THE PROPERTIES AND STRUCTURE OF $Ca_{10}(PO_4)_6(OH)_2$; ITS RELATION TO TIN (II) APATITE

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ABSTRACT

The refractive indices of synthetic hydroxyapatite are $\omega = 1.651$ and $\epsilon = 1.647$ (both ±0.002) and the unit-cell dimensions are $a = 9.416$ Å and $c = 6.883$ (both ±0.002). Measured and calculated intensities for powder diffraction reflections ($d > 1.720$ Å) are compared.

Apatites with complete substitution of stannous ions for calcium ions do not seem to form in hot aqueous solutions, but something approximating $Sn_9Ca(PO_4)_6(OH, F, Cl)_2$ was obtained. Its precise stoichiometry is uncertain. All attempts to produce Zn-substituted apatite resulted in a mixture of phases, one of which usually was hopeite [$Zn_3(PO_4)_2.4H_2O$].

INTRODUCTION

Apatites involving isomorphic substitution of CO_3 groups for PO_4 groups are of considerable interest because of their natural occurrences as hard parts of both vertebrate and invertebrate organisms. Such substances are not, in general, suitable for investigation by more refined, single-crystal diffraction methods because of the submicroscopic dimensions of the crystallites.

The situation is further complicated, insofar as the crystal chemistry is concerned, by the substitution of H_4O_4 groups (so-called tetrahedral hydroxyls) for PO_4 groups (McConnell, 1965). Both types of substitution (CO_3 and H_4O_4 for PO_4) alter the physical properties of apatites, as well as the Ca/P ratios, but it is not possible at this juncture to furnish quantitative data on these separate effects because, thus far, it has been impossible to obtain measurements involving one of these phenomena with the exclusion of the other.

Klement & Haselbeck (1963) discussed the character of certain tin phosphates; they prepared $Sn_8Ca_2(PO_4)_6Cl_2$, as well as $Sn_5Ca_5(PO_4)_6F_2$, both of which were apatites. Our stannous phosphate preparation more closely approximates $Sn_9Ca(PO_4)_6(OH,Cl,F)_2$; it is also an apatite. Stoichiometric apatites are difficult to synthesize, judging from an appraisal of results reported in the literature (McConnell, 1960).

SYNTHETIC HYDROXYAPATITE

The synthetic material which we investigated is thought to be an excellent approach to the stoichiometric substance; it was produced by the research laboratories of the Tennessee Valley Authority by hydrothermal methods in conjunction with leaching by citrate. It has the correct Ca/P ratio and does not contain a significant amount of carbon dioxide. The refractive indices are compared with other synthetic substances in Table 1, as are the unit-cell dimensions.

TABLE 1. COMPARISONS OF SYNTHETIC HYDROXYAPATITES

Reference	Dimensions		Refringence	
	a (Å)	*c* (Å)	ϵ	ω
This work	9.416 ± 0.002	6.883 ± 0.002	1.647	1.651
Collin (1959)	9.418 ± 0.003	6.883 ± 0.003	—	—
Trautz *et al.* (1955)	9.421 ± 0.003	6.881 ± 0.003	—	—
Lagergren & Carlström (1957)	9.42_3	6.88_4	—	—
Newesely (1963)	9.410 ± 0.005	6.867 ± 0.005	—	—
Winand (1963)	9.41 ± 0.01	6.874 ± 0.008	—	—
Simpson (1964)	—	—	1.648	1.652
Mitchell *et al.* (1943)	—	—	1.644	1.651
Posner *et al.* (1958)	9.43_2	6.88_1	1.643	1.649*

*Perloff & Posner (1956) *Science* **124**, 583–584.

It is noteworthy that the material used by Posner *et al.* (1958) for the "refinement" of the structure of hydroxyapatite shows not only the largest unit-cell dimensons, but also the lowest refractive indices (Table 1). The probability that this material was a good, stoichiometric hydroxyapatite seems quite remote. They did not report the analysis, the Ca/P ratio, or indeed what safeguards had been used to prevent contamination by carbon dioxide or sodium (replacing Ca). Under the circumstances their elaborate measurements of intensity values are quite meaningless with respect to their claimed refinement of the structure, despite their use of the single-crystal method.

