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PHYSICAL AND CHEMICAL COMPARISON OF MODERN AND

FOSSIL TOOTH AND BONE MATERIAL

by

Elizabeth B. Jaffe and A. M. Sherwood

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CONTENTS

	Page
Abstract	6
Introduction	7
Review of previous work	10
Optical and morphological changes	11
Changes in chemical composition during fossilization	12
Structural changes in fossilization	19
Summary and conclusions	20
References	21

TABLES

	Page
Table 1. Identification of samples studied in this report ...	8
2. Partial chemical analyses of Recent and fossil bones and teeth	13
3. Chemical analyses of selected Recent and fossil manatee ribs	15
4. Chemical analyses of Recent and fossil manatee bones, recalculated from Carnot	16
5. Chemical analyses, calculated to apatite, of mineral matter of selected Recent and fossil manatee ribs	17
6. Carbonate content of Recent and fossil bone before and after leaching	18

PHYSICAL AND CHEMICAL COMPARISON OF MODERN AND
FOSSIL TOOTH AND BONE MATERIAL

by

Elizabeth B. Jaffe and A. M. Sherwood

ABSTRACT

Ten samples of manatee ribs and shark teeth from the land-pebble phosphate deposits of Florida are here compared chemically and physically to one Recent manatee rib collected in Florida waters. Experimental studies comparing the Recent bone with the fossil manatee bones revealed that the fossil bones have lost free carbonate and combustible organic matter, that they have gained in fluorine and ignited insoluble residue, and that some of the fossil bones have gained in uranium content. The refractive index, birefringence, and apparent homogeneity of the fossil bones are greater than those of the Recent bone. The X-ray diffraction pattern of the fossil bones matches a carbonate-apatite pattern; that of the Recent bone is a weak apatite-group pattern with diffuse lines. These variations indicate that some modification in the structure of the mineral matter of the bone has taken place during fossilization.

INTRODUCTION

Several manatee ribs and shark teeth from the Florida land-pebble phosphate deposits are here compared to a Recent manatee rib from Florida waters, in order to ascertain the changes that have taken place during fossilization of these bones. Because only one Recent bone was available for study, results of this comparison must necessarily be tentative.

Most of the fossil bones and teeth were collected by V. E. McKelvey, A. P. Butler, Jr., and Katharine Lutz in the spring of 1950. They were obtained from dumps of two phosphate mines, so that their original stratigraphic location is unknown. Two of the fossil manatee bones (samples M-1 and M-2) were collected by Z. S. Altschuler, E. J. Dwornik, and C. E. Boudreau in February and March 1950 and are from stratigraphically known horizons. Fossil manatee ribs are common in both the Hawthorn and Bone Valley formations (Simpson, 1932, pp. 425 and 445) but as the Hawthorn formation is less commonly mined for phosphate, it is assumed that the bones and teeth from dumps are from the Bone Valley formation of Pliocene age. However, at least a part of the Bone Valley formation may be reworked from the Hawthorn, and the bones may thus be of either Miocene or Pliocene age.

The locations from which these bones were collected are given in table 1.

The fossil manatee ribs probably belong to the genus Felsinotherium, a dugongid form, most common in the Bone Valley formation (Simpson, 1932, p. 453); the Recent rib, U.S.N.M. 228478, was made available to

Table 1.--Identification of samples studied in this report

Sample no.	Material	Location
M-1	Fossil manatee rib	Watson mine, Swift and Co., sec. 9, T. 32 S., R. 29 E.
M-2	Fossil manatee rib	Homeland mine, Virginia-Carolina Chemical Corp., sec. 4, T. 31 S., R. 25 E.
M-3	Fossil manatee rib	Boyette mine, American Agricultural Chemical Corp., sec. 14, T. 31 S., R. 21 E.
M-4	Fossil manatee rib	Boyette mine
M-5	Fossil manatee rib	Boyette mine
M-6	Fossil manatee rib	Peace Valley mine, International Minerals and Chemical Corp., sec. 15, T. 31 S., R. 25 E.
M-7	Fossil manatee rib	Peace Valley mine
M-8	Fossil manatee rib	Peace Valley mine
M-9	Fossil manatee rib	Peace Valley mine
M-10	Fossil manatee rib	Peace Valley mine
M-11	Fossil shark teeth	Sidney mine, American Cyanamid Co., sec. 28, T. 29 S., R. 21 E.
M-12	Fossil shark teeth	Boyette mine, American Agricultural Chemical Corp., sec. 14, T. 31 S., R. 21 E.
M-13A	Recent manatee rib (middle) <u>Trichechus latirostris</u> , U.S.N.M. 228478	Jupiter, Florida
M-13B	Recent manatee rib (end) <u>Trichechus latirostris</u> , U.S.N.M. 228478	Jupiter, Florida

