SITE PREFERENCE OF Gd IN SYNTHETIC FLUORAPATITE
BY SINGLE-CRYSTAL W-BAND EPR AND
X-RAY REFINEMENT OF THE STRUCTURE: A COMPARATIVE STUDY

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ABSTRACT
Fluorapatite containing 1.2(2) wt% Gd₂O₃ (sample AP30–1), synthesized from a CaF₂-rich melt in a Pt crucible, has been investigated by single-crystal W-band (~94 GHz) electron paramagnetic resonance (EPR) spectroscopy and X-ray structure refinement. The EPR spectrum of AP30–1 measured at ~287 K, with Zeeman field $B_\parallel z'$ and microwave field $B_{mw}\parallel x'$, gave a Gd site-occupancy ratio (Ca₂⁻Gd/Ca₁⁻Gd) of 1.4(4), indicating a weak preference between the two types of Ca sites. Similarly, X-ray refinement of the structure of AP30–1 suggests that Gd is essentially equally distributed between the two Ca sites: Ca₂⁻Gd/Ca₁⁻Gd = 0.8(2), although the Gd content in this sample is close to the practical limit of detection of this method. This agreement between the W-band EPR and X-ray structural data confirms that EPR is capable of determining the distribution of paramagnetic trace elements between structurally nonequivalent positions in minerals. X-ray refinement of the structure of another sample of fluorapatite [AP40–0, containing 2.9(1) wt% Gd₂O₃] synthesized in a sealed Pt capsule, yielded a Ca₂⁻Gd/Ca₁⁻Gd value of 3.1(6), indicating a marked preference for the Ca₂ site, consistent with the site preference of Gd in hydrothermally grown Gd-rich fluorapatite. The marked preference of Gd for the Ca₁ site observed in previous EPR studies of flux-grown fluorapatite samples [AP30–0, 0.8(1) ppm Gd and Ca₂⁻Gd/Ca₁⁻Gd = 0.13; AP30–5, 57(4) ppm Gd and Ca₂⁻Gd/Ca₁⁻Gd = 0.20] is now attributed to the presence of Ca⁺ vacancies at ppm concentrations in these crystals. These point defects are unlikely to reach appreciable (weight %) concentrations in fluorapatite crystals synthesized from CaF₂-rich melts, and hence the normal preference of Gd for the Ca₂ site in AP30–1 and AP40–0.

Keywords: gadolinium, fluorapatite, single-crystal W-band EPR, X-ray structure refinement, site preference, substitution mechanisms, point defects.
INTRODUCTION

Apatite-group minerals, particularly fluorapatite (FAp) and, to a lesser extent, hydroxylapatite (OHAp) and chlorapatite (ClAp), are among the most important hosts of rare-earth elements (REE) in igneous, metamorphic, and sedimentary rocks, as well as in the biomass (e.g., Gromet & Silver 1983, Pan & Fleet 1996, Pan & Stauffer 2000, Dymek & Owens 2001). Consequently, extensive studies have been made to investigate intrinsic and external controls on the uptake of the REE in apatite-group minerals (e.g., Watson & Capobianco 1981, Kovalenko et al. 1982, Watson & Harrison 1984), including our own recent efforts combining hydrothermal experiments and single-crystal X-ray studies of the structure (Fleet & Pan 1995, 1997a, b, Fleet et al. 2000a, b). Previously, all of our X-ray structure work on synthetic apatite was performed on REE-rich crystals, with REE contents ranging from 1.6(3) wt% La2O3 in ClAp (Fleet et al. 2000a) to 12.7(5) wt% Nd2O3 in FAp (Fleet & Pan 1995). Similarly, existing structural data about the REE in natural FAp samples are all obtained from REE-rich crystals (e.g., Hughes et al. 1991). A question that arises is whether these data from REE-rich crystals can be extended to natural apatite-group phases that commonly contain only part-per-million (ppm) levels of the REE. In order to answer this question, we turned to single-crystal electron paramagnetic resonance (EPR) spectroscopy for the structural characterization of ppm- and sub-ppm-level Gd3+, as a representative of trivalent REE, in flux-grown FAp (Chen et al. 2002a, b, Pan et al. 2002).

