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Chronometric Dating in Archaeology: A Review

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ABSTRACT
Most archaeological dating methods are based on decay of a naturally occurring radioisotope. ^{14}C activity of fossil bones and charcoal decreases with age, but must be calibrated for past changes in atmospheric activity. Uranium absorbed by shells and stalagmites is used to date on a 10^5-year scale by observing the decay of ^{234}U to ^{230}Th. Thermoluminescence, optical luminescence, and electron spin resonance detect trapped electronic charges generated by natural radioactivity in burned flint, beach sands, shells, and tooth enamel. Rate of racemization of amino acids in fossil shells is constant at constant T, and age can be tracked from an increase in the D/L ratio.

Introduction

Archaeology is the study of the material record of the history of our species. An essential part of the study of archaeology is the assignment of dates to artifacts and sites as well as to the skeletal remains of the former inhabitants of those sites. Conventionally, we distinguish between two types of dating systems. In *relative* dating, we locate artifacts, fossils, and sites on a time scale that is based on the generally recognized sequence of appearance of different styles or the evolutionary sequence of biological species. In addition, prehistoric human chronology is founded on the geological time scale, which arranges the past in a series of discrete, successive intervals of time bounded by shorter periods of changing climate, etc. On the other hand, scientists have been able to provide an *absolute*, or preferably, *chronometric* time scale that allows us to place events at a definite point in time by determining the length of time that some process has been running, a process that would have started at the time when the artifacts or fossils of interest were laid down.

Both of these modes of assigning ages have great utility, and they are not interchangeable. An archaeologist would be content to assign a Mayan site to the Early Classic period on the basis of ceramics found there but would likewise try to find organic material associated with the site with which to obtain a radiocarbon date. In a sense, the methods are complementary: as more chronometric dates are obtained for a particular period, the dates alone allow the archaeologist to assign the artifact, site, etc. to a given archeological period, and vice versa.

Techniques of chronometric dating have arisen partly through the active collaboration of archeologists and scientists and in some cases through the "borrowing" of existing methods of dating by well-informed archaeologists. The methods of dating largely emerged from geology, where they had been developed to determine the timing of events in the recent geological past. However, the first such method to be applied was the result of "pure" physics and physical chemistry research: radiocarbon dating.[1] All methods of archaeological dating are based on the existence of some process acting in nature at a more or less steady rate; if we can establish the time elapsed since the process began, and if this time corresponded to an "event" in the archeological past, then in principle, we can date that event. In this brief review, I shall give examples of each of the principal dating methods; more exhaustive descriptions are available in some current texts.[2]

Methods of Radioactive Dating

1. Radiocarbon. Radiocarbon (^{14}C) is produced in the upper atmosphere by the reaction $^{14}N\ (n,p)^{14}C$. The neutrons are the product of spallation on other air molecules by cosmic rays. Radiocarbon quickly reacts with atmospheric oxygen to form $^{14}CO_2$, which is transported into the troposphere and used by photosynthetic plants. As a result, all living matter is labeled with cosmogenic ^{14}C at a level of about 10^{-12} C-atom^{-1}. Since no additional radiocarbon is taken up post-mortem, it decays by emission of a β particle at a rate determined by its decay constant:

$$d(N_{14})/dt = -\lambda_{14}N_{14} \qquad (1)$$

where λ_{14} is the decay constant of ^{14}C. The age of fossil organic matter can be determined from the residual activity of the sample, A_{14}, by solving eq 1.

$$A_{14}(T) = A_{14}(0)\ \exp(-\lambda_{14}T) \qquad (2)$$

where T is the time elapsed since death, and $A_{14}(0)$ is atmospheric ^{14}C activity at the time of death.

