JOURNAL OF SOLID STATE CHEMISTRY 112, 78–81 (1994)

Site Preference of Nd in Fluorapatite [$Ca_{10}(PO_4)_6F_2$]

Michael E. Fleet and Yuanming Pan

Department of Geology, University of Western Ontario, London, Ontario N6A 5B7, Canada

Received June 30, 1993; in revised form November 1, 1993; accepted November 3, 1993

A Nd-bearing fluorapatite [$Ca_{10-x-2y}Na_yNd_{x+y}(P_{1-x}Si_xO_4)_6A_2$, with $x \approx 0.32$, $y \approx 0.51$, $A_2 = F_{1.63}(OH)_{0.37}$; $P6_3/m$], has been synthesized hydrothermally and its crystal structure refined at room temperature with single-crystal X-ray intensities to $R = 0.024$. The F content is consistent with the conditions of synthesis and the Ca(2)–*A* bond length. Site occupancies of substituents are 0.041(1) for Nd and 0.077(8) for Na in the Ca(1) position and 0.110(1) for Nd and 0.034(8) for Na in the Ca(2) position, with Nd determined by direct refinement and Na by iteration. The Nd and Na occupancies are consistent with site preferences deduced from bond valence calculations. The bonding requirements of the *A* (or O) anion exert a considerable influence on the site preference of cations in apatites. © 1994 Academic Press, Inc.

INTRODUCTION

The crystal structure of apatite [$Ca_{10}(PO_4)_6A_2$; A = F, OH, Cl; space group $P6_3/m$, but $P2_1/b$ for some ordered varieties] permits a wide range of cation and anion substitutions (1–16). In particular, the two Ca positions have distinct stereochemistries [Ca(1), equipoint 4(*f*), CaO_9 polyhedron; Ca(2), equipoint 6(*h*), CaO_6A polyhedron; see (7; 15, Fig. 1)] and are able to accommodate a variety of univalent, divalent, and trivalent cations as substituents.

Substitution of the trivalent lanthanides and Y (rare-earth elements, REE, R^{3+}) is charge compensated in various ways; for example,

$$R^{3+} + Si^{4+} = Ca^{2+} + P^{5+}, \quad Ca_{10-x}R_x(P_{1-x}Si_xO_4)_6A_2 \quad [1]$$

$$R^{3+} + Na^{1+} = 2Ca^{2+}, \quad Ca_{10-2y}Na_yR_y(PO_4)_6A_2 \quad [2]$$

$$R^{3+} + O^{2-} = Ca^{2+} + A^{1-}, \quad Ca_{10-z}R_z(PO_4)_6A_{2-z}O_z \quad [3]$$

$$2R^{3+} + \square = 3Ca^{2+}, \quad Ca_{10-3w}R_{2w}\square_w(PO_4)_6A_2. \quad [4]$$

The structural role of REE in apatite is currently unclear. Minor amounts of REE appear to replace Ca on the smaller Ca(2) position (17). Lanthanum in synthetic $Ca_4La_6(SiO_4)_6(OH)_2$ is reported to be randomly distributed on both Ca positions (10), but this conclusion is based on the intensities of only four Bragg reflections. For Nd-doped fluorapatite (FAp), the REE site preference appears to depend on the substitution mechanism (11). In NdF_3-doped FAp, Nd substitutes equally into both Ca(1) and Ca(2), but in Nd_2O_3-doped FAp, Nd substitutes only into Ca(2). In $NaY_9(SiO_4)_6O_2$, Y is ordered in the 6(*h*) position [Ca(2)] and disordered with Na in 4(*f*) [Ca(1)] (12). In a detailed single-crystal X-ray study of four natural apatites containing minor but variable amounts of light REE (La → Eu), Hughes *et al.* (15) observed REE in both Ca positions and on the basis of bond valence sums reasoned that La → Pr should preferentially substitute into Ca(2), whereas Pm → Sm should selectively substitute into Ca(1).

This study on Nd-substituted FAp is part of a broader project to investigate the crystal chemistry of REE in apatite from single-crystal X-ray structures of individual-REE-substituted FAp. We are particularly interested in exploiting the distinctive stereochemistries of the two Ca positions in apatite to compare the control of monotonic decrease in size and electronic structure of trivalent REE cations on site preference.