One notable finding of the single-crystal EPR studies at W-band frequency (~94 GHz) is that Gd at ppm- and sub-ppm-level concentrations in FAp has a marked preference for the Ca1 site (Chen et al. 2002b, Pan et al. 2002), opposite to that in REE-rich FAp as inferred from X-ray structure studies (e.g., Hughes et al. 1991, Fleet & Pan 1995). EPR has long been applied to the determination of the distribution of paramagnetic trace elements over structurally nonequivalent positions in minerals and their synthetic analogues (e.g., Schindler & Ghose 1970, Warren 1970, Calas 1988, references therein). However, the site occupancies determined in previous EPR studies usually were not verified because of the lack of independent techniques for structural characterization of trace elements in solids. Accordingly, a comparative study using both single-crystal W-band EPR and X-ray structure techniques was initiated on a flux-grown FAp, and the resulting data are reported herein. Specifically, sample AP30–1 selected for the present study was used previously for the characterization of a Gd3+ center by X-band (~9.4 GHz) EPR and was shown by electron-microprobe analysis to contain 1.2(2) wt% Gd2O3 (Chen et al. 2002a), which is amenable to EPR but is close to the capability limit of X-ray structure refinement (see below). Therefore, another FAp sample (AP40–0 containing a higher Gd content in the starting material) was synthesized for X-ray structure refinement to test the results obtained with AP30–1. The data reported herein confirm that EPR is capable of providing reasonable estimates of site occupancies of paramagnetic trace elements in minerals and their synthetic analogues. Moreover, the results of this study, in conjunction with data from our previous single-crystal W-band EPR studies (Chen et al. 2002b, Pan et al. 2002), provide new insight into the control of mechanisms of substitution (Mackie & Young 1973, Pan & Fleet 2002), particularly the role of vacancies at the Ca2+ sites, on the site preference of trivalent REE in fluorapatite.

BACKGROUND INFORMATION

Electron paramagnetic resonance (EPR) spectroscopy is based on the quantitative measurement of the net resonant absorption and emission of microwave electromagnetic radiations by molecules, free radicals
and defect centers with unpaired electron(s) (i.e., paramagnetic species). EPR is a powerful structural probe of dilute paramagnetic centers in various materials (including minerals and fluids), but has not yet been extensively applied in the Earth sciences (Calas 1988, Weil et al. 1994). The EPR transition energies of paramagnetic trace ions in minerals are sensitive to the surrounding crystal field. Therefore, quantitative analysis of EPR spectra can provide detailed information about the state and local structural environments of the paramagnetic ions, e.g., oxidation state, coordination number, and polyhedron symmetry, and local distortion. In some favorable cases, occupancies among different crystallographic sites can be obtained (Calas 1988, Chen et al. 2002a, b).

Field-swept (fixed-frequency) EPR spectra are commonly presented as the first derivative (dF/dB) of the absorption versus the magnetic field B, rather than the absorption line F(B) itself. The concentration (commonly expressed as the number of spins) of paramagnetic centers then is proportional to the integrated first-derivative signal (Calas 1988). Thus the relative concentrations of paramagnetic trace ions over crystallographically nonequivalent sites (i.e., site-occupancy factors) in minerals can be estimated by comparing such doubly integrated values, i.e., areas I beneath the F(B) curves (e.g., Schindler & Ghose 1970). Note that EPR also distinguishes paramagnetic centers among magnetically nonequivalent but chemically identical positions, which in favorable cases may be directly assignable to crystallographic sites in minerals.

**EXPERIMENTAL PROCEDURES**

Experimental details for the synthesis of sample AP30–1 (crystals up to 1 cm in length and ≥1 mm in diameter) in a tightly covered platinum crucible (in air), using the flux method of Premer (1967), were given in Chen et al. (2002a). Sample AP40–0 was synthesized by use of similar experimental procedures and starting materials, except that a mixture of ~100 mg starting powders of PET, synthetic CaF2, synthetic K2O, synthetic MgO, synthetic Na2O, synthetic MgO, synthetic CaF2, synthetic K2O, and synthetic MgO was sealed in a platinum capsule by welding. Crystals of AP30–1 and AP40–0 were analyzed on a JEOL JXA–8600 electron microprobe at the University of Saskatchewan, operated at an accelerating voltage of 10 kV, beam current of 10 nA, beam diameter of 5 μm, and counting times of 30 s for Ca, P and F. The same spots of the FAp crystals were re-analyzed at an accelerating voltage of 15 kV, but at the same beam current and diameter, to include Gd (counting time of 90 s), in addition to Ca, P and F (30 s). Following Stormer et al. (1993), all microprobe analyses of FAp crystals were made on sections approximately parallel to the c axis in order to minimize the possible diffusion of F anions under the influence of the electron beams. Standards included a natural FAp for Ca and P, synthetic phlogopite for F, and synthetic GdPO4 for Gd. Also, a well-characterized sample of Durango fluorapatite (Young et al. 1969) was used as a secondary standard to monitor the F results (Table 1).

