

APATITE STRUCTURES

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ABSTRACT

The structure of apatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, can be described in terms of an approximate hexagonal close packed set of spheres in which each sphere represents a tetrahedral PO_4^{3-} ion. This packing has octahedral interstitial sites that form channels through the structure parallel to the hexagonal axis. The F⁻ and 4/10ths of the Ca^{2+} ions are located in these channels forming columns of F⁻ and Ca^{2+} ions respectively. The remaining 6/10ths of the Ca^{2+} ions form Ca triangles around the F⁻ ions. The relation between the hexagonal closed packed and apatite cells is discussed. CO_3^{2-} ions are thought to replace PO_4^{3-} ions in the lattice in precipitated carbonate-containing apatite (CO_3Aps). Rietveld refinements based on powder X-ray diffraction data from a series of precipitated CO_3Aps containing Na with a maximum CO_3 content of 17 wt% are reported. An apatite model without explicit inclusion of the CO_3^{2-} ion was used. There was clear evidence (PO_4 volume, O and P occupancies) of the replacement of PO_4^{3-} by CO_3^{2-} ions in the apatite lattice. However, the observed P occupancy was much higher than expected if all the CO_3^{2-} replaced PO_4^{3-} ions.

INTRODUCTION

Apatites have the general formula, $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$ where X is typically F (fluorapatite, FAp), OH (hydroxyapatite, OHAp), or Cl (chlorapatite, ClAp). The apatite lattice is very tolerant of substitutions, vacancies and solid solutions, for example, X can be replaced by $\frac{1}{2}\text{CO}_3$ or $\frac{1}{2}\text{O}$; Ca by Sr, Ba, Pb, Na or vacancies; and PO_4 by HPO_4 , AsO_4 , VO_4 , SiO_4 or CO_3 [1].

Apatites are widely distributed as accessory minerals in igneous rocks and in small quantities in most metamorphic rocks. This wide-spread occurrence is an important factor in their extensive use in fission-track chronothermometry for the study of geological thermal history. Rock phosphates (microcrystalline apatites), mostly of biological origin, are the starting material for phosphate fertilizer manufacture and a source of phosphorus for the chemical industry.

The mineral of bones and teeth is an impure form of OHAp, the major departures in composition being a variable Ca/P mol ratio (1.6 to 1.7, OHAp is 1.66), and a few percent CO_3 and water. The mineral is microcrystalline. The crystals are very approximately 150 Å wide by 400 Å long in bone and dentine, and 400 Å wide by from 1000 Å to 5 : m or more in dental enamel. They are much thinner than they are wide. OHAp is also used as a biomaterial, for example, for bone replacement and augmentation, and for coating metal prostheses to improve their biocompatibility.

Synthetic apatites (Sb and Mn doped halophosphates, *i.e.* chlorfluorapatites) are used as phosphors in fluorescent light tubes. Microcrystalline OHAp are also used for chromatographic separation of polypeptides and proteins. Apatites have potential for use as lasers and microcrystalline apatites for

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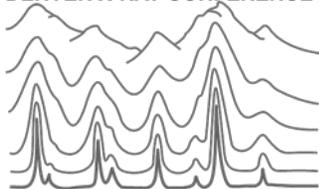
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catalysts (dehydrogenation and dehydration of alcohols) and decontamination of soils of heavy metal ions.

The basic apatite structure was published nearly simultaneously by Nary-Szabo [2] and Mehmel [3] in 1930. The structure is hexagonal with space group $P6_3/m$ and approximate lattice parameters $a = 9.37\text{Å}$ and $c = 6.88\text{Å}$. There are two crystallographically different Ca atoms, and three O atoms. The unit cell comprises $\text{Ca}(1)_4 \text{Ca}(2)_6 (\text{PO}_4)_6 \text{F}_2$, neglecting the distinction between O atoms. Beevers and McIntyre [4] have provided an excellent description of the structure, including good (coloured) "ball and spoke" drawings (Fig. 1). The structure is also depicted on the internet [5].