EXPERIMENTAL PROCEDURES

Single crystals of fluorapatite with about 12.5 wt% Nd_2O_3 were grown from a volatile-rich melt using a standard cold-seal hydrothermal reaction vessel. The starting material was a stoichiometric mixture of tribasic calcium phosphate (~$Ca_{10}(PO_4)_6(OH)_2$), Nd_2O_3 (99.99 wt%), CaF_2, and SiO_2, containing the equivalent of about 10 mol% $Ca_4Nd_6(SiO_4)_6F_2$. The charge consisted of 0.037 g of starting mixture, 0.040 g of NaF, and 0.01 cm^3 of deionized water contained in a sealed gold capsule about 4 cm in length. It was heated to 920–940°C at 0.17 GPa for 2 hr, cooled stepwise, maintained at 685°C and 0.11 GPa for 36 hr, and quenched in air and water. Apatite crystal size was a maximum of about 0.1 × 0.1 × 1.0 mm. By electron microprobe analysis (18), crystals similar to the one used

0022-4596/94 $6.00
Copyright © 1994 by Academic Press, Inc.
All rights of reproduction in any form reserved.

for structure analysis were essentially homogeneous. Average oxides/elements present were CaO at 44.7(4), Na_2O at 1.5(2), Nd_2O_3 at 12.7(5), P_2O_5 at 37.5(4), SiO_2 at 1.8(1), and F at 2.9(2) wt% (standard deviations are 1σ), yielding a formula of $Ca_{8.63}Na_{0.51}Nd_{0.82}(P_{5.71}Si_{0.32}O_4)_6F_{1.63}(OH)_{0.37}$. The formula used for the X-ray structure refinement was $Ca_{8.66}Na_{0.51}Nd_{0.82}(P_{5.68}Si_{0.32}O_4)_6F_2$.

All single-crystal measurements (made with an Enraf–Nonius CAD-4F diffractometer and graphite-monochromatized Mo$K\alpha$ X radiation) and structure refinements closely followed earlier procedures (19). Scattering factors for neutral atomic species and f', f'' were taken from Ref. (20). All computations were carried out with DATAP77 and LINEX77 (State University of New York at Buffalo). Further experimental details are given below, and the results are summarized in Tables 1–5.[1]

Unit-cell parameters are a = 9.3979(13), c = 6.8997(8) Å, V = 527.7 Å^3. Reflections (n = 3594) with indices $\pm h$, k, l to 2θ = 80° were measured in the ω scan mode. Transmission factors varied from 0.320 for $\bar{1}$, 1, 0 to 0.778 for 2, 10, 2 (crystal volume = 0.96×10^{-3} mm^3, μ = 45.7 cm^{-1}). There were 1081 unique reflections, with 325 considered unobserved on the basis of $I < 3\sigma(I)$. Two strong reflections (300 and 310) were deleted because of unsatisfactory extinction correction. Refinement in $P6_3/m$ converged to R = 0.024, R_2 = 0.025 [for reflections with $I \geq 3\sigma(I)$, S = 0.847, $g = 1.11(2) \times 10^{-4}$, $\Delta\rho$ = −0.84 e Å^{-3} at 0, 0, 0.25 ± 0.10 to 1.02 e Å^{-3} at 0, 0, 0.25 (both near F and attributable to omission of OH in the refinement)].

DISCUSSION

The present X-ray structure refinement of synthetic Nd-bearing FAp does not yield separate positional and thermal parameters for atomic substituents. The parameters reported in Tables 1 and 4 (see footnote 1) are average values for the various atomic substitutions documented above and the local atomic displacements resulting from these substitutions.

The analyzed F content is approximately consistent with both the conditions of synthesis (cf. 21) and the Ca(2)–A bond length (2.311 Å; Table 2). The latter is also 2.311 Å in end-member FAp (7), but decreases with substitution of REE to 2.302 Å in FAp with a REE content similar to the present (15) and increases with substitution of OH to 2.385 Å in hydroxyapatite (7).

