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CRYSTAL CHEMISTRY OF BONE MINERAL: HYDRATED CARBONATE APATITES

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ABSTRACT

The additive relation between composition and the unit-cell dimension (*a*) is explored for the few examples of francolites and dahllites for which adequate chemical data are available. This work yields estimates of coefficients for several atoms: Cl (+0.115), F (−0.015), C (−0.070) Å. A mean value for H (+0.0075) cannot at present be resolved to account for the several mechanisms by which protons may enter the apatite structure to produce hydrated carbonate apatites. The constant for the compositional model, $Ca_{10}(PO_4)_6X_2$, is evaluated as 9.404 Å.

Large coefficients for Cl, positive for *a*, negative for *c*, are significant with respect to several interpretations.

In carbonate apatites (CO_3F) or (CO_3OH) substitution for (PO_4) completely fails to account for observed cationic ratios. The substitution of (CO_3) for 2 F has *not* been demonstrated in any natural (well-crystallized) carbonate apatite; it has been *surmised* as an explanation for some poorly-characterized preparations, some of which certainly are not a single apatitic phase. Many reports in the literature are unreliable because only isolated aspects of the problem were considered.

INTRODUCTION

More than 30 years ago a structural model for francolite (carbonate fluorapatite (*carFap*)) was presented by Gruner & McConnell (1937) and the general aspects of this theory were applied to the elucidation of the crystal chemistry of teeth and bones (Gruner, McConnell & Armstrong, 1937). During succeeding years, the quantitative aspect of this theory has been greatly augmented by additional data on the francolites—which are of widespread occurrence as phosphorites, and therefore of concern to geologists and mineralogists.

Progress on the crystal chemistry of the dahllites (carbonate hydroxyapatites *carHap*, essentially without fluorine) has advanced at a slower pace—in part because of analytical difficulties, but also because of diversionary interpretations which are inconsistent with the fundamental principles of crystal chemistry.

At least 20 years ago most knowledgeable persons regarded the partial substitution of carbonate groups for phosphate groups as proven. They were concerned with such minor quantitative details as the small excess of fluorine in most francolites, the question of whether the carbon-for-phosphorus substitution is on a strictly one-for-one basis, whether the structure of francolite is rigorously hexagonal, and so forth. Even today it is not possible to answer some of these questions unequivocally, but this fact should not impede progress on the major objective: refinement of the general crystallochemical theory on bone mineral.

The remaining question of major significance in connection with the dahllite series involves the water content—which, in turn, is related to the Ca/P ratio. The analysis for chemically-combined water in an apatite is fraught with difficulty because of the tenacity of the structure for hydroxyl ions. Valuable insight on this problem has been presented by Little & Casciani (1966), and theoretical postulation of at least three different types of proton incorporation in such structures is contained in the works of McConnell (eight references from 1952 to 1965).

Some valuable analytical data on synthetic apatites (Simpson, 1968) will be combined with further recent data on francolites in order to deduce semiquantitative models for carbonate apatites. While the principal interest, at this time, involves the dahllite series (teeth and bones), it becomes necessary to consider the francolites again in order to approach a realistic solution of the difficult problem of the carbonate apatites.

No attempt will be made to refute many absurd statements, in the literature. These range from the statement that carbon dioxide in francolite is present as a separate calcium-carbonate phase (based solely on infrared absorption), through a "refinement" of the structure of hydroxyapatite (using a crystal which almost certainly was *not* hydroxyapatite), to the conclusion that bone contains in excess of 40 per cent of an inorganic "amorphous" phase although observations with the electron microscope and electron diffraction give no confirmation whatever of such a situation.

