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MINERALOGICAL STUDIES ON BONE APATITE AND THEIR IMPLICATIONS FOR RADIOCARBON DATING

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ABSTRACT. Infrared (IR) spectrophotometry and X-ray diffraction (XRD) were conducted on modern and fossil bone material from archaeological sites in the U S to determine post-mortem changes in bone apatite and to evaluate the effect of these changes on radiocarbon dating. IR absorption bands, XRD peak-broadening parameters, and XRD unit cell measurements indicated that during fossilization, bone apatite, a mineral similar to dahllite, was partially or completely recrystallized to francolite. Post-mortem changes involved then removal of some of the endogenous crystal carbonate both at surfaces and at internal OH-sites and introduction of exogenous carbonate into internal crystal PO_4 sites. Increased fluorine content accompanied carbonate substitution.

Both the carbon isotopic composition and the amount of exogenous carbonate introduced into the apatite structure will affect the radiocarbon dating of bone apatite. Special sample pre-treatment may remove most of the substituted carbonate in some cases. Simulated experiments are suggested for a better understanding of the nature and mechanism of carbonate substitution in bone apatite for the removal of the exogenously substituted carbon and the improvement of radiocarbon dates.

INTRODUCTION

Despite the abundance of bone material at archaeological sites, only a few radiocarbon dates have been obtained from them. Many workers regard bone dating with suspicion because of the inaccurate ages often obtained. The organic fraction in bone, namely collagen, does not exchange carbon with the bone post-mortem environment. Accordingly, inaccurate collagen dates are caused by physical contamination with other organic material, which has led many investigators to devise new techniques for separating pure collagen (Berger, Horney, and Libby, 1964; Krueger, 1965; Sellstedt and others, 1966; Berger and others, 1971; Longin, 1971; and Hassan, 1976). In many cases, however, the amount of collagen separated is insufficient for dating. Haynes (1968) used the bone mineral, apatite, as an alternative.

Many investigators are skeptical of radiocarbon dates obtained from bone apatite because of possible post-mortem exchange of carbon with the surrounding medium (Tamers & Pearson, 1965; Sellstedt and others, 1966). One of us (CVH), in collaboration with Austin Long, University of Arizona (unpub), demonstrated this exchange by radiocarbon analysis of about 2 my old bone from the Curtis Ranch locality in Arizona and obtained apparent ages of 21,000 ± 1000 BP (A-1028) on apatite CO_2 and 16,180 ± 300 BP (A-1027) on CO_2 from secondary carbonate. The mechanism and magnitude of such exchange had not been studied before. In the present study, modern and fossil bone apatites were subjected to X-ray and infrared investigation to trace the changes which might have

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TABLE 1

Frequency for IR absorption bands (in cm^{-1}) for the carbonate in dahllite, francolite, aragonite, calcite and bone apatite

Samples	ν_1	ν_2	ν_3	ν_4
Dahllite (Carlström, in press)		873	1416 1455	
Francolite (Carlström, in press)		866	1425 1455	
Aragonite (LeGeros and others, in press)	1080	842 852	1445 1485	700 710
Calcite (LeGeros and others, in press)		872	1420	710
Protein-free rat tibia, untreated (Termine and Lundy, 1973)		868 877*	1417 1441* 1476	
Protein-free rat tibia, air, 24 hr (Termine and Lundy, 1973)		870 876	1413 1457 1485*	

* Shoulder

occurred during fossilization and their possible effects on radiocarbon dating. The fossil bone specimens are from Folsom site, New Mexico; Murray Springs Clovis Level, Arizona; Blackwater Draw Clovis Level, New Mexico; Domebo Clovis Level, Oklahoma; and Boney Springs and Trolinger Bog, Missouri. They belong to *B bison antiquus, Mammuthus columbi, Mammuthus, imperator,* and *Mammut americanum.* The modern equivalents used in the study consist of buffalo (bison), cow, and elephant (*E indictus*)[1]. The elephant bones belong to two individuals; one died in 1967 and was left in open air while the other died in 1964 and was buried for 6 years prior to re-excavation.