The substitution of Nd is accommodated exclusively by compensating substitution of Si and Na (substitution mechanisms 1 and 2; cf. 14). For the structure refinement, Si was simply assigned a partial occupancy on the P position. However, the structural role of Na presented a problem. The crystal chemical analysis below points to a strong preference of Na for the Ca(1) position. This is observed in silicate oxyapatites (e.g., (12)), but cannot be assumed for FAp and hydroxyapatite. Hughes *et al.* (15) addressed this problem by assigning all Na to the Ca(1) position, to provide a limiting case for REE ordering. We have determined a value for the Na occupancy by an iterative procedure, in which the Na occupancy was reset between refinements. This procedure is not entirely satisfactory, but the occupancies of Nd and Na in the Ca(1) and Ca(2) positions cannot be varied independently during least-squares refinement with structure factors from Mo$K\alpha$ X-ray intensities. With Nd in the Ca(2) position as the variable compositional parameter, R was minimized with about 60% of the Na in Ca(1) (Table 3). Values for refinement of two limiting models [with all Na in Ca(1)

TABLE 1
Positional and Isotropic Thermal Parameters (Å^2)

	x	y	z	B_{eq}[a]
Ca(1)	$\frac{2}{3}$	$\frac{1}{3}$	0.0000(1)	0.89(3)
Ca(2)	0.99024(9)	0.24085(9)	$\frac{1}{4}$	0.75(1)
P	0.3687(1)	0.3975(1)	$\frac{1}{4}$	0.52(1)
O(1)	0.4830(3)	0.3253(3)	$\frac{1}{4}$	0.96(3)
O(2)	0.4661(3)	0.5859(3)	$\frac{1}{4}$	1.23(4)
O(3)	0.2561(2)	0.3406(2)	0.0714(2)	1.41(3)
F	0	0	$\frac{1}{4}$	2.93(12)

[a] $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

TABLE 2
Selected Bond Distances (Å) and Angles (°)

Ca(1)–O(1)	2.415(1)	×3	P–O(1)	1.531(2)	
Ca(1)–O(2)[a]	2.460(2)	×3	P–O(2)	1.534(3)	
Ca(1)–O(3)[a]	2.817(2)	×3	P–O(3)	1.535(1)	×2
Ca(2)–O(1)[b]	2.662(2)		O(1)–P–O(2)	111.46(15)	
Ca(2)–O(2)[c]	2.391(1)		O(1)–P–O(3)[e]	111.06(9)	×2
Ca(2)–O(3)	2.510(1)	×2	O(2)–P–O(3)	108.16(10)	×2
Ca(2)–O(3)[d]	2.352(2)	×2	O(3)–P–O(3)[e]	106.75(14)	
Ca(2)–F	2.311(1)				

[a] $-x, -y, -z$.
[b] $-y, x-y, z$.
[c] $y-x, -x, z$.
[d] $x-y, x, -z$.
[e] $x, y, \frac{1}{2}-z$.

[1] See NAPS Document 05078 for 10 pages of supplementary materials (including Tables 4 and 5). Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163-3513. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 for up to 20 pages, plus $0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15.00. Foreign orders add $4.50 for postage and handling, for the first 20 pages, $1.00 for each additional 10 pages of material, and $1.50 for postage of any microfiche orders.

TABLE 3
Refined Nd Site Occupancies

Position	Cation	1[a]	2[b]	3[c]
Ca(1)	Ca	0.882	0.823	0.971
	Na	0.077(8)	0.128	0.0
	Nd	0.041(1)	0.049(1)	0.029(1)
Ca(2)	Ca	0.856	0.896	0.797
	Na	0.034(8)	0.0	0.086
	Nd	0.110(1)	0.104(1)	0.118(1)
R index		0.02361	0.02365	0.02370

[a] Na occupancy defined by iterative refinement and error is estimated.
[b] All Na in Ca(1).
[c] All Na in Ca(2).

and Ca(2), respectively] are given in Table 3 for comparison. We have not attempted to evaluate the *R* values for the three refinements of Table 3 and indeed they are statistically similar using the Hamilton (22) test. However, the Hamilton test may not be applicable to this problem because the variable parameters and observations remain unchanged in the three refinements. The total uncertainty in the Nd occupancy on Ca(2) due to the structural role of Na is about 6% of the accepted value, and all other structural parameters are identical within error (1σ). For the currently accepted refinement (1 in Table 3), Nd is strongly but not exclusively partitioned into Ca(2); about 80% of the Nd in this FAp is accommodated in the Ca(2) position. In contrast, about 60% of the Na is accommodated in the Ca(1) position. The ratio of the Nd site occupancies [Nd : Ca(2)/Nd : Ca(1)] is 2.68, which is within the range of values (1.76–3.00) for four REE-bearing natural apatites (15).