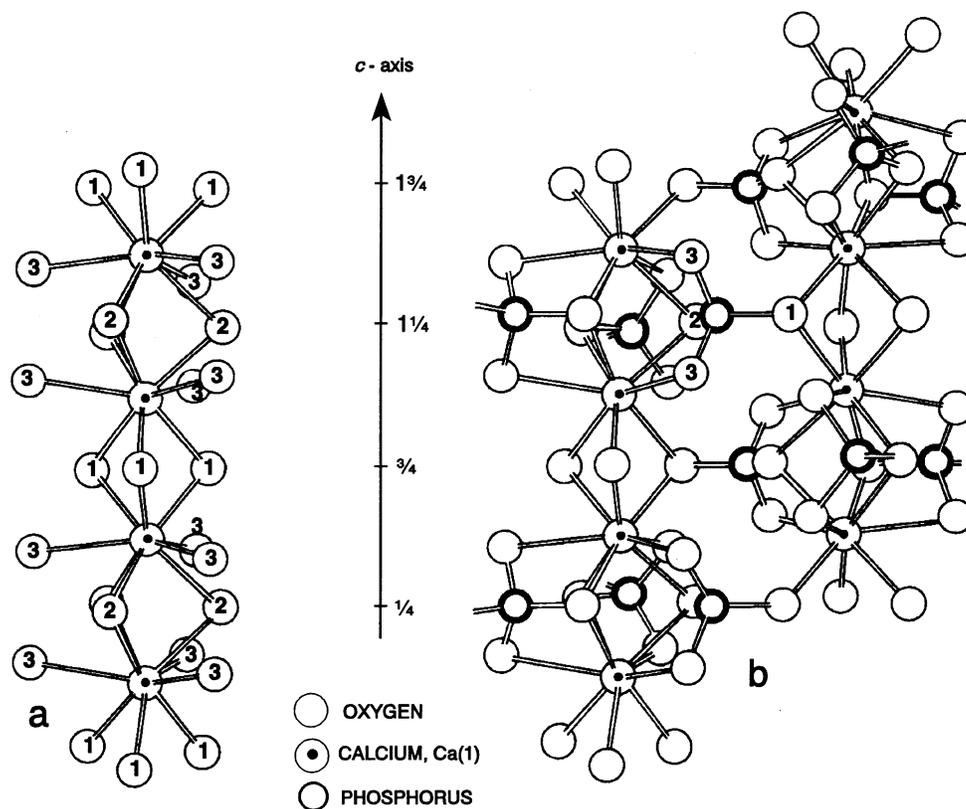


Fig. 1. (a) Oxygen coordination of columnar Ca(1) ions in apatite. (b) linking of columns via PO₄ tetrahedra. The oxygen atoms in (a) and in one tetrahedron in (b) have been numbered, and positions of the horizontal mirror planes at 1/4, 3/4 etc. marked on the c-axis. Fig. 2.2 of Elliott [1], after Fig. 3 of Beevers and McIntyre [4].

The ball and spoke representation conveys the structure as rather complex, but consideration of the packing of the largest ions (PO₄³⁻) reveals the structure has a basic simplicity: the structure comprises approximate hexagonally packed spheres (radius ~2.6 Å) in which each sphere represents a tetrahedral PO₄³⁻ ion [6]. In discussing this representation, the abbreviation hcp will be used for both exact hexagonal close packing and the approximate packing found in apatite. As is well known, the hcp structure [7,8] comprises sheets of touching spheres arranged on a hexagonal grid. The sheets are packed in an ABABAB sequence, so the 1st and 3rd, 2nd and 4th, etc. sheets are vertically over each other (Fig. 2). Each sphere is 12-fold coordinated, six from within a sheet and