INFRARED SPECTROSCOPY

Infrared (IR) absorption spectra from bone are usually composites of both protein and mineral absorption bands. The spectra of bone apatite are characterized by vibration bands produced by H_2O, OH, PO_4, and CO_3 groups. The characteristic vibrational bands of the CO_3 group in spectra of bone apatite are different from those observed in spectra of simple carbonate (table 1). The CO_3 IR bands of fresh bone apatite (table 1) are more complex than those of dahllite (carbonate hydroxyapatite with less than 1 percent F^-) and francolite (carbonate fluorapatite with more than 1 percent F^-).

Generally CO_3 exists in bone apatite at three different positions: (1) absorbed on the crystal surface, (2) at OH-, and (3) at PO_4-sites

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[1] The elephant bones were obtained from Charles McNulty, University of Texas at Arlington.

TABLE 2

Chemical analysis of fresh, modern, and fossil bone apatite*

Sample description	Ca%	PO_4%	CO_3%	F%
Fresh cow	36.18	53.96	—	.074
Fresh buffalo	36.06	52.93	5.75	.035
Modern elephant	35.04	49.13	—	.076
Modern buried elephant	34.94	48.93	6.50	.055
Folsom bison	39.08	50.24	5.80	1.404
Murray Springs mammoth	37.46	49.28	—	1.467
Blackwater Draw mammoth	37.59	49.89	6.56	1.830
Blackwater Draw mammoth III	37.16	45.24	—	3.958
Domebo mammoth	36.67	48.44	9.78	1.659
Boney Springs mastodon	38.70	49.35	—	1.561
Trolinger bog mastodon	38.88	50.50	5.52	1.781

* From Hassan (1976)

(LeGeros and others, 1967; LeGeros and others, 1969; Carlström, in press; and Elliott, in press). About one-third to two-thirds of the total carbonate occurs at the surface (Neuman & Mulryan, 1967; Termine & Eanes, 1972; Termine & Lundy, 1973). The remainder is distributed between PO_4- and OH-sites with the vast majority in PO_4-sites.

The spectra of bone apatite were made with a Perkin-Elmer Model 621 Spectrophotometer, purged with dry air from pellets of 300mg kBr and 2mg protein- and calcite-free samples.[2] Some samples were treated with triammonium citrate and acetic acid to test the effect of these chemicals on carbonate removal. Machine adjustment was as follows: slit program 1x, gain 4.5, attenuator 11.00, scan time 10×4.5, suppression 6, and source 0.8 amp. The infrared splitting function SP, which is proportional to percentage crystallinity as determined by XRD, was calculated according to Termine and Posner (1966). The carbonate percentage was calculated from the ratio A_1/A_2, the ratio of the areas under the peaks of the carbonate ion asymmetric stretching frequency (1550-1350 cm^{-1}) and the phosphate ion antisymmetric bending frequency (800-450 cm^{-1}), and a standard whose CO_3 content is known (Greenfield & Eanes, 1972). The standard used in the present study is the modern buried elephant femur in which the CO_3 content was previously determined by wet chemistry (Hassan, 1976). Some of the chemical analysis on the bones investigated appear in table 2.

The spectra (fig 1) and frequencies (table 3) for IR linear absorbance for bone indicate that during fossilization bone apatite had experienced some changes. The absorption at 1495 cm^{-1}, attributed to surface and/or amorphous carbonate, is absent or very weak in the fossil bone. The intensities of IR bands at 1542, 1445, and 880 cm^{-1}, which stand for CO_3-OH substitution, decrease while an increase occurs at the 1418 and 873 cm^{-1} bands, which stand for CO_3-PO_4 substitution, with fossilization. Despite these changes, the fossil bone apatites were still close to the dahllite-type of apatite with the exception of the bone of the Blackwater Draw Mammoth III, a francolite-type. It is noteworthy that this sample

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[2] See Hassan (1976) for sample pretreatment.

