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COMPARISON OF SYNTHETIC AND MINERAL FLUORAPATITE, $Ca_5(PO_4)_3F$, IN CRYSTALLOGRAPHIC DETAIL

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ABSTRACT

Detailed crystal structure refinements based on x-ray intensity data measured to ~1% precision in most cases (R_1 = 1.6% and 2.9%) show that the atomic positions in both synthetic and mineral fluorapatite (space group $P6_3/m$, $\underline{a}$ = 9.367(1) Å, $\underline{c}$ = 6.884(1), and Z = 2) agree within less than 0.001 Å. Observed differences of 10 to 30% in the thermal parameters are ascribed to the effects of impurity and vacancy substitutions. Although the new atomic parameters differ significantly (up to 0.1 Å) by current standards from those reported nearly 40 years ago by Náray-Szabó and refined by Beevers and McIntyre, the differences generally represent improvements in precision rather than corrections.

Introduction

Apatites occur in a wide range of substituted forms both biologically (in tooth and bone) and mineralogically. Apatites are also important to agriculture (in the production of fertilizer) to the lighting industry (as a phosphor in fluorescent lamps), and to the field of quantum electronics where rare-earth-doped fluorapatites are being studied as possible solid-state laser hosts (1). Some of the interesting and useful properties of apatites depend on the occurrence of minor substitutions (e.g., 1 wt. %) or alterations of the ideal apatite structure. These detailed structure-determined properties are, in principle, predictable from detailed knowledge of location and motion of each individual atom. For crystallographically distinct - or distinguishable - atoms, single-crystal diffraction techniques have the ability to yield this type of atomic-scale detail. On the basis of such data, atomic-scale models for certain apatite properties have been presented by Elliott and Young (2,3) and by Young, Sudarsanan, and Mackie (4).

Fluorapatite ($Ca_5(PO_4)_3F$) occurs naturally as a mineral and is easily prepared synthetically. The structure of naturally occurring fluorapatite has been described by Náray-Szabó (5) and by Beevers and McIntyre (6). Precision structure refinements have been carried out for the nearly isostructural compounds hydroxyapatite (4) and chlorapatite (7) from x-ray data. But such a refinement has not been reported for fluorapatite (FAp). The only published structure parameters are the positional coordinates (no temperature factors) given by Náray-Szabó (5) and partially modified by Beevers and McIntyre (6). Both to provide structure parameters with a precision consistent with current capabilities and to allow comparison of FAp from different origins, both a mineral and a synthetically prepared sample of FAp were studied with single-crystal x-ray diffraction techniques. Two different automated diffractometers and two different data collection strategies were used. In consequence, the results are thought to be characteristic of fluorapatite, $Ca_5(PO_4)_3F$, rather than being specimen or technique specific.

Experimental

The single-crystal mineral sample (hereafter referred to as Crystal M), from Auburn, Maine, was ground to approximate a sphere of radius of 0.14 mm. A punched-tape-controlled single-crystal x-ray diffractometer and $\mathrm{MoK}\alpha$ radiation were used to collect the Bragg intensity data for 1316 independent reflections. Information obtained from an initial rapid survey run (about 700 reflections per day) was used to adjust the scanning speed and background range to yield, in most cases, approximately 1%, or less, counting statistical error in the net intensities. Single-filter (Zr) 2θ scans were used in the range $25^\circ \le 2\theta \le 100^\circ$ and balanced-filter ω scans in the range $2\theta < 25^\circ$. The basic experimental conditions, including assignment of standard deviations for the observations, have been described in detail elsewhere (8).

The synthetic fluorapatite crystal (hereafter referred to as Crystal S) used in this study, ground to approximate a sphere of 0.165 mm radius, was prepared from a flux-grown sample supplied by Dr. J. S. Prener, General Electric Company, Schenectady, New York. A computer-controlled four-circle diffractometer was used to collect the Bragg intensity data for 1086 independent reflections with unfiltered $\mathrm{MoK}\alpha$ radiation. The data were collected only for the angular ranges: $40^\circ \le 2\theta \le 60^\circ$, $75^\circ \le 2\theta \le 85^\circ$ and $100 \le 2\theta \le 120^\circ$. Only the intensities of those reflections for which all Bragg peaks from the β radiation lay outside the range of the background measurements were measured. Simultaneous diffraction effects were assessed by remeasurement of each reflection intensity after the specimen was rotated about the diffraction vector by 1 degree. In most cases the reflections were measured to 1% statistical precision in the net intensity. Further details of the procedure have been described by Mackie (9).