**Single-crystal W-band EPR measurements**

Single-crystal W-band EPR spectra of AP30–1 were measured at ~287 K on a Mark-II spectrometer at the Illinois EPR Research Center, University of Illinois at Urbana–Champaign. Unlike those spectra obtained in the previous experiments (Chen et al. 2002a, b), which were measured with applied Zeeman magnetic field B in three orthogonal rotation planes designed for the optimization of the spin-hamiltonian parameters of unknown paramagnetic centers, the EPR spectra used in this study were collected for B in one plane (i.e., x'z') only. Following Chen et al. (2002a, b), we denote the actual experimental coordinate system by x'y'z' to distinguish it from the ideal coordinate system xyz to deal with the (unavoidable) errors in crystal alignment in W-band experiments, where axes y and z are chosen along the crystallographic axes a and c, respectively, and axis x is defined as perpendicular to both y and z. For measurements in plane x'z', a prismatic crystal of FAp was first mounted on a quartz rod by attaching a well-developed crystal face to the flat end of the quartz rod (i.e., the crystal face perpendicular to the rod axis), and was then inserted into the resonant cavity of the W-band spectrometer. Alignment was made by trial runs on the basis that the two well-characterized Gd3+ centers (‘a’ and ‘b’) do not exhibit any magnetic-site splitting at B // z and microwave excitation in a magnetic field Bp // x (Chen et al. 2002a, b). Field-swept EPR experiments were made at 5% and 10% intervals, with a spectral resolution of 4.9 G (i.e., 4,096 field data-points over 20,000 G).

<table>
<thead>
<tr>
<th>TABLE 1. COMPOSITION OF FLUORAPATITE CRYSTALS</th>
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<tr>
<td>Samples</td>
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<tr>
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</tr>
<tr>
<td>P2O5 (wt%)</td>
</tr>
<tr>
<td>CaO</td>
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<tr>
<td>Gd2O3</td>
</tr>
<tr>
<td>F</td>
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<tr>
<td>I(F)</td>
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<tr>
<td>Total</td>
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All oxide contents were obtained from EMPA at 15 kV, whereas the F values were obtained at 10 kV (see text for discussion); wt% is weight percent; n, number of analyses; σ, one standard deviation; apfu, atoms per formula unit. Ref denotes reference data for the Durango fluorapatite (FAp), from Young et al. (1969). * Total includes other oxides.
Single-crystal W-band EPR spectra were also measured on an elongate crystal of sample AP40–0 at room temperature. Unfortunately, these EPR spectra exhibit only very broad lines, making it impossible to distinguish the different paramagnetic centers (e.g., Chen et al. 2002a, b) in this sample. This pronounced line-broadening effect presumably is related to the high Gd content in this sample (see below).

Single-crystal X-ray refinement of the structure

Single-crystal X-ray-diffraction measurements were made at room temperature and atmospheric pressure with a Nonius Kappa CCD diffractometer and graphite-monochromatized MoKα X-radiation (50 kV, 32 mA, and λ = 0.70926 Å), at the University of Western Ontario. The reflection data were processed with the software packages DENZO and SCALEPACK (University of Texas Southwestern Medical Center at Dallas) and XDISPLAYF (University of Virginia Patent Foundation). SCALEPACK includes an empirical absorption-correction based on intensities of equivalent reflections. Structure refinements were made with LINEX77 (State University of New York at Buffalo). Scattering factors for neutral atomic species and values of f’ and f” were taken, respectively, from Tables 2.2A and 2.3.1 of the International Tables for X-ray Crystallography (Ibers & Hamilton 1974). Experimental details for the two crystals investigated, including the assumed formulae, are given in Table 2, and selected bond-distances and angles are given in Table 3. Tables of observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

Characterization of AP30–1 and AP40–0

The experimental products and characterization of sample AP30–1 have been described in Chen et al. (2002a). The synthesis of AP40–0 was undertaken in a sealed platinum capsule for the following three reasons: 1) to prevent F (and Ca) loss during the experiment, 2) to test the maximum uptake of Gd in FAp from CaF2-rich melts in the absence of extraneous charge-compensating ions (e.g., Na+ and Si4+; Fleet & Pan 1995), and 3) to produce FAp crystals with a higher Gd content than that of AP30–1, for X-ray structure study (see below). The experimental products of AP40–0 included subhedral FAp crystals (up to ~300 μm in maximum dimension), quenched CaF2 melt, and unreacted Gd2O3.