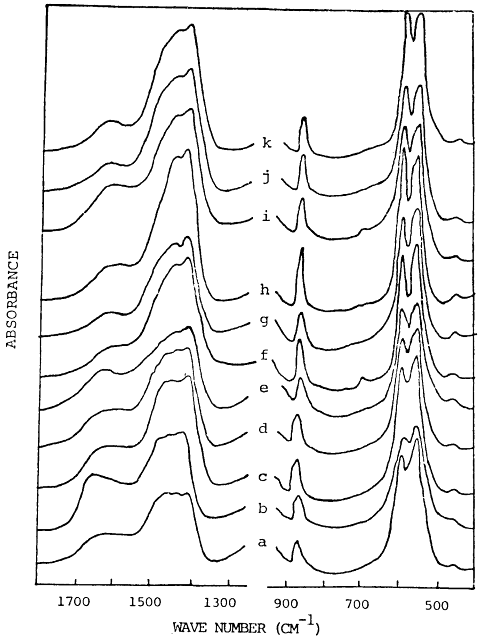


Fig. 1. Linear absorbance IR spectra from the bone of (A) fresh cow, (B) fresh buffalo, (C) modern elephant, (D) modern buried elephant, (E) Folsom bison, (F) Murray Springs mammoth, (G) Blackwater Draw mammoth, (H) Blackwater Draw mammoth III, and (K) Trolinger bog mastodon.

has an abnormally high F$^-$ concentration (3.96 percent) whereas the rest of the fossil bones have less than 1.9 percent and the fresh and modern bones contain less than 0.1 percent flouride (table 2). The fact that bone mineral dahllite may be converted into francolite because of fossilization, has been reported previously by Stevenson (1966).

The relative carbonate content of fossil bone apatite decreases sharply with triammonium citrate and acetic acid treatments (table 4). Prior to these chemical treatments, calcite was removed mechanically (Hassan, 1976). Any calcite remaining was below the detection limit of the IR, about 2 percent. The decrease in CO_3 after the above treatments may well result from the weakening effect of the post-burial-substituted carbonate on bonds within the apatite structure. This is in agreement with the explanation of LeGeros and others (1967) for the observed increase in rates of dissolution and solubility of apatites with carbonate substitution.

X-RAY STUDIES

X-ray diffraction (XRD) broadening analysis has been extensively employed in the study of biological apatite (Carlström, 1955; Carlström and Glas, 1959; Posner and others, 1963, 1965; Harper and Posner, 1966; Termine and Posner, 1967; LeGeros and others, 1967; Posner, 1969;

TABLE 3

Frequency for IR absorption bands (in cm^{-1}) for the carbonate in modern and fossil bone apatite

	No treatment		Triammonium citrate		Acetic acid	
Sample description	ν_2	ν_3	ν_2	ν_3	ν_2	ν_3
Fresh cow	873	1417	—	—	—	—
	880*	1445	—	—	—	—
		1470		—		—
		1495*		—		—
		1512*		—		—
Fresh buffalo	873	1418	—	—	—	—
	880*	1445	—	—	—	—
		1470		—		—
		1495*		—		—
		1512*		—		—
Modern elephant	873	1418	—	—	—	—
	880*	1445	—	—	—	—
		1470		—		—
		1500*		—		—
Modern buried elephant	873	1418	873	1418	—	—
	880*	1445	880*	1445	—	—
		1470		1470		—
		1495*		1495*		—
		1510*		1510*		—
Folsom bison	868	1417	—	—	—	—
	878*	1450	—	—	—	—
		1495*		—		—
Murray Springs mammoth	873	1423	873	1423	873	1423
	880**	1453	880***	1453	880***	1453
		1495***		1495*		1495*
Blackwater Draw mammoth	873	1423	873	1423	—	—
	880**	1453	880**	1453	—	—
		1495***		1495*		—
Blackwater Draw mammoth III	866	1427	866	1429	—	—
		1455		1455		—
Domebo mammoth	873	1420	873	1420	873	1420
	880***	1453	880*	1453	880***	1453
		1495*		1495*		1495*
Boney Springs mastodon	873	1420	—	—	—	—
	880***	1453	—	—	—	—
		1495*		—		—
Trolinger bog mastodon	873	1422	—	—	—	—
	880***	1453	—	—	—	—
		1495*		—		—

* Shoulder
** Very weak shoulder
*** Weak shoulder

Lundy and Eanes, 1973; and Russell, Termine, and Arcoli, 1973). Crystallite size can be deduced from the broadened X-ray diffraction peaks using Scherrer's equation (Klug and Alexander, 1954). However, the figures for bone apatite crystallite dimensions and its crystallographic orientation are controversial (Carlström and Glas, 1959; Posner and others, 1963; and Höhling, Themann, and Vahl, 1966) which suggests that the validity of accurate crystallite size determination for bone apatite has not been settled. However, it is generally agreed that the crystals are extremely minute with the smallest dimension less than 50 Å and the largest dimension much less than 1000 Å, paralleling the c-axis (Eanes, 1973).

