduction of sand plays a key role in obtaining the characteristic hue of the Egyptian Blue pigment, leading to the opportunity for tuning the properties of a given chromophore by modifying the structure of the insulating lattice where it is located (*115*).

The possibility of a technology transfer between the Western World (Egyptian blue) and the Eastern World (Han blue) seems not to be very likely. The development of these technologies required preceding evolutionary development (from approximately 1100 BCE in the case of China and 2,500 BCE in the case of the Mediterranean), suggesting parallel but independent advancement. ((*109*), p. 27).

Natural Ultramarine Blue (Lazurite)

Artists often refer to ultramarine blue by the term “lapis,” a shortening of the name of the mineral from which it is derived, lapis lazuli. It is chemically a tectosilicate with the formula $(Na,Ca)_8(AlSiO_4)_6(S,Cl,SO_4,OH)_2$. The proportions of aluminum, silicon, and oxygen are fixed in an aluminosilicate framework, whereas the other elements are present as ions in varying amounts. The overall structure is cagelike (chemically termed a clathrate) that can host the deep blue sulfur chromophore, S_3^-, a species unstable in the free state (*116*).

“Ultramarine” is a term that literally means “beyond the sea,” and this term was apparently first used in Italy when referring to the only known source of the of the material in ancient times, the Sar-e-Sang mining area in Afghanistan’s remote Hindu Kush, beyond the Caspian Sea. These mines, as well as the blue extracted from them, have always fascinated explorers and amateurs alike. In her delightfully-narrated pilgrimages in search of color around the world, the intrepid reporter Victoria Finlay describes her visit to Sar-e-Sang (*117*):

> One day many years ago somebody told me that all the true ultramarine paint in the world came from one mine in the heart of Asia. And that before it could be squeezed sparingly onto any European artist's palette…it had journeyed in rough sacks on the backs of donkeys along the world's ancient trade roads…[A]fter that I dreamed of a mountain with veins of blue, inhabited by men with wild eyes and black turbans, and when I woke up I knew that one day I would go there.

Due to the climate, the mines can only be worked four months out of the year, and indeed, the donkeys are indispensable since the road leading to them is impassable to jeeps. It took two tries over two years for Victoria to finally arrive, hindered not only geographically, but politically. She comments:

> After all, part of the mystery of lapis was that although for millennia it had travelled to Europe and Egypt it was always known to come from a mythical land so far away that…[e]ven Alexander had not managed to cast his greatly acquisitive eyes on the mines when he conquered the area 2,300 years ago, and Marco Polo in 1271 had only nodded in its direction from another mountain range to the north.

Since ultramarine is found embedded in lapis lazuli either as pale blue fine veins or as nuggets of good quality blue (Figure 13), it almost always has to be extracted from the mixture. While there are many methods given in artists' handbooks, they have these features in common: one must grind the blue material to a fine powder and then disperse it into a malleable fatty paste which is then kneaded and allowed to "rest" for periods of even longer than a week. When the paste is then kneaded in a hot alkaline aqueous medium, the fine blue particles of ultramarine fall to the bottom of the liquid and are carefully collected. The colorless material and impurities remain behind in the doughy mass, which is then kneaded again and a second fraction of ultramarine is deposited. The process is repeated for a third time to produce the least desirable fraction, sometimes called "ultramarine ash (*118*)." The process takes advantage of the hydrophilic nature of the lazurite particles contrasted with the less hydrophilic characteristics of the other minerals from which it must be separated.

Given the difficulty in obtaining the raw mineral in the first place, plus the labor-intensive extraction method to obtain the colorant, ultramarine blue was frightfully expensive, an ounce of pigment costing more than an ounce of gold in the Middle Ages. Therefore, although it was imported into the Mediterranean area for over 7,000 years, it found little use as a pigment, but rather as a semi-precious gemstone, attested to by the fact that archaeologists have found it again and again among the grave furnishings of tombs throughout the Mediterranean and Near East. The oldest published example of the use of ultramarine as a pigment is to

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

be found in Turkmenistan, Central Asia in the 2nd century BCE wall paintings of Mansur Depe (*119*). The first definitive occurrence of its use in the West is on a 2nd century CE Gallo-Roman statuette found in an excavation at Argenton-sur-Creuse, France ((*104*), p. 105).

Figure 13. A sample of lapis lazuli. The dark nuggets on top are examples of very fine ultramarine blue. Sar-e-Sang District, Koksha Valley, Badakhshan Province, Afghanistan. Courtesy of The Arkenstone (www.iRocks.com); Photograph by Joe Budd.

When Jean-Baptiste Guimet succeeded in producing artificial ultramarine in 1828, the natural product's hegemony was over, and prices dropped accordingly (*120*).

Azurite

Azurite has gone by many names in the past, all of which are now considered obsolete: mountain blue, *bleu d'Allemagne*, *azzurro della magna*, Armenian blue, to name a few. It is basic copper carbonate with the formula $2CuCO_3 \cdot Cu(OH)_2$, occurring in the upper oxidized parts of copper ore deposits along with its green counterpart, malachite, $CuCO_3 \cdot Cu(OH)_2$. It was not widely used in Egypt and other Mediterranean areas presumably because of the easy availability of Egyptian blue. Its principal source in Europe seems to have been Hungary, and it was a very important pigment in the paintings of the Far East (*121*). Azurite came into its own as the most important medieval blue pigment, a discussion that is beyond the scope of this endeavor. Despite the fact that it is a carbonate, it is a reasonably permanent pigment. It is sensitive to acid and darkens when exposed to sulfur vapor.

Blue verditer is the name given to artificial basic copper carbonate. Recipes for its synthesis abound since the early Middle Ages since it was a less expensive alternative to natural azurite and ultramarine (*102*, *103*).

Maya Blue

A misnomer gives credit to the Maya for the invention of this pigment although evidence of its use is found throughout Mexico and Central America. It may not properly belong in this discussion of mineral pigments since only part of it, and the colorless part at that, is inorganic. However, it is an extraordinary hybrid and, as such, deserves some discussion.

Maya blue, one of the most intriguing and technologically "savvy" of the ancient pigments, came to light in the mid-1940s through its use in polychrome wall paintings at the newly uncovered site called Bonampak (Chiapas, Mexico). When information about the site was published in 1955 (*122*), it attracted much interest because of the remarkable permanence of its fresco paintings despite the hot humid climate in which they were immersed from, it is estimated, the 5th century CE. Figure 14 depicts King Chan Muán and his dignitaries against a blue background that became famous around the world.

Once samples from this site became available, they were analyzed by X-ray diffraction, which confirmed that Maya blue was made of clay (*123*). However, since none of the usual metallic chromophores – copper, cobalt or iron – were detected in the samples in any appreciable amount, the paper suggested the presence of an organic dye derived from Campeche wood that forms a blue lake with aluminum and is one of the constituents of attapulgite. This hypothesis could not be confirmed experimentally, so numerous other suggestions were put forward until the true Maya blue was found to be indigo (from the Mexican indigo bush, *Indigofera suffructicosa*) intimately mixed with palygorskite, or other supporting clay structure such as attapulgite or sepiolite (*124*). The entire fascinating story is told by Delamare ((*104*), pp. 306-313).

The greatest difficulty in determining the cause of Maya blue's permanence was its relationship to the clay support. Was the dye bonded to the clay surface, or did it enter the channels inherent to the clay structure? Sonia Ovarlez and her co-workers finally solved the problem (*125*). Her group found that indigo in contact with sepiolite at temperature ranges below 130 °C behaved like pure indigo; the blue pigment formed was not true Maya blue and the reaction was reversible; the indigo remained surface adsorbed to the clay. On the other hand, upon thermal treatment in the range between 130-300 °C, the cumbersome indigo dimers and trimers separated from one another and the indigo monomers were able to enter the ion channels of the sepiolite more easily and, furthermore, indigo's nitrogen atoms were able to bond with sepiolite's magnesium ions to form a stable indigo/sepiolite complex. At higher temperatures (between 300 and 550 °C), the indigo carbonyl group could also bond with the sepiolite forming an even more stable complex with an even greater tinting strength. Furthermore, the sepiolite structure did not collapse at the higher temperatures because the presence of indigo in the sepiolite

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

nanotubes allowed it to retain its structure even up to temperatures approaching 800 °C. Figure 15 (*126*), graphically illustrates this structural change.

In Figure 15, the top model depicts the crystal mesh of attapulgite seen along axis c. Water molecules occupy the free space in the hydrated attapulgite channels. Center: The water molecules are replaced by indigo molecules during the Maya blue formation at around 120 °C. The indigo is still only surface adsorbed. Bottom: representation of a portion of a monoclinic attapulgite nanochannel with the indigo molecules in a stable position after heating at around 150 °C. This model shows the structure of true Maya blue.

Figure 14. Bonampak, Structure 1. Procession of King Chan Muán and the notabilities of his court. C. 790 CE. Photo © 2004 Jacob Rus - Photo © 2004 Jacob Rus. Licensed under CC BY-SA 2.0 via Wikimedia Commons.

Further work by Giustetto's group (*127*) has demonstrated that the nature of the host clay makes a difference in the stability of Maya blue. Since palygorskite has narrower channels than sepiolite, the indigo guest molecules can hydrogen bond to both sides of the channels, whereas the encapsulated indigo monomers can only form H-bonds to one side of sepiolite-based Maya blue, thus dramatically reducing host/guest interaction and providing a rationale for its greater fragility.

Another recent paper (*128*) suggests that dehydroindigo, the oxidized form of indigo, penetrates more deeply into the ion channels of the clay support, protecting the indigo and leading to an explanantion of its extraordinary stability. Maya blue, considered the first-ever artificial organic-inorganic hybrid pigment, has served as a source of inspiration for the design of new hybrid materials (*129*). Who knows where this research will take us in the development of new host/ guest hybrid materials? The Native Americans of Meso-America hardly knew that their extraordinary discovery would both baffle and inspire scientists around the world for generations to come.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

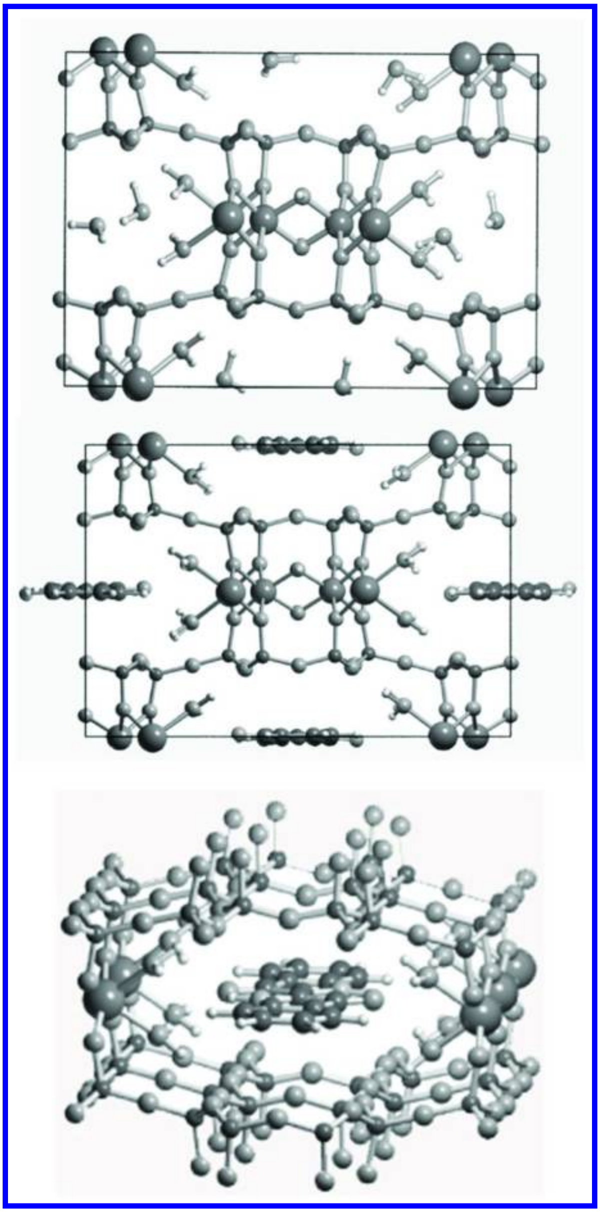


Figure 15. Atomic Model of Maya Blue. Adapted from Giustetto, R.; Llabrés i Xamena, F. X.; Ricchiardi, G.; Bordiga, S.; Damin, A.; Gobetto, R.; Chierotti, M. R. J. Phys. Chem. B 2005, 109, 19360-19368. Copyright 2005 American Chemical Society.

Violet (or Purple) Pigments

If it were not for the fact that a mixture of red and blue pigments can create a satisfactory violet shade, the case of violet mineral pigments would have been as exigent as that of blue pigments. However, the ancients had plenty of Egyptian blue and copper blues at hand, and plenty of cinnabar, red ochre, and hematite as well, so they produced their violet shades with ease. For example, the Roman *ostrum* was a mixture of red ochre and blue copper oxide (*130*). However, as every artist knows, the more pigments mixed together, the muddier the mix becomes, so the brightness of a mixed pigment is compromised.

From Table 6, we can see that there are not many options for a mineral violet pigment. Tyrian purple, of course, is the purple or violet color derived from shellfish of the *Murex* and other genera, and although it is a fabulous color with a legendary history (to which Victoria Finlay (*117*) devotes 40 pages), it is unambiguously organic in nature and will be discussed in detail elsewhere in this volume. Furthermore, it has not been detected in any of the wall paintings analyzed.

The other "violet" entry in Table 6 is burnt ochres. Raw and burnt sienna and umber are staples of the ancient palette; the burnt varieties have deeper color and one could, without a color-measuring instrument, conceivably call them "violet," at least in a more dilute form. There is also evidence that violet was obtained by heat treatment of hematite Siddall (*89*).

Gettens and Stout (*45*) list three violet mineral pigments, but none of them were available in antiquity. Ultramarine violet was developed in the 19th century by heating a mixture of ultramarine blue and ammonium chloride ((*45*), p. 167). Cobalt violet, also a 19th century creation, may be either cobalt phosphate, $Co_3(PO_4)_2$, or arsenate, $Co_3(AsO_4)_2$, or a mixture of the two ((*45*), p. 109). Managanese violet, reported to be manganese ammonium phosphate, $(NH_4)_2Mn_2(P_2O_7)_2$, was possibly synthesized in 1868 and found its way into the Winsor and Newton catalog in 1890 ((*45*), p. 128).

So, where did the magnificent violet color come from that is such an astounding feature of the mosaics in Imperial Roman times, especially those found in the basilicas and tombs of Ravenna? Fortunately, the collection of antiquities in the Martin von Wagner Museum in Würzburg holds about 250 samples of mosaic glass attributable to Roman origin. Using a combination of Raman microspectroscopy and electron microprobe analysis, 12 samples were analyzed and the coloring agents in the glasses were detected as well as the composition of the glass recipes – a first for Roman mosaic glass. And the violet component in every case was found to be Mn^{3+} by addition of Mn_2O_3; in an oxidizing furnace, manganese was expected to retain its tervalency. Depending on the content of Mn_2O_3, but also on the thickness of the glass, various shades of purple were observed, ranging from pink to violet and to dark purple with increasing Mn_2O_3-concentration: pink 1.7 wt.% in; violet 2.2 wt.%; dark purple 3.6 wt.% (*131*).

Far to the East in central China, a purple pigment called Han purple was being manufactured along with its near-relative, Han blue, by a method similar to that of Egyptian blue, but with a substituted barium counterion. Han purple has the

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

formula $BaCuSi_2O_6$ and can be generated in the presence of excess quartz and if a longer reaction time is maintained, although it is very difficult to obtain in the pure state, especially if ancient techniques are used. Berke ((*109*), pp. 18-19) has shown that pure Han purple is not purple at all, but a deep blue; its purple shade comes from varying amounts of cuprite, the red copper(I) oxide with the formula Cu_2O. He ascribes the composition of "normal" Han purple to 95% Han purple and 5% Cu_2O, which most closely approximates what would have been the synthetic result in antiquity, c. 1,100 BCE in the case of Han blue and purple. A notable occurrence of Han purple is its presence among the pigments used to paint the Terracotta Army found in the tomb (210 BCE) of the first Chinese Emperor Qin Shihuan (*104*).

With Han purple, we are back to Square One: purple or violet in antiquity had to be a mixture of pigments unless it could be stabilized as Mn^{3+} in glass!

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Properties of Pigments That Affect Their Appearance

Stability

The ideal pigment is chemically inert, stable to heat and light, and insoluble in its binding medium. If a pigment is even slightly soluble in a given medium, its particles tend to migrate, giving rise to a "bleed" effect which is highly undesirable unless it can be controlled. Some pigments change color when they react with a nearby substance. For example, cinnabar, HgS, darkens in the presence of lead, Pb, because of the formation of PbS, which is black. Stability can often be controlled by simply controlling the environment (*132*).

Light-Scattering: Effect of Refractive Index

An important property of a pigment is its light-scattering power. If a pigment in a paint is unable to effectively scatter the light striking it, a good deal of the light will simply travel through the paint, and the paint surface is said to be transparent. On the other hand, a high degree of light-scattering by a pigment allows only little transmittance of light. The higher the light-scattering power, the more opacity or hiding power the pigment has. The deciding factor is the difference between the pigment's and the binder's refractive index. Early artists learned how to control transparency and opacity by trial and error and succeeded very well.

Light-Scattering: Effect of Particle Size

Early artists knew very well the effect of the pigment's particle size on the degree of saturation of its color. They naturally ground their pigments in order to apply them to a surface, but they found that the more they ground their pigments, the more the color of the pigment seemed to fade. This is because scattering power increases as particle size decreases. For example, if we take a pigment sample of malachite and crush and grade the particles for size into the ranges 40-50 micrometers (µm), 20-25 µm and 10-12 µm, as the particle size decreases the amount of light scattered increases relative to the amount of light absorbed, so the smaller particles appear lighter in color. In fact, some pigments can only be ground very coarsely because too much grinding causes their colors to fade.

Degree of Selective Absorption

Pigments exhibit color because they selectively absorb a range of wavelengths of the visible light impinging upon them. The greater the amount of light absorbed, the more intense will be the color because the color you see is the range of wavelengths that are NOT absorbed, but reflected to your eye. The degree of selective absorption depends on the intrinsic chemical structure of the pigment and cannot be modified by any physical means. Absorbed light causes an electronic transition of the pigment from a lower to a high energy state, and it is the probability of this transition taking place that governs the intensity of the color. The pale colors of some pigments and the intense colors of other pigments are a direct result of the fact that not all transitions take place with the same probability. For example, Egyptian blue is a relatively pale color when compared with cinnabar. Our eye can tell that we are dealing with two entirely different kinds of transitions.

Once the parameters of these different variables are understood, the artist can exercise a certain amount of control over his or her creation.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

Conclusion

Our colorful journey has taken us from the vast reaches of unrecorded time up to the “relative present” of late antiquity, i.e., approximately 1,600 years ago. In that time span we have witnessed the development of materials and techniques relative to color usage by applying a battery of observational instruments from simple physical and chemical tests to the most sophisticated spectroscopic means available today. We have seen synchronous developments across Eurasia in the preparation of colorants and ancillary substances. In the Paleolithic era, there were no quantum leaps to entirely new materials, but a gradual and steady evolution of a discipline that was communicated intergenerationally for tens of millennia. As the human population began to increase and expand, and at the same time as the glaciers of the latter Ice Age receded, great civilizations developed that had no knowledge of what had gone before, buried as the Paleolithic artifacts were by landslides in forgotten climes and places. Today, thanks to the discoveries of these caves, largely in the 20th century, we are receiving a communication from our ancient forebears through their paintings on cave walls and ceilings. Their message is the first archaeological evidence of a chemical process other than combustion and the existence of a culture that perpetuated it.

Little by little, the color palette expanded. Sometime between 400 BCE and 100 CE, a large body of literature developed that, for the most part, was handed down to us to enable us to reconstruct colorant usage at and before that time. The 19th century archaeological expeditions and excavations unearthed civilization’s forgotten treasures in virtually every part of the globe. These priceless signposts to lost cultures continue to be revealed to us today. We marvel at the accomplishments

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch002

of our forebears, but let us not forget that their knowledge was hard won. It was based on empiricism and tradition, something almost unthinkable to those of us used to citing theories and applying equations to most modern problems.

In fact, apart from the breakthroughs of Isaac Newton (1643-1727) and John Dalton (1766-1844), science has been driven by empiricism. Empiricism carried through to intuitive pattern recognition in the cases, for example, of the development of the periodic table and the formulation of the Rydberg equation, eventually found theoretical bases in the work of Niels Bohr (1885-1962), Albert Einstein (1879-1955), and many others in the early 20th century. Today, these theories have penetrated and informed the thought and practice not only of scientists, but also of the thinking of the public at large. Theory enables controlled and systematic practice to advance our use of materials and prime our innovative thinking at an exponential, not an intergenerational, rate. But we must never forget that we still stand on the shoulders of those persistent practitioners of the Ice Age and beyond, and it is they who enable us to see into the beyond.

The practice of chemistry, as we have seen through this study of color, is ubiquitous in human societies, and it has been from the beginning of civilization. Therefore, the chemical-historical "tourist" can find material for study wherever human material culture has been well preserved. It is hoped that this comprehensive catalog of how chemistry, and in particular the use of color, has impacted human civilization from the dawn of history will give the ordinary citizen an appreciation of the civilizing influence of the chemical enterprise.

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Chapter 3

The First Artificial Material: Ceramics from Prehistory to the Fall of Rome

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The firing of clay is among the first chemical reactions humans intentionally used to create a new material. The earliest ceramic objects, ceremonial cult figurines from Dolni Vestonice (Czech Republic) have been dated to 28,000 B.P. The earliest utilitarian pottery are vessels from the Xianrendong cave (China), determined to be 20,000-19,000 old. The earliest ceramics from the Americas have been dated to 7,500-7,000 years ago. The archaeological record suggests that pottery was independently invented at multiple locations already by hunter-gatherers. Innovations in materials pro-cessing led to increasingly refined objects. These innovations include concepts such as using fillers to improve mechanical properties, control of reaction kinetics by particle size, carefully timed protocols for redox processes, and melting point depression by the addition of fluxes. The development of glazes, polychromy, and sophisticated kilns capable of higher temperatures and controlled kiln atmospheres will be discussed, as will the earliest chemical texts on ceramics.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

Introduction

Ceramics today represent a very important class of artificial materials that are indispensable in meeting the diverse needs of a technologically complex society. Contemporary advanced applications range from biocompatible implants, to high temperature superconductors currently tested for the construction of powerful magnets, to heat and radiation resistant materials able to withstand the rigors of prolonged space travel and survive atmospheric reentry. In view of the chemical complexity of modern ceramics it is often easy to forget that ceramics can be thought of as the earliest artificial material used by humans since prehistoric times to make objects that met their practical, emotional, or transcendental needs.

The history of ceramics is a vast and multifaceted subject. Archaeological and historic ceramic collections trace the evolution of human thought, reflecting our inventiveness, our aesthetic sensibilities and even our changing thoughts about Man's place in the Universe. Trying to do justice to this vast topic in a short symposium chapter would be a fool's errand. I have decided therefore to restrict myself to the vantage point of the chemistry historian, leaving out topics that might be of interest to the cultural anthropologist or art historian. For our purposes, the history of chemistry, broadly defined, traces the emergence of new materials and processes, and the evolution of concepts about the material world. And this is the vantage point I will primarily adopt in conjunction with the history of ceramics. Even so, I had to restrict myself to a few selected vignettes rather than attempt an exhaustive coverage of the topic.

When reconstructing the development of chemical technology in prehistoric times, the chemistry historian has by definition no written records to go by and must rely on supporting evidence from archaeological chemistry. Even in historical times the records may have survived only partially if at all and may be hard to interpret. When researching more recent topics from within the period of recorded history, information can also flow the other way. The chemical historian can provide the archaeologist or art historian additional context for the interpretation of field observations or archaeometric laboratory data (*1–3*).

In this chapter prehistoric dates determined by radiocarbon methods are given in BP (calibrated years before the present). For more precise dates during historical times the now standard convention BCE/CE has been adopted.

Because of space limitations I have omitted the section on clay geochemistry included in my oral presentation. For the interested reader that might benefit from a very cursory introduction to this bewildering subject, the geochemistry portion of my Symposium talk is however posted online and and is available at ACS Presentations on Demand.

Paleolithic Ceramics and the Material Culture of Hunter-Gatherer Communities

The dehydration and irreversible thermal dehydroxylation of clay are among the first chemical reactions humans intentionally used to create a new material. Our earliest evidence comes from artifacts discovered in Central Europe dating to 28,000-25,000 BP (Figure 1). The figure on the left is the very familiar Venus

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

of Willendorf, a carved limestone figure. The ceramic figure on the right, the Venus of Dolní Věstonice from the Czech Republic resembles closely the Venus of Willendorf. The two are of similar age and signal what has been called the transition from a lithic tradition to a ceramic tradition.

Figure 1. (Left) Venus of Willendorf, discovered 1908 near Willendorf, Austria. Carved from oolithic limestone, dated to c. 28,000– 25,000 BP, H. 111 mm (4.4 in). Photography by Don Hitchcock, Wikimedia (Right) Venus of Dolní Věstonice, discovered 1925 south of Brno, Czech Republic. Fired loessic clay, dated to 29,000-25,000 BP, 111 mm by 43 mm (4.4 in by 1.7 in). Photography by Petr Novák, Wikipedia.

The Dolní Věstonice site has yielded over 5000 ceramic artifacts made of local Pleistocene loess soil kneaded and shaped as moist paste, and then fired in walled structures serving as hearths or early kilns (*4*). The firing temperature was estimated to be 500-800 °C, in a reducing, carbon-monoxide-rich atmosphere judging by the grayish-black color of the artifacts. Impurity-initiated sintering allowed the consolidation of the clay into a ceramic object. Mostly animal and a few intact human figures but no utilitarian ceramics were recovered at this site.

Table 1 gives a thumbnail sketch of ceramics from Paleolithic Europe and related sites in Northern Africa. We see that all of them are non-utilitarian artistic objects, fired at low temperatures (<800 °C), some made of loessic sediment rather than true clay. The find at Tamar Hat may have been accidentally fired. The bison sculptures at Tuc d' Audoubert are formed out of clay but not fired at all, and they may represent a pre-ceramic tradition of working with clay. Finally at Klisoura cave, the clay lining of the hearth probably formed a ceramic material during use.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

Table 1. Other European Paleolithic Sites Yielding Ceramic Objects[a]

LOCATION	*DATE BP*	*ARTIFACTS*
Krems-Wachtberg, Austria	27,400	Zoomorphic
Kostenki I, Russia	25,300	Shards
Tamar Hat, Algeria	20,200	Zoomorphic
Vela Spila, Croatia	17,500	Zoomorphic
Maina, southern Siberia	16,000	Anthropomorphic
Klisoura cave, Greece	30,000	Hearthlining
Tuc dAudoubert, France	13,000	Bison sculptures

[a] Data compiled from Farbstein, R.; Radić, D.; Brajković, D.; Miracle, P. T. First Epigravettian Ceramic Figurines from Europe (Vela Spila, Croatia). *PLoS ONE 7(7)*: e41437. doi:10.1371/journal.pone.0041437 and sources sited therein.

As of 2012, the oldest known utilitarian ceramic object i.e. true pottery was excavated in the Xianrendong cave in China dating to 20,000 BP (Figure 2). The vessels were produced by mobile foragers and may have been used for cooking since many shards bear signs of burning on their exterior surface. The Xianrendong pottery is made of sandy silty clay, is low-fired and typically tempered with crushed quartzite or feldspar (*5*).

If written in 2009 the paper would have cited shards found in the Yuchanyan Cave (Hunan, China) and dated to ~18,000 to 17,000 BP as the oldest pottery (6). Infrared spectra indicate that the firing temperature was between 400 and 500 °C, with kaolinite being a major clay component. Both the interior and exterior surfaces were impressed for decorative purposes, possibly using cordage.

Figure 2. Typical shard from the West section of the Xianrendong Cave. The cave was originally excavated in 1993 and 1995, and trenches reopened in 2009. (From Supplementary Material for ref. (5), reprinted with permission).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

Traces of Paleolithic culture, mainly stone tools, occur in Japan from around 30,000 BC onwards. This culture is referred to as the Jōmon Culture. The earliest, so-called "Incipient Jōmon" phase began while Japan was still linked to continental Asia as a narrow peninsula. The most famous Jōmon site is the Ohdai-Yamamoto site. The earliest ceramic shards from Ohdai-Yamamoto are from 16,850-16,240 BP as determined by C-14 dating and made of loam (*7*). **And yes, ten years ago one would have stated that this is the oldest example of pottery.** Jōmon Pottery usage was recently investigated using GC/MS and GC/Combustion/Isotope Ratio MS. Lipids were recovered from charred surface deposits adhering to pottery dating from about 15,000 to 11,800 BP. In most cases it was found that these organic compounds were unequivocally derived from processing freshwater and marine organisms (*8*). From the perspective of the science and technology historian the examination of Paleolithic ceramics leads to four main points:

1. The technology to produce ceramic objects was invented and developed independently at several locations and at different times.
2. Utilitarian ceramics fired at relatively low temperatures (<800 °C) were developed by hunting-gathering populations and are not the consequence of the so-called “Neolithic Revolution”
3. Ceramics are not necessarily associated with the invention of agriculture and the emergence of permanently sedentary populations.
4. The addition of fillers into clay (temper) can be thought of as the first use of a composite. As such, it represents an early deliberate attempt at improving the properties of an existing raw material.

Neolithic Ceramics: The Emergence and Spread of Polychrome Decoration

The Neolithic period is marked by the introduction of utilitarian polychrome-decorated pottery during the 7th millennium BP, and a rapid expansion in its production within the Near East, southern Mediterranean and southeastern Europe, but also China and the Far East. Unfortunately Neolithic ceramics became part of the very contentious debate over the identity of the “first Europeans” (*9*). We will not wade into the muddy waters of colonization vs. the mere transmission of ideas (cultural diffusion) and restrict ourselves to simply chronicling material innovations. Polychromy was accomplished by slip-decoration. Slip is a water suspension of clay and pigment that is used as paint to decorate clay prior to firing. Typical vessels with geometric decorations from the Cucuteni-Tripolye culture, Romania/Ukraine (Figure 3) and the Majiayao culture, China (Figure 4) were selected here as globally representative examples.

The pigments used by Neolithic potters relied on essentially the same transition metal ions as those used on cave paintings during the Paleolithic, but with an added complication. They had to be modified to withstand the firing step in the production of the ceramic object. The advent of minimally invasive synchrotron radiation X-ray diffraction has enabled the identification of new

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

pigment phases on Neolithic ceramics using very small amounts of the pigment. Thus, pigments on Neolithic ceramics can now be easily compared with similar pigments used in the much earlier cave paintings. As an illustrative example we will briefly mention recent results obtained on shards from the Cucuteni culture dating to around 6300 BP (*10*). Red pigments based on hematite, Fe_2O_3, can survive the firing process under oxidizing conditions and thus continued to be used on ceramics. Other pigments had to be modified or substituted by alternative materials. Calcite used as a white pigment or to generate lighter shades of other pigments is stable up to 800 °C. When the object is fired at higher temperatures it reacts with the clay to form a white Ca-silicate, diopside ($CaMgSi_2O_6$). The formation of a black color represented a greater challenge. Black magnetite, Fe_3O_4, formed from hematite in a reducing kiln atmosphere, was one possibility. This approached was used in Neolithic Mesopotamian ceramics. The Cucuteni potters met the challenge of obtaining both black and red decorations on the same pottery fired under oxidizing conditions and at temperatures around 1000-1100 °C by using a novel black pigment, Mg-substituted jacobsite, Fe_2MnO_4.

Figure 3. An example of Neolithic painted pottery from Cucuteni/Romania, 6800-5000 BP. (Photography by CristianChirita, Wikipedia).

Ceramics from the Chinese Neolithic (10000-4000 BP) were similarly decorated. The black colors were due to various Mn-containing phases formed by the thermal decomposition of pyrolusite (MnO_2) during firing. Zhiyan has published an excellent review of Chinese ceramic prehistory (*11*), albeit from an archaeological/art historical point of view.

It is also noteworthy that around the same time, late forager communities in Northern Eurasia, covering an area from the Baltic to the Urals mountains and from the Barents Sea to the Black and Caspian Seas were still producing utilitarian ceramics resembling the much earlier Chinese Paleolithic objects we encountered

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

in the previous section. The objects by these northernmost late hunter-gatherers while contemporaneous with the Neolithic cultures of southeastern Europe and the Near East were fired at low to medium temperatures, were tempered with sand, crushed stone, gravel, ochre, and mollusk shells (*12*), or even organic matter and **lacked any polychrome decoration**. They were made from a paste often low in clay and with a high silt content (*13*).

Figure 4. Neolithic Chinese funerary urn, Majiayao Culture, Banshan Phase 4600-4300 BP, 175 by 175 mm (7 by 7 in), John Young Museum of Art, U. of Hawaii.

Early Recorded History: Egyptian Ceramics

As we enter the period of recorded history the art of the potter becomes a recognized profession. As the copy of an Egyptian mural from the temple at Beni-Hassan shows (Figure 5), the potter's wheel has been invented (presumably already before 6500 BP in Mesopotamia), pottery is mass-produced, and advanced, two-chambered kilns are employed (*14*). The status of the Mesopotamian potter in contrast was apparently not as prominent since few depictions of the potter's art from this region are known (*15*). Slip-decorated pottery flourished also in the Mycenaean world. The word for the profession of the potter and the root word for ceramics, is first encountered on clay tablet texts written in Linear B Greek from Pylos and Mycenae (*16*). Linear B was in use 1600-1000 BCE. This word in Mycenean Greek is ke-ra-me-we. It later became κεραμευς (= the potter in Attic Greek) and survives to this day

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

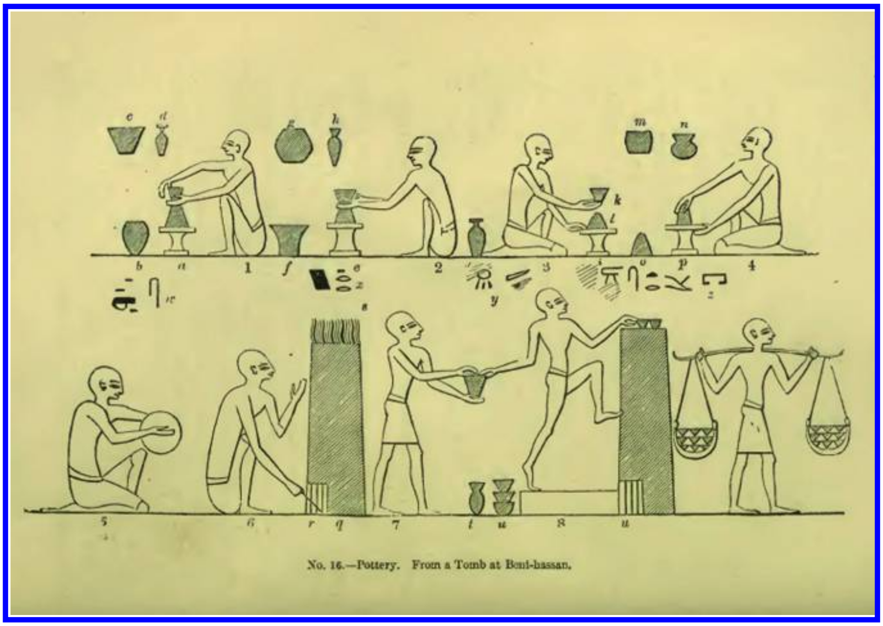

Figure 5. Representation of pottery making on a mural from a tomb at Beni-hassan, Middle Kingdom, 2800-2500 BCE.

In Europe and the Near East, there was no further progress in the composition of ceramic bodies beyond the stage of earthenware until the Late Middle Ages. The subsequent advances in the ceramic technology of Classical Antiquity were related to such surface treatments as the application of colored glazes and the control of complex surface reactions. Workers in ceramics, metallurgy and glassmaking exchanged ideas, and advances in one area drove advances in the others (*17*). However, potters and glassmakers appear to have retained some of their separate traditions in the choice of raw materials (*18*). In China, more highly vitrified ceramic bodies like stoneware and a so-called "proto-porcelain" material were developed already during the Shang Dynasty (ca. 1600-1046 BCE). The subject has been reviewed in detail by Kuishan et al. (*19*).

Ceramics were not the earliest glazed objects. They were preceded by artifacts made of quartz, carved steatite or crushed quartz paste (also known as Egyptian faience). These objects were typically coated by a blue copper-based glaze, a vitreous form of the Egyptian blue pigment discussed in the previous chapter by Orna. The chemistry of glazed Egyptian and Near Eastern objects has been reviewed by Tite et al. (*18*). Egyptian blue can be applied to ceramics only post-firing and tends to flake. Egyptian pottery was not glazed until the 1st century BCE and in general was rarely decorated. The period of the 18th and 19th Dynasties, a period of technological innovation in general, represents an exception. The technology for using cobalt colorants on ceramics was discovered during the reign of Tuthmosis III and became widespread during the reign of Amenhotep III (*20*). An example of these blue decorated so-called Malqata ware from the palace of Amenhotep III is shown in Figure 6.

The blue pigment on Malqata ware was identified by Riederer as a Co/Al spinel (*21*). It is probably very similar to Thenard's blue, the pigment in underglaze blue painted porcelain. The cobalt used for the colorant both on ceramics and for dark blue glass from this period was extracted from the cobaltiferous alum deposits in the Dakhla and Kharga oases of the Western Desert. Kaczmarczyk was the first to establish this link by comparing trace metal analyses of alum from Dakhla and Egyptian cobalt glass samples (*22*). It appears however that the composition of the alums for pigments used in the decoration of pottery was different than the ones used for making blue glass (*20*).

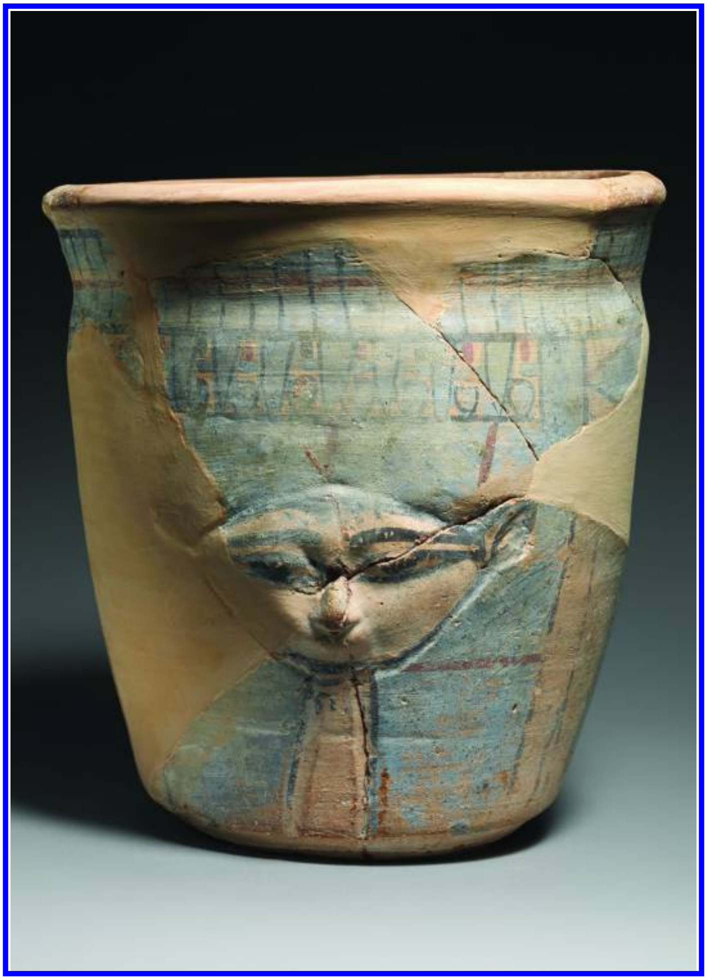

Figure 6. Blue-painted Hathor jar from Malqata, reign of Amenhotep III, New Kingdom, 18th Dynasty, 1390-1353 BCE, H. 24.5 (9 5/8 in.); diam. 25 cm (9 13/16 in.), excavated by the Museum's Egyptian Expedition at Malqata, Upper Egypt. (The Metropolitan Museum of Art, Rogers Fund 1911).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

Of interest to the science historian is the sophisticated process of extracting the cobalt from the alum raw material. A comprehensive study of the process involving replication experiments in the laboratory was published by Shortland et al. (*23*). The cobaltiferous alum as mined is composed of a mixture of aluminum, cobalt, manganese and magnesium sulfates. Preparation of the pigment involved the precipitation of aluminum and cobaltous hydroxides from an aqueous solution of the alum by the addition of natron (a natural deposit, mostly sodium carbonate). As observed in the replication experiments, increase in the pH of the solution by progressive addition of natron causes successive precipitation of the hydroxides based on their solubility product constants (the chemical equilibria are slightly more complex for Al). Aluminum, cobalt and manganese hydroxides precipitate first, magnesium hydroxide due to its higher solubility does not precipitate until the solution is considerably more alkaline. This may be the reason for the lower Mg/Co ratio found in the blue pigment compared to the alum samples collected and analyzed (*20*). If this supposition is correct, then the extraction of cobalt would represent the earliest example of fractional precipitation, a laboratory technique for the separation of ions in solution that is still practiced today. However, the alternative explanation that a source of alum was used that is different from the modern samples collected for analysis cannot be excluded.

The Earliest Chemical Records: The Glazed Ceramics of Mesopotamia

The successful deciphering of cuneiform script was completed in 1857. The script was first invented in Sumer around the late 4th millennium BCE and was adopted by a series of near Eastern languages from Akkadian to Old Persian. Today close to a million tablets have been recovered and several tens of thousands have been read and published. They shed light on diverse aspects of Near Eastern everyday life, literary culture and technological accomplishments. In this context, a work of significance to the chemistry historian is R. Campbell Thompson's seminal mono-graph "On the Chemistry of the Ancient Assyrians" published in 1925 (*24*) together with its 1933 critical review by A. E. Marshall in the Journal of Chemical Education (*25*). While the majority of the "chemical" tablets discussed by Thompson and others are of interest mainly to historians of glass technology, many of them also contain significant information about the glazing of ceramics.

Stone and wood were not readily available in Mesopotamia, so clay was used as a primary construction material. The first bricks were made of loam, shaped by hand and were irregular, often merely sun-baked and tempered with straw or gravel. Loam is soil composed mostly of sand and silt, and a smaller amount of clay (with a composition of roughly about 40%-40%-20%, respective-ly). Based on archaeological evidence, the earliest smooth, regularly shaped, loam bricks known from Mesopotamia date to 6300 BCE. Loam bricks of standardized size emerge around 5900 - 5300 BCE. The earliest clay bricks date to 3100 – 2900 BCE.

The production of the earliest glazed clay objects occurred in Mesopotamia some 2000 years after the first production of glazed quartz, steatite, and faience and coincided with the beginnings of glass vessel production. The calcareous clays of Mesopotamia give rise to a ceramic body with a coefficient of thermal expansion that can be matched to that of the glaze thus minimizing crazing and might have facilitated the development of the process as pointed out by Tite et al. (*18*).

A Middle-Babylonian clay tablet in cuneiform script, ostensibly from the reign of Gulkishar, 1700 BCE, shown in Figure 7 is probably among the earliest chemical documents. It was first translated by Gadd and Thompson (*26*). The authors in describing the content of the tablet write:

> "…what is still more extraordinary about the tablet is that it is unique in the history of chemistry, containing as it does, the earliest record known of the actual formulae for the making of glazes."

The tablet describes the preparation of a copper-based green glass specifically for the glazing of pottery. A summary of the recipe reproduced below gives a vivid impression of the glazing process.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

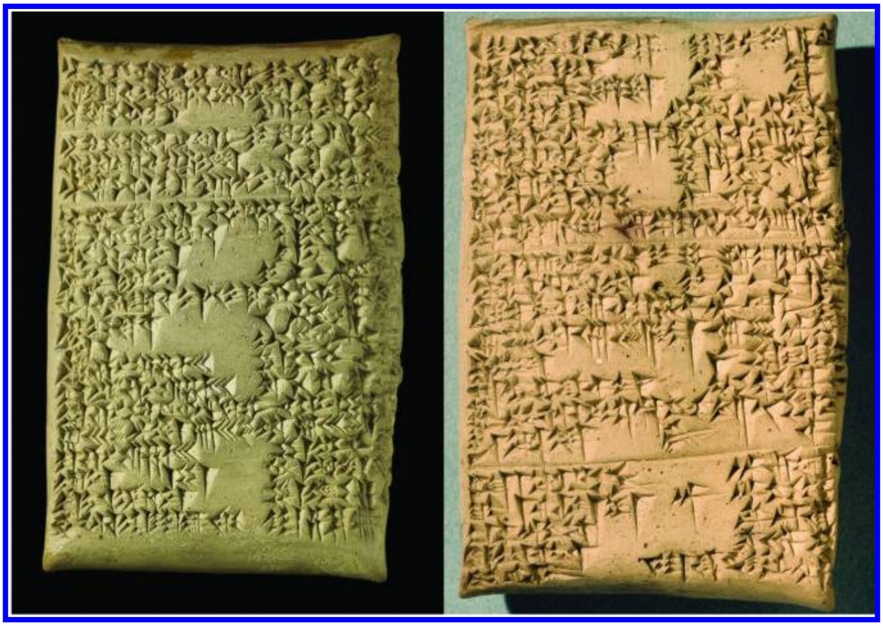

Figure 7. Recipe for copper-based green glaze. Middle Babylonian clay tablet in cuneiform script, reign of Gulkishar, 17th century BCE. L: 8.25 cm (3.25 in) W: 5.23 cm 2 1/16 in) with twenty (obverse, left) and twenty one (reverse, right) lines of inscription. The British Museum, Museum number: 120960 (published with permission).

Following the translation by Gadd and Thompson, lines 1-3 give a recipe for a form of green copper glaze called "lead-copper". It should consist of 60 parts *zukû*-glass, 10 parts lead (in the authors' interpretation of the word *abaru*), 15 parts copper, ½ part saltpeter and ½ part lime, all melted together. Lines 4-6 describe a

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

related green glaze called "Akkadian copper" consisting of 60 parts *zukû*-glass, 10 parts lead, 14 parts copper, 2 parts lime and 1 part saltpeter. These two glazes are next crushed, mixed together re-melted and crushed. To this 1-½ parts *zukû*-glass, and 1/24 parts each of saltpeter, copper and lead are mixed and the mixture is melted and ground, ready to be applied to the pot. But before this is done certain rites have to be followed for the propitiation of the "incompletely dead" to insure success. This is one more instance of the Babylonian belief in the intervention of the occult in the (chemical) processes of the material world (*27*). This ritualized process may also be behind the seemingly superfluous mixing and remixing of intermediate colored frits in the above recipe along the lines discussed by Shortland for Mesopotamian blue glass and Egyptian Amarna frits (*27*). Oppenheim (*28*) on the other hand gives a somewhat different translation of this text. relying on a stylistic analysis he concludes that the text was actually written somewhat later, perhaps during the 14th -12th century BCE. He also translates Gadd and Thompson's "saltpeter" as antimony and concludes that the glaze is a Cu(I)-based red rather than a Cu(II)-based green glass.

Figure 8. Glazed brick relief of an auroch (young bull). Detail of the Ishtar Gate in the city of Babylon, built around 575 BCE by King Nabuchadnezzar II. (Vorderasiatisches Museum-Pergamon Museum, Berlin, amateur photograph).

A number of recipes describing the manufacture of glazed bricks such as those used in the construction of the Ishtar gate (cf. Figure 8) are known from tablets in the library of Assurbanipal (668-627 BCE) and some have been translated by Zimmern (*29*). One of the basic starting materials for the preparation of colored glazes is a type of glass known as zukû-glass. At the Fifth Congress of the International Association for the History of Glass in 1970, Robert Brill (The Corning Museum of Glass) described the first successful laboratory replication of zukû following the process outlined in a cuneiform text (*30*). In his words “The resulting product was a well-melted, homogeneous piece of transparent pale bluish glass of very good quality”. Other recipes, however, could not be reproduced and zukû-glass appears to be the only successful replicate so far (*28*). The word “recipe” should be used with caution since the names for some of the ingredients cannot be unambiguously translated. Furthermore, important steps in the procedures are sometimes intentionally left out, to guard trade secrets. Interestingly, these problems seem to plague the chemistry historian across the ages, and are encountered even in documents from the Early Modern Era (*2*, *3*).

The Chemical Puzzles of Athenian Black and Red Figure Pottery

Around the late 7th century BCE Athenian potters began producing vessels of a very high technical sophistication and aesthetic refinement like the one shown in Figure 9. The vessels are known as Athenian black or red figure pottery. They are decorated with a characteristic black glaze that is used for drawing either the figures or the background. While these objects inspired the poet John Keats (1795-1821) to write his “Ode on a Grecian Urn,” scholars like the Comte de Caylus were already inquiring into the production techniques in 1752, well before Keats was born (*31*). Caylus described a small red and black decorated Etruscan vase and speculated that it as made of a ferruginous clay containing manganese. In 1842 the physician and explorer John Davy established that the black pigment was ferrous iron (*32*). In his words, the black pigment was “…powerfully attracted by the magnet” an observation consistent with magnetite, Fe_3O_4. The presence of Fe(II) compounds and absence of any significant manganese levels in the black glaze was demonstrated in 1910 by Foster using wet analytical techniques and a shard from the sanctuary of Hera at Argos (*33*). It was established that the paint consists of a slip made of iron-rich illitic clay. By 1929 Binns and Fraser put forth the outlines of the so-called three-stage firing process for the production of Athenian pottery (*34*). The process can be described as follows:

The initial firing stage is carried out in an oxidizing environment at 870−950 °C. During the second stage the atmosphere is changed to a reducing environment accompanied by a decrease in temperature. Under these conditions the red colored mineral hematite (Fe_2O_3) in the slip is reduced into a mixture of black colored magnetite (Fe_3O_4) and hercynite ($FeAl_2O_4$) while at the same time the clay platelets in the slip layer undergo sintering to form a black layer impervious to oxygen. The body remains porous. In the final, re-oxidizing stage, the kiln slits are opened again admitting oxygen into the kiln atmosphere. While the painted vitrified areas remain black, the iron minerals in the porous ceramic body are re-oxidized to Fe_2O_3 to produce the red color. The potter is confronted with an obvious chemical dilemma, namely how to retain the porosity and suppress reduction of Fe(III) in the red areas, while at the same time promoting vitrification and Fe(II) formation in areas that should turn black. The answer can be found in the potters’ experiential grasp of the properties of the clays they chose to work with.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

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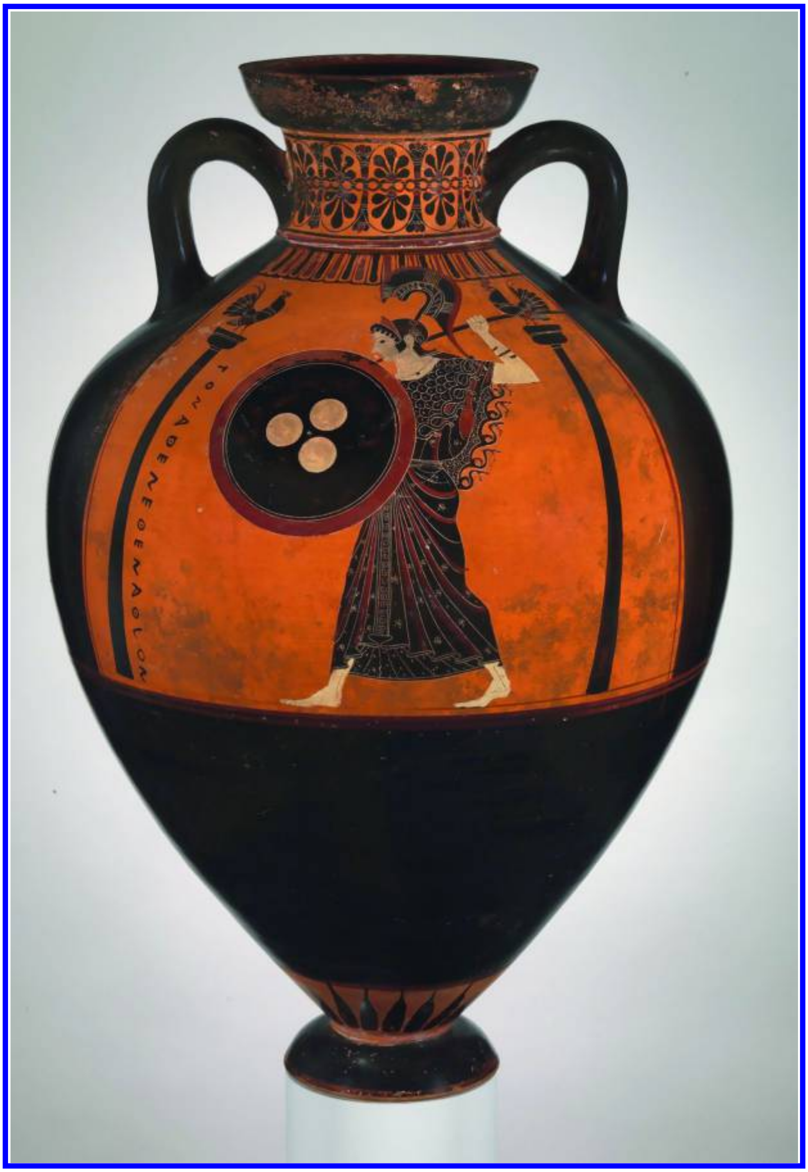

Figure 9. Panathenaic prize amphora, attributed to the Euphiletos Painter, ca. 530 BCE black-figure pottery H: 62.2 cm (24 ½ in). Metropolitan Museum of Art (Rogers Fund 1914).

Early studies (*35*) have shown that the slip is made of very fine clay particles separated from the clay through the process of levigation. In this process the clay is dispersed in water and the coarser grain particles settle to the bottom while the finer particles remain suspended and are harvested to prepare the slip. The Attic potters understood that small particle size accelerated the vitrification process and aided the formation of a smooth and glossy vitreous phase.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

Another key property of the slip is its exceedingly low calcium content compared to the calcareous clay used to make the ceramic body (*36*, *37*). Upon firing very different iron phases develop in Ca-rich vs. Ca-poor clays as was shown by Maniatis et al. using XRD, SEM and Mössbauer spectroscopy (*38*). In calcareous clays fired at 900 °C calcite reacts with the clay mineral to form gehlenite ($Ca_2Al_2SiO_7$) crystals. Gehlenite can accommodate a portion of the Fe(III) substitutionally in the lattice and protect it from reduction during the subsequent stage. Furthermore the development of a crystalline phase gives the ceramic body a coarser more porous structure and inhibits extensive vitrification. In the Ca-poor clays Fe(III) is expelled from the vitrifying lattice and forms a hematite phase. During the reduction stage, Fe(III) in the Ca-rich clay "trapped" in gehlenite is largely protected. In the Ca-poor slip hematite is reduced to black Fe(II) oxide phases. Wustite (FeO) is a very effective flux assuring the complete vitrification of the slip. With the difference in porosity now in place, the reoxidation stage creates the black/red contrast.

Because of the differences in the composition of the slip and the clay of the ceramic body it has been assumed that two different sources of clay were used, a calcareous clay for the body and a Ca-poor clay for the slip (*37*). However, recent work by Walton et al. offers circumstantial evidence that calcium was removed through a mild acidification of the clay during levigation in order to induce flocculation (*39*) suggesting a single source of clay. Similarly, the hitherto widely held view that the process involved a single multi-stage firing event is now in question, as new evidence supporting multiple firings has been recently published (*40*).

Concluding Remarks

Our brief excursion into the technical history of ceramics leads us to some general observations. Relatively early in the history of our species, our ancestors engaged in the processing and intentional chemical transformation of raw materials to make objects that met their practical and spiritual needs. The traditions relied on the stable transmission of know-how marked by continuous improvement through the steady accumulation of knowledge by experience and observation. Metallurgists, glassmakers and potters shared know-how and possibly equipment, as all three arts rely on the manipulation of similar materials at high temperatures, hence the name "arts of fire." We have already alluded to the interaction between glassmakers and metallurgists sharing materials that lead to the emergence of colored glazes (*17*). Equally interesting for the chemistry historian is the use of ceramic crucibles (for example in New Kingdom Egypt), to prepare colored glass and manufacture colored glass ingots for further trade. Rehren (*41*) has discussed the structure and thermal properties of these crucibles in considerable detail.

During prehistoric times the transmission of knowledge was obviously accomplished through an oral tradition. More surprising is the paucity of written texts even during historical times, when many other aspects of human activity and thought were painstakingly recorded. This may possibly be related to the low literacy levels of the craftsmen. More intriguing perhaps is the ambiguity, possibly intentional, of the chemical records that have survived as evidenced by the low success rate of replication experiments. The difficulties encountered in such attempts are not always linguistic in nature. They may reflect the desire to restrict the knowledge within a small group of iniates. Another reason may be the inability to distinguish between crucial details and marginal factors, especially in the absence of a hermeneutic narrative.

Nevertheless the early ceramists were able to develop very complex chemical processes that culminated with the production of Athenian pottery, a product that was highly artistic and extremely utilitarian at the same time. One is reminded of the remark by science historian Jacob Bronowski (*42*) that "the sciences and the arts have flourished together."

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch003

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Chapter 4

From Honey Wine to the Cultivation of the Grape: An Early History of Fermented Beverages

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It is generally believed that the origin of alcoholic fermented beverages is shrouded in the mists of human prehistory. While its specific origins are uncertain, it is clear that the production of alcohol via fermentation is one of the oldest forms of chemical technology, with the production of fermented beverages such as mead, beer, and wine predating the smelting of metals. As a result of the intoxicating effects of these drinks, as well as their perceived pharmacological and nutritional benefits, fermented beverages have also played key roles in the development of human culture, contributing to the advancement of agriculture, horticulture, and food-processing techniques. A general overview of the early history and chemistry of fermented beverages and their uses will be presented.

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Introduction

Ethyl alcohol, or ethanol, is one of the most ubiquitous chemical compounds in the history of the chemical sciences (*1*). In chemical applications, it has played the role of both solvent and reagent. At the same time, it served as a medium for the preservation of organic matter and an effective disinfectant in medical applications. Of course, ethanol was not known as a distinct chemical species until the 12th century (*1–8*), when it was ultimately isolated from wine by distillation, and it was the only alcohol known prior to the discovery of methanol in 1834 (*9*, *10*). Prior to the 12th century, ethanol was only encountered via a number of alcoholic beverages produced via fermentation, where it served as a psychoactive component resulting in euphoria and other mind-altering effects. Such beverages are thought to have been the most common and popular daily drinks, and provided essential sources of both nourishing fluid and calories (*8*, *11*). In addition, the alcohol content (ca 1-16% for the time period discussed here) of such fermented beverages is one of the oldest recreational drugs known, and is still the most widely accepted of such drugs in most cultures. As a result, ethanol plays a central role in the history of society in general.

The origin of fermented beverages is generally believed to be shrouded in the mists of human prehistory (*1*, *12–16*). While the details of these origins are unknown, it is clear that the production of alcohol via fermentation is one of the oldest forms of chemical technology and the production of beer and wine is thought to predate the smelting of metals. The first cases of alcoholic fermentation were likely a result of serendipity, and probably occurred while early humans were still nomadic (*14*, *16*, *17*). In addition, while some have tried to place the origin of intentional fermentation in either Africa (*18*), the Indus Valley (*12*), or the Fertile Crescent, there is little support for such claims of a single specific origin. In fact, the chances of such an event happening only in a single place and time would be expected to be extremely low. As such, it must be concluded that the consumption of alcohol by fermentation must have been discovered independently by various groups of prehistoric nomadic people (*15*, *17*, *19*).

Over the years, various authors have proposed possible pathways for the discovery of fermented beverages. The most common of these scenarios is based on the idea that collected food was stored for too long a period and began to ferment. For example, one can easily imagine sugar-rich foodstuffs such as honey or fruit being left to spoil, resulting in the fermentation of the high sugar content to produce noticeable amounts of alcohol (*13*, *15–17*, *20–22*). It has also been proposed that such circumstances could have been part of the learning process in the early handling and storage of grains during the beginnings of agriculture (*11*, *15*). Regardless of the specific details, these fermented materials were consumed at some point, most likely driven by thirst, hunger or simple curiosity, and people found that they liked the taste and the distinctive aftereffects.

An alternate theory stems from the observation that under the right conditions, some types of berries can ferment while still on the plant. In this process, the berries are attacked by molds which concentrate the fruit's sugar, leading to fermentation and the production of alcoholic content (*13*). Birds and other animals will then often eat such fermented berries, especially as food becomes scarcer

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during the winter months (*8*, *13*). The resulting odd behavior and uncoordinated movements of such animals after eating these berries could have been observed by early humans who, through either hunger or curiosity, could have sampled the fermented berries to experience firsthand the observed effects.

Once early humans had experienced the euphoria and mind-altering effects resulting from the consumption of such alcohol-contaminated food, they must have been stimulated to develop methods to produce a regular supply of alcoholic substances from locally available sugar sources (*15*, *19*). Because of the intoxicating effects of fermented beverages, as well as the perceived pharmacological and nutritional benefits, such drinks have played key roles in the development of human culture. In the process, the production of these drinks has contributed to the advancement of agriculture, horticulture, and food-processing methods (*19*).

The fact that humans have a gene for the enzyme alcohol dehydrogenase leads to the conjecture that over evolutionary time animals have encountered alcohol enough to have evolved a way to metabolize it (*8*, *23*). In fact, it has been proposed that primates may have ingested ethanol via the consumption of partially fermented fruit as early as 80 million years ago. However, recent studies have revealed that a dramatic evolutionary transition occurred in our hominin ancestors ca. 10 million years ago, which resulted in an increased activity of ethanol-metabolizing enzymes (*24*). This transition is thought to be the result of environmental changes brought about large-scale ecological transitions, which resulted in a reduction of available diet and a greater dependence on over-ripe fruit (*24*). This change implies that the genomes of modern humans began adapting at least 10 million years ago to dietary ethanol present in fermenting fruit. Even so, the deliberate production of fermented beverages is not thought to pre-date 10,000 BCE, although their use was widespread by 4000 BCE (*8*, *12*, *15*, *16*).

The problem with trying to support the production of fermented beverages as early as the Paleolithic period (before 10,000 BCE) is the improbability of finding a preserved sample with intact organic material or micro-organisms that can be pinpointed as specifically due to such beverages (*13*, *20*, *23*). Because of this, most authors feel that the most probable time period for the intentional production of fermented drinks is during the Neolithic period (ca. 10,000-4000 BCE), as this was the first time in human prehistory when various necessary preconditions for this discovery really came together (*12*, *21*, *22*, *25*).

It was during the Neolithic period that early humans transitioned from hunter-gatherers to living in permanent farming communities, some of the earliest of which were found in the area of the Middle East called the Fertile Crescent (Figure 1). This region of rich soil stretches from the Nile Delta of northeast Egypt, up the Mediterranean coast, along the mountains of Anatolia, and then down again to encompass the land in and around the Tigris and Euphrates rivers (*15*, *19*, *25–27*). The name stems from a happy accident of geography that provided a rich supply of native plants such as wheat and barley that were suitable for domestication, as well as upland environments for wild sheep, goats, cattle, and pigs (*15*, *26*, *27*). As such, the Fertile Crescent provided an ideal environment for the initial development of permanent, year-round settlements and is not surprising that farming developed so early in this region (*13*, *15*).

As a result of both the formation of permanent settlements and the more secure food supply provided by the development of farming, a Neolithic “cuisine” emerged in this region. This involved the development of a variety of food processing techniques, including fermentation, soaking, heating, and spicing (*13*, *20–22*, *25*). The earliest examples of fermented foods include leavened bread, beer, and wine via yeasts, as well as cheese via bacteria and molds. These were then later followed by East Asian fermented foods such as yogurt and other fermented milk products, as well as a variety of other alcoholic beverages (*13*). Although the discussion here will focus primarily on the developments from the Fertile Crescent, fermented beverages from China were also known during the Neolithic period (*17*).

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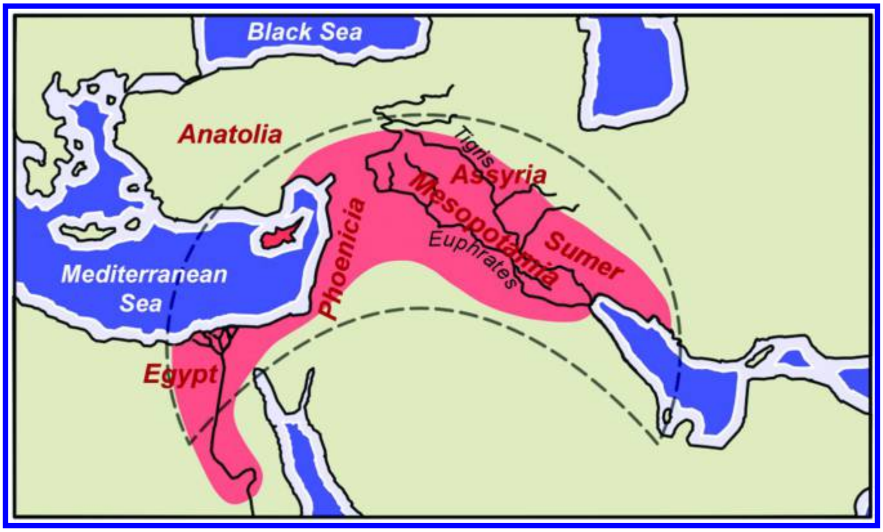

Figure 1. The Fertile Crescent (ca. 4th-2nd millennia BCE).