APPLICABLE THEORETICAL CONSIDERATIONS

As discussed elsewhere in detail (McConnell, 1967), an additive relation exists between the volume of a structure and the nature of the atoms which comprise this structure, with the result that atomic substitutions produce proportional dimensional changes. Although this relationship (Vegard's law) may not be rigorously accurate, nevertheless, it has been applied frequently as a useful criterion for evaluation of crystallochemical data. Thus, theoretical considerations permit the expression of a unit-cell dimension (a_p) of an apatite as the summation of a series of compositional functions in the following manner:

$$a_p = a_k + x(A) + y(B) + \cdots \qquad (1)$$

where

a_p is the predicted dimension a (in Å),
a_k is a constant inherent to the structure,
$A, B \cdots$ are numbers of atoms of different species, and
$x, y \cdots$ are coefficients related to the sizes of the particular atoms.

The applicability of this relation in simple cases, such as the substitution of Sr for Ca (Collin, 1960), has been demonstrated.

The extension of this method to the complex carbonate apatites involves difficulties, to be sure, but appears to be justifiable because of its potential usefulness. These difficulties are of two kinds: (i) inadequacies of the analytical data, and (ii) theoretical factors of a crystallochemical nature. In the latter connection, for example, the effect on a of the addition of a proton will surely differ depending upon the spatial environment in which it occurs; that is, the consequence of addition of a second hydrogen to OH^- to give H_2O must be somewhat different from that of addition of H^+ to H_2O to produce H_3O^+. However, it is deduced that a mean value of the coefficient for H will suffice until further resolution of the problem is feasible.

Equation (1) is now written in such form as to cover most of the principal constituents of francolites and dahllites:

$$a_p = a_k + x(\mathrm{H}) - y(\mathrm{C}) - z(\mathrm{F}) + m(\mathrm{Cl}) - n(\mathrm{S}) \qquad (2)$$

As before, H, C, etc. represent numbers of atoms of the several elements, and a_k represents the a dimension of $Ca_{10}(PO_4)_6X_2$. (Thus, a_k is smaller than a for hydroxyapatite and chlorapatite, but larger than a for fluorapatite.) Equation (2), then, is a quantitative description of the compositional model in which 10 structural sites are occupied by Ca (with minor substituents of Na, K, Mg, H_3O^+, H_2O, etc.), 6 structural sites are occupied by P (with minor substituents of S, Si, H_4, etc.), and 24 structural sites normally are occupied by oxygen atoms. The X_2 sites normally are occupied by F, OH and/or Cl (with minor substituents of O, H_2O or H_3O^+, possibly, but *not* CO_3!).

ANALYSIS OF THE DATA ON CARBONATE APATITES

Recently several authors have contributed chemical analyses which include water, as well as X-ray diffraction measurements. They have made their results most useful with respect to present purposes by casting the stoichiometry into the format suggested by McConnell (1952).

Although Skinner (1968) does not indicate the most plausible interpretation of her results, she has demonstrated that synthetic apatites prepared at different temperatures show small but significant differences in their a dimensions, depending upon the Ca/P ratios of the starting materials. Inasmuch as water was available, I will assume that her several products probably differed in their water contents. Simpson (1968) analyzed three synthetic apatites and found that they contained far in excess of the water content for theoretical hydroxyapatite (*Hap*). The results on phosphorites presented by Whippo & Murowchick (1967) similarly demonstrate that, despite the presence of more than 2F atoms, significant quantities of water are also present for a series of francolites which range from 9.29 to 9.40 Å for *a*. Unfortunately, the analyses given by McClellan & Lehr (1969) completely disregard the water contents.

Despite the dearth of good analytical data, estimates can be made for the several coefficients, and a_k, in equation (2). As stated previously, it is necessary to treat the protons in terms of their mean effect, without regard for the type of structural configuration involved. However, some clues to approximate effects can be obtained by consideration of *a* for *Hap* as compared with that of fluorapatite (*Fap*), as well as the effect of one (H_4O_4) group substituting for one (SiO_4) group in $Ca_3Al_2(SiO_4)_3$. In the latter case, it is deduced that the effect would be >0.006 Å per proton for apatite, whereas comparing *Hap* and *Fap* suggests that the effect of one proton would be <0.010 Å. Through trial of various reasonable approximations, it has become feasible to estimate the coefficients of equation (2) as follows:

Positive coefficients (*a*)	Negative coefficients (*a*)
H 0.0075	F 0.015
Cl 0.115	C 0.070

(expressed as Ångström units per atom per unit cell).

