magnetic rocks. South of these areas in western Antarctica the terrane is generally quite devoid of anomalies, with occasional exceptions. This is probably the result of sedimentary or metasedimentary rock, since 14 km of metasediments were reported in the Sentinel Range (*6*). The dividing line between this sedimentary province and the volcanic areas to the northwest and the Antarctic Peninsula is quite abrupt and can be traced reasonably accurately from profile to profile. It appears likely that the sedimentary rock extends east beneath the Filchner Ice Shelf.

The Trans-Antarctic Mountains have areas of numerous anomalies of narrow width and other areas with essentially smooth fields. It is quite possible that the anomalous areas are caused by the McMurdo volcanics (*7*) of late Cenozoic age. The dolerite sills (*7*) intruding into the late Paleozoic-Mesozoic Beacon system do not have susceptibilities high enough to produce the observed anomalies (*8*). The flight from McMurdo to Wilkes shows a number of anomalies which are probably associated with ancient intrusive or extrusive rocks of the pre-Cambrian shield in this area. The highest anomalies observed in Antarctica occur in the area around 67°S, 140°E. The Project Magnet flight in this area recorded one anomaly with an amplitude of about 3500 gamma.

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Radiocarbon Dating of Bone and Shell from Their Organic Components

Abstract. *A method of dating bone and shell by radiocarbon content has been developed. The mineral is removed by mild acid treatment and the residual carbon is dated in the usual manner.*

Until recently, the radiocarbon dating of archeological bone samples was based primarily on the dating of associated charcoal, and in some cases on the natural calcium carbonate contents of bones. However, dates by correlation with charcoal may not always be correct. Even greater doubts exist on the accuracy of dates based on calcium carbonate which may have been replaced by ground-water carbonate of varying age.

It is now possible to date bones directly from their content of organic carbon or collagen (*1*). There is no known natural mechanism by which collagen may be altered to yield a false age.

Generally dry modern bone is composed approximately of 50 percent calcium phosphate, 10 percent calcium carbonate, 25 percent collagen, and 5 to 10 percent bone fat, and the remainder is made up mainly of mucopolysaccharides, calcium fluoride, magnesium phosphate, sodium salts, and heavy elements such as iron and manganese.

Collagen is characterized chemically as a protein with a low content of aromatic amino acids and a high content of pyrrolidine amino acids (proline and hydroxyproline) as well as glycine. Also, it is specifically hydrolyzed by the enzyme collagenase. Collagen is found as fibrils 0.3 to 0.5 μ thick throughout bone. The individual fibrils are often collected into bundles of 3 to 5 μ. The physiological turnover of collagen is very slow as determined by isotopic measurements. Bone collagen is chemically indistinguishable from the collagen in cartilage, skin, and tendon.

The bone mineral is composed of crystals of chiefly calcium phosphate with the structure of a hydroxyapatite $[Ca_3(PO_4)_2]_3 \cdot Ca(OH)_2$. The crystals are oriented along the major axis of the collagen fibrils. Roughly speaking, bone has the structure of a brick wall. The bricks are apatite; the mortar consists of citrate, carbonate, and other ions; and the collagen fibers act as reinforcing strands in the loosely assembled intercrystalline matrix.

There have been attempts to use the carbonate portion of bones for radiocarbon dating by liberating carbon dioxide with hydrochloric acid. However, one may arrive very easily at fallacious dates because ground water contains atmospheric carbon dioxide of modern carbon-14 age. This carbonate can be exchanged with radioactively dead carbonate in the soil (limestone). Therefore, ground-water carbonate may possess a radiocarbon age of anywhere from 0 to 5730 years (50-percent exchange). Theoretically, bones immersed in modern carbonate water could be dated as being too young and bones in radioactively dead water as being too old. Since older bones have a much less preserved structure than young bones, the error will be most pronounced in older specimens owing to the possibility of greater exchange.

These considerations led to the dating of bones from their collagen—which does not suffer from exchange phenomena. However, the collagen content of bone decreases with age to such low concentrations that isolation of sufficient collagen for radiocarbon dating becomes difficult with the oldest bones. The oldest specimen that has been dated in this way had a collagen content of about 0.16 percent. It was about 9000 years old (UCLA–630). Unfortunately collagen does not decrease uniformly with age for finds around the world. For example, a 4000-year-old bone (UCLA–140) from Santa Rosa Island, California, buried in dry, permeable soil had a collagen content of about 15 percent whereas a 3300-year-old bone buried in moist English conditions had only 10 percent (*1*). When bones of different ages are found in the same general locality, they can be relatively dated, depending on their collagen content. Cook and Heizer were able to arrive at reasonably good absolute dates for bones derived from their collagen content for the general area of the southwestern United States (*2*).

Bones of the same age have a different collagen content in different environmental conditions in which they

were buried because of (i) invasion by saprophytes, possibly fungi or algae which feed on the organic material and perhaps also on the mineral matter (*3*), (ii) collagenase (*4*) activity in the bone, and (iii) ground-water erosion. Therefore, variations in local moisture, temperature, and microfauna or -flora will greatly influence the rate of bone destruction. Moreover, bones should be checked microscopically for excessive bore canals with associated possible foreign protein.

