American Mineralogist, Volume 60, pages 134–138, 1975

Fluoride in Apatite: Substitution of Monofluorophosphate for Orthophosphate

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Abstract

A monofluorophosphate apatite (MFP apatite) having the composition $Ca_6Na_4(PO_3F)_6O_2$ as determined by electron microprobe analysis was synthesized. X-ray diffraction studies show that MFP apatite, chlorapatite, and pyromorphite group are similar in that they are monoclinic and the ion in the "*X*" site, which is oxygen or chloride, is coordinated with six cations. There appears to be a definite coordination between sodium and fluoride in MFP apatite and related structures which promotes the stabilization of fluoride in apatite. MFP apatite contains three times the fluoride of fluorapatite and involves a different structural site for the halogen.

MFP apatite dissolves incongruently, and the released PO_3F ions are hydrolyzed. The solution is enriched in sodium and fluoride relative to calcium and phosphate. This indicates that the residue of the incongruent solution is a calcium phosphate rich material. A likely site for the natural occurrence of MFP apatite is a very calcium-poor fluoride-rich water that is near neutral in pH.

Introduction

Apatite is one of the most ubiquitous minerals in nature. It occurs in all rock types, it is an important constituent of the biosphere, and its ions are widely distributed in the hydrosphere. The mineral's distribution is indicative of its wide environmental tolerance. Many chemical analyses of apatite show that the mineral is a hospitable host for extensive substitutions. In fact, over one-third of all chemical elements can occur at appreciable concentrations as substitutes in apatite. This paper reports on the substitution of monofluorophosphate (PO_3F^{2-}) in apatite.

An idealized formula for apatite is $Ca_{10}(PO_4)_6(OH)_2$, and the crystals are normally hexagonal. There is voluminous literature concerning specific substitutions in the hydroxyl, calcium, or orthophosphate sites; and there are other studies which report on coupled substitutions. The substitution of monofluorophosphate in apatite was first proposed by Ericsson (1963) after finding that dental enamel treated with sodium monofluorophosphate reacts to form fluorapatite. Ericsson suggests that monofluorophosphate substitutes for orthophosphate in apatite, but subsequently there is hydrolysis to orthophosphate and fluoride. Ingram (1967) with similar experiments states that the presence of PO_3F^{2-} in apatite can be demonstrated; however, his results can have alternate interpretations, for example, those given by Ericsson. Simpson (1968) concluded that some apatite synthesized in a fluoride-rich environment contains fluoride in two structural sites. These sites corresponded to the normal halogen site and an oxygen site on the phosphate tetrahedron. This postulate was presented to account for more than two fluorides per unit cell of synthesized apatite, the necessity of balancing electrostatic charges, and anomalous results of the partitioning of fluoride between solution and crystals. Although the likelihood of PO_3F^{2-} in apatite was presented, there was no direct proof, nor was the effect of such substitution on the physical properties of apatite established.

Recent discussions concerning the various substitutions in apatite have been presented by Kreidler and Hummel (1970), Simpson (1972), McConnell (1973), and many others. It is widely accepted that: (1) there is continuous solid solution between hydroxyapatite and fluorapatite, (2) divalent cations larger than calcium can readily substitute for calcium, and (3) there is a coupled substitution of silicate and sulfate for phosphate. Furthermore, sodium and sulfate have been reported to form a coupled substitution for calcium and phosphate. All of these chemical variants of apatite are hexagonal.

Chlorapatite has two polymorphs. One is hexagonal, and the other is monoclinic. Similarly, the lead-chloride compounds of phosphate, arsenate, and vanadate are monoclinic. These compounds are pyromorphite, mimetite, and vanadinite respectively. In chlorapatite and the related lead compounds, the halogen is in six-fold coordination with calcium or lead. In fluorapatite and hydroxylapatite the fluoride or hydroxyl is in three-fold coordination with calcium. Because of this structural difference between the chlorapatite-type compounds and the fluorapatite-hydroxyapatite compounds, there is very limited solid solution between the two groups.

It is the purpose of this paper to report a monofluorophosphate-bearing apatite containing three times the normal halogen content. Yet this apatite contains oxygen in the normal fluoride site. A comparison is made to a sulfate compound, with an apatite structure, to develop a model concerning the distribution of sodium and fluoride in apatitic compounds.

