PARTITIONING OF FLUORIDE BETWEEN SOLUTION AND APATITE

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Abstract

The fluoride content of phosphorites and marine waters indicates that there is a strong partitioning of fluoride in favor of apatite. However, synthesis of fluorapatite at low temperatures required solutions enriched 10^2 to 10^3 in fluoride relative to sea water. Uptake of fluoride by sodium-bearing hydroxylapatite requires similarly enriched solutions, and with the uptake there is a concomitant release of sodium and phosphate from the crystals.

Agitation of Durango fluorapatite with water resulted in fluoride increasing to a pF $\sim$3 and hydroxyl to pOH$\sim$4.5 in the solution. A surface layer retards the exchange of hydroxyl and fluoride in apatite.

Introduction

The apatite phase of marine phosphorites commonly contains more than several percent fluoride, and in some specimens the fluoride level exceeds that of pure fluorapatite. It has been generally assumed that very low levels of fluoride in solution are sufficient to effect significant exchange of fluoride for hydroxyl in apatite, and in fact such an exchange was proposed, more than a century ago, as the basis of an age data method. It is the purpose of this paper to consider the partitioning of fluoride between solution and crystals, Such partitioning is established by crystallization of apatite in a fluoride-bearing environment, measurement of uptake of fluoride by hydroxylapatite, and equilibration of natural fluorapatite and water.

Nature of Low Temperature Apatite

Regardless of the manner of formation, apatite formed at 1 atmosphere pressure and a temperature of 30°C or lower lacks good crystallinity, is very fine-grained, appears isotropic under the microscope, and contains much more than the 1.8 percent water of ideal hydroxylapatite. Unless care is taken to exclude carbonate from the system, such apatite will contain carbonate. These characteristics are typical of the natural material called colophane. Artificial material with such properties will hereafter be referred to as low temperature apatite, a term used solely for convenience. At higher temperatures of synthesis there is a decrease in the water content of apatite and improvement in crystallinity, but even at 100°C the apatite contains water in excess of the ideal 1.8 percent. Such additional water will hereafter be referred to as excess water.

The nature of low temperature apatite has been a subject of contro-

versy in regard to the site or sites of the carbonate and excess water or its various ions.

EXPERIMENTS

Analytical Methods. For the analysis of apatite, sodium was determined by flame photometry and calcium by EDTA titration. Carbon dioxide was determined with a Beckman Infrared analyzer and volumetrically by the method described by Shapiro and Brannock (1956). Phosphorus was determined gravimetrically as the quinolinium salt of molybdophosphoric acid. Reproducibility of apatite analysis by these methods was shown by Simpson (1968a).

Fluoride in crystals was determined by solution of the crystals with a strong cation exchange resin, filtration of the solution and adjustment of pH~8 with a strong base. Fluoride activity was measured with a specific ion electrode. This ion exchange procedure has the advantage that divalent cation fluoride complexes are eliminated. Fluoride of the solution separated from crystals was measured without the ion exchange procedure because activity was desired.

Calcium activity was determined in some solutions as being greater than $pCa = 5$, the limit of measurement with the calcium liquid-membrane electrode.

Unless otherwise stated electrode measurements are ± 0.05.

Formation of Hydroxylapatite at 25°C. Low temperature apatite can be formed by interaction of calcium carbonate and alkali phosphate solutions as described by Ames (1959). For the present study, Ames' method of using a column and a flowing solution was modified (Simpson, 1964).

Apatite formed at 25°C by reaction of calcite and a sodium phosphate solution has a calcium to phosphate ratio less than the 1.667 of ideal hydroxylapatite, and contains much excess water (Simpson, 1964, 1967). This apatite has a low mean index of refraction and appears isotropic. Forms are commonly 10 μm in diameter; however, because of the isotropic nature it is impossible to determine whether such forms are an aggregate of crystals. X-ray diffractograms of the apatite are diffuse. In many heating experiments it has been found that there is a continuous weight loss with increasing temperature, with the apatite commonly losing about 8 to 10 percent by weight.