Fermentation

Alcoholic fermentation, also referred to as ethanol fermentation, is a biological process in which yeasts obtain energy through the conversion of sugars such as glucose and fructose (Figure 2) into ethanol and carbon dioxide, as illustrated by equation 1:

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2 \qquad \textbf{(1)}$$

Yeasts are eukaryotic microorganisms classified in the kingdom Fungi and are estimated to make up approximately one percent of all fungal species. The principal yeast species responsible for fermentation is *Saccharomyces cerevisiae*, which has been used in both the baking of breadstuffs and the production of alcoholic beverages for thousands of years (*25*, *28–30*).

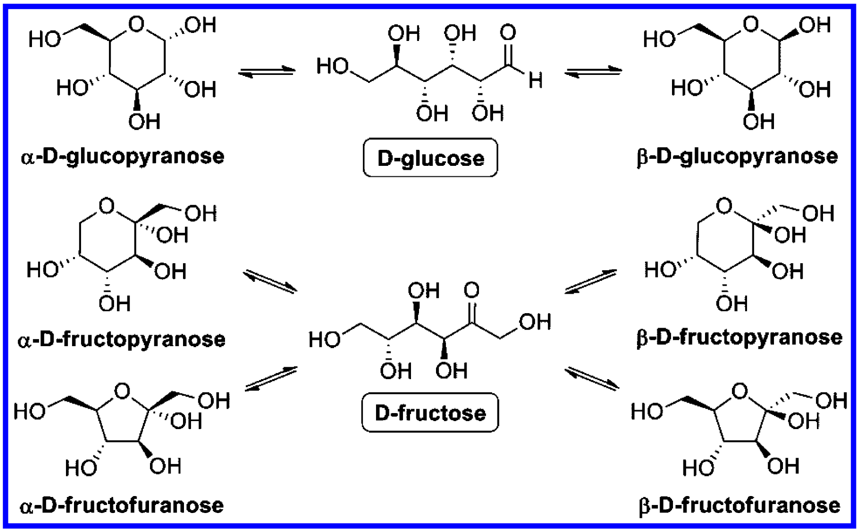

Figure 2. The sugars D-glucose and D-fructose in their linear forms, as well as the various cyclic hemiacetal isomers that predominate in solution.

Evidence of the presence of *Saccharomyces cerevisiae* has been found in material collected from Egyptian wine jars dating back to ~3150 BCE (*25*). The collected material, which was presumed to include dead cells and cellular debris from yeast, was extracted and subjected to two independent sets of PCR amplifications with the appropriate negative and positive controls. The results of these efforts were reported to reveal DNA from an organism that was confidently assigned to be *S. cerevisiae*. Of course, *S. cerevisiae* exists as a wide variety of strains (*29*) and differences in types of yeast were recognized as early as 1550 BCE. For example, the Ebers Papyrus mentions various types of yeasts, including wine yeast, beer yeast, mesta-yeast, growing yeast, bottom yeast, yeast juice, and yeast water (*31*). It has been proposed that early craftsmen may have gone so far as to cultivate successful yeast strains, potentially skimming the frothy yeast from the surface of the fermentation vats in order to use it again for later efforts (*25*). Some have even suggested that yeast was possibly cultivated before grain (*32*) and may be the oldest known domesticated plant (*32*, *33*).

A simplified scheme of the alcoholic fermentation process is outlined in Figure 3, although this process is significantly more complicated than this scheme may suggest. For example, the first overall step shown (i.e. glucose to pyruvate) actually represents ten distinct steps requiring ten different enzymes (*34*, *35*). Another important aspect that is not made clear by the simplicity of Figure 3 is the fact that in addition to the major products given in Equation 1 and Figure 3 (i.e. ethanol and carbon dioxide), there are a large number of other minor byproducts of yeast metabolism that contribute to the overall flavor of different fermentation products (*28*). In fact, the theoretical conversion predicted by Equation 1 (i.e. 180 g sugar to yield 92 g ethanol and 88 g CO_2) could only be expected in the absence of any yeast growth, production of other metabolites, or loss of ethanol as vapor (*35*). This is confirmed by model fermentation processes, which reveal that only about 95% of the sugar is converted into ethanol and CO_2. Of the remaining 5%, ~1% of the sugar is converted into cellular material, with the rest being used to give other products such as glycerol (*35*).

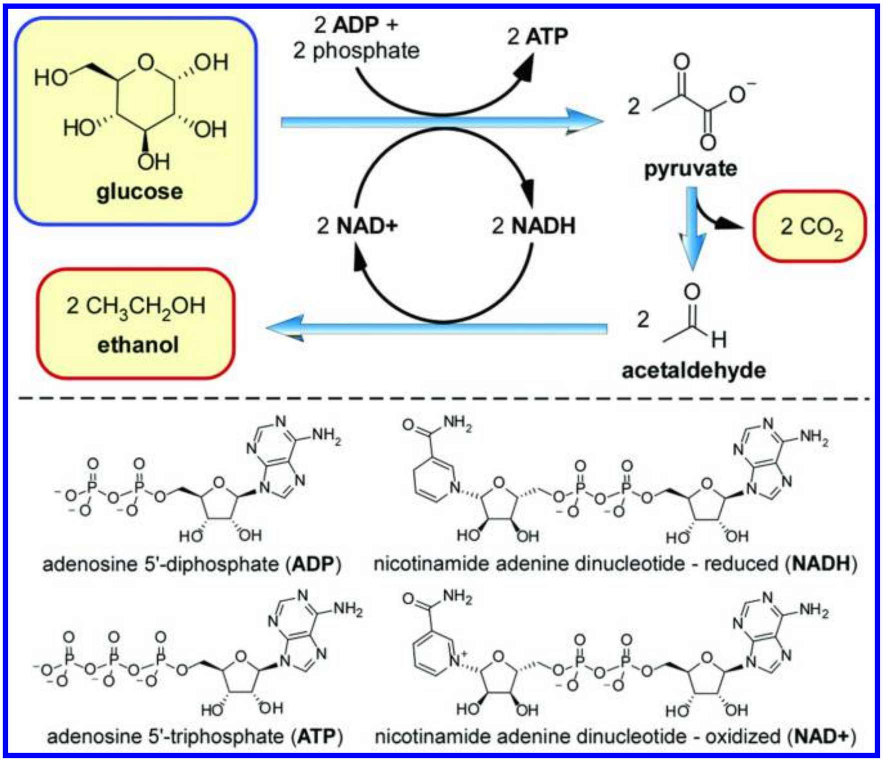

Figure 3. A simplified outline of the alcoholic fermentation process.

As illustrated in Equation 1 and Figure 3, the primary product of fermentation is ethanol with carbon dioxide as a significant by-product. In the production of fermented beverages such as beer, the dissolved CO_2 gas gives its carbonation and creates the head or froth on the beer. In addition, the gas production assists in preservation as a sealed cask that is retained under the pressure of CO_2 keeps air and microbes out of the empty portion of the cask (*32*). This same fermentation process is also employed in the making of leavened breads. Here, the gaseous CO_2 is caught in the glutinous dough, causing it to rise and producing bread that is soft, light, and fluffy in texture. Of course, ethanol is produced here as well, but the volatile liquid is lost due to evaporation at the elevated temperatures used during baking the bread (*32*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

Earliest Fermented Beverages

As fermentation only requires sugar and yeast, fermented beverages can be produced from a wide variety of sugar-containing species. Common fermented beverages include cider from apples, sake from rice, mead from honey, beer from grains, and of course, wine from grapes (*32*). Considering the primary sources of sugar readily available to early Neolithic cultures, however, this quickly becomes limited to wild berries and other abundant fruits, honey, tree sap, and to some extent, milk from animals. In warmer climates, various sources of sugar could have been fairly plentiful, even before farming became common. In temperate zones, however, there would have been few abundant sources of sugar besides honey (*14*). In addition, honey would be more likely to be stored for future use than much more perishable berries (*17*). As such, the earliest alcoholic beverage is generally believed to have been fermented honey (*8*, *14*, *16–18*, *30*, *36*).

Mead

The collection of bee honey by mankind is an ancient activity and is thought to date as far back as the Paleolithic period (before 10,000 BCE) (*36*). The earliest direct evidence of this can be found in Mesolithic rock art from Cuevas de la Araña near Valencia, Spain that dates to 6000-8000 BCE (*36*, *37*). As shown in Figure 4, this rock art illustrates the collection of honey from a wild nest. A number of similar examples have also been found in Europe, Africa, Asia, and Australia (*36*).

Figure 4. The reproduction of a portion of Mesolithic rock art from Cuevas de la Araña near Valencia, Spain. [created by Achillea, 2007; used with permission].

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Honey provided an abundant source of sugar, consisting of ~34% glucose, ~40.5% fructose, and ~1.9% sucrose (*37*). A fermented beverage could therefore be readily produced from diluted aqueous honey solutions, most commonly referred to as mead, hydromel, or honey wine (Table 1) (*14*, *38*). Such honey drinks are known from many sources of ancient history throughout Europe, Africa, and Asia (*14*, *18*, *38*) and it is thought that fermented honey was the first intoxicating beverage made by most early peoples, with its production occurring thousands of years before either beer or grape wine (*8*, *14*, *16–18*, *38–41*).

Unfortunately, firm evidence of fermented honey from archaeological investigations is relatively ambiguous. The basic problem lies in the fact that archeological confirmation of either beeswax or certain types of pollen can be indicative of the presence of honey, but provide little if any evidence of its fermentation. The correlation of the detection of honey to it being a component of mead or honey wine is usually based upon the container from which the sample is found (i.e. drinking horns or other drinking vessels), as well as the environment in which the material under analysis was discovered and the simple speculation of those carrying out the analyses. Of course, as honey has been used historically to sweeten various drinks, even the detection of honey in drinking vessels does not prove the production of mead (*14*).

Table 1. Fermented Beverages Made with Honey[a]

Beverage name	*Description*
mead (or hydromel)	fermented mixture of honey and water
sack mead	fermented mixture of honey with less water
metheglin	fermented mixture of honey, water, and spices
mulsum	wine mixed with honey
pyment (or clarree)	wine mixed with honey and spices

[a] Collected from (*39*).

One of the earliest archaeological studies relating to fermented honey is the analysis of a drinking horn recovered from a peat bog at Skudstrup, in northern Germany. Dated to before 100 CE, the horn provided evidence of both yeasts and pollen grains (indicative of honey), suggesting that it may have held mead (*39*, *41*, *42*). Additional archaeological evidence suggesting the presence of mead was found from the analysis of various bronze drinking vessels from the tomb of King Midas (ca. 700 BCE) in Gordion, central Turkey (*43*). A combination of infrared spectroscopy, liquid and gas chromatography, and mass spectrometry were used to analyze 16 residues, leading to the detection of tartaric acid and its salts as biomarkers of wine, calcium oxalate (“beerstone”) as a biomarker of beer, and long-chain, saturated hydrocarbons indicative of beeswax. This final result, coupled with the detection of gluconic acid, led to the conclusion that the residues contained honey. The combination of species detected in the residues led the investigators to propose that the analyzed vessels contained a mixture of grape wine, beer, and mead (*43*).

A more recent report provides the earliest possible evidence of the use of honey in the production of fermented drinks. This work details the chemical analysis of pottery sherds dating to 7000-5500 BCE from Jiahu, an early Neolithic village in the Henan province of China (*19*). A combination of Fourier-transform infrared spectroscopy (FTIR), gas chromatography–mass spectrometry (GC-MS), and high-performance liquid chromatography–mass spectrometry (HPLC-MS) was used to analyze material extracted from the sherds to reveal the presence of long straight-chain hydrocarbons (C_{23}–C_{36}) attributed to the presence of beeswax. In addition, IR signals were found that were consistent with the presence of tartaric acid. As introduced above, tartaric acid and its salts are commonly referenced biomarkers for grapes and other select fruits. The presence of tartaric acid was further supported by positive Feigl spot tests (*19*). Based upon these analyses and spectral matching of the FTIR and HPLC analyses with various modern samples, the authors suggested that the pottery objects were used to prepare, store, and serve a mixed fermented beverage of honey, rice, and a fruit postulated to be Chinese hawthorn.

The earliest written evidence of mead is believed to come from the Rigveda, an Indian collection of Vedic Sanskrit hymns. The Rigveda is dated to around 1700-1100 BCE and contains approximately 300 references to *mádhu*, the Sanskrit word for both honey and mead (*39*, *40*, *44*). Of course, it is unclear whether any of these occurrences of *mádhu* actually referred to mead and could just be simple references to honey (*39*, *40*). The Ramayana, a later Indian text dated to the 4th-5th century BCE, specifically mentions becoming intoxicated after drinking *mádhu*, strongly supporting the belief that this refers to mead (*39*).

Fermented honey drinks are frequently mentioned by various early Roman writers. Lucius Junius Moderatus Columella (4 - ca. 70 CE), considered one of the most important Roman writers on agriculture, discusses mead and its preparation in his *De Re Rustica* (written in 42 CE) (*39*, *45*). The first century historian Pliny the Elder (23-79 CE) also discussed hydromel in his *Naturalis Historia* (Natural History, published in 77 CE) (*46*) and differentiates it from grape wine sweetened with honey (a drink known as mulsum, Table 1) (*47*).

The species responsible for honey fermentation are various osmophilic yeasts naturally present in honey (*39*, *41*). Osmophilic yeasts are strains that are able to thrive in highly concentrated sugar solutions, which include the species *Saccharomyces rouxii*, *Saccharomyces bailii var. osmophilus*, and *Saccharomyces bisporus var. mellis* (*48*). As these types of yeast are naturally found in honey, its fermentation readily occurs at the right sugar concentrations. Unintentional fermentation could therefore occur if rain simply fell into a vessel containing honey combs or honey to produce a diluted honey solution (*39*). The ease and simplicity of honey fermentation is illustrated by the following preparation of mead as given by Pliny the Elder in his *Naturalis Historia* (*46*):

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> There is a wine also made solely of honey and water. For this purpose it is recommended that rain-water should be kept for a period of five years. Those who show greater skill, content themselves with taking the water just after it has fallen, and boiling it down to one third, to which they then add one third in quantity of old honey, and keep the mixture exposed to the rays of a hot sun for forty days after the rising of the Dog-star; others, however, rack it off in the course of ten days, and tightly cork the vessels in which it is kept. This beverage is known as "hydromeli," and with age acquires the flavour of wine. It is nowhere more highly esteemed than in Phrygia.

A more detailed preparation of mead is also given by Columella in his *De re rustica* (*45*, *49*):

> Therefore having set apart this bees-wax-water, and destinated it for preserving of fruits, mead must be made by itself of the very best honey; but it is not made after one manner: for some, many years before, put up rain-water in vessels, and set it in the Sun in the open air; then, having emptied it from one vessel to another, and made it very clear, (for, as often as it is poured from one vessel to another, even for a long time, there is found, in the bottom of the vessel, some thick settling like dregs) they mix a sextarius of old water with a pound of honey.
>
> Nevertheless some, when they have a mind to make the mead of a rougher taste, mingle a sextarius of water with three quarters of a pound of honey; and after they have, according to this proportion, filled a stone bottle, and plaistered it, they suffer it to be forty days in the Sun, during the rising of the Dog-star; then they put it up in a lost, which receives smoak. Some, who have not been at the pains to preserve rain-water till it becomes old, take that which is fresh, and boil it in to a fourth part: then, after it is grown cold, if either they have a mind to make mead sweeter than ordinary, they mix a sextarius of honey with two sextarii of water; or, if they would have it rougher, they put three quarters of a pound of honey to a sextarius of water; and, having made it according to these proportions, they pour it into a stone bottle; and, after they have kept it forty days in the Sun, as I said above, they put it up in a lost, which receives smoak from below.

The glucose and fructose content of honey undergoes fermentation as discussed above and, if fermented long enough, honey wines can be made with an alcohol content of up to 10-12%. Most honey wines are often characterized by a sweetness due to significant amounts of unfermented sugars (*41*, *50*, *51*). Although both sugars undergo fermentation in the same way and by the action of the same yeasts, fermentation studies have shown preferential uptake of glucose over fructose when mixtures of the two sugars undergo fermentation. In fact, it is estimated that *S. cerevisiae* preferentially ferments glucose at about twice the rate of fructose (*52*). This means that it is primarily the glucose content of honey that contributes to the alcohol content. The remaining sugar present in honey, sucrose,

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

is a disaccharide and must first by hydrolyzed to contribute to fermentation. In this case, the yeast first utilizes the enzyme invertase to hydrolyze the sucrose to a 1:1 mixture of glucose and fructose (Figure 5) (*53*). Fermentation of the hydrolyzed sugars then occur in an identical fashion to that previously discussed.

The osmophilic yeasts naturally present in honey are best suited for the fermentation of honey solutions with sugar concentrations above 15%. However, such osmophilic yeasts do not typically produce alcohol as well as *S. cerevisiae,* the most common yeast used in the production of beer and grape wine (*41*). Because of this, species of *S. cerevisiae* are the best yeasts for the fermentation of honey solutions with sugar concentrations below 15%. It has been found, however, that combinations of *S. cerevisiae* with various additives can successfully ferment honey solutions with sugar concentrations up to 25%, resulting in alcohol concentrations of 12-15% (*41*, *50*).

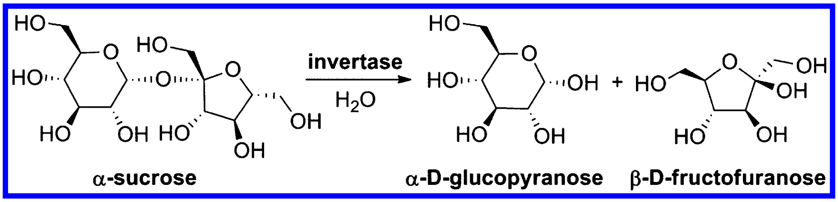

Figure 5. Enzymatic hydrolysis of sucrose to glucose and fructose.

Fermented honey drinks can be made from nearly any type of honey and many of the characteristics of the specific honey utilized are retained in the resulting mead produced. For example, light honeys will yield lighter meads, while dark honeys of stronger flavor can lead to a more beer-like beverage, sometimes referred to as honey ale (*41*, *50*). A number of mead variants can also be produced, one of which is produced by fermenting an aqueous solution of honey with grain mash, which is then strained after fermentation. Additional variants include those flavored with spices (metheglin, Table 1), fruit, or hops, the latter of which produces a more bitter, beer-like flavor.

Despite improved hivekeeping, honey always remained a precious and somewhat expensive commodity. Thus, when agriculture and viniculture led to the production of cereals, grapes, and other fruits in some quantity, mead suffered in competition with beer and grape wine. Even in Egypt, where bee-keeping was significant and honey was produced in quantity, beer and wine became the predominate fermented beverages (*17*). Likewise, in the Mediterranean region and the warmer, temperate parts of Europe, wine obtained a higher social status and displaced honey-based alcoholic drinks (*39*). The Romans, however, still retained a taste for honey-wine, even though it was considered to be an expensive drink (*17*). Elsewhere beverages from fermented honey often remained important (*39*). This was particularly true in the Germanic north (*44*) and among the Saxons in Britain (*17*). Mead was also popular in central and northern Europe at least as early as 334 BCE (*41*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

Date Wine

Perhaps the most abundant and widely used source of sugar in antiquity came from the date palm (*Phoenix dactylifera* L., Figure 6), particularly in the Fertile Crescent (*37*, *54*). This source of fermentable sugar therefore offers the most likely means by which alcoholic drinks were first produced with any degree of regularity (*14*). The date palm grew abundantly in the Fertile Crescent (*55*), especially throughout Babylonia (*54*). In warm dry places such as northern Iraq, there is evidence of its presence dating back to earlier prehistoric periods. Middle Palaeolithic layers excavated in Iraq show that the palm was flourishing it that period, although climatic changes in the later Mesolithic period had made the environment less favorable to the date palm (*55*). Thus by the Neolithic period, the palm was not indigenous to northern Mesopotamia, Syria, or Asia Minor (*54*), but was prolific in both southern Mesopotamia and Egypt (*56*). In Mesopotamia, the date palm was a critical component of the diet and its tremendous value is well recorded in Assyrian and Babylonian texts. In the same way, dates were also an important and commonly used food in ancient Egypt (*55*).

Figure 6. Phoenix dactylifera L. [Botanical print (dated 1884); Tree photo by Symac (2004); Fruit photo by Mariluna (2005); used with permission].

The date palm had been domesticated by 4000 BCE, most likely in southern Mesopotamia (*14*, *57*, *58*) where it was well established by 3000 BCE (*59*). It is highly adapted to a xeric habitat and thrives in desert environments that are unsuitable for most crops (*59*), although it does require plenty of water. Unlike any other cultivated tree, however, the date palm can tolerate water of high salinity

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

and thus it can survive with a supply of brackish water (*57*, *58*). In Palestine, its natural habitat is the Rift Valley, although some small plantations might be also found in the southern coastal plain (*57*).

Economically, the date palm is considered a very valuable plant with high productivity (*57*). As a result, ancient Egyptians considered it the most important of the cultivated fruit-trees (*60*). The date palm furnishes sources of sugar via both fruit (dates) and sap, with dry dates containing 70-80% sugar (*14*, *57–59*). In addition, the date fruit provided a source of date honey (a date-sugar syrup) that was more common than bee honey in antiquity throughout the Fertile Crescent (*54*). Trees are able to bear fruit for 60-100 years and the average palm can produce as much as 40 kg of fruit each year (*58*), with the most productive trees producing as much as 100 kg or more (*59*). In modern Israeli plantations, it has been reported that the annual harvest of a typical tree is 100–200 kg of sugar. This means that a typical plantation can produce up to 10 tons of sugar with a relatively small investment of labor (*57*).

As with fermented honey beverages, it is not known when the production of date wine (or date beer, as it is sometimes referred) began (*57*). The oldest, solid evidence of its production dates to 3000-2000 BCE (*56*, *58*), but it is believed to have been prepared in Mesopotamia and Egypt long before that. In general, it is thought that the production of date wine probably preceded that of barley beer (*56*, *57*) and some believe that the date palm and barley provide the earliest direct evidence that both the Mesopotamians and the Egyptians were making fermented drinks (*56*). In Egypt, date wine was known as *benά*, where its consumption was largely limited to the lower classes (*31*). In Mesopotamia, date wine was known as *dašpu* and represented a favorite drink that would keep for up to a year (*54*). In its popularity, however, it was still secondary to barley beer until the beginning of the Iron Age, after which it became the Mesopotamian alcoholic drink of choice (*57*). The classical Roman authors also wrote of date wine, such as Pliny the Elder who described it as one of the varieties of artificial wines (i.e. non-grape wines) and stated that it was prepared by the Parthians, the Indians, and throughout all the countries of the East (*61*). In some cases, herbs or other additives were also used to flavor the wine. Surviving records describe numerous varieties of date wines and it has been proposed that the additions made to these drinks and the exact methods of manufacture were jealously guarded secrets (*56*).

The production of date wine was not a very involved process and was much simpler than that required for cereal beers produced from barley or wheat (*8*, *56*, *57*). The yeast needed for fermentation is naturally present in the date fruit and thus fermentation is fairly rapid in the warm climates of the Fertile Crescent (*56*). As a result, all that was fundamentally required was a container in which to put the date mash during fermentation and a method to separate unwanted solids from the liquid when complete (*56*). In order to produce the mash, however, it was first necessary to press the date fruit (*57*, *58*). As crushed pits in the mash might be a nuisance, it is generally assumed that the dates were initially pitted. Another motivation for pitting the dates is that date pits are known to have nutritional value and have been compared to barley in that respect. In fact, shredded or ground date pits are currently used as animal fodder and in times of desperation can be added to wheat or barley flour (*57*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

Pressing the dates could be achieved by simple foot-treading, but the use of heavy stone rollers was much more efficient. Four such rollers have been found to date, with one large roller estimated to weigh 900 kg discovered at Ein Feshkha, on the northwestern shore of the Dead Sea (*57*). It has been proposed that such rollers were operated by two or three people. While such cylindrical stones were quite heavy, it is thought that rolling these stones would not have been that difficult, as the crushed dates could theoretically serve as a lubricant (*57*).

The mash was then diluted with a nearly equal amount of water (*56*). In his *Naturalis Historia*, Pliny the Elder described this as follows (*61*):

> A modius of the kind of ripe date called "chydææ" is added to three congii of water, and after being steeped for some time, they are subjected to pressure.

As described by Pliny, this gave a ratio of ca. 0.83 equivalents of dates to each equivalent of water. In Egypt, this wine was made in January as that is when the water collected from Nile was the clearest (*31*). This diluted mash was then allowed to undergo fermentation and finally strained. As the yeast stops functioning when the alcohol content becomes too high, the same dates could be used a number of times to produce multiple batches of date wine. Thus, after fermentation stopped, the mash could be strained and fresh water could be added to the remaining date mash. As this would produce a new mash with little alcohol but significant remaining sugar, the yeast would then start the fermentation process again (*57*).

Palm Wine

A related, but distinctly different beverage was known as palm wine. It too was produced from the date palm, but resulted from the collection and fermentation of the palm sap, rather than the fruit (*14*, *31*, *58*). The sap has a lower sugar content than the fruit, but still contains about 10% sugar. Significant amounts of sap can be extracted from the palm and it has been reported that a typical tree can generate as much as 8 L of sap per day and up to 400–500 L each year. However, trees harvested for their sap in this way are significantly weakened (*58*), and thus stop bearing fruit (*57*, *60*, *62*). It has been reported that it then requires at least 4-5 years for a palm to recover enough to start producing fruit again (*51*), although others have noted that the tree often dies rather than recovering (*60*, *62*). Because of this, sap is generally harvested only from either male or fruitless old trees (*57*, *58*), or in regions in which the palm grows in great abundance (*60*).

The palm sap was collected by making an incision in the heart of the tree below the base of the upper branches (*60*, *62*). A jar was then attached below the incision in order to catch the juice (*60*). The initial liquid extracted from the date palm can be drunk in large quantity, but after fermentation it became a strongly intoxicating beverage (*60*, *62*). Fermentation occurs very rapidly and sap collected in the morning can contain as much as 4–5% alcohol by the evening.

In Egypt, the lower classes drank palm wine (áama) in the same way as date wine (*31*). Although there is not explicit evidence of such, it is believed that palm wine was also produced in ancient Palestine. This is largely due to the mention of ‘palm water’ as a thirst quencher in the Mishnah (the first major written redaction of the Jewish oral traditions), and it is thought that such ‘palm water’ would have been fermented for wine (*57*). In addition, Pliny mentions the production of palm wine in his discussion of Arabia (*63*):

> ...and that the other nations, like the Indians, extract a sort of wine from the palm-tree, and oil from sesame.

Palm wine is still being produced in modern times, particularly in Egypt (where it is now called *lowbgeh*) and Libya (where it is called *lakbi*) (*31*, *57*, *60*, *62*). It is also still made in West Africa and Madagascar, as well as most of the East Indian islands, where it is known as Indian toddy (*31*).

Cereal Beers

The cereals were among the earliest food plants to be domesticated and cultivation of wild wheat and barley is thought to date to around 10,000 BCE (*26*). Although such cereal grains are thought to have begun as relatively unimportant foodstuffs, they took on greater significance following a couple of simple discoveries. The first such discovery was that when grain gets wet, it begins germination and develops a sweet taste (*15*). This sweet taste is due to the conversion of starch into maltose sugar (Figure 7), which is catalyzed by diastase enzymes such as β-amylase, which are present in the germinated grain (*11*, *15*, *32*, *56*, *64–66*). This sweetened germinated grain is referred to as malted grain or simply malt. The malting of grains was common practice in the ancient Near East, not only for increased sweetness and palatability, but also for increased nutritional value and preservation (*65*, *67*).

Malted grains then led to a second important discovery. Such grains could be used as a component of soup, or they could be simply boiled in water to make a gruel or porridge (*15*, *66*). When such porridge of malted grain was allowed to sit too long, it fermented to result in an entirely new sensation (*67*). This process of fermentation was due to wild yeast present in the air. Exposure of the porridge to such yeast would result in its implantation and growth (*66*), which would then ferment the sugar content of the malted grains into ethanol (*15*). This process begins with the hydrolysis of maltose to produce two equivalents of glucose (Figure 8), which is facilitated by the enzyme α-glucosidase contained in the yeast. The glucose produced in this process then undergoes fermentation in an identical fashion to that previously discussed (*32*).

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Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

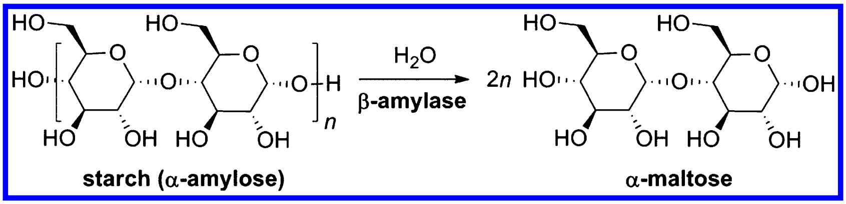

Figure 7. Enzymatic hydrolysis of α-amylose, the simplest form of starch, to produce the sugar maltose.

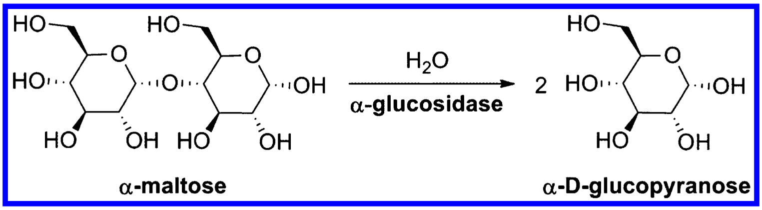

Figure 8. Enzymatic hydrolysis of maltose to glucose by α-glucosidase.

Beer vs Bread

The fermented gruel or porridge discussed above is thought to have evolved into the ultimate products of bread and beer (*15*, *65*). For example, a substantially thickened gruel could represent a form of dough which could be baked to make bread. In this case, the CO_2 released by fermentation would cause in the dough to rise, while the resulting ethanol would be cooked off during baking (*65*). Alternately, the fermentation of a thin, watery gruel could result in a new type of fermented beverage, which would be called a beer in the modern sense. Unlike the previous honey, date, or palm wines, such beers could be made from cereal crops. As such crops were both abundant and could be easily stored, beer could be produced reliably and in significant quantity (*15*, *57*).

Grain domestication and bread-making have long been thought to be inter-connected developments, with bread typically being cited as the primary motivation for the development of agriculture. Some, however, have suggested that cereals may have been domesticated initially for beer production rather than for the making of bread (*33*, *64*, *66*, *68–70*). Originally proposed by Jonathan D. Sauer (1918-2008) of the University of Wisconsin, it is Robert J. Braidwood (1907-2003) of the University of Chicago that formulated this question in 1953 (*33*):

> Could the discovery that a mash of fermented grain yielded a palatable and nutritious beverage have acted as a greater stimulant toward the experimental selection and breeding of the cereals than the discovery of flour and bread making? One would assume that the utilization of wild cereals (along with edible roots and berries) as a source of collected food would have been in existence for millennia before their domestication (in a meaningful sense) took place. Was the subsequent impetus to this domestication bread or beer?

This question generated significant debate, with the majority still favoring bread as the primary motivation for agriculture. This majority was by a fairly narrow margin, however, and arguments for the contributions of beer still remain (*33*, *66*, *68*). Either way, it is likely that the preparation of unleavened bread and beer (and possibly even leavened bread by accident) occurred before the development of agriculture. While no direct evidence is yet known for the production of beer before the practice of agriculture, the large number of wild grains suitable for use in beers, the simple methods involved, and the number of groups who prepare beers are all thought to support such a possibility (*33*).

The connection between bread and beer is further reinforced by the fact that bread was used as an ingredient in some early beers (*32*, *69*). It is such references to the use of bread in brewing in early Mesopotamian and Egyptian cultures that has led to much debate among archaeologists and historians as to the proper chronology of bread and beer. While it is typically argued that bread came first and was later used as a component in beer, some have suggested that bread must be a derivative of beer making and was developed as a means of storing the raw materials of the fermented beverage (*15*). Paul C. Mangelsdorf (1899-1989) of Harvard University gave the following argument in support of beer being the initial cereal product (*33*):

> A fairly good case might be made for an earlier utilization of cereals for brewing than for bread-making, not because thirst was a stronger motive than hunger, but because the earliest grains available were more suitable for beermaking than for bread. The earliest cereals of the Near East - the wild wheats, *Triticum aegilopoides*, *T. thaoudar*, and *T. dicoccoides* and their cultivated counterparts, *T. monococcum* and *T. dicoccum*, and species of barley - are all characterized by the adherence of the glumes (husks or chaff) to the grains after the grains have been removed from the heads. Such glume-enclosed grains are, without additional processing, virtually useless for bread-making but all can be used for brewing and one, barley, is the cereal par excellence for this purpose.

A group of French researchers attempted to address this debate in 2007 (*29*). These efforts involved study of the genetic diversity of *Saccharomyces cerevisiae* via a large-scale evaluation of various yeast populations, including strains associated with both beer and bread (*29*). The genetic differences observed between various yeast groups suggest an ancient divergence leading to local natural populations, from which multiplication may have then been favored by humans. Comparing the genetic relationships of the bread, beer, and wine strains studied, it was proposed that the main group of bread strains could have resulted from a tetraploidization event between an ale beer strain and a wine strain. If correct, this would imply that the production of bread appeared after the production of both beer and wine (*29*).

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Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

Barley Beer

While a number of cereal grains have been successfully used to produce fermented beverages, beer traditionally comes primarily from barley (*Hordeum vulgare L.*, Figure 9). Barley was one of the earliest of the grains to be domesticated, with the cultivation and domestication of emmer wheat (*Triticum dicoccum*), einkorn wheat (*Triticum monococcum*), and barley thought to date to ca. 10,000 BCE (*26*). While the domestication of barley is commonly thought to have first appeared in or near Mesopotamia (*32*, *69*), it has been said that botanical evidence points to its domestication being not in the Near East, but the Far East, possibly Tibet (*33*). It is thought that barley domestication came later in Egypt, although it was firmly established there by the 6th millennium BCE (*71*).

The brewing of barley beer is thought be linked to the early development of formal agriculture (*33*, *68*, *69*). Chemical evidence cited in the support of early barley beer comes from remains in pottery vessels that were unearthed at Godin Tepe, in the Zagros Mountains in Iran (*57*, *70*, *72*, *73*). While the analyzed pottery dates to only the 4th millennium BCE, it is believed that such beer existed even earlier and most date the origin of beer production to ca. 6000 BCE (*32*, *65*).

Figure 9. Hordeum vulgare L. [Botanical print (dated 1885); barley ear photo courtesy of Syngenta].

Of the various grains utilized in beer production, barley produces the greatest amount of diastase enzymes upon germination, with wheat producing only about 50% that of barley (*15*, *32*, *66*, *74*). As a result of the higher diastase enzyme content, the malting of barley produces the greatest quantity of maltose and therefore provides a near ideal grain for the production of beer. Once it was discovered that beer could be produced from watery gruels of barley, the beverage was improved and optimized through trial and error. For example, it was found that the more malted barley there is in the original gruel and the longer it is left to ferment, the stronger the resulting beer. In hindsight this makes sense, as more malt means a greater amount of sugar and longer fermentation times allows more of that sugar content to be converted to the alcohol product (*15*).

As desirable chemical changes occur during the baking of bread, it was ultimately found that cooking the mash of malted grain enhances the strength of the resulting beer. This is due to the fact that the malting process converts only about 15% of the starch in barley to maltose (*15*). However, diastase enzymes become more active at higher temperatures (60-70 °C) which converts more of the grain's starch to sugar, thus providing more maltose for fermentation and even greater amounts of alcohol in the final product (*15*, *32*, *65*). The resulting mixture produced from cooking the malt is referred to as the wort and the final barley beer results from fermentation of the cooled wort (*32*).

A point of clarification needs to be made in differentiating beer in antiquity from modern beverages of fermented grains. The word beer in its modern sense typically refers to a beverage of malted barley or wheat that is brewed in the presence of hops (*Humulus lupulus* L.). The addition of hops to beer gives it a more bitter taste, but more importantly improves its storage properties due to the preservative properties of hops (*75*). However, hops as a component of beer was not introduced until the Middle Ages (*32*, *76*). This innovation is usually attributed to the Dutch (*32*), although it has been pointed out that this practice was introduced into Holland from Germany (*76*). Others point to either the Finnish, Latvians, or Slavs as the first to introduce hops to beer (*31*, *75*). As a result of this late introduction of hops to the beer-making process, the term beer in a historical context refers to all fermented products of the cereal grains and is not limited to just those beverages that contain hops.

Beer maintained a widespread popularity in the cultures of the Fertile Crescent throughout antiquity. Particularly in Mesopotamia and Egypt, beer remained the favorite drink for millennia, fit not only for mortal consumption but deemed worthy of the gods as well (*67*). The Babylonians knew of at least seventy different varieties of beer, and texts of the Anatolian Hittites suggest that only bread surpassed the importance of beer (*32*, *67*). Beer was also popular among both the Phrygians and the Armenians (*67*, *77*), as stated by Xenophon in his *Anabasis* with the following description of Armenian beer (*78*):

> ...and wine made from barley in great big bowls; the grains of barley malt lay floating in the beverage up to the lip of the vessel, and reeds lay in them, some longer, some shorter, without joints; when you were thirsty you must take one of these into your mouth, and suck. The beverage without admixture of water was very strong, and of a delicious flavour to certain palates, but the taste must be acquired.
>
> The high standing of beer in most early cultures is such that it only suffered a decline in popularity after the Greeks Hellenized the Near East. It has been suggested that this change was due to the fact that the Greeks championed wine as a replacement to beer (*67*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

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Beer vs Wine

Of course, it is not possible to properly discuss the history of beer without addressing its often debated chronology in relation with grape wine. The long-standing debate as to which is the older fermented drink, barley beer or grape wine, is complicated by the lack of specificity of the basic terms of beer and wine themselves. In their modern use, the term beer refers exclusively to those beverages made from fermented grains, while wine is almost always associated with those obtained from fermented fruits. Historically, however, these modern associations were much less definite and older terms that are typically correlated to the modern words beer or wine could commonly be used interchangeably. This problem is exemplified by the fact that date wine was often referred to using terms that correlate better to beer than wine (*57*), as well as references in the Old Testament that do not distinguish between beer or wine. Even the Old English word for beer, *beor*, was commonly used to refer to both beer and honey wine (*79*). This underlying issue can been seen among various classic Greek texts as shown by the quote given by Xenophon above, as well as the following by Herodotus, both of which use the term barley-wine to refer to beer (*80*, *81*):

> ...they use habitually a wine made out of barley, for vines they have not in their land.

Besides barley-wine, some Greek writers also referred to beer as barley-mead (*81*).

Even ignoring the complicating factor of ambiguous language, it is quite difficult to ascertain with any certainty whether grape wine or beer was the earlier of the two drinks (*74*). Both are thought to date to ca. 6000 BCE (*32*, *65*), although some have proposed that a “wine culture” was established by at least 7000 BCE (*22*). A common argument to support the claim that grape wine pre-dated beer is to point to the common reference to wine in the Bible, while high-lighting that beer is never mentioned (*74*). It should be noted, however, that the Hebrew words used in the Old Testament for wine are *šêkar* (*shekar* or *shekhar*) and *yayin* (*82*, *83*). While *yayin* specifically refers to wine made from grapes, *šêkar* refers to non-grape wine (*83*) and is typically defined as just an intoxicating drink (*82*). Thus, while both are translated into English as the generic “wine”, *šêkar* most likely refers to date wine (i.e. the most common wine of antiquity), but could also refer to either honey wine or barley wine (i.e. beer) (*82*, *83*). Others have instead quoted the opinions of various classic Greek authors, which emphasize grape wine over beer (*74*). However, the strongest argument given for grape wine over beer has been the fact that unlike the grains used in beer, the principal yeast species responsible for fermentation, *Saccharomyces cerevisiae*, occur naturally in grapes (*25*, *84*).

The combination of the natural presence of *Saccharomyces cerevisiae* in the grape and doubts by some about the airborne transmission of either the yeast or its spores, has led to the argument that a practical understanding of the use of yeast in fermenting grapes must have preceded its use for grain-based foods and beverages such as bread or beer. (*25*, *84*). Through such an argument, it is postulated that yeast used to ferment the later cereal products initially came from grapes, with the yeasts eventually evolving into specific wine, beer, or bread strains over centuries of human selection (*25*). This argument, however, ignores the fact that yeasts also occur naturally in both honey and dates. Thus, a practical understanding of yeast could have logically come from the hundreds to thousands of years of fermentation of these sugar sources before either grape wine or beer. Claims that grape wine predated beer also point to a line in the *Hymn to Ninkasi*, a 1800 BCE hymn to the Sumerian goddess of brewing, (*69*, *85*), that suggests the addition of wine, grapes, or raisins to the wort (*25*, *69*).

As described previously above, a group of French researchers studied the genetic diversity of *S. cerevisiae* via a large-scale evaluation of yeast populations in 2007 (*29*). One of the core questions that this study sought to address was whether evidence could be found that beer strains evolved from wine strains as proposed by the argument given above. Not only could no such supporting evidence be found, but the study's results actually revealed that the beer strains were quite poorly related to wine yeast, leading the researchers to state (*29*):

> However, as beer strains are obviously far from wine yeast, our results do not support the classical hypothesis of wine technology as an origin for beer.

Without the discovery of significant new evidence, it is just not possible to state explicitly which of the two fermented beverages was produced first. What is known at this point is that the dominant drink during the early periods of both Mesopotamia and Egypt was beer (*67*) and the popularity of grape wine only increased with the later influx of Greek influence (*74*). Therefore, it is quite reasonable to propose that both beer and grape wine were introduced at approximately the same time, but that due to the greater accessibility of large amounts of grain, beer became more available and widespread at an earlier time period than grape wine and thus was the more common drink initially (*64*). Others have come to similar conclusions, stating that the restriction of wine production to a limited number of areas during the Bronze Age undeniably resulted from the lack of agricultural conditions necessary for large-scale, sustained production. In contrast, barley was the pervasive cereal staple throughout the archaeological and cultural records of these regions (*74*, *86*).

Beer in Mesopotamia

The production of beer is thought to have first emerged in Mesopotamia as early as ca. 6000 BCE (*32*, *65*). The name Mesopotamia comes from the Greek meaning "[the land] between the rivers" (*57*) and refers to its placement between the Euphrates and Tigris rivers (Figure 1). The floodplains between these rivers were rich with fertile soil due to silt spread during flooding. In addition, the Mesopotamians learned how to irrigate this land by digging canals to carry water from the rivers, thus resulting in a near perfect region for the development of agriculture. Among such efforts was the domestication of cereals such as barley, the optimal grain for beer production (*72*). Because of this, it is perhaps not

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

surprising that the preferred fermented beverage of the ancient Sumerians was beer (*66*, *72*). Of course, the popularity of beer was not limited to just the Sumerians and the consumption of beer was common throughout Mesopotamia during all time periods and by all social classes, both men and women alike (*68*).

While a growing number of chemical archeological findings have been reported for early wine, this is not the case for beer and the only real chemical evidence relating to beer in Mesopotamia comes from the analysis of a pale yellowish residue found in the grooves of a jar from Godin Tepe (*57*, *70*, *72*, *73*). Godin Tepe is a site of strong Lower Mesopotamian influence and resides in the Zagros Mountains of modern Iran. The double-handled jug dates to the Late Uruk period (~3500-2900 BCE) and was recovered from a room also containing a wine jar (*73*). Based on this and other contextual evidence, the authors felt confident that this vessel served as a container of beer.

The yellow residue was isolated and analyzed via a Feigl spot test for oxalate (Figure 10) (*87*), which gave a positive response (*70*, *72*, *73*). The residue was then assumed to consist of calcium oxalate, a principal component of "beerstone," an insoluble deposit which accumulates on the inner surfaces of fermentation and storage vessels for beer. Due to this formation of beerstone during brewing, the presence of calcium oxalate has been used to support the evidence of beer in such archeological studies (*68*, *70*, *72*, *73*). For comparative purposes, tests were also carried out on scrapings from an Egyptian New Kingdom blue-painted jar (which tomb paintings and reliefs suggested was used for beer) (*68*, *72*, *73*), beerstone from a modern brewer's vat, and a pure sample of calcium oxalate. In all cases, similar results to the isolated yellow residue were obtained (*72*, *73*) and the oxalate in the jar was thus attributed to fermented grain products once held by the jar (*72*). As such, the chemical analysis was reported to confirm the archaeological and pictographic evidence that the vessel was a beer jug (*73*).

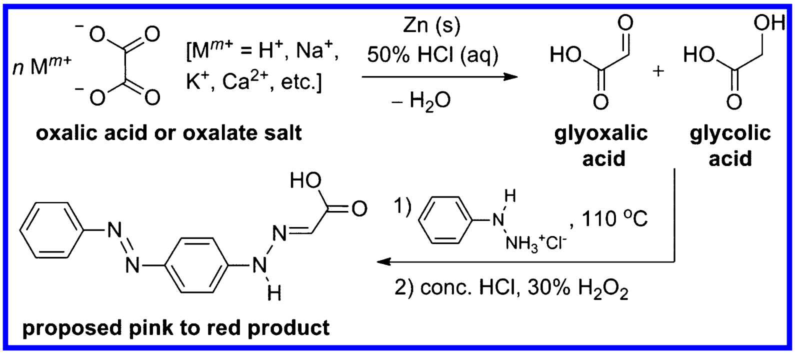

Figure 10. Feigl spot test for oxalate.

It must be pointed out, however, that oxalate salts are very simple chemical species and can be present as the result of a number of sources. The calcium salt is known in three primary forms: the monohydrate $Ca(C_2O_4)\cdot H_2O$ (whewellite), the dihydrate $Ca(C_2O_4)\cdot 2H2O$, and the polyhydrate $Ca(C_2O_4)\cdot(2+x)H_2O$ (weddelite) (*88*). Microcrystals of the polyhydrate are found in some plants, and can sometimes be found as a sediment in cooled urine. In fact, human kidney stones are primarily crystals of the polyhydrate (*88*). Microcrystals of the monohydrate are also common in higher species of plants and the authors of the archeological study above point out that oxalates occur naturally in spinach and rhubarb (~5-10% by fresh weight), species of which grow today in the Iranian highlands (*72*, *73*). In addition, both the monohydrate and polyhydrate are known mineral species whewellite and weddelite, respectively (*88*). Because of the facts outlined here, it has been pointed out by some that deposits of oxalates could just as well result from the pottery being buried in oxalate-rich soil (*64*, *68*).

Another point that needs to be clarified is that while the Feigl spot test for oxalate is quite sensitive (detection limit of 1 μg), Feigl warns that samples containing either glyoxalic or glycolic acid will give a false positive (*87*). In order to eliminate such false positives, it is necessary to first precipitate the sample as the insoluble calcium oxalate salt and wash well with water in order to remove the presence of any other acids or salts (*87*). Assuming that the sample isolated from the pottery sherd was beerstone, washing first with water prior to the chemical test should be sufficient, but no pretreatment was reported (*72*, *73*).

To be fair, the authors did analyze the exterior of the jar from which the yellow residue was isolated, as well as the interior of one of the wine jars from the same site in order to rule out various environmental oxalate contributions as discussed above. The Feigl spot test was again used, for which both cases gave negative results (*72*, *73*). Still, it is not possible to reliably say that any oxalate detected is from beerstone and it is recognized that there are currently no reliable biomarkers for confirming the presence of beer in ancient residues (*68*). Others have gone so far as to state that all organic residues from antiquity can be challenging and unreliable samples for analysis (*68*, *86*), a topic which will be discussed in more detail in the following section on wine.

In general, the history of alcoholic beverages in Mesopotamia can be more complex than that of other regions such as Egypt or the Levant. This is largely due to the fact that older societies typically provide more fragmentary evidence of their history and practices. Still, various pieces of evidence have been collected over the years to help create a strong circumstantial case for the place of alcoholic beverages in early Mesopotamian history (*11*). For example, written records have provided much useful information. The Mesopotamians wrote the bulk of their records on clay tablets, and such tablets containing recipes for beer have been found dating back to ~2800 BCE (*66*, *68*, *70*). Some sources have even claimed recipes dated to yet older periods (*8*, *89*). Additional information relating to beer in Mesopotamia includes laws pertaining to beer parlors as detailed in the *Code of Hammurabi*. This text is dated to the 18th century BCE and details laws codified by King Hammurabi of Babylon (*32*, *69*). Archaic texts from the Sumerian city of Uruk also list quantities of goods manufactured, stored, and distributed, including beer (*11*, *70*). One such archive records the production of at least eight different types of beer (*11*).

The recipes included in these ancient tablets were generally not true detailed recipes and some are really too fragmented to be of much use. More commonly, these tablets are temple accounts which document the type and amount of grain issued to brewers and the amount of beer produced in return. As a result, these texts at least provide a list of the ingredients used in beer production and the ratios

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

involved (*68*). Perhaps the best studied of these is known as the *Hymn to Ninkasi*, which was written about 1800 BCE and has been found on tablets at Nippur, Sippar, and Larsa (*32*, *68–70*). This hymn is in praise of Ninkasi, the Sumerian goddess of brewing, and in the process gives a basic outline of the brewing process (*32*, *66*, *69*, *70*, *85*). The hymn was translated in 1964 by Miguel Civil of the Oriental Institute at the University of Chicago (*85*). In 1991, however, he revisited the hymn (*68*, *69*) to give the following refined translation (*69*):

Borne by the flowing water [...],
Tenderly cared for by Ninhursag,
Ninkasi, borne by the flowing water [...]
Tenderly cared for by Ninhursag.

Having founded your town by the sacred lake,
She finished its great walls for you,
Ninkasi, having founded your town by the sacred lake
She finished its great walls for you.

Your father is Enki, Lord Nudimmud,
Your mother is Ninti, the queen of the sacred lake.
Ninkasi, your father is Enki, Lord Nudimmud,
Your mother is Ninti, the queen of the sacred lake.

You are the one who handles the dough [and] with a big shovel,
Mixing in a pit, the bappir with sweet aromatics.
Ninkasi, you are the one who handles the dough [and] with a big shovel,
Mixing in a pit, the bappir with [date]-honey.

You are the one who bakes the bappir in the big oven,
Puts in order the piles of hulled grain.
Ninkasi, it is you who bake the bappir in the big oven,
Puts in order the piles of hulled grain.

You are the one who waters the malt set on the ground,
The noble dogs keep away even the potentates.
Ninkasi, you are the one who waters the malt set on the ground,
The noble dogs keep away even the potentates.

You are the one who soaks the malt in a jar,
The waves rise, the waves fall.
Ninkasi, you are the one who soaks the malt in a jar,
The waves rise, the waves fall.

You are the one who spreads the cooked mash on large reed mats,
Coolness overcomes,
Ninkasi, you are the one who spreads the cooked mash on large reed mats,
Coolness overcomes,

You are the one who holds with both hands the great sweetwort,
Brewing [it] with honey [and] wine.
[You the sweetwort to the vessel].
Ninkasi, [...],
[You the sweetwort to the vessel].

The fermenting vat, which makes a pleasant sound,
You place appropriately on [top of] a large collector vat.
Ninkasi, the fermenting vat, which makes a pleasant sound,
You place appropriately on [top of] a large collector vat.

When you pour out the filtered beer of the collector vat,
It is [like] the onrush of the Tigris and the Euphrates.
Ninkasi, you are the one who pours out the filtered beer of the collector vat,
It is [like] the onrush of the Tigris and the Euphrates.

The hymn has been taken to be a linear account of brewing and seems consistent with the basic steps for the production of barley beer. It has been pointed out, however, that as some passages are relatively obscure, the translation is influenced to a large extent by knowledge of modern brewing methods. Because of this, opinions on the meaning of various aspects differ greatly in the literature (*70*). One point of considerable interest is the fact that the hymn does not mention the process of malting (*68*), although one verse has been translated to include the word malt (*69*, *85*). As a result, some have proposed that malt preparation was not a part of brewing in Mesopotamia (*68*), while others feel that malted barley was probably added at a later point (*69*). Interpretation of the hymn as a recipe for beer was finally put to the ultimate test by Solomon Katz of the University of Pennsylvania and Fritz Maytag of the Anchor Brewing Company (*68*, *69*). Using the hymn as the basis for the modern brewing of a Sumerian beer, they produced a beer that they named *Ninkasi*. The resulting beer had an alcohol content of 3.5%, with what was described as a dry flavor lacking in bitterness, tasting similar to a hard apple cider with the fragrance of dates (*69*).

Based on the evidence currently available, it is generally thought that beer in Mesopotamia was prepared via the following processes. The initial step was preparation of the malt by soaking the barley in water and allowing it to germinate for a short time (*56*, *68*). The germinated barley was then dried, either by laying it out in the sun for about three weeks, or by lightly heating it in a kiln. The result of this process was "green" malt, which was then kilned at a slightly higher temperature to produce "cured" malt (*68*). This malt is then thought to have been crushed by pounding and sieved to remove husks and other debris. The crushed grain was then either stored or converted into dough and baked in a domed oven (*56*, *68*) to produce small malt loaves called *bappir* in Sumerian or *bappiru* in Akkadian (*68*). These loaves normally contained various aromatic components and represented one of the primary raw materials for fermentation (*68*). Records indicate that such loaves were kept in storehouses and were eaten only during food shortages, leading to the conclusion that they were a convenient way to store the

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Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

raw material for making beer, rather than a foodstuff (*15*, *69*). The loaves of bappir were then crumbled into water (possibly with more grain), heated, and mixed to make the mash (*56*, *68*). After cooling, sweeteners such as honey or date juice were often added to the mash, which was then allowed to ferment with regular stirring. Once fermentation was complete, the mash was transferred to a clarifying vat that permitted the removal of some sedimentation (*68*). The final beer was then drawn off and placed into stoppered jars to prevent the further fermentation which would make the beer acidic (*56*, *68*).

Beer in Mesopotamia from the oldest periods was thought to be served unfiltered, which is supported by evidence from ancient Phrygia (8th-7th century BCE) in Anatolia that indicates that brewing left barley husks and other solid matter in the beer. To avoid consuming this solid material, these unfiltered beers were drunk through a straw from an open vessel or from a jug with a sieved spout attached to the main body (*32*, *66*). This practice is illustrated by iconographic evidence (3rd millennium BCE) that depict banquet scenes in which individuals are drinking from vessels through large tubes or straws (Figure 11) (*15*, *90*, *91*). Such scenes appear in both glyptic and decorative arts, and objects such as drinking vessels and straws have been found in elite burial sites, especially the Royal Cemetery at Ur (*68*). However, not all Mesopotamian beer was unfiltered, with historical evidence also indicating the brewing of filtered beers. It is believed by some that the move to filtered beer constitutes a major change in brewing technology during the mid-3rd millennium BCE (*68*).

Figure 11. Sketch of a Mesopotamian seal depicting drinking from tubes, ca. 2500 BCE. [Reproduced with permission from reference (64). Copyright 2014 Springer Science and Business Media].

An increase of spouted jars and flasks found from the Ubaid and Uruk periods has led to the view that the consumption of beer increased throughout the 4th and 3rd millennia BCE. In contrast, the study of texts of the 3rd and 2nd millennium BCE reveal that while beer rations are regularly referenced in the 3rd millennium, they rarely occurred in the 2nd millennium and were mostly replaced by documentation of the royal distribution and consumption of wine (*11*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

Beer in Egypt

Bread and beer were dietary staples of the ancient Egyptians (*92–97*) and written records of the Early Dynastic period (3100-2686 BCE) indicate that beer was an important and well-established feature of Egyptian culture (*74*). Additional evidence for Egyptian beer production extends even further back to the Predynastic era (5500-3100 BCE) (*31*, *74*) and this long record of beer-making is most likely why many Greek authors credit the Egyptians with having invented beer. This assertion, however, is not supported by modern historians (*74*).

Early Egyptians made beer from malted barley, emmer wheat, and combinations of both grains to produce a number of different varieties (*11*, *71*, *81*, *92–95*). In addition, textual evidence suggests that some beers were also flavored by the addition of dates, lupins, fruits, or wines (*11*, *31*, *81*, *92–94*). Egyptian beers were drunk by all social classes, from the Pharaoh downwards (*74*, *93*, *95*, *96*), and beer was integral part of daily life (*74*). This was in stark contrast with the Hellenistic period site of Alexandria. Here, Greek influence devalued beer such that it was said to be primarily limited to the lower classes (*31*).

While at least some of these beers were said to be strongly intoxicating, it has been thought by some that typical Egyptian beer would have been drunk daily as a refreshing and reliable substitute for water, which may not always have been especially clean (*8*, *71*, *94*). Such beers brewed for daily consumption would most likely not have been very alcoholic and would have had a relatively short shelf-life. These properties would have required frequent brewing and immediate use with no long-term storage (*74*).

Evidence of beer in Egypt has been claimed from the analysis of jars at Abadiyeh, a Predynastic site on the east bank of the Nile in upper Egypt, as well as at Naqada on the west bank of the Nile, one of the largest Predynastic sites in Egypt (*74*, *97*). The most extensive evidence for Egyptian beer production, however, comes from excavations of two Predynastic sites at Abydos and Hierakonpolis, which uncovered what is considered to be the remains of breweries, including double rows of large vats (*11*, *93*, *97*). A hardened black residue with embedded cereal grains was recovered from these vats, with initial chemical analysis suggesting that the contents of the vat could have been beer (*93*). Two additional samples recovered from these vats were later analyzed in efforts to determine their composition. Characterized as amorphous charred residues, macro- and micro-scopical examination were reported to reveal the presence of intact remains of wheat and barley, as well as fragments of dates and grape pips.

Chemical analysis was performed on the residues and while most of these were determined to be ash, three water-soluble fractions were isolated via ion exchange chromatography, which were reported to be sugars, amino acids, and organic acids (*97*). The sugar fraction was then *O*-silylated and analyzed by gas chromatography (GC), with the authors reporting that it contained xylose, mannose, galactose, glucose, galacturonic acid, and glucuronic acid, as well as three unknown chemical species. In a similar fashion, the carboxylic acid fraction was treated with diazomethane and analyzed by gas-liquid chromatography, with the fraction reported to contain oxalic, succinic, tartaric, lactic, and malic acids (*97*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

Finally, the amino acid fraction was analyzed by high pressure ion exchange chromatography, with the authors reporting the fraction to consist of ~30% ammonia, with the remainder attributed to 16 different amino acids (*97*). It needs to be stressed, however, that at no point did the authors report the use of any chemical method to confirm the identity of any of the species reported and all conclusions were based solely on comparison to the retention times of commercial standards (*64*). Regardless, the authors were confident that this data confirmed that the vat residue samples were fermentation products of cereal grains and fruit material (*97*). In addition to concerns by some concerning the rigor of the analysis methods reported (*64*), Delwen Samuel of Kings College London has pointed out that such studies ignore any potential contamination by microorganisms or effects of degradation due to the age of the residues (*93*).

One of the earliest known written descriptions of Egyptian beer production methods was given by the alchemist Zosimus of Panopolis in ca. 300 CE. A 1922 translation of this account states (*74*):

> Take fine clean barley and moisten it for one day and draw it off or also lay it up in a windless place until morning and again wet it six hours. Cast it into a smaller perforated vessel and wet it and dry it until it shall become shredded and when this is so pat it (i.e. shake, or rub) in the sunlight until it falls apart. For the must is bitter. Next grind it and make it into loaves adding leaven, just like bread and cook it rather raw and whenever the loaves rise, dissolve sweetened water and strain through a strainer or light sieve. Others in baking the loaves cast them into a vat with water and they boil it a little in order that it may not froth nor become luke-warm and they draw up and strain it and having prepared it, heat it and examine it.

Interpretations of early Egyptian brewing activities have also resulted from the numerous artistic records of ancient Egypt (wall-reliefs, paintings, models, statues, etc.) (*74*, *92–95*). Although there is vague general agreement on the basic brewing methods utilized, no consensus of opinion concerning the precise details has developed and most interpretations vary in particular aspects of production (*94*, *95*). Nevertheless, the general process proposed for the Egyptian brewing methods based on these artistic sources is as follows. First a calculated quantity of grain would be moistened, placed into a mortar, and ground. Yeast would then be added and the mixture worked into a dough which would be placed into earthenware vessels. This was then heated over a slow-burning fire to partially bake the dough (*31*, *74*, *93*, *94*). The resulting loaves were then crumbled into a large vat of water, where fermentation would occur (*31*, *74*, *89*, *92–94*). Some believe that honey was also added in some cases, which might explain the term barley-mead used by some authors (*81*). As this additional sugar source could produce a higher alcohol beer, this could explain the description by some classical authors of Egyptian beer's highly intoxicating nature (*31*).

Following fermentation, the porridge-like mixture would be transferred to a woven basket-work sieve, where it would be kneaded by hand to force the separation of the liquid fraction into a large, wide-mouth jar situated below. This

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

filtered beer was then transferred into the final beer jars, which are normally shown as being held in some sort of rack, and sealed with a ball of mud in the neck of the jar (*31*, *74*). Of course, it has been pointed out that the artistic evidence is not completely clear and notable discrepancies in these interpretations persist (*92*, *94*, *95*). The most critical point of debate is to what extent malt was used in this process (*31*, *94*). Another consideration is the lack of knowledge of how these brewing practices might have changed over time (*93*, *95*).

As outlined by the descriptions above, the Egyptian methods are usually described as utilizing partially baked barley loaves in a similar manner to the previously discussed Mesopotamian processes, which probably accounts for the view that Egyptian bakers often doubled as brewers (*67*). As with beer, traditional descriptions of ancient Egyptian bread-making also rely on artistic depictions and written sources. Unfortunately, it has been noted that little information on bread ingredients is included in known written sources (*92*).

In efforts to provide new perspectives on Egyptian brewing and baking methods, the systematic analysis of desiccated bread loaves and cereal residues by optical and scanning electron microscopy (SEM) was reported by Delwen Samuel in 1996 (*92*, *94*). The cereal residues studied were from two sites: Deir el-Medina (1550-1307 BCE), on the west bank of the Nile (*74*, *92–94*), and the Workmen's village of Amarna (~1350 BCE) in middle Egypt (*92–94*). The bread analyzed came from various sites dating to 2000-1200 BCE. The samples were first examined optically to provide data about ingredients and their quantities, texture, and any unintended inclusions (*92*). While the texture of both groups of samples ranged from fine to coarse, a common feature limited to the cereal residues was the presence of large amounts of chaff. In addition, substantial quantities of coarsely shredded husks were found in residues from large jars and thin coatings revealed embedded husk slivers along with small bran pieces.

The beer residue microstructure was then investigated by SEM examination to reveal a wide range in starch morphology, from undistorted but pitted granules to fully fused starch. This observed microstructure was attributed to the use of a two-part brewing process – one involving coarsely ground, well-heated malt or grain; and another based on unheated malt (*92–95*). Samuel points out that it seems plausible that ancient Egyptians used a variety of techniques to kiln germinated grain or to process unsprouted brewing grains, which might account for the variety of named beer types listed in ancient sources (*94*). Samuel goes on to stress that the microstructural data does not match the accepted use of lightly baked bread for brewing as described in the generally accepted process detailed above. It is believed that such loaves would contain unblistered, undistorted, and pitted starch granules, but would not provide the large quantities of well-fused starch found in the analyzed residues. Alternatively, if moist loaves had been baked long enough to create the completely merged starch observed, few unblistered and undistorted starch granules should have remained (*92*, *93*).

The yeast content in the residues investigated was then used in an attempt to gain insight into the fermentation stage of Egyptian brewing. Most of the large samples obtained from whole jars revealed no traces of yeast, but coarse grain fragments and large pieces of chaff, which was attributed to the contents consisting of spent grain (i.e. residues left after sugars, dextrins, and starch were rinsed from the processed malt). Samuel thus proposed that fermentation began in the rinsed sugar- and starch-rich liquid obtained by removal of the husk (*92*, *93*).

Clearly, Samuel's conclusions (*92–94*) are in stark contrast with those formed from artistic depictions and later period sources (*74*, *89*, *92*). However, no single study has yet been able to provide a definitive view of ancient Egyptian brewing methods and the existence of multiple proposed processes indicates that our current understanding of these methods is far from complete, with ample room for further research (*94*). Of course, it is entirely possible that the Egyptians did not use a single, uniform process for brewing. This view was proposed by 1911 by John Arnold (*81*), reasoning that number of different beers known to be produced by the Egyptians could be the result of different ingredients, but could quite reasonably also be the result of multiple brewing processes.

Grape Wine

Of course, when one discusses wine, it is usually in reference to wine produced from grapes, even if it is commonly accepted that other wines predated the traditional grape wine. The earliest grape wine was thought to be produced from the wild ancestor of the Eurasian grape, *Vitis vinifera sylvestris*, which was generally limited to the higher elevations north of the Fertile Crescent (*13*, *16*, *86*, *98–100*). Small isolated populations of the wild grapevines can still be found from the Atlantic coast of Europe to Tajikistan and the western Himalayas (*16*, *99*) and the use of these wild grapes as a food source by Paleolithic hunter-gatherers has been well documented at many sites across Europe (*99*).

