

## THE CRYSTAL CHEMISTRY OF DAHLLITE

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### ABSTRACT

Chemical and powder diffraction data are given for fossilized dental enamel from a mastodon tooth. The specific gravity is 2.968 (20°/4° C.) and  $a_0=9.454$ ,  $c_0=6.892$  Å.

Calculations, analogous to those previously made for francolite, indicate that the carbonate groups enter the structure as substitutions for phosphate groups. However,  $(\text{CO}_3\text{OH})$  does not appear to be an accurate representation. The recent supposition that carbonate groups can substitute for (F, OH) groups of normal apatite is untenable.

### INTRODUCTION

Through personal conversations with several mineralogists, it has become evident that they regard the problem of the carbonate apatites as solved. They find such formulations as  $\text{Ca}_5\text{F}/(\text{PO}_4, \text{CO}_3\text{OH})_3$  in recent reference books, and are quite willing to accept this representation as a close approximation, at least. However, they are not mindful of the reluctance of the physiological chemists to accept any portion of the mineralogical investigations as analogous to the problem of tooth and bone composition.

Certain chemists are more than mildly perturbed about "amorphous  $\text{CaCO}_3$ ", various synthetic concoctions which produce apatitelike diffraction patterns but show a range of Ca/P ratios, how the carbonate ions can substitute for phosphate ions in the structure whereas citrate ions cannot, and numerous *non-sequiturs* that have been presented as "conclusions" after heating and dissolving various solid materials, both natural and synthetic and with or without other treatment. A summary of most of these views, including an extensive bibliography, has been presented by Carlström (1955), who states: "Summarizing the views on the structure of the carbonate-apatites, it may be concluded that they do not exist as homogeneous single phase compounds but are composed of a microcrystalline, somewhat 'impure,' fluorapatite with 'amorphous' carbonate mainly in the form of  $\text{CaCO}_3$ , and from that point of view they are of great interest in relation to the state of the carbonate in calcified tissues." Although this statement will astonish numerous mineralogists who have had first-hand experience with carbonate apatites (see: McConnel and Gruner, 1940), it is more or less typical of numerous "mineralogical" interpretations by persons completely unfamiliar with mineralogical methods of investigation.

Being familiar with the fundamental principles of solid-state physics and chemistry, mineralogists raise questions which are quite different

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from those which disturb the physiological chemists, and there is no need to explain to the former group that the "citrate ion" (containing seven oxygens) cannot enter the apatite crystal structure to produce an isomorphic variant whereas the carbonate group can do precisely this. Furthermore, crystal chemists quickly recognize that some minor changes in the structure would necessarily result as a consequence of the introduction of carbonate groups:

- (1) The optical properties, particularly the birefringence, might be altered.
- (2) The cell dimensions, intensities of diffraction from certain planes, and specific gravity might be altered.
- (3) The structure might be converted from hexagonal to lower symmetry and the optical properties and twinning might reveal that the structure is merely pseudo-hexagonal.

All of these criteria are satisfied in the case of francolite, but the data for dahllite are not nearly so adequate.

A recent book, *The Chemical Dynamics of Bone Mineral*, for example, states: "It is difficult to attain a clear-cut comprehension of the crystallography of hydroxy apatite when the mineralogists themselves do not agree on rather fundamental interpretations." The authors, Neuman and Neuman (1958), also refer to such substances as phosphorite as forming at "high temperatures," apparently without realizing that the temperatures need be no greater than temperatures encountered in present-day oceans. Certain portions of their chemistry are as confused as their geology and mineralogy, particularly such statements as: "One cannot approach the same *equilibrium* from the two directions—precipitation and dissolution." (Italics added.) It is to be remembered that the title of this book contains the word "mineral." Although it seems unlikely that workers in these areas can be expected to consult mineralogical literature with comprehension, there is good reason for recording the fundamental data and interpretations, nevertheless.

Accordingly, certain fundamental investigations have been carried out on a sample of post-Wisconsin fossilized dental enamel from a mastodon, found near Bluffton, Ohio. It was furnished through the courtesy of Dr. Mildred Marple of the Geology Department. The x-ray diffraction data were supplied by Dr. Leslie C. Coleman of the Mineralogy Department. The chemical analysis was made at the Laboratory for Rock Analysis at the University of Minnesota under the direction of Dr. S. S. Goldich. Most of the remaining sample has been deposited with the National Museum (U.S.N.M. 113977).