To determine the effect of temperature of synthesis on the nature of the apatite, calcite was reacted with sodium phosphate solutions at 4°C, 25°C, and 80°C. It was consistently found that there was an inverse relationship of quantity of excess volatiles to temperature of formation. For example, apatite formed at 4°C contains more than 10 percent expellable volatiles in the temperature range of 25 to 800°C; whereas apatite formed at 80°C contains less than 4 percent expellable volatiles in the same temperature range.

A series of low-temperature apatite formed in solutions of different phosphate concentrations were analyzed chemically. After these crystals had reacted in frequently changed solutions for six months, they were ball milled in the mother liquor and permitted to equilibrate for an additional four years. By X-ray and optical examination apatite was found to be the only solid phase. Two typical analyses (Table 1) of apatite formed in solution of different phosphate concentration show the crystals to contain soda and carbonate. The $Na + Ca/PO_4 + CO_3$ ratio is less than the 1.667 of ideal hydroxylapatite, and both samples contain much excess water.

The chemical analyses were cast into structural formula with the following assumptions: 1) The calcium site to phosphate site ratio is to be 1.667; 2) Sodium and hydronium ions are possible substitutions in the calcium site; 3) Carbonate and $H_4O_4^{4-}$ can occur in the

TABLE 1.

ANALYSES OF LOW TEMPERATURE APATITE

	pH formation $\sim$8	
	C-2	C-5
Na_2O	2.44	1.29
CaO	49.21	49.81
P_2O_5	38.00	38.75
CO_2	2.25	3.38
H_2O^a	8.10	6.77
Cat/An[b]	1.633	1.493

[a] By difference.

[b] Moles $Na+Ca/PO_4+CO_2$.

STRUCTURAL FORMULAS OF LOW TEMPERATURE APATITE

	Na^+	H_3O^+	Ca^{2+}	PO_4^{3-}	CO_3^{2-}	$H_4O_4^{4-}$	OH^-	H_2O°
Ideal			10	6			2	
C-2	a. 0.81	0.19	8.99	5.48	0.52	0.00	1.50	0.50
	b. 0.73	1.15	8.12	4.95	0.47	0.58	0.00	2.00
C-5	a. 0.40	1.04	8.55	5.26	0.74	0.00	1.29	0.71
	b. 0.37	1.80	7.83	4.81	0.68	0.51	0.00	2.00

Mole values ±0.01 except OH^- and H_2O° which are dependent on all other oxides.

[a] formula for minimum water.

[b] formula for maximum water.

C-2 apatite formed in solution containing 0.3 molar total phosphate, and C-5 formed in a 0.05 molar solution.

phosphate site; and 4) Either water or hydroxyl can occur in the hydroxyl site. Water shown in the analyses was established by difference; and TGA shows that there is water lost below 110°C, a temperature at which all samples were dried before the analyses. The structural formula must account for this loss of water without the appearance of a second phase.

Considering the substitutions, the following is possible and will have no effect on the calcium site to phosphate site ratio nor will it change the charge on the resulting crystal.

Calcium Site	*Phosphate Site*	*Hydroxyl Site*
Addition of 1.43 H_3O^+	Addition of 0.86 $H_4O_4^{4-}$	Substitution of 2.00 H_2O for 2.00 OH^-

The above substitutions are efficient for incorporating water in the crystals and they are limited only by the availability of hydroxyls in the hydroxyl sites. With this mechanism all of the water shown in the analyses can be incorporated in the crystals, and in fact the

mechanism can accommodate the larger quantities of water found in crystals formed at 4°C.