Experimental Methods

Synthesis of pure monofluorophosphate apatite was by heat treating charges containing sodium metaphosphate glass ($NaPO_3$) and calcium fluoride. This monofluorophosphate apatite will hereafter be referred to as MFP apatite. For the high temperature treatment, charges were contained in gold capsules welded at both ends. Throughout the preparation and synthesis, care was taken to keep the material anhydrous. All syntheses were at one kilobar, for one to twenty weeks, at temperatures greater than 500°C. After heat treatment, the charge contained five or six phases. These were identified by optical and X-ray diffraction methods. One phase was unreacted sodium metaphosphate glass. The crystalline phases in order of decreasing abundance are MFP apatite, $\beta Ca_2P_2O_7$, CaF_2, $Na_5P_3O_{10}$, and rarely fluorapatite. The metaphosphate glass and $Na_5P_3O_{10}$ are readily soluble and thus easily removed by washing with water. MFP apatite was found to float in tetrabromoethane heavy liquid and the other sparingly soluble phases sank. Thus, final concentration of MFP apatite was by heavy liquid separation, with the floats being used for chemical and physical determinations.

The best crystals of MFP apatite were obtained at about 500°C, but the greatest yield is obtained at about 700°C. The crystals of MFP apatite decompose at 740° ± 3°C.

Chemical Analysis and Formula

Calcium, phosphorous, sodium, and fluorine content of MFP apatite was determined, but oxygen was not measured. An ARL electron microprobe at 10 kV accelerating voltage and 0.5 mA beam current was used to determine the chemical composition of MFP apatite. The analyses were made on carbon coated polished sections of MFP apatite crystals. X-ray counts were generated by scanning a slightly defocused electron beam over an 8 × 10 micrometers area of the crystal. The data were computer-corrected using a program by Rucklidge and Gasparrini (1969).

The primary standard used for the analysis was Faraday Township apatite. The uncertainties in the analysis were estimated by comparing the results obtained by using as separate standards cryolite, fluorite, and albite.

Oxygen was not determined, and it is only in accord with convention that the analysis listed in Table 1 is reported as oxides.

The ratio of calcium plus sodium to phosphorous is 1.67 for MFP apatite. This is the same as the calcium to phosphorous ratio of fluorapatite. The fluoride to phosphorous ratio is 1.00 for MFP apatite. The formula of MFP apatite is $Ca_6Na_4(PO_3F)_6X_2$, where X represents sites for an anion. Considering the chemistry of the system and the electrostatic balancing, oxygen is the only possibility for the X site. Thus, the formula for MFP is: $Ca_6Na_4(PO_3F)_6O_2$.

Crystallography

MFP apatite crystals are colorless, have a prismatic form, and most contain inclusions of glass. Crystals rarely exceeded 100 μm in length. The indices of refraction are: $\alpha = 1.512 \pm 0.002$ and $\gamma = 1.517 \pm 0.002$. The crystals are biaxial negative with $2V = 56°$, and they have length slow

TABLE 1. Composition of MFP Apatite

	MFP Apatite	Ideal Fluorapatite		MFP Apatite	Ideal Fluorapatite
	(weight percent)			(moles)	
Na_2O	13.0±1.0	0.0	Na	0.42	0.0
CaO	35.7±0.5	56.0	Ca	0.63	1.0
P_2O_5	44.7±0.5	42.6	P	0.63	0.6
F	12.0±0.5	3.8	F	0.63	0.2
-O=F	5.1	1.6	$\frac{Ca+Na}{P}$	1.67	1.67

elongation. There is moderate dispersion with $v > r$. Crystals of MFP apatite show polysynthetic twinning. Most prismatic crystals appear to have parallel extinction, but some show a small extinction angle. The optics therefore, require that the crystals be triclinic or monoclinic.

One polymorph of chlorapatite is monoclinic, and the apatite-like minerals pyromorphite, mimetite, and vanadinite are monoclinic. These monoclinic crystals have $a/2 = c$ and $\beta \sim 120°$. Thus, the monoclinic apatite is related to hexagonal apatite such that b monoclinic equals c hexagonal. With such orientation and parameters, X-ray diffraction is inadequate for establishing the monoclinic nature of the crystals. Therefore, consistent with chlorapatite, the X-ray diffraction of MFP apatite was indexed as a hexagonal apatite, although the optics deny such symmetry. The powder diffraction data were obtained using Ni filtered copper K_α radiation. Calcium fluoride was mixed in the mount as an internal standard. The X-ray diffraction data is given in Table 2, and the calculated cell parameters are: $a = 9.90 \pm 0.01$ Å and $c = 6.48 \pm 0.01$ Å. Calculated and observed d values are in good agreement and could not be further improved by considering the cell monoclinic.