Separate analyses of FAp crystals, including the Durango FAp, at 10 and 15 kV did not reveal any systematic differences in the measured F contents either in individual grains or between grains. Table 1 shows that the FAp crystals of AP30–1 are close to being stoichiometric with respect to F (considering that a minor amount of F is replaced by O in the incorporation of Gd into the Ca2 site; Chen et al. 2002a) and contain 1.2(2) wt% Gd2O3. Similarly, the FAp crystals of AP40–0 are approximately stoichiometric with respect to F, but contain a higher Gd content [2.9(1) wt% Gd2O3; Table 1].

Single-crystal W-band EPR spectra

The single-crystal W-band EPR spectra of AP30–1 measured with B in the plane x’z’ are similar to their respective counterparts of AP30–0 (Pan et al. 2002) and...
AP30–5 (Chen et al. 2002b). These spectra (e.g., Fig. 1a) are characterized by the presence of two distinct Gd\(^{3+}\) centers (i.e., the recently established centers ‘a’ and ‘b’ containing Gd\(^{3+}\) ions at the sites Ca2 and Ca1, respectively; Chen et al. 2002a, b). The individual spectral lines of the Gd\(^{3+}\) centers in AP30–1, however, are noticeably broader than their counterparts in AP30–0 and AP30–5 (Fig. 1), largely because of the appreciably higher Gd content and resulting stronger dipolar interactions between the Gd\(^{3+}\) ions in the former (Chen et al. 2002a). Other spectral lines related to unknown paramagnetic center(s) are also present in the spectra of AP30–1 (Fig. 1a). However, the Mn center and a defect center possibly involving two \(^{19}\)F or \(^{31}\)P nuclei (Pan et al. 2002), which are clearly resolved in the single-crystal W-band spectra of AP30–0 and AP30–5 (Fig. 1b, c), are not detectable in AP30–1.

The relative abundance of centers ‘a’ and ‘b’ in AP30–1 has been estimated by comparison between observed and simulated single-crystal W-band EPR spectra, because a direct double integration of the first derivative of the absorption lines (e.g., Schindler & Ghose 1970) is not possible here owing to significant line-broadening and consequent peak-overlap (at the central electronic transitions) related to the high Gd content in this sample. Specifically, the spectrum selected for this purpose was that with \(B//z'\) and \(B/H//x'\) (Fig. 1a), in which all spectral lines of ‘a’ and ‘b’ are best separated and are not appreciably affected by magnetic-site splittings (Chen et al. 2002a, b). The actual orientation of the crystal for the spectrum with \(B//z'\) and \(B/H//x'\) was determined by angle correction on the basis of all spectra in plane \(x'z'\) and using the spin-hamiltonian parameters of centers ‘a’ (Chen et al. 2002a), obtained with the EPR–NMR software package of Mombourquette et al. (1996). Spectral simulations for centers ‘a’ and ‘b’ at \(B//z'\) and \(B/H//x'\) were first made separately by use of their respective spin-hamiltonian parameters, measured linewidths and appropriate lineshapes (i.e., lorentzian; Chen et al. 2002a, b) and were then added together for various trial proportions (Fig. 2). These simulated spectra were then compared with the observed spectrum by minimizing their differences using the criterion \(\Sigma(I_{\text{observed}} - I_{\text{simulated}})/\Sigma I_{\text{observed}}\), where the symbol I represents EPR absorption intensities (i.e., areas) and the sum \(\Sigma\) is over all electronic transitions.

The simulated spectrum giving the best fit for the observed spectrum of sample AP30–1 has an ‘a’/‘b’ value of 2.0(6) (Fig. 2), corresponding to a site-occupancy ratio of Gd between the Ca2 and Ca1 sites (i.e., Ca2\(_{\text{Gd}}\)/Ca1\(_{\text{Gd}}\)) of 1.4(4); the multiplicities of Ca2 and Ca1 sites are 6 and 4, respectively (Hughes et al. 1989). Note that the uncharacterized centers, related to Gd\(^{3+}\) ions or not, account for only approximately 5% of the total observed spectrum in AP30–1 and therefore are not expected to cause significant deviations from the site-occupancy ratio that is based on centers ‘a’ and ‘b’.