There have been several proposals to rationalize the Ca(1) and Ca(2) site occupancies of REE in apatites. Urusov and Khudolozhkin (23) noted that divalent cations larger than Ca preferentially occupy the smaller Ca(2) position, whereas divalent cations smaller than Ca occupy Ca(1). They suggested that site occupancy was determined very largely by bond type, with cations more electronegative than Ca favoring the more covalent Ca(1) position. Mackie and Young (11) concluded that the substitution mechanism was the factor controlling the site occupancy of Nd in Nd-doped FAp. Hughes *et al.* (15) used calculation of bond valence (23) to show that heavy REE (Gd → Lu) are underbonded in either Ca position, whereas La, Ce, and Pr are slightly overbonded in the Ca(1) position and therefore should prefer Ca(2), Pm and Sm should favor Ca(1), and Nd should readily substitute into either Ca(1) or Ca(2).

A simple average of bond lengths gives a misleading estimate of the relative sizes of the Ca polyhedra in the apatite structure, because the coordination of Ca(1) is really 6 + 3 rather than 9. The six closest oxygens to Ca(1) [O(1), O(2); Fig. 1] form a trigonal prismatic cluster, sharing basal faces to link into chains parallel to the *c*-axis (cf. 25). The distant near-equatorial O(3) atoms are bridged to O(2) by P (Fig. 1).

Calculated bond valences (24) for end-member FAp (e.g., 15) are Ca(1), 2.02; Ca(2), 1.88; P, 5.07; O(1), 2.00; O(2), 2.07; O(3), 1.96; and F, 0.89, with a bond valence sum for ligand atoms of 49.7, in good agreement with the ideal value of 50.0. Thus, minor amounts of trivalent Nd substituted into FAp, as in the present case, should favor the Ca(2) position, to increase the bond valences of both Ca(2) and F. Conversely, Na should favor Ca(1). Our preferred structure refinement (Table 3) is in agreement with these predicted site preferences, recognizing that the moderately high temperature of crystal synthesis could account for the lack of complete ordering. The bond valence requirements of the *A* (or O) anion alone must exert a considerable influence on the site preference of cations