Radiocarbon activity can be determined by counting the rate of emission of β particles. Samples are oxidized to CO_2, which is then reduced with Li metal to LiC. Reaction with water produces C_2H_2, which is then catalytically converted to benzene. The benzene is then mixed with a fluorescent "cocktail" and placed in a scintillation counter.[3] β counting typically requires carbon sample weights >10 mg. Since the 1970s, accelerator mass spectrometry (AMS), by directly counting the number of carbon atoms, has allowed us to date samples as small as 100 μg with comparable or higher precision.[4] After the sample is converted to CO_2, it is reduced to graphite with

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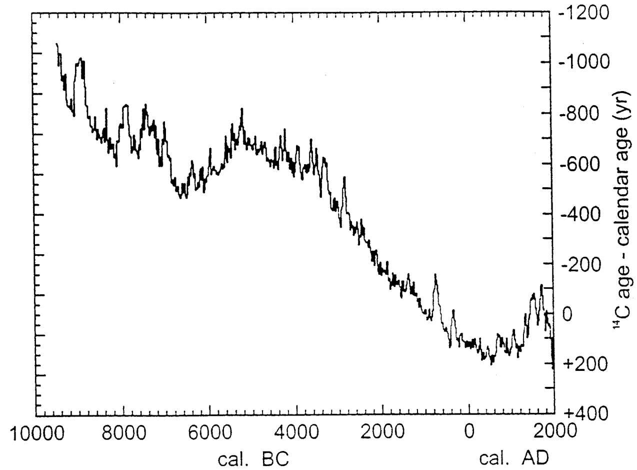

FIGURE 1. Dendrochronological calibration curve for radiocarbon dates.[54]

nickel[5] to produce a target that is then sputtered with Ar or Cs ions to generate negative carbon ions; the lower stability of negative nitrogen ions ensures a low background at a mass/charge ratio of 14. The age limit for radiocarbon dating is set by the AMS detection limit at an effective age of ~50 ka.

The rate of production of ^{14}C in the atmosphere, and therefore $A_{14}(0)$, has varied through time; as a result, it is necessary to calibrate the radiocarbon “clock’ by determining $A_{14}(0)$ in samples of independently known age. For the period up to 11 000 years before the present (11 ka BP), the calibration is performed by analysis of tree rings (dendrochronology), including those of fossil wood. Continuous sequences of tree rings have been patched together on the basis of similarities in their climatically controlled thickness. Calibration to the limit of the dating method has been obtained by radiocarbon analysis of submerged corals that were also dated by uranium series (see below)[6] and more recently by analysis of lake sediments from Japan that exhibited annual laminations (“varves”).[7] Unfortunately, as a result of “wiggles” in the consequent calibration curve, a given ^{14}C value corresponds to multiple possible ages that may range over >100 y (Figure 1); independent archaeological evidence may be required to establish the correct date.

High-resolution AMS radiocarbon dates have been used to demonstrate the late survival of Neanderthals in Europe[8] and to define the earliest arrivals of humans in North America.[9] Thanks to the large number of dating facilities worldwide, this method is responsible for the majority of chronometric dates published in archaeology.[10] The journal *Radiocarbon*, published at the University of Arizona (radiocarbon.org) contains date lists from many laboratories.

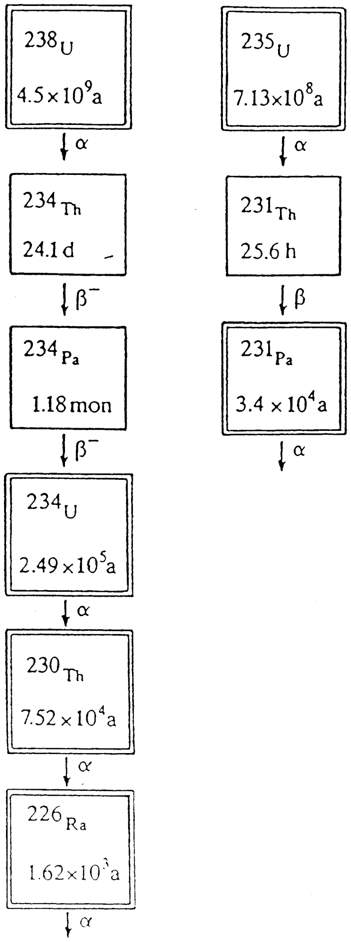

FIGURE 2. Uranium series daughter isotopes.[11]