**Fig. 1.** Single-crystal W-band EPR spectra, with \(B//z'\) and \(B/H//x'\): a) AP30–1 containing 1.2(2) wt% Gd\(_2\)O\(_3\), measured at \(T \approx 287\) K, frequency = 94.3767 GHz and spectral resolution of 4.9 G, b) AP30–5 containing 57(4) ppm Gd (Chen et al. 2002b), and c) AP30–0 containing 0.8(1) ppm Gd (Pan et al. 2002), collected at similar orientations and experimental conditions, are shown for comparison. Note that centers ‘b’ and ‘a’ corresponding to Gd\(^{3+}\) at the Ca1 and Ca2 sites are labeled as “1” and “2”, other spectral lines of unknown center(s) in AP30–1 are marked by “?”; Center Mn corresponding to \(^{55}\)Mn\(^{2+}\) at the Ca1 site is evident in AP30–5, and an as-yet uncharacterized defect center possibly involving two \(^{19}\)F or \(^{31}\)P nuclei (Pan et al. 2002) in AP30–0 is labeled as “x”. Note that the relative intensities of ‘a’ and ‘b’ in AP30–1 are opposite to those in AP30–0 and AP30–5.
Single-crystal X-ray structure refinements

The precise X-ray reflection intensities measured in this study confirm the observations of our previous X-ray study; the FAp crystals of AP30–1 are not twinned (Chen et al. 2002a). The X-ray structure refinements of AP30–1 and AP40–0 closely followed the procedures of Fleet & Pan (1995) and Fleet et al. (2000a, b), who investigated hydrothermally grown apatite, refined the REE occupancy of the Ca2 site, and assumed that the total occupancy of both Ca1 and Ca2 positions is unity (i.e., that all formulae are stoichiometric). For the present crystals of Gd-bearing FAp, the Gd occupancy of the Ca2 position was refined, and the total cation occupancy of Ca1 and Ca2 was constrained to be equal but less than unity, as required by the EPMA data (this is a refinement of type-1 in Table 4). The resulting site-occupancy ratios \( \frac{\text{Ca2Gd}}{\text{Ca1Gd}} \) are 3.1(6) for AP40–0 and 0.8(2) for AP30–1. The Gd occupancy of the Ca1 position was refined (i.e., refinement of type 2 in Table 4); the \( \frac{\text{Ca2Gd}}{\text{Ca1Gd}} \) value is 2.8(3) for AP40–0 and 1.2(2) for AP30–1, values that are broadly within a one-sigma standard deviation of the type-1 refinement. The assumed nonstoichiometry for AP40–0 [the total content of cation vacancies is 0.03 per formula unit (pfu), Table 2] is relatively insignificant compared to the Gd content (0.17 atoms pfu), but that for AP30–1 (total cation vacancy content: 0.03 pfu) is possibly significant (the Gd content is 0.06 atoms pfu), and may have introduced a significant error in the refined site-occupancy ratio. However, refinement of AP30–1 assuming a total occupancy of unity for Ca1 (refinement of type 3 in Table 4) gave a site-occupancy ratio consistent with the previous two refinements. Therefore, uncertainty in apatite composition (including vacancies), as estimated from EMPA, is unlikely to significantly affect the calculated site-occupancy ratios of Gd. Finally, when the occupancies of Ca in Ca1 and Ca2 are varied along with Gd in Ca2 (refinement of type 4 in Table 4), a higher value of 1.7(7) is obtained for the site-occupancy ratio. This refinement did converge (albeit slowly), but the resulting site-occupancy ratio is suspect, because the Gd and Ca occupancies are now highly correlated.