Powder diffraction methods surely have limitations, but, assuming that the whole composition of the sample has been determined by chemical analysis, compensating advantages also exist. In order to establish a basis for comparison with microcrystalline substances, we have applied the powder method to synthetic hydroxyapatite, with the results shown in Table 3. The atomic positions, to be sure, cannot be stated as precisely as attempted by Posner *et al.* (1958). We have used the values shown in Table 2.

The atomic scattering factors used in the calculations were taken (for Ca^{+2}) from the *International Tables for X-ray Crystallography*, vol. III (1962) and (for P^{+5}, O^{-2} and F^{-}) from the earlier German edition (1935). Although our calculated F values are not identical with those of Posner *et al.*, the differences are not entirely attributable to the differences in atomic positions. The atomic scattering factors which they used, the sources of which were not stated, may be the explanation for certain differences between our results (using their atomic positions and their temperature factors) and the F_c values in their table. (They do not give calculated or measured values for pinacoidal reflections inasmuch as their measurements involved merely rotation about *c*.)

TABLE 2. ATOMIC PARAMETERS FOR HYDROXYAPATITE

Atom	*x*	*y*	*z*
Ca_{I}	0.33	0.67	0
Ca_{II}	0.25	0	0.25
P	0.40	0.37	0.25
O_{I}	0.33	0.50	0.25
O_{II}	0.60	0.48	0.25
O_{III}	0.35	0.26	0.07
OH	0	0	0.25

SYNTHETIC TIN (II) APATITE

Possible cationic substitutions in apatite have been extensively investigated and, while coupled anionic substitution frequently occurs also, it might be supposed that fairly complete substitution of Sn^{+2} for Ca^{+2} could be attained. This does not seem to be the situation, however, according to Klement & Haselbeck (1963), and we are not in a position to further elaborate on the reasons, although our product indicated approximately 9 of the 10 Ca positions contained tin, as indicated by gravimetric analysis of tin as the sulfide. The CaO and P_2O_5 were not determined and it is suspected that our preparation was not simply $Sn_9Ca(PO_4)_6(OH,F,Cl)_2$ because this compound should have smaller unit-cell dimensions—considering the comparative radii of Sn^{+2} (0.93) and Ca^{+2} (0.99), according to Ahrens (1952).

The dimensions of our tin apatite were $a = 9.45$ and $c = 6.89$ Å. This increase in *c* surely cannot be attributed to chloride ions, so another explanation is required.* No simple alternative suggests itself for these increases in *a* and *c* except the substitution of H_4O_4 for PO_4, accompanied by H_2O substitution for OH, as was reported for the mineral from Sabinas Hidalgo, Mexico (McConnell, 1965).

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*Inasmuch as the Cl^- ion has a *z* parameter of 0.50 (as compared with 0.25 for F^- or OH^-), this ion does not tend to cause an increase in the *c* dimension, despite its significantly larger ionic radius, because it is surrounded by 6 Ca^{+2} ions whereas F^- or OH^- is surrounded by 3. The value of *c* for chlorapatite is probably 6.77 Å, as compared with about 6.88 Å for both hydroxyapatite and fluorapatite.

Presumably the stannous ions would more readily substitute in one type of site for Ca than in the other, thus giving rise to three different models, as follow:

(i) The *remaining* Ca atom would occur as Ca_I,
(ii) it would occur as Ca_{II}, or
(iii) it would be statistically distributed between Ca_I and Ca_{II}, either in accordance with the relative abundance (4:6) of the two different Ca sites or without regard for such a difference.

Using the scattering factors for Sn^{+2} of Thomas & Umeda (1957), we were unable to decide which model gave calculated values that would most closely approximate the experimental intensities. Inasmuch as the calculated F values are appreciably different for certain reflections of these three models, we concluded that the composition of our preparation probably was not simply $Sn_9Ca(PO_4)_6(OH, F, Cl)_2$.

Judging from our own experiences, those of Klement & Haselbeck (1963) and several other persons who have attempted it, the preparation of tin apatite is fraught with many failures to obtain a single phase that has the structure of apatite, rather than a mixture. Our numerous efforts to prepare Zn-Ca apatites in aqueous media likewise have consistently yielded mixtures, one phase commonly being hopeite, $Zn_3(PO_4)_2.4H_2O$. The ionic radius of Zn^{+2} (0.74) seems to be too small to permit significant substitution of this element for Ca^{+2} (0.99).