#### EXPERIMENTAL DATA AND INTERPRETATIONS

Shown in Table 1 are the results of chemical analysis and the calculations used to determine the contents of the unit cell. From the "molec-

TABLE 1. SUMMARY CALCULATIONS ON ANALYSIS OF DENTAL ENAMEL FROM MASTODON TOOTH

(C. O. Ingamells, Analyst)

Oxides	Weight per cent	Oxide ratios	Relative charges of cations	Cation charges $\Sigma = 53.0$	Atoms per unit (cations)	Structural locations*
CaO	51.44	.9173	1.835	18.21	9.11	Ca, Mg, Na 9.45
MgO	0.34	.0084	.017	.17	.08	C [.19]
Na <sub>2</sub> O	0.80	.0129	.026	.26	.26	H <sub>3</sub> .55
						Ca Positions 10.00
CO <sub>2</sub>	2.72	.0618	.247	2.45	.61	H <sub>2</sub> O (excess) .24
H <sub>2</sub> O+	2.83	.1570	.314	3.12	4.00	
H <sub>2</sub> O-	0.80	.0444	.089	.88		10.24
						P 5.58
P <sub>2</sub> O <sub>5</sub>	39.92	.2812	2.812	27.91	5.58	C .42
						P Positions 6.00
Cl	0.42	.0118‡				
F	0.03	.0016‡				
Others†	0.19	—				Cl, F .13
						OH 1.87
						F Positions 2.00
	99.49					
Less O	.10					
	99.39			53.00§		

\* The method of calculation, which includes assignment of H<sub>3</sub>O<sup>+</sup> and C structurally replacing Ca (although the H<sub>3</sub>O<sup>+</sup> and C are not additive), causes the accumulated error to occur in the summation of the Ca positions. There is an excess of 0.24 expressed as H<sub>2</sub>O.

† Others: Al<sub>2</sub>O<sub>3</sub> 0.07, Fe<sub>2</sub>O<sub>3</sub> 0.03, K<sub>2</sub>O 0.05, Insoluble 0.04, SO<sub>3</sub> trace, and N<sub>2</sub>O<sub>5</sub> trace.

‡ Chlorine and fluorine must be adjusted by the same factor that was applied to other oxide ratios, namely 9.925.

§ The summation of cationic charges is taken as 53.0. To the usual 26 large anions (O+F+Cl) must be added any oxygens which occur as H<sub>3</sub>O<sup>+</sup> (see first note above) but compensating deductions must be made for Cl and F.

ular" weight, the specific gravity is calculated to be 3.062, whereas the experimental value with reference to water at 4° C. was found to be 2.968 by means of a Roller-Smith torsion balance. The disagreement is attributed to porosity of the fossilized dental enamel; it is approximately three per cent.

No difficulty was encountered in separating an adequate sample of pure dental enamel from the dentin, and microscopic examination failed to reveal any lack of homogeneity (Fig. 1). Ingamell's analysis does not show a particularly satisfactory summation despite repetition of most of the determinations. It is assumed that the explanation lies in the tenacity of hydroxyl ions, even at high temperatures. The calculations have been made, of course, on the actual analytical constituents reported and, of necessity, would be subject to slight modification if more water were assumed to be present.

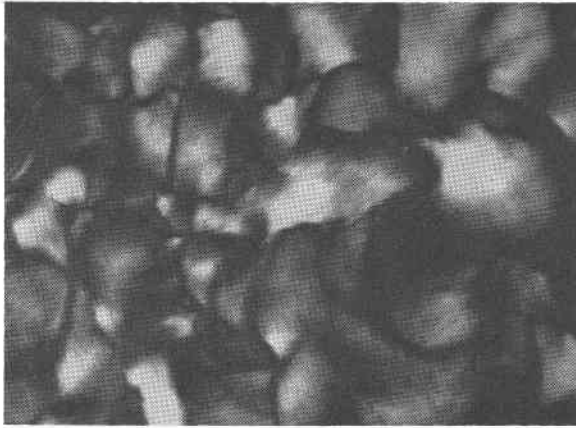


FIG. 1. Fossilized dental enamel of mastodon in section cut approximately parallel with the enamel surface. Shown are the peculiar convolutions (bending and grouping) of the enamel rods (bundles or aggregates of crystal with their  $c$  axes more or less parallel). Mag. 30 $\times$ ; polarizing prisms slightly rotated from "crossed" position.