**DISCUSSION**

Comparison of site-occupancy ratios from W-band EPR and X-ray structure methods

The X-ray structure refinement of AP40–0 containing 2.9(1) wt% Gd2O3 shows that Gd in this sample has a marked preference for the Ca2 position. This site preference is similar to that observed by Mackie & Young (1973), who reported that Nd in Nd2O3-doped FAp occupies exclusively the Ca2 position. Similarly, Fleet & Pan (1995) reported that the site-occupancy ratios of REE in FAp decrease monotonically with increase in atomic number through the 4f transition series (see also Hughes et al. 1991, Fleet et al. 2000a, b) and reported a \( \frac{\text{Ca2Gd}}{\text{Ca1Gd}} \) value of 2.03 for a hydrothermally grown

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**FIG. 2.** Comparison of observed (solid line) and simulated [dashed line; \( \frac{\text{Ca2Gd}}{\text{Ca1Gd}} = 1.4(4) \)] single-crystal W-band EPR spectra of AP30–1, with \( \vec{B} \parallel \hat{z} \) and \( \vec{B} \parallel \hat{x} \), at ~287 K, frequency = 94.3767 GHz and spectral resolution of ~4.9 G. Also shown is the difference between the observed and simulated spectra.

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**TABLE 4. SITE OCCUPANCIES OF Gd IN SYNTHETIC FLUORAPATITE**

<table>
<thead>
<tr>
<th>Site occupancies of Gd</th>
<th>SITE OCCUPANCY RATIO</th>
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<tbody>
<tr>
<td>Refinement</td>
<td>Ca1</td>
</tr>
<tr>
<td>AP30–1</td>
<td></td>
</tr>
<tr>
<td>1 Gd in Ca2</td>
<td>0.00245</td>
</tr>
<tr>
<td>2 Gd in Ca1</td>
<td>0.00189(22)</td>
</tr>
<tr>
<td>3 Gd in Ca2, Ca1 full</td>
<td>0.00212</td>
</tr>
<tr>
<td>4 Gd in Ca2, Ca in Ca1, Ca2</td>
<td>0.00149</td>
</tr>
<tr>
<td>AP40–0</td>
<td></td>
</tr>
<tr>
<td>1 Gd in Ca2</td>
<td>0.00250</td>
</tr>
<tr>
<td>2 Gd in Ca1</td>
<td>0.00272(23)</td>
</tr>
</tbody>
</table>

Type of refinement: 1. Gd in Ca2 varied, \( \vec{B} \parallel \hat{z} \); 2. Gd in Ca1 varied, \( \vec{B} \parallel \hat{z} \).
Gd-rich FAp. Conversely, the structure refinement of AP30–1, containing only 1.2(2) wt% Gd₂O₃, indicates a site-occupancy ratio close to unity. Although the content of Gd in this apatite is approaching the limit of detection by the structure-refinement method, the differences in Gd site occupancies between the type-1 and type-2 refinements (Table 4) are equivalent to about 0.4 electrons, which are still well within the intrinsic sensitivity of the method. The discrepancy in the site-occupancy ratio for these two refinements of AP30–1 is the result of systematic errors in the reflection data, which, of course, become significant as the theoretical limit of the method is approached. The site-occupancy ratio from the type-1 refinement, in which the Gd content of the Ca2 position was refined, [0.8(2)] is the preferred value because this refinement procedure was adopted in all of our previous structural studies on REE-substituted apatite-group minerals (Fleet & Pan 1995, 1997a, Fleet et al. 2000a, b).

The progressive change in size of the (Ca1)O₉ polyhedron with increasing Gd content from FAp (Sudarsanan et al. 1972) to AP30–1, AP40–0, and the Gd-rich FAp of Fleet & Pan (1995) supports the presently accepted site-occupancy ratio for Gd in AP30–1. The spatial accommodation of REE³⁺ cations and anions X (F⁻, OH⁻ and Cl⁻) in the apatite structure was discussed in Fleet et al. (2000a, b). The two Ca positions (Ca1, Ca2) offer quite different stereochemical environments. The nearest-neighbor environment of the Ca1 position (site symmetry 3) is a CaO₉ tricapped trigonal prism, which also can be regarded as a 6 + 3 coordination-polyhedron sphere, whereas that of Ca2 (site symmetry m) is a CaO₆X irregular polyhedron. The bond distances and volumes of both (Ca1)O₉ and (Ca2)O₆X polyhedra increase progressively with increase in radius and content of substituting REE³⁺ cation, and with increase in size and content of the anion X (from F⁻ to OH⁻ and Cl⁻).