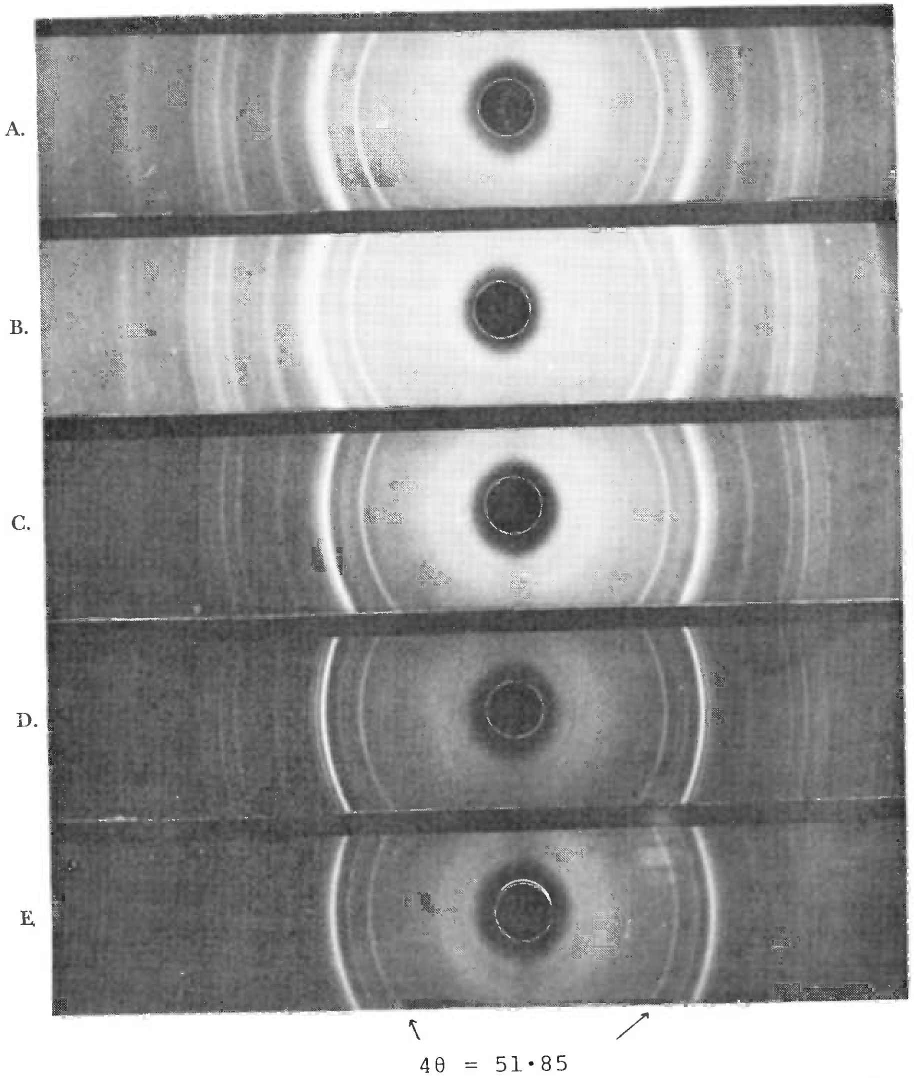
Variability in unit cell dimensions of biological apatites resulting from chemical substitution and the mechanism of such substitution has also been a matter of controversy. Among the substitutions which may occur in the apatite structure is that of carbonate. Carbonate substitution was investigated by McConnell (1938, 1952a and b, 1959, 1962, 1965), Borneman-Starinkevich and Belov (1953), Trautz (1960), McClellan and Lehr (1969), Elliott (1965, in press), LeGeros (1965), LeGeros and others (1967), LeGeros and others (1968, in press), Simpson (1972), and Carlström (in press). Generally agreed is that in francolite, one carbonate and one fluorine substitute together for one phosphate in the apatite structure resulting in a nonlinear decrease in the a-axis. Experimental studies on bone powder and on synthetic apatite by Neuman and Mulryan (1949, 1967), Neuman and others (1949), Neuman (1950), Neuman and Weikel (1954), and Simpson (1967) indicate that surface exchange, ionic and isotopic, as well as recrystallization, may also occur in bone apatites.