Although grapes of the wild ancestor are generally smaller and more sour than cultivated grapes, they are thought to have been suitable for wine production (*16*, *86*). However, due to the confined areas of wild grapevine populations, early availability of the grape was much limited in comparison to either the date palm or cereal grains. As such, the widespread and common use of grape wine is closely tied to the domestication and cultivation of the wild grape (*32*), resulting in the domesticated Eurasian grape (*Vitis vinifera sativa*) (*20*, *99*) and ultimately the domesticated common grape (*Vitis vinifera vinifera*) (*21*, *86*, *100*).

Wine production is thought to have most likely originated in the mountainous region between the Black Sea and the Caspian Sea around 6000 BCE (*8*, *16*, *32*, *98*, *99*), although some have claimed that a "wine culture" existed by at least 7000 BCE (*20*, *22*). Molecular archaeological data from Haiji Firus Tepe in the northern Zagros Mountains of Iran provides the oldest known evidence of large-scale wine production dating back to 5400-5000 BCE (*13*, *16*, *86*, *90*, *100–102*). Reports claim that even earlier chemical evidence has been obtained, relating to what appear to be remains of domesticated grapes, from the early 6th millennium BCE in the Neolithic village of Shulaveris-Gora in the Transcaucasus region of modern Georgia (*25*). Domesticated grape pips dating from the 6th millennium BCE have also been reported from Chokh in the Dagestan Mountains of the northeastern Caucasus, as well as grape remains dating from the 5th through early 4th millennia BCE from Shomutepe and Shulaveri in Transcaucasia (*13*,

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

102). Chemical analyses from other sites, generally dated between 6000-3000 BCE, have also provided evidence of ancient grape remains or wine jars (*16*, *22*).

Once winemaking was established as a viable endeavor in the Neolithic period, the trading of wine followed (*102*). It is thought that such trade then introduced grape wine to the royalty and the upper classes of Egypt and Mesopotamia, resulting in the development of viniculture and wine production in those early civilizations (*13*, *15*). As a demand for grape wine was built up among the elite during the 4th millennium BCE, it was traded broadly overland and via available waterways (*13*), and wine became a focal point for the economy of emerging societies during the Early Bronze Age (*11*).

As the demand for wine developed, the domesticated grapevine was transplanted south and ultimately into lowland regions, thus allowing the development of local wine production (*13*, *102*). This is demonstrated by the well documented wine trade between southern Palestine and the Nile Delta, which resulted in early Egyptian viniculture (*13*). Wine production then continued to spread and wine became the drink of choice for the Greeks, Romans, and Celts, in part because many areas in Europe were well suited to the grapevine (*32*).

Our current view of the history of grape wine comes from a variety of sources, of which artistic, linguistic, and archaeological records play critical roles. However, in comparison to the fermented beverages discussed above, a greater number of chemical archeological studies have been reported on residues related to wine. As such, it is worth reviewing the extent of knowledge provided by these reports.

Chemical Archaeological Studies Relating to Grape Wine

Over the last few decades, considerable advances have been made in the analysis of organic deposits in attempts to detect potential remnants of wine (*86*, *103*, *104*). Residues of interest include either preserved contents of ancient vessels or material absorbed in the ceramic matrix of unglazed pottery sherds (*86*, *103*), the unambiguous identification of which is notably challenging due to low trace levels and the overall chemical complexity of the residues analyzed (*104*). The primary difficulty in the confident identification of residues is the specificity of appropriate chemical biomarkers, as many chemical species are distributed widely in the environment. Additional complications arise from biomarker loss or degradation, as well as sample contamination (*86*).

The earliest chemical analysis of wine-related residues was reported in 1962 with the study of wine jars recovered from the tomb of Tutankhamun (ca. 1300 BCE) in Thebes and the Monastery of St. Simeon near Aswan (*86*). The residues were analyzed via a combination of wet chemical spot tests, solubility, and melting point determinations, from which the detection of potassium carbonate and potassium tartrate was reported. As the latter of these is present in grapes in high concentration (ca. 4000 ppm) (*86*, *103*), the authors concluded that the contents were wine residues. Tartaric acid and its salts have since become the favored biomarkers for the detection of wine.

Wine residues were then reported in the 1970s from wine vessels recovered from the shipwreck of La Madrague de Giens (75-60 BCE). One of the intact

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

and sealed vessels was reported to contain both liquid and solid phases, although the contents had been contaminated by sea water (*86*). Here, the samples were analyzed by GC to identify tartaric acid and various phenolic acid derivatives (tannin and anthocyanin degradation products). It should be pointed out, however, that while retention times from chromatography techniques can be compared to known standards, retention times are not unique. As such, retention times alone are not conclusive identification of chemical species.

The modern era of wine analysis then really began in 1993, with the study of a red deposit from jars recovered from Godin Tepe, in the Zagros Mountains of Iran. Dating to the Late Uruk period (~3500-2900 BCE), the jar contents were felt to be wine remains based on contextual evidence (*20*, *73*). The sample was analyzed by transmission and diffuse-reflectance FTIR spectroscopy, the results of which compared favorably to that of the naturally occurring L-(+) isomer of tartaric acid. Its presence was further supported by a positive Feigl spot test for tartaric acid, leading to the conclusion that the jars likely contained wine (*73*).

The Feigl spot test (*105*) (Figure 12) used here treats tartaric acid with [1,1′-binaphthalene]-2,2′-diol (BINOL) in concentrated sulfuric acid at 85 °C for 30 min to generate a green fluorescent dye (*73*, *105–108*). While the identity of the green dye is unknown, the test is quite sensitive and can detect tartaric acid down to 10^{-5} g (*105*). However, Feigl points out that a number of related acids (Figure 12) react under these conditions to also give a green dye (*105*) and thus the presence of any of these acids in the samples could give a false positive (*98*).

The oldest known chemical evidence to date was reported in 1996, with the analysis of a jar from the Neolithic village of Jajji Firuz Tepe in the northern Zagros Mountains (*13*, *101*). Dated to 5400-5000 BCE, the jar contained a yellowish residue that was analyzed by diffuse-reflectance FTIR spectroscopy, HPLC coupled with ultraviolet spectroscopy, and Feigl spot tests (*13*, *20*, *101*). The collective results were consistent with the presence of calcium tartrate and resin of the terebinth tree (*Pistacia atlantica Desf.*). This tree grows throughout the Middle and Near East, and terebinth resin was widely used as an early wine additive (*13*, *101*). Based on their analysis, the authors concluded that the residue was the remains of a mixture of a grape product and terebinth resin, with the grape product most likely grape wine (*13*, *20*, *90*).

Between 1996 and 1998, several additional reports of residue analysis appeared, including analysis of residue from Uruk in southern Mesopotamia dated ca. 3500-3100 BCE (*108*), residue from Malkata, the palace complex of Amenhotep III (14th century BCE) in western Thebes (*107*), and analysis of wine jars from a royal tomb at Abydos (ca. 3150 BCE) (*13*, *23*, *106*). In all cases, these analyses utilized the same methods as applied at Jajji Firuz Tepe above to provide evidence of tartaric acid and tartrate salts, as well as a tree resin (*13*, *23*, *106–108*). While some resins were suggested to be from terebinth (*106*, *107*), the chromatographic results were inconclusive (*13*, *107*). As before, the authors concluded that the residues were the remains of a grape product, with the jars from which they were isolated strongly suggesting wine (*13*, *106–108*). Further support for at least one sample coming from wine was the identification of a DNA segment that belonged to the wine yeast, *S. cerevisiae* (*23*).

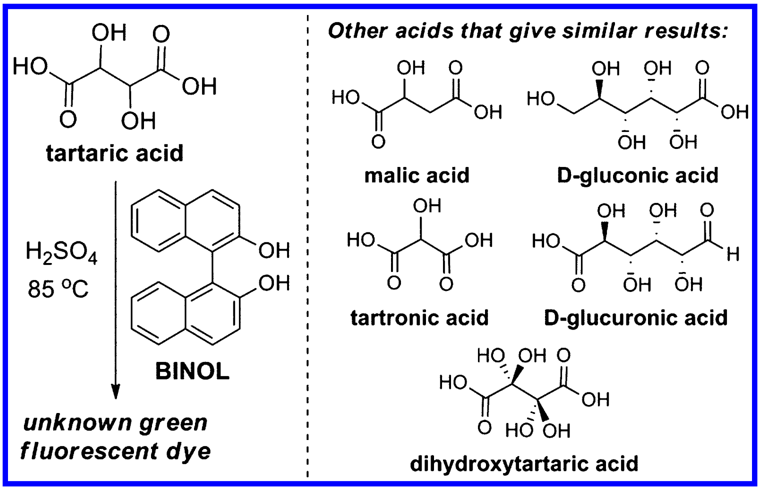

Figure 12. Feigl spot test for tartaric acid.

A new method for the detection of tartaric acid was then introduced in 2004. In efforts to overcome the lack of selectivity and sensitivity of the previously applied methods, special extraction procedures using NH_4OH were developed in order to obtain samples with higher tartrate concentrations (*20*). Liquid chromatography (LC) was then used to separate the sample into its components, which were directly analyzed using a triple quadrupole tandem mass spectrometer (MS/MS) (*109*). Three jars from the British Museum in London and two jars from the Egyptian Museum in Cairo were analyzed using these new methods, with the jars originated from various sites, including Abydos, Nubia, Thebes, and El Amarna, with associated dating ranging from ca. 3100-1300 BCE (*109*). Tartaric acid was detected in four of the five cases, although all but one sample required the use of the MS/MS multiple reaction monitoring mode, providing the highest sensitivity. Tartaric acid was identified in all cases by both LC retention time and MS/MS fragmentation patterns, both of which compared well to the standard analyzed under the same conditions (*109*).

While the various methods discussed above can offer convincing evidence for the presence of tartaric acid and its salts, tartrate alone does not conclusively prove that the analyzed residues originated from grape wine. Supporters of its use as an identifying biomarker for grapes and wine claim that tartaric acid and its salts occur “in large amounts only in grapes” (*20*, *21*, *73*, *101*). While it is true that grapes contain large amounts of tartaric acid (~4000 ppm), this concentration does vary based on the ripeness and variety of the grape, as well as the geographical latitude in which it is grown (*103*). Those doubting its reliability as a biomarker, however, have pointed to multiple plant sources with even greater tartaric acid content (*103*). Such examples include the fruit of the hawthorn tree (*Crataegus monogyna*, 16,000 ppm) (*19*, *103*), tamarind (*Tamarindus indica*, 180,000 ppm), star fruit (*Averrhoa carambola*, 25,000 ppm) and the yellow plum (*Spondia mombin*, 15,000 ppm) (*103*). Although most of these are not native to the Near East, hawthorn was used in the Anatolia as early as the 2nd millennium BCE. In addition, it has been pointed out that the amounts of tartaric acid have only been quantified for a limited number

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

of species and additional plants may yet be found to also contain high amounts of tartaric acid (*103*).

Another issue is the high water solubility of tartaric acid, which can cause it to leach readily out of buried vessels, as well as potentially leaching into adjacent ones. This then makes the presence or absence of tartaric acid in archaeological samples difficult to interpret (*103*). While less of an issue for its calcium or monopotassium ($KC_4H_5O_6$) salts, the dipotassium salt ($K_2C_4H_4O_6$) exhibits a solubility even higher than that of the acid. Because of these issues, tartrate species can only serve as reliable biomarkers for the grape in dry conditions favorable for the preservation of organic materials. Lastly, even if grapes are the source of the tartrate, this does not confirm the presence of wine, but could instead point to unfermented species such as grapes, its juice or syrup, and even raisins (*103*).

As an alternate approach, the biomarker malvidin (Figure 13) was introduced for the detection of red wine in 2004 (*109*). Malvidin and malvidin-3-glucoside are the major species responsible for the red-purple color of grapes and wines (*103*, *109–111*). Over time, these compounds react with other species in the wine to generate more stable pigments (Figure 13), resulting in the darker dusky red-brown hue of mature wines (*103*, *109–111*). These oligomeric and polymeric pigments exhibit low water solubility and cause the persistent nature of red wine stains. As such, these pigments would be expected to be well preserved in archaeological contexts. However, their isolation and identification has proven difficult due to their large molecular weight, their heterogeneous nature, and the fact that they are present in much lower amounts relative to the monomeric parents (*103*, *110*). These species, however, can be decomposed with strong base to release syringic acid (Figure 13) which can then be detected by analytical methods (*103*, *109*). To test the viability of malvidin as a wine biomarker, a sample previously analyzed to reveal tartaric acid was analyzed by LC-MS/MS both before and after treatment with aqueous KOH (*109*). Using the more sensitive multiple reaction monitoring mode of the MS/MS, syringic acid was successfully detected after alkaline treatment. As syringic acid was not detected from the sample before the alkaline treatment, the authors felt confident that the syringic acid detected was the result of the base-mediated cleavage of malvidin (*109*).

Malvidin was used as a biomarker again in 2011 during the analysis of four ancient potsherds from Armenia and Syria (*103*). The Syrian sherd (ca. 2200 BCE) had been suggested to possibly contain red wine, while the three Armenian samples were from a site dated to 4223-3790 BCE that was believed to be a grape pressing facility, based on the presence of various grape remains (grapes, seeds, rachises, and skins) (*103*). The primary improvement to the methodology was the use of solid phase extraction to clean the samples and remove any background syringic acid from the polymeric material before the base treatment. Such sample preparation is critical as syringic acid is present in a number of plant products, as well as soil and other organic environments due to microbiological activity. The pretreated samples were then treated with aqueous KOH to decompose the pigments and analyzed using LC-MS/MS. The positive detection of malvidin was

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

obtained for two of the Armenian potsherds, while the Syrian sherd gave a negative result, thus casting doubt that it had contained wine (*103*).

The authors are careful to point out that malvidin is present in pomegranate, which was sometimes added to wine. Significant amounts of malvidin are also present in whortleberry (*Vaccinium myrtillus*), red clover (*Trifolium pratense*) and high mallow (*Malva sylvestris*), all of which are collected and used by humans. As previously discussed for the presence of tartaric acid in plants, the amounts of malvidin in plants have only been quantified for a limited number of species, although it is expected to be present in fewer species than tartaric acid (*103*). Still, as with tartrate, the detection of malvidin alone cannot be used to reliably specify the presence of grapes and it gives absolutely no information as to whether or not the analyzed material was a fermented product.

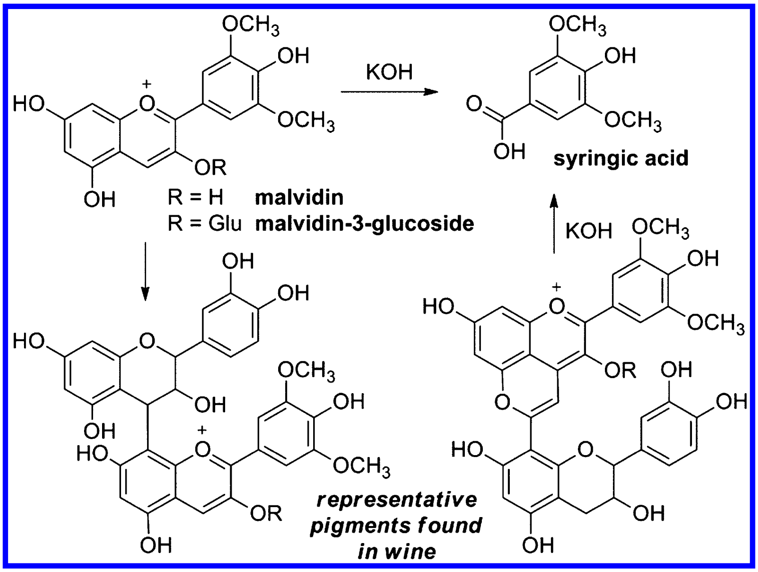

Figure 13. Malvidin and its reactions.

In an attempt to provide methods for the direct evidence of fermentation, the potential detection of ergosterol as a possible biomarker for yeast was proposed in 2010 (*104*). In this way, the detection of biomarkers for both yeast and grapes in a chosen sample would then provide more confidence that the residue was from a fermented product. As ergosterol is a sterol specific to the fungal kingdom, its detection in organic pottery residues could provide evidence of the presence of yeasts. However, the authors acknowledge that the growth of mold and other fungi on the potsherds could also contribute ergosterol and could therefore compromise its viability as a useful biomarker (*104*).

As can be seen from the summary above, the ability to obtain definitive historical context from the analysis of organic residues is still quite difficult, even with recent innovations in the chemical analysis of archaeological samples (*98*). Some authors have even gone so far as to say that it may never be possible to get reliable confirmation from such samples (*86*):

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

> Ancient organic residues are, quite simply, bad and rather intractable samples; by definition, residues are alteration products, modified by unobservable cultural practices, subjected to poorly understood degradation processes, and often contaminated during burial through to recovery, storage, and even analysis.

Viniculture

The cultivation and ultimately domestication of the wild grape eventually led to viniculture (also known as viticulture). Of course, the question is exactly how early did the domestication of the Eurasian grapevine occur and whether this transpired in a single place at a certain time, or whether it was domesticated in many different places and times (*16*, *20–22*, *99*). These queries have led to the formulation of two basic divergent hypotheses, the first of which favors a restricted origin hypothesis in which domestication took place from a limited wild stock in a single location, followed by the transplantation of those cultivars to other regions (*20*, *21*, *99*). Supporters of this theory sometimes refer to it as the 'Noah Hypothesis' (*16*, *20*, *21*, *98*, *100*), as one of the biblical patriarch's first acts following the great flood was to plant a vineyard and make wine (*112*):

> Noah, a man of the soil, proceeded to plant a vineyard. When he drank some of its wine, he became drunk...

Others envision a multiple-origin hypothesis in which domestication involved a large number of originating stock evolving over an extended time period and across the entire distribution range of the wild antecedent species (*99*).

In an attempt to address these two hypotheses, chlorotype variation and distribution were analyzed for 1201 samples of *sylvestris* (wild type) and *sativa* (domesticated) genotypes in order to study their genetic relationships. The results of this study support the existence of a genetic contribution of eastern and western *sylvestris* population groups to the genetic makeup of current grape-vines. This could then suggest the existence of at least two origins for the cultivated grapevine, one in the Near East and another in the western Mediterranean region. It is said that the latter of these two potential origins could have been that for many of the current Western European cultivars (*99*). The authors are careful to point out, however, that it is unclear whether this second origin signifies an independent domestication event or developed as an effect of the east to west transmission of the cultivated vine (*99*).

In spite of some dispute about the exact location (or locations) of the first domesticated grapevine (*86*), it is clear that crops of grapes, olives, dates, and figs were all being used in the Levant by the 4th millennium BCE (*11*). In terms of the grape, its domestication has been linked to the production of its wine. As grape wine production required sufficient access to grapes, as well as suitable containers for appropriate storage and preservation, it is generally thought that this did not occur prior to the Neolithic period (ca. 10,000-4000 BCE) (*16*, *21*, *22*, *99*).

In terms of the geographical origins of viniculture, most typically point to higher elevations of the north where *Vitis vinifera sylvestris* was known to

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

thrive. The upland regions of the northern Zagros Mountains, the eastern Taurus Mountains, and the Caucasus Mountains contained well established Neolithic communities and are thought to be the best candidates for early winemaking and viniculture based on current archaeological and historical knowledge (*13*, *20*, *22*, *99*, *100*, *102*, *113*). As a result, the origin of viniculture is typically attributed to the Transcaucasia region (Figure 14), where the greatest genetic diversity of the grape is found, and occurring ca. 6,000 BCE (*32*, *86*, *99*, *100*). The view of the Transcaucasia region as the first site of wine production is also supported by the theory that the hypothetical proto-Indo-European root for the word 'wine' (*woi-no or *wei-no) had its origin in eastern Turkey or Transcaucasia (*100*). Sadly, a limited number of sites have been excavated within this ethnically diverse and politically divided region, let alone published in a Western language (*13*, *21*). Still, archaeological research has found grape pips of the domesticated grape from Chokh in the Dagestan Mountains of the northeast Caucasus, dating to the early 6th millennium BCE, as well as from Shomutepe and Shulaveri along the Kura River in Transcaucasia, dating to the 6th-4th millennium BCE (*13*, *21*, *102*).

The cultivation and domestication of the grapevine seems to have involved the initial favoring and selection of hermaphroditic members of the wild species over either the barren male vines or female vines that were dependent on pollination via insects and a nearby male vine (*13*, *16*, *99*, *101*). As hermaphrodite genotypes include the male (stamens) and female (pistil) features on the same vine, such plants can pollinate themselves via even airborne transfer and are thus able to produce more fruit on a predictable basis (*13*, *16*, *20*, *22*). Such vines were then eventually able to sire offspring that were hermaphroditic themselves (*13*) and these self-fertilizing plants could then be selected for larger, sweeter, and better tasting fruit, with a higher ratio of juice to skin and fewer seeds (*16*, *20*, *22*, *99*). The final domestication step then involved the development of propagation techniques or cloning of the vine (*20*, *22*, *86*, *99*). Such cloning methods involved the transporting of branches, buds, or rootings, and eliminated the need for sexual reproduction via seeds to result in consistent and reproducible progeny. As a result, the most desirable qualities could all be selected and reproduced (*20*, *86*).

While most agree on Transcaucasia as the original site of viniculture, the details of the transmission of cultivated grapevines into the south remains a topic of debate (*98*). It is generally believed that wine production first moved to the cultures of the Sumerians, Assyrians, Babylonians, and Hittites (*100*), with some claiming the grapevine appeared in Mesopotamia as early as 6000 BCE (*35*, *39*). However, others favor later dates for this event. Evidence cited to support proposed timelines include archaeobotanical samples from Kurban Hüyük in Anatolia, which have shown that grapes were there in increasing amounts during the 4th-3rd millennium BCE (*11*). Based on the written evidence, the introduction of grapes into the Mesopotamian lowlands and Iran has been proposed to occur in the early 4th to late 3rd millennium BCE, as the Sumerian sign for grapes does not appear before then. However, this argument is complicated by another sign interpreted as wine, which appeared as early as the mid-4th millennium BCE. Still, it is only in the second half of the 3rd millennium BCE that references to grapes, raisins, and wine become more frequent in cuneiform sources (*11*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

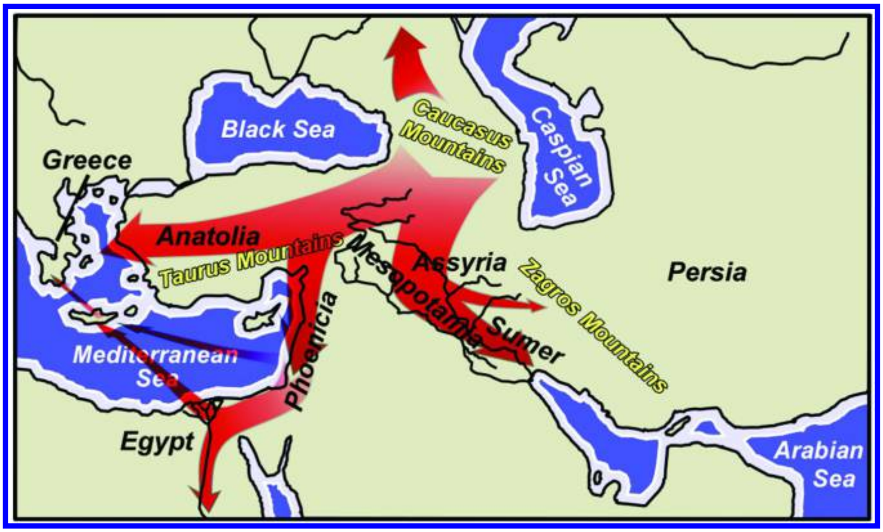

Figure 14. Proposed path of the transmission of viniculture. [Adapted with permission from reference (98). Copyright 2014 Springer Science and Business Media].

Sometime around 4000 BCE, it is believed that the domesticated grapevine was then transplanted southwards to reach the Jordan Valley, a region in which the wild grapevine did not grow (*13*, *20–22*, *99*, *102*). This is supported by evidence found at Chalcolithic (ca. 4000-3300 BCE) and Early Bronze Age (ca. 3300-3000 BCE) sites in the Jordan Valley that suggest active viniculture. Although the grape pips from the latter sites are of the proposed wild type, it is thought that *Vitis vinifera sylvestris* was unlikely to have grown in this climate and it is argued that the pips must therefore derive from domesticated vines transplanted into the Jordan Valley (*13*).

The grape was then introduced to the Nile Delta around 3000 BCE, where it formed the basis of the newly established royal winemaking industry (*11*, *15*, *20–22*, *90*, *99*, *102*). The introduction of the domesticated grape into Egypt was thought to have come from the Levant (*20*, *86*), with the Egyptian royal industry established under the tutelage of Canaanite winemakers from Lebanon and the southern Levant (*8*). Once introduced, vines were grown throughout Egypt and tomb paintings have provided an extensive record of their viniculture (*32*, *109*).

A similar progression of viniculture can be traced along the eastern side of the Fertile Crescent (*102*) with the spread of the cultured vine to the central and southern Zagros Mountains (Figure 14) by ca. 3000 BCE (*22*, *99*). Grape pips and grapevine wood have been identified from the late 4th-3rd millennium BCE site of Tepe Malyan, suggesting that the domesticated vine had been transplanted to the southern Zagros Mountains by the mid-3rd millennium BCE (*102*).

The cultivation of the grape is thought to have emerged in Greece and Asia Minor sometime during the 4th-3rd millennium BCE. It has also been stated that it was during this period that viniculture moved from a simple aspect of local consumption to an important component of local economies. Western expansion of grape wine is documented in Crete around 2200 BCE (*15*, *99*), and later along the coasts of the Italian and Iberian Peninsulas in ca. 800 BCE (*99*).

Although some believe that viniculture was introduced into Italy as early as 1000 BCE, it has been said that wine was still a scarce commodity in Rome during the 4th century BCE (*113*). It is thought that Italian viniculture came to play an important role by the beginning of the 2nd century BCE and became widespread in Italy after 150 BCE. While the quality of this wine was not thought to be significant, such wines now satisfied local demand and the importation of Greek wine diminished (*113*). Once introduced into Greece, Italy, and Gaul, wine became a beverage used by all levels of society (*32*). A general timeline of the cultivation of the grapevine is summarized in Table 2.

Table 2. General Timeline of Vine Cultivation[a]

Time period	*Region*	*Time period*	*Region*
6000 BCE	Caucasus	1000 BCE	Italy, North Africa
6000-4500 BCE	Mesopotamia	500 BCE	Spain, Portugal, France
4000 BCE	Jordan Valley	100 BCE	China, northern India
3000 BCE	Egypt, Phoenicia	100 CE	Northern Europe
2500-2000 BCE	Greece, Crete	1500 CE	North America

[a] Compiled from (*11*, *15*, *16*, *20*, *22*, *29*, *35*, *39*, *99*, *102*).

Wine Production

The ownership of vineyards in Mesopotamia and Egypt was thought to be limited primarily to the ruling class and grape wine was not typically available to the common man (*98*). It has even been said that some felt that this wine was reserved entirely for the gods (*56*) and its use as an offering is known, with both wine and grapes regularly placed in tombs (*31*). In its early years of production, the extreme cost of grape wine restricted it to the upper classes (*15*, *16*, *31*). This was primarily due to the fact that grapevine cultivation in the south had not yet occurred during this period, which meant that all production was still carried out in the mountainous regions of the northeast and then exported to the south (*15*, *16*). It has been estimated that the cost of transporting the wine down into Mesopotamia made it at least ten times more expensive than beer, and thus it was initially regarded as an exotic foreign drink (*15*). Textual and archaeological evidence indicate that the northern Mesopotamian city of Mari had become a major importer and distributor of wines by the 2nd millennium BCE (*11*).

Even after wine production was established in the southern regions, the import and export of grape wine still played a major role. For example, it has been reported that while most wine produced in the Levant appears to have been intended for local distribution, an unknown amount was also exported to Egypt (*11*), which imported such grape wines primarily as a drink of the upper classes (*20*, *86*). Such wine was imported primarily from Syria and Palestine, but also

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

from Greece in the later periods (ca. 6th century BCE) (*20*, *31*). Once Egypt began producing its own local wines, however, the dependency on Levantine wines diminished (*11*), with the best Egyptian wines thought to be those produced in the Nile River Delta and the Western oasis (*109*). Wine trade also had enormous economic significance during the Roman era, during which the wine amphora became one of the most common ceramics of the time. It has been reported that an estimated 40 million amphorae of wine were imported into Celtic territories during a single century at the end of the Iron Age, corresponding to 2.65 million gallons of wine per year (*32*).

Textual and pictorial evidence of wine production from the ancient world show that the processing of grapes into wine was not necessarily that complex (*73*). While the most detailed knowledge available is of the processes utilized in Egyptian wine production, these methods of are thought to be representative of other regions as well. Overall, available evidence seems to indicate that the processes for the production of grape wine used in antiquity generally follow the same basic processes known today (*56*). This began with harvesting the grapes (*31*, *86*), in which the collected grapes were placed into baskets for transportation (*86*). Such baskets of collected grapes have sometimes been shown covered with palm leaves or vines, which some believe may have been methods to protect the fruit from the sun. The baskets of harvested grapes were then emptied into large vats in order to collect the juice from the grapes (*86*).

Throughout the Mediterranean and Near East, the traditional method to isolate the juice was to tread the grapes underfoot in crushing vats (*31*, *56*, *73*, *86*). Pictorial evidence from Egyptian tombs clearly illustrate that this method was also employed in Egypt (Figure 15) (*86*). Such methods are more gentle than modern wine presses and are considered the most effective way to release the grape juice without crushing large amounts of the seeds and stems that can add unwanted tannins, astringency, and color to the collected juice (*86*).

In Egyptian scenes of the 3rd millennium BCE, the treading vat is shown as very shallow with upright poles at either end of the vat, which support a crossbar. Those treading the grapes would use this crossbar to increase balance, resulting in more efficient treading of the grapes. Later scenes also show a type of vat that retains the upright poles and crossbars, but appears to be rounded and much deeper than the earlier forms. These later vats also often utilize a spout for collection of the extracted juice (*86*).

A final type of treading vat found in some scenes is much more elaborate and often appears with steps leading up to the vat on a raised platform. Rather than the upright poles and crossbars pictured in the other forms, these vats are sometimes shown with a full roof from which support ropes hang down for those treading the grapes (Figure 15). Vats of this final form also contain a spout at the base for collection of the extracted juice (*86*).

It has been estimated that foot treading extracts only about two-thirds of the juice from the grape (*86*). To collect a greater fraction of the juice, the mash (i.e. crushed skins, flesh, stalks and seeds) remaining after treading was then transferred to a bag press (Figure 16), which could be used to squeeze the remaining juice from the mash (*31*, *73*, *86*). The earliest such presses consisted of a simple bag or sack with poles attached at each end (Figure 16a). Twisting the poles would then

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch004

compress the bag to extract any remaining juice (*16*, *86*, *98*). It has been proposed that the bag material consisted of either linen or possibly some type of basketry. This initial design was improved during the 2nd millennium BCE by attaching one end of the bag to a fixed post, requiring only a single pole to twist the bag (Figure 16b). After the 16th century BCE, a final innovation was added, consisting of one or both ends of the bag attached to poles outside a frame (Figure 16, c and d), which allowed the bag to be fixed securely in place so that the poles could to be twisted using maximum leverage (*86*, *98*).

Figure 15. Scene from a Theban tomb showing the treading of grapes (96).

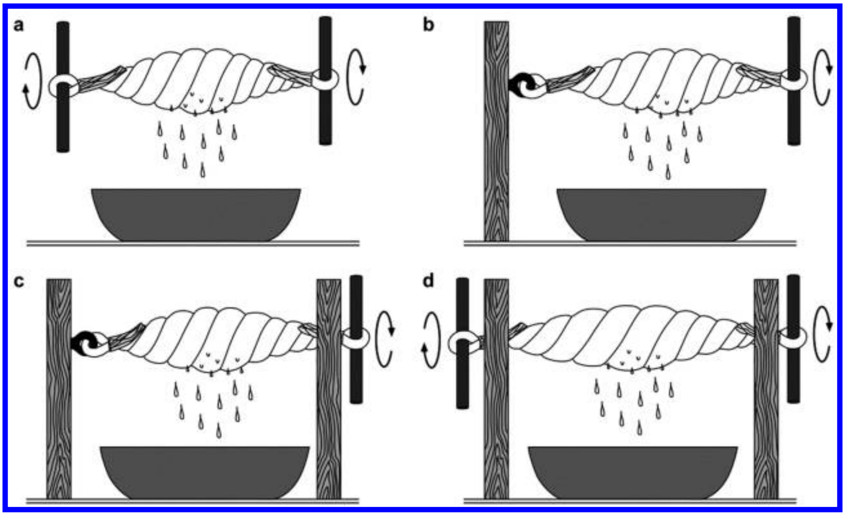

Figure 16. Evolution of the bag press - simple bag press (a); single-post design (b); double-post design with one handle (c); double-post design with two handles (d). [Reproduced with permission from reference (98). Copyright 2014 Springer Science and Business Media].

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The yeast-containing juice extracted from the grape is known as *grape must* or the *must of wine* (*16*, *73*, *86*) and grade of the must depended on how the juice was isolated (*16*, *86*). The highest quality is referred to as 'free-run' must, which consists of the juice pressed out of the grape simply by their own weight without any treading or pressing. As one might expect, rather little of this must is produced and fermentation of pure 'free run' results in a pure, sugar-rich, and long-lived wine (*86*). Most of the isolated juice, however, is obtained via treading, which is known as 'first run' must. Finally, the juice obtained via pressing is referred to as 'second run' must. As expected, the level of impurities increases with the each sequential grade of must, as does the potential to generate either acetic or lactic acid (*86*). It is unclear if each type of must was more commonly fermented separately or if they were instead mixed for different types of wine.

The necessary yeasts for fermentation are found in the white, powdery coating visible on some grapes, which is called the *bloom* (*86*). As such, the yeast mixed with the juice during isolation via treading and pressing (*73*). As previously discussed, the primary yeast involved in the fermentation of the grape juice is *S. cerevisiae*, although a variety of wild yeasts of the genera *Saccharomyces* and *Candida* have been found in the grape bloom (*73*). Other authors have even shown that that contrary to popular belief, *S. cerevisiae* occurs at extremely low populations on healthy, undamaged grapes and this yeast is rarely isolated from intact berries and vineyard soils. In fact, the predominant species on the grape surface are yeasts of the genera *Kloeckera* and *Hanseniaspora*, which account for ~50-75% of the total yeast population of the bloom (*35*). Even so, *S. cerevisiae* is still by far the primary yeast species colonizing surfaces in wineries, which has been said to illustrate the selective effects of grape juice and wine as growth substrates (*35*). It wasn't until the 19th century CE that wine must was produced by adding pure yeast cultures to sterile grape juice (*32*, *35*).

After isolation, the must was then transferred to large, wide-mouth pottery jars and allowed to ferment (*16*, *31*, *73*). Glucose and fructose make up about 20-30% of the grape (*32*, *35*, *86*) and fermentation converts these sugars to ethanol until the alcohol content reaches between 13-16% (*86*). At this point, the jar was either stoppered and sealed (*16*, *73*, *86*), or the fermented material was strained and transferred to secondary sealed containers (*56*, *86*).

Wine was commonly stored in large amphorae, which were tall pottery jars that were pitched outside and closed with a stopper (*96*). It has been suggested that the interior of these jars was also coated with resin or bitumen in order to seal the porous ceramic, as well as to potentially help preserve the wine (*16*, *86*). The jar stoppers commonly consisted of a variety of materials, including reeds, straw, pottery, wood, or clay (*86*, *96*). The stoppered amphorae were completed with the addition of either handmade or molded seals (*31*, *86*, *96*). The handmade seals consisted of placing dampened mud on the mouth of the jar, shaping it by hand, and allowing it to dry (*86*, *96*). In contrast, the molded seals were more elaborate and were made by either filling an open-ended mold with mud and forcing it onto the amphorae neck, or by covering the neck with mud followed by application of the mold (*86*). The rapid sealing of the wine jars was important as the availability of oxygen after fermentation could result in the growth of bacteria responsible for the conversion of ethanol to acetic acid (*73*, *86*).

Alcohol-soluble plant resins were sometimes added to wine, most commonly pine, cedar, frankincense, myrrh, and terebinth (*13*, *20–22*, *31*, *101*). In addition to serving as flavoring agents, these resins would inhibit the growth of acetic acid bacteria (*Acetobacter aceti*, *Acetobacter pasteurianus*, and *Gluconobacter oxydans*), which act to convert ethanol to vinegar (*13*, *20*, *22*, *35*). Columella detailed the use of pitch and resins to preserve wine in his *De re rustica* (*114*):

> When we shall have, in this manner, prepared the pitch, and have a mind to preserve our wines therewith, when they have now twice left off fermenting, we must put two cyathi of the foresaid pitch into forty-eight sextarii of must, in this manner: We must take two sextarii of must out of that quantity we are going to preserve; then, from these two sextarii, we must, by little and little, pour the must into the two cyathi of pitch, and work it with our hand as it were honey and water, that it may the more easily mix with the must: but, when the who two sextarii of must are mingled with the pitch, and make, as it were, an unity of substance, then it will be proper to pour them into the vessel from whence we took them, and to stir it about with a wooden ladle, that the medicament may be throughly mixed with it.

It is thought that the practice of adding resins to wine was introduced into Egypt during the Ptolemaic period (323-30 BCE) (*86*). Others, however, assert that the use of terebinth resin in wine dates to the 6th millennium BCE (*21*).

In most cases, both white and dark grapes produce a white juice, although the majority of modern wine is made primarily from white grapes. Contrary to common perceptions, the color of the resulting wine is generally not related to the color of the grape used, but is determined by how long the grape skins and seeds are left in the juice before isolation (*86*). As such, white wine is the result of fermentation of from the initial clear juice, while red wine uses juice that was left in the mash for longer periods (*32*, *86*). While there is little clear evidence of the color of Egyptian wines, artistic and textual records both suggest that red wine was the most common (*86*), even though at least six kinds of wine are mentioned in Egyptian sources, including white, red, black, spiced, and wine of the Delta (*31*). In the same way, Bronze Age texts from Mesopotamia mention only the color red in relation to wine (*86*). References to spiced wines are consistent with the fact that wines were occasionally flavored with herbs (*56*).

Conclusion

Althought the origin of fermented beverages was most certainly an accident, curiosity and experimentation resulted in the development of a range of alcholic beverages throughout antiquity. The earliest of such intentionally produced drinks are commonly thought to have been made from readily available sugar sources, particuarly bee honey and the fruit of the date palm, and may originate as far back as 10,000 BCE. In contrast, the more commonly referenced drinks of beer and grape wine were later innovations, as they were dependent on the development of

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agriculture and viniculture. While the chronology of these two primary fermented beverages is still actively debated, there is no definitive proof that either preceded the other and both drinks are commonly dated to ca. 6000 BCE. What is known, however, is that beer became more widespread at an earlier date due to better access to the necessary grains, while the transmission of wine was tied to the slower development of viniculture. Because of this, beer was initially the more prominent beverage in both Mesopotamia and Egypt until the Greek period, after which grape wine overtook beer in most Greek-influenced cultures.

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Chapter 5

The Metals of Antiquity and Their Alloys

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The first metals discovered by man were likely gold and copper, as native deposits of these elements can be found in forms pure enough for immediate working. The other "metals of antiquity" were silver, lead, tin, iron and mercury, bringing to seven the number of metals known to ancient man. Most of these metals had to be won from their corresponding ores by treatment under a controlled temperature and atmosphere. The most important alloys of these metals were bronze (copper and tin) and electrum (gold and silver). In all cases, the metals had to be worked to give the final desirable properties and shape. The processes used to refine and work metals were some of the most technologically advanced practices in ancient times. An historic account of how such relatively complicated processes evolved and what chemistry was involved will be given.

Introduction

The first metals known to humans were likely those occurring in the native state: gold, copper, silver, and meteoritic iron (Figure 1). The gold and copper were usually found in streams and rivers downstream of their ore deposits, and likely the copper was more plentiful.

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Figure 1. Native gold (By Aramgutang/Wikimedia Commons/Public Domain); native copper (By Jonathan Zander (Digon3)/Wikimedia Commons/ CC-BY-SA 2.5); meteoritic iron (By Opsoelder (own work)/Wikimedia Commons/ CC-BY-SA 2.0 Germany); native silver. (By U. S. Geological Survey, Image 252679, Public Domain).

Although widely known during antiquity, these metals are by no means common. Of the 88 elements occurring naturally in the earth's crust, oxygen and silicon are by far the most abundant (as calculated by mass) (*1*). For comparison:

Iron is the 4th most abundant (5.63% by mass)
Copper is 26th (60 ppm)
Lead is 36th (14 ppm)
Tin is 51st (2.3 ppm)
Mercury is 67th (85 ppb)
Silver is 68th (75 ppb)
Gold is the 75th (4 ppb)

Yet all were known and available in tangible quantities in ancient times.

In order to discuss the development of metallurgy, it is helpful to use the three-age classification system for technological change established by Christian Jürgensen Thomsen (Figure 2) in 1825. He defined the ages based on the change in artifacts such as pottery and metallic objects for European cultures, giving us the terms Stone Age, Bronze Age, and Iron Age (*2*). These ages occurred at different specific times for different cultures (Figures 3 (*3*) and 4 (*4*)), with some cultures skipping the Bronze Age and going directly from the Stone Age to the Iron Age.

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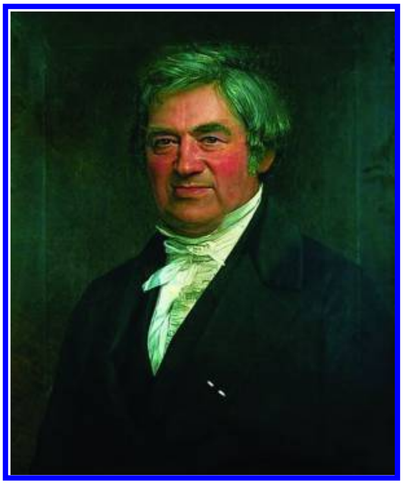

Figure 2. Christian Jürgensen Thomsen (1788-1865). (J. V. Gertner/National Museum of Denmark/Public Domain).

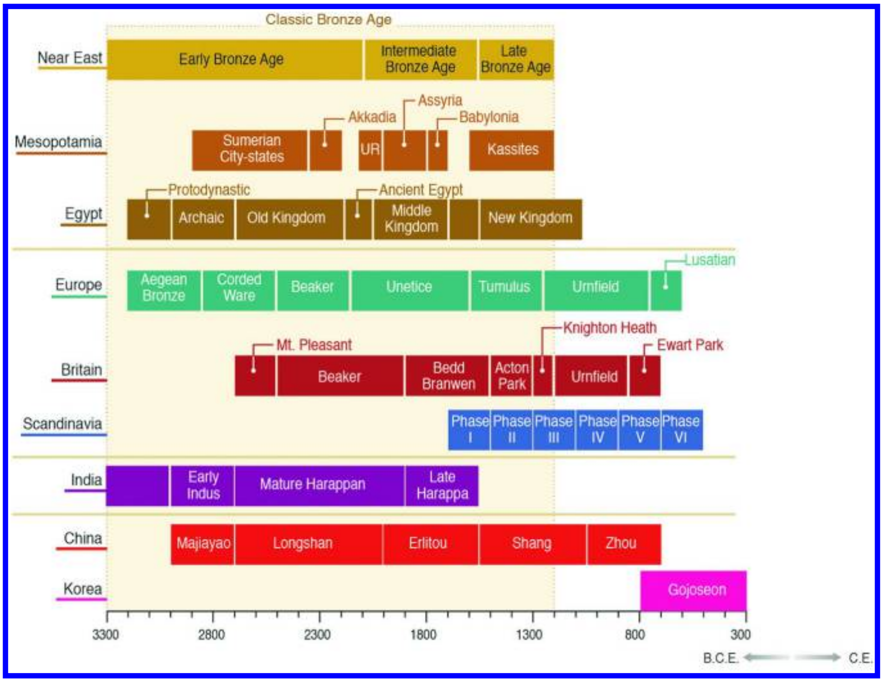

Figure 3. Bronze Age Timelines. (data from reference (3)).

This chapter will focus on the period from prehistory to 500 CE and the regions of the Ancient Near East (Figure 5) and the Mediterranean coasts. The map in Figure 6 shows the sites of metal production in the Ancient Middle East (*5*). Some excellent general references for this topic are available (*6*–*9*).

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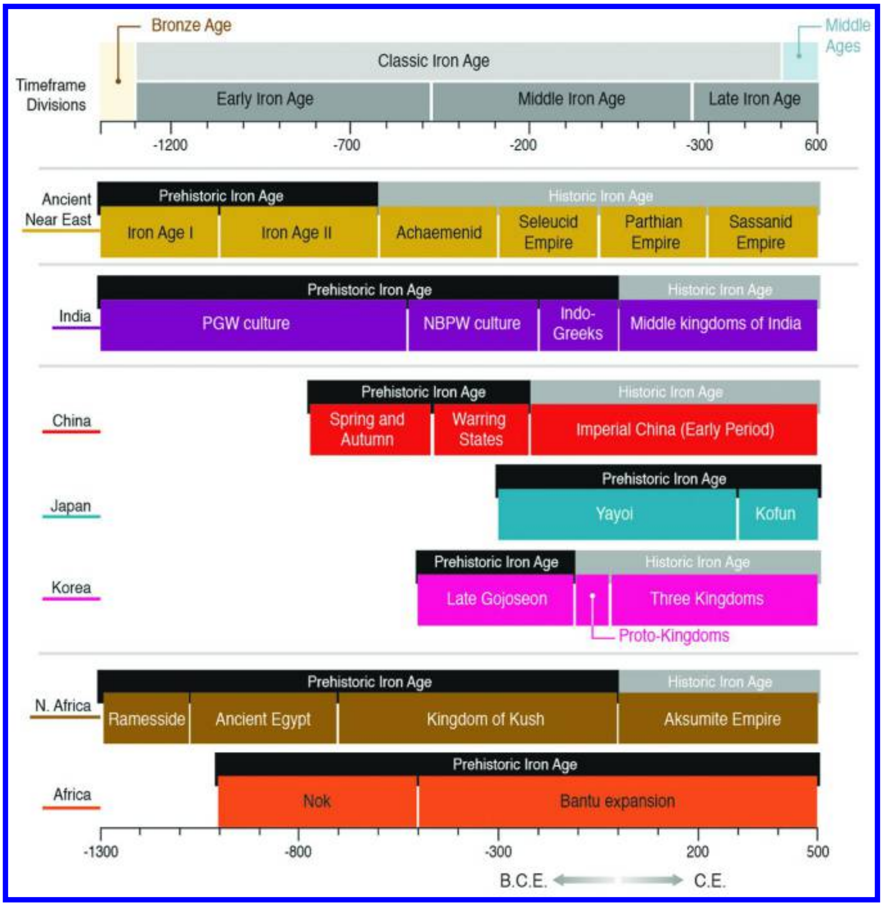

Figure 4. Iron Age Timelines. (data from reference (4)).

The first attempt to systematize mineralogy and describe the processes and methods critical to the science of mining and metallurgy was made by Georgius Agricola (1494-1555) in his *De Re Metallica*, published in 1556 (*10*). This book was so useful that it was continuously in print for over 200 years (*11*) and translated into English in 1912 (*12*). This is an important text for many reasons, but two stand out:

1) Agricola espoused the abandonment of inductive speculation in favor of direct observation (Figure 7), and
2) Agricola, at a time when guilds and trades zealously guarded their secrets, published everything he could find out and confirm about mineralogy, mining, and metallurgy.

Figure 5. Ancient Near East (Dbachmann at en.wikipedia (http:// en.wikipedia.org))/Public Domain) with some important archaeological sites marked.

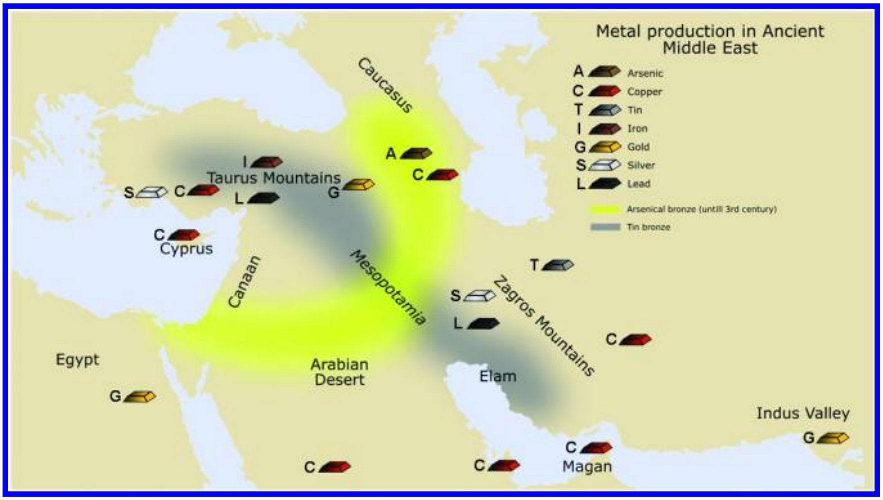

Figure 6. Metal production sites in the Ancient Middle East. (By Phirosiberia / Wikimedia Commons / CC BY-SA 3.0).

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De Re Metallica is lavishly illustrated, containing hundreds of woodcuts that depict the practices of the time. In the preface, Agricola states (*10*):

> *I have hired illustrators to delineate their forms, lest descriptions which are conveyed by words should either not be understood by men of our own times, or should cause difficulty to posterity.*

Although it is difficult to know with any certainty, it is likely that the technology described by Agricola in 1556 differed in numberous ways from those practiced 1000 years and more previously. Some of the practices described, however, such as striking a rock to break it into pieces, likely have not changed for millennia. Keeping these caveats in mind, we will use some of Agricola's images to illuminate the technology of the Bronze and Iron Ages.

Quae omnia cum oculis cernamus, et que sensibus percipiuntur,
verius percipiuntur quam si ex demonstratione cognosceretur,
satis habemus id quod de terrarum ortu sentimus,
hac inductione docere.

"Those things which we see with our eyes and understand by means of our senses are more clearly to be demonstrated than if learned by means of reasoning."

Figure 7. Georgius Agricola (1494 – 1555) (Wikimedia Commons/Public Domain); Quote emphasizes the importance he placed on direct observation (13).

Properties of Metals and Alloys

The technology needed to separate and work metals generally depends upon the melting point of the metal, all other things being equal. The metals of antiquity have low melting points, with iron being the obvious exception (*14*): mercury (−39°C), tin (232°C), lead (327°C), silver (962°C), gold (1064°C), copper (1085°C), and iron (1538°C).

Melting points of the various ancient metals and their alloys are shown below (Figure 8) (*15*). Generally, alloys have lower melting points than that of the highest concentration "parent" metal. Thus, bronzes and brasses melt at a lower temperature than copper. That means that bronzes, for example, could be melted and therefore cast at temperatures available in a simple campfire with a good draft whereas copper requires much higher temperatures than a campfire can provide (see discussion in next section on Fires and Furnaces).

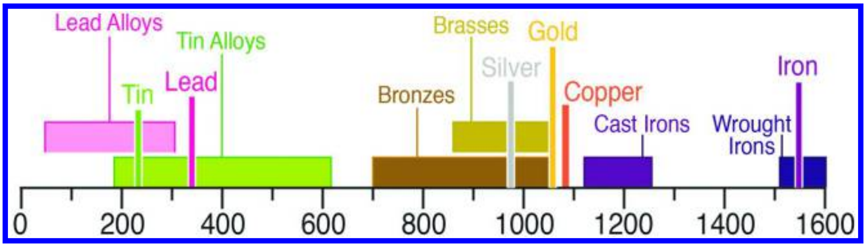


Figure 8. Melting point temperatures of selected elements and alloys.

Alloying results in a number of changes in physical and mechanical properties as shown in Table 1 (*16*). The final use of an object dictated whether it was best made from a "pure" metal or an alloy. Thus, if a spear head was the object of interest, the lower melting point of an alloy such as bronze made the object easier to cast and work, and stronger, and the loss in ductility and malleability would not be critical to its function. If decoration was the object of interest, then the loss in ductility and malleability might not be acceptable as fine detail work such as repousse (method in jewelry making of banging out relief in metals), granulation (method in jewelry making to create beads out of metal) and filigree (method in jewelry making that uses metal wires) depend upon those properties, leading to the use of the pure metal instead of an alloy.

Table 1. Alloys and Mechanical Properties (*16*)

Alloy	*Effect of alloying on base metal*	*Implication*
Melting point	Lower	Alloy easier to cast and work than the base metal
Strength	Higher	Alloy stronger than the base metal
Ductility and malleability	Lower	Gain in strength more than offsets the loss in these properties

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Fire and Furnaces

The development of metallurgy and pottery go hand in hand. The oldest known ceramic objects are cult figures from the Czech Republic and have been dated to 28,000 B.P. (*17*) (B.P. stands for Before Present, where dates are given from C.E. 1950 (*18*).) The earliest utilitarian pottery vessels are from the Xianrendong Cave in China and have been dated to 20,000 - 19,000 B.P. (*19*) The earliest known pottery found in the Near East dates to 7000 BCE and appears to have been independently invented (*20*). It is generally accepted that pottery was discovered serendipitously when a clay container was placed in a campfire and found to be rendered water-proof and harder as a result (*21*).

The maximum obtainable temperature in a campfire is roughly 700°C; if air flows over and through the fire then the temperature can reach approximately 800°C. Ancient potters often employed temperatures higher than those available in a campfire for firing clay pots, from 800°C to 900°C, and up to 1200°C for some glazed pottery. Egyptian predynastic pottery (the period before 3100 BCE) has been found that was fired at temperatures up to 1100-1200°C (*22*). At Tell Halaf, Syria, where the Halaf culture flourished between 6100-5400 BCE, well before the discovery of smelting in this area, highly fired pottery has been found, showing that the furnace technology to reach these higher temperatures was available (*23*).

The first firings of clay were likely carried out by burying the article within a mound of fuel, which was subsequently burned around it. The next development was separation of the baking chamber from the fire box, leading to the development of two-tier furnaces (Figure 9). These types of kilns have been found in various sites in the Middle East, such as Susa and Khafajé, and indications are that they were in wide-spread use in western Asia before 5000 BCE (*22*).

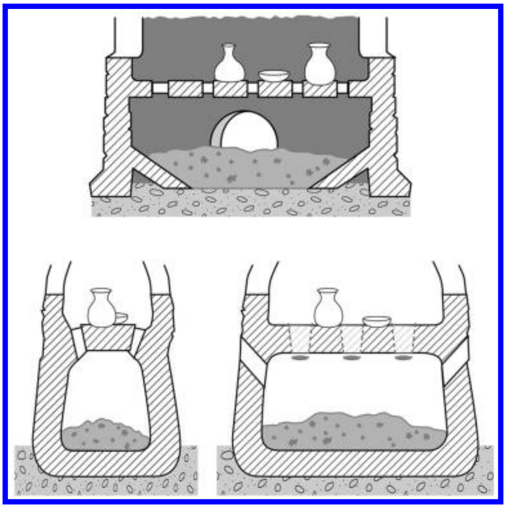


Figure 9. Top: Reconstruction of remains of a two-tier pottery kiln, Khafaje, ca. 5000 BCE; Bottom: Reconstruction of remains of a two-tier pottery kiln, Susa, ca. 4000 BCE; Left: tranverse section; Right: longitudinal section. (Data from reference (22)).

Pottery kilns, however, are not suitable for smelting ore and we now come back to the importance of the melting points of the various metals under discussion. Figure 10 shows the development of ore-smelting furnaces, starting from a simple campfire (Figure 10(A)). The next change was likely the addition of a blowpipe to allow oxygen to be introduced into the fire (Figure 10(B)), raising the achievable temperature to approximately 900°C. The next critical step was the lining of the hole with stones, sinking a crucible (a clay pot, for example) into the fuel, and enclosing the fuel with earth in order to concentrate the heat (Figure 10(C)), giving a maximum temperature of approximately 1050°C. Finally, using a bellows to force air over and into the heated area (Figure 10(D)) would allow the temperature to reach approximately 1200°C.

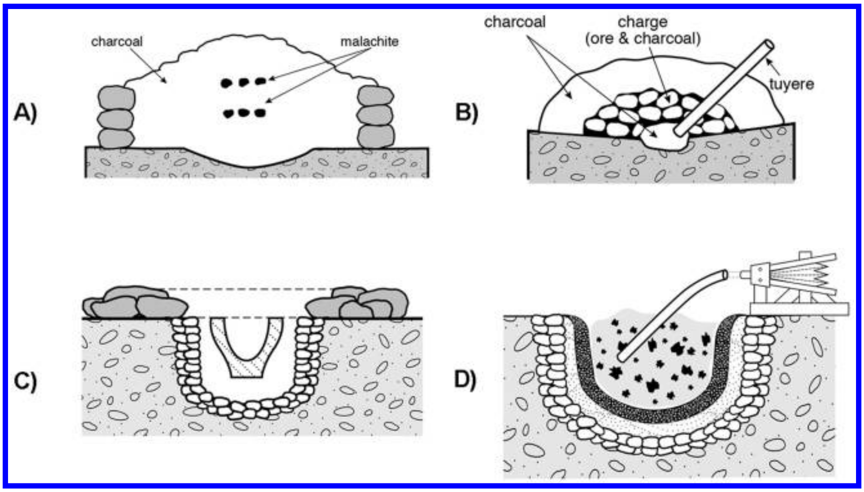


Figure 10. Development of the furnace. A) Campfire – Max temperature approximately 700°C; With air flowing over and through the fire, temperature can go up to approximately 800°C (data used from reference (25)); B) Campfire with oxygen source (tuyere) – max temperature approximately 900°C; C) Campfire with the center sunk to take a crucible; with stone lining and oxygen source – max temperature approximately 1050°C; D) Simple iron smelting furnace, temperatures approximately 1200°C. (Data from references (24, 25)).

Smelting

It is generally thought that the development of metallurgy went through distinct stages (*26*):

1. Native metal used as found. In this stage the native metal was worked in the same way as stone, with stone tools.
2. Native metal stage, in which the metal is worked cold, by hammering, cutting, etc. This would involve copper, gold, silver, and meteoric iron.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

3. Ore stage, in which the metal is worked hot (methods of melting, casting, welding, soldering, etc. are important) and the metal is produced from ore (smelting), leading to alloys, for which composition is a primary factor in development. This stage would lead to the isolation and working of lead, silver, copper, antimony, tin, bronze, and brass.
4. Iron stage, in which the methods of processing such as hot hammering, tempering, quenching and annealing are important. This stage leads to the development of wrought iron, steel and the chance cast iron.

In order to discuss various methods of treating ores, including smelting, some definitions are necessary (*27*, *28*):

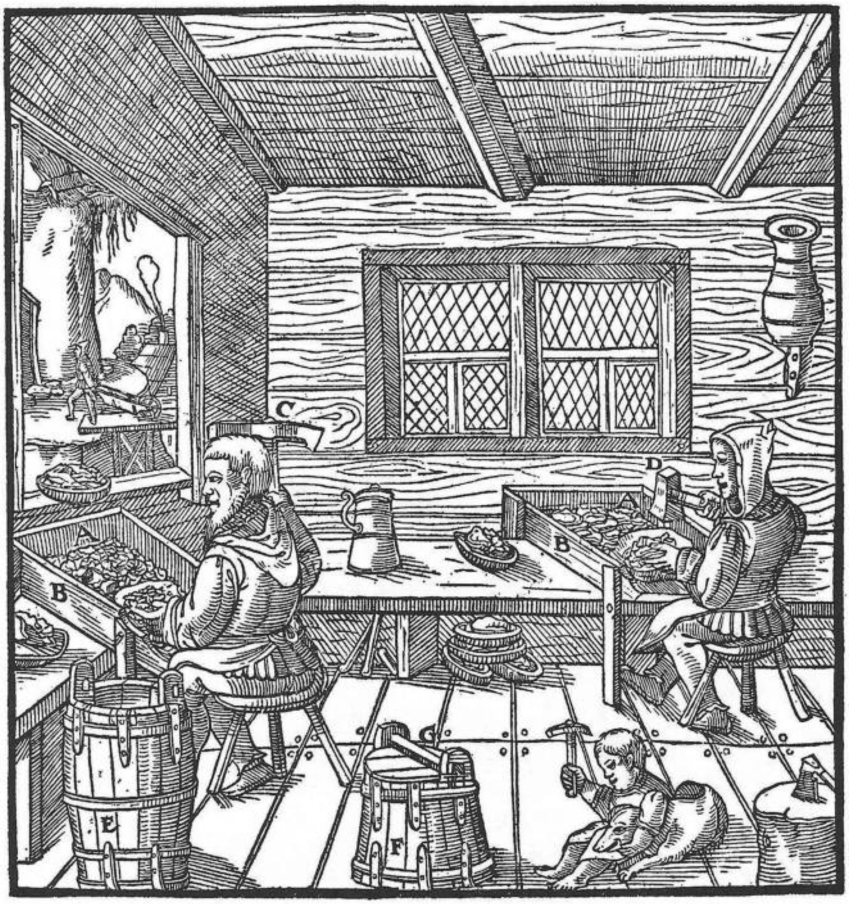
- *Roasting* – heating minerals while an abundant supply of air is maintained. Metal rich minerals and ores are generally roasted to make them suitable for smelting
- *Tuyere* - a vent in a furnace through which oxygen was injected into burning fuel either by natural draft or bellows
- *Flux* - a solid that, when added in minimal amounts, promotes the melting of another solid
- *Reducing gas* – gas generated in the smelting furnace which reduces the ore to free molten metal
- *Smelt* - to melt or fuse (as ore) often with an accompanying chemical change usually to separate the metal; to refine or reduce
- *Gangue* – the worthless rock or vein matter in which valuable metals or minerals occur, which endanger the efficiency of the smelting and the purity of the metal produced
- *Bloom* - a spongy mass of fused stone full of air-holes, containing the gangue, slag, cinders and metal of interest. The choice of the proper flux material allowed the efficient separation of the metal from the gangue and slag
- *Ore dressing* – a process intended to separate and concentrate the metal-rich minerals from the *gangue*
- *Slag* or *dross* – the waste products of smelting process, which contain the nonmetallic elements of the ore

After an ore is dug out of the ground, it must first be broken into sortable chunks (Figure 11) (*29*). One method of making stone into smaller pieces is hitting it with a hammer or some other tool. Once the ore has been broken into smaller pieces, it needs to be sorted and further pulverized. Figure 12 (*30*) shows workers inspecting the various chunks of ore and separating it into piles according to the quality of the ore. Then these pieces would also be crushed futher. The next step would be roasting the ore. Figure 13 (*31*) shows arranging the ore with wood in alternating layers. The ore was kept at temperature for as long as thirty days, depending upon the specific ore.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Figure 11. Breaking up ore with hammers (29). (Agricola, De Re Metallica, Public Domain).



A—TABLES. B—UPRIGHT PLANKS. C—HAMMER. D—QUADRANGULAR HAMMER.
E—DEEPER VESSEL. F—SHALLOWER VESSEL. G—IRON ROD.

Figure 12. Sorting ore (30). (Agricola, De Re Metallica, Public Domain).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

A—HEAP OF CUPRIFEROUS STONES. B—KINDLED HEAP. C—STONES BEING TAKEN TO THE BEDS OF FAGGOTS.

Figure 13. Method of roasting copper-bearing ore. Bundles of sticks, twigs and branches are laid out, ore is laid over them, then more layers until a mound is formed. Firing is on the right side, away from the wind (note the wind, top left) in order to prolong the burning. These piles might burn as long as thirty days (31). (Agricola, De Re Metallica, Public Domain).

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The flowchart for the smelting process in shown in Figure 14 (*32*).

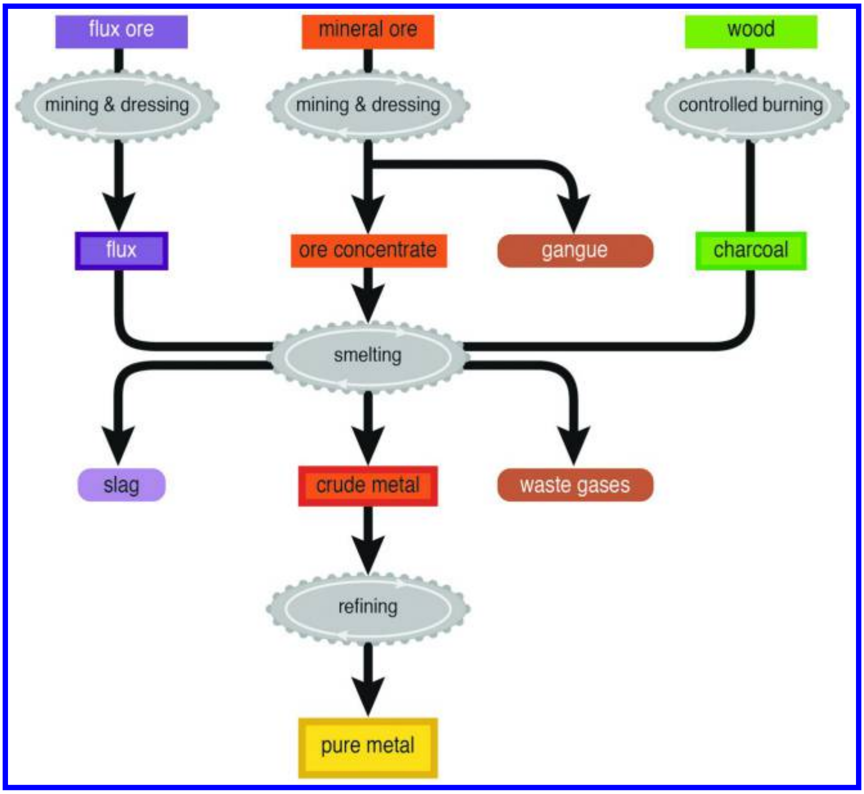


Figure 14. Smelting Flowchart. (Data from reference(32)).