The calculations indicate, as has been shown previously for francolite, that  $(\text{CO}_3)^{-2}$  groups enter the structure in substitution for  $(\text{PO}_4)^{-3}$  groups. The data on francolite do not fit the assumption that  $(\text{CO}_3\text{OH})^{-3}$  substitutes for  $(\text{PO}_4)^{-3}$  because there is not a straightforward relation between the water and the carbon dioxide contents. The best interpretation still postulates  $(\text{CO}_3)$  groups entering the structure in such a manner that some Ca ions are omitted, i.e. some  $(\text{CO}_3)$  groups lie parallel to  $(00.l)$ , whereas approximately three times as many  $\text{CO}_3$  groups are essentially perpendicular to  $(00.l)$  and are distributed symmetrically about an axis which has essentially (pseudo) threefold symmetry (McConnell, 1952A and 1952B).

Powder diffraction data obtained goniometrically are contained in Table 2, which also gives supplementary data on precise measurements made with the North American Philips goniometric apparatus.

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR DAHLLITE  
(Dental Enamel of Mastodon)

Line number	$hkl$	I	$d_{\text{calc}}$	$d_{\text{exp}}$
1	20.0	1	4.094	4.092
2	11.1	2	3.899	3.897
3	00.2	3	3.446	3.446
4	12.0	3	3.095	3.096
5	$\left\{ \begin{array}{l} 12.1 \\ 11.2 \end{array} \right\}$	>10	$\left\{ \begin{array}{l} 2.823 \\ 2.785 \end{array} \right\}$	2.811
6	30.0	8	2.729	2.730
7	20.2	2	2.636	2.627
8	30.1	<1	2.537	2.533
9	13.0	3	2.271	2.270
10	11.3	1	2.066	2.056
11	22.2	3	1.950	1.947
12	13.2	1	1.896	1.893
13	23.0	1	1.878	1.878
14	23.1	1	1.812	1.808
15	14.0	1	1.787	1.785
16	$\left\{ \begin{array}{l} 40.2 \\ 30.3 \end{array} \right\}$	1	$\left\{ \begin{array}{l} 1.760 \\ 1.758 \end{array} \right\}$	1.757
17	00.4	1	1.723	1.723

Precision measurements made with North American Philips apparatus:

$$d_{12.0} = 3.0959 \pm .0021$$

$$d_{13.0} = 2.2696 \pm .0006$$

$$d_{30.0} = 2.7295 \pm .0004$$

$$d_{00.2} = 3.4460 \pm .0013$$

$$a_0 = 9.454 \pm .004$$

$$c_0 = 6.892 \pm .0025$$

CuK radiation, Ni filter

Wallaey's (1954) has described a synthetic carbonate apatite for which he concludes that the  $(\text{CO}_3)$  groups are all arranged in such positions as to substitute for  $(\text{OH})$  ions, i.e. arranged essentially parallel to  $(00.l)$  but on the  $6_3$  axes. His cell dimension for the  $a$  direction greatly exceeds any previously reported for any carbonate-containing apatite. He reports  $a = 9.518 \text{ kX}$  as compared with  $9.454 \text{ \AA}$  obtained in the present work for a substance containing more than an adequate amount of  $(\text{OH}, \text{F})$  to fill these positions. Again, as was the situation with francolite, it seems highly improbable that  $(\text{CO}_3)$  groups would enter this structure in positions on the  $6_3$  axes—other monovalent anions being present in excess. The larger  $a$  dimension obtained by Wallaey's may be the result of  $(\text{O}_4\text{H}_4)$  groups substituting for  $(\text{PO}_4)$  groups; neither the precise composition of his original synthetic "hydroxyapatite" nor its carbonated product were determined by direct analytical methods.