Table 4

Splitting functions (SP), the ratio A_1/A_2, and carbonate percentage calculated from A_1/A_2 using the wet chemical analysis for the modern buried elephant as a standard

Sample description	No treatment			Triammonium citrate			Acetic acid		
	SP	A_1/A_2	CO_3%	SP	A_1/A_2	CO_3%	SP	A_1/A_2	CO_3%
Fresh cow	0.042	0.880	4.3	—	—	—	—	—	—
Fresh buffalo	0.033	1.350	6.6	—	—	—	—	—	—
Modern elephant	0.036	1.314	6.4	—	—	—	—	—	—
Modern buried elephant	0.023	1.327	6.5	0.023	1.296	6.3	—	—	—
Folsom bison	0.047	1.345	6.6	—	—	—	—	—	—
Murray Springs mammoth	0.086	1.568	7.7	0.057	1.064	5.2	0.076	0.708	3.5
Blackwater Draw mammoth	0.059	1.327	6.5	0.047	1.067	5.2	—	—	—
Blackwater Draw mammoth III	0.075	1.947	9.5	0.054	1.643	8.0	—	—	—
Domebo mammoth	0.057	1.515	7.4	0.038	1.048	5.1	0.049	0.870	4.3
Boney Springs mastondon	0.039	1.452	7.1	—	—	—	—	—	—
Trolinger bog mastodon	0.032	1.525	7.5	—	—	—	—	—	—

PLATE 1



Exact positives of X-ray films of (A) fresh cow bone, (B) modern buried elephant bone, (C) Folsom bison bone, (D) Blackwater Draw Mammoth III bone, and (E) Domebo mammoth bone.

XRD peak broadening analyses were obtained from protein-free finely hand-ground samples[3] adapting the method and experimental conditions of Russell, Termine, and Arcoli (1973). The apatite c-axis (002) and a-axis (310) reflections were step-scanned between 23.60-27.60° 2θ and 36.00-44.00° 2θ, respectively. Russell, Termine, and Arcoli (1973) ob-

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[3] See Hassan (1976) for sample pre-treatment.

TABLE 5

X-ray diffraction broadening and intensity parameters

Sample description	$B_{002}^{1/2°}2\theta$	$B_{310}^{1/2°}2\theta$	$B_{002}^{I°}2\theta$	$B_{310}^{I°}2\theta$	$\Sigma B^{I°}2\theta$	I_{002} (area)	I_{310} (area)	Brass Count	I/Brass 002	I/Brass 310	I_{xin}	$D\mathring{A}_{002}$	$D\mathring{A}_{310}$
Fresh cow	0.41	1.29	0.54	1.60	2.14	21,251	29,372	5,851	3.632	5.020	8.652	371	91
Fresh buffalo	0.39	1.31	0.49	1.66	2.15	20,372	31,663	5,844	3.486	5.418	8.904	408	89
Modern elephant	0.40	1.28	0.52	1.56	2.08	21,575	29,739	5,821	3.706	5.109	8.815	388	92
Modern buried elephant	0.39	1.23	0.49	1.53	2.02	21,705	30,390	5,874	3.695	5.174	8.869	408	97
Folsom bison	0.35	1.02	0.45	1.33	1.78	23,750	34,306	5,776	4.112	5.939	10.051	510	128
Murray Springs mammoth	0.32	0.95	0.39	1.09	1.48	25,144	34,615	5,867	4.286	5.890	10.176	628	143
Blackwater Draw mammoth	0.32	0.96	0.40	1.20	1.60	30,884	35,419	5,831	5.297	6.074	11.371	628	141
Blackwater Draw mammoth III	0.29	0.49	0.36	0.97	1.33	28,006	39,081	5,818	4.814	6.717	11.531	816	650
Boney Springs mastodon	0.35	1.11	0.43	1.36	1.79	29,932	34,787	5,794	5.166	6.004	11.170	510	113
Trolinger bog mastodon	0.36	1.20	0.45	1.48	1.93	31,473	36,354	5,921	5.316	6.140	11.456	480	101
Fluor-apatite[a] Standard	0.19	0.36	—	—	—	—	—	—	—	—	—		