Uranium-Series Dating. U isotopes decay through a series of short-lived daughters (Figure 2). The decay of ^{234}U to ^{230}Th can be used to date the time range $0.01-5 \times 10^5$ y; decay of ^{235}U to ^{231}Pa can be used to date events up to about 150 ky. At pH 7, U is geochemically separated from insoluble Th and Pa. Carbonate minerals precipitated from these waters contain traces of U but no Th or Pa. We can thus determine the time of formation of these materials (shells, stalagmites, travertines, tufas, etc.) from the present-day ratio of daughter to parent. For samples with an activity ratio $^{234}\mathrm{U}/^{238}\mathrm{U} = 1.00$, the activities of the isotopes in a sample in dpm/g are given by

$$^{230}\mathrm{Th} = {}^{234}\mathrm{U}\,(1 - \exp\,[-\lambda_{230}\,t]) \qquad (3)$$

where λ_{230} is the decay constant of ^{230}Th. Commonly, $^{234}\mathrm{U}/^{238}\mathrm{U} > 1.0$ in natural waters, in which case a more complex expression is used.[11]

The isotopes are determined either by counting α particles or γ rays or by mass spectrometry. Both require complete chemical separation and isolation of each parent and daughter (Th, U, Pa, Ra).[12] The elements may be plated onto planchets for α counting, onto Ta or Re filaments for thermal ionization mass spectrometry (TIMS), or injected as a solution into a multicollector inductively coupled plasma mass spectrometer (MC-ICPMS).[13] $^{230}\mathrm{Th}/^{234}\mathrm{U}-^{234}\mathrm{U}/^{238}\mathrm{U}$ ages can be obtained over the time range 10^2 to 5×10^5 y with errors of ±0.5−1% using TIMS or MC-ICPMS, while α counting gives errors of ±5−10%. Errors on ^{231}Pa dates by TIMS are ~1%.[14] Decay of ^{226}Ra deposited in excess over the activity of its parent ^{230}Th can be used to date some materials up ~6000 y.

Chemically precipitated $CaCO_3$ (stalagmites and travertines) behave most like closed systems (neither gaining

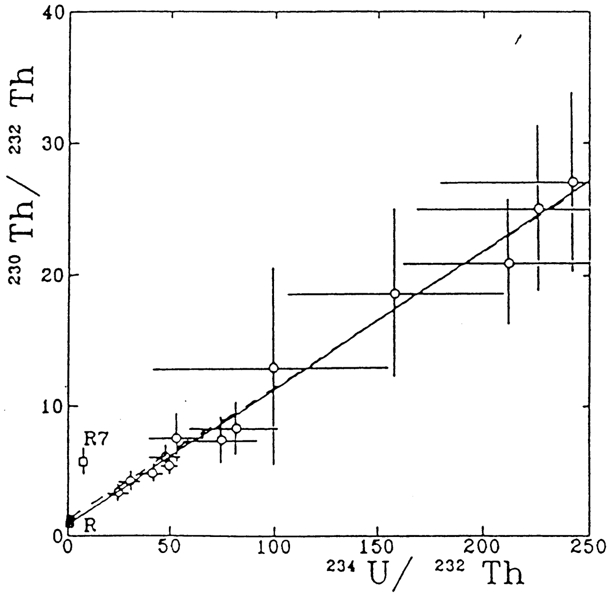

FIGURE 3. U-series isochron for contaminated samples: Plot of ^{230}Th/^{232}Th vs ^{234}U/^{232}Th. Slope of line gives the ^{230}Th/^{234}U ratio of the chemically precipitated calcite component, which was used to calculate the age. A similar plot was used to determine the ^{234}U/^{238}U ratio of this component. The ^{232}Th was entirely derived from detritus ("dirt") in the sampl.[55]

nor losing parent or daughter isotopes except by radioactive decay), but ^{230}Th and ^{231}Pa, unsupported by their parent isotopes, may be present in particles of detritus deposited with the calcite.[15,16] These can be dated using *isochrons* in which nonradiogenic, detritus-associated isotope ^{232}Th is used to normalize the activities of the U-series daughter isotopes in a series of coeval samples containing varying amounts of detrital contaminant (Figure 3). Stalagmitic layers and travertine deposits associated with archaeological sites have been dated, mainly by α spectrometry, at sites in Europe,[17,18] Israel,[19] and elsewhere. TIMS was used in a study of a cave in China where *Homo erectus* was recovered.[20] MC-ICPMS will soon displace TIMS due to its higher sensitivity and faster throughput.