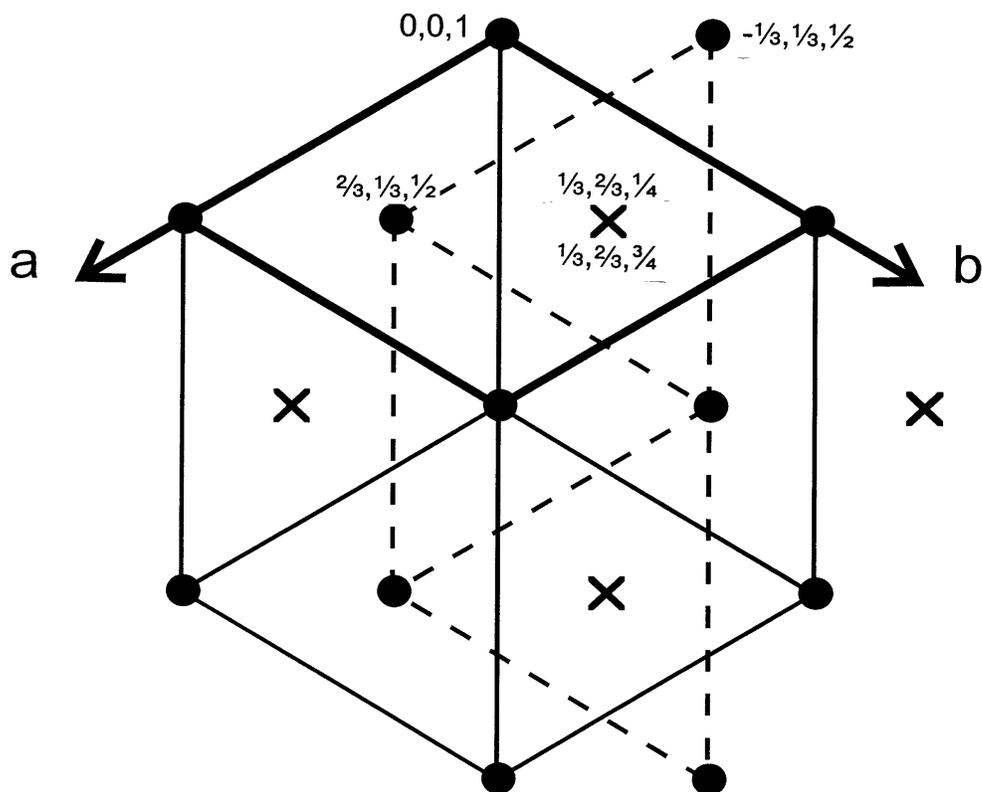


Fig. 2. Unit cell (heavy line) of hcp spheres (●) viewed down hexagonal c -axis. Spheres connected by full lines are at $z = 1$ (they overlie a similar sheet at $z = 0$) and dashed lines are at $z = \frac{1}{2}$. Octahedral holes (X), coordinated by 6 spheres, overlie each other in the c -axis direction. Some positional parameters are given. After Fig. 8.6b of Phillips and Williams [7].

three from above and three from below. The structure contains two different sized holes. If the spheres have a radius r , the smaller holes can accommodate spheres of radius $0.225r$ ($= 0.58\text{\AA}$), which is too small for most ions, so they are of no further interest. The larger holes can accommodate spheres of radius $0.41r$ ($= 1.1\text{\AA}$), so can be occupied by ions (Ca^{2+} radius 1.06\AA , F^- radius 1.33\AA), particularly if the hcp packing is distorted. The larger holes are midway between the sheets (X in Fig. 2) and are coordinated by six spheres (three from each sheet) at the corners of a regular octahedron and are therefore called "octahedral holes". These holes lie vertically over each other forming long channels or columns in the c -axis direction through the structure.

The unit cell for the hcp structure (Fig. 2) has a sphere (●) at each corner (from A sheets at $z_{\text{hcp}} = 0$ and $z_{\text{hcp}} = 1$), and one inside (from a B sheet at $z_{\text{hcp}} = \frac{1}{2}$) and octahedral holes (X) at $z_{\text{hcp}} = \frac{1}{4}$ and $\frac{3}{4}$. Thus the hcp cell comprises two spheres and two octahedral holes. As the apatite cell contains six PO_4^{3-} ions, three hcp cells are needed to describe it (Fig. 3), giving six octahedral holes per apatite cell. The mirror planes through the sheets of spheres (*i.e.* PO_4^{3-} ions) at $z_{\text{hcp}} = \frac{1}{2}$ and 1 are retained, so, as $z_{\text{ap}} = z_{\text{hcp}} - \frac{1}{4}$, the apatite cell has mirror planes at $z_{\text{ap}} = \frac{1}{4}$ and $\frac{3}{4}$, but some other symmetry elements of the hcp structure are lost. The parameters (referred to the apatite cell) of the octahedral