us through the courtesy of F. S. MacNeil and the U. S. National Museum. Its location is given as Jupiter, Florida. It is identified as Trichechus latirostris, a trichechid: thus it belongs to a different branch of the Sirenia. The bone material, however, should not have been substantially different originally, as both sea cows presumably inhabited similar environments.

Without knowing the stratigraphic location of the fossil bones and teeth it is impossible to compare their composition with that of stratigraphically comparable apatite of the phosphate deposits; therefore this study has no direct bearing on the problems of long-term epigenetic alteration and enrichment in uranium and phosphorus of the phosphorite deposits. Any future work should be carried out on samples of known stratigraphic location, so that the results will be of more than purely academic interest. It would also be desirable to study several Recent manatee ribs, preferably from different parts of the world, to see whether differences in availability of U, P_2O_5 , and F have any influence on the composition of fresh bone, or whether the enrichment in U and F is purely an effect of fossilization.

Acknowledgments and thanks are due to our associates at the Geological Survey: Harry Levine, Norma Guttag, and J. J. McGee who did preliminary chemical analyses; H. L. Waring and Helen Worthing who made spectrographic analyses; Sol Silverman, Ruth Fuyat, and Jeanne Weiser who made solubility tests for fixed and free carbonate and allowed the use of their unpublished results (Silverman, Fuyat, and Weiser, 1951); and Evelyn Cisney who did the X-ray work.

REVIEW OF PREVIOUS WORK

The changes that take place in bone during fossilization have been studied by many geologists. Carnot (1893) showed that the fluorine content of bone increases with fossilization and may be used as a rough index of geologic age; however, owing to the variation in the amounts of fluorine available in different localities, the fluorine content of bone can be used to indicate a relative age only. Oakley (1950) determined the fluorine content of human and animal remains from the Piltdown gravels, and was able to show that all of the animal remains "of undoubted Lower Pleistocene (Villafranchian) age proved to contain 2-3 per cent. fluorine, while all those of certainly later date showed less than 1.6 per cent. fluorine" whereas, on the basis of their average fluorine content of 0.2 percent, "all the specimens referred to Eoanthropus are contemporary, and ... their age is not Lower Pleistocene, but considerably later." Many other papers tend to confirm these results. Hendricks, Hill, Jacob, and Jefferson (1931) postulate that not only bone, but carbonate-apatite, hydroxylapatite, and tricalcium phosphate must change to fluorapatite as they age; according to their hypothesis, Pleistocene bones and phosphorites should consist chiefly of fluorapatite.

The structural nature of fresh bone is still under discussion by many authors. Hendricks, Hill, Jacob, and Jefferson (1931) believed that bone consists chiefly of carbonate-apatite, because its $\text{Ca:P}_2\text{O}_5$ ratio is greater than that required by tricalcium phosphate, because it gives a weak apatite pattern before ignition and a good apatite pattern after ignition, and because no crystalline impurities are

perceptible by X-ray diffraction methods even after heating. Dalle-magne, Brasseur, and Melon (1949), however, believe that bone consists of a mixture of hydrated tricalcium phosphate with absorbed calcium carbonate; such a mixture would give the required $\text{CaO:P}_2\text{O}_5$ ratio; would, before heating, give a weak apatite group X-ray diffraction pattern; would react, on heating to 700°C , to form an apatite, thus preventing the inversion of tricalcium phosphate to the anhydrous structure. The product of this reaction would give a good apatite pattern. This hypothesis is indirectly confirmed by the work of Sobel, Hanok, Kirschner, and Fankuchen (1949), who found that when the molar ratio of Ca to P in the enamel of rat teeth is less than 1.50, ignited enamel gives a beta tricalcium phosphate pattern. When this ratio is greater than 1.59, ignited enamel gives an apatite group pattern; ratios between these limits give a mixed pattern. In a recent paper Hendricks and Hill (1950) present the hypothesis that carbonate is adsorbed on inner surfaces of an apatite-like lattice. According to this latest view, bone is most likely to be composed of a neutral phosphate (tricalcium phosphate) or may approach a more basic composition (hydroxylapatite).