Using these estimates, the calculated a_p values are compared with experimental values in Table 1. In view of the inadequacies of the data it does not seem feasible to estimate a coefficient for sulfur from the analyses of phosphorites, but recent work by Kreidler & Hummel (1970) suggests that the coefficient for S is very small.

Determination of a_k [that is, *a* for $Ca_{10}(PO_4)_6X_2$] includes errors of all the coefficients simultaneously. Thus, a merely approximate value of 9.404 Å can be obtained from these data; however, it can be assumed that it lies between the *a* dimensions of *Fap* and *Hap*, inasmuch as their coefficients have opposite signs.

Using these values for the coefficients and 9.404 Å for a_k, some dimensions for theoretical compositions are given in Table 2. With the exceptions of *Fap*, *Hap* and Cl-apatite, the reliabilities of these predictions are unknown. They range from 9.294 to 9.487 Å and thereby encompass values for naturally occurring substances with low Cl contents, as well as many synthetic substances for which reliable measurements are available for *a*. However, the possibility of still greater hydration exists, so 9.487 Å does not necessarily represent a maximum value.

DISCUSSION

An important consideration is the fact that *c* remains fairly constant except when Cl is involved, in which case *c decreases* significantly. The

TABLE 1. COMPARISONS OF MEASURED AND PREDICTED a DIMENSIONS FOR HYDRATED APATITES

No.[a]	a in Å (meas.)	a in Å (calc.)	Atoms per unit cell					Key to Source
			H	Cl	F	C	S	
1-*f*	9.29	9.341	1.32	0.01	2.17	0.59	0.07	W-M, 3
2-*f*	9.30	9.359	1.23	—	1.90	0.35	0.04	W-M, 7
3-*f*	9.31	9.358	1.02	—	2.18	0.30	0.02	W-M, 2
4-*f*	9.32	9.353	1.24	0.03	2.22	0.43	0.10	W-M, 1
5-*f*	9.34	9.323	0.52	none	1.98	0.79	none	SHM.
6-*f*	9.343	9.323	0.68	—	2.08	0.78	—	W-L, M83
7-*f*	9.346	9.342	0.67	—	1.84	0.55	—	B-N, f
8-*f*	9.35	9.347	0.74	—	2.03	0.47	—	W-M, 5
9-*f*	9.356	9.349	0.84	0.06	1.00	0.76	—	H-T
10-*f*	9.36	9.337	2.33	—	2.17	0.73	0.20	W-H, 4
11-*f*	9.370	9.376	0.52	—	1.60	0.12	—	W-L, M90
12-*f*	9.371	9.375	0.46	0.01	1.66	0.12	—	W-L, M91
13-*f*	9.377	9.361	0.48	0.01	1.82	0.30	—	W-L, M87
14-*f*	9.383	9.385	0.74	0.01	1.34	0.08	—	W-L, M85
15-*f*	9.396	9.387	0.82	0.08	1.28	0.18	—	W-L, M84
16-*f*	9.40	9.397	3.06	—	1.48	0.12	0.01	W-M, 6
17-*d*	9.419	9.358	1.59	—	0.22	0.79	—	B-N, d
18-*h*	9.420	9.426	4.48	—	—	0.17	—	S, K-3
19-*h*	9.427	9.447	6.80	—	—	0.12	—	S, K-2
20-*h*	9.432	9.440	4.94	—	—	0.01	—	S, K-1
21-*d*	9.454	9.405	4.00	0.12	0.02	0.61	—	M
22-*ch*	9.615	9.538	0.82	1.12	0.06	—	—	W-L, M86
Idem	9.615	9.605	do.	[1.7]	do.	—	—	Idem

[a] Letters following the numbers are: *f* = francolite, *d* = dahllite, *h* = *Hap* and *ch* = chlorapatite.