In order to carry out a radiocarbon analysis with maximum accuracy in the carbon dioxide proportional counter of this laboratory, about 5 grams of carbon or 10 grams of collagen are needed for a complete counter filling. Since it is often desirable to estimate how much bone has to be sacrificed for a carbon-14 analysis, the nitrogen content of the bone is determined (*1*). The amino acids of collagen all contain nitrogen which is proportional to the amount of carbon present. Usually only 50 to 100 mg of bone is needed for a micronitrogen determination. If one multiplies the result by 3.0 ± 0.5, the expected quantity of collagenous carbon is obtained. And because collagen contains roughly 50 percent carbon, the total collagen content may be quickly estimated. Modern bone has about 4.7 percent nitrogen.

For the chemical treatment of bones after cleaning and inspection, one of the following methods may be selected.

1) The bone is treated in 1.0*N* hydrochloric acid at room temperature, which dissolves the mineral matter but leaves behind about 95 percent of the collagen as insoluble material. Sometimes the mineral matter may not dissolve entirely and short treatment with more concentrated hydrochloric acid is advisable. Because none of the insoluble mineral matter after treatment with hydrochloric acid can contain inorganic carbonate, it may be filtered off with the collagen on a glass paper filter.

2) The bone is dissolved completely in concentrated hydrochloric acid under refluxing which destroys both the inorganic and the collagen matrix. After evaporation to dryness to remove all hydrochloric acid, a minimum of water in a polyethylene or Teflon beaker is used to dissolve the residue. Then hydrogen fluoride is passed into the solution and the calcium fluoride precipitate is removed by centrifugation. The supernatant is allowed to evaporate. This method permits recovery of all organic compounds originally in the bone sample.

3) Bone is treated in a dialysis bag with 10 percent aqueous ethylenediamine tetraacetic acid (EDTA) or another tertiary amine carboxylic acid. This removes the inorganic ions by chelate formation. The collagen remains behind in the dialysis bag. It is then washed with distilled water and collected.

Of all these methods the first is most convenient in terms of ease and man-hours; it needs the least chemical manipulation and does not introduce any carbon compounds during the treatment. Small amounts of carbon of different age introduced into the sample may give rise to appreciable errors which call for painstaking care in processing. In any carbon-14 age determination, ~ 0.1 gram of carbon of infinite age will increase the age of a 6000-year-old sample to almost 7000 years if only 1 gram of the sample carbon is available.

After drying the collagen or residual organic mixture, it is converted in a stream of oxygen to carbon dioxide. The combustion train contains, for purification, traps filled with 0.1*N* silver nitrate, a Vycor tube filled with hot copper oxide (600°C), chromic acid traps, and a tube containing hot copper (475°C).

For some unknown reason, the carbon dioxide obtained in this way is not yet suitable for proportional counting, which demands gas samples of very high purity. Therefore, the crude carbon dioxide is absorbed in ammonium hydroxide and precipitated from the heated solution with hot calcium chloride. The resulting calcium carbonate is washed extensively with distilled water. Then carbon dioxide is liberated with hydrochloric acid and counted. If the Ca^{++} used is low in radium, then this process will remove radon also. The presence of radon would lower the accuracy of the analysis. The nature of the impurities which necessitate one or sometimes even two precipitation steps is unknown.

In order to show that collagen of bone and other simultaneously living material is of the same age, an American Indian mummy called "Whiskey Lil" from Chimney Cave, Lake Winnemucca, Nevada, was studied (*5*). Bone collagen (~ 20 percent) gave an age of 2500 ± 80 years (UCLA–689). The skin yielded an age of 2510 ± 80 years (UCLA–690), and a cedar bark knotted mat in which the body was wrapped was 2590 ± 80 years old (UCLA–692).

Another comparative analysis was performed on some partially charred bison bones from an ancient barbecue at Sage Creek, Wyoming (*6*). The sample was split into ordinary bones and those that were charred. The regular bones were 8750 ± 120 years old based on 4.3 percent collagen (UCLA-697A). The charred bones were treated with concentrated hydrochloric acid, which hydrolyzed all organic matter but left charred carbon pieces intact. These were isolated and gave an age of 8840 ± 140 years (UCLA–697B). The same sample had been analyzed in the original Chicago Radiocarbon Laboratory, where a lower age had been obtained by the solid carbon counting method. The difference is probably due to alcohol not uniformly "dead" used in the preparation of the very early samples before ethylene as a quenching agent was introduced.

Other human bones from a Santa Rosa Island canalino were 3970 ± 100 years old (UCLA–140) (*5*) when dated with collagen. Associated charcoal yielded an age of 4260 ± 85 years (UCLA–140). The discrepancy may be due to an intrusive burial. Similarly, human bones from India were 1800 ± 100 years old (UCLA–684) and associated charcoal 2270 ± 110 years (TF–90) (*7*). Some Indian bones from a site near Chillicothe, Ohio, were 2180 ± 80 years old (UCLA–685) (*8*). A dwarf mammoth bone from Santa Rosa Island, California, yielded an age of 8000 ± 250 years (UCLA–705) (*5*).