Because low-temperature apatite loses water below 110°C, the drying temperature for analyzed material, the specific water content of the crystals at 110°C has little meaning. For this reason the structural formula are cast in terms such that they contain the minimum water necessary to yield a calcium site/phosphate site ratio of 1.667 and such that components of the crystals sum to zero charge. Structural formulas are also presented (Table 1) such that they contain the maximum water, a condition where the crystal contains water, and no hydroxyl, in the hydroxyl site. It is concluded that the apatite synthesized at 80°C is best represented by the structural formula containing the minimum water; whereas the apatite synthesized at 4°C is best represented by the structural formula containing the maximum water.

Uptake of Fluoride by Hydroxylapatite at 25°C. Sodium-bearing hydroxylapatite was synthesized by reaction of 0.2 M. sodium phosphate solution with calcite. By X-ray and optical examination, the apatite, after reaction of several months, was free of unreacted calcite. This apatite is similar to that described in the previous section.

Samples of 0.8 gram of this low temperature apatite were agitated in 150 ml of solution containing either 10^{-2}, 10^{-3}, or 10^{-4} M. NaF. The uptake of fluoride was monitored with a fluoride electrode over a period of 125 days. The experiment was at 25°C under atmospheric pressure.

Uptake of fluoride by low temperature hydroxylapatite is rapid, with the major decrease in fluoride level of solution occurring in less than 10 days and a steady state being reached in about 50 days. The pH and pF of the solutions after 125 days and analysis of the crystal are shown in Table 2.

After 125 days the solutions show high levels of total phosphate and are less than 10^{-5} M. in calcium. Because fluoride was added as the sodium salt, there was initial sodium in all solutions. However, the sodium concentrations of the final solution demonstrate that the sodium level increased. Thus in the course of the experiment the crystals show some uptake of fluoride and appreciable loss of sodium and phosphate. Casting the analyses into structural formulas for the minimum water arrangement (Table 2) shows that with increasing substitution of fluoride, there is a decrease of water in the hydroxyl site. The incorporation of fluoride in these crystals is illustrated by the following idealized reaction:

$$1.25[Ca_8Na_2(PO_4)_6(H_2O)_2] + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2.5Na^+ + 1.5PO_4^{3-} + 2H_2O.$$
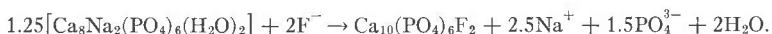
The data indicate that the uptake of fluoride by this apatite is not a simple replacement of hydroxyl, but rather involves a major compositional change and recrystallization of the apatite with the actual substitution being a replacement of water in the hydroxyl site.

These experiments were on crystals formed at 25°C. With decreased temperature of formation there is increased water content in the crystals, a feature that can be accounted for by casting the structural formula such that they contain maximum water. With the maximum water arrangement the structural formula contains water and no hydroxyl in the hydroxyl site. It is such water that is found to be readily removed, and where the water in the initial crystals is maximized the uptake of fluoride should be at a maximum.

Synthesis in Fluoride-bearing Solution at 25°C. Apatite was formed by the 0.2M. sodium phosphate solution—calcite reaction at 25°C; however, these solutions were also 10^{-1}, 10^{-3}, and 10^{-3} M. in fluoride.

Averages and standard deviations of analyses of fourteen samples of apatite formed in a 10^{-2} M. fluoride solution were presented and discussed by Simpson (1968b). Fluoride con-

TABLE 2.

COMPOSITION OF SOLUTION AND CRYSTALS AFTER 125 DAYS

Solutions					
Initial pF	pNa[a]	pCa	After 125 days		
			pPO$_4$[a]	pF	pH
a. 2.0	1.99	>5.0	2.57	2.43	8.71
b. 3.0	2.55	>5.0	2.82	4.70	7.98
c. 4.0	2.69	>5.0	2.08	5.00	7.71

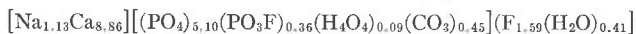| Crystals				
Na$_2$O	CaO	P$_2$O$_5$	CO$_2$	F
a. 1.05	51.53	39.88	0.73	1.46
b. 1.57	49.82	39.74	1.42	0.24
c. 1.36	49.38	39.77	1.21	0.03

[a] Measured as concentration and uncorrected for activity. PO$_4$ indicates total phosphorous in the solution.