However, the dimensions of the (Ca1)O₉ polyhedron are more sensitive to incorporation of REE, and those of the (Ca2)O₆X polyhedron, to occupancy of the anion site X. As shown in Figure 3a and Table 3, and using the FAp of Sudarsanan et al. (1972) and the Gd-rich FAp of Fleet & Pan (1995) as reference compounds, the Ca1–O bond distances and (Ca1)O₉ polyhedron volume of AP30–1 and AP40–0 are consistent with the Gd site-occupancy data in Ca1, as obtained from the type-1 refinement. However, the bond distances and volumes for the (Ca2)O₆X polyhedron are not informative in this respect (Fig. 3b, Table 3). The response of this cation polyhedron to replacement of Ca by small amounts of the heavy REE is markedly non-linear. As noted in Fleet et al. (2000b), the Ca2–O3 distance of 2.384 is distinctly anomalous, and represents an abrupt discontinuity in the change of this bond length with progressive substitution toward end-member FAp. The other bond distances and the (Ca2)O₆X polyhedral volume vary erratically.

The (Ca2)O₆X polyhedron forms a trigonal cluster around the X anion in the c-axis channels, and the Ca2 cation is significantly underbonded on its channel side. In contrast, the nine oxygen atoms of the (Ca1)O₉ polyhedron enclose the Ca1 cation more-or-less symmetrically, so that this polyhedron responds proportionately to replacement of Ca ions by the REE. The variation in unit-cell volume with total Gd content is also non-linear (Fig. 3c) and again signals some complexity in the response of the FAp structure to replacement of Ca by the heavy REE.

In particular, the Ca₂Gd/Ca₁Gd value of AP30–1 obtained from the single-crystal W-band EPR technique (Fig. 2) is within one standard deviation of that from X-ray structure refinement (Table 4). This agreement between the single-crystal W-band EPR and X-ray structural data confirms that EPR is capable of determining the distribution of paramagnetic trace elements...
between structurally nonequivalent positions in minerals and their synthetic analogues. Care must be exercised in site-occupancy determination by EPR spectroscopy, however, because some paramagnetic trace elements may not be detectable under certain experimental conditions (e.g., microwave frequencies, sample temperatures). For example, the X-band EPR spectra of AP30–1 disclosed only the presence of center ‘a’ (Chen et al. 2002a), whereas the higher-frequency W-band spectra (e.g., Fig. 1a) clearly demonstrate that Gd is not exclusively restricted to the Ca2 site in this sample. These results point to the advantage of multi-frequency EPR studies. For example, lower frequencies (ν) permit the investigation of relatively larger samples, which generally is convenient (e.g., in orienting single crystals and in yielding simpler spectra in some cases). On the other hand, increases in ν not only yield greater sensitivity per sample volume but also can lead to easier spectral analyses, enabling discrimination between B-dependent terms and B-independent terms in the spin-hamiltonian of a given species, as well as better discrimination between spectra of different species. Of particular relevance to the monitoring of the Gd centers ‘a’ and ‘b’ of this study is the fact that higher frequencies enhance observation of some of the magnetic species that are EPR-silent at lower frequencies (thus, ‘b’ is not spectroscopically active at the X-band frequency, but is “loud and clear” at the W-band frequency) because the spin-energy-level separation can then be spanned by the photon energy (hv).

**Controls of substitution mechanisms on site occupancies**

The $^{144}$Ca$^{3+}$/Ca$^{2+}$ value 1.4(4) of sample AP30–1 is significantly higher than those of AP30–0 (0.13; Pan et al. 2002) and AP30–5 (0.20; Chen et al. 2002b). Chen et al. (2002b) first noted that the marked preference of Gd for the Ca1 site in flux-grown AP30–5 is opposite to that in the hydrothermally grown Gd-rich FAp of Fleet & Pan (1995). Chen et al. attributed this discrepancy to: 1) different temperatures of synthesis, and 2) the presence of charge-compensating Na$^+$ and Si$^{4+}$ ions for the incorporation of Gd into the latter. However, sample AP30–1 was synthesized under the same temperature conditions and from similar starting materials (i.e., without Na or Si) as AP30–0 and AP30–5. Therefore, the two factors proposed by Chen et al. (2002b) cannot be responsible for the marked increase in $^{144}$Ca$^{3+}$/Ca$^{2+}$ in going from AP30–0 and AP30–5 to AP30–1, although they most likely have contributed, at least partly, to the absolute abundances of Gd in FAp (see below).