U-series dating has been attempted on bones,[21,22] mollusk shells,[23] eggshells,[24] and mammalian tooth enamel.[25] These materials are initially deposited with no U; the timing of absorption of U greatly affects the calculated age,[26] often leading to controversial results.

Nondestructive dating is needed for unique samples found out of stratigraphic context (e.g., human skulls). γ-ray U-series dating is possible.[27,28] Combined ^{231}Pa/^{235}U and ^{230}Th/^{234}U dating of the same sample partly constrains the U-uptake history of the sample,[29] knowledge of which is essential for calculation of the age.

Potassium–Argon Dating.[30] Potassium-40 decays to ^{40}Ar and ^{40}Ca. K-bearing minerals are formed at high temperatures by crystallization of volcanic magmas, which results in the loss of all argon from the crystal. Thereafter, Ar may be trapped indefinitely in the crystal as long as it is not heated above a few hundred degrees Celcius. The age of the crystals can be determined by direct measurement of the abundance of K and ^{40}Ar. For very young samples, this entails an error due to the possible presence of atmospheric argon (99.6% of which is ^{40}Ar). Separate analysis of K can be avoided by neutron activation of the sample, which forms ^{39}Ar by neutron capture on ^{39}K. The age is then determined from the ^{40}Ar/^{39}Ar ratio of argon released as the sample is progressively heated in a vacuum line; the component released at low temperature typically contains most of the atmospheric contaminant. Ages are calculated from the ^{40}Ar/^{39}Ar ratio obtained at each heating step. A well-behaved sample yields a series of constant ^{40}Ar/^{39}Ar ages over a significant temperature interval ("plateau").

^{40}Ar/^{39}Ar dating is ideally suited for archaeological or paleoanthropological deposits containing layers of volcanic ash. These are found in many areas where our early ancestors (hominids) lived, notably the rift valleys of East Africa. The first dates for the genus *Australopithecus* and the ancestral species of *Homo* were obtained there beginning with the work of Evernden and Curtis.[31] Argon dating has continued to be the mainstay of East African geochronology. Other areas where this method has been fruitfully applied include Indonesia and Israel.[32]

Samples for argon dating may be whole rocks that contain a mixture of glassy and crystalline material (e.g., particles of pumice). However, the ideal samples are small single crystals of a K-rich mineral, such as high-temperature K-feldspar (sanidine), extracted from volcanic rocks. Neutron-irradiated crystals can be individually fused in a vacuum system using a laser beam whose intensity is gradually increased to liberate Ar in stages. This method (single-crystal laser-fusion Ar/Ar dating) has the advantage that minor amounts of older, contaminant crystals can be identified and excluded. These could include bits of older volcanic rock from the same volcanic vent that were entrained in younger eruptions of ash.

For Ar-isotopic analysis, a dedicated, small-volume mass spectrometer attached to an all-metal vacuum line that can be evacuated to a pressure $< 10^{-10}$ Torr is used. Errors of $<1\%$ are readily obtainable for samples in the age range >0.5 My and containing $\sim1\%$ K. The minimum age determinable for freshly erupted volcanic rocks appears to be ~0.05 My.