Several animal bones were dated from one of the most important African archeological findings, that of *Homo rhodesiensis* from the Broken Hill cave (*9*) in Northern Rhodesia. The results, by this new technique, gave an age greater than 9000 years (UCLA–630B) (*10*). There is unfortunately no clear-cut relation between these bones and the skull of *Homo rhodesiensis*.

However, there may be a way of dating this or similar finds. First all pertinent bones must be collected. Then all the bones are analyzed for their nitrogen, organic carbon, uranium, and fluorine content. The older bones will have less nitrogen and organic carbon than the younger ones, but more uranium and fluorine. All

analytical data of a bone should be considered because of inconsistencies, as pointed out by Oakley (*11*). Based on these data, the bones are arranged in order of their relative age. Where there is a sufficiently large bone sample with enough collagen, the radiocarbon age is determined. This then will yield an age scale with a number of fixed points to which the analytical data of a small amount of bone sample, say from the skull of *Homo rhodesiensis*, is compared. With prudent interpolation one may arrive in this manner at its age.

Besides collagen, dentin—the organic matter in teeth—can also be utilized for dating except that modern dentin has inherently only approximately two-thirds of the collagen content of bone. But the possibility of dating ivory, such as tusks from mammoths, and so forth, is indicated.

Radiocarbon laboratories have reported many shell dates from the carbonate of the shell as the sample. Recently several papers have appeared that point to the unreliability of data from river shells (*12*) and land snail shells (*13*) because of the varying and unknown amounts of "dead" carbonate from limestone that are incorporated by the living organism.

This problem is not encountered with marine shells. But when they are dead and buried they may be subjected—like bones—to various groundwater environments (*14*). Usually investigators have attempted to circumvent possible errors arising from carbonate exchange by removing the outer layer of shells with hydrochloric acid and using only the central portion for dating.

Similar to bones, shells also contain an organic protein constituent, conchiolin, which is present in 1- to 2-percent amounts in modern shells. The two major inorganic components of shells are calcium carbonate in the form of calcite and harder aragonite, which are arranged like bricks in a wall with the conchiolin being the mortar. In contrast to collagen, conchiolin contains mostly glycine, alanine, aspartic acid, and serine (*15*). Its solubility characteristics are similar to those of collagen.

Thus conchiolin can be prepared for dating in a manner analogous to the treatment of collagen in bones. Usually kilogram amounts of raw material of shells are required in contrast to decagrams for bones.

Shells suffer destruction in time mainly from boring organisms which are smaller shells or sponges. These organisms excrete from their accessory boring organ a fluid which dissolves carbonate and eases the mechanical work of the borer. After general loosening of the carbonate layers ground-water erosion can act more destructively than before. In the absence of organisms, even in a moist environment only moderate changes occur in the protein of shells which affect its solubility. After about 10^4 to 10^5 years, only about 1 to 5 percent of the peptide bonds are broken, and the protein fragments are leached out of a shell (*16*).

It is interesting to note that while bones have an initially higher collagen content, after 8000 to 10,000 years or much more, shells can have comparable amounts of conchiolin left, indicating a faster decay rate of the more loosely assembled bones in contrast to the much tighter structure of shells.

Several abalone shells (*Haliotis*) from Santa Rosa Island, California, were dated. One set of shells gave an age of 7120 ± 120 years for the outer carbonate layers (UCLA–663) and 7230 ± 120 years for the inner layers (UCLA–663). The organic portion (~ 0.4 percent) yielded a corrected date of 7210 ± 400 years (UCLA–663). Similar results were obtained from a sample about 1000 years younger (UCLA–659). The correction (*17*) used (250 ± 50 years) takes into account the threshold which atmospheric carbon dioxide experiences before it enters the ocean and the upwelling characteristics of the ocean currents on the Southern California coast.

Besides such large shells as abalone, smaller shells commonly associated with Central American burials may be dated. For example, a Lunarca-type shell of 2700 ± 90 years (UCLA–687–1) still had a conchiolin content of 0.15 percent which is sufficient for conchiolin-based dating provided kilogram amounts of sample are available.

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Site of Preference Energy and Selective Uptake of Transition-Metal Ions from a Magma

Abstract. *Results of absorption spectra measurements on silicate glasses of various compositions indicate that ions of the first transition-metal series are present in tetrahedral and octahedral sites in silicate melts (glasses). The fractionation patterns observed for transition-metal ions between magmas and silicate minerals can be interpreted according to crystal field theory in terms of octahedral "site preference energies" of transition ions in crystal lattices.*

Numerous explanations have been offered for the distribution of trace elements during magmatic crystallization (*1*, *2*). Most of the proposals are modifications and extensions of the classical Goldschmidt criteria (*3*) of ion size and charge, but all of the explanations lack generality, particularly