OPTICAL AND MORPHOLOGICAL CHANGES

The Recent manatee rib is soft, porous, and cream-colored; the bone material is isotropic, has dark inclusions of undetermined nature, and a refractive index close to 1.545, with some spots of higher index and high birefringence. The fossil bones range in appearance from black

and hard with a black coating to cream colored and soft throughout; however, the refractive index and birefringence of all the fossil bones and teeth were about 1.61 and 0.010, respectively. The difference in appearance of the various fossil bones seems to be due, not to any difference in composition of the apatite, but to the amount, arrangement, and character of opaque inclusions of undetermined nature. Although the bone structure in the fossil bones is well preserved, the fossil bones are less porous in appearance than the Recent bone.

CHANGES IN CHEMICAL COMPOSITION DURING FOSSILIZATION

Two samples of one Recent bone, ten of fossil bones, and two of fossil shark teeth were analyzed for U, F, P_2O_5 , and acid insoluble after ignition. As the Recent bone is part of an articulated skeleton, only small samples could be drilled out of it without destroying its value as a museum specimen; therefore spectrographic analyses were first made to aid in the chemical determinations.

The results of the chemical analyses are presented in table 2. In the fossil bones and teeth, the ratio of P_2O_5 to F is about 10:1; in the Recent bone, the ratio is of the order of 100:1. Although the Recent bone is very low in U, the U: P_2O_5 ratio does not differ from the U: P_2O_5 ratio in the fossil bones poorest in uranium: in other words, the uranium content of the mineral matter of the Recent bone is of the same order as that of the least enriched fossil bones. The acid insoluble content of the Recent bone is zero; that of the fossil bones

Table 2.--Partial chemical analyses of Recent
and fossil bones and teeth

Analysts: H. Levine, N. Gutttag, and J. J. McGee

Sample no. and material	Percentage			
	U	F	P ₂ O ₅	Acid insoluble <u>1/</u>
M-1 fossil manatee rib	0.007	3.57	36.5	2.9
M-2 fossil manatee rib	0.007	3.42	37.4	0.52
M-3 fossil manatee rib	0.015	3.75	36.5	0.12
M-4 fossil manatee rib	0.008	3.55	36.8	0.04
M-5 fossil manatee rib	0.006	3.14	36.1	0.22
M-6 fossil manatee rib	0.005	3.52	37.2	0.16
M-7 fossil manatee rib	0.006	3.81	36.7	0.78
M-8 fossil manatee rib	0.006	3.69	36.8	0.98
M-9 fossil manatee rib	0.004	3.64	37.5	0.06
M-10 fossil manatee rib	0.010	3.67	36.6	0.04
M-11 fossil shark teeth	0.006	3.62	36.2	0.66
M-12 fossil shark teeth	0.016	3.67	36.5	3.6
M-13B Recent manatee rib	0.002	0.21	23.8	0.00

1/ Percent insoluble is the weight percent of material remaining after boiling 0.5 g of the sample in 50 ml of (1 + 2) HNO₃ for 30 minutes and then igniting the residue at 100°C for one hour.

probably represents clay, colloidal silica, or manganese and iron minerals, as the spectrographic analyses show trace to minor amounts of Al, Fe, Si, and Mn.

Further analyses of a selected group of the fossil bones, and of the Recent bone samples, are shown in table 3. Organic matter, indicated approximately by the loss on ignition between 450° and 480°C, is much higher in the Recent than in the fossil bones. In the sample of Recent bone taken near the articulation, organic matter insoluble in HCl and HF is higher than in the other sample of Recent bone and in the fossil bones. The ratio of CaO to P₂O₅ is approximately the same in the Recent and in the fossil bones. The Recent bone contains more nonessential water than do the fossil bones. Strontium and magnesium are of about the same order of magnitude in Recent and in fossil bones. Table 4 shows, for comparison, results obtained by Carnot (1893, pp. 164, 167, and 173) in his analyses of Recent and fossil manatee ribs.