FORMULAS FOR APATITE AFTER UPTAKE OF FLUORIDE

	Na$^+$	H$_3$O$^+$	Ca^{2+}	PO$_4^{3-}$	Co$_3^{2-}$	H$_4$O$_4^{4-}$	F$^-$	H$_2$O$^\circ$	OH$^-$
a.	0.3	0.4	9.2	5.6	0.2	0.2	0.8	0.0	1.2
b.	0.5	0.5	8.9	5.6	0.3	0.0	0.1	0.6	1.3
c.	0.4	1.3	8.1	5.6	0.3	0.0	0.02	1.5	0.5

a, b, c correspond to different initial fluoride activities. Splits of the same hydroxylapatite sample were used for the three conditions.

tent of the crystals averages 3.7 percent and the range is 3.3 to 4.1 percent. This average value is close to the 3.8 percent of ideal fluorapatite, but these fluorapatites contain an average of 4.6 percent water. Simpson (1968b) deduced that H$_4$O$_4^{4-}$ occupies some phosphate sites and the resulting surplus negative charges are compensated by substitution of PO$_3$F^{2-} for PO$_4^{3-}$. Such a substitution may effect a double reduction in negative charges, because it removes a fluoride from its considered position in the hydroxyl site and permits occupation of that site by uncharged water. The structural formula based on the average of the analyses illustrates the substitutions:

$$[Na_{1.13}Ca_{8.86}][(PO_4)_{5.10}(PO_3F)_{0.36}(H_4O_4)_{0.09}(CO_3)_{0.45}](F_{1.59}(H_2O)_{0.41}]$$

Apatite containing 3.7 percent fluoride formed in a 10^{-1}M. fluoride solution; however, fluoride may occupy two different sites. Thus the partitioning of fluoride between these crystals and solution cannot be directly compared to the fluoride uptake previously reported.

It was found that solutions 10^{-2} M. in fluoride yielded apatite averaging 2.57 percent

TABLE 3.

FORMULA FOR SODIUM-FLUORAPATITE SYNTHESIZED AT 100°C

Sample	Na$^+$	H$_3$O$^+$	Ca^{++}	PO$_4^{3-}$	PO$_3$F^{-2}	F$^-$	OH$^-$	H$_2$O
12A	0.67	0.30	9.03	6.00	0.00	0.52	0.50	0.98
12B	0.79	0.19	9.02	6.00	0.00	0.68	0.35	0.98
12C	0.79	0.17	9.04	5.94	0.06	1.10	0.00	0.99
12D	0.83	0.23	8.87	5.80	0.15	1.09	0.00	0.89
12E	0.85	0.00	9.15	5.83	0.16	1.33	0.00	0.67

PARTITIONING OF FLUORIDE BETWEEN SOLUTIONS AND CRYSTALS
SODIUM-FLUORAPATITES FORMED AT 100°C

Sample	pF solution[a]	F wt.% in crystals
12A	4.22	1.00
12B	4.35	1.30
12C	3.36	2.06
12D	2.42	2.54
12E	1.92	2.68

[a] Measured after cooling from about 100°C to 25°C.

fluoride with a standard deviation of 0.17. Apatite formed in a 10^{-3} M. fluoride solution averaged 1.29 percent fluoride with a standard deviation of 0.08. Thus by this method of synthesis, unnaturally high fluoride concentrations in solution are necessary to yield a fluorapatite.

Formation of Apatite at 100°C. Apatite of good crystallinity can be formed by boiling a solution of calcium EDTA and phosphate. A series of five sodium fluorapatites were prepared and analyzed (Simpson, 1968b) and the results cast into structural formulas (Table 3). All samples contained less than 0.01 percent CO_2. Fluoride values ranged from 1.00 to 2.68 weight percent, and water values ranged from 2.59 to 3.27 percent.

