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Radiocarbon: Analysis of Inorganic Carbon of Fossil Bone and Enamel

Abstract. *Carbon dioxide from calcium carbonate in fossil bone can be selectively separated from carbon dioxide in bone apatite by hydrolyzing the sample first in acetic acid and then in hydrochloric acid. Radiocarbon analyses of the inorganic carbon dioxide in three samples of known age clearly show calcium carbonate in fossil bone to be secondary and the carbonate of bone apatite to be indigenous and suitable for dating in some cases. Agreement between dates on collagen-bone apatite pairs increases the level of confidence.*

In a previous publication in which radiocarbon analyses of organic fractions of fossil bones was reported (*1*), I concluded that only collagen that has been purified of humic acids and other secondary organic matter gives reliable ages with the C^{14} method. The analyses of inorganic carbon of fossil bone and enamel reported here is a continuation of this research to investigate the reliability of fossil bones and teeth for radiocarbon dating.

It has long been recognized that most of the calcium carbonate in fossil bone is secondary and hence younger than the host. Therefore, carbon from this source is not reliable for age dating the animal (*2*), although it may provide useful geochemical data on secondary carbonate deposition and levels of ancient water tables (*3*).

The precise chemical structure of the inorganic matter of living bone and tooth enamel has been under investigation for over a century. The main constituent of bone and tooth inorganic matter is calcium phosphate (bone apatite) with varying proportions of fluoride, hydroxyl, and carbonate ions (*4*) Unless exchange has taken place the carbonate from bone apatite should be indigenous and reliable for age dating by the radiocarbon method.

In order to analyze the carbonate from bone apatite, that from calcium carbonate must first be completely removed before the bone apatite can be hydrolyzed. Experimentation with mineral specimens of carbonyl apatites, fossil tooth enamel, and calcite revealed that acetic acid would completely hydrolyze calcium carbonate and not appreciably affect apatite even after prolonged treatment. Apatite could then be hydrolyzed with hydrochloric acid and the carbon dioxide thus released analyzed in the standard way for C^{14}.

In order to test the possibility that bone apatite carbonate is indigenous, three of the same bone samples that had been used for analysis of the organic fraction were selected for analysis of bone carbonates. In addition mammoth tooth enamel was included for comparison with bone. The Lehner and Hell Gap samples yielded x-ray powder diffraction patterns typical of bone apatite. The data, including the earlier analyses corrected for fractionation of the standard, are presented in Table 1.

The Lehner archeological site, Arizona, is where Clovis hunters killed mammoths 11,260 years ago, as determined by the radiocarbon method (*5*). Both calcium carbonate (*6*) and bone apatite of mammoth bone from the Lehner site were analyzed. The calcium carbonate (A-806C) is 10,000 years younger than the bone deposit and is obviously secondary, but the bone apatite carbon (A-874C) is only a little more than 1000 years younger than the bone. It is, in fact, the oldest of the four fractions dated, suggesting that under the geochemical conditions at the Lehner site carbon from bone apatite is more stable than collagen.

Table 1. Carbon-14 analyses of organic and inorganic carbon of fossil bone. Laboratory numbers of the samples are given in parentheses.

Fraction	Lehner mammoth bone	Lehner mammoth tooth	Hell Gap bison bone	Murray Springs bovid bone
	C^{14} age*	C^{14} age	C^{14} age	% Modern standard
First $CaCO_3$	1,190 ± 90 (A-806C)		700 ± 260 (A-753C_1)	125 ± 4.6 (A-819C)
Second $CaCO_3$			6,130 ± 500 (A-753C_2)	
Apatite CO_2	9,980 ± 220 (A-874C)	7,780 ± 150 (A-876C)	9,050 ± 160 (A-753C_3)	
Organic residue	5,610 ± 350 (A-806A)†		8,890 ± 110 (A-753A)	103.5 ± 3.0 (A-819A)
Humates and soluble organic carbon	7,930 ± 490 (A-806D)		5,430 ± 110 (A-753D)	102.4 ± 2.8 (A-819B) 100.9 ± 2.4 (A-819D)
Fulvic acids				98.8 ± 6.7 (A-819E)
Total percentage of organic carbon				
	0.63		3.68	1.28
Percentage of apatite carbon‡				
	0.82	1.55	0.66	
True age				
	11,260 ± 360	11,260 ± 360	8,600 ± 300	50 to 500

* Expressed as years B.P. (before 1950). † Not collagen, but probably includes some decay products of collagen. ‡ Based on weight of sample after removal of calcium carbonate.

Carbonate from the apatite of a Lehner mammoth tooth (A-876C) was younger than that from bone by 2000 years, which indicates that tooth apatite is less stable than bone apatite under the geochemical conditions at the Lehner site. It will be surprising if this turns out to be true generally, because tooth enamel is more dense than bone and therefore believed to be less subject to replacement or exchange by diffusion of solutions. On the other hand, the apparent difference in age could be due to differences in permeability between the sedimentary matrices of the bone and tooth, where the tooth was in a coarser, more permeable sediment than the bone was.