TABLE 2. Powder X-Ray Diffraction Data for MFP Apatite.

"d" obs. Å	"d" cal.* Å	hk·l	I/Io
4.98	4.95	110	3
3.60	3.65	201	5
3.24	3.24	210,002	50
3.03	3.03	102	80
2.89	2.90	211	50
2.86	2.86	300	100
2.55	2.59	202	10
2.45	2.47	220	10
2.30	2.31	221	7
2.28	2.29	212	6
2.06	2.08	302	7
2.01	1.98	113	3
1.96	1.97	222,320	6
1.82	1.80	411	15
1.79	1.79	402	5
1.73	1.72	303	10
1.68	1.68	322	3
1.53	1.54	114	7
1.44	1.45	422	6

* "d" calculated on the basis of hexagonal cell with $\underline{a} = 9.90_5$ Å, $\underline{c} = 6.48$ Å.

Solubility of MFP Apatite

Experiments aimed at the precipitation of MFP apatite from an aqueous solution either failed or were nondefinitive. However, some information on the behavior of MFP apatite in water was obtained by stirring the crystals in water for 25 days. Two samples were treated, one in plasticware and the other in glassware. The determinations of H^+, F^-, Ca^{2+}, and Na^+ were made using ion selective electrodes. Phosphorous was measured by conversion of the monofluorophosphate ion to orthophosphate which was then determined gravimetrically as the quinolinium salt of molybdophosphoric acid. Results are listed as the negative log of the activity of the ions and molarity of the phosphate. Several analyses by atomic absorption are indicated with an (AA). The precision is estimated from differences between the two samples and on sequential readings. The results are the following:

pH = 7.12 ± 0.02
pF = 2.55 ± 0.05
pCa = < 5 10^{-4}M. (AA)
pNa = 2.64 ± 0.05 $10^{-2.7}$M. (AA)
PO_4 = $10^{-4.4}$M.

The results show the solution to be near neutral. Sodium and fluoride levels are roughly equal, and they are about 100 times greater than the phosphate. Calcium activity of the solution is extraordinarily low. If MFP apatite $[Ca_6Na_4(PO_3F)_6O_2]$ dissolves congruently and hydrolyzes, the calcium, fluoride, and phosphate values should be equal and about 1.5 times the sodium value. The differences found indicate that the crystal dissolves incongruently, with sodium and fluoride being preferentially released. Such release of fluoride requires hydrolysis of some monofluorophosphate ions.

Sodium monofluorophosphate (Na_2PO_3F) is readily soluble in water. Commercially available material is of technical grade. In a series of solutions prepared from this material, it was found that the fluoride activity is very nearly an order of magnitude less than the molarity. Thus, a 10^{-3}M solution has a 10^{-4} fluoride activity. This fluoride activity is probably the result of impurities in the sodium monofluorophosphate for the following reasons: (1) the activity of fluoride is 10 percent of the molarity over a range of 10^{-1} to 10^{-3} molar, and (2) the activity of fluoride could not be increased with aging or boiling of the solution. If the fluoride activity results from the hydrolysis of PO_3F, the activity should increase with time and thermal treatment. This indicates that the PO_3F^{2-} ion is either stable in these solutions, or it has an extremely slow rate of hydrolysis. In contrast, the limited solution of MFP apatite appeared to require the hydrolysis of the monofluorophosphate ion.

The contrasting behavior of the PO_3F^{2-} ion in a solution from Na_2PO_3F and another solution from MFP apatite may be the result of the presence or absence of calcium in the crystals and solution. MFP apatite's release of sodium and fluoride to the solution greatly exceeds the calcium and phosphate. This suggests that the crystals dissolve incongruently, leaving a residue of calcium phosphate on the crystal surface. This residue inhibits further solution. It is probable that such a coating residue would be apatite or brushite. This requires hydrolysis of the PO_3F^{2-} ion in the solution or at the crystal surface. The hydrolysis is probably promoted by the removal of orthophosphate by combination with calcium.

Sulfate Apatite

The compound $Na_6Ca_4(SO_4)_6F_2$, first synthesized by Klement and Dihn (1941), has an apatite structure. This sulfate apatite involves the substitution of divalent sulfate ion for trivalent phosphate ions. Electrostatic neutrality is maintained by the concomitant substitution of sodium ions for calcium ions. Sulfate apatite was synthesized to permit comparison of its properties with those of MFP apatite (Table 3). The difference between the calculated and measured density is probably the result of inclusion of sodium sulfate.