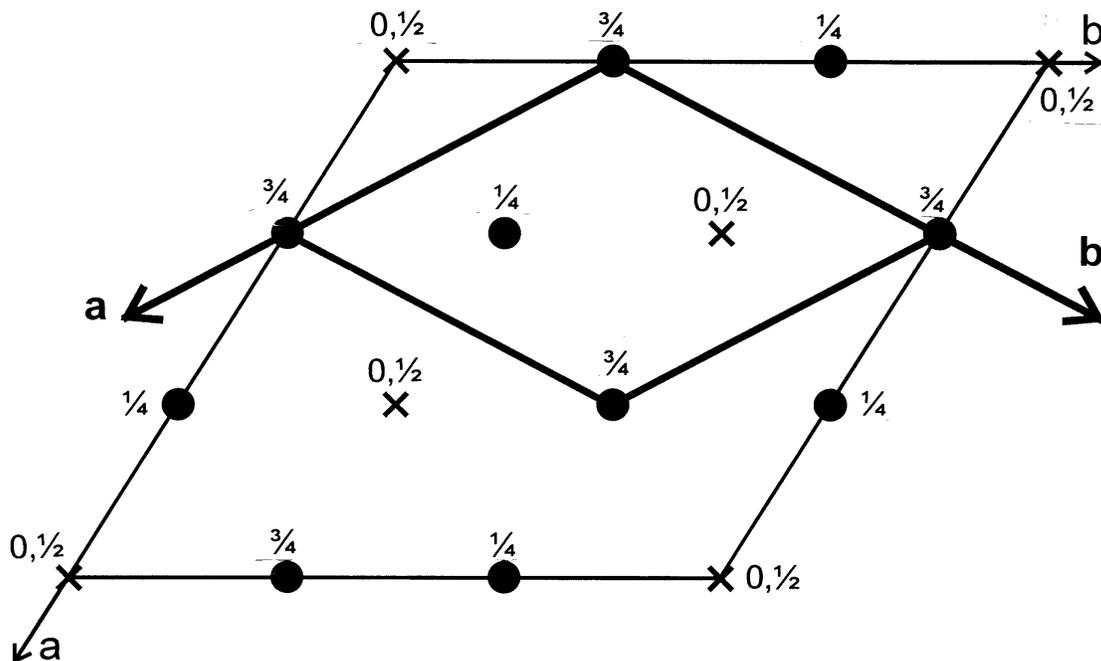


Fig. 3. Relation between hcp (heavy line) and apatite (light line) unit cells. Spheres (●) and octahedral holes (X) are marked. Parameters referred to the apatite cell for z are given; those for x and y are multiples of $\frac{1}{3}$ and can be determined by inspection. Corresponding parameters referred to the hcp cell are in Fig. 2.

holes are $0,0,0$; $0,0, \frac{1}{2}$; $\frac{1}{3}, \frac{2}{3}, 0$; $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$; $\frac{2}{3}, \frac{1}{3}, 0$; and $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$ (Fig. 3). In apatite, the first two octahedral holes (on the c -axis) are occupied by X ions if they are very large (e.g. Br [9]). Smaller X ions, e.g. F, are at $z = \frac{1}{4}$, but intermediate sized ions move along the c -axis towards $z = \frac{1}{2}$ (see later discussion). The remaining four octahedral holes are filled with Ca(1) ions (typically displaced $\sim 0.01 \text{ \AA}$ in the c -axis direction). As the octahedral holes occur in long columns in the c -axis direction through the structure, the X and Ca(1) ions form long columns, in fact the Ca(1) ions are often called the columnar calcium ions. Thus it is seen that the arrangement of the two X and four Ca(1) ions in the apatite unit cell arise naturally from a consideration of the packing of the six large PO_4^{3-} ions. The remaining 6 Ca(2) ions are accounted for by forming two Ca(2) triangles (Fig. 4) around the c -axis centred at $0,0,\frac{1}{4}$ and $0,0,\frac{1}{2}$, e.g. with F ions at their centres in FAp.

As Beevers and McIntyre [4] described it, the Ca(2) ions are located within "caves" formed by the O(3) atoms that line the c -axis channels. The detail of the positions of the O atoms of the PO_4^{3-} ion can be seen from Fig. 1. Assuming there is no departure from the hcp structure, trigonometric considerations give the following relations: $a_{\text{hcp}} = 2r$, $c_{\text{hcp}} = 8r/\sqrt{6}$ and $a_{\text{ap}} = \sqrt{3}a_{\text{hcp}}$, $c_{\text{ap}} = c_{\text{hcp}}$. The relations for the apatite cell parameters confirm, as expected, that the apatite cell is three times the volume of the hcp cell.