[a] obtained from Mr. B. O. Fowler at NIH.

tained a precision in half-width (B 1/2) and integral breadth (B^I = peak area/peak height) values within ±1.5 percent. Debye-Scherrer, 114.6mm diameter powder cameras were used for study of unit cell dimensions. With Ni-filtered Cu radiation (CuK_2 = 1.542 Å), XRD patterns were recorded at 35 kv and 20 ma. The exposure time was 2 hrs. The 002 and 300 X-ray diffraction lines were used to calculate c Å and a Å dimensions, respectively.

The crystallite dimensions, D $Å_{002}$ and D $Å_{310}$, of modern bone apatite obtained in the present study (table 5) have their small dimension parallel to the a-axis, in agreement with Carlström and Glas (1959). The crystallite size of bone apatite and/or the percent crystallinity increases with fossilization. The XRD lines (pl. 1) are sharper in fossil than modern bones which most probably results from crystallite enlargement. The calculated unit cell dimensions (table 6), even though not very accurate, show a distinction between modern and fossil bone apatite. The slight decrease in the a-axis with fossilization is consistent with the observed increase in fluorine and carbonate content detected with fossilization (tables 2 and 4).

CONCLUSIONS AND PROBLEMS

Fossil bone apatite undergoes a number of post-mortem changes which distinguishes it from its biological predecessor. Among those changes critical for radiocarbon dating is carbonate substitution. The present study reveals a definite change in the mode and amount of carbonate contained within bone apatite upon fossilization which suggests post-mortem exchange with exogenous carbon. Whether the exchange is ionic and/or isotopic is still unclear. Chemical treatments with triammonium citrate and/or acetic acid remove some of the carbonate in the apatite structure. Carbon isotopic studies (Hassan, 1976) indicate that the carbonates thus removed are contaminants. Hydrochloric acid leaching of the finely ground samples (fractional hydrolysis technique) removes more of the contaminated carbonate which then may improve the radiocarbon dates (Hassan, 1976).

TABLE 6

Unit cell measurements

Sample description	θ_{002}	θ_{300}	d_{002}	d_{300}	c Å	a Å
Fresh cow femur	12.9500	16.5750	3.4371	2.7001	6.87	9.35
Modern buried elephant femur	13.0125	16.6000	3.4215	2.6961	6.84	9.34
Folsom bison bone	13.0000	16.6125	3.4241	2.6945	6.85	9.33
Murray Springs mammoth bone	13.0250	16.6250	3.4176	2.6922	6.84	9.33
Blackwater Draw mammoth III bone	12.9625	16.6500	3.4345	2.6882	6.87	9.31
Domebo mammoth bone	12.9625	16.6500	3.4345	2.6882	6.87	9.31
Boney Springs mastodon bone	13.0250	16.6750	3.4176	2.6843	6.84	9.30
Trolinger bog mastodon bone	12.9825	16.6250	3.4393	2.6922	6.86	9.33
Francolite*	—	—	—	—	6.881	9.356
Dahllite*	—	—	—	—	6.890	9.391
Bone**	—	—	—	—	6.88 ± 0.01	9.38 ± 0.01

* Trautz, 1955

** Posner and others, 1963

In order to evaluate the magnitude and mechanism of post-mortem exchange of carbon in bone apatite, simulated lab experiments are essential. Carbonate substitution in both very old and fresh bone powder using either active or dead carbon should be investigated. Data derived from such studies test the validity of the above mentioned fractional hydrolysis and demonstrate the limitations of its applicability to this problem.

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REFERENCES

Berger, R, Horney, A G, and Libby, W F, 1964, Radiocarbon dating of bone and shell from their organic components: Science, v 144, p 999-1001.

Berger, R, Protsch, R, Reynolds, R, Rozaire, C, and Sackett, J R, 1971, New radiocarbon dates based on bone collagen in California Paleoindian: Berkeley, Univ California Archaeol Research Facility Contr, no. 12, p 43-49.