Sample numbers of original authors are given when appropriate; other symbols are: B-N is Brophy & Nash (1968); *f* is francolite from Staffel; *d* is dahllite from Allendorf, Saxony, for which the oxide sum is 98.17%. H-T is Hoffman & Trdlička (1967), francolite from Kutná Hora. Sulfur and silicon were assumed to be elemental impurities by the authors. M is McConnell (1960A) fossil dental enamel of mastodon, Ohio; sum of oxides is 99.39%. SHM is Sandell, Hey & McConnell (1939), francolite from Tavistock, Devon. S is Simpson (1968), K-1 to K-3 contained respectively 0.68, 0.84 and 0.97% K_2O. W-L is Walters & Luth (1969). The water was "determined by difference." Their M86 is reported to contain merely 1.12 atoms of Cl, but their c value suggests the amount should be 1.7 atoms, which would yield a predicted $a = 9.605$ Å. W-M is Whippo & Murowchick (1967); all samples "recalculated to an impurity-free basis," including leaching with tri-ammonium citrate to remove $CaCO_3$.

coefficients for c for Cl is estimated to be -0.055, and an illustrative example is given in terms of the two calculations for 22-*ch* (Table 1). Although Walters & Luth (1969) indicate merely 1.12 atoms of Cl, the amount estimated from the c dimension is 1.7 atoms, and this amount permits prediction of $a = 9.605$ Å (versus 9.538 Å) as compared with the

TABLE 2. PREDICTED DIMENSION (a) FOR THEORETICAL APATITES

Formula	Ca/P	a (Å)
$Ca_{10}(PO_4)_6(OH)_2$	1.67	9.419[a]
$Ca_{10}(PO_4)_6F_2$	1.67	9.374[a]
$Ca_{10}(PO_4)_6Cl_2$	1.67	9.634[a]
$[Ca_9(H_2O)](PO_4)_6(H_2O)_2$	1.50	9.449
$[Ca_9(H_3O)](PO_4)_5(H_4O_4)(H_2O)_2$	1.80	9.487
$Ca_{10}(PO_4)_5(H_4O_4)(OH)(H_2O)$	2.00	9.457
$[Ca_9(H_2O)](PO_4)_4(CO_3)_2(OH)_2$[b]	2.25	9.294

[a] Bhatnagar (1968) obtained for synthetic hydroxy-, fluor- and chlorapatites, respectively, 9.42, 9.36, and 9.63 Å; analyses [including CO_2] were not reported for the materials examined, however. Fluorapatite from Cerro de Mercado, Durango, Mexico is reported as 9.386 (Altschuler, Cisney & Barlow, 1952), 9.387 (Trautz, 1955), 9.39 (Rooney & Kerr, 1967), 9.391 (Young *et al.*, 1969), 9.39_5 (McConnell, 1952), and 9.398 (Simpson, 1965), 9.40 (Newesely *et al.*, 1968). Measurements, such as 9.352 ± 0.001Å for synthetic fluorapatite (Wallaeys, 1952), obviously are erroneous. For hydroxyapatite $a < 9.413$ or > 9.425 probably represent spurious values; it is noteworthy that the often-cited "refinement" of the structure was made on a crystal outside of this range (9.43_2). [*Added to proof*] Bhatnagar (*Rev. Roumaine Chim.* **15**, 87–89 [1970]) gives for synthetic *Fap:* $a = 9.3680$, $c = 6.8868$ Å.

[b] This *compositional* model assumes one-for-one substitution of C for P, which probably is not correct structurally [see text].

measured $a = 9.615$ Å. The c dimensions for all specimens (except 22-*ch* and 1-*f*) in Table 1 were 6.880 ± 0.015 Å.