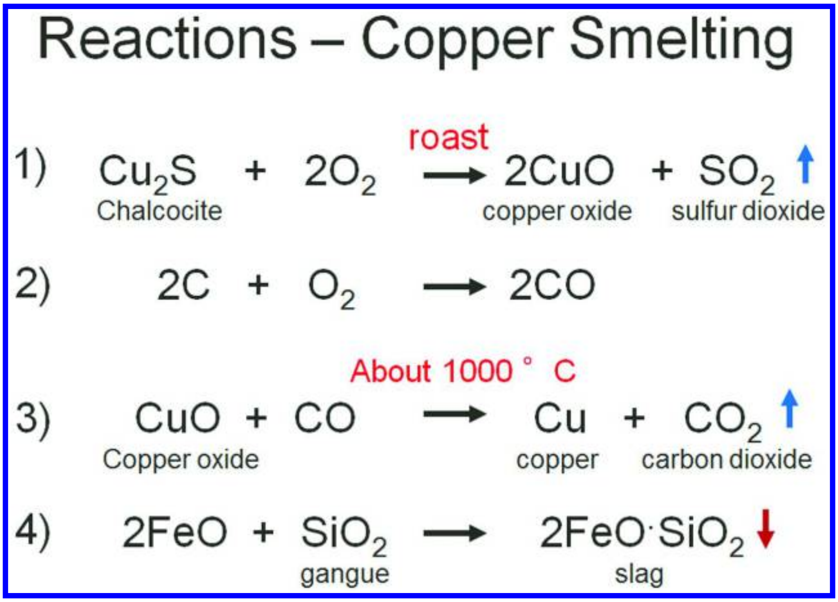
The reactions involved in copper smelting starting from a copper sulfide mineral are shown in Figure 15. The necessary reactions involve a roasting/oxidation step, which transforms the copper sulfide into copper oxide, and the reaction of charcoal with oxygen to form carbon monoxide, which provides the reagent for reducing copper oxide to copper metal. Copper oxide ores, such as malachite, are not reduced at temperatures lower than 700-800°C, but to melt the copper product requires temperatures of at least 1085°C, which requires more than a simple campfire technology.

It was suggested by Gowland (*33*) and accepted for many years that the discovery of copper smelting was the result of the serendipitous inclusion of a copper oxide ore such as malachite in the stone ring of a campfire. The metal in the stone would be reduced, then melt, run into the bottom of the campfire and be recovered as a button or cake of copper metal (Figure 16).

This suggestion, however, is improbable in view of the temperatures and conditions required for these reactions and those available in a simple campfire.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Coghlan (*34*) carried out a series of experiments with campfires configured as in Figure 10(A) and 10(C). He found that the simple campfire (Figure 10(A)) does not provide a sufficiently high temperature nor a suitably reducing atmosphere to convert copper oxide to copper metal. He did find that putting copper oxide into a covered crucible (Figure 10(C)) and maintaining it for several hours at red heat did produce a copper sponge. He believed that this configuration allowed some of the carbon monoxide produced in the charcoal fire to penetrate the porous material of the pot before it was oxidized externally to carbon dioxide. His conclusion was that copper was probably first accidently smelted in a pottery kiln, possibly when a copper ore used as a pigment was accidentally reduced to metallic copper.



Reactions – Copper Smelting

1) $Cu_2S + 2O_2 \xrightarrow{\text{roast}} 2CuO + SO_2 \uparrow$

Chalcocite, copper oxide, sulfur dioxide

2) $2C + O_2 \longrightarrow 2CO$

3) $CuO + CO \xrightarrow{\text{About 1000 ° C}} Cu + CO_2 \uparrow$

Copper oxide, copper, carbon dioxide

4) $2FeO + SiO_2 \longrightarrow 2FeO \cdot SiO_2 \downarrow$

gangue, slag

Figure 15. The reactions (1-4) involved in copper smelting.

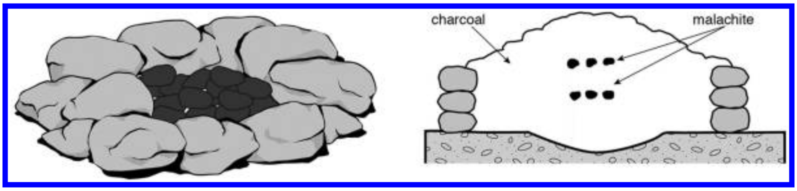


Figure 16. Campfire charged with malachite and charcoal. Maximum temperature approximately 700°C; with air flowing over and through the fire, temperature can go up to approximately 800°C. Left: Top view; Right: Side view. (Data from reference (24, 25)).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

The copper smelting furnaces excavated at Timna, in the southern Sinai, Israel, date from about 3500 BCE (Figure 17) (*35*). There is evidence of copper mining in the Timna area since the fifth or sixth millennium BCE (*36*) and Timna has been considered by many as the site of the earliest copper smelting furnace (*37*). Recent investigations (*38*) have shown that copper smelting operations in Belovode, a Vinča culture site in Eastern Serbia, date from 5000 BCE, approximately 1500 years earlier than those found at Timna.

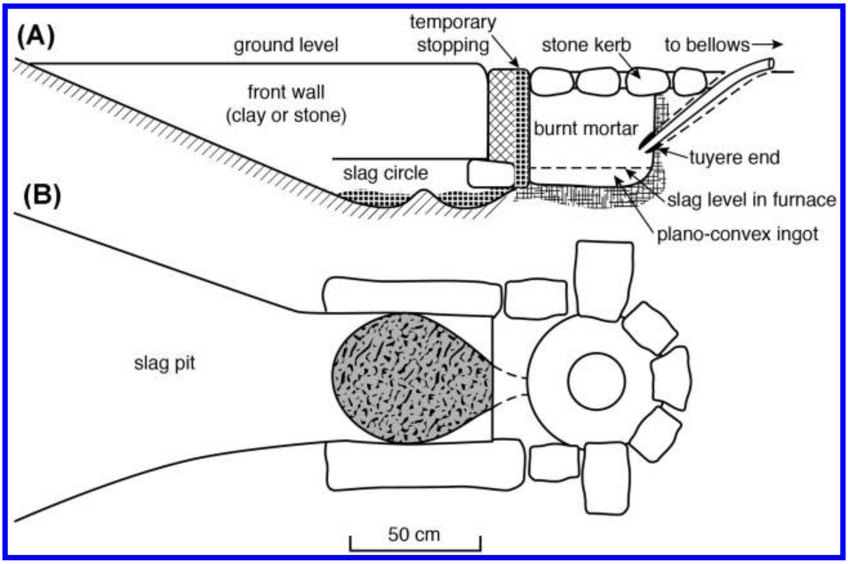


Figure 17. Copper smelting furnace, Timna, Israel, circa 3500 BCE. (A) Side view; (B) view looking down. (Data from reference (35)).

A slightly later copper smelting furnace, dating from 2000 BCE (Figure 18) (*39*), shows how the copper smelting operation worked in practice. The furnace was charged with charcoal, oil, flux and ore and heated while oxgen was pushed in with a bellows via the tuyere. The slag formed and was drained out of the furnace by removing a stone in the lining. The copper was then removed as an ingot (usually semi-hemispherical in shape) and purified, usually by remelting.

Other views of the smelting process are shown below. Figure 19 (*40*) is specific to a lead smelting operation and shows a covered furnace and roasting furnaces. This furnace configuration allows the trapping of volatile but possibly valuable impurities such as sulfur in the ceiling of the furnace. Figure 20 (*41*) shows a copper smelting operation with multiple furnaces and lots of activity. These figures are included to give an idea of the complexity of even simple processes.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

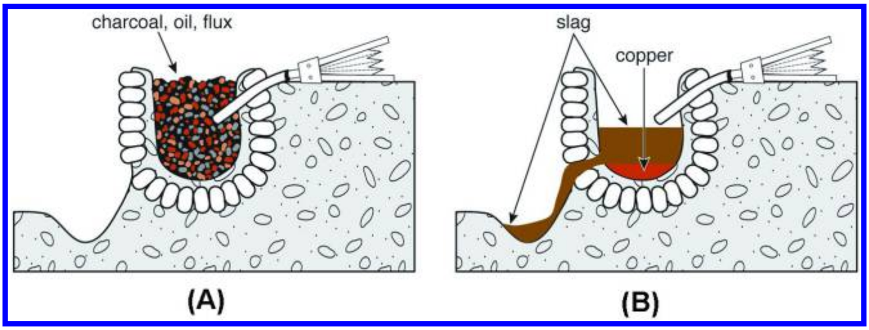


Figure 18. Copper smelting furnace, Egyptian, circa 2000 BCE. (A) Furnace loaded with ore, charcoal and flux; (B) furnace at the end of the smelt. (Data from reference (39)).

A—BURNING PYRE WHICH IS COMPOSED OF LEAD ORE WITH WOOD PLACED ABOVE IT. B—WORKMAN THROWING ORE INTO ANOTHER AREA. C—OVEN-SHAPED FURNACE. D—OPENINGS THROUGH WHICH THE SMOKE ESCAPES.

Figure 19. Roasting and smelting lead ore. The ore is roasted in a sloping furnace with logs that are placed on top of the ore. The slope allows the melting lead to flow out of the furnace. It is further refined in the covered furnace (40). (Agricola, De Re Metallica, Public Domain).

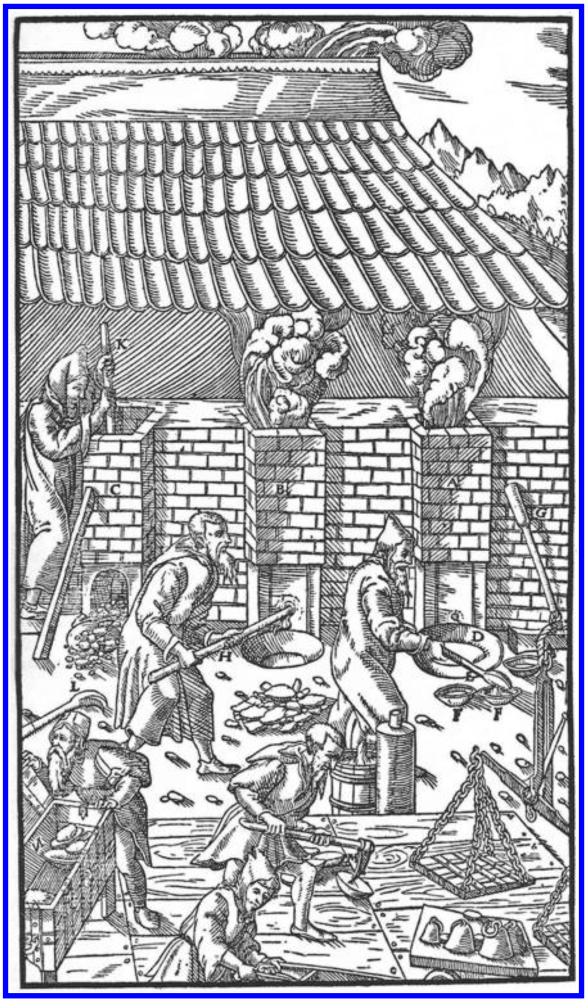
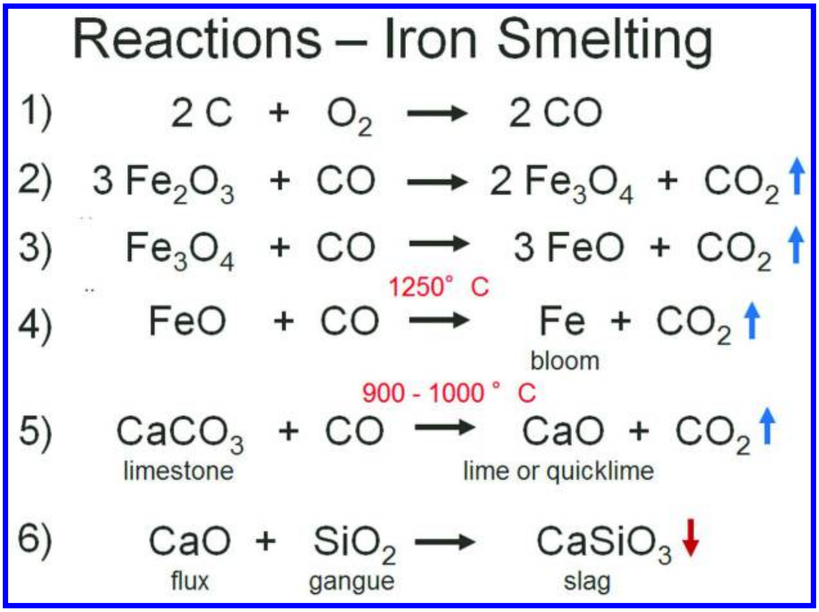


Figure 20. Copper smelting operation. The following is the original caption: A, B, C - Three furnaces. At the first stands the smelter, who with a ladle pours the alloy out of the forehearth in the moulds. D - Forehearth. E - Ladle. F. Moulds. G - Round wooden rammer. H - Tapping-bar. At the second furnace stands the smelter, who opens the tap-hole with his tapping-bar. The assistant, standing on steps placed against the third furnace which has been broken open, chips off the accretions. I - Steps. K - Spatula. L - The other hooked bar. M - Mine captain carrying a cake, in which he has stuck the pick, to the scales to be weighed. N - Another mine captain opens a chest in which his things are kept (41). (Agricola, De Re Metallica, Public Domain).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

The reactions involved in iron smelting (Figure 21) are similar to those for smelting copper and could be considered simpler as most iron ores are oxide or carbonate ores. One of the major issues that had to be conquered, however, was finding a flux to assist in the separation of the gangue from the bloom and the isolation of the pure iron. Every ore needs a different flux. Since there are many iron ores, the ancient iron smelters needed a lot of skill and experience (*28*).


Reactions – Iron Smelting

1) $2\,C + O_2 \longrightarrow 2\,CO$

2) $3\,Fe_2O_3 + CO \longrightarrow 2\,Fe_3O_4 + CO_2\uparrow$

3) $Fe_3O_4 + CO \longrightarrow 3\,FeO + CO_2\uparrow$

4) $\underset{}{FeO} + CO \xrightarrow{1250^\circ\ C} \underset{\text{bloom}}{Fe} + CO_2\uparrow$

5) $\underset{\text{limestone}}{CaCO_3} + CO \xrightarrow{900 - 1000^\circ\ C} \underset{\text{lime or quicklime}}{CaO} + CO_2\uparrow$

6) $\underset{\text{flux}}{CaO} + \underset{\text{gangue}}{SiO_2} \longrightarrow \underset{\text{slag}}{CaSiO_3}\downarrow$

Figure 21. The reactions (1-6) involved in iron smelting.

The Seven Metals of Antiquity

We now turn to details of the working of the seven metals of antiquity - gold, copper, silver, lead, tin, iron, and mercury. Although it is true that all but tin and lead occur natively, only gold and silver are commonly found as the native metal. No temperature higher than 900°C (easily reachable with charcoal and bellows) would be required to extract these metals from their ores.

When considering the seven metals of antiquity, we will treat them in the (approximate, as considered by historians and archeologists) order of their appearance. This section will discuss the form of the metal, whether native or ore, a timeline for the development of separation methods for the metal, and images of artifacts made from the metal.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Gold

Gold is often found in pure form in nature, as nuggets or grains, in rocks, in veins, and in alluvial deposits. It is easily worked, being both ductile and malleable, and does not tarnish or corrode. It may have been all of these properties that first caught the eye and interest of ancient man (*42*). In the beginning, it is likely that if a nugget were large enough it could have been hammered by Stone Age man into attractive shapes. During antiquity gold was almost always used as an ornament. Even when weapons were made of gold, they likely served as models or symbols and were intended for ritual purpose, not actual combat. Gold nails have also been found, but usually as part of an ornamental or funerary object (*43*).

Figure 22 shows the timeline for development of methods used to separate gold, usually from silver. The naturally occurring alloy of gold and silver, electrum, varies in color from pale yellow to white and in composition (from 90% gold - 10% silver to 80% gold - 20% silver (*44*).

The *cupellation* process is probably both the oldest and most efficient method of separating gold from base metals. Gold and/or silver is alloyed with lead in a special pot (*cupel*) by exposure to high temperature in a blast of air by which the unwanted metals are oxidized. A special crucible made of bone ash is needed. That is, porous enough to absorb the oxidation products of the base metals while retaining the gold or silver (*45*).

The *Salt process* requires the addition of salt to a silver-gold alloy and then heating with a reducing agent such as straw or charcoal. The salt reacts with the silver, forming AgCl, which is absorbed by the sides of the crucible. This process is still used in Japan (*45*).

The *amalgamation* process uses mercury to form an alloy with another metal that is solid or liquid at room temperature according to the proportion of mercury present. This method is usually used for extracting gold from rich gold ores (*45*) but was impractical until the production of mercury began on a commercial scale during the Roman era.

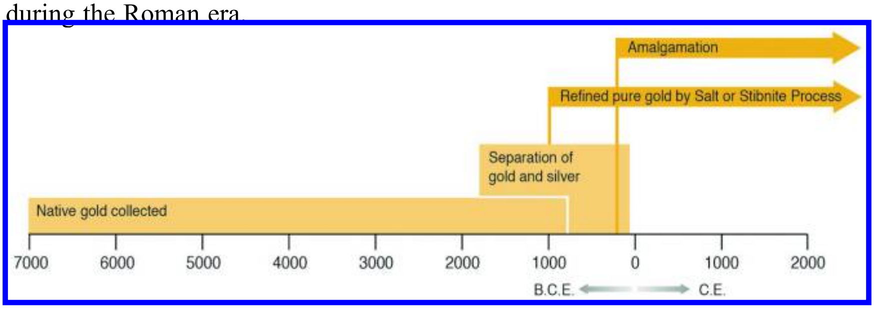


Figure 22. Timeline for gold separation methods. (data from reference (8)).

Figure 23 shows the famous "Mask of Agamemnon," which dates to 1500-1550 BCE. It was found by Heinrich Schliemann in 1876 and is a burial mask. In Figure 24 are shown some smaller ornamental objects, earrings and a brooch, which date from 600-300 BCE. The earrings in Figure 24(A) and (B) show the use of granulation and filigree decoration.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Figure 23. Gold death-mask known as the "Mask of Agamemnon." It is made of a gold sheet with repoussé details, 1550-1500 BCE. (By Xuan Che (Self-photographed (Flickr), 20 December 2010 /via Wikimedia Commons /CC BY 2.0).

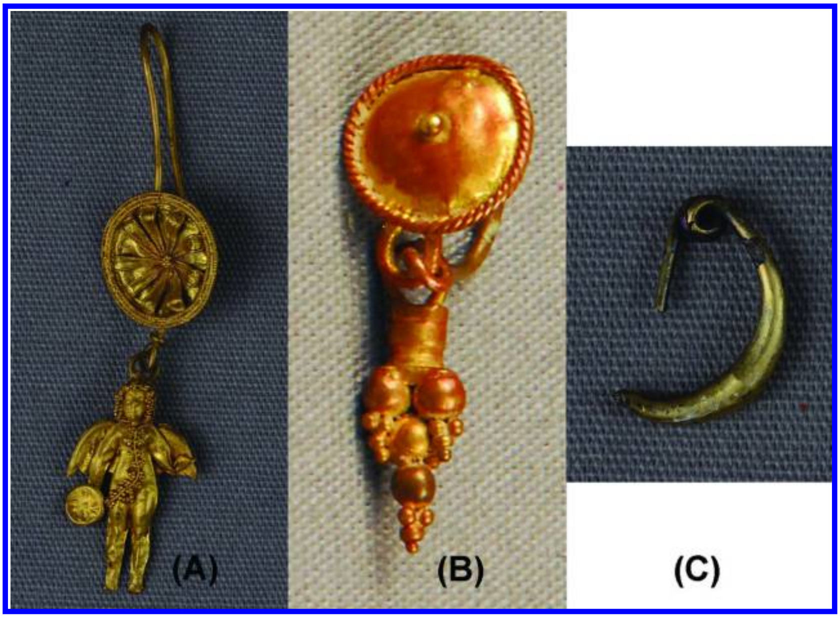


Figure 24. (A) Eros figurine earring, Greece, 300 BCE, 1929.01.0006A, gold, Spurlock Museum; (B) earring, Syria, 300 BCE, 1915.03.0001A, gold, Spurlock Museum; (C) Fibula (brooch or pin used to fasten garments), Italy, 600 BCE, gold, 1915.03.0231, Spurlock Museum. (Courtesy of The Spurlock Museum, University of Illinois at Urbana-Champaign).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Copper

Copper is found in the native state and was first used in a manner similar to that of gold, as an ornament. It was then discovered that, when cold-worked, hammered, for example, the metal became appreciably stronger and harder, and had uses that were utilitarian. These uses included tools, such as those from sites in Egypt which date from 2778-2423 BCE. These implements - chisels, gravers, points -- have exactly the same shapes as their modern counterparts (*46*). Figure 25 shows the various techniques by which copper is worked and transformed from an ore to metal.

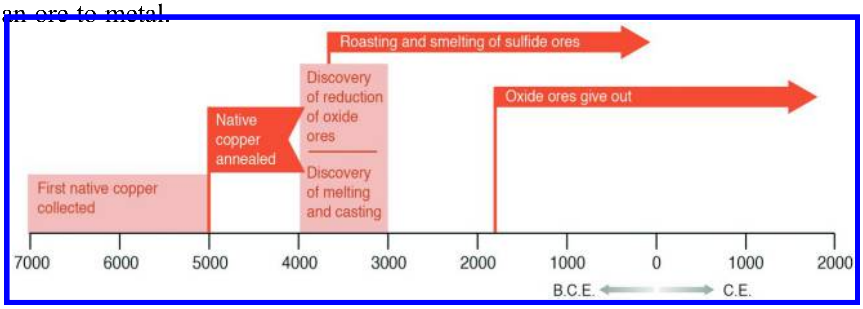


Figure 25. Timeline for copper separation methods. (data from reference (8)).

Native copper occurs in widely scattered deposits in the Ancient Middle East, but is found more usually in the form of its ores. Copper ores can be divided into two types, the easily reducible oxide and carbonate ores (Table 2 (*47*), Figure 26) and the more complex and less easily reduced sulfide ores (Table 3 (*47*), Figure 27), which can contain other metals and non-metals. It has been postulated that the more easily found and reduced copper oxide and carbonate ores were the first ones worked (*48*, *49*). The availability of these ores led to the production of cast copper objects (Figure 28), such as those found in the the Cave of the Treasure at Nahal Mishmar, Israel, and date from 4500-3600 BCE. These objects are the earliest examples of the use of the lost-wax cast method (*50*). Copper was also cast into coins, such as that shown in Figure 29, honoring Nero's father Germanicus.

Table 2. Principal Copper Ores (*47*)

Copper Ore	*Description*	*Cu Content*
Cuprite	Red oxide of copper, ruby ore, Cu_2O	88.8%
Malachite	Green (basic) carbonate of copper, $Cu_2CO_3(OH)_2$	57.3%
Azurite	Blue (basic) carbonate of copper, $Cu_3(CO_3)_2(OH)_2$	55.1%
Chrysocolla	Copper silicate, $(Cu,Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O$	36.0%

Continued on next page.

Table 2. (Continued). Principal Copper Ores (*47*)

Copper Ore	*Description*	*Cu Content*
Atacamite	Copper chloride, $Cu_2Cl(OH)_3$	59.5%
Tenorite	Copper oxide, CuO	79.9%

Figure 26. Principal copper ores: (A) cuprite (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0); (B) malachite and azurite (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0); (C) chrysocolla (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0); (D) atacamite (By Stefan Schorn [GFDL Wikimedia Commons/ CC-BY-SA-3.0; (E) tenorite. (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0).

Table 3. Copper Sulfide Ores (*47*)

Copper Ore	*Description*	*Cu Content*
Chalcocite	Vitreous copper, redruthite, copper glance, Cu_2S	79.8%
Covellite	Indigo or blue copper, CuS	66.5%
Bornite	Purple copper ore, peacock ore (a rarer variety of chalcopyrite), Cu_5FeS_4	55.5%
Tetrahedrite	Compound of copper, sulfur, and antimony, $(Cu,Fe)_{12}Sb_4S_{13}$	52.1%
Enargite	Compound of copper, sulfur, and arsenic, Cu_3AsS_4	48.4%
Chalcopyrite	Copper pyrites, towanite, yellow copper ore, $CuFeS_2$	34.6%
Chalcanthite	Copper sulfate, $CuSO_4{\cdot}5H_2O$	25.4%

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

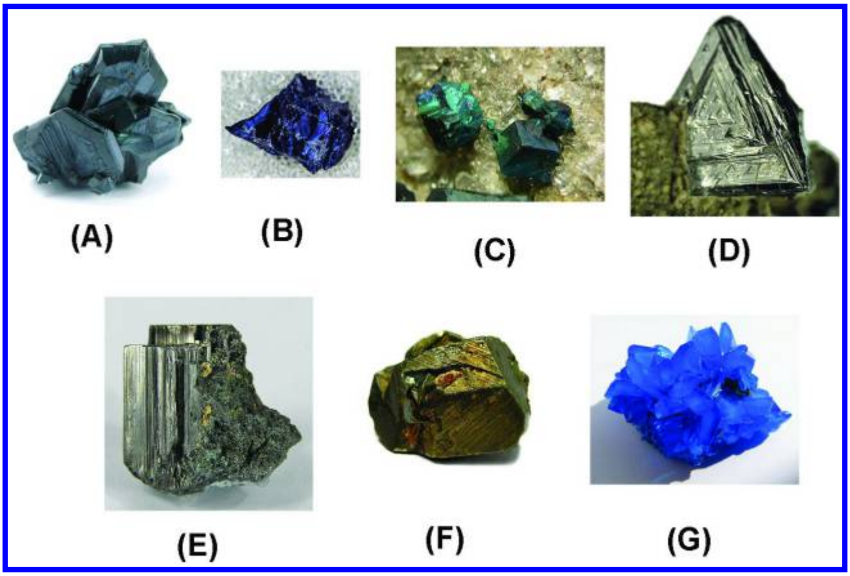


Figure 27. Copper sulfide ores: (A) chalcocite (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0; (B) covellite (by James St. John / Wikimedia Commons /CC BY 2.0); (C) bornite (by Leon Hupperichs/ Wikimedia Commons /CC BY-SA 3.0); (D) tetrahedrite (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0);); (E) enargite (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0); (F) chalcopyrite (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0); (G) chalcanthite. (By Ra'ike (Own work) Wikimedia Commons/ CC BY-SA 3.0).

Figure 28. Copper objects from the Cave of the Treasure, Nahal Mishmar, 4500-3600 BCE as dated by the reed wrappings in which the objects were found. (By Photo: Ella Zayith / Wikimedia Commons / CC BY-SA 3.0).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Figure 29. Coin as issued by Caligula in honor of his deceased father Germanicus (Roman; Italy), 40-41 CE, copper, 1919.63.1415, Spurlock Museum. (Courtesy of The Spurlock Museum, University of Illinois at Urbana-Champaign).

Silver

Silver is another metal which has high ductility and malleability but is very soft when compared to copper or gold. Silver is rarely found in the native state as nuggets, which is likely why it was recognized and used later than gold and copper. It can be easily smelted from its chloride ores, but as these ores are not plentiful silver was usually rarely available as the metal until about 2500 BCE, when almost all silver was produced from argentiferous galena. The lead and silver were separated by smelting and then by cupellation (*51*). Figure 30 shows the timeline for silver and lead separation techniques, and the principal silver ores are given in Table 4 (*52*) (Figure 31). Figure 32 shows an object shaped like a bull's head that dates to the sixteenth century BCE. It is a drinking vessel meant to be used in a ceremonial way. The horns and rosette are made of silver.

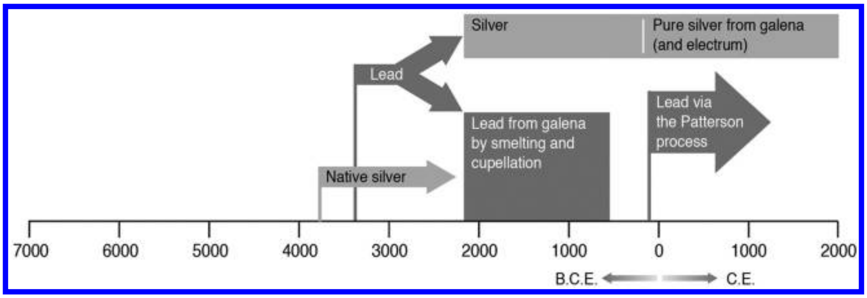


Figure 30. Timeline for silver and lead separation methods. (data from reference (8)).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Table 4. Principal Silver Ores (*52*)

Silver Ore	*Description*	*Ag Content*
Argentite	Ag_2S	87.1%
Chlorargyrite	AgCl	75.3%
Pyrargyrite	ruby silver, red silver ore, Ag_3SbS_3	59.8%
Galena	PbS and Ag_2S as an impurity	

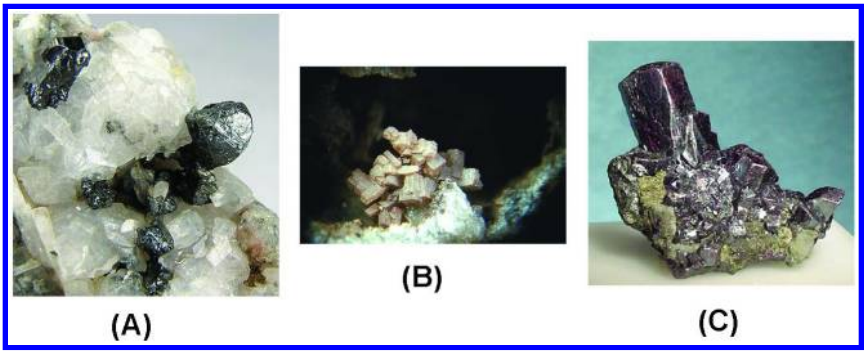


Figure 31. Principal silver ores: (A) argentite (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0); (B) chlorargyrite (By Manfred Groß Wikimedia Commons/ CC BY-SA 3.0); (C) pyrargyrite. (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0).

Figure 32. Silver Mycenaean vase (rhyton) in the shape of a bull's head, 1600-1501 BCE, Athens National Archaeological Museum. (By Giovanni Dall'Orto. (Own work) / Wikimedia Commons).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Lead

Lead is a very malleable and dense metal, easily worked into sheets (and thence into pipes), as well as easily cast into objects both small and large. It is simply extracted from its most abundant ore, galena. Galena was used as a cosmetic, kohl, when finely crushed. If galena is roasted with charcoal it reduces to the metal at relatively low temperatures. The liquid lead was then allowed to solidify at the bottom of the furnace. Because the technology for its extraction is so simple, little trace of its methods of production have remained in the historic record. It became a secondary material when it was discovered that it was easy to remove its precious impurity, silver. As noted above, this was done via smelting and cupellation or via what we now call the Pattinson process. The *Pattinson process* takes advantage of a property of the lead-silver mixture, that the first crystals formed upon cooling the melt are pure lead and the remaining liquid is enriched in silver. The lead can be enriched up to 97.6% lead and 2.4% silver, and at this point the material can be cupellated to remove and purify the silver (*51*, *53*). The principal ores are given in Table 5 (*52*) (Figure 33). Several small cast objects and some lead ingots from Roman Britain are shown in Figure 34.

Table 5. Principal Lead Ores (*52*)

Lead Ore	*Description*	*Pb Content*
Galena	PbS	86.6%
Cerussite	$PbCO_3$	77.5%
Anglesite	$PbSO_4$	68.3%

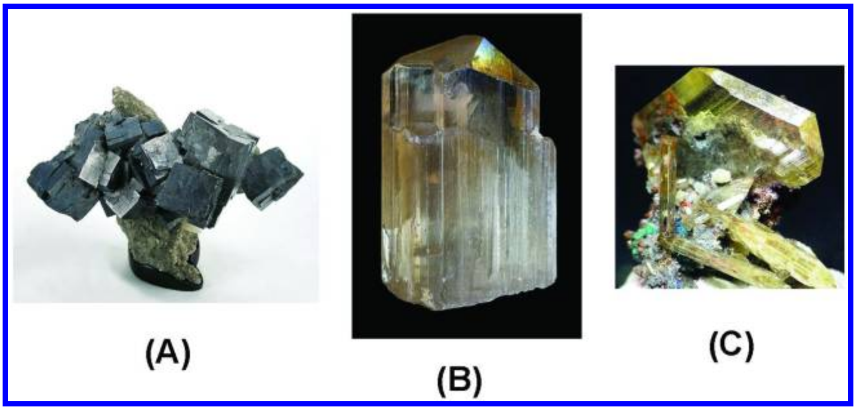


Figure 33. Principal lead ores: (A) galena (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0); (B) cerussite (By Didier Descouens (Own work) Wikimedia Commons/ CC BY-SA 3.0); (C) anglesite. (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Figure 34. (A) Cast lead figurine, China, Han dynasty, 206 BCE - 220 CE (Courtesy of Los Angeles Museum of Art); (B) cast lead amulet with Greek inscription, Egypt, 332 BCE - 395 CE (Courtesy of Los Angeles Museum of Art); (C) cast lead ingot, Roman Britain, 43-410 CE. (By Rodw (Own work) / Wikimedia Commons / Public domain).

Tin

The previous metals, gold, copper, silver, and lead, were all were used in their elemental state. Our next metal, tin, was normally not used at all in antiquity except as a constituent of its alloy with copper - *bronze*. Bronze is composed mostly of copper (80-95%), tin (20-5%), and many times smaller amounts of other metals such as zince and lead. Bronze is harder and has a higher tensile strength than copper but is less malleable. Because it melts at a lower temperature than copper, it is more easily cast than copper. Bronze is strong and wear- and corrosion-resistant. All of these properties made it useful, and it became the metal of choice for tools, weapons, small ornamental objects, large statues and other monumental pieces (*54*). Bronze gave its name to an entire age because of the utility of the alloy but it replaced copper as the metal of choice very gradually and slowly (*55*). It could not be produced reproducibly until it was made by mixing melted copper and smelted tin. The most common ore of tin is tinstone (cassiterite, SnO_2, 77.78% tin) which

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

needs a reduction temperature higher than the melting point of gold (1064°C). There was only one problem - tin was only available from a few selected localities, such as Britain, and had to be exported to the locales where copper was mined. This both limited the spread of bronze at first and stimulated inter-region trading and the spread of technology as it grew to be a more popular metal (*56*).

Figures 35 and 36 show a selection of small decorative cast bronzes from a large space in time (3000 BCE to 200 CE). A figure of an ibis made of mixed wood and bronze is shown in Figure 37. Two monumental statues from Greece, produced approximately 125 years apart, are shown in Figures 38 and 39. Both are beautiful but portray very different aesthetics. The last figure of a bronze piece, Figure 40, shows a fragment of the Antikythera Mechanism (*57*), as recovered from the sea off the Greek island of Antikythera, and a modern reconstruction of the complete device. The mechanism is an astrolabe: it dates between 205-100 BCE (*58*), and contains over 30 interlocking gearwheels. Nothing similar in complexity to it will be invented for another 1000 years.

Figure 35. (A) Head of bull figurine, 3000-700 BCE, bronze, Greece (Minoan), 1927.01.0001, Spurlock Museum; (B) Horse figurine or pendant, Iran, 1500-500 BCE, bronze, 1996.13.0003, Spurlock Museum; (C) Osiris funerary figure, Egypt, 1570-1070 BCE, bronze, 1900.38.0018, Spurlock Museum. (Courtesy of The Spurlock Museum, University of Illinois at Urbana-Champaign).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

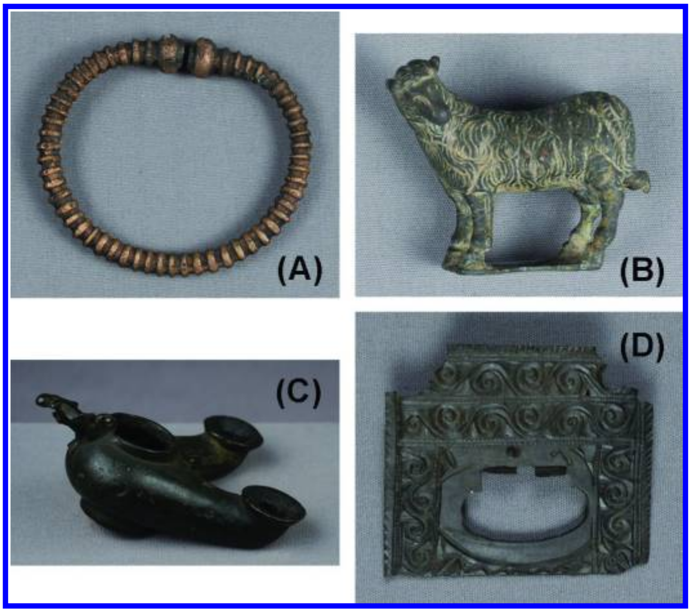


Figure 36. (A) Bracelet, Western Europe, 600-200 BCE, bronze, 1924.02.0177, Spurlock Museum; (B) Figurine of ewe, Greece, 323-30 BCE, bronze, 1929.01.0002, Spurlock Museum; (C) Oil lamp, Greece, Turkey (Roman), 100-200 CE, bronze, 1922.01.0232, Spurlock Museum; (D) Buckle plaque fragment, France, 500 CE, bronze, 1924.02.0072C, Spurlock Museum. (Courtesy of The Spurlock Museum, University of Illinois at Urbana-Champaign).

Figure 37. Votive figure of Ibis, Egypt, 700 BCE, wood and bronze, 1992.04.0003, Spurlock Museum. (Courtesy of The Spurlock Museum, University of Illinois at Urbana-Champaign).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005


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Figure 38. Left: Charioteer of Delphi (Greece), bronze, 475 BCE. (By Vera Mainz (own photo), 2007); Right: Detail of Charioteer of Delphi. (By Adam Carr at English Wikipedia; Later version(s) were uploaded by Ericd at English Wikipedia / Public domain / Wikimedia Commons).


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Figure 39. Left: "Boxer at Rest." Greek bronze, circa 350 BCE; Right: Detail of sculpture. (By Mary Virginia Orna, Museo Nazionale Romano, Rome, Italy).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Figure 40. Left: Antikythera Mechanism fragment (A), bronze, 205-100 BCE (ii), Greece (By Marsyas Edit: Cornischong at Luxembourgish Wikipedia / Wikimedia Commons) / CC-BY-SA-3.0); Right: Modern reconstruction of Antikythera Mechanism, Athens Archaeological Museum. (By Giovanni Dall'Orto. (Own work) / Wikimedia Commons).

Iron

Arguably the most important metal of antiquity is iron. Iron is not found as the free metal except as meteoritic iron. Iron is one of the most abundant elements in the earth's crust and deposits of its major ores are numerous, wide-spread and easily accessible. Its use came much later than copper, probably because of its high melting point and the consequently high temperatures needed for smelting it. However, after several millennia of experience with copper and bronze smelting, the smelting of iron ores was fairly widespread between 1200-1000 BCE (*59*, *60*). The major advantage of iron is its ability to form steel, which is an alloy with carbon, giving a material with increased malleability, toughness and ductility (see Table 6 (*61*, *62*) for alloy compositions and properties). In the steel form, iron is stronger and more elastic than bronze and will both take and keep a finer cutting edge. The timelines for technical developments for iron are given in Figure 41. The principal iron ores are shown in Table 7 and Figure 42.

Because iron reacts with oxygen, many early iron artifacts have likely disintegrated over time. It is therefore possible that iron objects of various types were made earlier than the timeline in Figure 41 indicates but have disappeared. Two daggers are shown in Figure 43, both made of iron but about 1600 years apart. Figure 44 shows various utilitarian artifacts from 100-800 CE. The Iron Pillar of Delhi, which dates from about 400 CE, is shown in Figure 45. The pillar is 23 feet tall. It was manufactured by the forge welding of pieces of wrought iron. It is unusually resistant to corrosion because of an even layer of crystalline iron hydrogen phosphate forming on the high phosphorus content iron, which serves to protect it from the effects of the local Delhi climate (*63*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Table 6. Alloys of Iron and Properties (*56*, *57*)

Alloy	*% Carbon Content*	*Implication*
Wrought Iron	< 0.1% carbon	Ductile; can be heated and welded but not hardened
Steel	0.65% carbon 1% carbon 1.5% carbon	Increase in tensile and compressive strength; ductile; can be welded and hardened. Steel for tools composition. Hardness increases but ductility and welding properties drop
Cast Iron	2% or higher	Loss of ductility; cannot be welded or tempered.
Pig Iron	1.8 - 3.0% carbon	Impure and brittle form of iron; cannot be worked or shaped as is but must be remelted and cast; the common form of iron from a smelter.

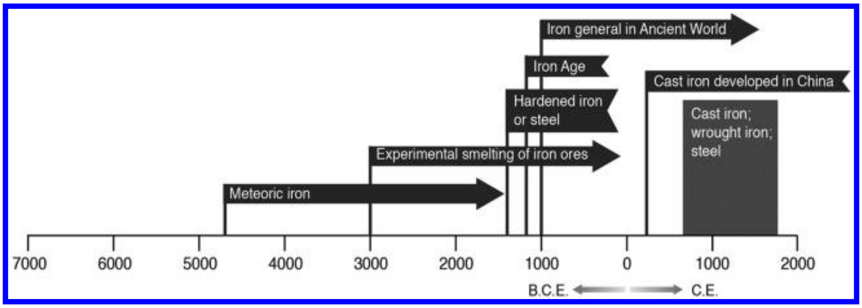

Figure 41. Timeline for iron separation methods. (data from reference (8)).

Table 7. Principal Iron Ores (*59*)

Iron Ore	*Description*	*Fe Content*
Magnetite	Lodestone, Fe_3O_4	72.4%
Hematite	Fe_2O_3	69.9%
Siderite	Ironstone, $FeCO_3$	48.2%

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

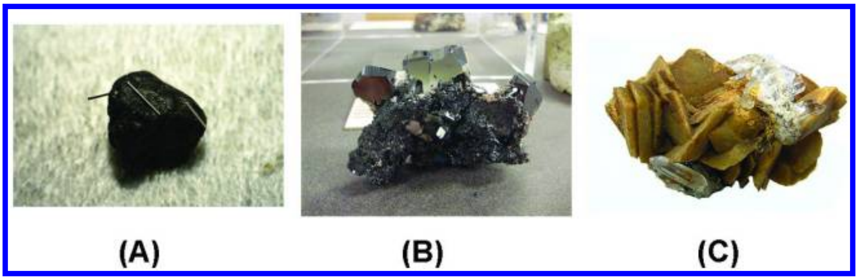

Figure 42. Principal Iron Ores: (A) magnetite (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0); (B) hematite (By Teravolt (talk) Wikimedia Commons/ CC BY-SA 3.0); (C) siderite. (By Rob Lavinsky, iRocks.com/ Wikimedia Commons/ CC-BY-SA-3.0).

Figure 43. Top: An antenna-hilted Iberian dagger, circa 399-200 BCE (Luis García / Wikimedia Commons / CC-BY-SA-3.0); Bottom: Dagger with iron blade and gold hilt from Alaca Höyük near Hattusa, circa 2000 BCE. (By Noumenon (Own work) / Wikimedia Commons / CC-BY-SA-3.0).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

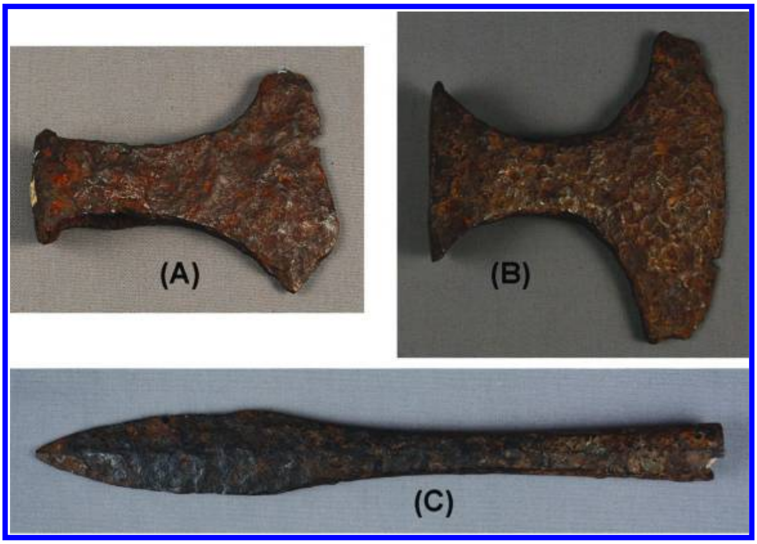

Figure 44. (A) Hatchet head, France, 100-600 CE, iron, 1924.02.0408, Spurlock Museum; (B) ax head, France, 100-600 CE, steel, 1924.02.0312, Spurlock Museum; (C) Spear head, France (Roman), 375-800 CE, iron, 1924.02.0030, Spurlock Museum. (Courtesy of The Spurlock Museum, University of Illinois at Urbana-Champaign).

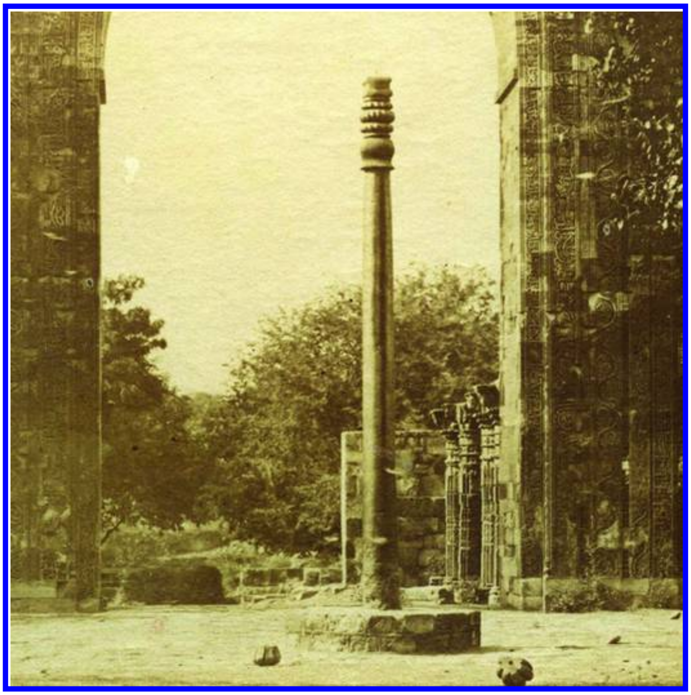

Figure 45. Iron Pillar of Delhi (India), circa 400 CE. (Image Public domain/ Wikimedia Commons).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Mercury

Mercury was the last of the metals of antiquity to make its appearance, sometime in the first millennium BCE. Aristotle (384-322 BCE) refers to the metal as “fluid silver,” but does not mention how it is obtained. Theophrastus (371-287 BCE), his student, wrote that mercury was obtained from cinnabar (HgS) rubbed with vinegar in a brass mortar with a brass pestle (*64*) from mines in Spain and elsewhere. Dioscorides (40-90 CE) was the first to describe distillation as a method for its recovery (*65*):

> *Quicksilver (liquid silver) is made from ammion, which is called cinnibari. An iron bowl containing cinnabari is put into an earthen vessel and covered over with a cup-shaped lid smeared with clay. Then it is set on a fire of coals and the soot which sticks to the cover when wiped off and cooled is quicksilver. Quicksilver is also found in drops falling from the walls of the silver mine. . . . It can only be kept in vessels of glass, lead, tin(?), or silver, for if put into any other substances it consumes them and flows through.*

The primary mercury ore is cinnabar (HgS), shown in Figure 46. The smelting process is simple and straight-forward, as one heats the ore at a relatively low temperature in an oxidizing atmosphere to convert it to HgO. Further heating (at 500°C or slightly higher) results in the decomposition of the oxide and the release of Hg (bp 360°C), which is recovered by distillation. This process is shown in Figure 47 (*66*) using an *opercula*, a rounded clay vessel with a nozzle, to collect the liquid mercury.

Aitichison noted (*67*):

> *It seems likely that no change in the method of making mercury occurred during the whole of antiquity.*

As mentioned under Gold, above, the primary use of mercury was in the purification of gold and silver via amalgamation.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

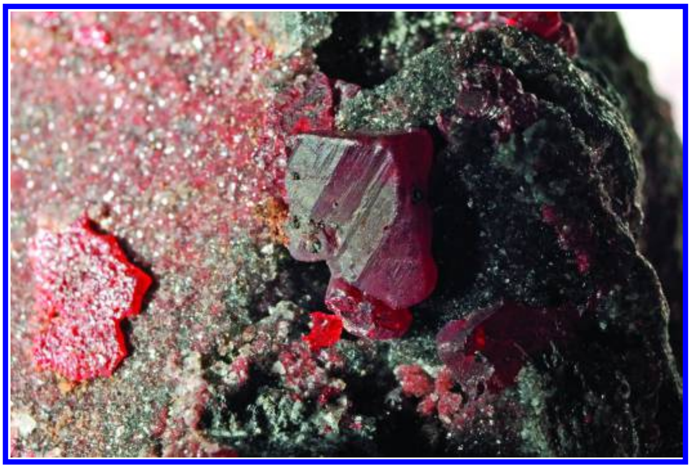

Figure 46. Crystals of cinnabar, droplets of native mercury from the Almadén Mine, Castile-La Mancha, Ciudad Real, Almadén District, Almadén, Spain. (By Parent Géry (Own work) /Wikimedia Commons / CC BY-SA 3.0).

Figure 47. A method of extracting mercury from its ore. Clay pots (A) holding the ore are placed in the furnace and covered with opercula (B) with nozzles that lead to the collecting vessels (D) (66). (Agricola, De Re Metallica, Public Domain).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch005

Conclusion

This short summary of the first metals used by man in antiquity has shown how the search for ways to use them in turn led to the development of technology to isolate them from their ores, purify them, alloy them with other materials to alter their properties, and many other advances, both good and bad.

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Chapter 6

The Skin They Were In: Leather and Tanning in Antiquity

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As the prehistoric human creature expanded geographically toward more extreme climates, early man began to use the pelts of other animals for clothing or shelter and for protection from the elements or other physical dangers. With further technological development, skins and hides found additional uses as shoes, writing material, armor, or other equipment such as livestock harnesses. In order for this to be practical, means of retarding or preventing the rapid decomposition of the hide material was necessary. A variety of treatment processes were developed, with many of them also altering the physical properties of the hides, rendering the leather material harder, stiffer, or more durable than the original hides. The treatment methods available to early tanners will be discussed, including archaeological evidence of these methods and discussion of the chemical changes that occur during these tanning processes.

Introduction

The production of leather from raw skins and hides is widely considered to be one of mankind's most ancient technologies (*1*, *2*). In fact, the quintessential visual representation of prehistoric man is that of a humanoid figure clad in pelts or furs, jumping around with the excitement of having harnessed the power of fire for the first time. As humanity spread geographically from the warm equatorial regions to more hostile and extreme climates, the use of animal skins for clothing and shelter to serve as protection from the elements would have been critical to survival.

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While the technologies and techniques needed to weave plant materials into robust fabrics would eventually be developed, it is generally accepted that animal skins would have been among the first materials used for clothing and other such applications. Unfortunately for these early prehistoric people, nature's mechanisms for recycling materials would have rapidly rendered raw pelts unpleasant to wear, as decomposition and putrefaction processes set in to cause various odors while undermining the structural integrity of the skins. While the circumstances surrounding their discoveries may never be known, these early humans were nonetheless able to develop methods of slowing the rate of decomposition of their acquired pelts and hides, likely though dehydration initially, and eventually utilizing the application of foreign substances which not only slowed the rate of putrefaction, but also changed the physical properties of the skin tissues, in some cases rendering the hide useful for a variety of other applications. Over the millennia, these techniques have been refined and adjusted, but the resulting material is still important to the modern civilized human, and for many of the same purposes.

The term leather refers to the skins of animals that have been "tanned" or treated through some process (*3*). While one of the main purposes of tanning is to enable the skin to resist decomposition, the resulting leather also is imparted with other physical changes such as increased durability, elasticity, and flexibility as well as water and puncture resistance. These improved physical properties allow the leather to be applied to a wide variety of applications within our modern world, including uses for jackets, shoes, gloves, and other clothing, bags and purses, upholstery for automobiles and furniture, tack, saddles, and harnesses for horses and beasts of burden, book bindings, and as coverings for athletic equipment such as baseballs, basketballs, and footballs (Figure 1).

Leather Usage

Most of the current applications of leather are at their basis the same as those from antiquity. While it is readily apparent that the use of fabrics derived from plant, animal (wool), and insect-based (silk) fibers has largely supplanted leather for clothing in general apparel, the use of leather for protective equipment continues to be rather common. The durability and puncture resistance of leather renders it well suited for uses in shoes, particularly as a material for the sole of the shoe. Motorcycle riders often wear leather jackets and chaps as protection from injury in the unfortunate event of an accident. The water resistance of leather also provides the side benefit of protection from wind and rain while riding. The elasticity and flexibility of leather makes it well suited for uses as belts, straps, or harnesses, where a brittle or rigid material might break or cause abrasive damage or injury. The physical appearance of leather is also often considered to be desirable, whether it be the natural earth tones of the raw leather or other colors imparted by various dyes and surface treatments.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch006

Figure 1. Examples of modern use of leather. (Courtesy of the author.)

Evidence of leather usage can also be found continually in the historic record, through written accounts, paintings, or the discovery of actual leather artifacts (*2*). However, since leather is ultimately still an organic material subject to weathering and decomposition, physical artifacts are increasingly rare. While the tanning process does impart a resistance to decomposition, this resistance merely retards the decomposition process as opposed to completely stopping degradation. Further slowing of the artifacts' decay can occur if the object is in a dry, anaerobic environment. Unfortunately, it is exceedingly rare for an item to find itself under these conditions for any significant period of time, much less for thousands of years. As such, the number of extant examples of leather from antiquity is rather small. There is, however, still ample evidence to support the assertion that leather was not only used, but quite important to ancient civilizations across the globe.

Ancient Mesopotamia had an entire thriving leather industry, with written inventory records having been discovered describing in detail both the numbers and types of hides procured and stored. Further records indicate leather usage for scabbards and quivers, sole leather for the shoes of soldiers, harness material for oxen and donkeys, wagon parts, hinges, and for the production of religious objects, with cuneiform tablets (dating to 1600-1000 BCE) providing some insight into recipes and procedures used for leather tanning (*1*, *4*, *5*). Translations of the ancient Sumerian epic of Gilgamesh clearly differentiate the wearing of "skins" from the wearing of "garments", indicating that the use of preserved pelts or leather for clothing, while perhaps considered uncivilized, was not unheard of (*6*).

Ancient Egypt also provides a host of evidence of leather production and use. Artifacts from graves include burial garments made of pieces of leather stitched together (*2*). Wall paintings in tombs dating from as far back as the 4th millennium BCE appear to show workers soaking hides in pots, then drying and working them over a beam (*2*). Evidence also exists to indicate that while papyrus was most often used as a writing material, sacred documents were often written on leather or parchment (*2*, *5*).

Eastern Asia also has a long history of leather use for clothing, armor, and other implements. Leather garments such as coats, aprons, and shoes have been dated to the 3rd millennium BCE (*7*). Examples of lacquered leather armor from China dated from the 5th to 3rd centuries BCE have been reported (*8*). In 2006, the contents of a tomb believed to date back to ~600 BCE included a bronze sword in a scabbard wrapped in leather (*7*).

The Ancient Roman army utilized a substantial amount of leather, with specialized tradesmen devoted to the production of leather shoes, tents, saddles, wine and water skins, breastplates, and shields (*2*). The use of leather implements of war are referenced in Homer's epic poem "The Iliad", including the use of leather coverings for shields during the Trojan War (*9*). Roman charioteers are depicted with leather lacings to secure their tunics as they rode (*10*). The Celtic tribes of northern Europe were reported to have had significant skill with leather production and craft by the time the Roman Empire made contact (*2*).

Parchment, a thin skin treated under tension and used as writing material, was commonly used during the Middle Ages, and the use of leather as a writing material can be traced back to Egypt in the middle of the 3rd millennium BCE (*2*, *11*). Textual evidence suggests the use of parchment in Mesopotamia before the 8th century BCE, with evidence suggesting that the Assyrians possessed a method of preparing the material (*2*, *4*).

These are just a few examples of evidence to support the assertion that leather has had wide usage geographically and chronologically. It is commonly believed that leather usage predates recorded history, with multiple cultures' ancient texts referring to leather or tanning in ways to suggest its presence was commonplace, such as the aforementioned Sumerian story of Gilgamesh (*6*) and the Old Testament of the Bible (*12*). However, physical artifacts dating to the 3rd millennium BCE or earlier have proven quite elusive, for reasons to be discussed later in this text.

Circumstances for study of ancient leather artifacts improved in the early 1990's, when the famous "Iceman", later nicknamed Ötzi (Figure 2), was discovered on the Schnalstal glacier in the Alps near the modern Austria/Italy border (*13*). Carbon-14 dating placed the frozen mummy to approximately 3300 BCE (*14*). Having met an untimely and apparently violent end upon the glacier,

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch006

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch006

Ötzi was preserved in the ice with his complete gear which included his clothing, consisting of a fur cap, a hide coat, and leggings composed of numerous pieces of leather sewn together (*13*). This find provided the oldest physical evidence of leather usage by ancient people.

Skins and Hides

The internal structure of skins and hides can be generally divided into three layers: the epidermis, dermis, and hypodermis, often referred to as the subcutaneous layer (Figure 3). The epidermis is the outermost layer, consisting primarily of layers of dead skin cells which serve as a barrier between the environment and the interior of the body (*15*). Epithelial cells are produced in the lowest portions of the epidermis, where continual production pushes them toward the surface where they eventually flake off. These flakes are primarily composed of keratin proteins, with the entire layer lacking robust connective tissues (*15*) necessary for the conversion of raw skins to useful materials. The hypodermis is the lowermost layer of the skin, composed of fatty tissues, vasculature, and some connective tissues which attach the skin to the deeper muscle tissues. Like the epidermis, this layer also is lacking robust connective tissues.

The central layer of the skin, termed the dermis, is the portion of the skin almost exclusively utilized in the production of leather (*4*). The bulk of the dermal material is composed of the protein collagen, a fibrous structural protein consisting of three peptide chains with approximately 1000 amino acid residues each (*16*). These chains are formed through a condensation reaction between carboxylic acid and amine groups of various amino acids (Scheme 1), forming the polypeptide backbone. While the exact composition is somewhat variable dependent upon the specific tissue and species, approximately one third of the amino acid residues in a typical collagen chain are glycine residues (*16*). Additionally, some number of aldehyde groups are also present to participate in cross-linking bonds (*16*).

The polypeptide chains are then ordered in microcrystalline triple-helical units (*15*, *17*). The collagen helices aggregate into parallel bundles, which in turn interconnect to form strong, flexible fibers (*16*). Interactions between fibers occur through a combination of intermolecular interactions (hydrogen bonds, dipole-dipole interactions, van der Waals interactions) as well as through covalent bonds. Increasing the number of covalently-bonded cross-links between the collagen fibers, as occurs during the tanning process, serves to increase the thermal and chemical stability of the skin (*16*), thereby increasing resistance to decomposition due to biological activity and changing the material's physical properties.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch006

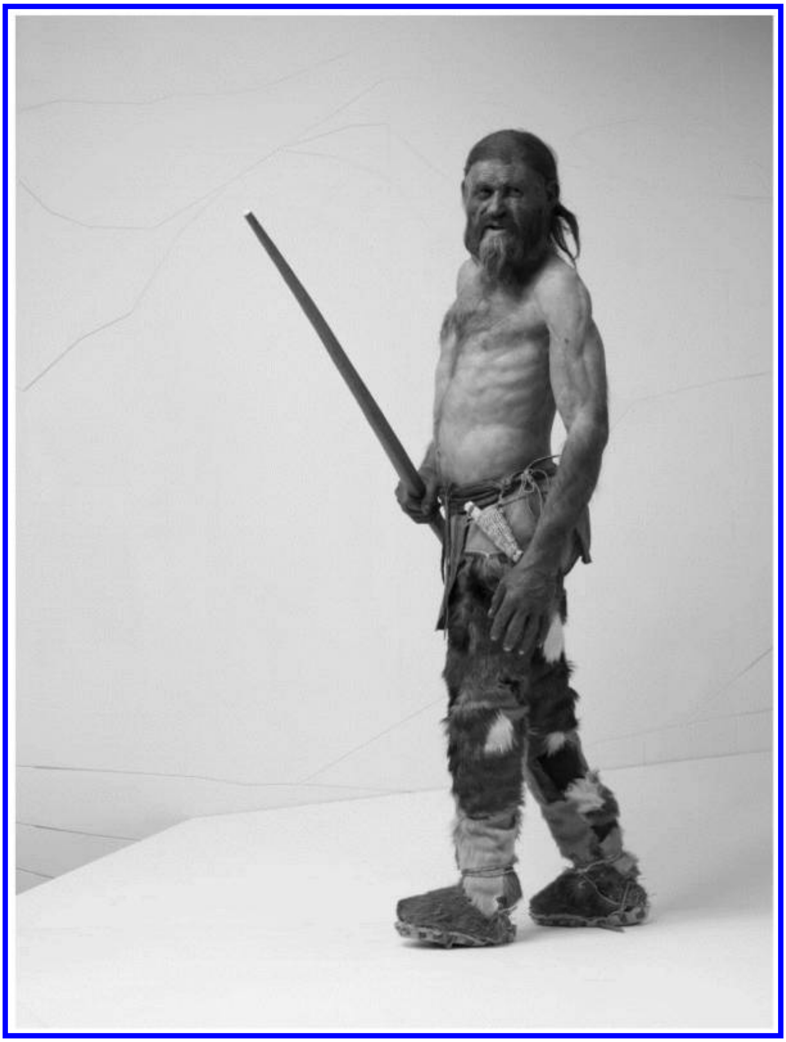

Figure 2. Reconstruction of Ötzi the "Iceman". [Reprinted with permission of the South Tyrol Museum of Archaeology. www.iceman.it.]

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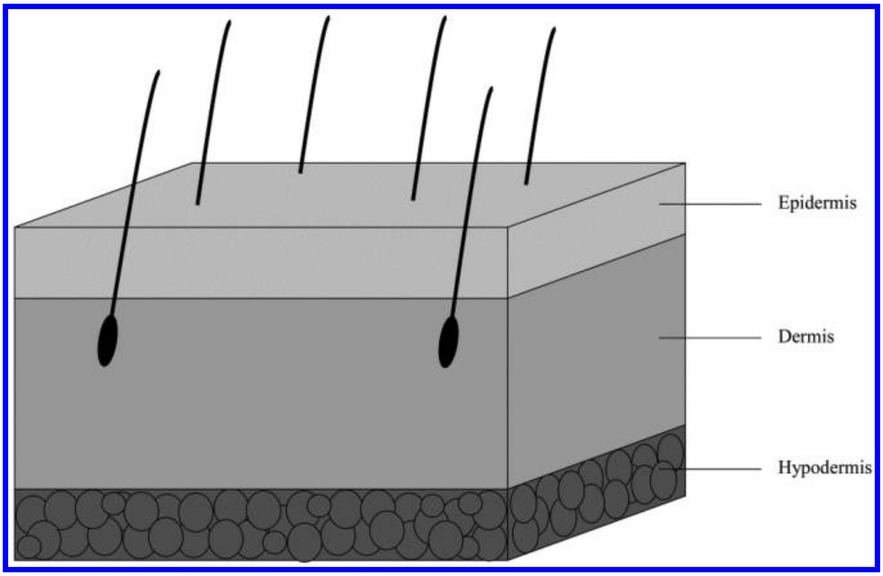
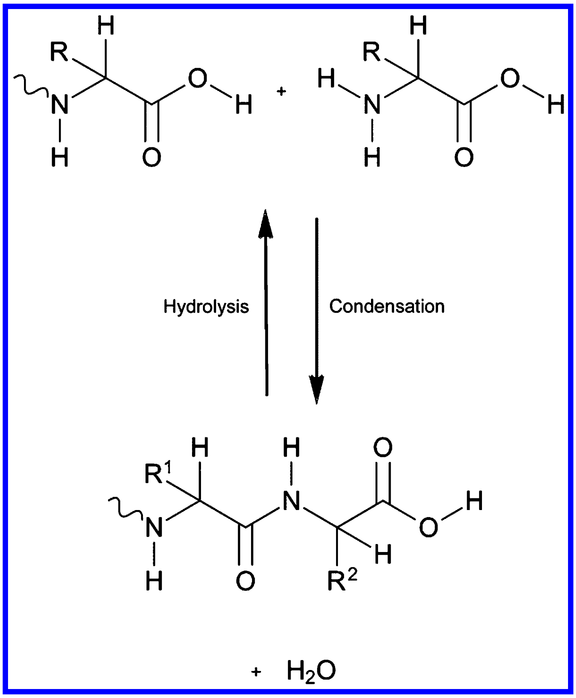


Figure 3. Typical skin morphology.