Absorption corrections were made for both spherical crystals, M and S, on the basis of the tabular data in the International Tables for X-ray Crystallography (10).

The structure models were refined by the full-matrix least-squares technique, the Busing, Martin and Levy (11) ORFLS program, modified by Johnson (12) and called XFLS, being used. The atomic scattering factors used for Ca^{2+}, P, O^{1-}, and F^{1-} were taken from the International Tables for X-ray Crystallography (10). Relevant corrections for anomalous dispersion were made with values of $\Delta f'$ and $\Delta f''$ calculated by Cromer (13). The observed structure factors were corrected for secondary extinction with Zachariasen's approximate method (14).

Results and Discussion

The unit cell dimensions and refractive indices of the two samples are:

FAp Specimen	a (Å)	c (Å)	n_ω	n_ϵ
Mineral	9.363(2)	6.878(2)	1.632	1.629
Synthetic	9.367(1)	6.884(1)	1.633	1.629

The two structures were refined to the final R values given below:

	R_1	R_2	wR_2
Crystal M	0.029	0.032	0.036
Crystal S	0.016	0.016	0.028

where $$R_1 = \frac{\Sigma(|F_o| - |F_c|)}{\Sigma|F_o|}, \quad R_2 = \frac{\Sigma(|F_o|^2 - |F_c|^2)}{\Sigma|F_o|^2}$$

$$wR_2 = \frac{\{\Sigma w(|F_o|^2 - |F_c|^2)^2\}^{\frac{1}{2}}}{\Sigma w|F_o|^4},$$ and w is the reciprocal of the variance arising from counting statistics. The difference between the two final R factors can be explained partly by the fact that for the synthetic specimen, only, an experimental assessment was made of simultaneous diffraction effects and those reflections which appeared to be significantly ($>3\sigma$ in net intensity) affected were eliminated from further consideration. Other differences in

the data collection strategies and the presence of impurities in the mineral specimen may also account, to a degree, for this observed difference.

The positional parameters and temperature factors, with their standard deviations, are given in Table 1. Previous experience (8) indicated that the estimated standard deviations as reported here, though small, are correct indications of the precision and that differences in the atomic parameters can be considered physically significant if they exceed 3σ.

Although the two specimens are from very different origins and although the two sets of data were collected on different diffractometers with different data collection strategies, the two sets of refined structural parameters are generally in excellent agreement. The fact that the new positional parameters differ as little as they do from those of Náray-Szabó (as modified by Beevers and McIntyre) may be regarded as something of a testimonial to the quality of the crystal structure work being done 40 years ago and on which many of Professor Pauling's insights were, necessarily, then based.

All the positional parameters except those of O_I agree within one standard deviation whereas the differences are as large as seven standard deviations for O_I. However, the temperature factors of the PO_4 group appear to be systematically larger for the mineral specimen while those for Ca and F appear to be systematically lower. These differences, which do meet the criterion of physical significance discussed above, may reflect either increased static or dynamic dispersal, or both, induced by the presence of impurities in the mineral sample. In particular, attention is directed to the presence of Mn, discussed below.

Table 1 shows that there are real differences in some of the site occupancy factors. For an analysis of these factors that would not be affected by possible errors in the overall scaling of observed to calculated intensities, ratios of the atomic multipliers were formed. They were formed with respect to the oxygen multipliers in the expectation that the oxygen atoms would be present in the same, essentially stoichiometric, amount in the two specimens (Table 2).