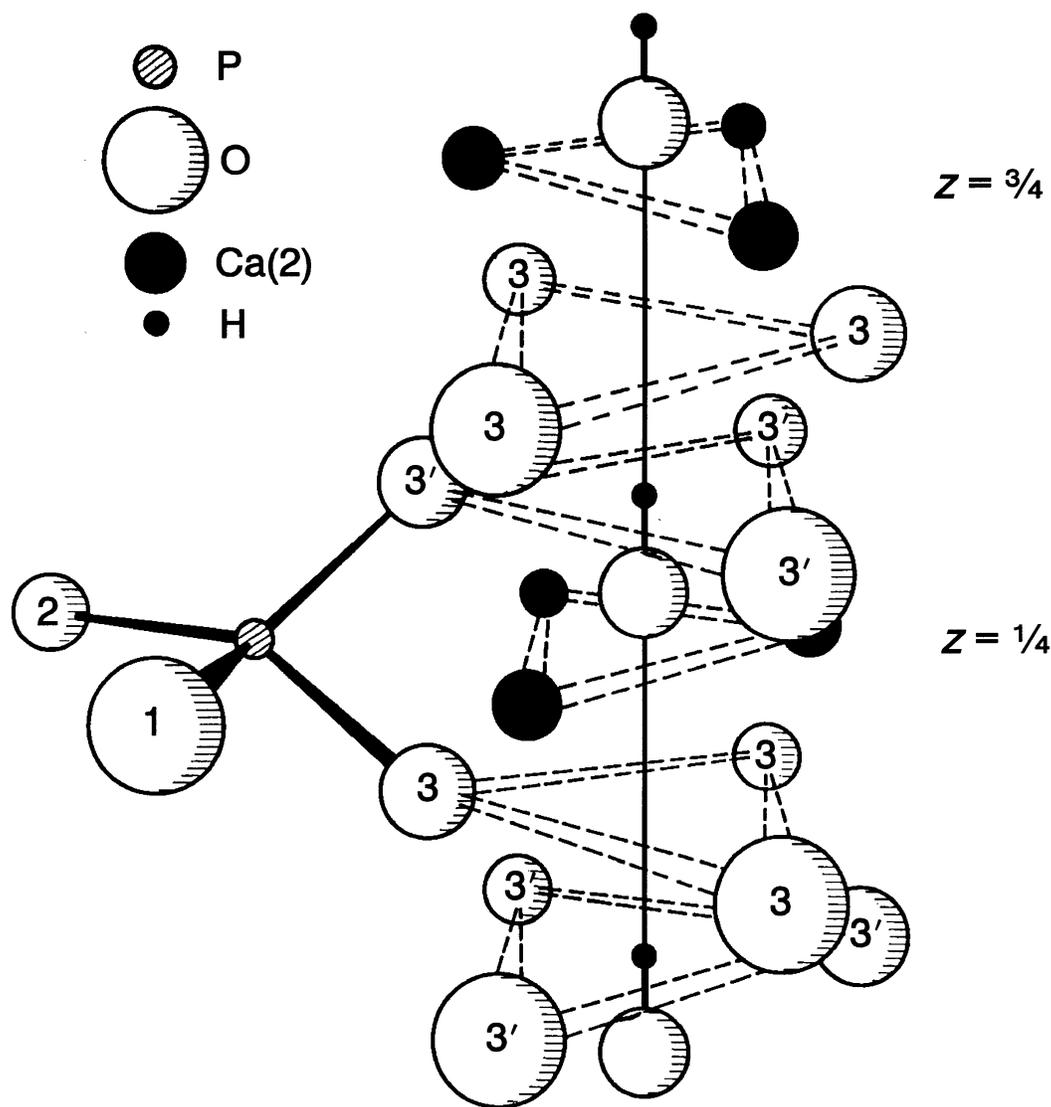


Fig. 4. Arrangement of ions around the c -axis in OHAp (see text for discussion of possible OH^- ion disorder). In other apatites, the F^- ion is at the centre of the Ca(2) triangle at $z = 1/4$, but the Cl^- ion (like the OH^- ion) is above this position. The Br^- ion is at $z = 1/2$, at the centre of an octahedral hole. (Fig. 4 of Elliott and Mackie [10], adapted from Fig. 3 of Young [11]).

For $r = 2.6 \text{ \AA}$, the relations give apatite cell parameters: $a = 9.0067 \text{ \AA}$, $c = 8.4916 \text{ \AA}$ and $a/c = 1.0607$. The corresponding figures for FAp [12] are 9.367, 6.884 and 1.3607 respectively. The fact that a/c (independent of the somewhat arbitrary choice of r) is larger in FAp than in hcp indicates that the Ca^{2+} and F^- ions have expanded the structure more within the "close-packed sheets" than perpendicular to the sheets. This is as expected as neither the F^- or $Ca(1)$ ions are coordinated by PO_4 spheres in the c -axis direction, so they will expand the a -axis more than the c -axis. In addition, the $Ca(2)$ ions lie in the same plane as the PO_4 spheres, so are also likely to expand the a -axis more than

the c -axis. The greater expansion in the a -axis direction is also consistent with the well-known observation that, when Ca^{2+} or F ions are replaced by larger ions, the most marked change in lattice parameters is an increase in a . Another approach to measuring the departure of the packing of the PO_4^{3-} ions in apatite from hcp is to compare their respective P positional parameters. In FAp, P is at 0.3982, 0.3689, $\frac{1}{4}$ [12], which is significantly different from the centre of a sphere (*i.e.* PO_4^{3-} ion) in the hcp structure ($\frac{1}{3}, \frac{1}{3}, \frac{1}{4}$, referred to the apatite cell). The P position is virtually the same in other apatites.