Trapped Charge Dating (TCD). Naturally occurring insulating solids are exposed to ionizing radiation from environmental radioactivity. As a result, electron–hole pairs are produced that are mainly annihilated through recombination. A small proportion of both charge types may be stored metastably at charge defects in the solid, such as vacant lattice sites. The gradual buildup of these trapped charges provides a clock to determine the time elapsed since the solid was formed or since trapped charges were last released by heating or exposure to light (bleaching). The abundance of the trapped charges can be determined by at least three methods: thermoluminescence (TL), optically stimulated luminescence (OSL, or IRSL where infrared radiation is used), and electron spin resonance (ESR). We determine the age of a deposit by measuring the equivalent radiation dose D_E that would

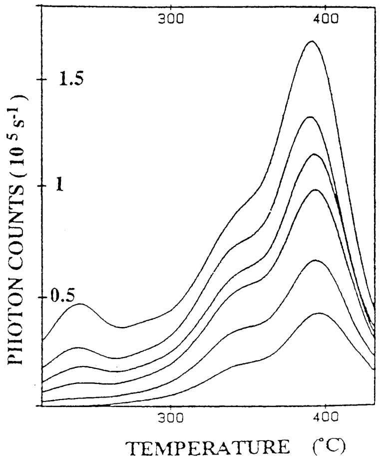

FIGURE 4. Thermoluminescence glow curve. Luminescent intensity observed as sample was heated at a constant rate; intensity is proportional to the number of stored charges in the sample material. Distinct peaks in the curve correspond to discrete charge traps in the material. In general, higher-T peaks correspond to deeper, longer-lived traps. The signal intensity increased with added doses; the lowest curve is the natural signal; the highest received 136 Gy.[56]

have been required to generate the observed charge density. Then for a sample that had been buried at time t at a site where it was exposed to a dose rate, d, we see that

$$t = D_E/d \tag{4}$$

In general, all TCD methods depend on the following assumptions: (1) at $t = 0$, D_E was set to zero by heating, bleaching, or by growth of new crystalline material (stalagmites, tooth enamel, etc.); (2) the signal has not faded significantly during storage; and (3) the dose rate has remained constant and equal to the value observed today at the site. Alternatively, part of the dose rate may have increased as a result of uptake of U in a determinable fashion.

Thermoluminescence Dating.[33] Historically, TL was the first of these methods to be developed. The minerals of ceramics fired in a kiln are zeroed by heating or growth of new minerals and can then acquire a dose as a result of exposure to the radioactive elements U, Th, and K in the soil and the ceramic itself as well as the corresponding U- and Th-series daughter isotopes. The measurement of TL is done by grinding a portion of a sherd and distributing the powder as a thin layer on a metal disk, which is then heated on a hot plate viewed by a photomultiplier tube. Recombination of electrons and holes results in emission of visible and ultraviolet light, the intensity of which is proportional to the amount of trapped charge. The sample is typically heated over a range of temperatures from 100 to 600 °C while the emitted light is continuously measured, resulting in a "glow curve" (Figure 4). Part of the curve corresponds to light emitted from energetically low-lying traps whose lifetimes are short compared to the time of burial of the sherd, while light emitted at temperatures above about 250 °C corresponds to trapped charges with archaeologically long lifetimes ($\gg 10^5$ y).

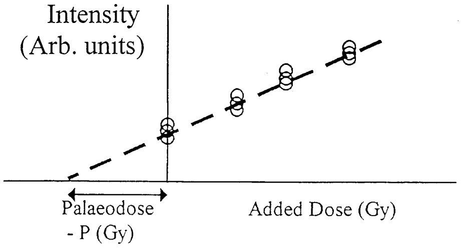

FIGURE 5. Growth curve for TL (or OSL or ESR) signals showing the additive dose method. Multiple aliquots were given additional doses of artificial radiation (β, γ), causing an increase in the intensity of the TL signal. The negative intercept is assumed to equal the dose corresponding to the natural intensity (before irradiation).

To determine D_E, part of the sample is artificially irradiated with β or γ radiation, and the increase in TL signal intensity as a function of added dose is recorded. By extrapolating this "growth curve" to zero intensity (Figure 5) we arrive at an intercept of negative added dose, which corresponds to D_E. This so-called additive dose method is widely used in all trapped-charge dating methods. The precision of the date is principally determined by errors in determination of D_E, typically on the order of 5−10%. The external β and γ doses are partly attenuated by the moisture content of the sediment. Some uncertainty in the age arises from unknown past variations in this quantity. Part of the dose (<10%) is from cosmic rays, which can penetrate up to 1 m into a sediment layer. Where samples were never buried deeply, unknown past variations in the cosmic dose rate constitute another potential source of error. Overall, errors in TL and other trapped charge dates are on the order of ±10%.