Compared to the synthetic specimen, the mineral specimen shows an increase in the site occupancy factor for phosphorus, which could suggest that some heavy-atom impurity substitution has occurred in the mineral specimen. Manganese, known to substitute as MnO_4 for PO_4 (16), was shown by chemical

TABLE 1

Structural Parameters of Mineral and Synthetic Fluorapatite
(All Positional Parameters and Temperature Factors, Except Those Expressed as Fractions, have been Multiplied by 10^4)

ATOM	SPECIMEN*	SITE OCCUPANCY	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O_I	M	0.988(4)	3268(1)	4850(1)	1/4	40(1)	28(1)	41(2)	26(1)	0	0
	S	1.000(6)	3262(1)	4843(1)	1/4	35(1)	26(0)	41(1)	23(0)	0	0
	NS	1.000	3330	5000	1/4						
O_{II}	M	0.988(4)	5881(1)	4668(1)	1/4	19(1)	25(1)	79(2)	8(1)	0	0
	S	1.000(6)	5880(1)	4668(1)	1/4	16(0)	24(1)	70(1)	7(0)	0	0
	NS	1.000	0	4670	1/4						
O_{III}	M	0.989(3)	3415(1)	2569(1)	704(1)	73(1)	35(1)	30(1)	36(1)	24(1)	15(1)
	S	0.998(4)	3416(1)	2568(1)	704(1)	61(1)	31(0)	31(1)	29(0)	21(0)	14(0)
	NS	1.000	3330	2500	620						
P	M	1.008(2)	3982(1)	3689(1)	1/4	20(1)	19(1)	19(1)	11(1)	0	0
	S	0.992(2)	3981(0)	3688(0)	1/4	14(0)	12(0)	17(0)	7(0)	0	0
	NS	1.000	4160†	3610	1/4						
Ca_I	M	0.990(3)	1/3	2/3	12(1)	28(1)	28	15(1)	14	0	0
	S	0.975(3)	1/3	2/3	11(0)	30(0)	30	20(0)	15	0	0
	NS	1.000	1/3	2/3	0						
Ca_{II}	M	0.986(2)	2415(1)	71(1)	1/4	20(1)	21(1)	20(1)	9(1)	0	0
	S	0.976(2)	2416(0)	71(0)	1/4	20(0)	20(0)	27(0)	11(0)	0	0
	NS	1.000	2500	0	1/4						
F	M	0.906(6)	0	0	1/4	26(1)	26	124(4)	15	0	0
	S	0.942(4)	0	0	1/4	25(1)	25	129(3)	12	0	0
	NS	1.000	0	0	1/4						

* M = Mineral, S = Synthetic, NS = Náray-Szabó's 1932 results.

† This value has been later revised to 3900 by Beevers and McIntyre.

TABLE 2
Ratios of Multipliers

Sites	Synthetic	Mineral	Ideal
$P/\Sigma O$	0.2482 (12)	0.2549 (10)	0.2500
$F/\Sigma O$	0.0786 (12)	0.0764 (7)	0.0833
$Ca(1)/\Sigma O$	0.1627 (16)	0.1669 (12)	0.1667
$Ca(2)/\Sigma O$	0.2442 (23)	0.2494 (16)	0.250

analysis* to be present in 0.62 wt % in the mineral sample. In least-squares refinement of structural models, the fractional increase, y, of the multiplier of an atom with scattering factor f_1, due to a fraction 'x' of its site being filled with another atom of scattering factor f_2, is given by

$$y = x(\langle \frac{f_2}{f_1} \rangle - 1)$$

where $\langle \frac{f_2}{f_1} \rangle$ is the volume-weighted reciprocal space average of the ratio of the scattering factors (8, 15). For the $\frac{\sin\theta}{\lambda}$ range used in this work (0 to 1), $\langle \frac{f_2}{f_1} \rangle = 1.85$ for Mn and P, respectively. With this relationship, the observed increase in multiplier could be explained by the presence of 0.74 wt % Mn substituting for P in the mineral. This result is considered to be in sufficient agreement with the chemical analysis to verify the occurrence of significant Mn-for-P substitution.

It is concluded (i) that the positional parameters in Table 1 obtained in the present work fairly represent $Ca_5(PO_4)_3F$, as such, within the precision indicated and (ii) that the small differences in thermal parameters most probably reflect real mineral-vs-synthetic differences in impurity and, possibly, vacancy substitutions.

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[*] Ca = 39.6%, PO_4 = 55.6%, F = 3.8% and Mn = 0.62% by weight. Chemical analysis was carried out by N. M. Braun, General Electric Company, Cleveland, Ohio, to whom we express our thanks.

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