The structural formula shows most samples to require H_3O^+ in the calcium site to yield the ideal calcium site to phosphate site ratio of 1.667. The three samples richest in fluoride require PO_3F^{2-} ions to reduce the negative charge, and these three samples contain no OH^- in the hydroxyl site.

Partitioning of fluoride between solutions and crystals is given in Table 3. Again it is found that unnaturally high fluoride activities are required in solution to yield a fluorapatite.

Natural Fluorapatite. Crushed Durango fluorapatite was agitated with deionized water to determine the pH and pF of the resulting solution. All samples were agitated on a shaker table and the temperature of the system was 25°C.

After the duration of the experiment, measurement of the pF and pH show that there is an increase in fluoride activity with an increase in hydroxyl activity (Fig. 1). Furthermore, these increases are coincident with increased solid to liquid ratio.
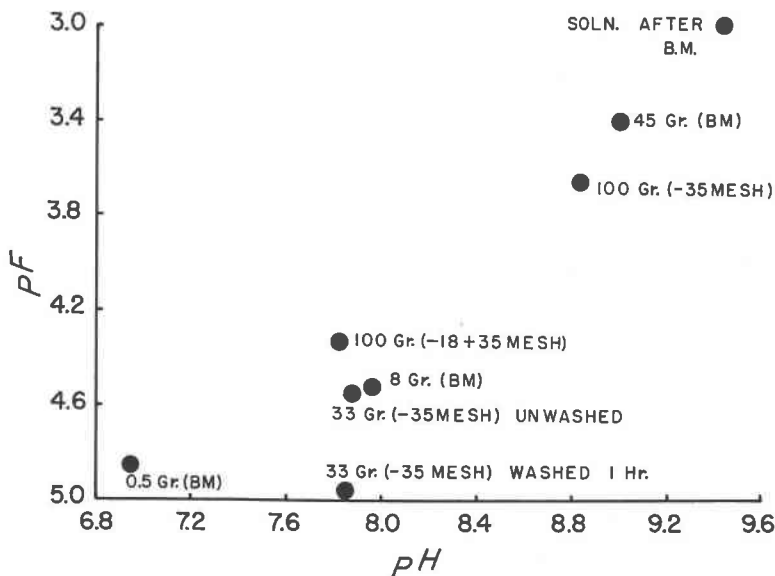
FIG. 1. Durango fluorapatite in water. Mesh size and weight of apatite per 150 ml of solution is indicated. BM = ball milled material.

Two samples were handled identically except that one was washed in water for one hour prior to starting the experiment. After such washing it yielded a solution pF of 4.96 after 120 hours; however, the unwashed sample yielded a solution pF, during the same period, of 4.55. The pH of the solution over both samples was similar. It appears that washing for even one hour removes labile ions from the surfaces of apatite fragments.

Another sample of Durango apatite ($-18 +35$ mesh) was quickly washed to remove dust resulting from the crushing. The washed crystal fragments were then agitated under water for 120 hours. At the completion of the experiment the liquid was turbid. The fine suspension from this solution was collected by filtration. Optically, it was found to be fragments of fluorapatite and a finely divided isotropic appearing material with $n \sim 1.612$. The isotropic nature and low mean index are atypical for fluorapatite; however, such properties are typical of collophane and artificial preparations of low temperature apatite. X-ray diffractograms show only apatite in this finely divided material. An analysis shows the material to contain two weight percent fluoride; a value far too low for the material to be pure fluorapatite. It is concluded that this material either (1) formed as a surface coating and was subsequently abraded from the coarse fragments of fluorapatite; or (2) small abraded fragments of fluorapatite are being converted to this collophane-like phase. With either possibility, Durango fluorapatite is being destroyed in a solution with pF = 4.33 and a second phase is forming, and all evidence indicates that the second phase is typical of low temperature apatite.