While some of the large a dimensions which Bonel & Montel (1964) have attributed to substitution of CO_3 for F_2 [or $(OH)_2$] may not be the consequence of Cl substitution, it is important to note that the c dimensions of some of these concoctions are significantly less than 6.88 Å Also LeGeros *et al.* (1969) indicate that Elliott's carbonate apatite with CO_3 groups supposedly lying on the 6_3 axis, shows at least 5 diffraction maxima that cannot be attributed to apatite (2θ from 28–35°). Not only are some of these unjustifiable conclusions based on unanalyzed mixtures (certainly two or more phases for Elliott's material supplied to LeGeros), but the location of a CO_3 group on a 6_3 axis in a position other than parallel with the basal pinacoid involves some drastic symmetry changes for which Elliott has come forward with no explanation whatever.

Indeed, before accepting the supposition that CO_3 can substitute for 2F in apatite, it must be demonstrated that the required molecular weight increase actually occurs, and that the resulting density and refractive indices are compatible with such an interpretation. Furthermore, it would make such speculations more realistic were the advocates to demonstrate that their concoctions were actually a single apatitic phase.

The calculated value for *Hap* (9.419 Å in Table 2) is reasonably close to that (9.416) given by McConnell and Foreman (1966). Some measured *a* values for *Fap* from Durango are given in the notes (Table 2); they are considerably larger than those reported for synthetic *Fap*. The predicted *a* for Cl-apatite is necessarily self-consistent inasmuch as this was the value used for estimation of the coefficient for Cl.

Two significant discrepancies exist (17-*d* and 21-*d*) which could result from the pronounced tenacity of some hydrated apatites for water. The summations of oxides for these samples are indicated as notes, following Table 1.

Among the *f* series (Table 1), some of the differences between measured and predicted values may be attributable to removal of carbon dioxide from the apatite structure during leaching with tri-ammonium citrate. For example, the amount of CO_2 used to predict *a* for 3-*f* was 1.32 percent whereas the analysis of the sample prior to leaching gave 2.16 percent of CO_2. However, this explanation is not applicable for 4-*f* and 1-*f* because the CO_2 contents were greater for the leached materials.

A similar problem arises in connection with the treatment of bone with ethylenediamine (in order to remove organic matter), because there is no straightforward evidence that the composition of the carbonate hydroxyapatite will not be altered by such treatment. In connection with a study of the calcareous algal genus *Halimeda* (McConnell & Colinvaux, 1967) it was found that the abundant inorganic material, aragonite, was completely destroyed by this reagent.

Most of the examples presented in Table 1 were calculated by the original investigators to include (H_4O_4) substitution for (PO_4), and this fact must be set in contradistinction to Elliott's (1969) statement: "There is as yet no direct evidence that this replacement [(H_4O_4) for (PO_4)] occurs in apatites." On the other hand, Young & Elliott (1966) seem to believe that the position of the proton of the (OH) group can be located precisely by a refinement of low-precision diffraction data on hydroxyapatite—that is, relative intensity data obtained from a crystal that almost certainly was not simply $Ca_{10}(PO_4)_6(OH)_2$. In view of the absence of adequate quantitative chemical information on the carbonate apatites, many of the interpretations in the literature—particularly those based solely on such methods are infrared absorption spectroscopy —should be disregarded as meaningless.

On several occasions it has been suggested—most recently by Walters & Luth (1969)—that there is substitution of F or OH with each CO_3 group to form (CO_3F) or (CO_5OH). Previously it has been indicated (McConnell,1960a) that there is no direct correlation between [(F,OH, Cl)-2] and carbon, and this situation is reiterated in Table 3. For the *f* series the ratios range from 0.6 to 5.2, but for the *d* and *h* series they

TABLE 3. SIGNIFICANT RATIOS OF HYDRATED CARBONATE APATITES

Example[a]	Ca′/P′	$\frac{Ca'}{(P'+C)}$	$\frac{(F+OH+Cl-2)}{C}$	Example[a]	Ca′/P′	$\frac{Ca'}{(P'+C)}$	$\frac{(F+OH+Cl-2)}{C}$
1-*f*	1.82	1.64	2.4	10-*f*	1.87	1.64	3.4
2-*f*	1.75	1.65	3.2	16-*f*	1.71	1.67	5.2
3-*f*	1.73	1.64	4.0	17-*d*	1.60	1.41	−0.2
4-*f*	1.79	1.69	3.5	18-*h*	1.71	1.66	15.
5-*f*	1.80	1.57	0.6	19-*h*	1.62	1.58	40.
7-*f*	1.78	1.61	0.9	20-*h*	1.53	1.53	294.
8-*f*	1.78	1.64	1.6	21-*d*	1.69	1.53	3.5
9-*f*	1.87	1.67	2.6				