In the late 1960s with funding from the National Institute of Dental Research, Dr R.A. Young undertook a series of precise and detailed single crystal X-ray and neutron diffraction studies of the apatites [12-21]. Apart from the unprecedented precision of these studies, particularly the determination of meaningful anisotropic thermal parameters, the studies revealed a number of interesting structural features. First, the X ion need not be in a special position on the c -axis as had previously been assumed; instead it was the Ca(2) to X ion distance that primarily determined the z parameter of the X ion [22]. In OHAp, the O(H) atom was about 0.36 Å above the mirror plane at $z = \frac{1}{4}$ [13,14] as shown in Fig. 4. In order to reconcile this with the mirror plane at $z = \frac{1}{4}$ usually observed by diffraction methods, the O(H) ions had to be disordered randomly above and below the plane. This presented a problem because neutron diffraction studies [13,14] showed that the H atoms were also on the c -axis, so frequent occurrence of the head-to-head configuration, OH HO was required. However, there was insufficient separation between the OH ions for this to occur easily. Thus a "disordered column" model was postulated in which, within one column, the sequences ...OH OH OH OH... and ...HO HO HO HO... occurred, separated by reversal points. This idea was consistent with the fact that the diffraction studies were made on mineral OHAp that contained F ion impurities (typically 0.28 wt %) that could provide reversal points via the sequence OH F HO. Alternatively, an "ordered column" model was postulated in which all individual columns were ordered, but the mirror plane was satisfied by having whole columns randomly up and down. It was subsequently found that in synthetic single crystals of OHAp without F ion impurities, the b -axis was doubled and the space group became monoclinic $P2_1/b$ [16]. In effect, the mirror plane was lost because the structure had an ordered arrangement of ordered OH ion columns. Pure ClAp also had the space group $P2_1/b$ for rather similar reasons [15,22].

Although these single crystal studies gave considerable insight into the apatite structure, frustratingly, because of the absence of suitable single crystals, they gave no information about one of the main puzzles in the crystal chemistry of the apatites, namely the relation between the few percent CO_3 many apatites contain and the apatite lattice (the " CO_3Ap problem"). This is an important question because CO_3Aps are generally more chemically reactive. For example, they dissolve more readily in acids, which is probably an important factor in understanding the role of dental enamel mineral in dental caries and erosion (direct loss of surface tissue by acids of non-bacterial origin) and of bone mineral in acid-base balance. CO_3Aps are also thermally less stable; this, and their more easy acid dissolution, are important considerations in the industrial processing of rock phosphates.

The study of the structures of CO_3Aps has a long and controversial history [1]. Proposals that have been made for synthetic, mineral and biological apatites include: CO_3^{2-} in an amorphous phase or adsorbed on the surfaces of apatite crystals; CO_3^{2-} replacing OH or PO_4^{3-} ions in the apatite lattice; and CO_4^{4-} replacing PO_4^{3-} or 4CO_3^{2-} replacing 3PO_4^{3-} in the lattice. The present generally accepted

belief for biological and precipitated CO₃Aps is that all, or nearly all, of the CO₃²⁻ ions are in the apatite lattice, mostly replacing PO₄³⁻ ions, but with up to 10% replacing OH⁻ ions. In poorly crystallised CO₃Aps, there is some evidence that small amounts might occupy less well-defined sites, possibly surface species.

The development of the whole-pattern fitting method for the analysis of neutron powder diffraction patterns by Rietveld in the late 1960s, as described by him in the book edited by Young [23], clearly seemed to provide a way forward to solve the CO₃Ap problem. Young and colleagues [24], as well as others [23], extended the Rietveld method for use with X-ray data in 1977. Young and Mackie [25] published the first Rietveld refinement of a CO₃Ap (dental enamel) using neutron and X-ray data in 1980.