Flint and other siliceous rock types (microcrystalline SiO_2) were widely used to fabricate artifacts (arrowheads, etc.) in the past. Some objects were intentionally heated (perhaps to harden cutting edges), thus zeroing the TL signal acquired during the geological history of the material. Subsequent growth of the TL signal occurs during burial in weakly radioactive soil. The lifetime of trapped charges in flint appears to be >1 My. Therefore, it is possible to date sites to an age of ~0.5 My without having to make appreciable correction for fading of the signal.[34] The lower limit of dating is about 10 ka, below which the regrowth in signal intensity during burial is not detectible above noise. TL dating of burned flint has been used extensively to date Palaeolithic sites in Europe and the Levant.[35,36]

TL dating has also been applied to sediment whose TL signals was bleached by sunlight.[37] Although this removes a large part of the TL signal from quartz and feldspar, a residual signal is usually left which must be corrected for; many methods for doing this have been described.[38] This method has been used at a few archaeological sites,[39] although OSL (see below) has been more widely applied because of the problems of correcting for a residual signal. Another problem is that the trapped charges released by bleaching are from shallower traps and, therefore, have shorter lifetimes. As result, TL dating of bleached sediment is only applicable for sediments <200 ka in age.

Optically Stimulated Luminescence (OSL). It is possible to excite trapped charges using light. The sample is irradiated with light of one wavelength (usually a green light from a laser or filtered white-light source), and emitted light is detected at a longer wavelength as the untrapped charges recombine with holes at a recombination center.[40] Charges that are released by OSL have been trapped at shallow traps, with relatively short lifetimes and, as with TL dating of bleached sediment, the maximum date attainable by this method is <200 ka. An important difference from TL is that the OSL signal of a sediment is completely bleached to zero in a relatively short time (as little as 10 min of exposure to full sunlight). Therefore, no correction for a residual dose is required. OSL dating of young archaeological deposits is still in its infancy,[41] but the method has the capability of supplementing radiocarbon dating over the time interval 0.1−50 ky.

Electron Spin Resonance (ESR).[42] Trapped charges, like free radicals, can be detected by ESR because of their unpaired spins. They have g values close to 2.00, but signals from many different charge traps can be easily resolved. The intensity of the signal (usually measured as the first derivative with respect to magnetic field) is proportional to the number of trapped charges and, therefore, is an increasing function of D_E. Partial zeroing of ESR signals may occur by heating or bleaching, but the most common application of ESR in dating is the analysis of newly formed minerals, especially hydroxyapatite [$Ca_5(PO_4)_3$ (OH, CO_3)] which is the mineral component of tooth enamel and bones. Teeth are very stable with respect to chemical alteration and are present as a ubiquitous component of archaeological sites. An ESR signal with $g = 2.0018$ is generated in tooth enamel as it is exposed to environmental radiation. The lifetime of this signal appears to be $\gg 10^8$ y. Equivalent doses are determined by the additive dose method with a precision of a few percent. Determination of the dose rate to which fossil teeth are exposed during burial presents some problems, however. The external dose to the enamel consists of the β and γ doses arising from U, Th, and K in the sediment as well as a β particle dose from adjacent dentine that penetrates up to 2 mm in the enamel. Uptake of U by the dentine (to levels that may be many times that of the surrounding sediment) as well as growth of U-series daughters from the absorbed U leads to a gradual increase in the dose rate, d. In addition, during burial, the enamel absorbs some U, which adds to the β dose as well as contributes an α-particle dose (with a range of 30 μm). The total dose rate depends on the U-uptake history. Conventionally, we assume that the uptake trajectory $\{[U] = f(t)\}$ lies between two models: early uptake (EU), in which the present day [U] was acquired soon after burial; and linear uptake (LU), in which an equal amount of U is absorbed yearly. For a given value of D_E and other measured parameters, the EU age is always smaller than the LU age, and for samples with large amounts of U in the dentine, $t(EU) \approx 0.5\, t(LU)$. Where [U] in the tooth is low, $t(EU) \approx t(LU)$. As with TL and OSL, the moisture content of the surrounding sediment and depth with respect to cosmic ray exposure affect the dose rate. The thickness of the enamel layer being analyzed is also critical because of its effect on the attenuation of β particles.[41]