Scheme 1. Formation and decomposition of collagen.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch006

Chemistry of Leather Tanning

Decomposition Processes

Arguably the principle motivation behind the development of the tanning process was the desire to retard or halt the decomposition of the skin or hide. Decomposition occurs primarily through hydrolysis of the polypeptides making up the collagen network (Scheme 1). These hydrolysis processes can be catalyzed through the action of acids, bases, or enzymes. Decomposition due to bacterial action is primarily the result of acidic and enzymatic attack, and begins almost immediately after the hide had been removed from the animal carcass, as anaerobic bacteria gain access to the hide and begin the putrefaction process (*18*). Not surprisingly, the best means to minimize degradation due to bacterial action was to immediately begin some preservation process on the hide, be it dehydration or tanning. If this was not practical, preliminary treatment of the raw hide could be performed in order to inhibit bacterial action as much as possible.

While modern chemistry and processing methods allow for the use of bactericidal treatments for short-term storage, the primary methods of preservation in ancient times were likely concerned with the removal of water, thus inhibiting bacterial growth and retarding hydrolysis processes (*18*). The most likely methods would have involved salting, either directly (*18*, *19*) or by soaking in a saline solution (*4*). This pretreatment could then allow the tanner to store the hides until such time as the tanning process could be completed.

Dehydration

One of the simplest and most obvious means to slow the action of bacteria is dehydration or desiccation of the hide. Removal of water from the hide would protect the collagen through both inhibition of bacterial growth and prevention of hydrolysis due to the lack of water for the reaction. While the stated goal of protecting the hide from decomposition could indeed be accomplished through dehydration, the resulting material would lose the pliability necessary for useful applications, as can be seen in modern rawhide. The material could be formed to some degree by wetting and shaping, followed by redrying. A limited flexibility can sometimes be imparted with repeated bending or working. Unfortunately, the hide also becomes quite brittle and prone to cracking or breaking when dry, rendering it unsuitable for most desired uses of ancient people. Additionally, this resistance to decomposition can only be maintained as long as the hide remains dry. Moisture from perspiration, rain or other precipitation, or other sources would rapidly counteract the dehydration treatment of the material and result in degradation (*20*).

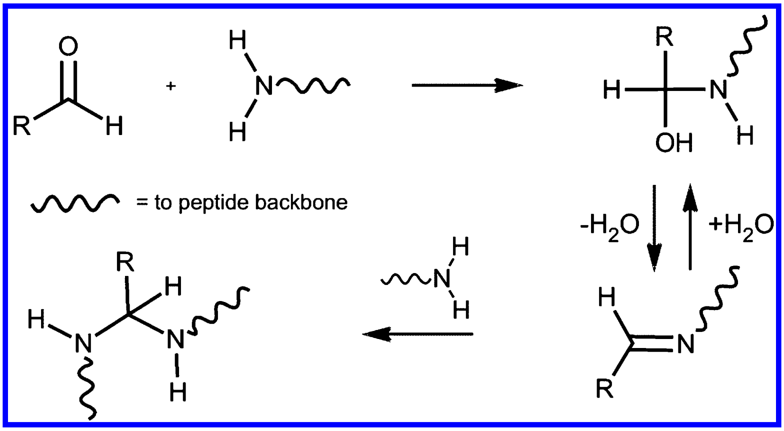
Smoking/Aldehyde Tanning

It seems a logical step to imagine attempts by prehistoric humans to preserve hides and skins would begin with simple drying, perhaps over a fire. While it was likely discovered by accident, it has been asserted that the first real tanning process used by these early people was treatment of the hides with smoke (*2*). It is unclear if this was a conscious decision or simply a serendipitous side-effect from drying skins over a campfire, but regardless of why it occurred, this technique was certainly a precursor to what is modernly known as aldehyde tanning.

Smoke is a mixture of a variety of organic and inorganic byproducts from the combustion of wood and other fuels. The exact composition of the complex mixture of materials seen as wood smoke is highly variable depending upon the fuel, moisture level, extent of oxidation, and temperature. Among the common components of this mixture are various aldehydes, including formaldehyde, acetaldehyde, and furfural, ranging in amount from 0.6-5.4 g/kg wood (*21*).

Exposure of collagen to aldehydes can result in a reaction between pendant amine functional groups found in a polypeptide chain (predominately the primary amine side chain of lysine) and the aldehyde moiety, as seen in Scheme 2. First, nucleophilic attack by the amine nitrogen occurs on the aldehyde carbon, resulting in formation of a hemiaminal intermediate. This intermediate then eliminates water to produce an imine product. Cross-linking to an adjacent collagen fiber then occurs through aminal formation due to reaction of a pendant amine group on the second fiber with the imine to form an aminal, covalently bonding the two collagen fibers.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch006



Scheme 2. Mechanism for cross-linking of collagen via aldehyde tanning.

Aldehyde tanning is often referred to as a “curing” process as opposed to a tanning process due to its ultimate reversibility when the hide is soaked in water. The final cross-linked animal product can be rather easily hydrolyzed, breaking the bonds between collagen fibers and regenerating the Schiff base imine product, which readily adds an additional equivalent of water to hydrolyze the peptide bond and reform the original amine and aldehyde species. Additionally, the number of lysine residues is rather limited, on the order of 2.5% of all amino acid residues in rabbit, pig, and cattle skins (*16*). This limited extent of cross-linking in combination with the instability of the bonds under wet conditions would render this type of tanning non-ideal. However, there would be expected to be some benefits to the method compared to the use of dehydrated or raw hides.

Some treatments of hides also involve the application of oils or fats to the skin (*2*, *4*, *13*). The breaking of unsaturated bonds in fatty acids during their degradation could also serve as a source of aldehydes to contribute to the tanning processes. While these aldehydes would likely be of rather low concentration, this treatment would have served to not only waterproof the hide due to the hydrophobic nature of the fats, but to also increase the extent of aldehyde tanning to some degree. The Native American tribes have been reported to use the brains of the animal to preserve the hide (*2*), although it is unclear when this practice may have begun. Studies of the chemistry of this method are sparse, but considering the high lipid content in myelin, the material that forms a protective sheath around neurons in mammals (*22*), the practice of tanning through treatment with brain tissue is likely another method of aldehyde tanning.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch006

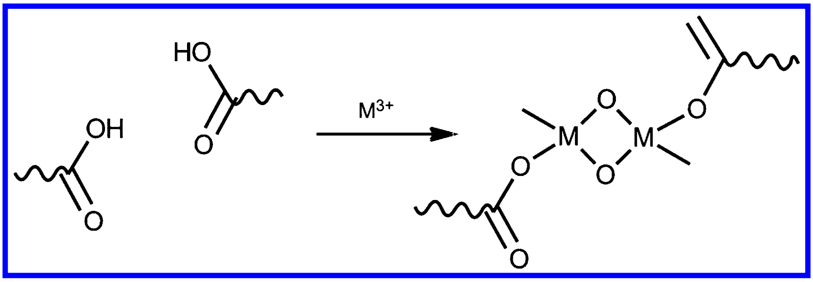
Mineral Tanning

The use of salts to slow the putrefaction of a hide through dehydration has already been discussed. However, it has also been reported based on depictions in tomb paintings that the use of mineral salts as a tanning agent was known in ancient Egypt, using a process known as “tawing” (*2*, *13*). Similar methods have also been reported to have been employed in ancient Mesopotamia (*4*). While simple sea salt, composed primarily of sodium chloride, would have been effective as a dehydrating preservative, salts which could be utilized for mineral tanning would have needed to contain a large portion of metal ions in higher oxidation states (Al^{3+} or Fe^{3+}, for instance) in order to chemically alter the collagen matrix. While chromium(III) solutions are used in modern processes, the most commonly described mineral tanning agent in antiquity was alum.

Alum at the time was likely an impure mixture of ionic species, composed primarily of various aluminum sulfate salts along with any number of other trace impurities. Among the most likely impurities were salts containing iron(III) cations (*4*), although other trivalent metal species may have also served as mineral tanning agents. It is not a coincidence that many of the salts potentially used for mineral tanning were also used as mordants in dying processes, as both processes involve the formation of insoluble metal complexes (*17*).

The mineral tanning process occurs through coordination of metal cations to potential hydrolysis sites, specifically carbonyl groups, in the collagen matrix. This coordination serves to compete with degradation processes, as well as to create cross-links between collagen fibers through metal ion bridges. In aqueous solution conditions as described for the Mesopotamians and the Egyptians (*1*, *2*, *4*), this would likely result in the formation of metal clusters bridged by oxide ligands under basic conditions, as seen in Scheme 3 (*17*). Other ligands (sulfate, for example) would undoubtedly be present in the tanning solution, and would likely also coordinate to the metal centers. It has been reported in studies of modern chromium tanning that sulfates can serve to stabilize the metal-collagen complexes (*17*).

The number of potential cross-linking sites available for mineral tanning is significantly higher than those available for aldehyde tanning. For rabbit, pig, and cattle hide, approximately 7.0% of amino acid residues are glutamic acid residues, with an additional 4.7% aspartic acid residues, providing four times more potential cross-linking sites compared to aldehyde tanning (*16*). While strong acids or bases could reverse the coordination process, the resulting leather would be much more stable under normal conditions, even quite damp conditions, than dehydrated or aldehyde tanned leather.



Scheme 3. Mechanism for cross-linking of collagen via mineral tanning.

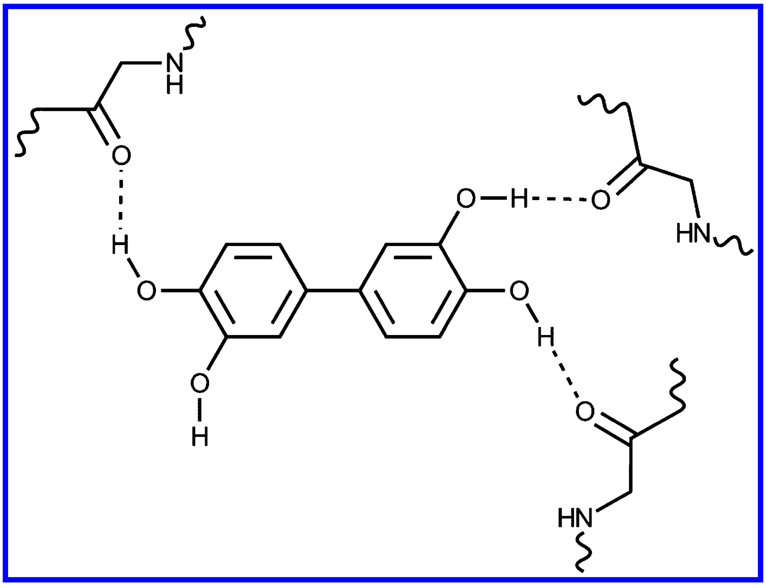
Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch006

Vegetable Tanning

Vegetable tanning is the technique from which the name “tanning” is derived. The use of organic components from a variety of plant sources including grains, nuts, barks, and roots results in the characteristic brown tones typically associated with leather. These vegetable tannins are any of a number of aromatic compounds containing phenolic groups that may be produced within the plant tissues. The cross-linking action of these tannins occurs through hydrogen bonding with any number of potential sites on the polypeptide backbone or the pendant groups on the amino acid residues. An example of one potential vegetable tanning agent, along with a potential bonding motif, can be found in Scheme 4.

A number of plant sources were used to supply the tannins necessary for leather production. In ancient Mesopotamia, accounts include mention of gall nut, oak bark, pomegranate rinds, and wheat and malt flour (*1*, *4*), while the ancient Greeks are reported to have used pine and alder bark, sumach, acorns, roots, and various fruits including grapes (*2*). As the organic tannins found in these materials would only be marginally water soluble, it is likely that processing steps such as pulverization and boiling of the plant material to produce a dark tea-like extraction occurred, followed by soaking of the hide for some period of time.

The effects of vegetable tanning are remarkably stable considering that the interactions are not covalent bonds as seen in aldehyde and mineral tanning, but rather weaker hydrogen bonding interactions. The stability and significant resistance to degradation can be attributed to the extremely large number of potential cross-linking sites found on each collagen fiber. Since the phenolic tanning agents can form hydrogen bonds with carbonyl moieties on the polypeptide backbone itself, rather than with only a small portion of the total amino acid residues, there are approximately seven times more available interaction sites when vegetable tanning is compared to mineral tanning, and approximately 22 times more compared to aldehyde tanning (*17*). Combined with the hydrophobic nature of the aromatic tannins, which is enhanced once the tannin molecule is bound, the resulting leather possesses an optimum stability toward degradation, as well as a good resistance to hydrolysis.



Scheme 4. Mechanism for cross-linking of collagen via vegetable tanning.

The Tanning Process

While the overall process was likely somewhat variable, the work of tanners involved several additional steps or processes in addition to the actual treatment of the hide with tanning agents. It is likely that some soaking or washing step would have occurred early in the process (*4*, *23*). The act of dispatching the source animal and removing the skin is necessarily messy. The skin may also have been salted in order to preserve it until such time as the formal tanning process could begin. While not always described in written accounts, an initial washing step to remove mud, feces, blood, and other foreign material from the hide is a logical first step.

Since the dermal layer of the skin is the collagen rich material that is acted upon and preserved through tanning, it was desirable to remove any remaining flesh, fat, and other connective tissues from the hide prior to treatment with a tanning agent. While examples of prehistoric leather itself does not generally survive intact for millennia, tools used by prehistoric cultures stand up better to the tests of time and are the most readily available evidence that some treatment of skins was done (*4*, *20*). Scraping tools made of stone or bone have been identified as likely being used to work skins (*20*).

If the hide was intended to be used as an insulating garment, the hair may have been left on the hide. For most applications, however, it was desirable to

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch006

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch006

remove the hair from the skin prior to tanning. This could be done though several mechanisms. For early tanners, this was likely accomplished through a controlled putrefaction (*4*). Soaking the hide in water would allow natural bacteria to act on the hide until the hair would begin to fall out, after which the hide could be removed and the tanning process continued. Other means by which this could have occurred include treatment with urine (*4*) or by simply allowing the raw hides to sit in storage for a length of time, generally stacked flesh to flesh to allow heat from the process to be trapped, thus accelerating bacterial action further (*23*). Due to the general unpredictability of bacterial action, depilation using this method would have been somewhat difficult to control.

Another method used to remove hair from the hide included treatment with lime or other strong alkaline sources (*23*). Treatment with a lime or lye solution would act directly on the hair itself, rather than degrading the follicle and allowing the hair to come loose. While lime was certainly known in antiquity, it is unclear if this method was regularly used. Descriptions of the tanning process in ancient Mesopotamia taken from cuneiform tablets make no mention of additional substances used for the depilation process (*4*).

The process of bating, where proteolytic enzymes were allowed to act upon the hide, may have served as a final step prior to treatment with tanning agents. This was done by treating the hides with a dung infusion, utilizing protein-digesting enzymes that were carried through the digestive tract of the animal and could therefore be found in the resulting excretions (*4*). These enzymes served several purposes, including removal of non-collagen proteins still residing in the skin, globular proteins, and other cellular residues from earlier processing steps, as well as serving to loosen the collagen network to allow the tanning agent better access to binding sites and resulting in a finer leather (*23*).

The final step in the process was the application of tanning agent. The method would necessarily vary depending upon the tanning agent to be applied (smoke tanning vs. vegetable tanning, for example). Additionally, the steps outlined above may have been rearranged to some extent, and some steps may have been combined or omitted entirely based upon the methods of the particular culture and time frame. To further complicate things, it is possible that multiple tanning agents may have been used simultaneously. For example, Mesopotamian literature indicates a process wherein both mineral and vegetable tanning agents were added to a bath, after which a sheep or hog skin was steeped in the resulting solution to produce leather (*1*). Another account found on tablets describes forming the raw hide into a bag, filling the bag with a tanning solution, then soaking the filled bag in a vat of the same tanning solution (*1*). While the details of the steps have evolved over the centuries, the base process described above is still largely in use today by both industrial and more primitive cultures across the globe.

Perhaps not surprisingly, the tanning process was not without its shortcomings, specifically with respect to aroma. The smells arising from refuse after flaying and scraping, combined with the pungent aromas associated with putrefying skins and dung, would have produced a highly objectionable odor. As a result, many highly populated communities placed tanners and leather workers in a specific district some distance from the city, separating the citizenry from the unpleasant but unavoidable stench associated with these trades (*4*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch006

Archeological Leather

Leather objects can be recovered from archeological excavations, although with increasing rarity as the age of the site increases. Unlike artifacts such as pottery, cave drawings, stone tools, and metal objects, leather artifacts are organic in nature. While the tanning process does serve to slow down the decomposition process, it does not stop it completely. Given time frames of several thousands of years, even well-tanned leather will slowly degrade under nearly all ambient conditions. When such artifacts are discovered, they are often found in highly anaerobic conditions such as waterlogged in the bottom of waterways or in peat bogs (*19*).

Studies have been undertaken to analyze ancient leather finds in order to identify the tanning process used in their production, but with limited success. A number of challenges exist when attempting such studies. First is the natural deterioration of the leather material itself. In addition, the chemical and morphological complexity of the collagen matrix can make many analytical methods impractical, with latent signals masking those indicative of particular cross-linking motifs.

Perhaps the most problematic, however, is the challenge that results from exposure of the artifact to its environment. This problem could manifest as simple contamination, be it latent contamination from the environment that the artifact was found in, secondary contamination occurring upon collection and storage, or preservation treatments applied to the artifact later. While the latter possibilities can be avoided or accounted for, the effects of exposure to the latent environment often extend well beyond simple contamination. Over time, agents within the environment can serve as *de facto* tanning agents themselves, causing untanned hides to appear as treated leather, or further tanning a leather object by methods not employed by the original artisans (*19*). Aluminum or iron minerals found in soils can coordinate to the leather resulting in mineral tanning. More commonly, tannins from natural sources such as peat bogs, or situational sources such as oak logs used for coffins, impart vegetable tanned character to artifacts otherwise untreated with these methods (*19*).

As a result, determinations of tanning methods are limited to those occurring within recorded history (*4*). Some suppositions can be made based on tool finds (*20*), and it is quite evident that leather production was widespread from mankind’s earliest days. Evidence can be found to suggest any or all of the discussed tanning methods may have existed prior to recorded history (*4*, *13*). Consequently, we may never know for sure exactly what methods were first used, how they were discovered, or how the processes were developed over time.

Conclusions

The conversion of raw skins and hides to leather is one of mankind’s oldest technologies, already a mainstay in the beginnings of recorded history. Several methods existed to necessarily preserve skins to slow decomposition, while also changing the physical properties which increased the general usefulness of the material. Regardless of whether smoking, mineral tanning, or vegetable tanning was performed, it was the cross-linking of collagen fibers within the dermis of the skin which served to stabilize the material against hydrolysis and bacterial action. However, due to a number of factors, definitive determination of the exact methods used in antiquity based on analysis of leather artifacts remains elusive.

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Chapter 7

Modern Chemistry of the Ancient Chemical Processing of Organic Dyes and Pigments

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The ancient dyer was an advanced empirical chemist. While inorganic pigments produced magnificent colors, the most elaborate chemical processing of colorants in antiquity – from the source to the final product – involved organic dyes from flora and fauna sources. Towards this end, the dyer applied his – or her – practical chemical knowledge to botany, entomology, and malacology. By controlling the temperature and the alkaline or acidic pH of the dye bath, the dyers were able to create colorful textile dyeings with some surviving even after six millennia. In order to produce stable products, the ancient dyer mastered the methods that are based on advanced chemical topics, such as, ionic, covalent, and intermolecular bonding, coordinate complexation, enzymatic hydrolysis, photochemical chromogenic precursor oxidation, anaerobic bacterial fermentative reduction, and redox reactions. This paper discusses various chemical principles that were applied by the ancient master of colorful chemistry.

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Introduction: Historical Overview

Two decades have elapsed since the first paper on the subject of ancient Near East dyestuff sources was published in an ACS Symposium Series by this author (*1*). In that work, emphasis was given to the yellow, red, and blue colorants that were obtained from flora dyestuff sources and the molecular structures of their main dyes were discussed. In the last two decades, more analyses of archaeological dyes have been performed with greater emphasis on the more important fauna origins of the red dyestuffs from scale insects and the purple and violet pigments from sea snails. This current paper, besides being a continuation and update of our knowledge in this field, focuses on the ancient dyer's advanced level of control and the highly complex chemistry applied in the process.

A number of classical English-language books have treated the history of organic dyes and pigments from botanical, entomological, and malacological sources used in ancient times. Some of the more prominent texts discussing these flora and fauna dyestuff sources include, chronologically, the works of Leggett (*2*), Forbes (*3*), Robinson (*4*), Brunello (*5*), and Sandberg (*6*, *7*)*;* and more recently by Cardon (*8*), Balfour-Paul (*9*), and Orna (*10*). The ancient and historical literature on dyestuffs includes the Natural History in Latin of the 1st century CE Roman historian, Pliny the Elder, and the 16th century Plictho of Gioanventura Rosetti in Italian (*11*). In fact, the full title of The Plictho, as translated into English, is: "Instructions in the Art of the Dyers Which Teaches the Dyeing of Woolen Cloths, Linens, Cottons, and Silk by the Great Art as Well as by the Common".

It is practically impossible to determine the geographical origin of textile dyeing. To the question of "where in the world was dyeing first performed?" one undoubtedly needs to answer that in all probability it was performed in various locations at about the same time by using the locally available dyestuff sources. Today, we have definitive archaeological and chemical evidence that this craftsmanship dates back at least six millennia, and these textile dyeings are the oldest yet found to date, and were excavated from the Cave of the Warrior in the Judean Desert, Israel (*12*). In these Chalcolithic linen textiles, the dark-brown (blackish) decorative yarns were dyed with an acidic organic macromolecule dyestuff source, but whose exact nature has yet to be determined, prior to weaving them into the textile. As for the famous purple molluskan colorant, the production of this water-insoluble compound as a paint pigment dates from about four millennia ago while its conversion to a soluble textile dye probably occurred about half a millennium later (*13*). Similarly, the use of the dark blue-violet indigo pigment (also known as indigotin) is from over four thousand years ago as analyzed by this author and observed from various surviving Pharaonic textile fragments in the collections of, for example, the British Museum in London and the Metropolitan Museum of Art in New York.

The primary thrust of the current work is to portray a picture of marvel at the scientific abilities of the ancient dyer, undoubtedly achieved via empirical trial and error experimentation, and probably with an added dose of accidental successes. He – or she – utilized vast empirical know-how to produce colorful long-lasting dyeings that have withstood the ravages of time. When the dyer used the full spectrum of the natural dyestuff sources available, he also applied his practical knowledge of botany, entomology, and malacology. Further, he incorporated into his scientific craft the methodologies generally associated with the following topics in inorganic, organic, physical, and biochemistry:

- ionic, covalent, and intermolecular chemical bonding
- coordinate complexation
- pH control of alkalinity/acidity
- enzymatic hydrolysis
- photochemical chromogenic precursor oxidation
- anaerobic bacterial fermentative reduction
- air-oxidation

A discussion of the colorants used in ancient – and modern – times requires a clear understanding of the difference between a “pigment” and a “dye”, which unfortunately have sometimes been erroneously used interchangeably. Figure 1 outlines the properties of these two colorants. Without any additional treatment, a natural pigment is a relatively water-insoluble colorant and is used to paint a surface. Examples are painting on a wall (as in a fresco), canvas (paintings), vessel, on a body, and even to paint on a textile (if that textile will not be washed such as a shroud on a coffin). In ancient times, most paint pigments were of an inorganic, mineral, nature. Conversely, a dye is a water-soluble organic colorant and that word should be specifically used when this colorant is utilized to perform a true textile dyeing. Historically, some dyes were chemically transformed into paint pigments by complexing with a metallic ion to form a “lake” used in various historic paintings or in mordant dyeing – indirectly fixing the dye into the textile (discussed below). Inversely, certain pigments (such as indigo from plants and related compounds from mollusks) were transformed into a dye by, for example, reducing the pigment to its water-soluble counterpart, and after the dyeing this was then followed by air-oxidation back to the original pigment.

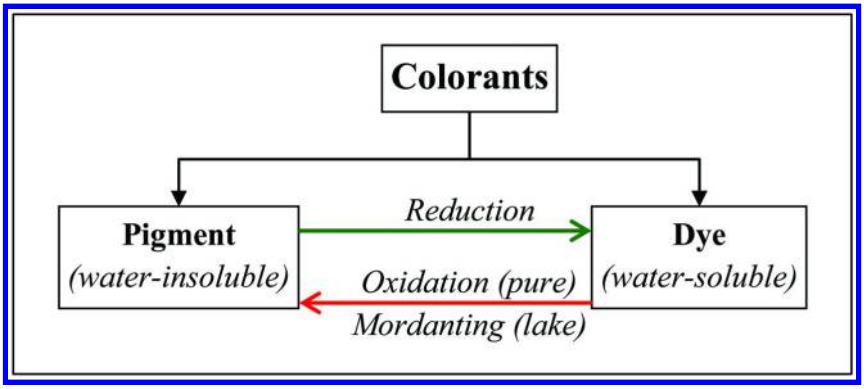

Figure 1. The properties of water-insoluble pigments vs. soluble dyes.

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Ancient Coordination Compounds

Historical Mordanting with Alum

It was well known at least as far back as the Roman Period that a salt was needed in order to act as an intermediary and fix the dye to the textile fibers. This fixative is known as a "mordant" from the Latin *mordere*, which means "to bite" or "biting", and it "bites" (i.e., attaches to) the dye as well as to the textile fiber. The Roman historian Pliny clearly mentions the use of the mordant alum in dyeing, and this mineral contains the trivalent aluminum ion and is generally accepted to be $KAl(SO_4)_2 \cdot 12H_2O$. The relevant passages in Pliny are from Book 35, Chapter 52, as follows in Latin and in English (*14*, *15*):

> *Nec minor est aut adeo dissimilis aluminis opera, quod intellegitur salsugo terrae. plura et eius genera. in Cypro candidum et nigrius, exigua coloris differentia, cum sit usus magna, quoniam inficiendis claro colore lanis candidum liquidumque utilissimum est contraque fuscis aut obscuris nigrum.*
>
> Not less important or very different is the use made of alum *(aluminis)*, by which is meant a salt exudation from the earth. There are several varieties of it. In Cyprus there is a white alum and another sort of a darker color, though the difference of color is only slight; nevertheless the use made of them is very different, as the white and liquid kind is most useful for dyeing woolens a bright color whereas the black kind is best for dark or somber hues.

Complexing the Dye with Alum

Alizarin and the related purpurin are the well-known di- and tri-hydroxyanthraquinone hydrolysis products extracted from various madder plants (*Rubiaceae* species), with the most famous being Dyer's Madder (*Rubia tinctorum*), shown in Figure 2. This plant was the most widely used red dyestuff source of the ancient Near East and also available in various European regions.

In wool, the Al^{3+} ion – a Lewis acid – bonds to an oxygen atom in the proteinic fiber and also to certain oxygen atoms in the dye molecule via ionic and covalent bonds, the latter including coordinate covalent bonding. Thus, in the schematic $O_{(wool)}$–Al–$O_{(dye)}$ bridge, the Al intermediary serves as a bridging agent – a "matchmaker" – between the fibers and the dye. However, the exact molecular structure of this wool–alum–dye complex is still not known, and further research into this area would be important.

Without wool, the structures of alizarin-mordant complexes have been studied for bivalent and trivalent metal mordants and two of the proposed general structures are shown in Figure 3. In order for the C=O → M–O coordination bond to form in the hydroxyanthraquinones, the carbonyl and hydroxyl groups in the ligand must be adjacent. In the structure proposed for a metal–alizarin complex in neutral media, Figure 3 *(left)*, the hydrogen atom is replaced by the metal ion, which is followed by the ionization of the M–O bond, and the ionized hydroxyl group in position 1 is bonded through the intramolecular hydrogen bond (*16*). This complex can have more tautomeric forms that contain the six-membered chelate cycle, and other structures have been proposed for the metal–alizarin complex in acidic and alkaline media (*16*).

The metal-alizarin coordination compound in Figure 3 *(right)* has often been given (*1*, *17*), in which coordinate covalent bonds are formed; however, the M–O bond in similar structures has been found to be partly covalent (*18*), so that a partial ionic character can be present, and even a more fully ionized bond may exist, as mentioned above (*16*). Resonance structures are also possible for this 2:1 complex.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

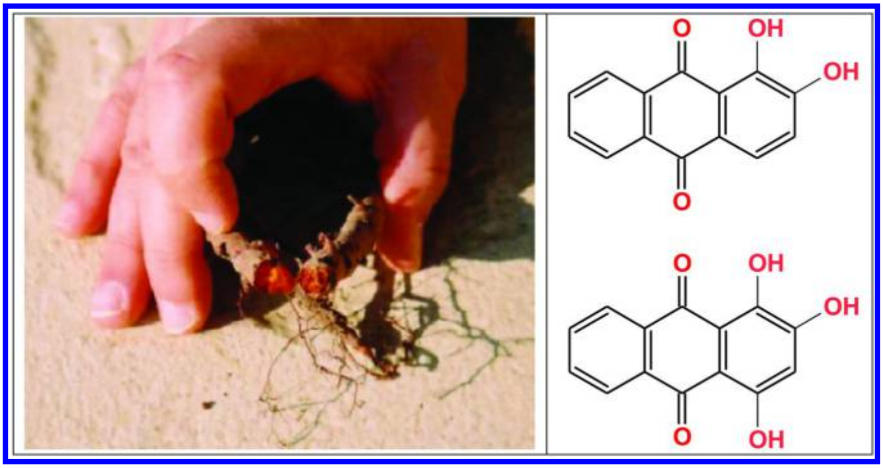

Figure 2. Left: roots of the Dyer's Madder plant (Rubia tinctorum) with the interior showing the presence of the red dyestuff source. Right: molecular structures of alizarin (top) and purpurin (bottom); intramolecular H-bonds are also present between adjacent carbonyl and hydroxyl groups in both molecules.

Further studies have also included calcium ions into the complex, Figure 4, which is a logical extension since in antiquity naturally hard water rich in calcium was used. Further, the aluminum-calcium-alizarin complex is the dye known as Turkey Red for dyeing cotton (*18*). It was assumed that the groups around the central aluminum take on an octahedral structure (*18*). It is also noted that the two anionic oxygens are probably *cis* to each other in order to neutralize the Ca^{2+} counterion on their side. If this complex would be attached to the wool then probably the water molecule would be replaced by the oxygen from wool.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

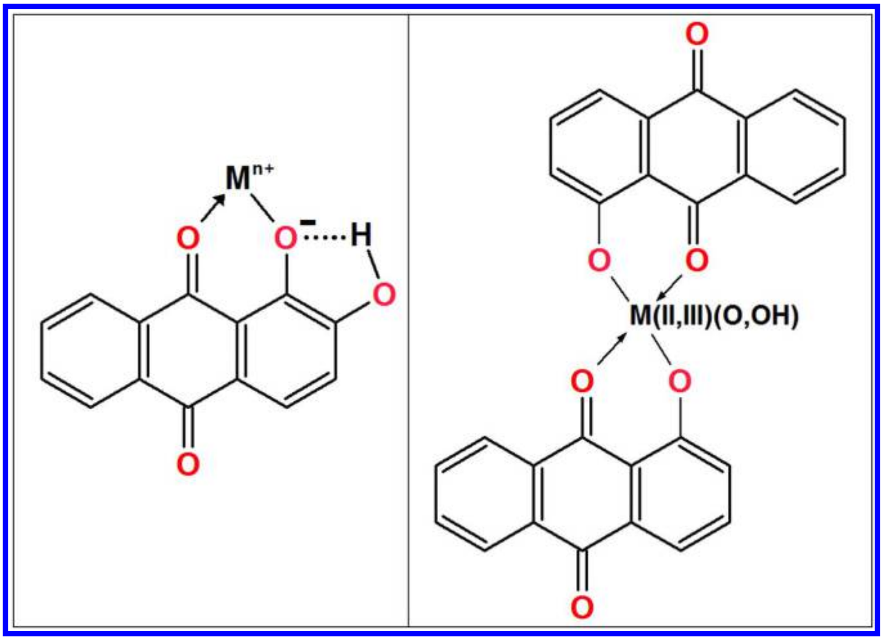

Figure 3. Proposed alizarin complexes with an M^{2+} or M^{3+} metal ion mordant.

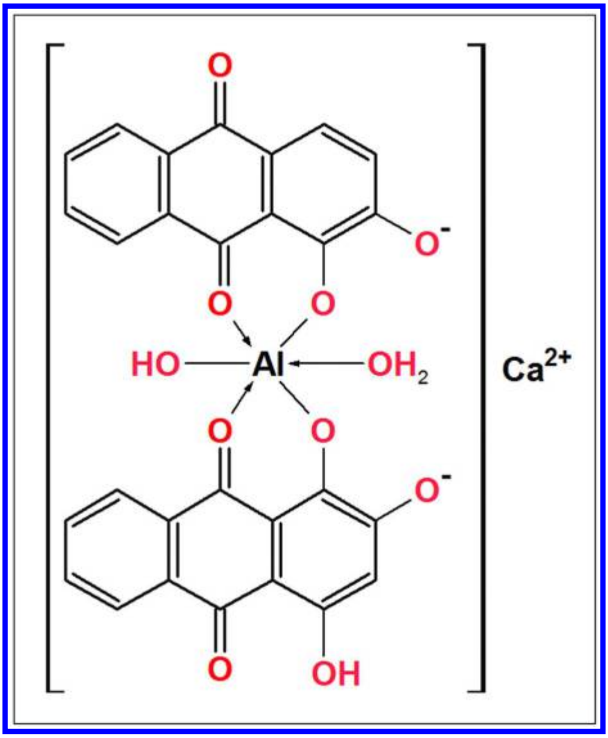

Figure 4. Alizarin–aluminum complex with calcium based on the structure proposed by Kiel & Heertjes (18).

Another elaborate structure for the alizarin–aluminum–calcium complex has been given and shown in Figure 5 (*19*).

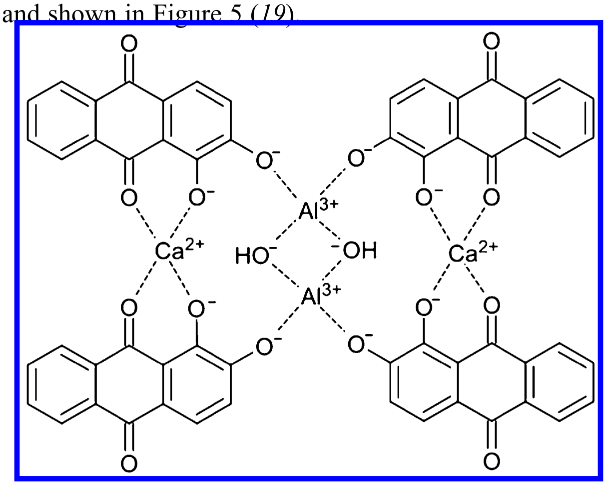

Figure 5. A proposed alizarin–aluminum –calcium complex. (courtesy of Mattern, R.; Wikimedia Commons).

Finally, Wunderlich and Bergerhoff (*20*) obtained single crystals of aluminum calcium alizarinate and purpurinate by two-phase crystallization. X-ray structure determinations showed tetranuclear complex molecules with four alizarins. The metal–oxygen interactions in this structure (Figure 6) are mostly coordinate covalent bonds with some ionic character. This structure is different from other proposed arrangements, and the authors state that this is the best structure. A similar complex is also given for carminic acid, which is also a hydroxyanthraquinone, and obtained from red-producing cochineal scale insects (*21*).

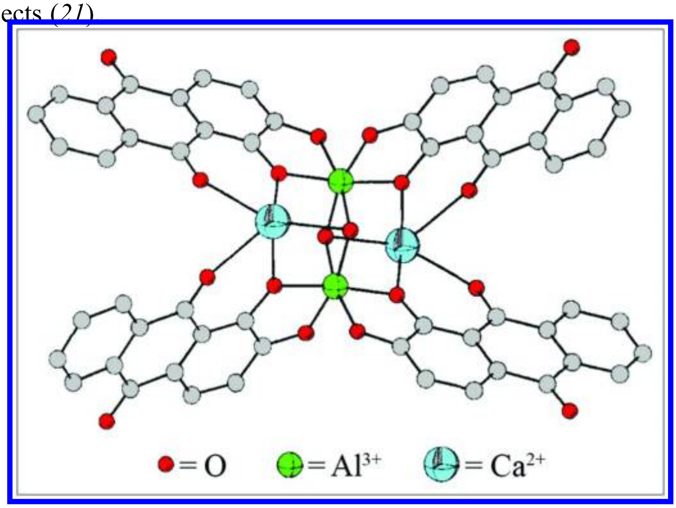

Figure 6. The alizarin–aluminum–calcium complex based on the work of Wunderlich and Bergerhoff (20).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

With all of the differing proposed molecular structures given in the literature for this complex, more research in this area would be most welcome. Whatever the correct structure is for these mordant dyes in wool, it is remarkable that the ancient dyer was producing metal complexes and utilizing the coordination chemistry associated with chelation several millennia before Alfred Werner (1866–1919) expounded on coordination compounds and Gilbert Newton Lewis (1875–1946) explicated his universal concepts of acid-base properties.

A beautiful example of the aluminum-alizarin complex that the ancient dyer created is from the 2nd century CE Roman Period (Figure 7).

Figure 7. Fragments from a multicolored 2nd century CE scroll wrapper from the period of the Bar Kokhba revolt found in the Cave of Letters, Judean Desert; the red background was dyed with madder containing mostly alizarin and complexed with an alum mordant.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

Redox Purple Chemistry of the Ancients

Fermentation and Vatting

As impressive as the ability of the ancient dyer to create coordinated complexes is, it is the dyeing with indigoid compounds from purple-producing sea snails that really showed off the chemical prowess of this artisan. These purple dyeings are famously renowned for the regalia of kings, priests, and the military, and referred to by various names, such as Royal Purple or Tyrian Purple. Direct archaeological evidence of dyeing with molluskan purple is based on various purple-stained and analyzed potsherds from dyeing vats, and dates back to at least three and a half millennia when the Levantine Phoenicians developed this chemical technology (*13*).

Performing a dyeing from the purple pigment produced from certain mollusks was similar to – but much more biologically challenging – than dyeing with the indigo pigment (also referred to as indigotin). The latter colorant was produced from various precursors in the leaves of certain plants, such as *Indigofera tinctoria* (the indigo plant, so-named because it is native to India and environs), and also from woad (*Isatis tinctoria*), a plant that was available in the ancient Near East and Europe (see Figure 8).

Figure 8. Left: the woad plant, Isatis tinctoria (Wikimedia commons). Right: the author holding a dark blue-violet indigo pigment produced from the isatans in the leaves via fermentative reduction and air-oxidation.

Photochemical Oxidation Production of the Purple Pigment

The pigment produced from most purple-producing Mollusca is of a reddish-purple coloration, an example of which is given in Figure 9. However, while a type of the *Hexaplex trunculus* sea snail species (also known as *Murex trunculus*), the most important purple-producing mollusk of the Eastern Mediterranean, can produce that coloration, another chromatic subgroup of *H. trunculus* mollusks produces bluish-purple or violet pigments. In any case, though the purple pigments from different sea snail species may contain different colorants, all purple-producing mollusks, whether from the waters off Japan, the

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

Atlantic Ocean, or the Mediterranean Sea, possess the same common chromatic marker, the red-purple 6,6′-dibromoindigo (abbreviated as DBI) colorant (*13*).

The formation of the colorants in the purple pigment from the colorless precursors contained in the hypobranchial gland of the living animal consists of complex steps (*22*) that can be schematically outlined for the case of DBI, as shown in Figure 10. Each precursor is hydrolyzed by purpurase, a sulfatase enzyme, which is present in the gland but is not in contact with these precursors as long as the snail is alive. When the snail expires or when the gland is cut or pierced, then the enzyme comes in contact with these precursors, which after hydrolysis followed by air-oxidation and photolytic processes, produce the indigoids, such as the DBI shown in the figure.

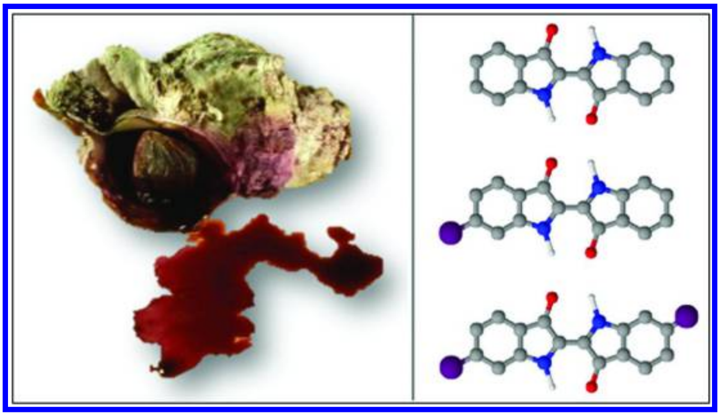

Figure 9. Left: an expiring Hexaplex trunculus sea snail expelling the colorless precursors from its hypobranchial gland, which under the influence of air and light, undergo photochemical oxidation to the red-purple pigment. Right: the molecular structures of the three indigoid components in the H. trunculus pigment (top to bottom): indigo (IND), 6-bromoindigo (also known as monobromoindigo, MBI), and 6,6′-dibromoindigo (DBI), the latter being the most abundant component of any red-purple colored pigment.

Not all snails were created equal. The major component in all red-purple molluskan pigment from all species is DBI, and it can even be more than 90% of the dye content in such pigments. However, *H. trunculus* sea snails produce other indigoids in varying amounts besides the red-purple DBI colorant, and these are the violet MBI and the dark blue IND colorants. This is summarized in Figure 11. The presence of a significant quantity of the violet MBI colorant is unique to *H. trunculus* snails and finding appreciable quantities of it in a purple pigment – whether archaeological or modern – indicates that its malacological dyestuff source is from *H. trunculus*. In fact, MBI may even be the colorant in greatest abundance in such pigments. Further, the pigments from *H. trunculus* snails can be categorized in two ways, depending on the relative quantities of DBI and IND in their pigment. Thus, one type produces a red-purple pigment because it is richer in DBI, while the other type is richer in IND and subsequently the pigment's color is blue-purple or violet.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

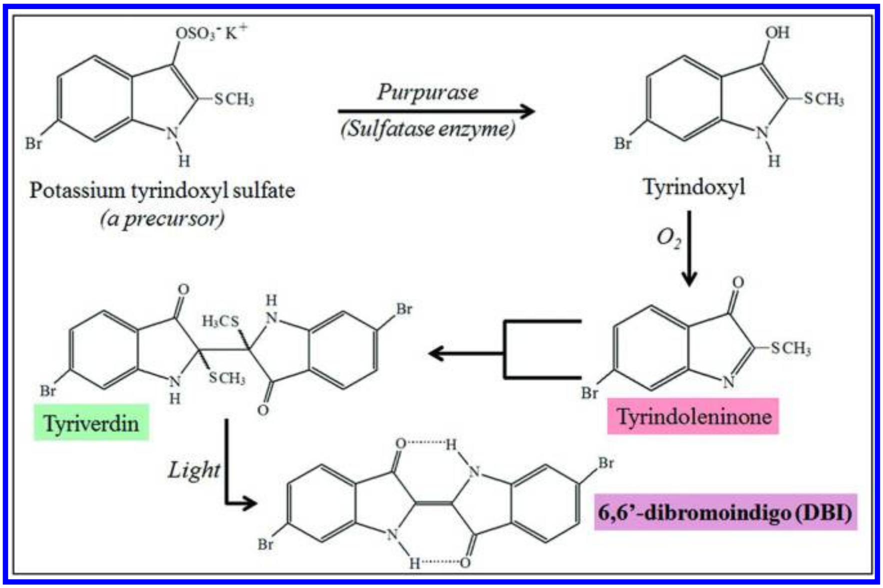

Figure 10. An outline of the spontaneous production of the DBI pigment via enzymatic hydrolysis of a precursor in Hexaplex trunculus sea snails followed by oxidative coupling and photochemical reactions.

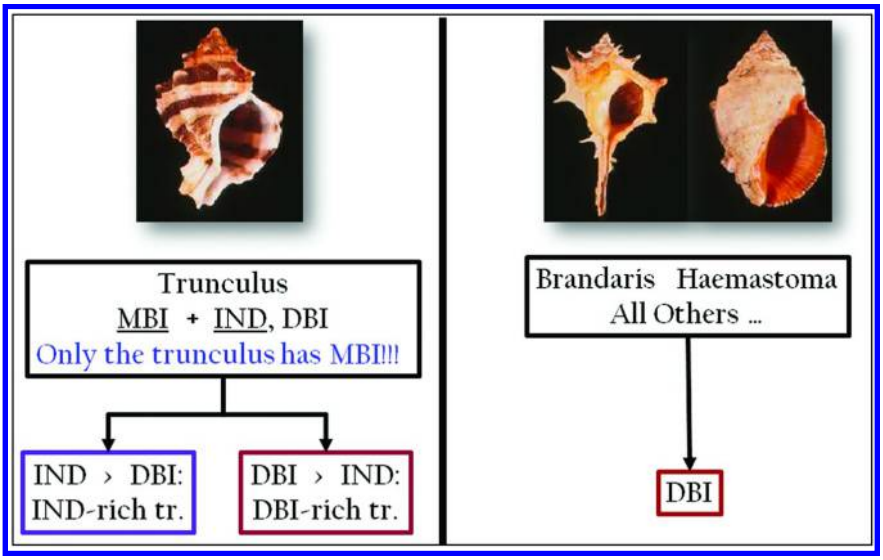

Figure 11. The three Muricidae family of sea snails from which purple pigments were produced in antiquity (from left to right), Hexaplex trunculus, Bolinus brandaris, and Stramonita haemastoma, and the main colorants that they produce.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

Fermentative Bacterial Reduction

All the indigoid colorants in the purple pigment are relatively water-insoluble colorants – pigments – due to the strong intra- and inter-molecular hydrogen bonds that they form, and the solubility decreases as more Br atoms are attached to the indigo skeleton. Thus, for any textile dyeing to be performed – whether natural or synthetic – the colorant must be dissolved. In the case of an indigoid, this dissolution is accomplished via reduction – or "vatting" – of the pigment to yield the reduced and less-colored or "whiter" dye known as "leuco". The natural reducing agent to effect the solubilization of the solid pigment via fermentation is the thermophilic bacteria present in – and feeding off – the meaty glands of the rotting flesh (*23*).

The first step in the reduction process produces the non-ionized leuco acid, which is only sparingly soluble (Figure 12). The affinity of the reduced dye to the textile fibers will be significant when the colorant is in a soluble and ionic state, and thus the reduction is performed in an alkaline environment to produce the soluble monoanion (*24*). If the pH is further increased then the more soluble dianion can also exist in appreciable amounts, but the pH should not exceed 9 when dyeing a proteinic material, such as wool, so as not to cause degradation of the textile.

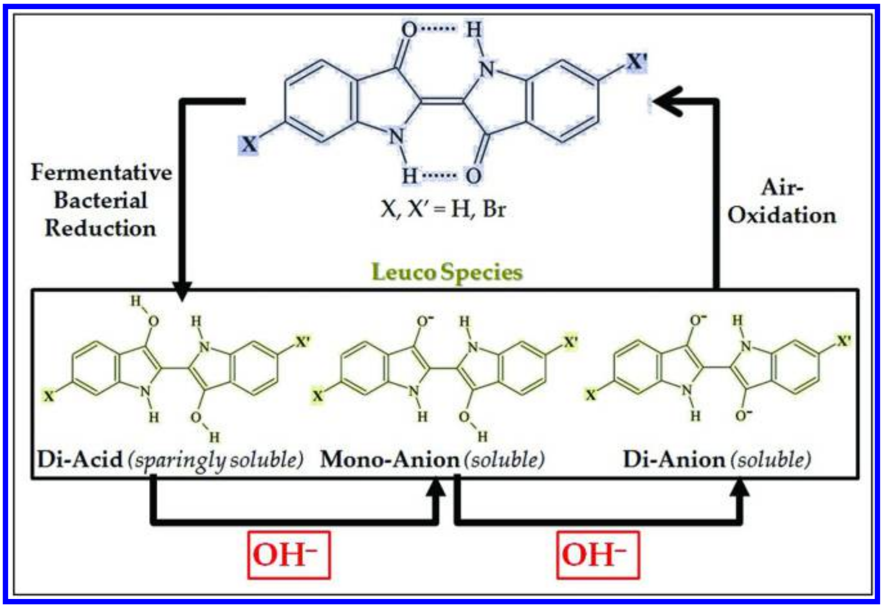

Figure 12. Fermentative bacterial reduction of the indigoids to their leuco species as a function of the alkalinity of the solution; the actual dyeing is effected by introducing the textile in the dye vat and after a few hours removing it into the air whereby it undergoes air-oxidation to the original pigment's components.

The fractions of the reduced brominated indigoids existing in equilibrium as a function of pH has not yet been researched, which would be of great interest, however the relevant quantities of the different species of indigo itself have been

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

studied. The two equilibrium dissociation constants for reduced indigo have been originally estimated from other data and reported to be 8.0 and 12.7 for pK_1 and pK_2, respectively (*24*). From an interpolation and extrapolation of the relevant curves in recently published graphs (*25*), it is found that the value for pK_1 is different and estimated at 9.45, while pK_2 is the same 12.7 value. Based on the more recent values for the dissociation constants of the reduced indigo species, the fraction of each species as a function of the pH can be evaluated from published equilibrium equations (*25*), and the classical mirror-image α-shaped curves are obtained (Figure 13). The diagram shows that at a working pH of 9, about 20% of the reduced indigo is in the monoanion state, whereas about 80% is the nonionized leuco acid species. However, from the recently published graphs (*25*), there is a steeper rise in the monoanion composition so that its fraction is at 20% already at pH 8. In any case, the monoanion species necessary to bond to the wool fibers is present under alkaline conditions. Similar results should be obtained for the reduced brominated indigo species.

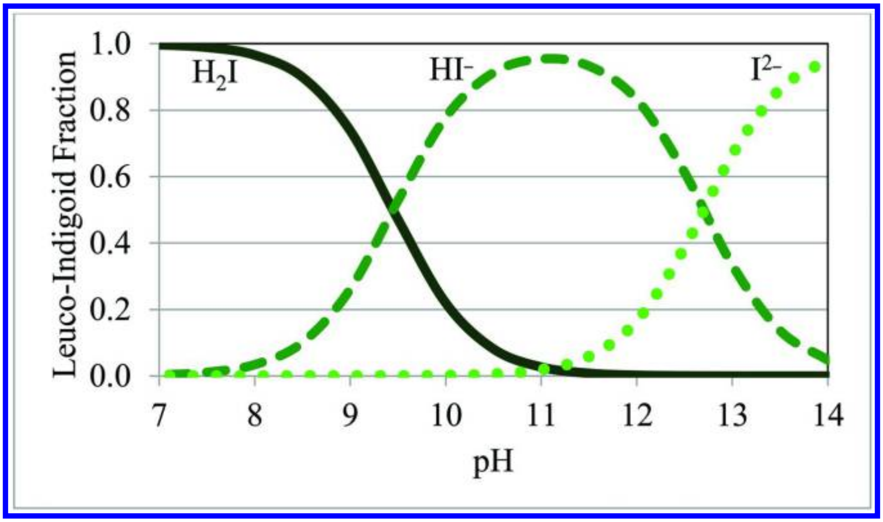

Figure 13. Mirror-image α-diagram showing the reduced indigo fractions based on the pK1 = 9.45 and pK2 = 12.7. H_2I refers to the reduced (leuco) indigo acid, HI^- and I^{2-} are the respective mono- and di-anions of reduced indigo.

The diagram shows that the dianion is indeed irrelevant at the moderate alkaline pH values that are needed so as not to destroy the proteinic wool structure. It is the monoanion that is substantive and attaches itself to the wool fibers via various intermolecular bonds. Hence, in effect, the relevant equilibrium is mainly between the reduced nonionic indigo (represented by "H_2I") and its monoanion, HI–:

$$H_2I(aq) \rightleftharpoons HI^-(aq).$$

Though, the mono-anion's presence in the reduced dye vat is much less than the nonionic species, nevertheless as more of the monoanion is removed from the solution and bonds to the fibers, then the equilibrium of the conjugate acid-

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

base pair shifts to produce more of the monoanion from the nonionic acid. This right-shift in the equilibrium was practiced by the advanced ancient chemical dyer thousands of years before the famous French chemist, Henry Louis Le Châtelier (1850–1936), invoked his principle on the "lois des équilibres chimiques".

Redox Dyeing

After the purple pigment was reduced and dissolved, the actual dyeing could be performed. The overall dyeing process then follows a reduction-oxidation cycle, which is schematically shown in Figure 14. The anaerobic bacterial reduction requires that the vat – the clay vessel containing the dye bath – be covered to minimize the entrance of air into the solution. A few days of fermentation are normally required for the natural reduction of the pigment to occur, and this can be clearly observed as the purple-color of the aqueous mixture transforms to the green-colored solution (*23*). At this point, a cleaned woolen fleece is inserted into the solution and kept at a temperature of about 50 – 60 °C for a few hours. Afterwards, as the green-colored wool is removed from the solution and into the air, the reduced species in and on the fibers immediately begin to undergo oxidation by the atmospheric oxygen to the original purple pigment, though not exactly with the same composition as in the raw pigment.

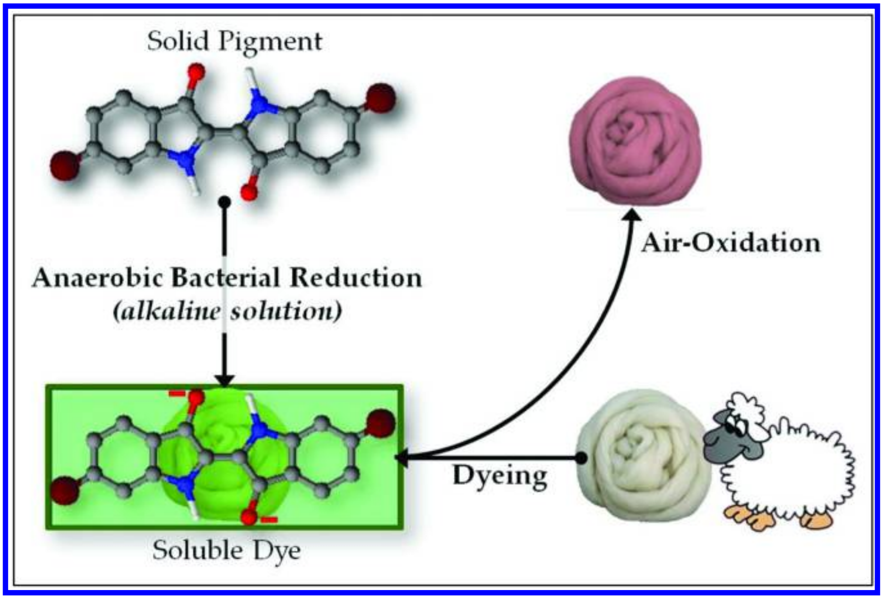

Figure 14. Overall dyeing process including the pre-dyeing reduction stage, wool insertion into dye bath, followed by air-oxidation of the reduced indigoids.

The essence of this dyeing strategy was in getting the pigment, which originally was not connected to the textile, to impregnate the fibers, which could have only occurred in the dye's dissolved state. Then, when air-oxidized to the pigment again, this pigment is now "imprisoned" inside the interior of the fibers,

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

and is also attached to the external fibers, by means of various intermolecular forces. In short, the colorant is a pigment before and after the dyeing, but in the middle stage it is in a water-soluble reduced state as a dye.

A most beautiful example of such a Royal Purple dyeing is from a miniscule weave fragment that is probably from the royal robe, cloak, or mantle of the 1st century BCE King Herod the Great (*26*), and shown in Figure 15.

Figure 15. A close-up of the miniscule fragment of only a few millimeters showing the purple-dyed yarns from the1st century BCE Herodian fabric found atop Masada in the Judean Desert; the few beige-colored yarns are undyed woolen fibers that have yellowed and been sullied over the archaeological time frame.

Analytical Methods of Dye Analysis

An investigation of ancient chemical technologies requires a three-pronged approach that incorporates historical accounts regarding dyeing technologies, physical archaeological findings, and scientific analyses on these historic artifacts as well as on modern dyestuffs that would have also been in existence in antiquity. The starting point for this study is, then, a dilemma, since the relevant question is “where best to start?”. However, because the triad topics are interconnected any of the subjects can be approached first as one investigation leads to the others and back again to the first.

A necessary stage in the investigation is to identify the dyestuff sources discussed in the historic literature and be hopeful that they also exist in modern times so that these can be analyzed via advanced analytical instrumentation. Scientific analyses of these sources will produce a chemical library of the various colorants in each dyestuff. Towards this step, it is crucial to use the correct analytical instrumentation for such a purpose. Unfortunately, in some cases, various instrumental techniques have been used for dye analyses without an understanding of these limitations. Not every instrumental technique – advanced as it may be – is automatically useful for analyses of these colorants (*27*). The main limitation of all spectrometric techniques is that they produce an "overlap of data", i.e., these techniques measure the bulk sum of all species, which can result in an overlap of information from different components. The latter property is crucial to unambiguously identify the exact dyestuff species because every natural dye source consists of several components.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

Analytical instrumental chemistry is inundated with a myriad of acronyms representing many advanced methods of analyses. Accordingly, the analytical chemist is faced with such abbreviations as NDT, NDI, FORS, FAB, DESI, DART, HRMS, TOF, SERS, TERS, DRIFTS, DAD, and the list goes on. With all these methods, it can be confusing as to which technique to use for dye analyses, and a variety of techniques have indeed been used. In this regard, it is important to differentiate between inorganic pigments, which are typically characterized by a metallic entity that can be relatively easily analyzed via various elementary spectrometric techniques (such as, XRF, SEM-EDX, AA, ICP, etc.), and organic pigments and dyes.

An additional dilemma for museum officials – the "Curator's Quandary" – is whether to use a destructive technique or a non-destructive one. This Shakespearean predicament – "to destroy or not to destroy?" – is the question that curators and conservators must ask themselves. It is well acknowledged for many years now that the optimal method for dye analyses is HPLC (high-performance liquid chromatography) – or its more modern "ultra" version, UPLC (also referred to as UHPLC). This technique provides the most detailed information regarding the various dye components constituting a dyestuff or pigment. Though this is a destructive technique, it is micro-destructive – actually nano-destructive – in that it has been shown that it can produce detailed results on even a single fiber of a few millimeters in length representing nanogram levels of dye (*28*). There is no other technique that can compete with LC for the full analysis of the dyestuffs and pigments. Thus, an Ecclesiastical answer to the Shakespearean question can be that "there is a time to build, and a time to destroy", and with the nano-destructive LC method, producing the most detailed results far outweighs the negligible invasiveness of this technique (*29*).

An example of the detailed information produced by HPLC is the chromatogram obtained for the various colorants that may be present in a molluskan purple pigment (Figure 16). The chromatogram curve shows the separation of each component at the time that the mobile phase elutes it out of the stationary phase – known as the retention time (R.T. or t_R) – and the absorbance

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

at this time. In essence, a chromatic “fingerprint” of the dyestuff is produced so that not only a qualitative analysis is obtained of what colorants are present in the dyestuff, but also a quantitative analysis indicates how much of each colorant is present. Metaphorically, the human analogy is that the peaks in the chromatogram represent fingers and their position in the chromatogram show which fingers they are; the heights (technically the areas under each peak) indicate the lengths of these fingers. For example, the red-purple and blue-purple (or violet) pigments produced from *H. trunculus* snails can contain about 10 colorants, with yellow, orange, blue, violet and red-purple colors as shown in the figure (*30*).

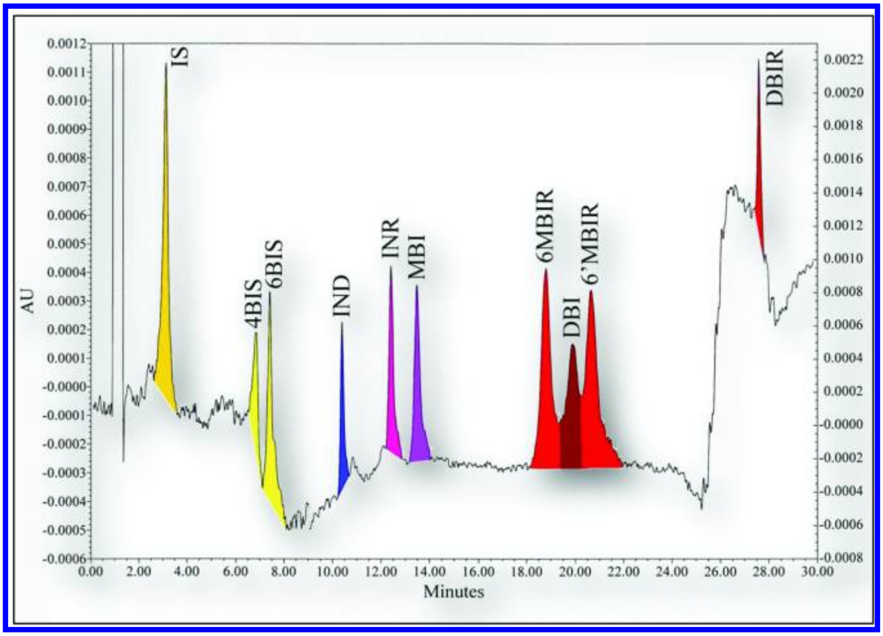

Figure 16. HPLC-produced chromatogram of the various indigoids (IND, MBI, and DBI) and related components, with their representative colors, which may be present in a molluskan purple pigment. The other components are: IS = isatin, 4BIS = 4-bromoisatin (not present in a molluskan pigment but included for standardization), 6BIS = 6-bromoisatin, INR = indirubin, 6MBIR = 6-(mono)bromoindirubin, 6'MBIR = 6'-(mono)bromoindirubin, and DBIR = 6,6'-dibromoindirubin; the right absorbance scale is for the first three peaks representing the isatinoids.

Together with the spectrometric detection of each peak, which produces a UV/Visible spectrum with the PDA (photo-diode array) detector (also abbreviated as DAD), these two properties – chromatographic retention time and spectrometric – can be used to positively identify the colorants present when compared to a standardized library of analytical results performed on the possible natural colorants. An additional detector that is helpful in the dye identifications would be MS (mass spectrometric).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

A normalized quantification has been made (Figure 17) on the three above-mentioned Murex sea snails that inhabit the Eastern Mediterranean – including the two chromatic species of the *H. trunculus* snails – and compared with an archaeological pigment found on a King Darius marble jar from 2,500 years ago (*31*). To date, all the archaeological purple pigments that have been properly analyzed via HPLC have shown the significant presence of MBI. This clearly indicates that *H. trunculus* snails were used in all the dyeings and paintings, alone or sometimes together with the other *Muricidae* snails, in all archaeological purple pigments found to date.

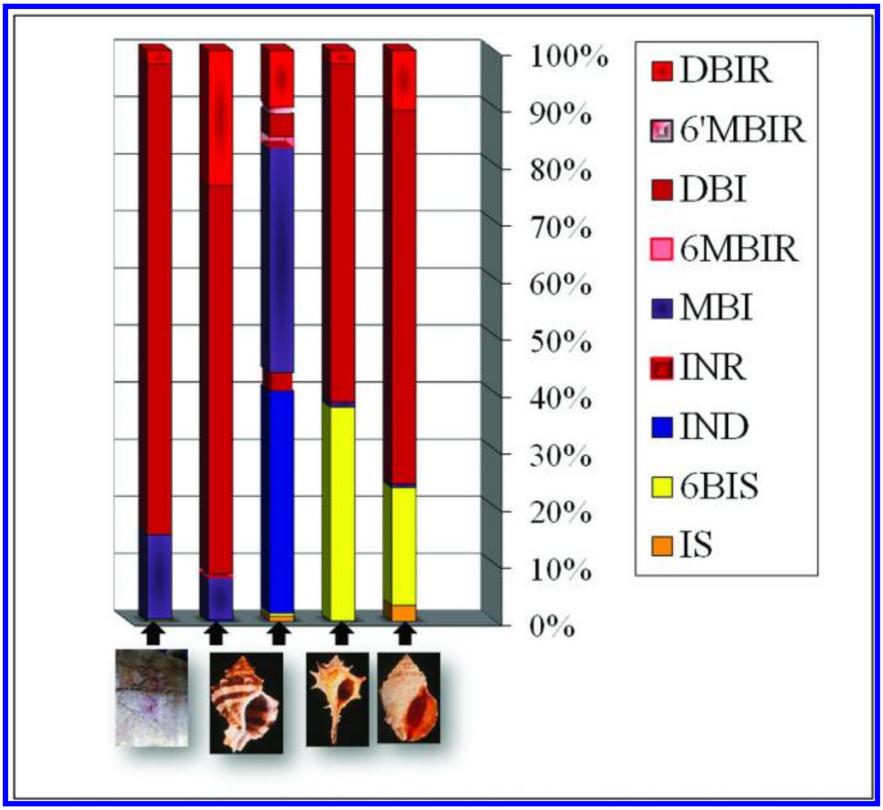

Figure 17. A multi-component normalized quantification of the integrated peak areas (measured at the standard 288 nm wavelength), which can be used as semiquantitative measures of the relative amounts of the dyes in the purple pigments from various sea snail sources; (bottom, left to right) red-purple paint residue on a 2,500 year old King Darius marble jar, red-purple and blue-purple pigments from modern H. trunculus, and red-purple pigments from modern B. brandaris and S. haemastoma.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

Conclusions

The production of colorfully dyed textiles from more than four millennia ago required an advanced degree of practical chemical knowledge that was based on inorganic, organic, and physical chemistry, and biochemistry. As such, the long-lasting stable dyeings that we are witness to nowadays are the results of strong intermolecular bonds between the colorants and the textile fibers that the ancient dyer created. Today, with all of the accessible modern tools, we can only marvel at the high degree of empirical chemistry that the ancients practiced. In their hoary past, with only primitive tools and primeval conditions, they exhibited a modern mastery of chemical principles. These ancient dyers were truly Nobles of Chemistry.