Borneman-Starinkevich, I E, and Belov, N V, 1953, Carbonate-apatites: Akad Nauk SSSR Doklady, v 90, p 89-92.

Carlström, D, 1955, X-ray crystallographic studies on apatites and calcified structures: Acta Radialosia Supp, v 121, p 1-59.

——— Mineralogical carbonates containing apatites, *in* Brown, W, and Young, R, eds, Internat symposium on the structural properties of hydroxy apatite and related compounds, 1968: New York, Gordon & Breach (in press).

Carlström, D, and Glas, J E, 1959, The size and shape of the apatite crystallites in bone as determined from line broadening measurements on oriented specimens: Biochem Biophys Act, v 35, p 46-53.

Eanes, E D, 1973, Eleven X-ray diffraction of vertebrate hard tissue, *in* Zipkins, I, ed, Biological mineralization: New York, John Wiley & Sons, Inc, p 227-256.

Elliott, J C, 1965, The interpretation of the infrared absorption spectra of some carbonate-containing apatites, *in* Stack, M V, and Fernhead, R W, eds, Tooth enamel, its composition, properties and fundamental structure: Bristol, John Wright & Sons, Ltd, p 220, 50-58.

——— Synthetic and biological carbonates containing apatite, *in* Brown, W, and Young, R, eds, Internat symposium on the structural properties of hydroxy apatites and related compounds, 1968: New York, Gordon & Breach (in press).

Greenfield, D J, and Eanes, E D, 1972, Formation chemistry of amorphous calcium phosphates prepared from carbonate containing solutions: Calcified Tissue Research, v 9, p 152-162.

Hassan, A A, 1976, Geochemical and mineralogical studies on bone material and their implications for radiocarbon dating: PhD dissert, Southern Methodist Univ (Univ microfilms, Ann Arbor, Michigan).

Harper, R A, and Posner, A S, 1966, Measurement of non-crystalline calcium phosphate in bone mineral: Soc Expt Biol Med Proc, v 122, p 137-142.

Haynes, C V, Jr, 1968, Radiocarbon analysis of inorganic carbon of fossil bones and enamel: Science, v 161, p 687-688.

Höhling, H J, Themann, H, and Vahl, J, 1966, Collagen and apatite in hard tissues and pathological formation from a crystal chemical point of view, *in* Fleisch, H, Blackwood, H J J, and Owen, M, eds, Calcified tissues, European symposium on calcified tissues, 3rd, Davos, 1965, Proc: New York, Springer-Verlag, p 146-151.

Klug, H P, and Alexander, L E, 1954, X-ray diffraction procedures for polycrystalline and amorphous materials: New York, John Wiley & Sons, Inc, p 491-537.

Krueger, H W, 1965, The preservation and dating of collagen in ancient bones: Internat conf on radiocarbon and tritium dating, 6th, Pullman, Washington, 1965, Proc (CONF-650652), p 332-337.

LeGeros, R Z, 1965, Effect of carbonate in the lattice parameters of apatite: Nature, v 206, p 403-404.

LeGeros, R Z, LeGeros, J P, Trautz, O R, and Klein, E, 1968, Crystallographic studies on the CO_3 substitution in the apatite structure: Soc Chim France Bull, spec no., p 1712-1718.

LeGeros, R Z, Massuyes, M, Trombe, J C, Bonel, G, and Montel, G, Infrared and X-ray properties of synthetic carbonate apatites, *in* Brown, W and Young, R, eds, Internat symposium on the structural properties of hydroxy apatite and related compounds, 1968: New York, Gordon & Breach (in press).

LeGeros, R Z, Trautz, O R, Klein, E, and LeGeros, J P, 1969, Two types of carbonate substitution in the apatite structure: Experimentia, v 15, p 5-7.

LeGeros, R Z, Trautz, O R, LeGeros, J P, and Klein, E, 1967, Apatite crystallites: effects of carbonate on morphology: Science, v 155, p 1409-1411

Longin, R, 1971, New method of collagen extraction for radiocarbon dating: Nature, v 230, p 241-242.

Lundy, D R, and Eanes, E D, 1973, An X-ray line-broadening study of turkey leg tendon: Arch Oral Biol, v 18, p 813-826.