CONCLUSIONS

All evidence indicates that Durango fluorapatite forms a surface coating in solutions containing low levels of fluoride, for example, 10^{-4} M.,

and that this surface coating contains less fluoride than the starting solid. In fact, solutions containing 10^{-3} M. fluoride are obtained when Durango apatite is ball milled in water. Thus it is concluded that fluorapatite would be in disequilibrium with a solution containing several ppm fluoride.
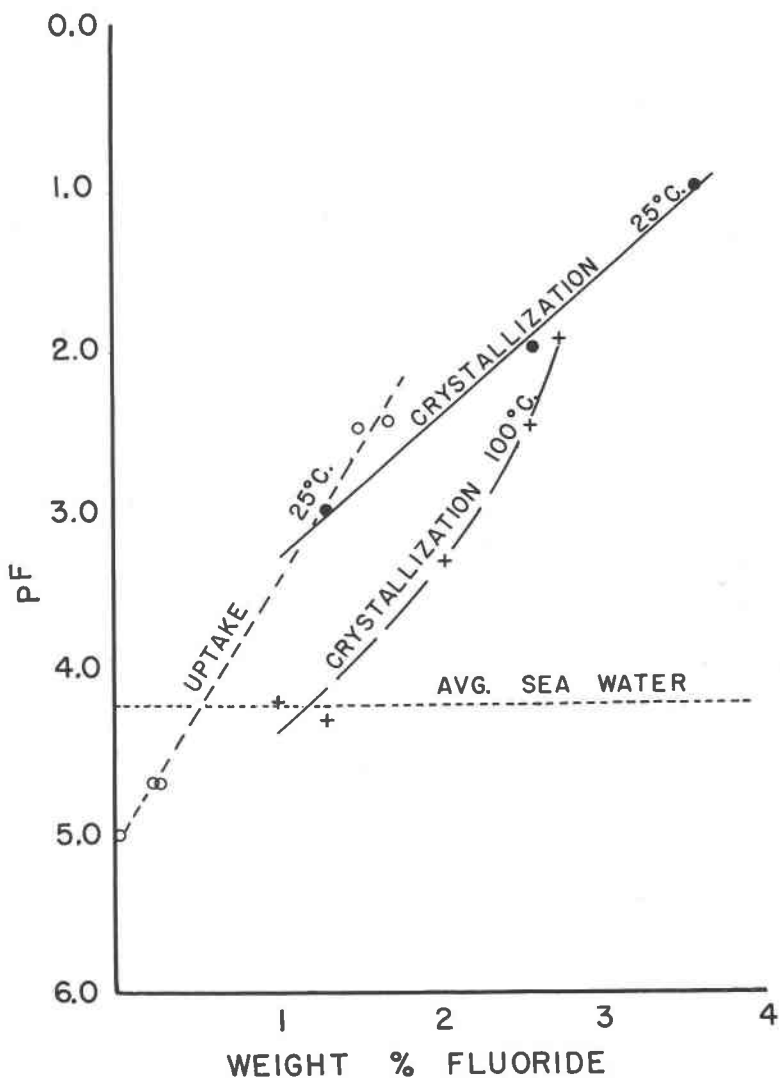

FIG. 2. Weight percent fluoride in apatite resulting from synthesis or uptake in solutions of different pF. Approximate fluoride concentration of sea water shown for reference.

Studies on uptake of fluoride by low temperature hydroxylapatite show that a solution with pF~4.2 yield an apatite containing about 0.5 weight percent fluoride (Figure 2). Crystallization of apatite at 25°C in a solution with a fluoride concentration of 10^{-3} M. yields apatite containing 1.3 percent fluoride. Unless the activity is more than three orders of magnitude lower than the concentration, the crystallization studies at 25°C also indicate that fluorapatite or fluor-carbonate apatite with 3.8 percent fluoride cannot form in solutions with fluoride levels of several ppm. To the extent that these experiments model nature, it is concluded that the fluor-carbonate apatite of marine phosphorite persists metastably in sea water.

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