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Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch007

Chapter 8

Scented Oils and Perfumes

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Scented oils and perfumes have fascinated mankind with their very existence. The first knowledge and use of these materials is buried within the layers of time, with evidence of their usage thought to date back to the beginning of civilization. Over this time period, both men and women have used oils in one form or another, be it as a cure to an ailment or simply as a fragrance-enhancing component. Although various materials and archeological evidence has been collected over the years on the use of oils and perfumes, the lack of written documentation makes it difficult to paint a picture of their status in early human life and its history tends to exist via numerous interesting anecdotes. This chapter will summarize what is known of the history of the development and use of oils and perfumes in antiquity with a closer look at the scientific claims and analysis perfomed on the artifacts recovered from the antiquity period.

Introduction

Perfumery, like many other fundamental technologies, evolved during antiquity (*1*). The word “perfume” stems from the Latin words *per*, “through,” and *fumum*, “smoke” (*2*). However, the materials described here predate this modern word, and the origin of scented oils and perfumes can be traced back to the birth of urban life in the Fertile Crescent. The first ‘scented oils’ or ‘perfumes’ were aromatics used as incense to please the gods.

The earliest evidence of human understanding of plants and related aromatic properties are found in cave paintings in the Lascaux region in France, dated about 17,300 years old. Archaeologists suggest that the people who lived during that period might have had an understanding of herbs and spices in the context of medicine and flavoring food based on the pictorial representations drawn on the cave walls. This does not give us any information about whether these people used oils or perfumes, but it is one of the oldest records of human knowledge of flavors and fragrances in nature (*3*).

Olfaction, or the ability to smell, is a faculty that evolved when mankind's predecessors lived in the ocean. In a liquid medium the sense of smell serves many purposes. For example, fish use smell for detection of prey, mating and danger. The clues of smell have been shown to serve an important role in annual salmon migrations. When our ancestors moved from the oceans to the land, the quality of olfaction declined to a certain extent. This is evident from the fact that primates lack the keen sense of smell found in canines (*4*). Smell or odor is not an intrinsic property of a molecule, as color is. The odor of molecules also depends on the receptor molecules in the human body. Most of the receptor molecules are enzymes, and these enzymes bind to specific molecules which cause signals to be sent to the brain, thus allowing us to detect smell in air for example (*5*).

Odors play an important social role in our society, and this was also true during antiquity. Every civilization and society has held certain fragrances to a prestigious level. The Greeks and Romans considered the smell of rose to be of great value (*6*, *7*). Before that time, myrrh and frankincense were of great importance in the Fertile Crescent. Anthropologically, perfumes are often considered as liquid memory (*8*). For example, the modern lacing of natural gas with thiol derivatives is a common procedure that has been in use for decades. The recognition of the scent immediately warns one of a gas leak.

Scent also plays an important role in some animal and insect reproduction. The term 'pheromone' was coined in 1959 from the Greek words *pherin*, meaning to bear along, and *hormon*, meaning an excitement (*9*). Humans who lived during antiquity were familiar with the pheromones secreted by insects and animals and used them to anoint themselves and gods. The pheromone excreted by the musk deer was used by the ancient Egyptians and Mesopotamians. People of different cultures understood the links between sex and scent during antiquity, and the use of scented oils and perfumes was often for sexual appeal (*10*).

Essential Oils

At the very core of the perfume enterprise lie the "essential oils". The definition of an essential oil is given differently by different dictionaries. For scientific purposes, "an essential oil can be defined as an odoriferous material existing in liquid or semisolid form at normal temperatures and obtained mostly from plant sources" (*11*). Since most essential oils come from plants, the essential oils used throughout history in different regions are connected to the geographical nature of the place. Analysis of the archaeological specimens left by early civilizations thus reveal to us the culture, lifestyle and many other details of those civilizations (*12*).

The essential oils are classified today according to the rate at which they diffuse in the atmosphere, which depends on their volatility. Top notes are the

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

most volatile material and the first perceptible odor. Middle notes are the floral and spicy ones and usually add body to the perfume. These notes can last for up to thirty minutes to an hour. Base notes are the least volatile materials, and persist for a long period of time. Oils and sometimes resins are used commonly as base notes, such as frankincense, myrrh, rose, sandalwood, lavender and jasmine (Table 1). Comparing the composition of the perfumes and scented materials used during antiquity and today, one realizes there are many similarities in their basic skeleton (*13*).

Today, perfumes are commonly made using ethyl alcohol as an extender or solvent with one or more essential oils that impart scent. The ratio is commonly eight parts alcohol to two parts essential oil. An “eau de toilette” is a further-diluted solution of similar ingredients in ethyl alcohol. The “after shave lotion” or “cologne” used by men contains about one to five percent scent-imparting components in ethyl alcohol. Alcohol was an important component in perfumes during antiquity, as well as today, as the diluent or carrier, which is often alcohol based. The solubility of essential oils containing terpenes was much less and probably compelled the use of alcoholic solvents by the perfumer. Given the fact that alcohol was not isolated until the 12th century, alcohol-containing reagents such as wine were used for this purpose during antiquity (*15*).

Steam distillation is a modern process used in day-to-day preparation of perfumes by manufacturers. The chemistry behind this process is that two immiscible liquids such as a semi-volatile oil and water have their own respective vapor pressures. When they are mixed, the total vapor pressure increases according to Raoult’s law. Some of the essential oils in plant ingredients may decompose close to or below the boiling point but most of the oils responsible for fragrance boil at higher temperatures. These oil mixtures could be made into a mixture with water, and be purified by steam distillation. During antiquity, a related process commonly used for the preparation of scented oils and perfumes was to boil the natural ingredients in a pot with water. The reason we are able to use chemical techniques to identity most of the major organic compounds is because these compounds from natural sources have been shown to be able to withstand the amount of heat possible from heat sources during antiquity. Some of the major organic compounds with high boiling points in commonly found natural sources are listed in Table 2 (*16*).

Almost all of the scents that have been discovered and used during antiquity or synthesized in modern times can be classified into seven sets or categories: floral, greens, citrus, oriental, chypre, aldehydic, and leather or animal scent. There were other common terms used during antiquity such as mossy, spirituous, vanilla-like, metallic, fishy, sulfurous, burnt, spermous, anisic, fruity, ammonia-like, waxy, putrid, fecal, etc. Several classification models arose in the earlier part of the twentieth century (*17*). One of the earlier versions, for example, was called the “smell prism” and was developed by philosopher Hans Henning in 1916 (Figure 1) (*18*). In this model, Henning classified all the known odors into six primary odors and represented them in a space as a prism. He claimed that any odor we experience could be pointed to a region in the prism as a combination of the

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

primary odors. The tone of a fragrance or scent is a term that describes whether the particular odor is piercing, mild, or muffled.

Cultural affiliations of scents and perfumes differed among civilization and societies. For example, as introduced above, the Greeks considered rose to be of high value compared to other fragrances. Throughout most of ancient Egyptian history, however, it was lilies that were highly prized. Thus the abundance of a certain fragrant material in residues from excavations as well as written records sheds light on the culture of people (*19*).

Table 1. Essential Oil Use Found in the Fertile Crescent[*]

Oil sources	*Egyptian*	*Sumerian*	*Akkadian*
Bitter almonds	?	-	✓
Anise	✓	-	✓
Calamus	✓	✓	✓
Cassia	✓	-	✓
Cedar	✓	✓	✓
Cinnamon	✓	-	?
Citron	✓	✓	✓
Ginger	?	-	✓
Rose	✓	✓	✓
Peppermint	✓	✓	✓
Rosemary	✓	-	✓
Rushes	✓	✓	✓
Sandal	?	-	✓
Gingergrass	?	✓	✓

✓ − record of usage found. ? − possible use. [*] Data from reference (*14*).

Table 2. Essential Oils, Main Ingredients, and Boiling Points

Essential oil source	*Main ingredient*	*Boiling point (°C)*
Aniseed	Anethole	234
Bergamot	Linalyl acetate	220
Clove	Eugenol	254
Dill	Carvone	231
Juniper	Camphene	159
Oranges/Lemon	Limonene	176

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Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

Table 2. (Continued). Essential Oils, Main Ingredients, and Boiling Points

Essential oil source	*Main ingredient*	*Boiling point (°C)*
Lavender	Camphor	204
Rose	b-Damascenone	274
Peppermint	Menthol	212
Thyme	Thymol	232
Pine	Terpineol	219
Wintergreen	Methyl salicylate	222
Pine	Pinene	155
Rose	Methyleugenol	255
Lavender	Linalool	199
Spruce	Isobornyl acetate	229
Ylang-ylang	Benzyl acetate	212
Lavender	Terpineol	219

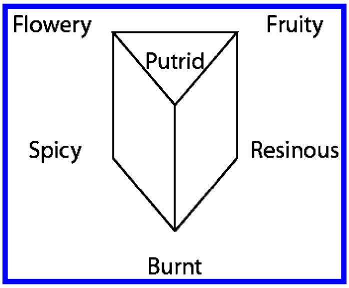

Figure 1. Henning's Smell Prism.

Carriers and Additives

Fats and oils were major carriers of scent during antiquity. Fat material could be both plant- and animal-based. The source of animal fat is often a topic of interest to an archaeological chemist with an anthropological perspective. Depending on the nature of the spice or scent source, a suitable fat material should be selected to extract the scents. Most of the fat was probably derived from the butchering of wild and domesticated animals for meat and hides. This included mainly cattle, goat, sheep, donkeys, and pigs.. Many of these domesticated animals were available during the Old Kingdom period (3rd millennium BCE). In some instances, crocodile fat was used around the Nile Delta due to the abundance of its sources. Ducks and geese also supplied fat, along with doves, herons, quails, and some migratory birds. Some historians mention the use of fishes, such as carp and eel, as a source of fat (*20*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

Specific details on fat-rendering techniques are yet to be found (*21*). With the current knowledge it is safe to assume the ancient Egyptians used both dry and wet rendering methods for the purpose of perfume production. In the dry method the fatty tissue was cooked until dry in an open vessel at a temperature around 120 °C. Another process involved slow cooking at low heat; this fat might have been used for food preparations. In the wet preparation, the fat was steamed with a small amount of water in a closed container at a much lower temperature, and after the mixture was allowed to settle, the fat was skimmed off from the top. If the preparation of rendered fats was carried out in a copper vessel, then the fats would become rancid much faster (*22*). The current sources point us to scenes from the tomb of King Seti I from the New Kingdom; there are scenes of fat-rendering and a scene of a butcher's yard with men chopping fat near a large vessel over a fire. One hypothesis is that, their knowledge of fat rendering could have stemmed from applying the methods they knew for oil extraction to fats (*23*). The New Kingdom jars from Amarna with oils and fats were signed by a same person named *ps sgnn.* Some of the identification of the artifacts are still speculative in nature concerning the fats and oils used in the preparation of scented oils. Gums, resins, and balsams, on the other hand, are more complicated than simple fats. Their main use was as a fixator, or if a scented oil required maceration for a certain amount of time. Dutch historian R. J. Forbes has listed out the gums and resins that are commonly used in the fertile crescent during antiquity (Table 3) (*24*).

Beeswax was another important ingredient in unguent preparation (*25*). Egyptian knowledge of bee-keeping can be understood from wall paintings and papyrus records. Due to the hot climate and the rich land around the Nile, beekeeping was not a difficult task. Archaeological remains from the tombs, ritual articles, and texts point us to the fact that the Egyptians believed the beeswax had magical properties (*26*, *27*). The inflammable nature of beeswax was well-utilized in the preparation of incense cones, and the ability to mold the beeswax provided an opportunity to make scented human and divine idols (*28*).

The uses of perfumes as well as the kinds of scented oils and fragrances have been recorded by historians through different periods, but the essential technology, processes, and equipment used by the perfumers are often obscure. The advent of new technologies of the 21st century such as X-ray diffraction, mass spectrometry, and magnetic resonance imaging, has resolved many unanswered questions.

The chemical fingerprints of oils, fats, resins, and waxes shed more light on what went into the preparation of scented oils and perfumes. Common components of fats and oils are triglycerides, cholesterol, saturated fatty acids, and mono- and polyunsaturated fatty acids. The fatty acids can be identified by the number of carbon atoms present in the molecules. For example, palmitic acid contains 16 carbon atoms, and stearic acid contains 18 carbon atoms. The ratio of C16 and C18 fatty acid can tell us the possible major components in a sample (*29*). These fatty acids are also found in animal fats and dairy products. The more unsaturated fatty acids that are in the fat material, the lower the melting point of the fat. Unsaturated fatty acids are often found in vegetable sources. The chemical nature and composition of the oils and fats cause changes in properties over time. For example, some oils tend to become rancid faster than others. Fourier transform infrared spectroscopy (FT-IR) and gas chromatography-mass spectrometry (GC-

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

MS) have proved to be valuable tools in understanding the nature and composition of these fat residues as well as their degradation products (*30*).

Table 3. Gums and Resins Use Found in the Fertile Crescent*

Gums and Resins	*Egyptian*	*Sumerian*	*Akkadian*
Myrtle	?	✓	✓
Mecca balsam	✓	-	✓
Galbanum	✓	✓	✓
Liquid amber	✓	✓	✓
Sagapenum	-	-	✓
Pine	✓	✓	✓
Juniper	✓	✓	✓
Wormwood	-	-	✓
Elder	-	✓	✓
Cypress	✓	✓	✓
Ladanum	✓	-	✓
Indian myrrh	-	-	✓
Benzoin	✓	-	-
Ammoniakon	✓	-	-
Cedar	✓	✓	✓
Cedar-pitch	✓		
Fir	✓	✓	✓
Pine-cone gum	✓	✓	✓
Broom	-	✓	✓

✓ − record of usage found. ? − possible use. * Data from reference (*24*).

Scented Oils and Perfumes in Mesopotamia

The use and evolution of perfumes and scented oils most likely originated in the ancient Near East around the fourth millennium BCE. The first use of perfumes or scented oils was most likely as medicine. The art of perfume-making was known to early Mesopotamians (*31*). Excavations from Mari, a location near present day Iran, have revealed scented and unscented oils stored separately in a room. Records of the amounts of scented oils and unscented oils were found on tablets in the same location (*32*). Tablets dated as early as the third millennium BCE detail how essential oils and water extracts of essential oils from plants were used for common ailments.

In addition to scented oils, the Sumerians also exhibited knowledge of cosmetics. For example, the Sumerian people used yellow ochre as face powder, and it was often referred to as “the golden clay” or “face bloom”. The Egyptians also used this face powder, but the women of Egypt used the powder in minor quantities compared to the Sumerians. Later on, the people of Mesopotamia started using plant derivatives such as henna or asa foetida in the preparation of make-up for men and women (*33*).

In Akkadian, the word for an ointment came from the name of the priest who prepared that concoction. Every anointing oil was distributed in its own vase and spatula, and the name of a utensil was often associated with the name of the oil prepared in it (*34*).

Archaeological excavations have shown that perfumery was a major chemical industry in the Babylonian time period. Preparation of aromatic substances had four main areas of impact in Babylonian society. They were used in rituals, magical practices, medicine, and cosmetics. The knowledge of the Babylonians on the topic of sepsis is debatable; nevertheless, the application of essential oils to wounds was a common practice (*35*). On a comparative ground, the archeological studies on Babylonian and Assyrian sites have been very frequently discussed in early twentieth-century texts compared to other regions.

The list of names identified for apparatus used during the Babylonian period was described in detail by chemical historian Martin Levey in his book on chemistry and chemical technology in ancient Mesopotamia (*36*). Figure 2 illustrates commonly used apparatus in perfume-making operations. Shown are apparatus for sublimation, condensing, a primitive form of distillation, and regular heating. The apparatus excavated in ancient Mesopotamia has remarkable similarities to distillation apparatus and other alchemical apparatus that came into use during the Arabic civilization and later. And the evolution of these apparatus could well be attributed to the development of cooking wares (*36*).

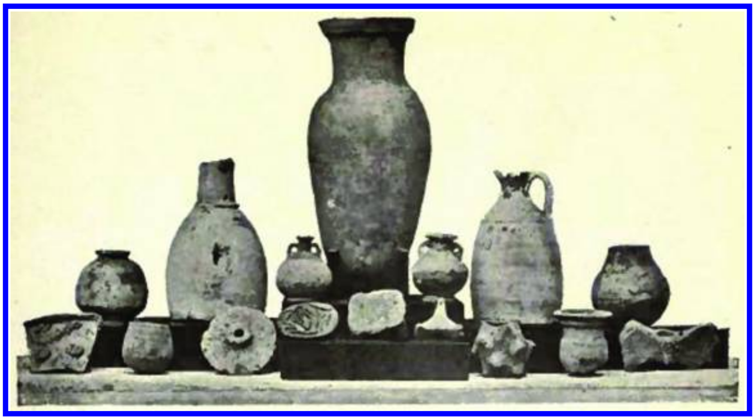

Figure 2. Apparatus possibly employed for perfume-making processes in ancient Babylonia. (from The Civilization of Babylonia and Assyria by Morris Jastrow Jr, JP Lippincott and Co., 2nd ed., 1915).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

Some important texts on the manufacture of scented oils and perfumes in Mesopotamia were translated from second-millennium Akkadian cuneiforms mostly excavated from Assur. The translations were mainly carried out by Assyriologist E. Ebeling. Martin Levey, a famous chemical historian, in reference to some of the translated texts mentions the importance of this technology in latter Arabic chemical practices (from al-Kindi). A Sumerian medical tablet currently at the University of Pennsylvania Museum describes the preparation of an aromatic mixture. A translation is given below (*36*, *37*):

> “On the fourth time of pouring together, you heat fresh good well water and pour it onto a hirsu pot; then you pour ½ qa calamus and ½ qa myrrh, expressed and filtered, on the heated water in the hirsu pot. The mixture stands overnight and is steeped. In the morning, you filter the water and aromatic, using a cloth sieve, into another hirsu pot. Remove the dregs. Then you measure 3qa calamus, 3qa expressed, filtered myrrh, and 40 qa water which had been overnight with the calamus and myrrh. Light the fire. When the water necessary for the mixture is heated pour in the oil and stir. When the oil, water and aromatic penetrate one another, you need not shake it further. Cut down the fire under the diaqru pot and let it stand for two or three days.”

Levey, in his description of Babylonian techniques, mentions that “the chemists who lived during the period must have had low yields with many impurities present such as decomposition products of the non-volatile plant components”. The multiple extraction methods remarkably resemble the techniques used by the Alexandrian alchemists who came much later. Some of the apparatus excavated from the apparent perfumery installations strongly resemble the alchemical apparatus described by al-Kindi. The descriptions of Babylonian apparatus and the equivalent names given by al-Kindi are listed in Table 4 (*36–38*).

The cedar of Lebanon (*Cedrus libani*) was one of the most valued scented products recorded in Mesopotamia. The product was used as an incense and imported from the forests of Marduk in Lebanon and brought in to the settlements around the Tigris and Euphrates valley. The word Lebanon comes from the Akkadian word *lubbunu*, meaning “incense”. Besides cedar, materials such as pine, cypress, and myrtle were also imported from Lebanon (*39*, *40*). The use of myrrh and Frankincense was also prevalent among the Akkadians, who are believed to have imported them from regions around present day Yemen. The kingdom of Larsa mentioned in letters from the fifth year of Sumuel’s reign is believed to have been a great market-place for perfumes, fragrances, and several raw materials (*41*). Oils mentioned in the Ebers papyrus from Egypt (dated to the same time period) includes aber oil, abra oil, beetle wax, adu animal oil, cats oil, clear oil. Cows fat, cedar tree fat, crocodile oil, hippopotamus oil, marrow of an ox, mouse oil, olive oil, sefet oil, shad fish oil, tallow oil, and van tree oil were all traded in these regions (*42*). During pre-classical antiquity, castor oil remained as the poor man’s option, while olive oil was available only to priests and the rich (*43*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

Table 4. Description of Babylonian Apparatus and Respective Names Given by Al-kindi

Description of Babylonian apparatus	*Al-kindi's Name*
Condensing apparatus	Anbiq
Fireplace or hearth (in which to place a still, clay or metal vessel)	Mustauqad
Clay or metal vessel (Matter to be purified is placed on this.)	Tingir, qurat
Receiver	Qabila
Condenser	Ihlil
Beaker	qadah
Flask for oil	Barbiyya, qarura
Glass/clay bowl with varying shape	Gam, batiya
Basin	tast
Cup	fingan
Pot made of white stone	Baram
Perfume/wine vessel	Batia
Drinking vessel	Taur
Pot	Qidr, gamr
Mug	Kuz
Large wooden bowl	qasa

Aromatic woods were used in architecture shortly after the fall of the Sumerians. For instance, imported cedar, sandalwood and other aromatic woods were plentiful in the royal architecture of the palace of Sargon II at Khorsabad (722-750 BCE). Records dated to sixth century BCE reveals the import of sandalwood from distant lands (*44*).

To conclude, Mesopotamian medical tablets are so far the oldest texts found to contain detailed descriptions of methods for extracting essential oils from plant sources and their aromatic and medical properties. Mesopotamian knowledge of the chemical technology of scented oils and perfumes spread to the Egyptian, Indus Valley, and Mediterranean cultures. This empirical knowledge, even though more applied in nature, served as a basis for the evolution of scientific technology through the times.

From Birth to Afterlife: Perfumes in Egypt

The Egyptian outlook on perfumes can be inferred from their lifestyle revealed by ancient records, the objects found in connection to death and afterlife, and mummified remains. The ancient Egyptians were concerned with the odors of everyday life and death. Dated to 1550 BCE, the Ebers papyrus gives us a wealth of knowledge of Egyptian medical preparations for ailments, perfumed anointing oils, and incense plants. As we move back through time, as early as the third millennium BCE, it becomes difficult to differentiate between the uses of oils, scented oils, perfumes, and fragrances for spiritual and pharmacological purposes (*45*). The Egyptian term used for smell is always associated with the word used to refer to perfumes, which means “fragrance of the gods”. This is a clear indication that perfumes and fragrances were used mostly for religious purposes in the beginning (*46*).

Scented oils, along with resins and ointment preparations, were widely used in the funerary process, preparing the body for mummification and the afterlife. Often, after organs were removed, the empty cavities of the body were filled with linen cloths dipped in resins and oils enriched with fragrances. These facts are attested to by texts recovered, grave articles, and systematic chemical analysis of the burial sites using advanced techniques such as GC-MS and liquid chromatography-mass spectrometry (Table 5) (LC-MS) (*47*)

Table 5. Compounds Identified in Tomb TT14 at Luxor-Egypt through GC-MS and Possible Sources of the Compounds[*]

Sample	*Identified Compounds*	*Possible sources*
Mummy abdomen	Saturated fatty acids	Beeswax
	Hydroxyl fatty acids	
	Linear alcohol CLinear alcohol C_{24}-C_{30}	
	Linear alkanes CLinear alkanes C_{28}-C_{31}	
Mummy thorax	Di terpenes	Pinacea resin
	dehydroabetic acid	Pinacea resin
	Linear alkanes CLinear alkanes C_{28}-C_{31}	Beeswax

[*] Data from reference (*47*, *48*).

Elemental analysis is the quintessential part of chemical analysis on the residues. A small portion of the sample is usually taken and qualitatively analyzed using energy-dispersive X-ray fluorescence with a microprobe. This analysis reveals some key information, such as the origin of samples. For example, the analysis of filling material from the sarcophagus of Queen Hatshepsut and King Thutmose I revealed a red paint-like material. Analysis showed that the sample was mostly organic in nature and some amounts of inorganic materials. Combination of this technique with FT-IR revealed the presence of kaolinite and quartz as components possibly crushed with mastic resin, animal fat, and sugary materials to prepare the red material. A detailed look at the way the material was attached revealed the possible use of plant gum during altercation of the sarcophagus (*49*).

Egyptians used perfumes, essential oils, and scented oils for personal adornment during the New Kingdom. During the Old Kingdom, the production of perfumes was reserved for priests, and its use was reserved for priests, use in funeral ceremonies, and for kings since most of the kings were considered to be representation of gods. Records dating back to as early as 4500 BCE indicate the use of balsamic substances. This archaeological evidence also indicates that the use of such aromatic substances could very well have been for food (*50*).

In addition to the major use of scented oils and perfumes during the funeral process, they also found a place among queens and high-society women. Around the sixth dynasty (2300 BCE) the use of scented oils for personal adornment increased. The walls of mortuary temples in Thebes depict the extensive use of perfumes by women and men to anoint themselves (Figure 3) (*51*, *52*).

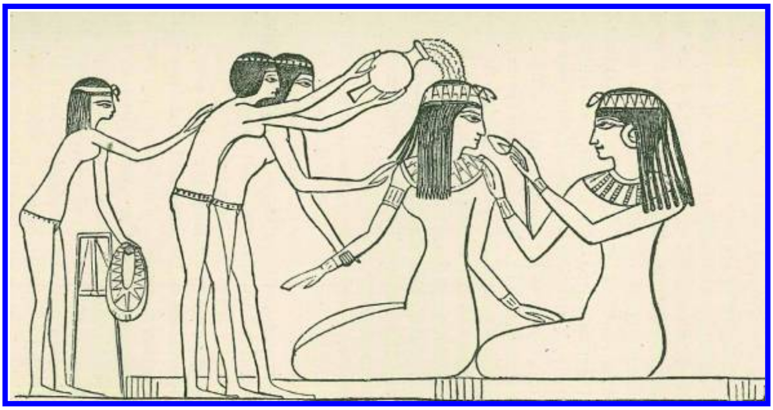

Figure 3. Egyptian Queen adorned with scented oils. (image from The Ancient Egyptian, Vol-II by Sir J. Gardner Wilkinson, 1883).

Analysis of hieroglyphs reveals that Egyptians most commonly used enfleurage as a method for the preparation of perfumes. This method is still used in rural Egypt for the preparation of incense. In this process, the natural fragrance source such as a flower or leafy material is placed on the top of purified fat under sunlight every day for certain number of days. The essential oils present in the material diffuse through and the fat becomes enriched with fragrance. Finally the fat is melted and filtered to obtain the scented oil. The choice of the fat used depended on the nature of application of the unguent. For example, sometimes the oils that solidified out upon cooling were used as pomades. The famous Egyptian wax cones often found in paintings and papyri were made this way. Aristocratic women wore these cones on their head; as the day passed, the heat of the sun and their body heat caused the aroma in the cone to dissipate (Figure 4) (*53*, *54*).

Two other methods used in the perfume-making process were maceration and expressing. Maceration involved dipping flowers in hot fats or oils at temperatures over 60 °C. This is a technique that was often used when the perfumer was told to heat his herbs in oil and to strain the mixture when hot. Excavated kitchen utensils from ancient Egypt support this fact. Also, the ancient perfumers, who

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

were equivalent to current day pharmacists, depended heavily on the cooking techniques and utensils available at that time (*55*).

Pictures of women gathering flowers, especially lotus and lilies, were carved in mortuary temples and papyri. Scenes of women carrying baskets of lilies and walking towards a factory where the essence will be extracted have also been found (*56*).

Figure 4. Egyptian queen adorned with scented wax cones. (Life in Ancient Egypt by Adolf Erman, Translated by H. M. Tirard, MacMillan and Co., New York, 1894).

A method adjunct to boiling, enfleurage, and expressing is torsion pressing. The earliest records on the use of a torsion press are from the First Dynasty. Similar paintings have been found from the Fourth Dynasty and into the Old Kingdom Period. Many papyrus records and records from mortuary temples pertain to the wine-making process. To some extent there is evidence that the processes were essentially the same for oil and wine presses. A problem arises, however, when there are no texts accompanying the pictorial representations. The god depicted for the preparation of oils is the same as that for the preparation of wine. Knowledge from the Fifth-Dynasty tomb of Iymery at Giza helps us understand the similarity between the processes. There are pictures representing women holding poles with a simple sack above a container. When the poles are twisted, the juices and essential oils from the leaves or flowers would drip into to the container. The same method was used in the Old Kingdom for pressing grape pulp. In a picture from the Ptolemaic tomb of Petosiris, two women work sticks inserted in the looped ends of a bag. The linen bag contains blossoms and is inserted into a jar (Figure 5) (*57*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

Figure 5. Two Egyptian women working a bag-press and another carrying a lily flower. (Wikimedia commons ID E11162, author: Guillame Blanchard, 2004).

The operation of crushing and squeezing the blossoms would usually take place near the field. Most of the inscriptions from the temple walls indicate that these installations were rather temporary and moved once the harvest was completed (*58*). Paintings from Rekhmireh's tomb (ca 1430 BCE) depict perfumers mixing and crushing resins and other ingredients in mortars (Figure 6) (*59*). The mixture would be combined with oil and heated in a cauldron to allow the oil to become saturated with scents.

Figure 6. Egyptian hieroglyphs showing flower-crushing operation and storage. (Forms reproduced from Saqqara Mastabas).

While the interest of scented oils and perfumes reached its peak among the Sumerians around 2800 BCE, a thousand miles to the southwest, in Egypt, King Isesi sent expeditions to the land of Punt (current-day Somalia) for procuring fragrances. Owing to the importance of scented oils and perfumes in Egyptian society, oils of cypress and cedar were imported from distant lands to Egypt. The use of animal-based perfumes and scents has been found throughout Egyptian hieroglyphs. Perfumes such as musk, ambergris, and civet were available only from distant lands through trade or conquer (*60*).

The Egyptian word for incense, *ntyw* appears in the earliest pieces of literature found, but the extensive use of essential oils and other aromatics rose to its peak during the New Kingdom, around 2100 BCE. During the reign of Queen Hatshepsut, many expeditions were made to the land of Punt. The flowering plants and shrubs brought back were planted in her temple *Deir al-Bahari* (*61*).

Kyphi was a preparation used by people in the Old Kingdom. It was a mixture of 16 ingredients such as scented barks, resins, spices, oils, and plant pastes. The preparation was used as incense, perfume, and as medicine (*62*). In the Ebers papyrus there is a recipe for another perfume also called "kyphi" made of dried myrrh, juniper berries, incense, gyu plant, twigs of mastic, fenugreek, nebyt of northern Syria, yukun, and zemen plant, which were ground, mixed, and cooked. It was used for perfuming houses and clothes; when prepared with honey and made into pills, it was used by women for perfuming their breath (*63*).

In Egypt, perfumes and cosmetics were closely associated and the Egyptians used cosmetics to a greater extent than the Sumerians. For example, the Egyptians' use of eye-makeup is well known and found in paintings from the oldest pyramids and mortuary temples. The use of eye-makeup was not only for beauty but was also thought to serve as protection against eye diseases (*64*). The excavated tubings to hold the eye-paints bear inscriptions saying, "to stop bleeding", "good for the sight" and "to lay on the lid and the lashes". Ingredients such as burnt almond shells and manganese dioxide were eventually either added to galena and green malachite, or replaced them. The advent of trade and transport with the Mesopotamian region and the land of Punt brought unguents and green resins of coniferous trees and unguents to add to the eye-makeup. During the New Kingdom period, the preparation of eye-makeup was carried out using fats or oils and mineral ingredients. The mineral ingredient was first ground well on a stone and then made up into a paste with water or with the gum of Akkadians or a gum-water mixture (*65*).

Even during the Old Kingdom, scented oils and perfumes were used for magic or religious purposes as well as for hygiene. The evolution of the use of essential oils for everyday purposes in Egypt stemmed from the geographical conditions that prevailed in the northern regions of Africa. The human skin contains a thin layer of fat to protect against natural forces such as dirt, bacteria, and dehydration through sweating. The use of essential oils and cosmetics to protect against the hot and humid conditions of the Nile Delta was necessary for the Egyptian people. Ptah-Hotep mentions in his texts, "Oils is the remedy of the body". During the Amenhotep III period there was a dedicated "apportioner of ointment". During his reign, King Seti I increased the ration of ointment for the army (*66*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

Historians have been able to identify recipes for 35 specific unguents from the Middle Kingdom, 22 of which were used commonly as cosmetics in addition to being mentioned for their pharmacological properties. There exists plenty of evidence that scented preparations were used as incense as well as in cosmetics. Pyramids from the Old Kingdom contained incense burners; the residues tested positive for gums, resins and plant based materials. The presence of long handles on the incense burners indicate that they were used for ritual offerings (*67*).

The addition of bitumen to these scented oils and unguent preparations is one of the notable features found during residue analysis of mummies and empty jars. Analysis of two Eighteenth-Dynasty samples by GC-MS, one from a coffin and another from a canopic chest has revealed the presence of hopanes and black varnish material consisting mostly bitumen. Thus, the association of bitumen in funeral practices as well as its inclusion in the preparation of cosmetics has been established. Many mummies from the New Kingdom have blacker skins than to mummies from the Old Kingdom or Middle Kingdom. This difference is attributed to the treatment of the bodies with resin, pitch, and scented oils, although other possibilities, including fungal growth under damp conditions, are reasonable (*68*). When exposed, the heads of some mummies—for example, the mummy of King Seti I—were first brown in color and later changed to black over time. This suggests some oxidative decomposition of the essential oil ingredients used in the preparation of the mummies. The amounts of essential oil residues and resin residues from the linens used to fill the cavities were much higher compared to the amounts on the skin. A recent analysis by the British Museum on a mummy from the Third Intermediate Period showed the presence of 7-oxodehydroabietic acid, possibly from pine, cedar or fir. Other materials found include pitch and beeswax. Lucas et al also noticed and reported the reddish brown color of desiccated mummies resembling remarkably with the resinous ingredients used during that time frame. GC and GC-MS remains one of the reliable tool in identifying and characterizing the resins and oils found in mummies (*69*).

King Tutankhamun's burial chambers shed more light on the use of scented oils, perfumes, spiced wine, and fragrances during the New Kingdom (Figure 7) The annex chamber next to the coffin of King Tutankhamun contained numerous jars of dried wine and fragrances. One of the excavations revealed a double box consisting of two cartouches that were traditionally inscribed with the name of the king. Both sides are covered by one lid made up of two pairs of feathers with solar disks. The throne name of Tutankhamun is written four times in code. The scarab beetle inscribed along with King Tutankhamun's name signifies that the container is dedicated for his perpetual regeneration in afterlife. The container was found to contain perfume oil residues. Another article with scented oil residues was a jar with a lion lid. The jar was made with alabaster and decorated with gold and ivory. The lid of the jar could be swiveled sideway by the pin on the left-hand pillar. Egyptologists propose that these types of highly decorated jars were often used for storing perfumes made from ingredients imported from distant lands (*70*).

Another alabaster jar, with a carved head of Hathor, was found to contain similar residues. The plants entwined around the jars include lily and papyrus. The goddess Hathor was closely associated with beauty and cosmetics, and at times she was also associated with love, joy, and eroticism. Such containers for perfumes used by kings and queens are direct proof of the role of scented oils and perfumes in ancient Egyptian society (*71*).

Figure 7. Perfume jars in King Tutankhamun's annex chamber. (Wikimedia commons, author: Frank Rytell, August 1987).

Perfumes in Ancient Greece and Rome

Greeks indulged in hygiene and care for the human body. During Homeric times, beauty was requested from the gods. Girls would enter beauty contests freely and with a sense of responsibility (*72*). The development of perfume technology among the Greeks and, during the later periods, among the Romans was largely based on knowledge from the Egyptians and Mesopotamians. The Greeks employed the following process mostly for the preparation of scented oils: fats were made astringent by heating with plants and mixed with aromatic substances such as flowers, spices and resins. The mixture would be heated, although sometimes no heat is applied depending on the desired product. Resins were often added to make the perfume less volatile (*73*).

An ointment containing myrrh was used by soldiers around 400 BCE for infections from battle wounds. Hypocrites (460-377 BCE) recorded the medicinal uses of over 400 plants and spices. He mentions in his writing, "A perfume bath and a scented massage is the way to healthy life" (*74*).

Olive is an evergreen tree and an indigenous species to Mediterranean costal lands. To the people in those regions, it has remained a symbol of health and prosperity to this date. It has also continued to be a good source of nutrition for the people through the centuries. Olive oil contains high amounts of mono-unsaturated fats, phenolics, and good amounts of vitamin E and other micronutrients. The oil made from green olives was called "oleum omphacium" in Latin. The oil from unripe berries is white, and it was considered better than the green oil. Both Pliny and Dioscorides mention that the white oil was considered to be the best for perfumery (*75*).

Archaeological remains reveal the existence of perfume shops in the centers of cities. Remains from Delos, Paestum, Pozzouli, Capula and Rome during the Hellinistic and Roman periods reveal the importance of perfumes in society, the methods of preparation, and the raw materials used. In the late 1990s, excavations at Delos Paestum revealed the details of perfume-making during the Hellenistic period (*76*).

During the Roman period, the practice of palestrae and baths led to the "democratization" of perfume usage. The difference between the perfumes used by the common man and the aristocrat was the quality of the perfumes (*77*). The major contemporary outlooks on classical perfumes and fragrances were written in Greco-Roman literature by Pliny the elder (23-79 CE) and Theophrastus (371-287 BCE). To a good extent, Dioscorides (40-90 CE) in his *De Materia Medica* talks about perfumes, fragrances, oils, and scents. The importance of perfumes and scented oils and the resources spent for them during Roman times is explained in Pliny's words (*78*):

> "a hundred million sesterces every year, that is the sum which our luxuries and our women cost us: for what fraction of these imports, I ask you, now goes to the gods or to the powers of the lower world?"

Pliny and Dioscorides both mention a variety of perfumes such as mendesion, metopium, cheap unguent, malbrathum, nardinum, faliatum, rhodinum, krokinon, sampsuchinon, melinon, susinum, kuprinon, telinum, megalinum, kinnamominon, myrtle-laurel, royal unguent, Illyrian iris, amarakinon, elatinon, oinathinon, olaminon, abrotominon, anethimon, narcissinon, irinon, gleucinon, and metopium. In his writings, Theophrastus talks about the different spices whereas Pliny the Elder includes the regions in which these spices originated (*79*).

Theophrastus's writings start with basic questions such as *What is odor, taste and smell?* He defines odor (*80*):

> "Odor in general, like tastes are due to mixture; for therefore simple substances such as water, air and fire; on the other hand earth is the one elementary substance which has a smell, or at least it has one to a greater extent than the others, because it is of a more composite character than they".

Theophrastus believed every animal and plant has its own innate smell and cites the fact that some animals have a great olfactory sense.

His description of rose perfumes goes as follows (*81*):

> “being very delicate and acceptable to the sense of smell, by reason of its lightness it penetrates and fills up the passages of the sense, so that being entirely taken up and filled with it, it is unable to judge of others… the sense may be preoccupied with superior odour, so it is not easy to introduce after it what is inferior, since the sense of smell refuses it”

Theophrastus describes the use of scents in wines in several of his chapters. He also talks about the manufacture of artificial odours with perfumes in wines and the general process for manufacture of scented oils and perfumes (*82*):

> “...the method of the maker of spices and perfume powders (diapasmata) is to mix solid with solid, that of those who compound unguents or flavor wines is to mix liquid with liquid: but the third method which is the commonest is that of the perfumer, who mixes solid with liquid that begins the way in which all perfumes and ointments are compounded. Further one must know which odours will combine well with which, and what combination makes a good blend, just as in the case of the taste; for there two those which makes combinations, and as it were season their dishes, are aiming at the same object.”

Records on perfume production and importance are found in ample amounts in Hebrew literatures and the Bible. As early as the 14th century BCE, there were recipes for making sacred perfumes with myrrh, frankincense and cinnamon which were used in ceremonies by the priests. In the New Testament, scented oils were also used for bathing and medicinal rubs. Palestine is mentioned throughout in the history as a major perfume producing region. Judean balsam oil originated in the Palestine region and was an often-used commodity in antiquity. The En-Gedi oasis is located on the west coast of the Dead Sea; it is a place known for its production of Judean balsam oil. Excavations revealed several furnaces, jars, and metal and bone artifacts dated from 630 to 582 BCE (*83*, *84*).

The use of perfumes and their manufacture was found in Jerusalem, dating to 70 CE during the Roman period. When Titus captured the city, he burned down the buildings. Analysis of a particular installation revealed several furnaces, scales, weights, measures, and terracotta containers for storing unguents (*85*).

China and Indus Valley Civilization

The first use of scents, oils, and fragrances in China was recorded between 2697 and 2597 BCE. Huang Ti, mentioned as the Yellow Emperor, describes several aromatic preparations in his book *The Yellow Emperor's Book of Internal Medicine,* Some of the methods of preparation are still in practice in eastern Asia (*86*).

The Indus Valley civilization is comparatively the less-studied Bronze Age civilization. Owing to the geographical location and lack of accessibility to the industrially advanced western world, research at the sites of Harappa and Mohenjedaroh was not initiated until the 1920s (*87*). Vedic literature that is

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known to have existed as early as 300 BCE mentions hundreds of materials such as cinnamon, ginger, myrrh, sandalwood, and oily plants and fragrant wood barks. Records indicate extensive use of scented oils and aromatic plant derivatives for medicinal purposes. The exact period of Ayurvedic literature is still under debate, but current eastern historians indicate that records on ayurvedic practices date back to the time of Buddha; again ca. 300 BCE (*88*).

Notes on the use of aromatic oils have been found at various instances in literature dated prior to 1st century BCE. In the Indian epic Valmiki Ramayana, the king of Ayodhya, Dasaratha, upon death was kept in a wooden bath filled with aromatic oils and medicines called "taila droni". The ingredients used during the process were sandalwood, pinus roxberghii, prunus cerasoides, aquilaria agallocha and cedrus deodra. The use of sandalwood paste seems to have been a common practice (*89*). Incenses are referred to by the name 'dhupa'. The preparation of dhupa often involved the use of resins. The use of molasses-type materials was also found in some instances (*90*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch008

Sea Routes and Transfer of Knowledge

The word *Meluha* is a Sumerian name for the Indus Valley civilization. Reference to this name has been found sporadically throughout the Mesopotamian tablets. This could be an indication of trade routes between these two civilizations (*91*). Excavations in the Indus Valley reveal the use of bitumen, cotton textiles, and chicken, which were not native to the region and were brought from Mesopotamia though trade. Timber, sandalwood, ivory, lapis lazuli, carnelian, glazed stone, beads from Persian Gulf, and bone inlays were among the goods sent to Mesopotamia in exchange for silver, tin, woolen textiles, oils, and copper ingots. The land of Ophir mentioned in Hebrew texts (Kings 10:11, Chronicles 9:10) reached by the Phoenician vessels of King Solomon could have been in the Indian subcontinent. The goods imported by the vessels included spices such as pepper and cardamom, gold, ivory, precious stones, sandalwood, and peacocks (*92*).

According to many historians it is difficult to distinguish, based on excavations and residue analysis, between spices of Indian origin and those from Arabia or eastern and southeastern Africa. Herodotus mentions that cinnamons came from Dionysus's birthplace, referring to India or eastern continents in general. Systematic archaeo-botanical analysis reveals that cinnamons originated from Indonesia and slowly moved to the southern region of India. The scented baths during Roman and Greek antiquity contained turmeric, which could have come from trade with the southern region of India. Evidence of trade between Rome and India was established on the golden coins of Rome, carrying Julius Caesar's symbol, found in the southern peninsula (*93*, *94*). The evidence that Romans used *piper longum* or long pepper for spicing their wine reveals the existence of trade with northern regions of India. Aquilaria agallocha, commonly known as aloe-wood, is indigenous to the Himalayan region and was a commodity of trade with the Romans (*95*).

Just like the well-known Silk Road during antiquity, an incense route existed for the trade of raw materials such as flowers, aromatic wood, and resins from the Eastern Hemisphere into Egypt and Rome. Several desert cities, benefiting from the incense trade, arose during the 1st century CE near current day Arabia. The Nabateans, who were nomadic people settled around the Arabian peninsula, controlled the sea routes to the port of Gaza on the Mediterranean, where Roman ships set out to procure incenses from India. Eventually, the Nabateans became a part of the Roman Empire and thrived on agriculture. Ruins from the cities of Avdat and Shivta reveal temples with perfumery (*96*).

Epilogue

The manufacture of scented oils and perfumes from the Semitic period until later antiquity was reviewed. In the Semitic world the religious aspects of fragrances and scented oils were much more prominent than in later antiquity. The archaeological evidence that is currently available leaves us with a lot of unanswered questions on the evolution of perfume-making technology and the spread of knowledge. However, combining the information that is currently available from the excavations with the knowledge from systematic analysis, we are able to paint a picture of how perfume might have been produced during antiquity. The most recent knowledge of perfume preparation and uses was found in the writings of Dioscorides, Theophrastus, and Pliny.

Southeast Asia and China remain elusive to archeologists as well as to historians. Though these regions remained as major suppliers of spices, fragrant woods, and dried flowers to the Fertile Crescent, the use of scented oils and perfumes in the Indus Valley civilization is yet to be understood.

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Chapter 9

An Ancient Cleanser: Soap Production and Use in Antiquity

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The production of soap is one of the later forms of chemical technology in the ancient world. Yet, it is also one of the least studied. Unlike inorganic materials such as glass or ceramics, soap does not leave any archeological treasures that can be studied to chart its history. Instead, our understanding of the chemical technology of soap must rely primarily on the written record. The earliest evidence of soap production dates to the 3rd millennium BCE from Mesopotamian clay tablets. As soap can be produced through the simple combination of plant ash and animal fat, it is quite possible that it was formed prior to that time period, although no empirical evidence for its earlier existence has been found. An overview of the historical production and usage of soap will be presented, as it pertains to its origins in antiquity through the Roman era.

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Introduction

The modern definition of soap is a salt of a fatty acid, either saturated or unsaturated, which contains at least eight carbon atoms in the hydrocarbon chain. Such soaps can consist of a single fatty acid salt or a mixture of such salts (*1*). The application of soap in cleaning is necessary because it eliminates contaminants that cannot be completely removed by water alone. Soap is mainly used for cleansing, by solubilizing the insoluble contaminants of dirt, grease, and oil in water, thus allowing them to be washed away. This works because soap is a surfactant – a substance that lowers the surface tension between the water-oil interface. The insoluble contaminant is removed by associating with soap-based micelles in solution, spheres formed by soap molecules with hydrophilic (water-attracting) heads and lipophilic (fat-attracting) tails, which encase it and make it soluble in water. These contaminants are then removed with the water once they are solubilized.

Soap is also a detergent, which is defined as a surfactant, or a mixture containing one or more surfactants, having cleaning properties in dilute solutions (*1*). However, detergents in general are a much broader class of cleansing agents than soap. Most modern detergents are usually alkylbenzene-sulfonates, which are a family of compounds similar to soap but have the advantage of being more soluble in hard water than soap (*2*). Because of their reduced sensitivity to water hardness relative to soap, synthetic detergents have overtaken soaps as the cleansing substance of choice in the modern era because they do not interact adversely with the metal ions in hard water. However, such modern detergents are a relatively recent innovation and thus traditional soap has dominated the history of such detergents.

Chemistry of Soap

The principal method for soap production is the combination of a triglyceride and an alkali salt, in a reaction known as saponification, as shown in Figure 1 (*3*, *4*). Soap can also be manufactured from the neutralization of a fatty acid such as stearic acid with an alkali metal salt such as sodium hydroxide. However, because the isolation of the fatty acid would first require the hydrolysis of the triglyceride to the fatty acid, with subsequent removal of the glycerin (*5*), it would not have been a viable method of production throughout antiquity.

Triglycerides are found in fats, such as tallow and lard, as well as various oils. Common oils include palm, palm kernel, coconut, and olive oils, where palm oil is extracted from the pulp of the palm fruit and palm kernel oil is extracted from the inner kernel of the palm fruit. Triglycerides that are semi-solid or solid at room temperature are classified as fats, and are primarily found in animals. Triglycerides that are liquid at room temperature are classified as oils, and are primarily found in plants, but can also be found in fish. Depending on the source, triglycerides can vary in both chain length and degree of unsaturation (i.e. the number of alkene bonds in the carbon chain). Fats are predominantly composed of saturated fatty acids, whereas oils are largely composed of unsaturated fatty acids (*6*, *7*). Table 1 lists the fatty acid content of some fats and oils found in nature.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch009

Natural fats and oils primarily consist of triacylglycerols (triglycerides), along with minor quantities of monoacyl-glycerols, diacylglycerols, free fatty acids, coloring matters such as chlorophyll and carotenes, and vitmains such as A, D, E, and K (*6*). Simple triglycerides are those that have three identical acyl chains, while mixed triglycerides, which are more common in nature, are composed of different acyl chains.

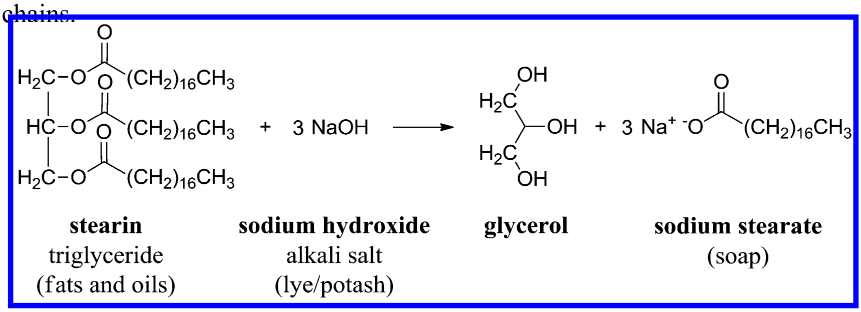

Figure 1. Synthesis of sodium stearate from triglyceride and alkali salt.

The nature of the fatty acid with which the alkali is combined can affect the consistency of the soap formed. For example, sodium salts of lower molecular weight fatty acids have no soap-like properties, dissociating into ions and dissolving in water as true molecular solutions (*8*). With soaps made from caproic acid (C_6 carbon chain), there is a faint trace of soap-like properties with a slight foaming occurring in cold solutions. As the chain length increases, the soap becomes harder in consistency and more insoluble, with lauric acid (C_{12}) producing a soap that is very soluble, lathering freely in cold water, while stearic acid (C_{18}) produces a slightly soluble soap in cold water (*8*).

Fats and oils were historically obtained from a variety of different sources, where locally available materials were primarily used so there was minimal trade over long distances. The main carcass fats produced industrially today are tallow (beef and mutton) and lard (pork), which are used for human food, animal feed, and as source material in the oleochemical industry, the majority of which is used in the production of soap and other surface-active compounds (*6*). The first fats were probably obtained through rendering, since this is a relatively easy operation that only involves simmering of the fatty animal tissue. Animal fats are relatively easy to render because the cell walls and membranes in animal tissue rupture upon cooking when the intercellular fat expands (*10*). In comparison, the extraction of oil from plant matter was also relatively simple. Sesame, linseed and castor oil were extracted through pressing in Egypt in the 3rd century BCE. In the 1st century BCE, screw and wedge presses, filters, and edge runner mills were used in Rome to facilitate the extraction of various oils (*11*). The modern refinment of edible oils through neutralization, bleaching, and deodorization processes, however, did not occur until the 19th century CE (*10*). The origin of the fats and oils used in soap production, whether obtained from animal or plant sources, would affect the quality of soap produced. As seen in Table 1, different plant and animal sources contain varying amounts of several fatty acids. Thus the origin of the fats and oils influences the final composition and solubility of the soap produced.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch009

Table 1. Fatty Acid Distribution Found in Samples of Tallow Fat and Coconut, Palm, and Palm Kernel Oil[a]

Fat or oil source	*Fatty acid[b]*	*% Distribution[c]*
Beef tallow	Myristic (14:0)	3
	Palmitic (16:0)	27
	Stearic (18:0)	7
	Palmitoleic (16:1)	11
	Oleic (18:1)	48
	Linoleic (18:2)	2
	Other fatty acids	2
Coconut oil	Caprylic (8:0)	8
	Capric (10:0)	7
	Lauric (12:0)	48
	Myristic (14:0)	16
	Palmitic (16:0)	9
	Stearic (18:0)	2
	Oleic (18:1)	7
	Linoleic (18:2)	2
	Other fatty acids	1
Olive oil	Palmitic (16:0)	10
	Stearic (18:0)	2
	Oleic (18:1)	78
	Linoleic (18:2)	7
	Other fatty acids	3
Palm oil	Palmitic (16:0)	44
	Stearic (18:0)	4
	Oleic (18:1)	40
	Linoleic (18:2)	10
	Other fatty acids	2
Palm kernel oil[d]	Caprylic (8:0)	4
	Capric (10:0)	4
	Lauric (12:0)	45
	Myristic (14:0)	18
	Palmitic (16:0)	9
	Stearic (18:0)	3
	Oleic (18:1)	15
	Linoleic (18:2)	2
	Other fatty acids	trace

[a] Data collected from references (*6*, *9*). [b] The ratio (X:Y) signifies length of carbon chain (X) and degrees of unsaturation (Y). [c] Variation exists for these natural products depending on growing conditions (plants) and environmental and dietary conditions (animals). [d] Oil extracted from the kernel (seed) of palm fruit.

The source of the alkali salt used in soap production can also have an effect on the nature of the soap formed, where salts such as lye (NaOH), potash (K_2CO_3), and soda (Na_2CO_3) are all used in soap manufacturing. By convention, soaps that are hard in consistency are called hard soaps and soaps that are soft in consistency are called soft soaps. The type of alkali salt, and thus the identity of the cation,

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch009

can contribute to the physical properties of the soap, such that soaps formed from sodium (Na^+) salts tend to be hard and soaps formed from potassium (K^+) salts tend to be soft (*3*, *4*). For example, sodium palmitate [$NaCO_2(CH_2)_{14}CH_3$] is a hard soap and potassium palmitate [$KCO_2(CH_2)_{14}CH_3$] is a soft soap (*12*). This is because the sodium cation is a harder acid than the potassium cation and is thus less polarizable. In addition, the radii of sodium and oxygen are similar in size. As a result of these combined effects, sodium salts produce a more favorable lattic energy leading to a harder soap. Insoluble soaps, which are not soluble in water, can also be formed from non-alkali metal ions such as calcium (Ca^{2+}) or lead (Pb^{2+}).

Alkaline substances such as soda and potash were historically obtained from the burning of halophytic (high salinity) and alkaline plants, and also from the burning of wood, which primarily produces potash. These plants tend to tolerate high alkaline environments, absorbing alkaline salts in their tissues during growth. Geographically, costal marine areas, alkaline and saline lakes, and semi-deserts are all excellent environments for the growth of mineral-rich plants that can then be burned for plant ash (*13*). The mineral ash produced, whether potash or soda ash, depends on multiple factors, including the soil and ground water in which the plants are grown, the plant species, the stage in the growing season and the component of the plants (wood part or leaves), and the way in which the plants are ashed (*13*). Inland plants tend to produce potash, while high alkaline plants tend to produce soda.

There are many such plants that have been used historically for their high alkaline content, many belonging to the *Chenopodiaceae* family (*13*). The *Chenopodiaceae* family is found worldwide, and contains some 1300 species in 120 genera (*13*). When these mineral-rich plants are burned in low-oxygen conditions, so as to allow only partial oxidation, they generate ash which is rich in sodium carbonate, with some potassium carbonate and other mineral salts as impurities (*14*). The soda and potash could then be obtained by leaching the plant-ashes in water, whereby the more soluble carbonate species would dissolve in the water to form solution of potash or soda. The insoluble mineral salts could then be disposed of, and the solution could be concentrated to give potash and soda (*15*). This method of leaching, however, is a later process and would not have been used in most cases for the time periods discussed here.

Salsola kali and *Salicornia* (Figure 2) are two examples of plants that have been historically burned for their alkali (*13*). The genus *Salsola*, recently re-circumscribed, historically refers to a group of plants containing high soda content found traditionally in the central Asian and Middle Eastern deserts and sub-deserts, the Mediterranean, and Africa (*16*). The *Salicornia* genus grows in the periodically wet saline coastal and inland habitats such as salt marshes, salt lake shores, mud flats and salt pans of Europe, Asia, North America and South Africa (*17*), and was also used in the past for its plant ash.

Natron was another source of alkali in antiquity. It is important to note that natron historically referred to a mineral not found in plant ash. Rather, natron, or sodium sesquicarbonate ($Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$), was mined from evaporite lakes such as the Wadi Natrun in Egypt (*14*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch009

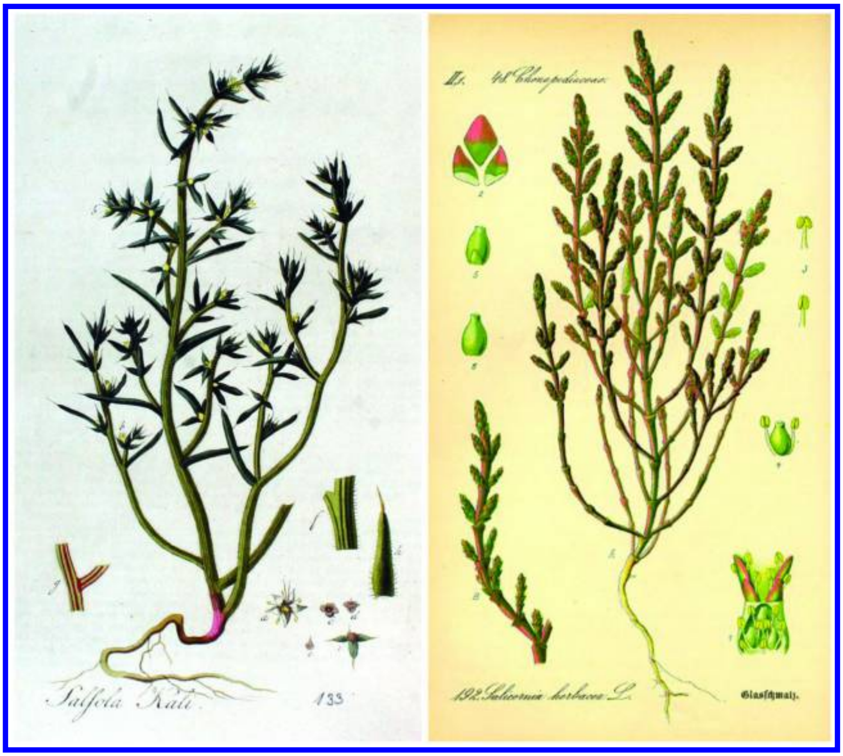

Figure 2. Salsola kali and Salicornia herbacea L. [Botanical Prints from Flora Batava by J. Kops – 1807 and Flora von Deutschland by O. W. Thomé – 1885].

As the soap produced today is a mixture of alkaline salts and fatty acids, a question arises of what cleansing alternatives might have been employed before the discovery of soap. The simplest cleaning materials were most likely abrasives such as sand or ash. However, the bile of animals and the sap of some plants also contain natural juices which are of soapy quality and can be employed in place of manufactured soap (*18*).

The best examples of such species found in nature are the soap plants, which contain *saponins* – glycosides that dissolve in water and create a froth with cleansing qualities (Figure 3) (*19*). The term saponin originates from the plant genus *Saponaria*, which are native to Europe and Asia, and are generally known as soapworts. The common soapwort, *Saponaria officinalis*, is one such plant that can produce a soap-like substance by soaking the leaves or roots in water (Figure 4). The fuller's soap mentioned in the Bible (*20*) was another possible saponaceous plant with cleansing properties, where the plant was possibly the soap-weed *struthium* (*21*), or it could have been an alkali made from plant ashes. Even though the saponins are of widespread occurrence, there is no evidence that aqueous extracts of plants were made in antiquity for cleansing purposes. This is despite the fact that aqueous extraction was well-developed from perfume manufacturing in the 2nd millennium BCE in Babylonia (*22*).

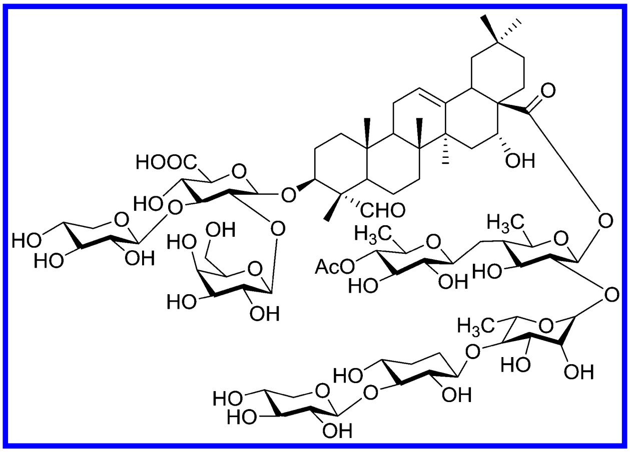

Figure 3. Saponin saponarioside B found in S. officinalis plant.

Figure 4. Saponaria officinalis L. [Botanical Print from Flora Batava by J. Kops – 1849].

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch009

Origins of Soap

Investigation of the etymology of the word *soap* could potentially provide some indication of its historical development. The word soap originates from the Proto-Indo-European root **seib*, meaning to pour out, drip, or trickle (*23*). The romance language words for soap are from the late Latin *sapo*, mentioned in the writings of Pliny (*24*), which is a Germanic loan-word. Keeping in mind that in many languages the pronunciation of certain letters is interchangeable, translations of the word soap are quite similar and are cognates of one another (Table 2) (*22*, *25*). *Ezov*, the classical Hebrew name for a plant used for ritualistic cleansing in the Bible, translates to *hyssop* in English (*26*). A connection could be made between the plant used for cleansing purposes and *soap*, which has the identical consonants as *hyssop*. In more ancient civilizations, the concept of soap was not always recognized with its own distinct word. For example, the Sumerians had no specific word for soap, however the same Sumerian cuneiform symbol is used for the *calamus* plant (a type of soap plant), for potash, and for the idea of washing (*27*).

Table 2. Cognates of Soap Utilized in Different Languages[a]

Language	*Translation*
Latin	*sapo*
Greek	*sapon*
German/Middle High German	*seife*
Old High German	*seiffa*
Middle Low German	*sepe*
Finnish	*saippua*
Hungarian	*szappan*
Dutch	*zeep*
Arabic/Persian/Turkish	*sabun*
Hebrew	*sabon*
French	*savon*
Spanish	*jabón*
Italian	*sapone*
English	*soap*

[a] Data collected from references (*21*, *22*, *24*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch009

A word corresponding with the hieroglyphic *anzir* has been found in Demotic papyri, which may translate to soap. Also, the similar Coptic word *anchir* is generally translated as soap (*22*, *28*). Demotic corresponds to the period of Egyptian language 8th century BCE – 5th century CE, which was preceded by the Late Egyptian period (14th – 8th century BCE) (*29*). The Coptic language developed from the Demotic and Greek systems, and was utilized from the 3rd – 12th century CE, and is still in use today in the Coptic Church (*30*). However, the validity of the translations for Demotic and Coptic is disputed (*31*). The word detergent is much more recent in origin, from the Latin *detergere*, meaning to wipe away or cleanse, and its usage dates to the 17th century CE (*32*). Although there is some etymological evidence that can be interpreted as reference to soap in the Egyptian hieroglyphs, Sumerian cuneiform symbols, and from its Proto-Indo-European origins, the etymology of the word soap does not support any civilization as the cradle of its invention. Rather, it can only be concluded that these civilizations may have been familiar with the substance.

The central issue with determining the origins of soap is that, unlike with other forms of chemical technologies such as glass or ceramics, there are no significant examples of soap that survive intact to modern-day. In addition, the detection of soap as a part of archaeological studies is complicated by the fact that organic residues can undergo saponification through exposure to basic media over the millennia between their genesis and any modern analysis. As such, almost all reliable knowledge of the development of soap must come from written historical records.

Soap in Mesopotamia

Mesopotamia is a geographical region in the Near East, referring to the land lying between the Euphrates and Tigris rivers (*33*). The name is based on a term local to the area, given in the time of Alexander the Great (326 – 323 BCE), which corresponds to modern-day Iraq, and to a lesser extent Kuwait, Iran, Turkey, and Syria (Figure 5). The ancient city-states of Mesopotamia, and the civilizations that spawned them, are among the earliest known non-nomadic agrarian societies. Mesopotamia included Sumer, as well as the Akkadian, Babylonian and Assyrian empires (4th – 1st millennia BCE). Of the ancient civilizations, it is the Mesopotamians that have had a large volume of their records survive to the modern day, because they wrote on the durable writing material of clay tablets, their primary form of record keeping (*34*). These texts provide a rich record of their daily life, including their accounts and usage of soap.