At the Hell Gap, Wyoming, site of early man, bone (probably bison) was collected from an archeological horizon that is correlated with a similar unit nearby that has been dated at 8600 ± 380 years old (A-501) (*3*, p. 15). Both the collagen date (A-753A) and the bone apatite date (A-753C_3) are in statistical agreement with each other and with the correlated date, which indicates that carbonate from the bone apatite is indeed indigenous. The calcium carbonate was hydrolyzed in two stages; the resulting dates (A-753C_1 and A-553C_2) clearly indicate it to be secondary. The difference in age is probably caused by the fact that the outermost layers of secondary carbonate are the youngest and the first to be attacked by acid during hydrolysis.

The Murray Springs bovid bone is from a sedimentary unit that is believed to be between 50 and 500 years old. All the organic fractions show a slightly post-thermonuclear age (1960), which suggests contamination from bomb-produced C^{14}. This interpretation is supported by the result of the calcium carbonate analysis (A-819C): 125 ± 5 percent of the C^{14} content of the modern standard. However, because the buried bovid skeleton is known to be of prenuclear age and because there was a 2.5-percent increase in the atmospheric C^{14} budget approximately 250 years ago (*7*), I believe that the yearling lived within a few years of A.D. 1700. Unfortunately, the bone apatite fraction has not been analyzed.

From the research reported here it is concluded that the inorganic carbon of fossil bone is in two separate mineral phases, one of which (calcium carbonate) is of secondary origin, whereas the other (bone apatite) is indigenous. Collagen free of secondary organic matter and bone apatite free of calcium carbonate can yield reliable radiocarbon dates, but contamination by insoluble noncollagenous organic matter (for example, saprophytes) and exchanged carbonates in bone apatite cannot always be precluded. Agreement between analysis of the two fractions is probably reasonable, but not conclusive, assurance that the radiocarbon age is correct.

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Seismic and Bathymetric Evidence of a Fracture Zone on Gorda Ridge

Abstract. *Swarms of seaquakes have been located hydroacoustically on Gorda Ridge near 41.5°N, 127.6°W, where detailed bathymetric charts indicate a slight dextral offset of the rift valley in the center of the ridge. It is suggested that a fracture zone may be nascent in the area.*

Recent work has shown that smaller submarine earthquakes (seaquakes) are located hydroacoustically than by the existing land-based seismographic network (*1*). During the years 1965 through 1967, seaquakes have been routinely located in the Pacific Ocean Basin from arrival times of earthquake T-phases at hydrophones placed in the deep-ocean SOFAR (SOund Fixing And Ranging) channel at Eniwetok, Wake, Midway, and Oahu islands and off California (*2*); in the eastern Pacific most of those located were on the East Pacific Rise. The accuracy of location, relative to published earthquake epicenters (*3*), depends on the source-receiver geometry, accuracy of reading of arrival times, and knowledge of sound speed in the SOFAR channel. In the area of Gorda Ridge off the coasts of Washington and Oregon, location of sources by T-phase is especially good because the phones are distributed about the source, a nearby detection hydrophone off Cape Mendocino was used, and sound speed in the SOFAR channel is well known.

Epicentral times of earthquakes located by the U.S. Coast and Geodetic Survey on Gorda Ridge, Blanco Fracture Zone, and Juan de Fuca Ridge were compared with those of the corresponding T-phase source times; there was a mean difference of 5 seconds, with a standard deviation of 24 seconds, for 70 events between August 1965 and December 1966. (A 5-second error in time of origin means an error in location of about 7.3 km when a sound speed of 1.47 km/sec is used.) These epicenters were plotted on a large-scale (1:828,000) chart along with 955 additional epicenters located by T-phase that were presumably too low in magnitude to be detected by the Survey (which routinely locates earthquakes of magnitude 4 or greater). This plot was then laid over a detailed topographic map of the area. Figure 1 shows the Gorda Ridge section, scene of 78 percent of the epicenters located by T-phase. The epicenters are in two major zones: (i) a north-trending belt between 41° and 43°N, near 127.5°W; and (ii) a northwest-trending belt between 43° and 45°N and between 127° and 130°W. These seismic belts correspond to Gorda Ridge and Blanco Fracture Zone, respectively, as defined on the basis of bathymetry (*4*, *5*). Thus, as has been demonstrated (*6*), the earthquakes are not restricted to fracture zones.

The greatest concentration of epicenters is at 41.5°N, 127.6°W. South of this cluster the epicenters are in the central rift valley [Escanaba Trough (*5*)] of Gorda Ridge. North of the cluster, epicenters occur along a line trend-