ESR dating has been applied to tooth enamel from sites throughout the Old World, including Europe,[43] Israel,[44] Africa,[45] China,[46] and Australia.[47] Rink[42] has summarized many of the ESR studies of archaeological sites. Using ESR methods, Swisher et al.[48] showed that *Homo erectus* persisted in Java (Indonesia) until at least 55 ky.

In quartz (SiO_2), holes trapped where Al and Ti atoms have substituted for Si can be bleached by sunlight.[49] This raises the possibility of dating archaeologically associated quartz sands that were exposed to sunlight before deposition. The lifetime of these trapped holes appears to be a few My, as inferred from agreement between ages calculated for geological deposits of known age, but the stability of these signals is not yet well-established.

Amino Acid Racemization. All amino acids except glycine exhibit stereoisomerism. Biologically synthesized amino acids are almost entirely L-enantiomers. The amino acids of proteins extracted from fossil bones and other organic materials are partially or wholly racemized or epimerized. The rate of racemization of a given amino acid in a specific protein is principally determined by the temperature, the first-order rate constant, k, being given by

$$k = \mathrm{A}\exp[\mathrm{E}/\mathrm{RT}] \qquad (5)$$

The ratio of D- to L-isomers in a sample increases with time according to the relationship[50]

$$\ln[\{1 + (\mathrm{D}/\mathrm{L})\}/\{1 - (\mathrm{D}/\mathrm{L})\}] = 2kt \qquad (6)$$

For some fossil materials, specifically ostrich eggshells[51] and mollusk shells,[52] the rate constant for epimerization of isoleucine to alloisoleucine is slow enough that this process can be used to determine the age of a sample from an archaeological site as long as (a) the rate can be calibrated for that site and (b) the rate remained relatively constant during the burial history of the site. Over a time scale-up to ∼0.3 My, the *AI/I* rate allows us to date ostrich shells from regions such as the Sahara and Kalahari Deserts, or marine shells from coastal sites in temperate regions. This method, called amino acid racemization (AAR) dating, has been used to establish the chronology of some important sites in Africa, including Border Cave in South Africa.[53] The calibration of the rate constant is usually based on radiocarbon dating of a shell <40 ky in age, although U-series dating of associated carbonates has also been used. Many sites are intrinsically poorly suited to AAR dating, because they have experienced large shifts in temperature during the burial history of the analyzed material.

Analysis of shell samples (both molluscan and avian) generally begins with demineralization with dilute acid. This is followed by treatment for 24 h with hot HCl to hydrolyze the protein into its component amino acids. The measurement of the D/L ratio can be done by automated chromatography, using a chiral column to separate D and L isomers.

Conclusions

The history of the scientific study of archaeological dating is relatively brief, and we have already witnessed surprising novelties that opened new avenues of analysis. Until a few years ago, most of the new methods of dating that became available arose as byproducts of geological research, but in the past few years a discrete cadre of dedicated "archaeometrists", scientists dedicated to the analysis of archaeological sites and their constituent materials, has arisen. These scientists, in collaboration with chemists, physicists, and other scientists, are actively developing new methods that are specifically adapted to the kinds of materials found at sites. Despite this, we still find a marked level of scepticism on the part of archaeologists when presented with chronometric dates that are in conflict with current opinions. Of course, we disregard these concerns at our peril: we must be aware that the archaeological record itself exhibits a chronological, evolutionary sweep that provides an independent, somewhat fuzzy record of the relative timing of hominid evolution.

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