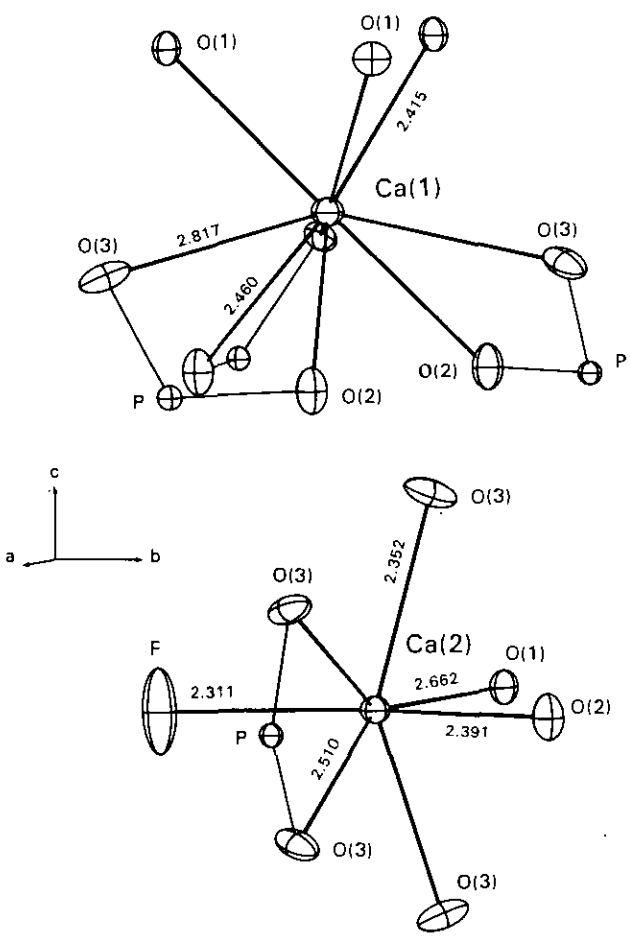

FIG. 1. Stereochemical environment of Ca in Nd-bearing fluorapatite. Ca(1) polyhedra share faces to link into chains parallel to *c*-axis, and F is in triangular coordination with Ca(2): bond distances are in Å.

in apatites and readily explain the strong preference of trivalent REE for the Ca(2) position in oxyapatites (12) and Nd_2O_3-doped FAp (11).

ACKNOWLEDGMENTS

We thank two unknown referees for helpful comments on the manuscript and the Natural Sciences and Engineering Research Council of Canada for financial support.

REFERENCES

1. S. Náray-Szabó, *Z. Kristallogr.* **75,** 387 (1930).
2. M. Mehmel, *Z. Kristallogr.* **75,** 323 (1930).
3. M. I. Kay, R. A. Young, and A. S. Posner, *Nature* **204,** 1050 (1964).
4. P. E. Mackie, J. C. Elliott, and R. A. Young, *Acta Crystallogr. Sect. B* **28,** 1840 (1972).
5. J. C. Elliott, P. E. Mackie, and R. A. Young, *Science* **180,** 1055 (1973).
6. K. Sudarsanan, P. E. Mackie, and R. A. Young, *Mater. Res. Bull.* **7,** 1331 (1972).
7. J. M. Hughes, M. Cameron, and K. D. Crowley, *Am. Mineral.* **74,** 870 (1989).
8. J. M. Hughes, M. Cameron, and K. D. Crowley, *Am. Mineral.* **75,** 295 (1990).
9. M. R. Hughson and J. G. Sen Gupta, *Am. Mineral.* **49,** 937 (1964).
10. A. G. Cockbain and G. V. Smith, *Mineral. Mag.* **36,** 411 (1967).
11. P. E. Mackie and R. A. Young, *J. Appl. Crystallogr.* **6,** 26 (1973).
12. R. P. Gunawardane, R. A. Howie, and F. P. Glasser, *Acta Crystallogr. Sect. B* **38,** 1564 (1982).
13. P. R. Suitch, J. L. Lacout, A. Hewat, and R. A. Young, *Acta Crystallogr. Sect. B* **41,** 173 (1985).
14. J. G. Ronsbo, *Am. Mineral.* **74,** 896 (1989).
15. J. M. Hughes, M. Cameron, and A. N. Mariano, *Am. Mineral.* **76,** 1165 (1991).
16. R. W. G. Wyckoff, "Crystal Structures," 2nd ed., Vol. 3, p. 228. Wiley, New York, 1965.
17. S. V. Borisov and R. F. Klevcova, *Struct. Rep.* **28,** 188 (1963).
18. Y. Pan, M. E. Fleet, and N. D. Macrae, *Geochim. Cosmochim. Acta* **57,** 355 (1993).
19. M. E. Fleet, *Am. Mineral.* **77,** 76 (1992).
20. J. A. Ibers and W. C. Hamilton (Eds.), "International Tables for X-ray Crystallography," Vol. IV. Kynoch Press, Birmingham, England, 1974.
21. M. A. Korzhinskiy, *Geochem. Int.* **18,** 44 (1982).
22. W. C. Hamilton, *Acta Crystallogr.* **18,** 502 (1965).
23. V. S. Urusov and V. O. Khudolozhkin, *Geochem. Int.* **11,** 1048 (1974).
24. I. D. Brown, in "Structure and Bonding in Crystals" (M. O'Keeffe and A. Navrotsky, Eds.), Vol. II, p. 1. Academic Press, New York, 1981.
25. J. Huang and A. W. Sleight, *J. Solid State Chem.* **104,** 52 (1993).