Studies of dental enamel [25,26] and precipitated CO₃Aps [27,28] using Rietveld methods undoubtedly show evidence for replacement of PO₄³⁻ by CO₃²⁻ ions in the apatite lattice. X-ray [29] and neutron diffraction [30] studies of francolite, a CO₃-containing mineral FAp, also show clear evidence for partial replacement of PO₄³⁻ by CO₃²⁻ ions. Despite these efforts, the location (locations?) of the CO₃²⁻ ion has not yet been convincingly determined. The most obvious effect of the CO₃²⁻ ion on the structure modelled without its explicit inclusion is an apparent reduction of the PO₄ tetrahedron volume and a small reduction in P occupancy. For dental enamel (typical CO₃ content 3 wt%) for example, the volume is reduced from 1.87Å³ (for stoichiometric OHAp) to 1.787Å³ (about a 3.6% reduction) and the P occupancy by 8% [26]. A small volume reduction can also be seen in francolite [26,29]. Recently, we have studied Na-free CO₃Aps precipitated at 95 °C and found that the apparent PO₄ tetrahedral volume falls systematically from 1.814 to 1.616 Å³ as the CO₃ content increases from 0.13 to 8.6 wt% (upper limit before calcite precipitation).

LeGeros [31] reported in 1967 that a set of 44 Na-containing CO₃Aps precipitated at 95 °C showed a linear decrease in the *a*-axis parameter from *a* = 9.4276Å to 9.304 Å as the CO₃ content increases from 0.80 to 22.22 wt %. This observation, plus chemical analyses, showed her that there was a coupled substitution of Na⁺ for Ca²⁺ and CO₃²⁻ for PO₄³⁻ ions in the lattice. We report here preliminary results using Rietveld analysis of X-ray diffraction data from similar samples.

EXPERIMENTAL

Five samples of Na-containing CO₃Aps were provided by Dr Racquel LeGeros. These were made by the dropwise addition (0.05 ml per s) of 250 ml of 0.02 M Ca(CH₃COO)₂ to 750 ml of 0.016 M Na₂HPO₄ containing variable concentrations (0 to 0.54M) of NaHCO₃ at 95 °C [31,32]. The precipitates were filtered, washed with distilled water and air-dried. Chemical analyses of these samples were not available, so their compositions were estimated from measured *a/c* ratios by interpolation of the composition as a function of *a/c* for the 44 samples published earlier by LeGeros [31]. Interpolation was based on the *a/c* ratio as this reduced systematic errors between the different sets of lattice parameter measurements.

Diffraction patterns were collected over 1-120E in 2θ with an INEL CPS-120 curved position-sensitive detector [33,34]. A Ge 111 monochromator provided monochromatic CuK_α radiation (λ = 1.5406Å). 1-3mg samples were spread on a (711) cut Si single crystal specimen holder rotated during data collection. Patterns were collected with ~4000 points about 0.03° apart in 2θ for 1000 -

1300 minutes. Patterns were calibrated with lead nitrate run before and after data collection. Further details of the data collection can be found elsewhere [26,27]. The GSAS [35] Rietveld refinement programme and March-Dollase model for preferred orientation were used. Initial atomic parameters (including anisotropic temperature factors) were taken from a single crystal neutron data refinement of Holly Springs OHAp [14]. Occupancies, atomic positions, lattice parameters, peak profile, sample displacement, 2 θ zero, and background parameters were allowed to vary. Anisotropic thermal parameters and the occupancy of either Ca(1) or Ca(2) set to the stoichiometric value (unity), were kept constant.

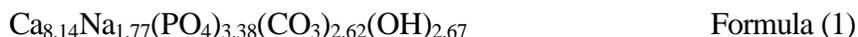
RESULTS AND DISCUSSION

Parameters that varied significantly as the CO₃ content increased are give in Table 1. The reduction in P-O bond lengths, PO₄ volume and O(3) and P occupancies with increased CO₃ content clearly show changes that are consistent with an increasing replacement of the PO₄³⁻ ion by the smaller CO₃²⁻ ion. The fact that it is the O(3) occupancy that changes most (for sample 18, O(1), O(2) and O(H) occupancies were 0.965 and 1.06 and 0.446 respectively), suggests that the CO₃²⁻ ion is in disorder about the mirror plane so that two of its O atoms approximately occupy O(1) and O(2) positions in the plane (Fig. 4), whilst the remaining O atom is disordered between O(3) and its mirror image, O(3)'.