McClellan, G H, and Lehr, J R, 1969, Chemical investigation of apatites: Am Mineralogist, v 54, no. 9-10, p 1374-1391.

McConnell, D, 1938, A structural investigation of the isomorphism of the apatite group: Am Mineralogist, v 23, p 1-19.

———— 1952a, The problem of the carbonate apatites. IV. Structural substitutions involving $CO_3^=$ and OH^-: Soc francaise mineralogie et crystallographie Bull, v 75, p 428-445.

———— 1952b, The crystal chemistry of carbonate apatites and their relationship to the composition of calcified tissues: Jour Dent Research, v 31, p 53-63.

———— 1959, The problem of carbonate apatites: Econ Geology, v 54, p 749-751.

———— 1962, The crystal structure of bone: Clin Orthopaed, no. 23, p 253-268.

———— 1965, Crystal chemistry of hydroxyapatite. Its relation to bone mineral: Arch Oral Biol, v 10, p 421-431.

Neuman, W F, 1950, Bone as a problem in surface chemistry, *in* Reifenstein, E, Jr, ed, Metabolic inter-relations, trans, 2nd conf: New York, Josiah Macy, Jr, Foundation, p 37-72.

Neuman, W F, and Mulryan, B J, 1949, Studies on the surface chemistry of bone 1—Recrystallization: U S Atomic Energy Comm, AECU-132, p 1-9.

———— 1967, Synthetic hydroxyapatite crystals, III. The carbonate system: Calcified Tissues Research, v 1, p 94-104.

Neuman, W F, Neuman, M W, Main, E R, and Mulryan, B J, 1949, The deposition of uranium in bone: Jour Biol Chem, v 179, p 325-348.

Neuman, W F, and Weikel, J H, Jr, 1954, Recrystallization in bone mineral: New York Acad Sci Annals, v 60, p 685-695.

Posner, A S, 1969, Crystal chemistry of bone mineral: Physiological Rev, v 49, p 760-792.

Posner, A S, Eanes, E D, Harper, R A, and Zipkins, I, 1963, X-ray diffraction analysis of the effect of fluoride on human bone apatite: Arch Oral Biol, v 8, p 549-570.

Posner, A S, Harper, R A, and Muller, S A, 1965, Age changes in the crystal chemistry in bone apatite: New York Acad Sci Annals, v 131, p 737-742.

Russell, J E, Termine, J D, and Avioli, L V, 1973, Abnormal bone mineral maturation in the chronic uremic state: Jour Clin Inv, v 52, p 2848-2852.

Sellstedt, H, Engstrand, L, and Gejvall, N-G, 1966, New application of radiocarbon dating to collagen residue in bones: Nature, v 212, p 572-574.

Simpson, D R, 1967, Effect of pH and solution concentration on the composition of carbonate apatite: Am Mineralogist, v 52, p 896-902.

———— 1972, Problems of the composition and structure of the bone minerals: Clin Orthopaed, v 86, p 260-286.

Stevenson, J S, 1966, Fluorine content of microsaur teeth from the Carboniferous rocks of Joggins, Nova Scotia: Science, v 154, p 1548-1550.

Tamers, M A, and Pearson, F J, Jr, 1965, Validity of radiocarbon dates on bone: Nature, v 208, p 1053-1055.

Termine, J D, and Eanes, E D, 1972, Comparative chemistry of amorphous and apatitic calcium phosphate preparations: Calcified Tissue Research, v 10, p 171-197.

Termine, J D, and Lundy, D R, 1973, Hydroxide and carbonate in rat bone mineral and its synthetic analogues: Calcified Tissue Research, v 13, p 73-82.

Termine, J D, and Posner, A S, 1966, Infrared determination of the percentage of crystallinity in apatitic calcium phosphates: Nature, v 211, p 268-270.

———— 1967, Amorphous/crystalline interrelationships in bone mineral: Calcified Tissue Research, v 1, p 8-23.

Trautz, O R, 1955, X-ray diffraction of biological and synthetic apatites: New York Acad Sci Annals, v 60, p 696-712.

———— 1960, Crystallographic studies of calcium carbonate phosphate: New York Acad Sci Annals, v 85, p 145-160.