Discussion

As summarized in Table 3, sulfate apatite and fluorapatite have nearly identical lattice parameters, but by comparison MFP apatite and chlorapatite have a contracted *c* and greatly enlarged *a*. Differences in parameters of chlorapatite and fluorapatite result principally from different sites for the halogen. In chlorapatite, the chlorides occupy sites as 0,0,0 and 0,0,1/2 and are thus between two trigonal groups of calcium ions. In contrast the chloride ions of fluorapatite are at 0,0,1/4 and 0,0,3/4. Thus, the fluoride is in the plane of the trigonal group of calciums. In MFP apatite, the two oxygens not associated with phosphorous occupy sites similar to chlorides of chlorapatite. As a result, they are in six-fold coordination with calcium. This is the major cause of the contraction of *c* and the enlargement of *a*, and the effect is greater in MFP apatite than in chlorapatite because of the reduced size and increased charge of oxygen relative to chloride.

TABLE 3. Properties of Fluorapatite, Sulfate Apatite, and MFP Apatite

Fluorapatite	Sulfate apatite	MFP apatite	Chlorapatite
		Optics	
$\omega = 1.626$	$\omega = 1.525$	$\alpha = 1.512$	$\omega = 1.668$
$\epsilon = 1.624$	$\epsilon = 1.523$	$\beta = 1.516$	$\epsilon = 1.667$
		$\gamma = 1.517$	
		2V = 56°	
Length fast elongation	Length fast elongation	Length slow elongation	Length fast elongation
		Polysynthetic twinning	
		Density	
3.15	2.82 ± 0.02 meas	2.80 ± 0.02 meas	3.18
	2.87 calc	2.87 calc	
		Parameters	
a 9.382 Å	9.399 ± 0.002 Å	9.90 ± 0.01 Å	9.629 Å
c 6.886 Å	6.892 ± 0.002 Å	6.48 ± 0.01 Å	6.777 Å
		Volume	
524.9 $Å^3$	527.3 $Å^3$	550.5 $Å^3$	544.2 $Å^3$
		Formula	
$Ca_{10}(PO_4)_6F_2$	$Ca_4Na_6(SO_4)_6F_2$	$Ca_6Na_4(PO_3F)_6O_2$	$Ca_{10}(PO_4)_6Cl_2$

MFP apatite contains six calcium and four sodium ions per cell. The calciums occur in trigonal clusters above and below the oxygens. These are the Ca_{11} sites. The sodium of MFP apatite is in the Ca_1 sites, or 1/3,2/3,0. In this arrangement there are calcium-oxygen bonds and sodium is coordinated to the fluoride of the PO_3F^{2-} ligand. In contrast, the compound $Ca_4Na_6(SO_4)_6F_2$ has fluoride in the normal fluoride site, namely, 0,0,1/4. The ratio of sodium to calcium requires that the six sodiums occupy the Ca_{11} sites and the four calciums occupy the Ca_1 site. Thus, in sulfate apatite, the sodium and calcium occupy opposite sites from those found in MFP apatite. However, the sodium-to-fluoride coordination and the calcium-to-oxygen bond is maintained by this site switching. It appears that the preservation of the sodium-fluoride coordination is of primary importance in these apatites. It further appears that a foreign cation, as sodium, can completely replace the calcium in the Ca_1 site or the calcium of Ca_{11} site. However, a limited replacement involving both sites appears unlikely. For example, attempted syntheses of $Na_6Ca_4(PO_3F)_6F_2$ and $Na_4Ca_6(SO_4)_6O_2$ were unsuccessful.

Specific conditions for the precipitation of MFP apatite from an aqueous solution remain unknown, nor is there proof of the natural occurrence of the PO_3F^{2-} ion. A likely environment for MFP apatite would require abundant sodium, phosphorous, and fluoride and very little calcium. The extent of solid solution between MFP apatite and natural apatite has not been established. However, such solid solution is probably comparable to that found between the structurally equivalent compounds fluorapatite and chlorapatite. Even limited solution of MFP ions in apatite would have a marked effect on the stability and solubility of the crystals. Finally, the experiments show the importance of sodium fluoride coordination in several chemical variants of apatite.

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Manuscript received, May 31, 1974; accepted for publication, August 13, 1974.