Table 5 shows, in molecular ratios, the amounts of Ca , P₂O₅, and F which should be present if the bones corresponded to the fluorapatite formula, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$, as well as the molecular ratio of CO₂. The fossil bones have an excess of fluorine, whereas the Recent bone samples are deficient in fluorine. Although some workers (Hendricks, Hill, Jacob, and Jefferson, 1931) have thought that the mineral matter of bone is carbonate-apatite, CO₂ was not included in the calculation of the apatite. The existence of carbonate-apatite as a distinct mineral species and the structure of carbonate-apatite, if it so

Table 3.--Chemical analyses of selected Recent and fossil manatee ribs (in percentages)

Analysts: A. M. Sherwood and H. Levine

Sample no.	U	CaO	P ₂ O ₅	F	CO ₂	SrO	MgO	Insoluble <u>1</u> /	Loss <u>2</u> / 230°C	Loss <u>3</u> / 450-480°C	Loss <u>4</u> / 1000°C	Insoluble <u>5</u> / matter
M-13A	0.001	33.6	27.0	0.41	4.55	0.15	0.99	---	16.06	14.18	3.52	0.30
M-13B	0.002	28.0	23.8	0.21	2.90	0.17	1.00	0.00	18.11	18.80	4.11	8.75
M-4	0.007	49.4	36.8	3.55	2.90	0.20	0.33	0.04	2.65	0.70	3.40	0.22
M-8	0.006	49.3	36.8	3.69	2.82	0.16	1.36	0.98	1.70	0.45	3.15	0.10
M-12	0.015	45.0	36.5	3.67	2.18	0.16	0.47	3.6	2.30	0.85	2.10	0.42

1/ Percent insoluble is the weight of matter remaining after boiling 0.5 g of the sample in 50 ml of (1 + 2) HNO₃ and then igniting the residue at 1000°C for one hour.

2/ Loss at 230°C is loss in weight of the sample heated to 230°C, and probably represents nonessential water.

3/ Loss at 450-480°C is additional loss in weight of the sample between 450° and 480°C, and probably represents combustible organic matter.

4/ Loss at 1000°C is additional loss which probably represents essential water and CO₂.

5/ Insoluble matter is the organic matter insoluble in HCl and HF.

Table 4.--Chemical analyses of Recent and fossil
manatee bones, recalculated from Carnot (1893,
pp. 164, 167, and 173) in percentages

Description	P ₂ O ₅	CaO	Fe ₂ O ₃	MgO	F	Cl	CO ₂	SiO ₂	Loss on ignition
Recent manatee rib <u>1</u> /	38.62	52.52	0.15	1.20	0.31	0.23	6.98	---	---
Tertiary manatee rib <u>1</u> /	36.73	48.00	4.61	1.01	1.86	0.19	7.68	0.35	---
Quaternary manatee rib	31.70	---	---	---	0.44	---	---	---	33.40

1/ This analysis was done on ashed bone.

Table 5.--Chemical analyses, calculated to apatite, of mineral matter of selected Recent and fossil manatee ribs 1/

A. Molecular proportions of oxides

Sample	CaO	P ₂ O ₅	F	CO ₂
M-13A	600	190	010	103
M-13B	500	168	005	066
M-4	882	259	093	063
M-8	880	259	097	064
M-12	804	257	097	050

B. Oxides in fluorapatite formula $3[Ca_3(PO_4)_2] \cdot CaF_2$, and excess oxides

Sample	Apatite			Excess over apatite formula			CO ₂
	CaO	P ₂ O ₅	F	CaO	P ₂ O ₅	F	
M-13A	570 010	190	010 <u>2/</u>	020	---	---	103
M-13B	500 <u>3/</u>	167	--- <u>4/</u>	---	001	005	066
M-4	777 086	259	086	019	---	007	063
M-8	777 086	259	086	017	---	011	064
M-12	723 081	241	081	---	016	016	050

1/ See table 3 for complete chemical analyses of these bones.

2/ Fluorine deficient by 054.

3/ Calcium deficient by 056.

4/ Fluorine deficient by 050.

exists, have long been a subject of controversy. A complete discussion of these problems is not within the scope of this paper; however, the fossil bones here discussed show similarities to the minerals accepted by some workers as carbonate-apatite. Although it is necessary to refer to "carbonate-apatite standards" and "CO₃ combined as in carbonate-apatite," use of the term carbonate-apatite does not imply that carbonate-apatite is here accepted as a distinct mineral species.