Tin apatite was prepared by adding successively to 10 ml of boiling water: 4 ml of molar $CaCl_2$ solution, 1 ml of saturated SnF_2 solution, and 5 ml of 0.6 M solution of NaH_2PO_4. These additions were repeated four times after refluxing for 15 minutes between each. The acidity was reduced by small additions of NaOH solution using methyl red as an indicator.

The resulting white precipitate was recovered on filter paper, washed with boiling water, and dried in a desiccator. After drying at 60° for 4 hours the product weighed slightly less than 0.6 g. The tin content was estimated by dissolution in HCl, by treatment with H_2S, and by weighing the brown precipitate as SnS. However, examination of this sulfide precipitate by *x*-ray diffraction suggested that some SnS_2 was present. Consequently, our preparation cannot be assumed to be free from stannic ions and the relative abundances of fluoride, hydroxyl and chloride ions is not precisely known. The mean refractive index of this preparation was 1.625.

CONCLUSIONS

Preparation of stoichiometric apatites in aqueous systems is by no means a simple procedure because of the possible isomorphic substitution of Na, K, and possibly water molecules for Ca ions. In general, carbonate substitution for phosphate will take place unless great care is exercised to exclude carbon dioxide from all reagents (including the water), inasmuch as all solid "reagent" phosphates that we have examined show significant effervescence with normal HCl.

TABLE 3. COMPARISONS OF OBSERVED (I_0) AND CALCULATED (I_c) INTENSITIES FOR SYNTHETIC HYDROXYAPATITE*

d_0	d_c	*hk.l*	I_0	I_c
8.147	8.158	10.0	10	15
5.267	5.259	10.1	5	8
4.711	4.710	11.0	2	<1
4.079	4.079	20.0	6	12
3.892	3.887	11.1	6	<1
3.506	3.509	20.1	5	7
3.441	3.440	00.2	35	34
3.175	3.170	10.2	10	12
3.083	3.083	21.0 12.0	19	14
2.812	2.814	21.1 12.1	103	98
2.778	2.778	11.2	65	43
2.718	2.719	30.0	74	61
2.628	2.630	20.2	26	24
2.525	2.529	30.1	5	4
—	2.355	22.0	—	<1
2.297	2.296	21.2 12.2	4	8
2.262	2.263	31.0 13.0	22	19
2.229	2.228	22.1	3	2
—	2.208	10.3	—	<1
2.148	2.149	31.1 13.1	5	7
—	2.133	30.2	—	<1
2.060	2.062	11.3	4	7
2.039	2.039	40.0	2	2
1.998	1.999	20.3	5	2
—	1.955	40.1	—	1
1.943	1.943	22.2	34	32
1.891	1.890	31.2 13.2	13	16
1.871	1.872	32.0 23.0	5	6
1.845	1.840	21.3 12.3	44	32
1.805	1.806	32.1 23.1	19	20
1.779	1.780	41.0 14.0	18	13
1.755	1.754 1.753	40.2 30.3	16	15 2
1.721	1.720	00.4	20	17

*Experimental data were obtained on a Philips diffractometer with filtered Cu radiation. Calculated spacings (d_c) are for $a = 9.42$ and $c = 6.88$ Å. Calculated I_c are for parameters shown in Table 2, using the same temperature factors as those used by Posner *et al.* (1958). The I_0 values in this table are insignificantly different from those previously given (*Arch. Oral. Biol.* **10**, p. 424); previous I values were visual estimates and some reflections with an intensity of 5 or less were omitted, particularly (10.1) and (20.1).

Even in cases where carbon dioxide can be eliminated completely, the substitution of H_4O_4 must be considered. If the phosphate concentration is greatly increased in order to eliminate such difficulties, there is a tendency to form mixtures with Ca:P < 1.667. So-called "Ca-deficient apatites" are readily explained on this basis or the types of isomorphic substitution mentioned in the paragraph above.

Most naturally-occurring apatites that have Ca:P > 1.667 are explainable by substitution of SO_4, SiO_4, H_4O_4, and/or CO_3 groups for PO_4 groups.

Although Sn^{+2} definitely can be caused to substitute for Ca^{+2} in apatite, $Sn_{10}(OH)_2(PO_4)_6$ does not seem to be obtainable in aqueous systems containing Ca ions. Zinc apatite has been reported, but we have been unable to confirm its preparation in an aqueous system. All crystalline substances so produced gave diffraction lines of hopeite.

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