$Ca' = Ca + Na + Mg + \cdots$ (on the basis of atoms per unit cell). $P' = P + S$. For $Ca_{10}(PO_4)_6F_2$, $Ca'/P' = 10/6 = 1.67$.

[a] The examples are numbered as in Table 1, except samples reported by Walters & Luth (1969) are omitted because these ratios cannot be obtained from their data.

are from −0.2 to 294. A negative ratio can be interpreted merely as the presence of the oxyapatite (voelckerite) component, but cannot be regarded as proof of its existence in view of the difficulty involved in the water determination. McConnell & Hey (1969) have discussed this topic.

Another ratio, Ca′/P′+C), is considered in Table 3. Were the (CO_3) for (PO_4) substitution on a one-for-one basis, this ratio should be 1.67, provided the ten Ca sites are filled with ordinary cations, that is $Ca' = Ca + Na + Mg + \cdots = 10$. Ca′ cannot be > 10.

Despite the fact that Ca′/P′ significantly exceeds 1.67 for the entire *f* series, the ratio Ca′/(P′+C) is < 1.67 for all examples except 4-*f*, 9-*f* and 16-*f*. There are only two interpretations: (i) either C substitutes for P in a ratio greater than unity, or (ii) all ten Ca sites are not occupied by Ca′ cations. It seems probable that both interpretations are correct; that is

$$3(PO_4)^{3-} \rightarrow 4(CO_3)^{2-}$$

and simultaneously $$Ca^{2+} \rightarrow (H_3O)^+$$

thus producing a balance of electrical charges $(-9+2=-8+1)$. These interpretations do not disprove the substitution of (H_4O_4) for (PO_4) (McConnell, 1965). Indeed 4-*f* is further tentative confirmation insofar as $Ca'/(P'+C) > 1.67$.

Finally, it should be stated that there is no question whatever regarding certain phenomena connected with apatites:

(1) In many cases the amount of (F+OH) significantly exceeds that required to fill sites at $(0,0,\frac{1}{4})$.

(2) The carbon dioxide content of natural, well-crystallized carbonate apatites may exceed 4.27 percent (the maximum for $Ca_{10}(PO_4)_6CO_3$) and there is no straighforward proof that (CO_3) ever substitutes for $(OH)_2$. In fact, this type of substitution has been postulated only for some dubious concoctions which have not been adequately investigated, and has ever been demonstrated for a well-crystallized natural substance.

(3) There is no good evidence of a direct correlation between (F+OH) and CO_2 for francolites or dahllites, so the supposition of substituion of (CO_3F) or (CO_3OH) for (PO_4) is untenable.

(4) Carbonate apatites of the fluorine-containing variety (francolite) and the low-fluorine variety (dahllite, less than 1 percent F) are widespread in nature, but their understanding involves some appreciation of fundamental crystallochemical principles, and their analysis involves difficult techniques.

Here, the attempt has been made to obtain a semiquantitative correlation between the diverse compositions and a single physical property (the dimension *a*). Other physical properties, including the refractive indices, have been discussed elsewhere, for example, Lehr, McClellan, Smith & Frazier (1967) confirm the observation made by McConnell & Gruner (1940) that the introduction of carbonate groups tends to decrease the mean refractive index, although the later work contains no reference to the earlier results. Optical observations on francolites (*i.e.*, their biaxial character and twinning) suggest that they are not hexagonal, but triclinic, and this may be true of carbonate apatites, in general. Demonstration that Al can substitute for both Ca and P (Fisher & McConnell, 1969) is illustrative of the complexity of the crystallochemical relationships.

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