Leaching experiments (Silverman, Fuyat, and Weiser, 1951) with 0.5 M triammonium citrate in aqueous solution were done on one very small sample of Recent bone and on fossil bone (Sample no. M-4) (table 6). This leaching should remove CO₂ present as calcite or some similarly soluble carbonate leaving behind that combined as in carbonate-apatite. Even taking into account the limiting precision

Table 6.--Carbonate content of Recent and fossil bone before and after leaching

	Total CO ₂ (percent)	CO ₃ combined as in carbonate-apatite (percent)
Recent bone (0.2 g)	4.55	0.9 ± 0.5
Fossil bone	2.90	2.88

of the CO₃ determination in the small amount of leached residue from the Recent bone, these results strongly suggest that, although some of the carbonate in the Recent bone may be combined as in carbonate-apatite, most of it is probably present as calcite or as some similarly

soluble carbonate and that the carbonate in the fossil bone is entirely combined as in carbonate-apatite. A differential thermal curve of the fossil bone showed no calcite peak; therefore the bone should contain less than 1.7 percent free calcite, equivalent to 0.75 percent CO_2 .

STRUCTURAL CHANGES IN FOSSILIZATION

X-ray diffraction patterns of the Recent and fossil bones and teeth were made with Debye-Scherrer powder cameras on a North American Phillips machine; spindles were made of the ground bone material using ethyl cellulose dissolved in toluene as a binder. The samples were otherwise untreated.

Electron diffraction patterns were made on an R.C.A. electron diffraction unit, model EMD-2. Ring patterns similar to Debye-Scherrer patterns were obtained from Recent and fossil bone material. As the X-ray diffraction pattern of the Recent bone material is diffuse, probably because of extremely fine particle size, electron diffraction patterns were made in the hope that the much shorter wavelength (about 0.05 Å) would produce a less diffuse pattern. The ground bone material was suspended in distilled water and evaporated onto 200-mesh copper screens; the screens were then placed in the specimen chamber of the electron diffraction machine, and the entire column, including the specimen chamber, evacuated to a pressure lower than 0.1 micron of mercury. Preliminary measurements with an accuracy of 0.5 mm were made on these patterns. The patterns show poor resolution in many of the lines.

The X-ray diffraction patterns of the fossil bones and teeth correspond to the carbonate-fluorapatite standard used in this laboratory (film no. 1468). No other phases are apparent in the X-ray diffraction patterns of these bones. The electron diffraction pattern of fossil bone M-4 corresponds to standard apatite patterns within the limits of error of the instrument. The Recent bone has an X-ray diffraction pattern similar to that of poorly crystalline apatite; the lines are diffuse, and only the strongest ones are present. The electron diffraction pattern of the Recent manatee bone does not correspond to the ASTM spacings for $\text{Ca}(\text{H}_2\text{PO}_4)_2$ anhydrous or hydrated, CaHPO_4 anhydrous or hydrated; it does not correspond exactly to whitlockite (beta tricalcium phosphate) or apatite spacings, but is similar to both, with more affinities for the whitlockite pattern. The lines are sharp, and more lines are present than in the X-ray diffraction pattern. The difference between the X-ray and the electron diffraction pattern of Recent bone may mean either that the electron diffraction pattern is due to some impurity imperceptible by X-ray methods or that some structural change (possible partial dehydration) of the bone has taken place in the vacuum and under the intense electron bombardment.

SUMMARY AND CONCLUSIONS

Because only one sample of Recent bone was available for study, conclusions reached here must necessarily be tentative.

In fossilization, the manatee bones have undergone chemical and physical changes which are probably related to some structural change.

Compared to the whole Recent bone, the fossil bones have gained in fluorine, P_2O_5 , CaO , carbonate fixed as in carbonate-apatite, ignited insoluble residue, and uranium, and have lost nonessential water, free carbonate, and combustible organic matter. The refractive index, density, apparent homogeneity, and birefringence of the fossil bones have increased. Considering only mineral matter, the fossil bones have gained in ignited insoluble residue and fixed carbonate; some have gained in uranium. It is impossible at present to come to any conclusion concerning the nature of the structural change that has taken place. Evidently some change has occurred that tends to fix carbonate and fluorine. Because the whole Recent bone gives an apatite group X-ray diffraction pattern indicative of poorly crystalline material, which pattern has been described as characteristic of hydrated tricalcium phosphate (Dallemand, Brasseur, and Melon, 1949), it may be supposed that the Recent bone is either hydrated tricalcium phosphate or very finely crystalline hydroxylapatite with adsorbed fluorine and carbonate. In crystallizing during fossilization, the bone material has incorporated in its lattice or adsorbed on inner surfaces (Hendricks and Hill, 1950) this excess fluorine and carbonate. This idea must be tested by further study.

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