Many peoples of the ancient Near East dedicated a great deal of attention to the concept of cleanliness. In an almanac from the Mesopotamian settlement of Assur, a man is cautioned not to enter a laundry, and thus cleanse his garments or himself, on the sixth and seventh days of the month of Teshrit, this being in a month of penance (*35*). Simple detergents that were commonly used in ancient Mesopotamia to cleanse were alkalis, clays, earths, and resins, although the alkalis, such as those leached from the ashes of plants, were most common (*22*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch009

A Sumerian tablet found in the Hittite capital of Boghazkoi discusses the use of soda for cleansing the body (*22*, *36*):

> With water I bathed myself. With soda I cleansed myself. With soda from a shiny basin I purified myself. With pure oil from the basin I beautified myself. With the dress of heavenly kingship I clothed myself.

A variety of plants were used for their alkaline substances in Mesopotamia. In an Akkadian text belonging to a private citizen during the reign of Ashurbanipal (7th century BCE), the author discusses using tamarisk, date palm, pine cone and the *mastakal* plant (which is unidentified) for their detersive properties (*22*):

> May the tamarisk, whereof the tops grow high, cleanse me; may the date palm, which faces every wind, free me; may the mastakal plant, which fills the earth, clean me; may the pine cone, which is full of seed corns, free me [...] I carry a container with an aqueous solution of mastakal plant to the gods of the heavens. As I would bring forth to you for purification, so will you cleanse me.

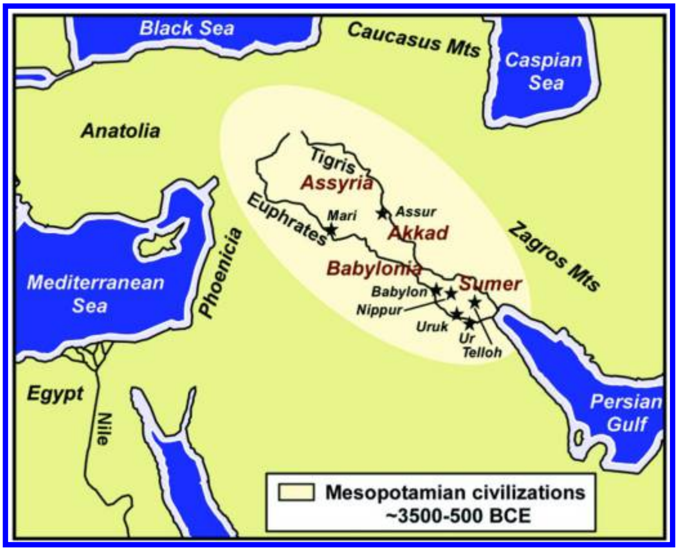

Figure 5. Map of Mesopotamia.

This description of cleansing agents is quite interesting in that it contains ingredients that form the two components of soap. The tamarisk, a genus of a group of saline and alkaline soil-tolerant flowering shrubs native to Eurasia and Africa (*37*), could be a potential source of alkali, along with the *mastakal* plant. Tamarisk is also mentioned in the Epic of Gilgamesh (Mesopotamian Epic poem, compiled ~1300 – 1000 BCE), when the goddess Ninsun, Gilgamesh's mother, bathes ceremoniously in a bath of tamarisk and soapwort (*38*). The date palm, which contains a number of fatty acids in both the seed and the flesh of the fruit (*39*), could provide the second component needed to produce soap.

It has been stated that the oldest literary reference to soap dates to clay tablets from ~2500 BCE concerning the washing of wool (*27*), but details concerning the identity and contents of these tablets have not been reported. In contrast, a text from the 3rd Dynasty of Ur (2200 BCE), discovered at Tello, gives a detailed economic account of cloth manufacture. Included in this account is the preparation of a substance made up of 1 *qa* (approximately 1 liter) of oil and 5 *qa* 1/2 (ca. 5½ liters) of potash is used to degrease and clean the cloth (*40*). This combination of potash and oil would make an impure liquid soap. The potash described would not have been pure, but rather the ash of a plant rich in potassium carbonate, which explains the large excess of alkali required in the recipe (*27*). A second account from the same text gives a slightly different recipe, containing 1 *qa* oil and 5 *qa* 1/6 potash (*40*). Another recipe that alludes to soapmaking can be found in the text of the cylinder B of Gudea (~2120 BCE) (*27*, *40–42*):

> So that he makes pure with water, so that he cleanses with potash, (?) and so he intermixes the pure oil with potash.

In a text from a later period, during the reign of Nabonidus of Babylon (556 – 539 BCE), a recipe for soap is given which specifies the oil source (*14*):

> 12 *qa* uḫulu [in ash form], 6 *qa* of cypress [oil], 6 *qa* of sesame [probably weighed out in seed form before pressing] for washing the stones for the servant girls.

In this recipe, *uḫulu* designates the potash or soda plant source (*40*). Unlike previous recipes, which indicate that the purpose of the soap is to clean cloth, soap at this time is being used for cleaning the stones by the servants.

Soap was found to be of value as a medicament very early, and soap is mainly mentioned in connection with medical writings in Mesopotamian records. Mesopotamians utilized the concepts of diagnosis and prognosis of illness, creating herbal remedies to treat the afflictions (*43*). Medicine was usually composed of a pharmacological ointment that contained oil, plant matter, and various other substances, which was applied to the affected area of the body. In an Assyrian medical prescription from the 7th century BCE, castor oil and horned alkali (*Salicornia* plant) are used, together with other drugs, as a mouth cleanser, in enemas, and to wash the head (*35*, *44*). Sulfur ointments, variants of which are used in modern times for the treatment of skin disorders such as acne, scabies, and dandruff, were also known in Mesopotamia. One sulfur ointment for the eyes involves using saltpeter, iron sulfate, *Salicornia* alkali, fir turpentine, niter, *Lepidium*, sulfur, ox-fat, and other substances (*35*, *44*). Another recipe from Mesopotamia directs (*35*):

> Take turpentine, sulfur, horned alkali and put in water, then oil and spittle are poured thereon forming an ointment.

The oldest known medical writing containing soap is a Sumerian pharmacological tablet (2200 BCE) from Nippur. A series of fifteen prescriptions

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch009

are given, but the ailments to be treated are not specified. In two of these, one is directed to wash the ailing organ with a specially prepared solution, followed by rubbing with oil. The final step involves covering the area with a substance that has been interpreted by some to be burnt plant ashes (*43*). In effect, producing a recipe for medicated soap. The first of these prescriptions gives instructions for the formation of the remedy (*42*, *43*):

> Sift and knead together – all in one – turtle shell, the sprouting (?) *naga*-plant (a plant used to obtain soda and other alkalies), salt, (and) mustard; wash (the sick spot) with quality beer (and) hot water; scrub (the sick spot) with all of it (the kneaded mixture); after scrubbing, rub with vegetable oil (and) cover (?) with pulverized fir.

The second prescription uses different ingredients, but also gives instructions that involve the components of soap (*42*, *43*):

> Pour water over a dried and pulverized water snake, the *amamashumkaspal*-plant, the roots of the "thorn"-plant , pulverized *naga*, powdered fir turpentine, (and) the feces of the *garib* (?)-bat; heat (the infusion), (and) wash (the sick spot) with this liquid; after washing with the liquid, rub with vegetable oil and cover with *shaki*.

Although little direction is given as to what part of the body this remedy was supposed to cure, this set of prescriptions was preceded by the passage directing arrangement of rushes over the hands and feet of the sick man, so it is possible it was to be applied in the same area (*43*). As the first recipe includes salt, this could suggest that "salting out" was practiced in antiquity, although there is no direct evidence of such. The process of salting out involves the precipitation of soap from the solution of glycerin, excess water, and impurities, thus making a hard soap (*22*). This is typically accomplished by adding salt (e.g. NaCl) to the soap solution, rendering the soap insoluble because of the large amount of electrolyte in solution (*3*). Otherwise, without filtration, the soap produced would most likely be soft and liquid in consistency because of the impurities. Also, from the recipes above, and other medical writings, it is quite possible that the Sumerians were familiar with resin soaps (compounds of soda or potash combined with coniferous resins i.e. pulverized fir/tree sap) (*22*).

As with all of these medical formulations, the efficacy was questionable, and they may have done more harm than good. Nevertheless, hundreds, if not thousands, of tablets containing medical prescriptions survive from Mesopotamia, some of which contain the components of soap manufacture (*44*). Whether these ingredients were purposely added together or rather just combined as a coincidence is still debatable.

There is no evidence that the alkaline substances used by the Mesopotamians for the production of soap were causticized (*22*). The preparation of a soap of pure salts of fatty acids would imply a caustification of the alkali by quicklime (CaO) (*45*). This means that lye (NaOH) or caustic potash (KOH) would be produced by treating the soda/potash with quicklime as follows:

$$CaO\ (s) + H_2O\ (l) \rightarrow Ca(OH)_2\ (aq) \quad (\mathbf{1})$$

$$Ca(OH)_2\ (aq) + Na_2CO_3\ (aq) \rightarrow 2\ NaOH\ (aq) + CaCO_3\ (s) \quad (\mathbf{2})$$

Caustic soda (i.e. lye) and caustic potash are used nowadays for the production of soap (*3*, *8*). The advantage of this caustification is that insoluble $CaCO_3$ is formed and the alkali metal (Na^+ or K^+) hydroxide remains free in solution. Rather, the Mesopotamian soap produced from alkali carbonates would have resembled that manufactured in some parts of the world today, known as cold or semiboiled soap (*22*). In either such case, the hydrolysis of the triglyceride would be ineffective, resulting in a mixture of soap and partially hydrolyzed products that would produce a liquid mixture.

Nor is there any evidence of how (or if) the alkali was extracted from the plants, although the Babylonians were familiar with alkali plants for the extraction of essential oils (*35*). It has been hypothesized that some more recent operations to extract the alkali may resemble those used by the Mesopotamians, which include the slow combustion or incineration of the dried plants, then a washing or leaching of the ash followed by drying until a salt cake forms on the sides of the vessel. The crude product would then be calcined to remove the water and destroy any organic substances remaining. However, this detailed process for the manufacture of soda or potash was most likely beyond the common laborer and was reserved for the use of royalty and the priesthood (*22*). For the more common household chores the ash was probably stirred in the water and the solution was then filtered before use to remove insoluble impurities. This method of containing the ash in a cloth bag which was then immersed in the wash water was utilized until the 19th century CE, when soap became cheap enough to displace the alkali plant ash (*22*).

Soap in Egypt

Egyptians, especially those of the priest caste, also placed great emphasis on personal cleanliness, with frequent washing of the hands and fingers both before and after eating (*28*). However, despite the frequent ritual ablutions and washings of the ancient Egyptian priests there is little evidence that soap was known to them, unless a mixture of natron and clay or steatite (soapstone) was used, both of which the Egyptians were well-acquainted with (*31*, *46*). There existed some unknown means of removing grease from clothing, which has been suggested to be either natron or fuller's earth (*47*). The Eber's papyrus (1550 BCE) contains a number of recipes in which alkaline substances are boiled together with oils and fats (*48*). While it is probable that soaps and plasters were obtained from these processes, they were never specifically mentioned (*28*). In a similar manner, the Berlin medical papyrus (Brugsch Papyrus) (1350 – 1200 BCE) contains a prescription which includes natron and tallow, which could indicate a soap being made *in situ* (*49*). While previous evidence of soap had been thought to be found on some Egyptian mummies, further analysis has led to the modern belief that this was instead formed by natron reacting with the fat from the body over time (*28*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch009

Recently, lead soaps, including lead palmitate, have been found in Egyptian cosmetic containers from the 18th dynasty (1549 – 1292 BCE) through the use of modern analytical techniques (*50*). However, it is difficult to determine whether the lead soaps found in archeological cosmetics were prepared willingly by the Egyptians, or if instead they were the result of slow degradation of the original material and the long-term interaction of oil with lead salts (*51*). Overall, there is no definitive evidence that soap was recognized as such by the Egyptians.

Soap and Cleaning in Greece and Rome

While the Greeks and Romans had high standards of cleanliness, soap did not play a role in personal hygiene. The Greeks would pour water over themselves and perform ritualized communal bathing in public baths. The Romans took personal cleanliness to a high art, bathing in the *thermæ* (public baths) located all across the Roman Empire in pools of waist-high water of different temperatures (Figure 6) (*22*). The strigil, a body scraper employed to remove perspiration, dirt, and oil that was applied before bathing, was especially used by Greek and Roman male athletes (Figure 6) (*52*).

In Homer's *The Odyssey* (~800 BCE) only water is used to wash the nuptial garments of Nausica, daughter of the King of the Phaeacians (*53*). In contrast, the comic playwright Aristophanes (445 – 386 BCE) mentions adulterated soda-lye being used with the Cimolian earth for washing (*54*). This "adulterated soda-lye", depending on translation, could possibly have been causticized alkali (*54*). More specific references to soap were made by the physician Dioskourides (40 – 90 CE) who wrote that the best soap was made from natron and Cimolian earth (*54*). Pliny the Elder (23 – 79 CE), the Roman natural philosopher, writes in his *Naturalis Historia* (*24*):

> Prodest et sapo, Galliarum hoc inventum rutilandis capillis. Fit ex sebo et cinere, optimus fagino et caprino, duobus modis, spissus ac liquidus, uterque apud Germanos maiore in usu viris quam feminis.
> Soap, too, is very useful for this purpose, an invention of the Gauls for giving a reddish tint to the hair. This substance is prepared from tallow and ashes, the best ashes for the purpose being those of the beech and yoke-elm: there are two kinds of it, the hard soap and the liquid, both of them much used by the people of Germany, the men, in particular, more than the women.

In this passage, Pliny implies that this soap was not to be used as a cleansing agent, but rather as a means of beautification. The Gauls that Pliny refers to are one of the northern Celtic tribes that were conquered and fell under Roman rule in the 2nd and 1st centuries BCE (Figure 7), and would include modern-day France, Luxembourg, and Belgium, along with parts of Switzerland, Italy, Germany, and the Netherlands (*55*). This soap, which was probably tinged with plants used to dye hair, was imported to Rome for use by fashionable Roman ladies and their gallants in order to dye their hair a coveted red-gold color. It was, in many respects,

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch009

a hair pomade (*18*, *54*). It is possible that the soap may have been causticized, because although Pliny does not speak of quicklime in his description, he mentions a mixture of goats' tallow and quicklime a little before, so it is probable that the use of the latter was known in Rome at that time (*18*). Marcus Valerius Martialis (Martial) (~38 – 104 CE), a Roman poet, also discusses the Roman use of soap from the Germans. He refers to it both as *pilæ Mattiacæ*, a preventative for grey hair and *caustica spuma*, with which the Romans could color their hair (*18*, *56*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch009

Figure 6. Top: Roman Baths in Bath, England [Photochromic color print 1890-1900, Library of Congress Prints and Photographs Online Catalog]. Bottom: Bronze Strigil, Roman Period (30 BCE – 395 CE) or later. [Courtesy of Los Angeles County Museum of Art]

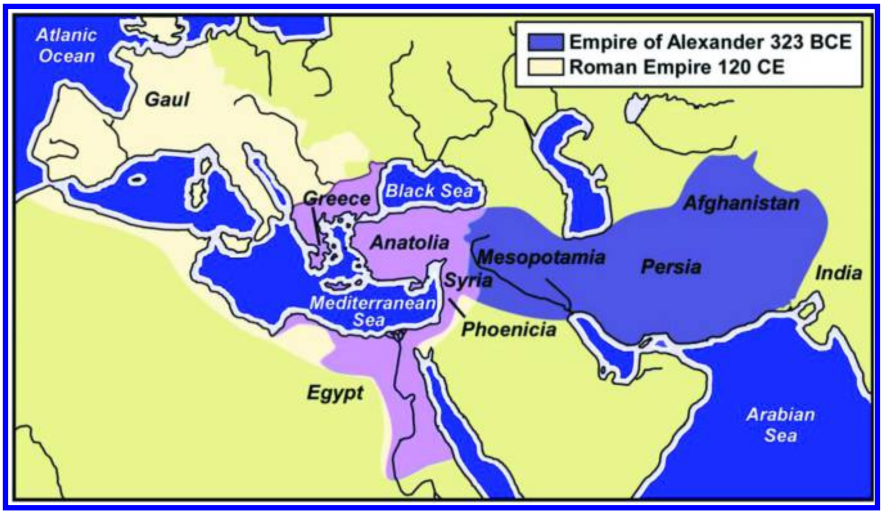

Figure 7. Map of the Roman Empire.

Galen (129 – 199/216 CE), a prominent Greek physician and philosopher in the Roman empire, both mentions the use of causticized lye in making soap and states that soap is a better detergent than soda (*57*, *58*). An account of soap-making attributed to Galen by some historians goes further (*22*, *54*, *59*):

> Soap is made from cooking beef, goat, or wether fat, mixed in with lye and quicklime. The best soap is judged to be Germanic, because it is the purest and the creamiest; after this ranks the soap of the Gauls. All types of soap can severely loosen and remove all filth from the body and from clothing […] and is put into caustics.

However, it has been reported that Galen did not write this and the source is rather a pseudo-Gallenic medieval handbook that has unfortunately propagated through the literature (*18*, *59*, *60*). It has been proposed that the German soap may have been soft soap made from the ashes of land plants (containing potash), while the soap of Gaul was a hard soap made from the ashes of sea-shore plants (containing soda) (*54*). Additional references to soap by Greek writers include the alchemist Zosimos of Panopolis (250 CE), who mentions both soap (σαπώνιον) and soap-making (σαπωναρικής τέχνης) in his writings (*54*, *61*), and Aretaeus of Cappadocia, a prominent Greek physician of the 2nd century CE, who included the medical use of soap in his writings (*54*).

Alternatives to true soap were also utilized for cleansing purposes. Putrid urine was collected on Roman street corners and from public urinals as a source of ammonia for use in various chemical processes, especially the washing of cloth (*18*). The Roman *fuller*, or cloth-launderer (Latin *fullo*), would wash the cloth by trodding upon it in a tub of putrid urine to clean it. The effectiveness of using putrid urine results from the high content of ammonium carbonate ($(NH_4)_2CO_3$) present, which reacts with fats and oils to produce a light saponification (*22*). This business of collecting putrid urine for washing was taxed by the government of

Emperor Vespasian (69 – 79 CE), and this tax, *urinae vectigal commentus est*, continued for a period of two centuries (*18*). On account of the disagreeable smell, *fullones* (plural) in Rome were obliged to reside in less-populated areas such as the suburbs (*18*).

The *Papyrus Graecus Holmiensis*, or Stockholm Papyrus as it is also known, is a codex from 300 CE containing recipes for the manufacture of dyes and colors, and includes soap in one of its preparations (*42*, *62*, *63*):

> To prepare Phoenician dye. Take and combine heliotrope [plant] with alkanet [plant]. Lay them in an earthen vessel and sprinkle then for three days with white vinegar. On the fourth day boil them, with the addition of water, until these float at the top. If you desire, however, to dye cedar color then take out the alkanet and boil lightly, but if you wish cherry-red then add krimnos (?) soured with a little soap. Put the wool in and boil it together with the substances until it appears to you to be good.

It should be noted that the Phoenician dye described here was not the same as the more famous mollusk-derived Tyrian purple. There are also numerous mentions in the Papyrus of using soap weed, which was most likely soapwort (*Saponaria officinalis*), in the cleansing of textiles (*62*, *63*):

> Take and treat soap weed with hot water. Make a ball from it as if from tallow. Then steep this in water until it is dissolved. The water, however, should go above the wool. Then boil up the water. Put the wool in and prevent it from becoming scorched. Leave it in there a little while until you see that it is clean. Lift out, rinse it and dry it.

This treatment of cleaning would have produced a light saponification and washed the wool. The Cimolian earth, mentioned by Aristophanes and Dioskourides for washing (*54*), would be another way of cleaning the wool. As the cloth was stamped with the feet during the washing process, the earth would both scour the cloth and absorb the greasy dirt (*18*). These earths were also used for whitening many types of cloth. This was done by rubbing fine white earth into the cloth to give it a brighter appearance, a similar process to that employed when cleaning leather (*18*). These clays went by a variety of names, including fuller's earth, and from the region they were produced, such as *terra Cimolia*, *Umbria*, and *Tympaea* (*18*). To render cloth completely white, fullers would fumigate the material with sulfur, many colors being destroyed by its vapors (*18*).

There is some analytical evidence to support the Roman manufacture of soap beyond the written record. Pompeiian mural paintings (2nd century BCE – 1st century CE) were studied in the mid-19th century through destructive analytical methods (*64*). These mural paintings have two or more dry preparatory layers (*tectorio*) on which the base pigment was spread, diluted in a mixture of water-lime and wax. A soap solution was intentionally added to the mixture by the muralist to avoid color alteration over time. All the samples studied contained beeswax and soap in both the painted backgrounds and in the upper paint layers. This soap mixture was generally a mixture of fat matter and potash.

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More recently, non-destructive methods have been utilized to analyze a Roman wall painting from the 1st century CE (*65*), in which the pigments were dissolved in a lime/soap/water solution, the function of the soap being to mitigate the negative effects of lime on alkali-sensitive mineral-based colors. The presence of calcium and strontium in the colored layers, in conjunction with the use of pigments that are incompatible with lime, suggests that a neutralizing additive must have been employed. The presence of potassium in all samples examined supports the hypothesis that a water/soap solution was employed that comprised a potassium-containing ash combined with fat (*65*). Similar preparations were also found in Roman wall paintings from the 1st century BCE (*66*). The characteristics of these paintings correspond to the Pompeiian wall paintings (*64*). It has also been shown that Roman artists used a water-soluble paint mixture of beeswax and soap in the encaustic painting technique on wall and wood (*67*). Encaustic painting, a technique utilizing beeswax and colored pigments, was practically the only technique used in connection with the execution of works of art in antiquity. This technique was gradually abandoned during the middle ages, later substituted by fresco in wall painting, and egg tempera and eventually oil paint. The use in Roman times of wax and soap encaustic in wall and easel paintings that are geographically distant (from Spain to Egypt from the 1st century BCE to the 2nd century CE) suggests that using soap in the encaustic process had a widespread use in classical antiquity (*67*).

Conclusion

The earliest written records of soap-making date to 2200 BCE in Mesopotamia (*40*, *43*). However, because saponification can occur by the simple combination of fat and plant-ash, it is highly likely that soap was made, whether intentionally or not, before this time. The slightly complicated process of rendering the fats and oils and combining it with alkali could not have been developed spontaneously. There must have been a series of steps or procedures that slowly evolved, where each step resulted in a process useful enough to be adopted in its own right. One proposed sequence of development is that people used sand or ashes to remove the grease from skin. If they rinsed the ashes off with water, the water and their skin would become slippery, which was because of the dissolved alkali salts. This water would clean better because the dissolved alkali reacts with the grease, converting it into soap. The more grease that was dissolved in the solution, the better it cleans because more soap is formed. At some point the ashes were discarded and the solution from leached ashes or concentrated alkali salts were used (*15*).

In the Mesopotamian period, soap was primarily made from oil and plant ash. The Mesopotamians used it mainly for medical purposes, but also for cleansing. The Egyptians did not identify soap as such, but it is possible that they were familiar with it, through the combination of alkali and animal fat (*48*, *49*). There is evidence of soap residue being found in ancient Egyptian artifacts, but it cannot be definitively concluded that this was not the result of slow degradation of the original material (*50*, *51*). The Greco-Roman world was familiar with soap and soapmaking, using it for medical, textile, and beautification purposes, but not for

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personal hygiene. There is also archeological evidence that soap was used in various Roman painting techniques (*64–67*). It is also quite probable that soap production was occurring in other parts of the world and other civilizations during this time, but no evidence has yet been found to confirm it (*25*, *54*).

Soap production in antiquity was most likely a small craft industry, especially in the Mesopotamian and Egyptian periods, where locally available materials were used in its formation. However, the large expanse of the Roman empire allowed for the movement of materials and processes, one of which was soap that was imported from the Gauls (*24*). It is possible that there was some sort of soap-works preserved in Pompeii (*11*, *54*). The term *saponarius* (soap-maker/soap-boiler) is mentioned in 4th century CE writings, so there was obviously some sort of recognized profession or industry at this time (*54*). Soap was known for its medicinal purposes by Arabian physicians Rhases and Serapion the Younger in the 10th and 12th centuries CE (*54*). A small soap industry started in Marseilles in the 9th century, and Venice and England in the 14th century (*11*, *54*). These industries expanded, but it really wasn't until the Industrial Revolution in the 18th and 19th centuries that large-scale production of soap was undertaken.

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Chapter 10

Modern Materials in Antiquity: An Early History of the Art and Technology of Glass

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Glass and its uses predate recorded history. Even before the ability to manufacture glass, early tribes discovered and shaped natural glass such as obsidian. The technology of synthetic glass production, however, is thought to date back to no later than 3000 BCE. This glass technology was not discovered fully fashioned, but grew slowly through continued development of both chemical composition and techniques for its production, manipulation, and material applications. This development had become fairly advanced by the Roman period, and the 1st to 4th century CE is often described as the First Golden Age of Glass. During this time, glass was widely used and certain kinds of glass were actually considered a household necessity by the 4th century, although many glass objects still remained luxury items. A general overview of the early history and chemistry of glass and its use will be presented.

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Introduction

Glass is unlike any other material in antiquity and its production required some of the most advanced methods of any of the chemical technologies of this time period. In terms of material properties, its closest modern analogues are the organic plastics utilized extensively today (*1*). In its molten state, glass could be poured into almost any shape and retains that shape upon cooling, thus making it a broadly versatile material for a vast range of applications. While characterized as a liquid at high temperature, glass is described as either a *supercooled liquid* or *amorphous solid* at room temperature (*1–4*). That is, glass is a solid. However, due to its highly disordered nature, glass has properties much like a liquid that is too viscous to flow at room temperature. A commonly cited myth is that glass is really a highly viscous liquid and thus observable flow can be detected in objects of sufficient age. This belief stems from the often stated observation that 800-year-old, stained-glass windows of 12th century cathedrals are thicker at the bottom (*5–8*). Theoretical calculations, however, have verified that the compositions used in either medieval and contemporary windows cannot flow at room temperature within the time scales of humanity (*4*, *6*) and physical measurements have showed that unless sufficient compressive stress is applied, glass does not flow below 400 °C (*6*, *8*). In truth, the uneven nature of medieval windows is a result of the limited techniques used in their manufacture. Because of this variable thickness, the thicker edges would all be mounted in the same direction, with the thicker edge logically mounted at the bottom (*6*, *7*).

The composition of most traditional glass is comprised primarily of silica (*9*), with an empirical formula of SiO_2. The most common form of natural silica is quartz, a crystalline solid as exhibited by a regular repeating lattice as shown in Figure 1 (*10*, *11*). In contrast, glass has no regular repetition in its macromolecular structure and exhibits a disordered structure similar to substances in the liquid state (*2*). Regardless of structural order, all silicate solids are extended three-dimensional networks of SiO_4 tetrahedra (Figure 2A) in which oxygens of adjoining tetrahedra share corners, resulting in a highly crosslinked polymeric framework of alternating silicon and oxygen (Figure 2B). Simplified two-dimensional models of crystalline and disordered SiO_4 networks are given in Figure 2.

Due to the extent of disorder in amorphous structures, the glass state of a material is higher in energy than its crystalline state. This common view that the glass structure represents a metastable state of increased energy is supported by the fact that glasses can suffer from devitrification (i.e. frosting and loss of transparency as a result of crystallization). That is, devitrification is the result of the glass modifying its structure to obtain the more thermodynamically stable crystalline state (*1*). Glasses that tend not to devitrify typically exhibit little energetic difference between the glass and crystalline states. As such, stable glasses are those that can form a disordered, three-dimensional network which is of comparable energy to the corresponding crystalline state (*3*).

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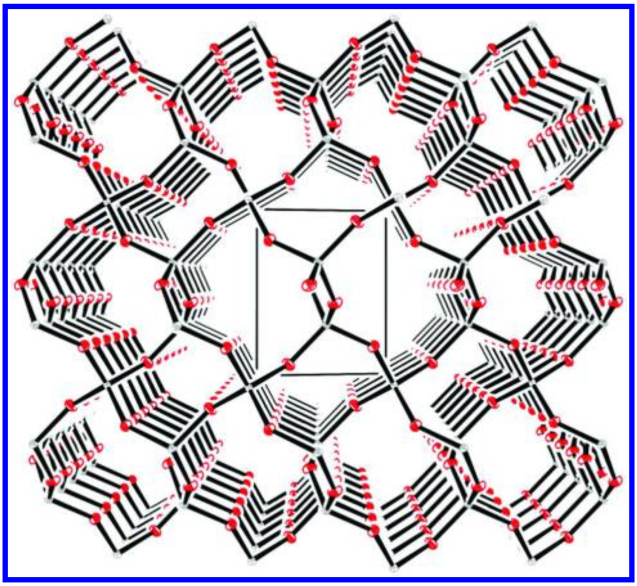

Figure 1. X-ray structure of quartz viewed down the a-axis. [thermal ellipsoid plot generated from data reported in ref (8)]

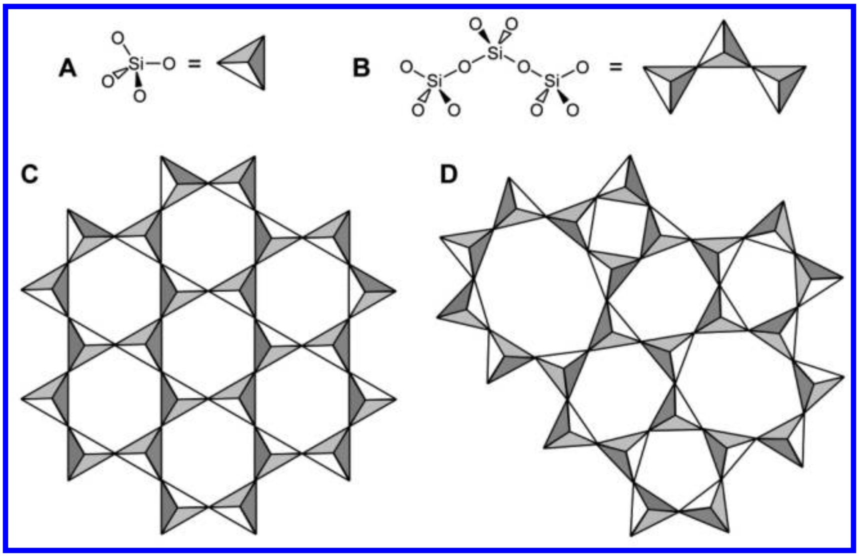

Figure 2. Simplified two-dimensional silicate structures: SiO_4 tetrahedron (A); polymeric structure (B); crystalline structure (C); amorphous structure (D).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

While the fusion of silica sources such as beach sand can result in a glass state, the temperature needed to melt silica (~1710 °C) is too high to have been achieved using the heating methods available in antiquity (*11–16*). This limit was overcome sometime around 2000 BCE, when ancient craftsmen discovered that the fusion of silica could be accomplished at significantly lower temperatures by the use of a *flux* (from the Latin *fluxus* - “flow”) (*12*, *15*, *16*). The origin of the flux has its roots in metallurgy, where it consisted of a species added to the furnace to render non-ore impurities (i.e. rock and other alumina-silicates) liquid at the smelting temperature (*17–19*). In its application to glassmaking, the most common flux was soda (sodium carbonate, Na_2CO_3) (*12*, *15*), and its use could reduce the melting point of silica to below 1000 °C (*4*, *11*, *14*, *16*, *20*).

While the temperature needed to produce molten glass can be significantly reduced via the application of soda, the sodium contained in the resulting glass is highly soluble and thus susceptible to attack by water. As a result, the use of soda as a flux produces a glass of low chemical stability (*1*). To counter this, viable glass materials require a third component which acts as a stabilizer for the resulting glass (*12*, *15*). Stabilizing species generally contain less soluble cations, with the most common species containing calcium or magnesium. While these ions could be obtained from sources such as lime, shells, or other mineral additives (*12*, *21*, *22*), their importance was not initially recognized and lime was not intentionally added as a major constituent before the end of the 17th century (*20–22*). Prior to that time, the calcium and magnesium content of glasses was introduced as the result of impurities in either the silica or soda sources (*22*, *23*). By combining quantities of both soda and calcium salts, the fusion temperature of silica can be reduced to as low as ~725 °C (*11*). The triple eutectic mixture resulting in the lowest melting temperature provides a glass of the composition 73.5% SiO_2, 21.3% Na_2O, and 5.2% CaO (*11*). The products produced through this combination are typically referred to as soda-lime glass, and most early glasses in the western world consisted of various soda-lime-silica compositions that depended upon the specific raw materials used (*2*, *4*, *14*, *16*, *21*, *23*, *24*).

In its fully developed form, most glass in antiquity was produced from beach sand and a crude source of soda, with both components contributing enough lime or magnesia to provide some chemical stability (*1*, *23*). Upon heating a mixture of these two species, the soda would quickly begin to fuse and then start reacting with the sand to generate various sodium silicates and the formation of liquid material. Lime and other basic species would then start to join the melt as it also began to react with the fusing mixture of silica and silicates. Any remaining excess silica would then be the last to fuse as the melt temperature increased and the viscosity was reduced (*25*). Throughout these processes, gases would be liberated due to the conversion of the various carbonate, nitrate, and sulfate components to their respective oxides (*14*). This release of gaseous byproducts would result in violent agitation of the fusing mixture and the generation of significant bubbles in the final melt (*25*).

In order to reduce the impact of these escaping gases, this process was often accomplished in two distinct stages. The silica-soda mixture would first be heated in shallow pans at a temperature which would allow the reaction of the soda and lime with the silica, but not hot enough to achieve homogenous fusion of the

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

complete mixture. As a result, the majority of the gaseous byproducts would be liberated and the mixture then cooled to give an intermediate product referred to as preliminary sintered mixture or *frit* (*15*, *26*). The intermediate frit would then be crushed to enhance more intimate mixing before being heated a second time at temperatures high enough to achieve complete fusion (*15*). In this manner, a final glass could be produced that was relatively free of bubbles (*26*).

While early glass is referred to as soda-lime glass, its composition was usually more complex than suggested by this simple description. Besides the primary components of silica, flux, and stabilizer, these glasses also contained coloring or decolorizing agents, as well as a variety of unintended impurities introduced along with the primary constituents. As a consequence, the resulting chemical composition and glass structure could be both quite complex and extremely variable, resulting in materials with a range of physical and chemical properties. To further complicate things, the character of glass depends not only on its chemical composition, but also the manner and degree of heating, as well as the rate of cooling the hot glass (i.e. annealing of the glass) (*13*, *26*, *27*).

Of course, the technology of synthetic glass production was not discovered as a fully established practice, but grew slowly through constant development of both chemical composition and techniques for its production, manipulation, and material applications (*28*). It is generally believed that the origin of this technology dates back to no later than 3000 BCE (*14*, *23*, *29–31*), yet by the Roman period its development had become fairly advanced (*14*, *29*, *30*). As a result, the 1st to 4th century CE is often described as the *First Golden Age of Glass* (*1*, *9*, *32*). It is this initial period of glass technology that is the focus of the current chapter, with the aim to present an overview of the known history of glass from its origins through its first peak in progress during the Roman period. In the process, the manufacture, development, and applications of glass throughout antiquity will be detailed.

Natural Glass

Glass use predates recorded history and initial applications did not depend on the synthetic production of glass materials. Long before the development of glass manufacture, early tribes discovered and shaped glass formed by nature (*1*). Such natural materials include volcanic glasses such as obsidian, as well as impact glasses (impactites or tektites) (*32–37*). As with the previously discussed glass, these natural forms are silica-based species, but differ from synthetic glasses in that they contain higher silica content (up to 83%), notably higher alumina (8-16%), and low amounts of alkali and alkaline earth elements (*37*).

Obsidian (Figure 3) is the most common of these glasses (*33*) and is the result of the rapid cooling of volcanic lava, often at the margins of a flow (*32*, *34*). As such, deposits of obsidian can be found in most locations that have experienced the melting of silica-rich rock due to volcanic eruptions (*32*, *33*). However, archaeological finds have also revealed evidence of obsidian very far from volcanic centers, which suggests that a vast and extensive trade in obsidian must have existed (*33–36*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Figure 3. Snowflake obsidian. [photo by S. C. Rasmussen].

Obsidian deposits were highly valued by prehistoric tribes (*32*) and the widespread use of this material dates back to the Neolithic period (ca. 10,000-4000 BCE) (*34–36*). The earliest evidence of obsidian use has been traced to the Upper Palaeolithic (late Stone Age, 50,000-10,000 BCE) in Greece and by 6000 BCE, evidence of obsidian is found at sites from Crete to Macedonia. Obsidian then remained an important material until it was ultimately supplanted by the increasing availability of metals around 2000 BCE (*34*). One factor that made obsidian a desirable raw material was its highly attractive cosmetic properties (*35*). Normally shiny in appearance and usually dark in color (black or gray), obsidian can also be red, green, or brown. As such, the glassy material was used to form decorative items such as small vessels, statuettes and mirrors (*34*, *36*).

Obsidian's greatest value, however, stemmed from the fact that the conchoidal fracture of obsidian allows for its easy transformation into objects with very sharp edges (*32–35*). This property, coupled with its relatively high strength, made obsidian well suited for the production of cutting and engraving tools (*35*). Known tool artifacts include various blades, scrapers, awls, bradawls, and saws (Figure 4) (*35*, *36*). Weapons, too, were produced in great abundance. This included arrow and spear heads, knives, and even swords (*32*, *33*, *35*). Obsidian-based swords, however, did not consist of a single large blade, but utilized a length of wood studded with sharp obsidian teeth (*35*). The manufacture of obsidian tools long predated the development of metal tools and thus played a significant role in the development of early civilizations (*33*).

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Figure 4. Obsidian blades from Syria, 3rd-2nd millennium BCE. [73.1.12, Collection of The Corning Museum of Glass, Corning, New York, gift of Mr. and Mrs. John Dessel].

Origins of Glass − Myth and Legend

The specific details of the origin of synthetic glass production are unknown and its discovery has been attributed by various authors to the Syrians, the Egyptians, and even the Chinese (*38–40*). In the process, assorted legends have been presented that claim to account the discovery of glassmaking (*39–42*). The most famous of these was recorded by the 1st century Roman historian Pliny the Elder (23-79 CE) (*39*), although it has been proposed that the story may have originated with the earlier Greek scholar Alexander Polyhistor (ca. 100 BCE) (*38*). As given in his *Naturalis Historia* (Natural History), Pliny states (*39*):

> In Syria there is a region known as Phœnice, adjoining to Judæa, and enclosing, between the lower ridges of Mount Carmelus, a marshy district known by the name of Cendebia. In this district, it is supposed, rises the river Belus, which, after a course of five miles, empties itself into the sea near the colony of Ptolemaïs. The tide of this river is sluggish, and the water unwholesome to drink, but held sacred for the observance of certain religious ceremonials. Full of slimy deposits, and very deep, it is only at the reflux of the tide that the river discloses its sands; which, agitated by the waves, separate themselves from their impurities, and so become cleansed. It is generally thought that it is the acridity of the sea-water that has this purgative effect upon the sand, and that without this action no use could be made of it. The shore upon which this sand is gathered is

> not more than half a mile in extent; and yet, for many ages, this was the only spot that afforded the material for making glass.
>
> The story is, that a ship, laden with nitre, being moored upon this spot, the merchants, while preparing their repast upon the sea-shore, finding no stones at hand for supporting their cauldrons, employed for the purpose some lumps of nitre which they had taken from the vessel. Upon its being subjected to the action of the fire, in combination with the sand of the sea-shore, they beheld transparent streams flowing forth of a liquid hitherto unknown: this, it is said, was the origin of glass.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Pliny's account places the site of this discovery in the north of modern Israel, just south of Lebanon (Figure 5). The Belus river referenced by Pliny is recognized with what is now known as the Na'aman river, which flows into the Bay of Haifa. The mouth of the Belus resided just south of Akko, now the modern city of Acre in Israel (*42–44*). Analysis of the sand at the mouth of the Belus has revealed that it indeed is a high silica sand (ca. 81%) with significant amounts of calcium (*22*). The calcium content has been reported to be in the form of calcium carbonate, mainly as fragments of beach shell and limestone, and made up about 15% of the sand (*44*). These analyses also have shown that these sands contain little other undesirable impurities such as iron oxides (*22*). In addition to Pliny, the sand at the mouth of the Belus has been referred to by a number of classical authors of the 1st century CE (*22*, *44*). As such, the Belus sand is thought to have served as major silica source for glassmakers working along this coast (*22*, *44*) and the exportation of this sand to other glassmaking centers has also been proposed (*22*).

It should be pointed out that the use of the term '*nitre*' by Pliny does not refer to sodium nitrate, but soda. The word nitre has only acquired its modern meaning of representing sodium nitrate within recent centuries. Originally it meant carbonated alkali and referred to the soda obtained from either evaporitic lakes or plant ash (*21*).

In order to evaluate the validity of successful glass production as described in Pliny's account, William L. Monro of the American Window Glass Co. attempted to recreate the conditions described via a series of experiments in the 1920s (*40*). In his first experiment, he built an open wood fire over a bed of glass sand mixed with an equal quantity of sodium carbonate. He kept the fire burning for two hours, during which he monitored the temperature generated using a standard pyrometer couple set into the bed of the fire. In this manner, he determined that the temperature reached a high of 2210 °F (~1210 °C). Once the fire had burned itself out, the ashes were removed and a portion of the bed mixture was reported to have been fused into a vitreous mass (*40*).

Monro then repeated the process, this time using nitre (*45*) in place of the sodium carbonate, to give similar results (*40*). Finally, the process was carried out a third time, in this case using a bed of glass sand unmixed with any potential flux species. In this last case, no evidence of fusion was found.

While Monro felt that his results confirmed the plausibility of the Pliny's story (*40*), a number of important points have been raised by other authors (*27*, *42*). One such point is that Monro maximized the potential of success by using a large quantity of soda mixed throughout the sand, rather than the relatively limited interface of soda and sand as described by Pliny (*27*). As a result, Munro's conditions were not an accurate recreation of Pliny's story and were thus much more favorable for the production of fused products.

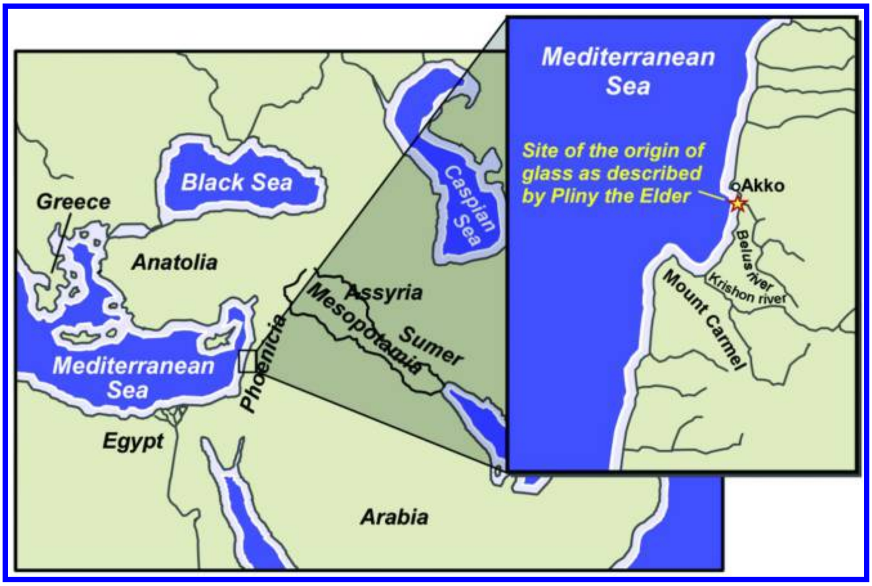

Figure 5. Discovery site of glass as described by Pliny the Elder. [adapted from reference (42) with kind permission from Springer Science and Business Media].

Another point made is that it can be assumed that the merchants in Pliny's account prepared a fire hot enough to cook, but not necessarily the extreme temperature achieved by Monro (*40*). It is generally accepted that an ordinary campfire reaches temperatures of 600-650 °C (*46*), with a possible maximum of 700 °C (*2*, *17*, *47*). In light of this information, the temperature claimed by Monro is nearly double that of accepted values and it is unclear exactly how this remarkable temperature was achieved (*42*). As previously discussed above, the fusion temperature of silica-soda mixtures is typically below 1000 °C (*4*, *11*, *14*, *16*, *20*). As such, the temperature of 1210 °C claimed by Monro should have resulted in fusion of a greater portion of the bed, if not complete fusion.

In the end, this all points to the general view that Pliny's account is not very likely. In his recreation of the events, Monro set up all of the conditions for the greatest chance of success. Yet, even under these optimal conditions, Monro still did not observe the free-flowing liquid glass described by Pliny (*42*).

Origins of Glass − Current Historical Knowledge

While accounts such as that given by Pliny make entertaining stories, they are rarely accepted as historically accurate. Although the true origin of glass is unknown, scholars believe glass resulted as either a byproduct of metallurgy or via an evolutionary sequence in the development of ceramic materials (*2*, *4*, *12*,

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

14, *29*, *38*, *42*, *48–50*). Either possibility is considered plausible as both early technologies had procedures that could be considered precursors of glass (*12*).

Metallurgical Byproducts

In order to consider the possibility that glass arose from metallurgical operations, we must look to the early smelting of copper, which was being regularly produced in the Sinai Peninsula by 3700 BCE. By about 3000 BCE, Cyprus became a major site for the production of copper and the modern word copper is derived from the name of this city (*2*). Copper smelting was accomplished by heating ores such as malachite ($Cu_2CO_3(OH)_2$) in the presence of a carbon source at temperatures of ~1200 °C (*46*). Incomplete combustion of the carbon would result in a strong reducing atmosphere of carbon monoxide, which would reduce the copper content of the ore to metallic copper. As temperatures employed were greater than the melting point of copper (1084 °C), the metallic copper was produced as a molten liquid, which could then be isolated and cooled to generate pure copper cakes (*46*, *47*).

A complication in the practice of smelting is that in the process of collecting the ore, various amounts of other material (rock, sand, and other minerals) were unavoidably collected as well. As previously discussed, sand is primarily silica, while common rock is comprised of various silicates and aluminosilicates, all of which do not easily melt at the temperatures applied for the smelting of copper in antiquity. As a consequence, the presence of these materials during smelting would result in a heterogeneous mixture of rock and raw metal.

To overcome this problem, a flux would be added to the smelting mixture to assist with the melting of these residual silicate and aluminosilicate species (*19*). The earliest applied fluxes have been said to be sea salt and potash (*19*). Other early common fluxes for copper smelting are thought to be easily fusible pyrites, and evidence confirming such iron ores as flux in copper smelting has been reported (*46*). Of course, a diverse range of species were utilized as fluxes, from various metal ores to a number of simple salts. Known examples of such simple fluxes include common salt, soda (Na_2CO_3), potash (K_2CO_3), saltpeter (KNO_3), and vitriols (metal sulfates) (*18*, *19*, *51*).

The use of such a flux during smelting would then result in a combination of molten metal and a liquefied mixture of fused rock and flux, commonly known as the *slag* (*19*). Due to their immiscibility, the liquefied slag would separate from the molten metal to form two separate molten layers (*14*). The less dense slag would reside on top of the molten metal, which could then be skimmed off as the liquids collected in the forehearth of the furnace (Figure 6).

When the isolated slag was allowed to cool, it would produce a rigid, glassy solid similar to obsidian, which would have intrigued early metalworkers with inquiring minds (*14*). It is easy to imagine that experimentation by such metalworkers with such siliceous slag species (variation in types and source of rock, variation in flux, etc.) could have eventually led to glass manufacture. (*2*, *14*, *48*). Such slaggy lumps from the Mesopotamian sites of Eshunna (ca. 2300 BCE) and Eridu (2100 BCE) have been pointed to as early examples of glass (*14*).

As the slag produced from the addition of melting fluxes during smelting consisted primarily of a mixture of silicates and aluminates, the application of these fluxes to the fusion of related silica sources such as sand was a logical progression and suggests a strong connection between metallurgy and the genesis of glassmaking (*1*). Support for such a connection between copper smelting and glassmaking has included the fact that many early glazes and glasses were colored blue due to the presence of copper (*2*, *48*, *50*). The analysis of 2nd millennium BCE light blue opaque Malkata glasses has revealed the presence of tin oxide, which suggests the potential use of bronze dross, scale, or corrosion products as the source of copper ions to color the glass. The analysis of blue New Kingdom glasses has also revealed copper and tin ratios compatible with the compositions of New Kingdom bronzes (*48*, *50*).

The most significant evidence for a relationship between ancient glass-making and metallurgy is thought to come from archaeological finds. One such example is the Ramesside Egyptian site of Qantir (late 2nd millennium BCE), which contains evidence for both the preparation of red opaque glass ingots and bronze casting. Such evidence thus provides a clear example of the production of colored glass occurring at the same site where metallurgical byproducts were being generated (*48*, *50*). Another cited example is the discovery of fragments of both glass and furnace slag at Tamassos in Cyprus, providing additional support for a connection between metallurgical slag and glass (*52*).

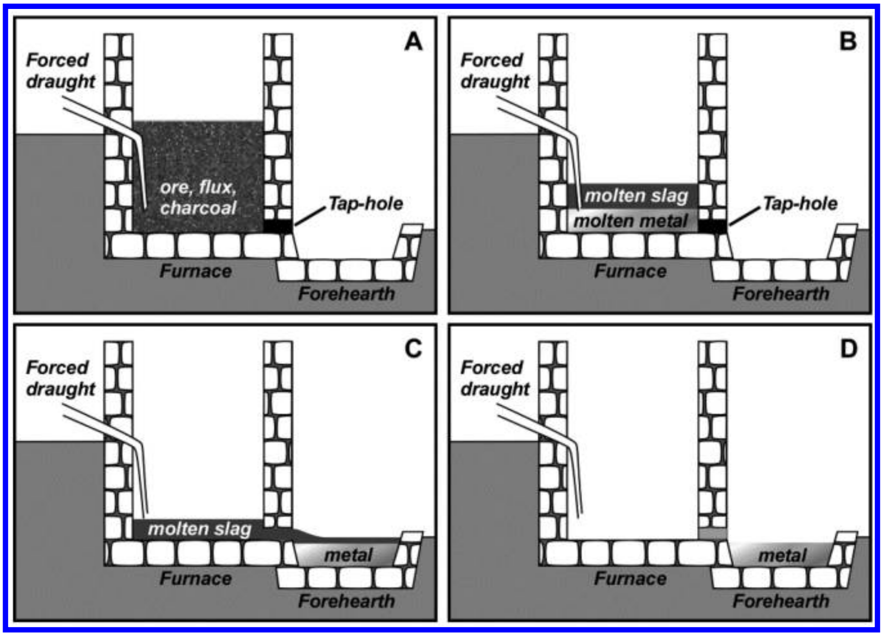

Figure 6. Basic smelting process: A) Ore, flux, and charcoal are mixed in the smelting furnace and fired; B) Heating produces immiscible layers of molten metal and slag; C) Tap-hole is removed. Metal/slag collected in the forehearth; D) Liquid slag skimmed off and metal allowed to cool.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

As a point of caution; it has been noted that slags from copper smelting contain only a small amount of copper and are much richer in iron than observed for either early glazes or glasses (*2*). Of course, it must be remembered that only very small amounts of copper would be needed to provide the blue color. In addition, the high amount of iron in such slag is not surprising considering a common early flux for copper was iron pyrites. The move to another flux via experimentation, however, could easily have resulted in early blue glass with low iron content (*42*).

Faience

The second potential origin of glass is considered to be due to an evolutionary development of a family of highly siliceous ceramics coated with alkali glazes (*2*, *14*, *53*). These ceramics originating in either Sumeria or Egypt and the material considered to be the immediate predecessor of glass in this developmental sequence is often called *faience* (Figure 7) (*2*, *14*, *53*). This ceramic dates to the 4th millennium BCE and was produced through a variety of techniques to create a glaze layer over a silica core (*12*, *14*, *28*, *49*, *50*, *53*). This results in a surface of transparent glass, usually blue or green, encapsulating a white or grey body of crystalline quartz grains loosely bound together by a glassy phase (*46*, *53*, *54*). Because these materials closely resemble glass and preceded it in the areas where true glass later appeared, they are considered by many to be the most logical candidates of a direct precursor of glass manufacture (*14*, *29*). As the term faience is more commonly used to refer to the tin-glazed earthenware pottery produced in Italy during the fourteenth century CE, the material considered to be the precursor to glass is usually called *ancient faience* or *Egyptian faience* to distinguish it from the later pottery (*53*). However, as the constitution of these two groups of materials is quite distinct, some authors have preferred the term *glazed quartz* over faience in the present context (*14*, *54*). Such materials may have been invented when accidentally heating an alkali or lime on a quartz pebble (*4*), and its application was mostly for the manufacture of small objects such as beads that are found in profusion at archaeological sites in Egypt and elsewhere (*2*, *12*, *49*, *50*, *53*).

As the faience body is comprised of quartz, the bodies themselves could provide the silica needed to form the external glassy glaze. As such, it is believed that the glazing was possible through the application of a paste or slurry consisting of alkalis (typically soda) and copper species to the body surface, followed by firing to a temperature to induce the glaze formation (*49*, *50*, *54*). An alternative proposed method is called cementation glazing, in which the quartz bodies are buried in a glazing mixture of alkalis and copper species. Upon firing, the glazing mixture in contact with the body surface reacts with the silica to form the glaze (*49*, *50*). Lastly, a third possible method is referred to as efflorescence glazing. Here, alkalis and copper species are mixed with the ground quartz and then moistened to form a paste to be shaped by modeling or molding. As the shaped body dries, a proportion of the glazing components are carried to the surface by capillary action. Upon firing this precipitated layer is then converted to the glaze (*49*, *50*, *53*).

In Chemical Technology in Antiquity; Rasmussen;
ACS Symposium Series; American Chemical Society: Washington, DC, 2015.

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Figure 7. Green-Blue Faience Scarab, Egypt, 12th - 25th Dynasty (1991 - 525 BCE). [M.69.91.232; Courtesy of the Los Angeles County Museum of Art].

In all cases, it is believed that in shaping the body of finely ground silica, a gum, fat, or other organic matter may have been added as a binder, the majority of which would then be removed by the thermal treatment during the glaze formation. The use of clay as a binding material has been suggested, but many regard this as improbable. If used at all, clay would have been added in quantities only just sufficient to hold the sand together (*54*). Chemical analysis of faience bodies have shown that they are comprised primarily of crushed quartz in the form of practically pure silica with small amounts of soda and other impurities (*2*, *14*, *53*). Such analysis has revealed that clay is not present in any appreciable quantity, with any detectable amounts believed to be the result of impurities (*53*). The X-ray diffraction analysis of several specimens has revealed that the grains of silica consist of α-quartz, indicating that the material was heated to a temperature no higher than 870 °C. The application of higher temperatures would have resulted in domains of tridymite in the body (*2*).

The formation of faience objects has been duplicated in the laboratory using the efflorescence glazing method (*2*). In these recreations, finely powdered quartz was combined with aqueous sodium carbonate to produce a firm paste, which can then be formed and fired. This heating resulted in fusion of the sodium with the quartz surface, giving rise to both a glass exterior and an interior glassy phase that binds together the domains of α-quartz. However, the crystalline domains still make up the majority of the body, with only a small amount of glassy material and a large proportion of empty space (*2*).

Based on what is known about the composition and fabrication of faience, it is clear that the initial discovery of glass could have occurred through simple variations in its production. Such variations could have been the result of investigating the effect of variable conditions on faience production. Of course, this could just as easily have occurred accidentally due to poor compositional or

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

temperature control (i.e. excess soda or heat) (*2*, *49*, *50*, *55*). For example, if the amount of soda had been increased, or if the heating had occurred at either a higher temperature or for an elongated period of time, the fusion of quartz and soda could have proceeded to a greater extent. Such modifications would have resulted in domains of α-quartz would have been fewer in number and of smaller size, so that the material would have been mostly glassy. Faience makers could then have easily carried out a little additional experimentation to produce a true glass without any crystalline domains (*2*).

This proposed origin of glass is supported by examples of a known subset of glazed quartz known as glassy faience, which exhibits an intermediate structure between traditional faience and that of true glass (*2*). Unfortunately, the chronology of glassy faience is not well documented and thus it is not certain if it actually preceded the origin of glass. In addition, it needs to be pointed out that a problem with this proposed path of discovery is the inconsistency that while the full development of faience was accomplished in Egypt (thus the common description of Egyptian faience) (*53*), glass is thought to have originated in Mesopotamia and Syria, with its later spread to Egypt (*23*, *29*, *42*, *49*, *50*, *55–57*). As the more advanced and significant production of faience occurred in Egypt, the logical transition from faience to glass would be expected to have taken place among these Egyptian artisans. A possible explanation for this inconsistency would be the possibility that Mesopotamia craftsman accomplished the jump from less advanced faience materials to glass, while faience production continued to be optimized in Egypt without the transition to glass.

Complementary Factors

In attempting to explain the delay of more than 2000 years between the production of faience and the transition to glass, it has been stressed that an important factor was the differences in the working temperatures utilized in the production of the two material types (*12*, *49*, *50*). Faience production involved only cold-working and reduced temperature sintering of the raw materials, while the routine production of glass objects involved the manipulation of hot, viscous fluids, a process that was more akin to metal working. Thus, while the production of glazed quartz and glass involved the same combination of essentially identical raw materials, the shift from cold-working for faience to hot-working for glass may not have been either a logical progression or an easy transition (*49*, *50*). Some have used this fact as an argument in support of metallurgy as the more likely path to glass (*14*).

Even if glass did derive from faience, such a transition would have at least required input from metal workers who were more familiar with such high temperature manipulations. As such, it can be argued that the discovery of the techniques necessary for hot-working glass was the result of interaction between the workers of faience and metal workers (*48–50*). Such interactions may have been facilitated by the changing organization of artisans following the political upheavals occurring in Egypt and the Near East during the 16th century BCE, which could have resulted in artisans skilled in different crafts being brought into close proximity in workshops and production centers. The transfer of technologies between crafts would have been facilitated in such an environment, paving the way for the eventual discovery of glass production (*49*, *50*).

While arguments can be made for either of the two commonly proposed pathways to the discovery of glass, it seems clear that neither path is totally independent of the other. In the first case, metallurgy is thought to originate in the pottery kilns, potentially as a consequence of using metal ores in glazes. In the second case, the production and working of glass required high temperature techniques, for which the most likely source of expertise would have been metal workers. It is therefore quite reasonable to propose a combined path in which transfer of knowledge between the two groups of craftsmen resulted in the discovery of glass with origins in both metallurgy and siliceous glazes (*42*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Early Glass Production

Regardless of the specific path to its discovery, glass as an independent material is not thought to really predate 3000 BCE (*29*, *55*, *56*, *58*). Glass beads claimed to date to as early as 2600 BCE have been reported, but at least some of these dates are questionable (*2*). Glass objects reported to date back to 2500 BCE have been found in Syria, and by 2450 BCE, glass beads were believed to be plentiful in Mesopotamia (*4*, *23*, *31*). A lump of blue glass was found at the Sumerian city of Eridu in southern Mesopotamia (*59*), in remains believed to date to earlier than 2300 BCE (*60*). Occasional small glass objects were produced in Egypt during the 3rd millennium BCE (*49*, *50*, *55*), with the oldest Egyptian glass of undisputed age believed to date from ~2200 BCE (*31*). Some early Egyptian objects originally thought to be brown or yellow glass were later proved to be amber (*61*). The first glass objects included beads, plaques, inlays and eventually small vessels (*23*, *29*, *30*, *55*). In Mesopotamia, beads, plaques, and cylinder seals of glass or glass-like compositions occur in varying frequencies from quite early periods. The occurrence of glass vessels, however, was not significant until after the middle of the second millennium BCE (*62*).

While glass was once thought to be an Egyptian discovery, this is no longer believed to be true (*29*). The earliest glass was probably developed in the Mitannian or Hurrian region of Mesopotamia (*29*, *63*) and there is little doubt that glass was made from an early period both in Babylonia and Assyria (*64*). Routine glass production is thought to have started in Mesopotamia around 1550 BCE (*56*). Glass came a bit later in Egypt, with its manufacture appearing as a major industry after 1500 BCE (*4*, *12*, *14*, *49*, *60*).

It is generally assumed that glass-working was introduced into Egypt during the reign of Tuthmosis III (1479-1425 BCE) through a combination of glass objects and ingots being imported as tribute (*49*, *50*, *55*, *56*). Tuthmosis III is also credited with importing Mesopotamian glassmakers into Egypt around 1480 BCE (*49*, *50*, *56*), ultimately resulting in the local production of glass in Egypt by the time of Amenophis III (ca. 1388 - ca. 1350 BCE) (*55*). During the initial period of Egyptian glassworking, however, it is unclear whether Egypt relied on imported raw materials (in the form of ingots and cullet) that were then worked in Egypt, or whether glass was actually being produced onsite (*49*, *50*, *55*). Nevertheless,

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

evidence supports onsite glass production in the Egyptian city of Amarna around 1350 BCE and glass objects were soon made exhibiting genuine Egyptian style, supporting their manufacture within Egypt, most likely by Egyptian artisans. This is further supported by the archaeological identification of several glass workshops in Egypt (*56*).

In addition to Amarna, the remains of such production sites have been found near the Ramesseum at Thebes, at El-Kâb, Tell Achmunein, and also in the Libyan Desert. Here, sand and alkali were first heated in fritting pans, after which the resulting frit was fused into glass in deeper pots. The produced glass was then removed and allowed to cool, during which the upper frothy scum and the lower sediment were broken off. Finally, the remaining clear block of good glass was broken up, reheated, and then moved onto a smooth surface in order to be rolled into a thick rod for latter working (*4*, *60*).

Glass manufacture soon become a major industry throughout the Mediterranean and was extremely successful for the next 300 years (*9*). The prevailing model of this industry involves the existence of only a few primary glass production sites. The trading of glass in the form of ingots or rods was then thought to occur from these primary sites to secondary glass workshops scattered around the Mediterranean, and even extending into the Aegean world (*56*). Glass objects of this early period (1500 - ca. 800 BCE) are characterized as being comprised of a typical soda-lime glass with a high magnesia (3-7%) and potash (1-4%) content (*4*, *14*, *24*, *50*, *55*, *60*, *63–65*), which is thought to be representative of glass produced or used throughout the Mediterranean area (*24*). These vitreous materials were commonly produced from a mixture of silica (sand or pebbles) and a crude source of alkali (most commonly some form of soda). Both the silica and alkali could then act as sources of lime or magnesia to give the resulting glass some chemical stability (*23*).

Silica Sources

For this early period, crushed quartzite pebbles and sand are usually cited as the two primary sources of silica (*2*, *22*, *65*). While generally considered to be the less common of the two, the use of quartzite pebbles is supported by the identification of a mineral called *immanakku* found in Assyrian cuneiform texts. This mineral was used as a raw material for glass production and has been interpreted as quartzite pebbles, probably collected from river beds (*26*, *55*). The analysis of such quartzite pebbles has revealed them to be a very pure form of silica (*50*, *65*), in some cases containing only trace impurities of barium (19 ppm), strontium (5 ppm), and cerium (6 ppm) (*65*). As such, the application of crushed quartzite pebbles in glass production should really only contribute silica to the final material.

When considering sand as the silica source, things become a bit more complicated. As well as providing the desired silica, sands are thought to have also provided considerable amounts of alumina, as well as iron oxide, lime, and magnesia (Table 1) (*14*, *22*, *50*). In addition, sands are not uniform and can provide a wide range of compositions depending on the local geology, as well as the degree to which they are subjected to weathering and other alteration (*65*).

As an example of the variability of these materials, sands from limestone areas, such as those near Amarna in Egypt, can have considerably higher lime contents (Table 1) (*14*, *22*, *65*). In contrast, sands from areas comprised of more mixed sandstone/limestone compositions can have lower lime content and increased content of iron and alumina (*65*).

Table 1. Compositions of Various Sands from Ancient Sites[a]

Component	*Egyptian sites*			*Syrian sites*	
	Amarna	*Karnak*	*Thebes*	*Haifa*	*Mouth of Belus*[d]
SiO_2	60.46	83.61	72.69	76.40	80.65
Al_2O_3	2.25	1.32[b]	8.18		4.27
Fe_2O_3	1.73		5.60		0.13
CaO	18.86	12.01	4.86	10.73	8.81
MgO	0.83	1.23	2.44	0.75	
K_2O	0.74		1.10		
Na_2O	0.30		1.21		
Water	0.42	1.57	1.04	0.40	
Organic[c]	13.90		1.60	7.80	6.23

[a] Data collected from (*22*); values represent % by weight. [b] Combined total of Al_2O_3 and Fe_2O_3. [c] Determined by loss on ignition. [d] Average of three different samples.

What is perhaps surprising is the purity of sands from large aeolian systems such as the Great Sand Sea, which provide widely available sources of high quality Egyptian sand. Because of this, it has been pointed out that although quartzite pebbles are normally suggested as the silica source of early Egyptian glass, the apparent wide availability of fairly pure sands provides the possibility that such sands were also used (*65*). The use of such sand is supported by the remarks of some authors concerning the superior quality of Alexandrian sand for glassmaking, leading to Alexandria becoming a center for glass production (*60*).