## SUMMARY

Despite what may be a slight increase in chlorine content brought about during the process of fossilization, the dahllite sample investigated still deserves every consideration as a carbonate apatite analogous to the inorganic substance of teeth and bones. Reference to the substance of teeth and bones as "hydroxyapatites" is a misnomer; statements con-

TABLE 3. RATIOS OF LARGE CATIONS TO PHOSPHORUS FOR CARBONATE-APATITE MINERALS

Mineral	Locality and reference	Ratio Atomic Ca'/P'	Ca'	P'
Dahllite	Bluffton, Ohio present work	1.69	Ca, Mg, Na	P
Dahllite	Mouillac, France McConnell (1938)	1.72	Ca, Na, K*	P, S
Francolite (Quercyite)	François Lake, B.C. Poitevin (1927)	1.82	Ca†	P
Francolite	Busumbu, Uganda Davis (1947)	1.77	Ca, Mg	P
Francolite	Staffel, Germany Gruner & McConnell (1937)	1.85	Ca, Mg	P, V
Francolite	Richtersveld, So. Africa de Villiers (1942)	2.02	Ca, Mg, Na	P
Francolite	Yorkshire, England Deans (1938)	1.81	Ca, Sr	P
Francolite	Tavistock, Devon Sandell, <i>et al.</i> (1939)	1.80	Ca, Mg	P

\* Oxides disregarded as "impurities" were Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>.

† Disregarded were: FeO, Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, SiO<sub>2</sub> and organic C.

cerning the non-existence of carbonate apatites are absurdities based solely upon conjecture.

Most of the investigations of synthetic "hydroxyapatites," particularly those showing an appreciable range of Ca/P, can be dismissed as meaningless with respect to crystal chemical interpretation because of inadequate evidence that the preparations consisted of a single, homo-

geneous crystalline phase. One of Carlström's precipitates for example, contains diffraction lines that cannot be attributed to apatite. Also, it is particularly noteworthy that mineral carbonate apatites, like teeth and bones, do not tend to have Ca/P ratios below the theoretical value (1.667) provided other divalent and monovalent cations are taken with calcium (Table 3). To be sure, the reason for these higher values depends upon the proportionally greater substitution of carbon for phosphorus. No constancy would be expected for this ratio, and this prediction is entirely consistent with the experimental results given in Table 3.

That several persons are pretending to have a knowledge of crystallography is evident from the fact that they have copied the atomic parameters of Náray-Szabó (1930) without discovering an obvious error. The literature (Carlström lists 195 references) is burdened with meaningless data, faulty logic and *non sequiturs*. Many papers which have been written on the problem of the carbonate apatites show no evidence that the authors were cognizant of previous investigations on closely related segments of the problem. The earliest reference to the problem seems to be a statement by Haüy (1822) in which Werner is taken to task for assuming that phosphorite is not merely impure apatite.

#### *Supplementary Discussion*

Subsequent to the preparation of the manuscript of this paper, an important contribution on the laboratory synthesis of carbonate apatite has appeared (The genesis of carbonate apatites, L. L. Ames, Jr., *Econ. Geol.* 54, 829-841, 1959). The author states therein (p. 837): "The reaction equilibrium data and structural formulae indicate that this carbonate can be entirely present in the apatite lattice when the apatite contains less than 10 per cent by weight of  $\text{CO}_3^{-2}$ ." The substance of teeth and bones, to be sure, is always far below this limit so there is no need for assuming any type of adsorptive process peculiar to the surfaces of the crystallites even for dentin and bone.

Ames concludes, furthermore, that the "structural formulae, equilibrium data, and  $\text{C}^{14}$  tracing show no indications of the carbonate being present in Hendricks' 'voids' or adsorbed to any great extent on apatite surfaces . . .," and "the variable composition of the apatite phase, even in this relatively simple system, shows the fallacy of attempting to apply the laws of sparingly soluble compounds to apatite." Not only do Ames' opinions coincide with my opinions based upon my investigations of mineral carbonate apatites, but they are consistent with my interpretations of certain phenomena observed during synthesis and dissolution studies by other investigators.

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