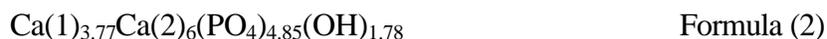
No	<i>a</i> -axis	<i>c</i> -axis	CO ₃	P-O(1)	P-O(2)	P-O(3)	PO ₄ vol	O(3)	P	Ca(1)
	Å	Å	wt. %	Å	Å	Å	Å ³	occup	occup	occup
1	9.425	6.898	4.4	1.474	1.474	1.554	1.778	0.959	0.942	1.005
5	9.411	6.913	8.2	1.426	1.452	1.555	1.717	0.864	0.894	1.007
10	9.368	6.918	13.6	1.435	1.409	1.549	1.674	0.886	0.834	0.979
15	9.357	6.925	15.8	1.425	1.396	1.532	1.627	0.882	0.812	0.976
18	9.341	6.924	17.3	1.367	1.443	1.503	1.572	0.806	0.808	0.943

Table 1. Principal changes with CO₃ content for model based on OHAp. The occupancy of Ca(2) was set to unity.

Both the chemical composition and occupancies from the diffraction studies give information about the unit cell contents which may be compared. Only the highest CO₃ content sample (No 18) will be discussed. If it is assumed that all P positions are occupied by either PO₄³⁻ or CO₃²⁻ ions and that their total is six, the estimated chemical composition gives unit cell contents of

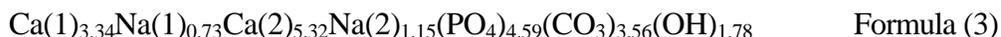


where OH is based on charge balance. On the other hand, occupancies given above give a unit cell

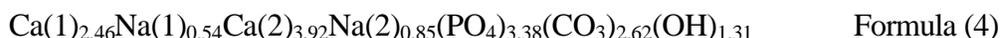


where it has been assumed that every P requires 4 O and that all the 6 Ca(2) sites are filled with Ca²⁺ ions. The total O(P) in Formula 2 is 19.4, which compares with 21.83, the total of O(1), O(2) and O(3) from the Rietveld analysis. However, Formula 2 neglects to take into account the Na and CO₃ contents. It will be assumed that Na and Ca are randomly distributed between Ca(1) and Ca(2) sites.

C is assumed to contribute only 25% of its scattering to the P site, as in previous studies of CO₃Aps [26,27]. Whether either of these assumptions is correct will not matter unduly as the scattering will be dominated by Ca and P. The results from calculations performed with 0% and 100% C contribution, whilst giving slightly different results, do not alter the conclusions drawn below. Corrected unit cell contents can now be calculated so that the total scattering at the Ca and P sites remains unchanged and the ratio of Na:Ca and C:P is as given by Formula 1. The result is



Formula 3 has an excess negative charge of 3.47, Ca/P mol ratio of 1.89 (compared with 2.41 from Formula 1) and a total of CO₃²⁻ and PO₄³⁻ ions in the P sites of 8.15. The total O atoms associated with the ions in P sites is 29.03 which compares with 21.83, the observed total O(P) from the Rietveld analysis given above. As the density is unknown, the unit cell contents can be multiplied by a factor, 6/(total of PO₄³⁻ and CO₃²⁻ ions), so that the P sites are just filled. This gives



The total of O atoms associated with ions in the P sites is now reduced to 21.38, fitting the observed value, but there is an excessive number of vacancies in Ca sites, the OH occupancy is now too low, and the charge balance is still in error. Most seriously, the Ca/P mol ratio is unchanged and so still much less than given by Formula 1 based on the estimated chemical analysis. This difficulty has its origin in the fact that the occupancy for P determined from the Rietveld analysis is much larger than would be expected for an apatite in which it was thought that *ca.* 17wt % CO₃ occupied P sites in the unit cell. This expectation requires a substantial number of PO₄³⁻ ions to account for the observed scattering which then leaves insufficient space for the number of CO₃²⁻ ions derived from the chemical analysis. One possible solution to this problem is that a substantial amount of CO₃ is not in P sites, possibly as amorphous CaCO₃, but there is, as yet, no independent evidence for this.

CONCLUSIONS

There are still many unanswered structural questions about the precipitated CO₃Aps, but it is clear that Rietveld analysis of powder diffraction data, particularly sets of synthetic samples with increasing CO₃ contents, is capable of yielding much detailed information.

ACKNOWLEDGEMENTS

Dr Racquel LeGeros kindly provided the apatite samples. This work was supported by the Medical Research Council grant G9824467

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