On the basis of the local structural environments of centers ‘a’ and ‘b’, Chen et al. (2002a, b) showed that Gd$^{3+}$ ions are incorporated into the seven-coordinated Ca2 ($^{VI}$Ca) and nine-coordinated Ca1 ($^{VII}$Ca) sites of the flux-grown FAp via the following two types of substitutions:

\[ 8 \text{Ca}^{2+} + \text{O}_2^{-} = 8 \text{Ca}^{2+} + F^{-} \] (1)

and

\[ 2\text{Ca}^{3+} + \text{X}^{-} = 2\text{Ca}^{2+} + \text{VII} \text{Ca}^{2+} \] (2).

Here, substitution (2) indicates that the incorporation of Gd$^{3+}$ into the Ca1 site involves a Ca$^{2+}$ vacancy ($\square$) located at the next-nearest-neighbor Ca2 site (Chen et al. 2002b). Therefore, this substitution is controlled by the availability of such vacancies at the Ca2 site in FAp. Although the flux method of Prener (1967) is known to produce highly stoichiometric crystals of FAp (Elliott 1994), point defects such as Ca$^{2+}$ (and F$^{-}$) vacancies along the c-axis channels (Serret et al. 2000, Pan and Fleet 2002) are expected to be readily available at ppm- and sub-ppm concentrations. Therefore, the marked preference of Gd for the Ca1 site in AP30–0 and AP30–5 containing only 0.8(1) and 57(4) ppm Gd, respectively, is most likely related to the availability of Ca$^{2+}$ vacancies at these concentrations. Calcium (and F) deficiencies (i.e., nonstoichiometry) is well known in FAp synthesized from stoichiometric melts (e.g., Mazelsky et al. 1968) and in nature (particularly biogenic apatite; Elliott 1994 and references therein). The maximum Ca deficiency in synthetic FAp corresponds to a loss of 10 at.% of total Ca (Mazelsky et al. 1968, Elliott 1994). However, Ca$^{2+}$ vacancies in FAp crystals synthesized from CaF$_2$-rich melts in tightly covered platinum crucibles (Prener 1967) and in sealed platinum capsules (e.g., AP40–0) appear to reach saturation at thousands and hundreds of ppm levels of concentrations, respectively (authors’ unpubl. results). Therefore, the amounts of Ca$^{2+}$ vacancies in AP30–1 and AP40–0 cannot match their respective Gd contents, hence the opposite site-preference of Gd (relative to those in AP30–0 and AP30–5). Also, the higher $^{144}$Ca$^{3+}$/Ca$^{2+}$Gd value in AP40–0 than that in AP30–1, as observed by X-ray structure refinements (Table 4), is consistent with a lower concentration of vacancies at the Ca$^{2+}$ sites in the former sample (prepared in a sealed platinum capsule). Therefore, the present study provides further evidence for important controls of substitution mechanisms (Mackie & Young 1973, Fleet et al. 2000a, b, Pan & Fleet 2002), particularly the roles of point defects, at ppm- and sub-ppm-concentrations, on the site occupancies of REE in apatite-group minerals.

The Gd content in FAp AP40–0 is significantly lower than that in the hydrothermally grown Gd-rich FAp of Fleet & Pan (1995), despite similar Gd$_2$O$_3$ contents in their starting materials. This discrepancy is partly attributable to the absence of extraneous charge-compensating ions (e.g., Na$^+$ and Si$^{4+}$) for the incorporation of Gd into the Ca positions in AP40–0. By analogy with other flux-grown FAp (i.e., AP30–0, AP30–1 and AP30–5), the Gd$^{3+}$ ions in AP40–0 are most likely incorporated into the Ca sites via substitution...
The coefficients of currently under way to determine the partition coefficients in apatite-group minerals. Experimental studies are chemical environments of the two Ca sites in this ppm-concentrations, because of the distinct stereo-

in FAp at ppm- and sub-ppm-concentrations that are the effects of defect equilibria on the uptake of the REE in AP30–0 and AP30–5 is expected to exert significant controls on the uptake of REE in FAp at ppm- and sub-ppm-concentrations, because of the distinct stereochemical environments of the two Ca sites in this mineral (Fleet & Pan 1997b). Experimental studies are currently under way to determine the partition coefficients of REE between FAp and CaF2-rich melts over a wide range of REE concentrations, with emphasis on the effects of defect equilibria on the uptake of the REE in FAp at ppm- and sub-ppm-concentrations that are commonly observed in natural apatite-group minerals.

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REFERENCES