In terms of one silica source over the other, the analysis of early glasses reveal that these early glasses contain very low alumina content (~1.3% or less) (*49*, *50*). As the majority of sands analyzed contain much higher alumina content (Table 1), the alumina content in these glasses seems inconsistent with the use of sand as the source of silica. As such, it is generally believed that these early glasses utilized crushed quartzite pebbles as the silica source, an interpretation which is supported by the fact that large angular quartz particles have been found to survive in frits analyzed from Amarna (*50*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Alkali Sources

The two primary sources of alkali for early glassmaking were natron, a naturally occurring mineral source of soda, and various types of plant ash (*2*, *14*, *22*, *26*, *65–70*). The mineral natron is a naturally occurring evaporite that forms in evaporitic lakes of Egypt and Syria, such as the Wadi Natrun near Cairo and Wadi Hillal near El Kab in upper Egypt (*2*, *14*, *22*, *65–69*). Of these evaporitic sites, the most notable is the Wadi Natrun, which lies in a geographical depression approximately 38 km to the west of the Nile and 100 km north-west of Cairo, just south of the 'desert road' between Cairo and Alexandria (Figure 8) (*66–68*). Here, a group of lakes rises up annually in this large, flat basin formed as the result of flooding of the Nile (*2*). The lakes are apparently fed by underground seepage and all of the lakes contain water during the winter months. During the hot summer, however, the desert sun evaporates the lakes, resulting in the formation of crusts of natron and other minerals along the lake edges (*2*, *66*, *67*). These crusts, typically 15-18 inches thick, would be collected using poles and spades and spread out to dry on the banks. The natron would then be carried in baskets to the Nile, where it could be shipped for use elsewhere (*67*). Natron was referred to in older texts by the Egyptian word *hsmn* ("hosmen" or "hesmen") and the Hebrew word *neter* (*66*, *67*, *69*).

It should be pointed out that there can be confusion in the literature regarding the chemical composition of natron. In its modern use, the term *natron* is the mineral name for sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$) (*66*). However, in older usage, the term *natron* or *natrun* was used in a more general sense to mean the deposits of the Wadi Natrun, which can include a variety of evaporite minerals as shown in Table 2 (*66*). In this respect, natron applies to a mixture of evaporites in which the mineral natron is limited and the most common form of carbonate is the mineral *trona* (the sodium sesquicarbonate $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) (*44*, *66*, *68*, *69*). It is this later use of the word that best describes the natron applied as an alkali source for the production of glass.

Even as a mixture of evaporite minerials, natron is still a generally pure sodium source, being relatively free of potassium and magnesium impurities, and glasses made with natron usually contain less than 1% of either MgO or K_2O (*44*, *65*). The actual composition of natron, however, is complex and can vary widely depending on the exact mixture of minerals collected. In addition, various impurities were often included in this collection, particularly sodium chloride, sodium sulfate, and silica (*14*, *22*, *44*, *53*, *66–68*). The analysis of an ancient natron mixture dating to the 14^{th} century is given in Table 3. As can be seen from this data, the majority of the sample is various sodium species, but the content of the expected carbonate and bicarbonates actually falls below that of the chloride and sulfate salts. As the mineral halite (NaCl) is found to be the most dominant mineral in most of the evaporitive lakes (*67*), its strong presence is not that surprising.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

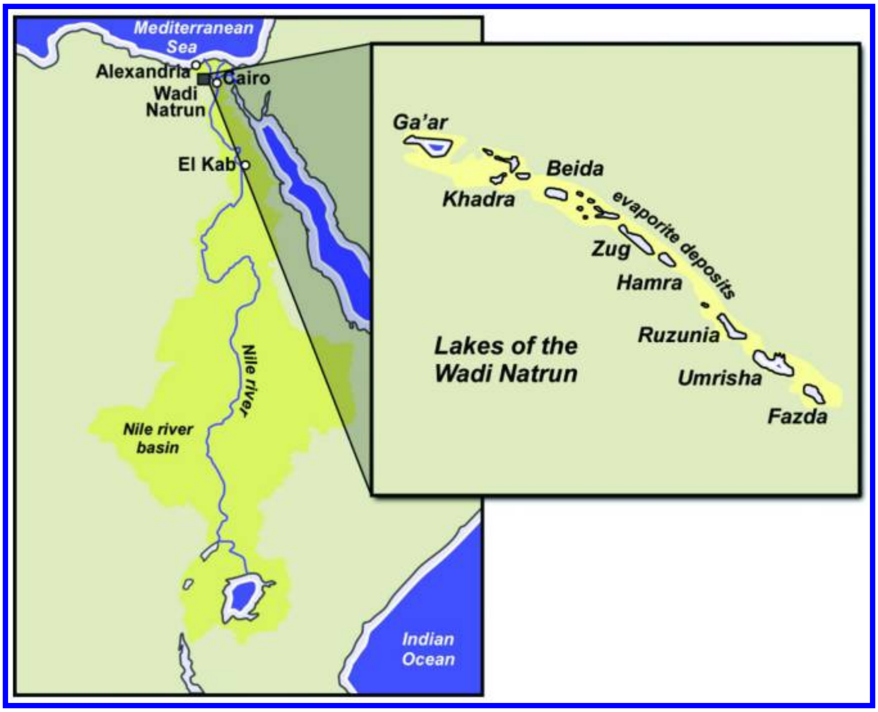

Figure 8. Evaporite lakes of the Wadi Natrun.

Table 2. Evaporite Minerals from the Wadi Natrun[a]

Modern mineral name[b]	*Chemical formula*
Natron	$Na_2CO_3 \cdot 10H_2O$
Thermonatrite	$Na_2CO_3 \cdot H_2O$
Pirsonnite	$Na_2CO_3 \cdot CaCO_3 \cdot 2H2O$
Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$
Nahcolite	$NaHCO_3$
Burkeite	$Na_2CO_3 \cdot 2Na_2SO_4$
Thenardite	Na_2SO_4
Mirabilite	$Na_2SO_4 \cdot 10H_2O$
Halite	NaCl

[a] Data from reference (*66*). [b] Nomenclature based on International Mineralogical Association recommendations.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Table 3. Analysis of an Ancient Natron Mixture (ca. 14th Century BCE)[a]

Component	*Chemical Formula*	*% by Weight*
Sodium chloride	$NaCl$	30.6
Sodium sulfate	Na_2SO_4	20.6
Sodium bicarbonate	$NaHCO_3$	12.6
Silica	SiO_2	10.0
Sodium carbonate	Na_2CO_3	4.9
Calcium carbonate	$CaCO_3$	2.0
Magnesium carbonate	$MgCO_3$	1.9
Alumina	Al_2O_3	0.7
Iron oxide	Fe_2O_3	0.3
Water	H_2O	4.7
Organic matter[b]	unknown[b]	1.7

[a] Data collected from (*53*). [b] By difference. [b] The organic material is thought to consist of impurities together with herbs and flowers, etc., introduced into the natron mixture for their fragrance.

The second common source of alkali came from the burning of halophytic and alkaline plants (*69*, *70*). These plants primarily belong to the *Chenopodiaceae* family, which tolerate highly alkaline environments and concentrate alkaline salts such as sodium carbonate in their tissues during growth. Such plants grow in saline maritime environments, inland salinas, and semi-desert conditions, often on the edges of deserts. Examples of halophytic genera include *Anabasis*, *Arthrocnemum*, *Halopeplis*, *Hammada*, *Salicornia*, and *Salsola* (*70*, *71*). When burned with a limited access of oxygen so as to allow only a partial oxidation, these plants generate ash which is rich in sodium carbonate with some potassium carbonate and other salts as impurities (*69*).

As one might imagine, the composition of plant ash could be even more convoluted and variable than that of natron. In addition to providing sodium and potassium carbonates, such alkali sources often furnished sodium and potassium salts of both chloride and sulfate, as well as calcium and magnesium salts of carbonate and phosphate (*22*). The exact chemical composition of these ashes could also be quite variable due to the fact that the mineral content of the ash depended largely on the soil in which the plants grew. As such, the same species of plants growing in different locations could result in ash of different compositions (*70*). This effect of the soil on composition is best illustrated by the fact that plants grown in salty soil or near the sea tend to produce ash high in soda, while those grown inland gave ash with higher potash content (*22*, *23*).

The detailed analysis of the ash from the Syrian desert plant *chinān* (*22*) is given in Table 4, and additional analysis of the ash from a variety of plants belonging to the genera *Anabasis*, *Arthrocnemum*, *Halopeplis*, *Haloxylon*, and *Salsola* have all revealed sodium levels that are high enough to make their ash potentially useful for the manufacture of glass (*70*, *71*) Overall, plant ash typically contains higher amounts of magnesia and potash in comparison to natron. As a result, glasses produced from these plant-based alkali sources generally exhibited higher concentrations of potassium oxide (K_2O, 1-4%) and magnesium oxide (MgO, 3-7%) (*26*, *65*).

Table 4. Analysis of Plant Ash from the Syrian Desert Plant *Chinān*[a]

Component	*Chemical Formula*	*% by Weight*
Sodium carbonate	Na_2CO_3	45.0
Calcium carbonate	$CaCO_3$	34.0
Potassium chloride	KCl	4.5
Calcium phosphate	$Ca_3(PO_4)_2$	4.0
Potassium sulfate	K_2SO_4	3.0
Sodium hydoxide	NaOH	2.5
Magnesium carbonate	$MgCO_3$	1.0
Carbon	C	1.0
Additional silicates, phosphates, etc.		5.0

[a] Data collected from (*22*).

A material called *ahussu* can be found in Mesopotamian tablets, which has been interpreted as a plant ash used by the Assyrians in glassmaking (*26*, *55*). This ash has been specified by some as coming from the *naga* plant (*2*, *70*). Nevertheless, whatever the plant source was, it is thought to be almost certainly a desert plant, most likely *Salsola kali* or related species (*55*). The proposed use of Salsola plant ash in the making of ancient glasses has been supported by the positive correlation found between magnesium, potassium, and calcium in both Salsola ash and in some ancient plant-ash glasses (*70*).

The use of this material in these texts suggests that Mesopotamian glassmaking most probably used a plant ash-based alkali (*26*, *55*). As such, it is generally believed that the glassmakers of Mesopotamia and Persia usually favored various types of plant ash as the alkali source (*55*), while natron was favored on the Eastern Mediterranean as it was readily available from northern Egypt (*23*). It has also been reported that lead species were sometimes used in Mesopotamia as an alternative to the more common sodium fluxes (*12*).

While alkali in the forms of both plant ash and natron were used in this initial period of glass production, glass throughout the Eastern Mediterranean, Egypt and Mesopotamia was characterized by high magnesia (3-7%) and potash (1-4%) content (*14*, *23*, *24*, *55*). This increased magnesia and potash content has been linked by many authors with the nature of the alkali used in the glass, resulting in the belief that plant ash was the predominant alkali source during this early time period (*14*, *55*). Thus, for the period of 1500-800 BCE, it is commonly held that the

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

majority of glass in both the Near East and Egypt was produced from a combination of ground quartz pebbles and the ash from halophytic desert plants (*49*). In addition to the necessary soda flux, the plant ash provided less soluble ions such as calcium and magnesium which would act as chemical stabilizers for the resulting glass (*49*). However, sea shells and calcinated corals have been mentioned in Mesopotamian tablets as reagents for glass production, both of which could also have acted as sources of calcium for glass stabilization (*2*, *26*).

Colorants

Finally, in addition to the primary components of silica and alkali, small amounts of transition metal species (~1-3% by weight) were often added as colorants (*49*). Even without such metal additive, early glass in antiquity was rarely colorless (*32*, *65*, *72*) due to impurities of iron in either the silica or alkali sources. All sands contain amounts of iron in the form of either FeO or Fe_2O_3 (*11*). The iron(II) species is especially problematic and acts as a very strong coloring agent to give a blue-green color to the glass (*2*, *11*, *12*). In contrast, the iron(III) oxide gives a yellow color, while mixtures of the two oxides can result in colors from amber to green (*2*, *11*, *65*). Glasses with as little as 0.4% iron have been shown to exhibit a pale translucent green (*65*). Although the coloring effect of these impurities might have been initially unintentional, glassmakers ultimately developed the ability to generate a variety of colored glasses through the proper choice of transition metal additives (Table 5) (*2*, *14*) and by 1375 BCE, the range of colors for both opaque and translucent glass had increased rapidly (*60*). Of these colors, only blue from copper and black from manganese were used to color faience prior to the production of true glass (*72*).

Blue colored glass could be produced using copper and/or cobalt colorants. Copper is generally considered the earlier colorant and, along with iron (*23*), was the most common coloring species, giving a glass that can vary from translucent pale blue to dark blue. For some blue glasses, the presence of tin ($\geq 0.05\%$) in addition to copper has suggested that either bronze or bronze scrap was used as the colorant (*55*, *65*). The analyses of glasses colored with copper have shown a range of 0.59-1.45% CuO, with the average of ~1% (*55*).

Cobalt was common in the production of deep blue, violet, and indigo glasses during the 2nd millenium BCE, although it virtually disappears after ca. 1100 BCE. The cobalt source for early Mesopotamian glass has been thought to be one of the arsenical ores (cobaltite or erythrite), which are found in several places in Persia (*59*). Cobalt in Egyptian deep blue glasses fall in the range 0.075 to 0.55% CoO (*55*). The cobalt source of Egyptian glass has been the object of a great deal of debate (*59*), but it has been suggested that the colorant was a cobalt-bearing alum available from the Oases in the Western Desert of Egypt (*49*).

Many blue glasses dating to the earliest time periods also contained significant amounts of antimony in addition to copper and/or cobalt (*72*). The addition of the antimony would render these glasses opaque (*48*, *65*) and would usually give the final glass a turquoise color, although glasses could also vary from opaque mid- to dark-blue (*65*). It is believed that the antimony was added to the glass in the form of antimony oxide (*65*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

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Table 5. Coloring Agents for the Generation of Colored Soda-Lime Glasses[a]

Color	*Transition or main group metal*	*Coloring oxides*	*References*
White	calcium/antimony, or tin	$Ca_2Sb_2O_7$; SnO_2	(*2*, *12*, *14*, *32*, *48*, *65*)
Yellow	lead/antimony, or iron	$Pb_2Sb_2O_3$; Fe_2O_3	(*2*, *11–14*, *32*, *65*)
Orange	chromium	CrO_3	(*11*)
Red	copper and/or lead	Cu_2O; Cu[a]; Pb_3O_4	(*2*, *12*, *14*, *32*)
Purple	manganese	Mn_2O_3	(*2*, *11*, *14*, *32*)
Blue	cobalt or copper	CoO; CuO	(*2*, *11–16*, *32*, *55*)
Blue-green	iron	FeO	(*2*, *11–14*, *32*)
Green	chromium	Cr_2O_3	(*11*, *16*)

[a] The coloring agents included here are not necessarily strictly limited to those utilized in antiquity. [a] Metallic copper nanoparticles can result in a ruby red color.

At about the same time the range of colorants used in glass was also extended to include other opaque glasses via antimony, including white from calcium antimonates ($Ca_2Sb_2O_7$ and $CaSb_2O_6$) and yellow from lead antimonate ($Pb_2Sb_2O_7$) (*23*, *48*, *49*, *72*). Such colored opaque glasses are among the earliest glasses, but do not occur in significant quantities until the middle of the 2nd millennium BCE (*48*). In the case of the white glasses, the lack of transparency is due to small particles of calcium antimonates (typically ~5 μm) which scatters the light, resulting in a milky or opaque appearance (*16*, *23*, *72*). These particles generally lack any evidence of definitive crystal faces or shape and are most commonly observed as delicate feathery crystals (*72*). As these glasses do not contain higher calcium content than other glasses, it is believed that antimony alone is added to create the white glass, with the lime content of the glass contributing to the formation of the calcium antimonate particulates (*65*, *72*).

The yellow opaque glasses contain particles of lead antimonate ($Pb_2Sb_2O_7$), which acts in a similar fashion to the calcium analogues in the white glasses (*65*, *72*). Analysis of such glasses has found nearly five times the required amount of PbO needed to produce the opacifier. Because of this, it is proposed that the excess lead must be added along with the antimony source, suggesting that the pigment added to the glass could be a mix of lead oxides, lead antimonates, and possibly antimony oxides (*65*, *72*). It is believed that the pigment might have been prepared beforehand by roasting antimony sources with excess lead species (*65*, *72*). Due to the high levels of lead and zinc found in such glasses, it is thought that the lead source was a Pb–Zn ore deposit. The most likely candidate for such a deposit is galena (PbS), presumably with significant amounts of sphalerite (ZnS). The most likely antimony source is the mineral stibnite (Sb_2S_3). The ultimate lead antimonate could then be produced by roasting galena and stibnite in the presence of excess lead as outlined below (*72*):

$$\boxed{\begin{array}{c} 2\ \mathrm{PbS}\ (s) + 3\ \mathrm{O_2}\ (g) \rightarrow 2\ \mathrm{PbO}\ (s) + 2\ \mathrm{SO_2}\ (g) \\ 2\ \mathrm{Sb_2S_3}\ (s) + 9\ \mathrm{O_2}\ (g) \rightarrow 2\ \mathrm{Sb_2O_3}\ (s) + 6\ \mathrm{SO_2}\ (g) \\ 2\ \mathrm{PbO}\ (s) + \mathrm{Sb_2O_3}\ (s) + \mathrm{O_2}\ (g) \rightarrow \mathrm{Pb_2Sb_2O_7}\ (s) \end{array}}$$

In the final step, heating a finely ground Pb-rich mixture of the oxides would begin to melt at 820 °C, resulting in a fully molten phase at below 850 °C. On cooling, this would produce a mix of $Pb_2Sb_2O_7$ and excess PbO (*72*). In addition to the common opaque yellow glasses, opaque green glass could also be produced if lead antimonate was added to a blue copper-colored glass (*48*, *65*).

Somewhat less common are purple glasses colored by the addition of manganese at an average level of 0.89%. Analyses of such glasses show no other elements at detectable elements, suggesting that the manganese source was relatively pure. Some of these high-manganese glasses do seem to have slightly elevated barium levels, which is thought to be linked to the use of the mineral psilomelane [$(Ba,H_2O)_2Mn_5O_{10}$] (*65*).

For all the colored glasses discussed so for, it is still uncertain whether the colorant was mixed with the initial raw materials or added to the crushed semi-finished glass (i.e. the frit) during the second stage. It is even proposed that there might have been a third stage where the colorant was finally added. Of course, it is possible that the coloring process was done differently at different workshops and for different colorants (*56*). Nevertheless, the added transition metal species would generate metal oxides during the formation of the molten mixture, providing strong coloring of the resulting glass. (*2*, *14*). The final color of the glass would depend not only on the resulting metal oxide, but also on the amount and mixtures of colorants used and the exact process used for the glass production, particularly the flux used and the manner of heating (*11*, *16*, *73*). Glass of black color can be produced through the use of almost any of the more powerful colorants in sufficient concentration. Such glasses are not truly black, but are so dark that they appear black. Analysis of very thin sections of such glasses, however, will reveal the true color of the chosen colorant. For example, a black glass can be produced via the addition of high quantities of manganese, although sufficiently thin samples appear to be a very dark purple (*11*, *73*).

A final class of colored glasses that deserves special discussion are the somewhat rare red glasses. Such red glass dates back to the 14th and 13th centuries BCE, but examples of such during this period were quite limited (*74*). In fact, such red glass was very rare in vessels and only slightly more common in jewelry (*23*, *65*). Red opaque glasses were colored and opacified with nanoparticles of either metallic copper or the red copper(I) oxide, Cu_2O (*23*, *48*, *74*, *75*). Such red glasses contain very high levels of copper, ~2–10 times higher than that typically found in the more common blue copper glasses (*65*). The coloring effect is accomplished by melting the glass under reducing conditions which converts cupric oxide (CuO) to cuprous oxide (Cu_2O), resulting in a nearly colorless to red glass, depending on the specific conditions utilized (*11*, *74*). The red color in this case results from the precipitation of minute, bright red crystalline particles of Cu_2O which results in a red opaque glass (*74*, *75*). The naturally occurring mineral form of Cu_2O is cuprite, which exhibits the same red color (*74*). The Cu_2O particles are typically so small that they can barely be seen under normal microscopic magnification. In some cases, however, crystals grown over longer time periods will generate dendritic formations. In extreme cases, such dendritic forms can be large enough to be seen by the unaided eye (*74*). In typical cases, the initial glass is nearly colorless to a pale yellow straw color. This glass is then reheated at a temperature somewhere between the annealing and the softening temperature, in a process commonly known as *striking,* during which the ruby color is developed via aggregation of Cu_2O in the glass matrix (*75*). Such red glasses are often referred to as *ruby* or *copper ruby* glasses due to the ruby red color of the glass (*11*).

In addition to the Cu_2O colorant discussed above, ruby glass can also be the result of metallic copper nanoparticles and it is thought that the color of copper-based ruby glass is due to the precipitation of both metallic copper nanoparticles and cuprous oxide crystallites (*75*). The copper nanoparticles color the glass via a combination of absorption and light scattering due to the metal particles, and the exact color depends on the size of the precipitated particles (~10-50 nm in diameter) (*16*, *23*). The size of the resulting nanoparticles produced in these glasses is determined by the specific temperature treatments used during their production (*16*).

The formation of the metal nanoparticles has been explained as the result in disproportionation of Cu(I) to give a mixture of Cu(II) and metallic Cu (*11*, *75*):

$$\mathrm{Cu_2O\ (solv)} \rightleftharpoons \mathrm{CuO\ (solv)} + \mathrm{Cu\ (s)}$$

Here the Cu(0) would then aggregate to form small particles of the metal, resulting in an intense red color (*11*, *16*). However, as the characteristic d-d band of Cu(II) is not found in a ruby glass, support for this explanation is limited. An alternate explanation is via Cu(I)-Cu(0) equilibria processes as outlined below, where solvated species are solvated by the glass matrix (*75*):

$$\boxed{\begin{array}{c} \mathrm{4\ Cu\ (s) + O_2\ (g)} \rightleftharpoons \mathrm{2\ Cu_2O\ (s)} \\ \mathrm{2\ Cu_2O\ (s)} \rightleftharpoons \mathrm{2\ Cu_2O\ (solv)} \\ \mathrm{2\ Cu_2O\ (solv)} \rightleftharpoons \mathrm{4\ Cu\ (solv)} \end{array}}$$

Modeling of the thermodynamics of these equilibria has suggested that while both types of particles contribute to the ruby color, the Cu_2O particles are the more dominate factor in the production of the ruby color in copper glasses (*75*).

Early Processing Methods for the Formation of Glass Objects

Core-Molding

The earliest hollow glass vessels were fabricated via a technique described as core-molding or core-forming, which dates to ~1500 BCE (*24*, *30*, *76*, *77*). This method is thought to originate from the Mitannian or Hurrian regions of Mesopotamia and is then thought to have spread fairly quickly to Egypt (*32*, *49*). Core-formed glass vessels found in other regions during this time period were thought to be probably imports from Mesopotamia, Syria, or Egypt (*76*).

The general process of this method is outlined in Figure 9, of which the initial step was the shaping of a form or core onto the end of a wooden or metal rod (Figure 9B) (*4*, *14*, *28*, *32*, *77*). The material used to shape the core needed to be pliable enough to form into the desired shape, while also solid enough to hold that shape without deformation. At the same time, it additionally needed to be weak enough to easily crumble for later removal from the interior of the finished vessel (*28*). The development of a satisfactory core material would have been difficult, as it had to possess a number of contradictory properties, including the ability to promote a sufficient interface with the glass so that it would adhere during the forming process, yet this interface could not be so strong as to disallow easy removal upon cooling (*28*). The precise composition of the core has been the subject of much speculation and a number of different materials have been proposed. Among those suggested are clay or mud (*2*, *14*, *28*, *55*), sand (*2*, *14*, *30*, *55*, *77*), fabric over a base material (*2*, *4*, *28*), sand-lime mixtures (*53*), mixtures of clay and horse dung (*78*), and camel dung (*28*). Once formed, the core could then be heated or fired to help set its shape (Figure 9C).

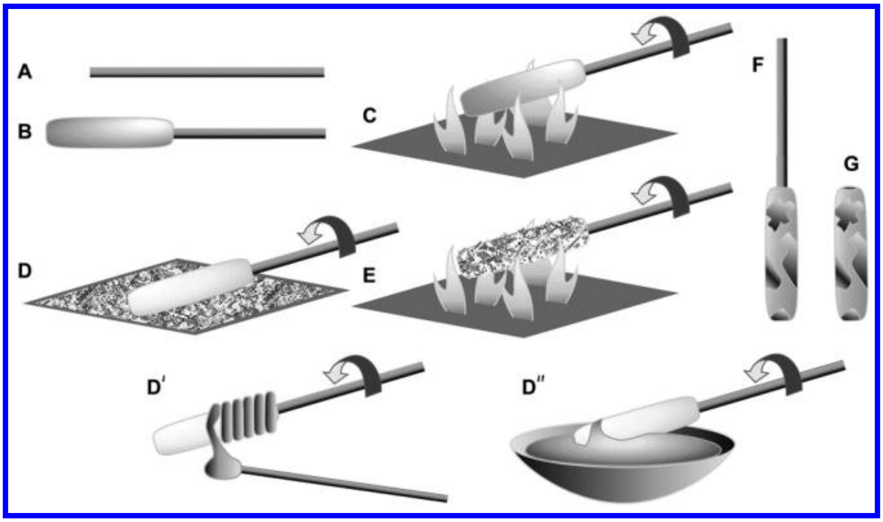

Figure 9. Proposed production of core-molded glass vessels: (A) metal or wooden rod; (B) formation of core form; (C) firing to set the core; (D) application of glass via rolling in crushed glass; (E) firing of applied layer; (F) completed object; (G) final vessel after removal of rod and core. Alternate methods for the application of glass included coiling strands of softened glass around the mold (D') or dipping the core in molten glass (D''). [adapted from reference (58) with kind permission from Springer Science and Business Media].

Once the core formation was completed, fabrication of the vessel would be accomplished by building up glass layers around the central set core. This was thought to be accomplished by a number of different methods, of which the most commonly cited are the following: treating the core with an organic binder such as egg white or honey, followed by rolling it in crushed glass (Figure 9D) (*14*,

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

28); winding strands of hot, softened glass around the core (Figure 9D′) (*4*, *28*, *32*, *55*); or repeatedly immersing the core in molten glass not much above the softening temperature (Figure 9D″) (*2*, *4*, *28*, *32*, *55*, *59*, *77–79*). The core would then be heated in order to generate a uniform layer of glass (Figure 9E), cooled, and another layer applied. Via such a repetitive process, the glass walls would be built up iteratively until the desired thickness was achieved (*32*, *77*).

With the fabrication of the vessel wall complete, the vessel could be rolled on a slab of stone while the glass was still soft in order to either smooth the surface or further decorate the exterior. Finally various manipulations could be accomplished to add details such as handles or rims (*2*, *4*, *14*, *28*, *60*). Once the final workings were completed and the object had cooled (Figure 9F), the rod was removed from the vessel so that the core material could be carefully dug from its center to give the finished hollow vessel (Figure 9G). Due to the nature of this process, vessels produced in this manner were limited in scale and the inside surfaces of the finished vessel were extremely contaminated with residual material from the core (*4*, *14*, *28*, *60*). Because of this, it is thought that the opaque nature of most early glass was beneficial for this method, as the lack of transparency masked the remaining residue of the forming core (Figure 10) (*28*). Generally, the hollow interiors of such vessels were not of significant volume, nor were objects produced by this method very large in size - probably five inches or less in height (*77*).

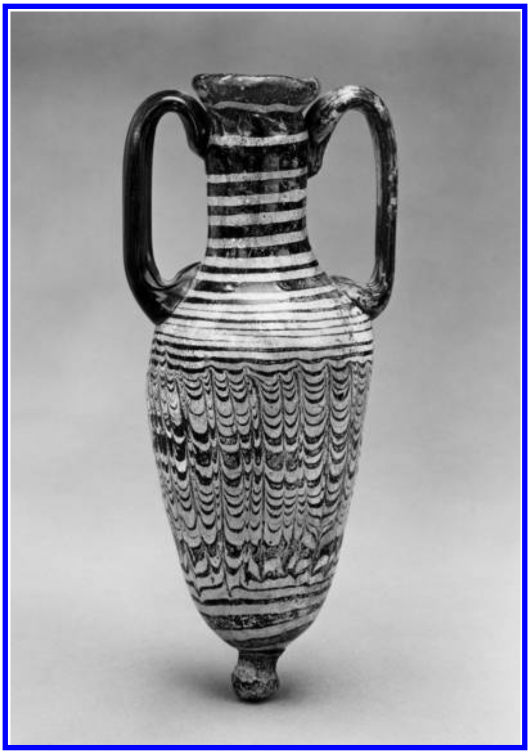

Figure 10. Core-formed glass Amphoriskos (2nd - early 1st century BCE). [M.88.129.4; Courtesy of the Los Angeles County Museum of Art].

Cast Glass

Glass forming then made another significant advancement in ca. 1200 BCE, when the Egyptians learned to press softened or molten glass into open molds (*4*, *60*, *77*). This development led to a stress on composite pattern rather than simple color (*4*). This now made possible the production of simple shapes such as bowls, dishes, and cups, the likes of which could not be made by the previous core molding methods (*4*). Casting involved melting glass (ingots, pieces, rods, or grains) into a mold which provided the simple, crude shape of the desired object (Figure 11) (*28*, *80*). The mold could then be removed after the glass had cooled (*80*) and the final finished product relied largely on the carving and polishing of the molded shape (*28*). Due to the limitations of this method, it seems to have been used primarily for the production of relatively simple shapes of limited sized and complexity (*28*).

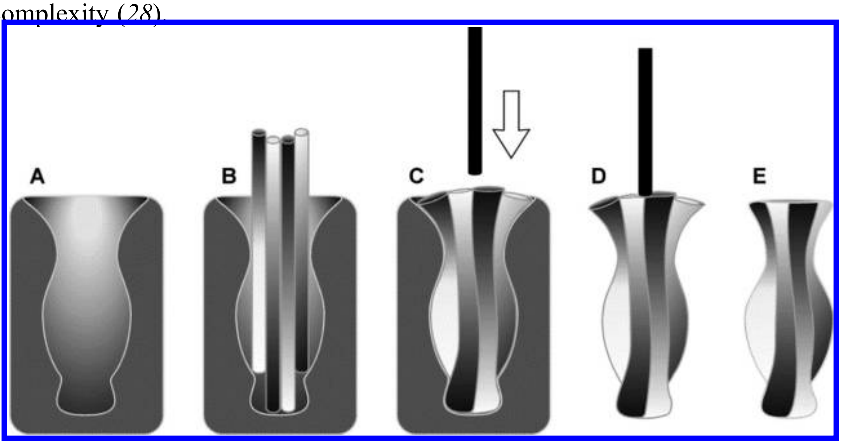

Figure 11. Fuse-casting of glass objects: (A) production of black mold; (B) glass pieces added, heated to fuse and fill mold; (C) metal rod inserted; (D) mold removed; (E) piece ground and polished to finish. [adapted from reference (58) with kind permission from Springer Science and Business Media].

Due to its viscous nature, the glass would need to be heated and kept at a relatively high temperature in order to make it fill the mold. At such elevated temperatures the glass would become plastic and take on the texture of the mold material. The materials utilized to construct the mold would have been relatively simple in nature and would have contaminated the glass surface during the process (*28*). In addition, it is quite difficult to obtain cast forms that were free from trapped air bubbles or unsightly portions of crystallized material resulting from the original exposed surfaces of the various glass pieces used to fill the mold (*80*). For these reasons, the object removed from the mold would require sufficient grinding and polishing to remove such surface contamination and defects. Unfortunately, such grinding and polishing has also removed all traces that could act as clues to the exact method used for the production of such cast glass objects (*28*).

In order to limit some of the defects outlined above, glass could be liquefied separately first and then poured into the mold from a pot or ladle. Even so, it would still be very difficult to prevent the inclusion of bubbles and such an approach

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

would be complicated by the fact that molten glass never attains the mobility of molten metal (*28*, *80*). Thus, the casting of glass is a much slower process and requires the gradual feeding of glass into the mold while subjecting it to continuous heating over long periods (*28*). This lower mobility also makes it so that the glass will not flow through small orifices or properly fill molds with intricate patterns. As a result, this limited the method to the production of larger objects of simple design (*79*). For these reasons, many of cast Egyptian objects were produced from simple flat-backed forms (*28*).

Decline and Renewal

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

After this period, the glass industry declined and there is little evidence of further evolution until glass production revived in Mesopotamia between 900-700 BCE (*2*, *9*, *14*). An apparently independent glass industry also arose in Syria and along the Palestinian coast during the period of 800-500 BCE (*2*). This was then followed by a similar revival in Egypt about 500 BCE (*9*). This general resurgence in glass technology is thought to be part of the Iron Age revival of culture that followed the period of turmoil in the Mediterranean between 1200 and 1000 BCE. After this initial revival, production spread to new glass-making centers, which introduced modifications of established processes, as well as the development of new techniques (*29*). For the next 500 years, centers of glass production continued to develop in Egypt, Syria, and other countries along the eastern shore of the Mediterranean Sea (*9*), with the Egyptian industry ultimately becoming centralized at Alexandria (*14*, *32*).

Glass during the period of ca. 6th century BCE to about 4th century CE is distinguished from glasses of other time periods by its antimony-rich nature (*12*, *14*, *24*). This glass was characterized by lower potassium (0.1-1.0 %) and magnesium (0.5-1.5%) content, along with a consistent high concentration of antimony (*14*, *24*, *55*). Many authors have linked the decreased magnesia and potash content with a change in the nature of the alkali used as the flux, proposing a change from the earlier application of plant ash to that of natron (*14*, *44*, *55*, *68*). This general glass composition represents that used in Greece, Asia Minor, and Persia during the 5th and 4th centuries BCE and continued to be popular in areas from the Euphrates eastward during the ascendancy of Rome (*24*).

In terms of glass color, there was little change from earlier glass other than that cobalt was reintroduced as a colorant after ca 600 BCE, where it is again used for the production of blue and dark blue-black glasses (*55*). A major change at this point, however, was a shift in emphasis from opaque to clear glass production. This move to clear and translucent colored glass is thought to be as much the result of a shift in viewpoint as with any specific improvement in technology (*29*). This view is supported by the fact that samples of colorless glass first appear at Thebes as early as 1400 BCE (*60*), which suggests that early glassworkers had the ability to produce colorless glass far before it became a major emphasis. The regular production of clear, antimony-rich glasses, however, dates back to only about the 7th century BCE (*2*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Colorless glass was achieved by the careful selection of very pure sand of low iron content and by the addition of antimony as a decolorizing agent (*12*, *60*). As discussed above, antimony was known in Mesopotamia quite early and was of crucial importance for the production of opaque glasses. With this shift in emphasis, however, antimony now became a commonly applied early decolorant for the production of colorless glass (*12*, *14*). The compositions of these colorless glasses are very similar to the previous white opaque glasses, which differ only in higher levels of antimony (average of 1.95%) for the opaque glasses (*65*).

As previously discussed for the opaque glasses, the source of the antimony was probably stibnite (Sb_2S_3) which can be found throughout the Mediterranean and the Near East (*48*). The stibnite would then be roasted to produce the decolorizing agent. In the initial step of this process, the sulfide would be converted to the corresponding oxide (Sb_2O_3). Further heating at temperatures of 460-540 °C in dry air would then convert this initial oxide to the mixed valence product Sb_2O_4 as shown in the reactions below (*58*):

$$2\ Sb_2S_3\ (s) + 9\ O_2\ (g) \rightarrow 2\ Sb_2O_3\ (s) + 6\ SO_2\ (g)$$
$$2\ Sb_2O_3\ (s) + O_2\ (g) \rightarrow 2\ Sb_2O_4\ (s)$$

When added to the glass batch, the Sb_2O_4 would act as an oxidizing agent to convert the strongly absorbing Fe(II) ions to the fairly colorless Fe(III), thus removing the coloring due to the iron impurities (*12*, *58*).

$$Sb_2O_4\ (s) + 2\ FeO\ (s) \rightarrow Sb_2O_3\ (s) + Fe_2O_3\ (s)$$

Colorless glass produced in this way would be relatively transparent unless it contains air bubbles or undissolved particles. The majority of ancient glass, however, contained much undissolved material and thus was not as transparent as modern glass. In addition, depending on the amount of Fe(III), the final object may still contain a slight yellow tint from the iron content.

Roman Glass

During the 4th century BCE, the wide-spread conquests of Alexander the Great (d. 323 BCE) extended Greek culture across the Near East, ultimately becoming the dominant cultural element in Syria, Egypt, Asia Minor, Mesopotamia, Southern Italy and Sicily (Figure 12) (*29*, *81*). Because of this, the Greeks became exposed to the combined technological knowledge of the Middle East (Mesopotamians, Babylonians, Syrians, Persians), as well as that of the Egyptians, Indians, and Chinese (*58*). On Alexander's death, his empire was divided into four separate Hellenistic Kingdoms - Egypt, Syria, Mesopotamia, and Greece-Macedonia (*29*). Rome conquered Greece in the 2nd century BCE and by 30 BCE, the entire Mediterranean basin was united under the Roman rule of Augustus (63 BCE - 14 CE) (*29*). In the process, Greek culture and natural philosophy was absorbed by the Romans, including the collected knowledge and technology of glassmaking.

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

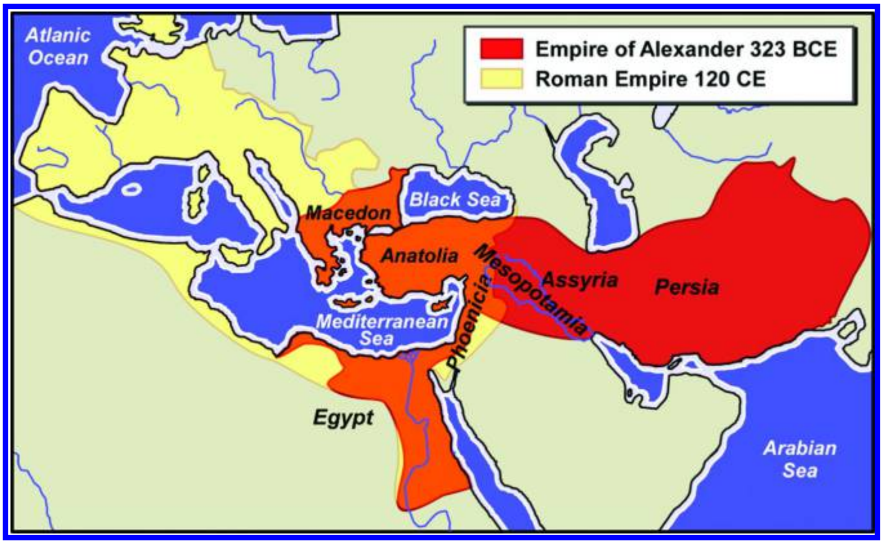

Figure 12. Maps of the territories occupied by Alexander the Great and the Roman Empire.

The term "Roman glass" is used to describe the normal composition of glass of the period 4th century BCE to 9th century CE. This composition was probably typical of glass produced throughout the coastal cities of Syria, as well as Egypt, Italy, and the western provinces (*24*). Such glass is thought to have been developed in the Syro-Palestianian area by the 3rd century BCE (*14*) and consists of a composition similar to that of the previous antimony-rich group, with the exception of a much lower antimony content and significantly higher manganese content. This has led to the conclusion that the distinction between Roman glass and the previous antimony-rich glass is a simple change in the choice of decolorant (*14*, *24*, *82*).

It is generally believed that the Roman period is also distinguished by another change in the type and origin of the raw materials used to produce glass (*49*). Based on the potassium and magnesium content of Roman glass, natron is thought to remain as the primary source of alkali, most probably from the Wadi Natrun in Egypt (*14*, *43*, *48*, *49*, *55*, *83*). Natron was extensively exported by the Romans and it remained the alkali of choice for glass production until the ultimate decline of the Roman Empire (*55*). However, the increased alumina (Al_2O_3, average 2.3%), TiO_2 (average 0.07%), and Fe_2O_3 (average 0.5%) content of Roman glass does suggest a change in the silica source, consisting of a move from ground quartz pebbles to sand (*49*, *83*). Due to the higher calcium content of typical siliceous–calcareous sands as shown in Table 1, these sands are thought to have acted as a source of lime as well as silica (*43*, *49*, *82*). The use of sand in Roman glass is confirmed by Pliny the Elder, as illustrated by his description of 1st century glass production given below (*84*):

> ...at the present day, there is found a very white sand for the purpose, at the mouth of the river Volturnus, in Italy. It spreads over an extent of six

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

> miles, upon the sea-shore that lies between Cumæ and Liternum, and is prepared for use by pounding it with a pestle and mortar; which done, it is mixed with three parts of nitre, either by weight or measure, and, when fused, is transferred to another furnace. Here it forms a mass of what is called “hammonitrum;” which is again submitted to fusion, and becomes a mass of pure, white, glass. Indeed, at the present day, throughout the Gallic and Spanish provinces even, we find sand subjected to a similar process.

Analysis of Pliny’s text has led to the proposal that sand to be used in glassworking was initial prepared by grinding and washing (*43*). Not only would this decrease the grain size, thus making it more suitable for more homogeneous fusion, but this would also remove the presence of various soft, non-quartz components (primarily carbonate, augite and feldspar) which could potentially reduce the suitability of the sand for glass production (*43*, *44*). This sand-natron glass formulation is thought to have been initially introduced during the 8th-7th centuries BCE with its origins somewhere in the eastern Mediterranean. This remained as the standard glass formulation throughout the Roman and Byzantine periods until about 850 CE (*49*).

As mentioned above, the most distinctive shift in raw materials for Roman glass was the shift from antimony to manganese as the chosen decolorant in the production of colorless glass (*12*, *14*, *24*). This increased manganese content, coupled with decreased antimony, is found in all regions with strong Roman influence and this change is considered an important chemical fingerprint for glass technology (*12*). As manganese had previously been used as a colorant for brown glazes, as well as purple or black glasses, it has been proposed that its initial use in decolorizing glass was perhaps made accidentally (*60*). For earlier colorless glasses that have been found to contain a mixture of both antimony and manganese, it is thought that the manganese was not intentionally added and was due to impurities in the silica source (*82*). The general and intentional use of manganese for decoloring glass is thought to have begun only in the Roman period (*60*), with the production of clear manganese glasses dating to the 1st century BCE (*2*). Still, colorless glass has been said to have not been initially that common and its large scale production may have been evolved in Alexandria as a result of the shift to blown glassware (*60*).

The most common source of manganese was pyrolusite (manganese dioxide or MnO_2) (*60*, *82*). The Mn(IV) of MnO_2 would act as an oxidizing agent, reacting with the strongly absorbing Fe(II) species to produce Fe(III) and Mn(II), both of which contribute little to no color to the resulting glass (*14*).

$$MnO_2\ (s) + 2\ FeO\ (s) \rightarrow MnO\ (s) + Fe_2O_3\ (s)$$

The successful oxidation of Fe(II) into Fe(III) was generally promoted by a MnO content of two to four times higher than that of iron (*83*). Nevertheless, such decolorizing methods typically did not fully counteract the colored contaminants and even the clearest Roman glass only really manages to limit their effects (*29*). Because of this, such decolorized glass was most commonly used in thin blown vessels where the thin nature of the glass walls would make any residual color less observable (*60*). Although manganese is recognized to be a less effective decolorant in comparison to antimony, it is thought that it was favored by the Romans due to its greater availability (*12*, *14*).

Other components reported to be utilized as additives in Roman glass include lead salts and various species that could have acted as potential sources of lime (*2*, *12*, *48*, *84*). In addition to the use of lead in the production of yellow opaque glasses (*65*, *72*), lead salts would sometimes be intentionally added to glasses and enamels in order to improve the working properties of the melt (*48*) or as a means to enhance the brightness of the glass (*12*). In terms of other additives, it has been claimed by some that the uniform calcium content found in Roman glasses is evidence of the intentional use of lime in glass during the Roman period (*2*). Thus, chalk or other forms of limestone ($CaCO_3$), as well as burned shells (primarily a mixture of chitin and $CaCO_3$), have all been suggested as raw materials which could have acted as convenient sources of lime for Roman glass (*2*). In support of this reasoning, authors have pointed to passages of Pliny the Elder which do mention in passing the addition of shells and fossil sand to glass (*84*). However, it has also been pointed out by others that the distinct lack of significant amounts of such components in known glass recipes does not really support these claims. In addition, as these components are not mentioned in the known glassmaking treatises of the Medieval and Renaissance periods, it is generally believed that the role of lime in glass was not yet recognized during the Roman period and that it was not intentionally added as a major constituent before the end of the 17th century (*21*).

In general, glass found throughout the Roman Empire is characterized by a very uniform compositional consistency (*43*, *49*). Some have proposed that this uniformity suggests that a limited number of sites were used for the production of glass during the Roman period (*49*). According to such a centralized glass production model, glass may have been produced from its raw materials in a limited number of large primary glass production sites, which would have been located near the necessary raw material sources (*43*, *44*, *49*). At such site, large quantities of raw glass could be produced in a single firing and the resulting glass cullet produced would then be transported around the Empire to a significantly larger number of local secondary production centers. Here, the cullet would be remelted and formed into the final vessels or other glass objects (*43*, *44*, *49*). This proposed production model is supported by both the scale of the tank furnaces known to have been used for glass production during this time period, and the fact that the only significant large-scale source of natron is the Wadi Natrun in Egypt (*49*). However, it must also be stated that such primary production sites are not that common in the archaeological record (*44*). Thus, while evidence exists for such sites in the Late Roman and post-Roman world, primary glass production sites have yet to be verified for the earlier Roman period (*43*, *44*).

An alternate model proposes that glass was made on a small scale at a large number of local or regional workshops. In such a multiple source model, compositional consistency is explained by the use of similar glassmaking recipes (*43*). However, even similar recipes would not eliminate compositional variance due to differences in raw materials and few glassmaking sites have been discovered where it can be suggested that glass was produced directly from

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

raw materials. Support for this alternate model is largely based on the view that long-distance trade in raw glass does not really fit what is known of Roman trade practices, which was related mostly to the provisioning of Rome and of its armies, as well as the fact that Pliny explicitly mentions glass-making at multiple centers (*43*). Opponents of this model, however, have pointed to the fact that as the majority of the natron is believed to have come from the Wadi Natrun, the multiple source model would require the transport of large quantities of natron around the Empire, which is significantly more bulky in volume and thus more difficult than the transport of glass cullet (*49*).

Most of the currently investigated sites for glass production are located in the Levant and Egypt, dating to the late Roman to early Byzantine periods (*44*, *49*). For at least these later periods, it is believed that raw glass was produced exclusively in these regions (*44*). The products of these different manufacturing sites can be distinguished on the basis of their chemical analysis, which reflect the compositions of the different quartz sands used at the various production centers. While this is supportive of the centralized glass production model theorized above, the glass from the currently known sites does not match the composition of earlier Roman glass dating from 1st to 3rd centuries CE (*49*). As such, it has been suggested that primary glass production must have also taken place in other areas, although this is still a point of debate (*44*). Therefore, it remains uncertain whether the centralized glass production model is reflective of the Roman Empire in general or just limited to the later Roman period (*49*).

Slumped Objects

The Roman Empire provided a ready market for high quality, material glass items. This in turn encouraged the development of new processes for the manipulation of glass and a more centralized approach to glassmaking. For the first time, the mass production of large numbers of similar object became an economic goal and new technological methods were developed to meet this demand. This began with the process of bending, also called sagging or slumping, as shown in Figure 13 (*28*). Large scale production of slumped objects has been dated to ca. 400 BCE (*29*).

In the formation of slumped objects, hot glass was first poured onto a flat surface (Figure 13A) and then pressed with a flat, disc-shaped former (Figure 13B). The removal of the former would then result in the creation of a glass disc (Figure 13C), which was then transferred onto a "former" mold of fired clay or cut stone (Figure 13D). The system was then reheated to soften the glass disc and the combination of heat and gravity would cause the disc to sag over the mold to give a bowl-shaped glass object (Figure 13E).

One of the most common objects made via this technique were distinctive ribbed bowls often referred to as pillar-molded bowls. Such bowls were popular from the 1st century BCE to the 1st century CE (*85*). Different theories regarding the rib-forming process have been proposed over the years, the most common of which consist of the stamping a disc of molten glass using a mold with radial grooves as illustrated in Figure 13. Others have proposed that ribs may have been raised by flattening an already slumped glass bowl using a metal bar (*85*). More

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

recently it has been proposed that the ribs were formed by using a pair of pincers to work a simple flat disc of molten glass. In this way, seven or eight ribs can be formed via pinching before the disc needs reheating, and when complete, the disc is slumped over a form (Figure 13D-E). Modern glassmakers have illustrated that this is a viable, easily repeatable, and relatively fast method which reproduces all of the characteristics of ancient ribbed bowls (*85*).

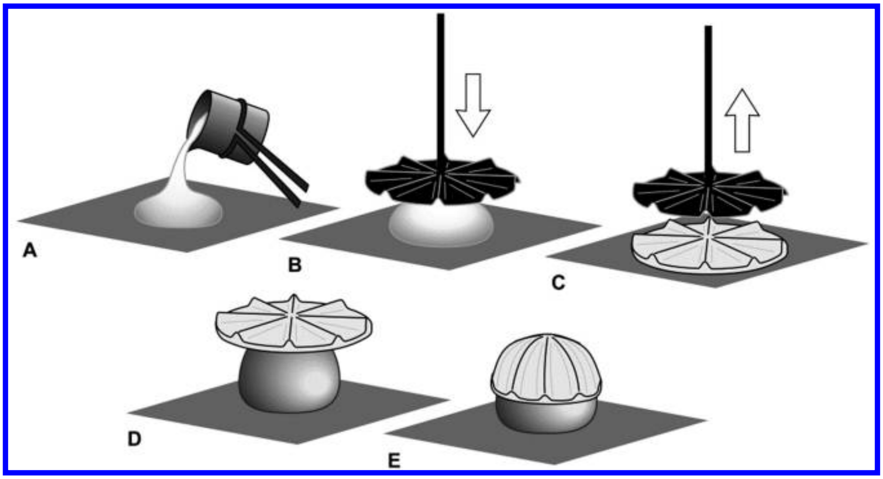

Figure 13. The formation of open-form bowls by sagging glass over convex "former" molds: (A) molten glass is poured onto a flat surface; (B) pressed with a flat, disc-shaped former; (C) cooled to create a glass disc; (D) transferred onto a "former" mold; (E) heated to cause the disc to sag over the mold giving the final bowl shape. [adapted from reference (58) with kind permission from Springer Science and Business Media].

In the case of all such slumped glass objects, the formed piece was finished by grinding and polishing, which was necessary to remove various mold markings or tool marks (*28*, *85*). In addition, these objects were often completed by the addition of a single horizontal ground band (*28*). Such grinding was believed to be accomplished using a rotating grinding wheel (*85*).

This glassforming technique was probably derived from the similar forming of a metal sheet over a preformed shape by hammering (*28*). Both the common horizontal band and the general profiles of slumped glass objects mimic analogous metal objects, which again strengthens the origin of this technique with previous metalworking methods. In comparison to metal species, however, the use of glass transformed the original metal objects into single-color, refined vessels that characterize the process (Figure 14) (*28*). The slumped glass pieces made by these methods were still individually made and would still have been exclusive items, produced primarily for the social elite (*28*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Glassblowing

Perhaps the most significant new advancement in the production of Roman-era glass objects was the introduction of glassblowing during the 1st century BCE (*2*, *23*, *32*, *49*, *60*, *76*, *86*). Some have proposed that glassblowing may have been invented as early as 250 BCE, but there is far too little evidence from this time period to support this earlier date (*86*). However, blown glass objects were common sometime after 50 BCE (*86*) and thus the time period of 50 BCE - 20 CE (*60*, *86*) is generally given for the invention of glassblowing.

Figure 14. Ribbed bowl (1st century CE). [52.1.79, Collection of The Corning Museum of Glass, Corning, New York].

The origin and development of glassblowing is typically attributed to craftsmen somewhere in Syria or the coastal strip of Phoenicia (*23*, *29*, *32*, *77*, *86*, *87*). While various cities in this region have been proposed for the site of glass-blowing's origin, many point to the Phoenician city of Sidon (on the coast of Syria) (*60*, *87*). Glass production was the most important industry in the Phoenician era and was conducted on a vast scale. The art of glassblowing is then thought to have migrated to Rome with craftsmen and slaves after the area's annexation by the Roman Empire in 63 BCE (*14*). Attracted by the extent of profitable commissions available in Rome, many Sidonian glassblowers migrated to Italy and set up shop in Rome, Campania, and Aquileia. It is thus thought that while glassblowing was invented in Syria or Phoenicia, it was perfected in Italy and glassblowing facilities soon began to spring up throughout the empire during the mid-1st century CE. The main exception was in Egypt where artisans were notoriously slow to adopt the new technique of glassblowing (*87*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Various possible origins for glassblowing have been proposed from blowing soap bubbles or derivative practices of metal working (*60*). One quite plausible route to its discovery was an accidental discovery resulting from the production of glass tubes. It has been suggested that while an artisan was working with such a glass tube (perhaps cutting it into beads), the end of the heated tube collapsed. Thinking to open it via forced air, the artisan could have blown into the tube. However, instead of opening the tube, this action formed a bubble which expanded as he continued to blow. Of course, there is no direct evidence to support this theory, but this path seems reasonable (*77*). Another proposed origin was via the production of mold-pressed bowls, during with an artisan may have found that blowing the molten glass into the mold was easier than pressing it. The step from this to free-blown glass would have then been a small one (*86*).

Technically, glassblowing required that the glass be very fluid which thus required working the glass at much higher temperature than for either casting or molding. Laboratory experiments reconstructing the conditions of ancient glassworking have shown that temperatures of least 1080 °C were required to make typical Roman glass fluid enough for glassblowing (*2*) and constant temperatures of 1050-1150 °C are needed for the duration of the work (*87*). To achieve such temperatures required a knowledge of and experience with the furnaces that had developed in the glass industries of the Middle East (*30*), but also required new modifications such as furnaces with a horizontal heat chamber which were specifically designed to facilitate glassblowing (*87*).

It is generally stated that initial blowpipes were about the same size and shape as it is today, consisting of a hollow iron tube 4-5 feet long, with a knob at one end and a mouthpiece on the other (*32*). However, others have postulated that early blowpipes could have initially been made from other materials. Support for such theories is largely indirect and stems from the fact that iron tubes are not present in the archaeological record of the Augustan period (*87*). In addition, sturdy iron tubes were difficult to make with ancient technology and could have therefore been cost prohibitive for glassworkers. As such, some believe that glassblowing may have begun with inexpensive clay blowpipes (*87*). This hypothesis could explain the rapid spread of the glassblowing technique as the glassblowers themselves could then easily make the needed blow-pipes. By 70 CE, however, it is clear that iron blowpipes were common (*87*).

In the hands of skilled artisans, the simple blowpipe now made possible the creation of an almost endless variety of hollow glass objects (*32*). The earliest known blown vessels are small bottles weighing 14-60 g and cups up to 166 g (*87*). Very thin, transparent glass could now be produced via glassblowing and this technique enormously increased the versatility of glass, as well as opened up potentially new uses (*30*). In addition, glassblowing could be combined with older techniques to result in new variants such as mold-blowing (Figures 15 and 16) (*86*). In this technique, glass was blown into two- or three-piece hollow molds made of either wood or clay. This would result in thin-walled, hollow molded vessels and the molds could be used and re-used indefinitely to allow the mass production of these glass objects (*86*).

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

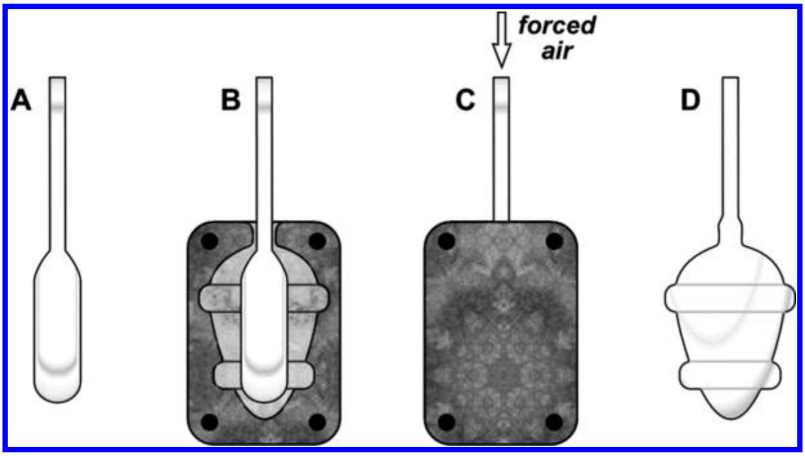

Figure 15. Blow-molding with a two-piece mold: : (A) hollow glass blank; (B) glass blank inserted into mold; (C) mold fashioned together and softened glass blown to fill mold; (D) mold disassembled and hollow vessel isolated.

Figure 16. Roman mold-blown glass bottle in form of grapes (1st-2nd century CE). [64.1.8, Collection of the The Corning Museum of Glass, Corning, New York].

As a consequence of these advances in glassworking, the whole character of glass vessels changed. The heavier forms of earlier periods began to be replaced by thin-walled vessels and the scale of glass production increased dramatically, with the use of large tank furnaces (2 × 4 m in size) claimed to be able to produce several tons of glass in a single firing (*49*). It was now possible for the rapid production of simple utilitarian vessels in much larger quantities, and glass transitioned from prestige objects to household commodities (Figure 17) (*2*, *49*). As a result, a middle-class Roman family probably owned glass storage containers, drank from glass vessels, and bought souvenir glass cups with the names of favorite gladiators molded into them. Even glass funerary urns served as the final resting place of many Romans (*2*).

Figure 17. Roman glassblown pitcher (1st century CE). [79.1.262, Collection of The Corning Museum of Glass, Corning, New York, bequest of Jerome Strauss].

Windows

Another significant Roman innovation was the application of glass to the construction of window panes and such window glass was produced by the Romans as early as the 1st century CE (*88–90*). The dating of this innovation is supported by the appearance of window glass in Pompei structures built or

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

restored after the earthquake of 62 CE, yet preceding the eruption of Vesuvius in 79 CE (*89*). Samples of window panes uncovered at Pompeii have been as large as 30 x 40 inches (*14*). Samples have also been commonly found in Roman sites in Britain (*90*). For the most part, such early glass windows were usually quite small, of irregular thickness, and not truly clear or transparent (Figure 18) (*88*).

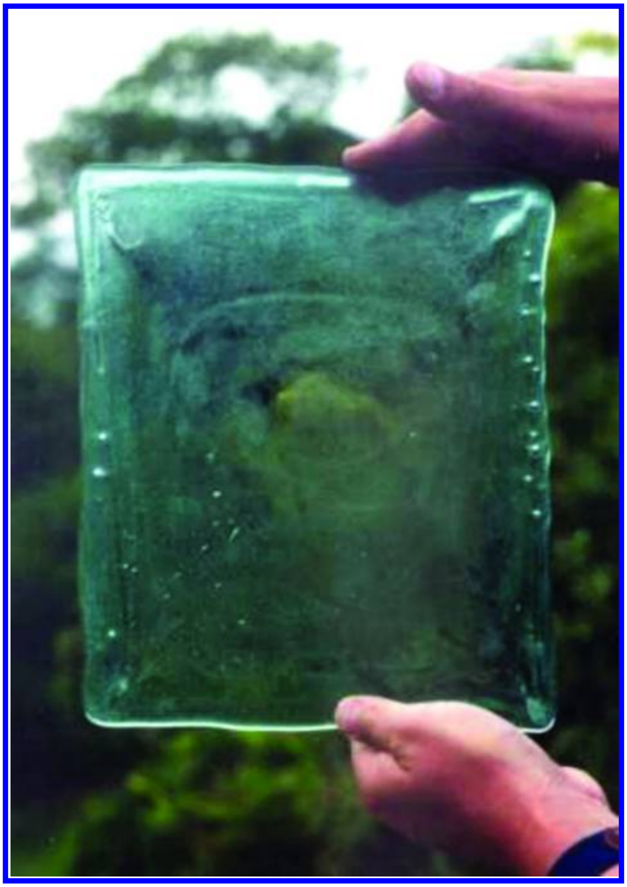

Figure 18. Modern reproduction of Roman window glass (~5 mm thick). [Copyright Roman Glassmakers, used with permission].

Early window panes were produced using one of several different processes (*83*, *88*–*93*). The earliest known method was the production of "cast glass" which produced panes of uneven thickness, with one side exhibiting a fire polished or smooth texture and the other side a pitted, rough finish (*89*, *91*). Casting seems to have been the prevailing technique during the Roman period up to the 3rd century CE, after which the technique feel into disuse and thus the precise technique of making cast glass has been lost (*83*, *90*, *91*, *93*). It has often been suggested that cast panes were produced by pouring molten glass into a rectangular stone or terracotta mold in which sand had been sprinkled to prevent the glass sticking to the

Publication Date (Web): November 20, 2015 | doi: 10.1021/bk-2015-1211.ch010

bottom (*89*). Arguments against this proposed method, however, are that it would not result in the specific edge and corner forms, nor the tool marks seen on original Roman glass (*89*, *90*). Some, however, include a processing component to the mold casting, in which the glass was stretched with tools to give the recognizable tool marks (*89*).

An alternate proposed method for the production of cast glass involves the casting of soft, hot glass onto a flat surface, which was then pressed into some semblance of flatness with a moist, wooden mallet (*88*). Using these methods, contemporary glassmakers have been able to produce glass panes that closely match authentic Roman-era panes (*90*, *91*). In the reported modern reproduction, molten glass was poured onto a damp surface and immediately flattened with a large block of damp wood. This resulted in the production of a flat disc of glass about 5 mm thick, which was then pulled and stretched in order to form a rectangular shape (Figure 18). This method utilized simple tools (metal rods, hooks, and pincers) and the marks produced on the finished panes closely match those seen on Roman samples (*90*, *91*). While somewhat crude, this method is simple and repeatable. As such, it is easy to imagine its use during the early Roman period.

Methods for the production of blown window glass (cylinder and crown glass) appeared at a later point, probably sometime after the 2nd century CE (*89*) By the beginning of the 4th century CE, both the cylinder and crown techniques started to become widespread (*83*, *93*). It is believed that cylinder-blown glass windows initially existed alongside the older casting technique (*93*).

In the cylinder processes, a molten glass bubble was blown and then rolled on a smooth surface to obtain a cylinder, which was then cut lengthwise in order to obtain a flat sheet. The glass produced in this way appears thinner than that produced by casting and has two smooth sides (*89*). The ability to distinguish between panes produced by the cylinder-blowing technique verses casting on the basis of their material characteristics is made difficult by the fact that both processes produce rectangular or square panes (*93*). Various features such as the surface appearance, the thickness of the glass, and the shape and orientation of the air bubbles within the glass are believed to distinguish between panes fabricated via the two methods (*89*, *93*), but the conclusiveness of these material features is still debated (*93*).

In contrast to panes fabricated by the first to methods, crown glass is simple to identify (*93*). This process consisted of first blowing a hollow sphere on the end of a blowpipe. The sphere was then either directly opened at the opposite end, or transferred to a pontil and then opened. The opened, soft sphere was then vigorously rotated such that centrifugal force would cause the glass to flatten out into a disc or wheel-like shape (*89*, *92*, *93*). As a result, this would result in a pane that was usually thick at its center and thinner towards the edges (*93*). The disc was then cooled and cut into small sheets (*92*). For the purpose of strengthening the thinner rim, the edges of the glass disc were sometimes folded over (*93*). Crown glass can be recognized by the characteristic lump of glass at the center (known as the ‘bullion’, ‘bull’s eye’, or ‘crown’) where the blow-pipe/pontil was attached and, if air bubbles or impurities are present in the glass, these would more often than not be spread in a spiral formation (*92*, *93*).

Conclusion

While soda-lime glass was the last of the major chemical technologies to be developed in antiquity, it had still been undergoing ca. 3000 years of refinement and continued development until its first height of technological advancement during the Roman era, often referred to as the *First Golden Age of Glass* (*9*). During this long span of time, the primary composition of glass underwent several major changes as the result in sources of either silica or soda, as well as the choice of decolorant. In terms of chemical properties, the earlier compositions gave perhaps the best glass. Changes in composition then largely occurred due to shifts to component sources (silica, soda, decolorant) that were readily available in greater quantities, even if they provided inferior properties. As such, it is quite possible that such changes occurred in order to meet a greater demand for glass objects.

Any deficiencies in the glass components were balanced by continued advancement of glassmaking and glassworking techniques. These efforts transitioned from core-formed vessels to molded cast glass, followed by slumped bowls and cups, before the ultimate development of glassblowing. At the same time, the variety in the visual quality of glass continued to be developed, thus increasing the palette of colored glass types available to the glassworker. As a result, glass in the Roman era consisted of both utilitarian household commodities, as well as exclusive objects of high art. In general, the Romans are usually praised primarily for their practical skills, rather than for their aesthetic achievements. However, in the case of glassworking, they excelled on both counts (*2*). Such glass objects from the Roman period are found in abundance out to the ends of the Empire, as far north and west as Scandinavia and Britain and as far east and south as Syria and Ethiopia.

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Subject Index

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