

## Crystal-structure refinement of a F-bearing spessartine garnet

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### ABSTRACT

The crystal structure of a F-bearing spessartine from the Henderson molybdenite deposit in Clear Creek County, Colorado, has been investigated by single-crystal X-ray methods. Electron-microprobe and infrared spectroscopic data indicate a composition of  $\text{Mn}_{2.67}\text{Fe}_{0.33}\text{Ca}_{0.05}\text{Al}_{1.97}\text{Si}_{2.70}\text{O}_{10.7}\text{F}_{1.0}(\text{OH})_{0.35}$  with up to 3.8 wt% F. The garnet has a cubic unit-cell edge of 11.628(1) Å. No reflections violating space group  $Ia\bar{3}d$  were observed.

The structure was refined to a final  $R$  of 0.054 ( $R_{\text{wt}} = 0.038$ ) using 2682 intensity measurements that reduced to 550 symmetry-independent reflections, of which 493 were greater than three times the standard deviation of the background count rate. The final oxygen positional parameters are  $x = 0.0336(1)$ ,  $y = 0.0481(1)$ ; and  $z = 0.6520(1)$ . The total Z-site occupancy was found to be 0.90(1) Si and is consistent with the chemical analysis that indicates a Si cation deficiency of approximately 10%. The Si-O distance of 1.656(1) Å is longer than observed for fully occupied Si sites in spessartines, indicating that F substitutes for O in Si-absent tetrahedra, similar to the OH substitution in hydrogrossular. The study indicates that it is not necessary to have the strong polarity of  $\text{OH}^-$  to achieve a  $\text{F}_4^-$  substitution for  $\text{SiO}_4^{4-}$ . Garnets may thus preserve a record of variable F activity in hydrothermal processes.

### INTRODUCTION

Porphyry molybdenum deposits are characterized, in part, by high F contents. These anomalies are expressed in such F-bearing minerals as fluorite, topaz, and F-bearing micas (Mutschler et al., 1981). Although experimental evidence (Candela and Holland, 1984) indicates that F does not form complexes with Mo under hydrothermal conditions (and therefore cannot be a direct factor in hydrothermal Mo transport), the high-F signature is significant in the exploration for porphyry molybdenum ore bodies.

During studies in 1978 of the geochemistry of alteration at the Henderson molybdenite deposit in Clear Creek County, Colorado, spessartine garnets were reported containing up to 3 wt% F (Gunow et al., 1980). F-bearing garnets have been described elsewhere in the literature and may be much more common than previously recognized. As early as 1922, von Eckermann reported a garnet with 0.63 wt% F from the Mansjo Mountain pegmatite in Sweden. More recent reports of F-bearing garnets include grossular from Adirondack calc-silicate metamorphic rocks (up to 0.76 wt% F, Valley et al., 1983), hydroandradites (up to 1.5 wt% F) from altered basalts (van Marcke de Lummen, 1986), hydrogarnet from alteration zones of the Ray porphyry copper deposit (up to 1.8 wt% F, Banks, 1976), hydrograndites from metasomatized ijolite xenoliths (up to 3.13 wt% F, Flohr and Ross, 1989), and vapor-phase spessartines in lithophysal

cavities in F-bearing rhyolite tuffs at Burro Creek, Arizona (T. Moyer, Vanderbilt University, personal communication, 1989). Also, cryolithionite ( $\text{Na}_3\text{Al}_2\text{Li}_3\text{F}_{12}$ ) has the garnet structure (Geller, 1971) as do several synthetic fluorides. Solid solutions between cryolithionite and Si-free katoite (hydrogrossular) ( $\text{Ca}_3\text{Al}_2(\text{OH})_4$ ) have been synthesized (Takamori et al., 1987), but these authors were unable to synthesize pure  $\text{Ca}_3\text{Al}_2\text{F}_6$ .

The object of this study is to determine the mechanism of F substitution by means of a crystal-structure refinement of one of the F-bearing spessartines from the Henderson ore body and to document the effects of this substitution on the garnet structure. Implicit in such a goal is a demonstration that F is actually in the garnet structure and not simply present as inclusions or as exsolution of other F-bearing minerals. Although F substitution in garnet is of considerable crystal-chemical interest, it is also essential to determine the mechanism of F substitution before a thermodynamic model of the substitution can be developed. With such a model, it may be possible to use F-bearing garnets as barometers of hydrothermal HF activity.

Meagher (1982) has given a thorough discussion of the cubic garnet structure. The general formula for the garnet group is  $\text{X}_3\text{Y}_2\text{Z}_3\text{O}_{12}$  with eight formula units per cell. Natural garnets possess a body-centered, cubic unit cell with X, Y, and Z cation sites at special positions that are fixed by space-group symmetry (Table 2). O occupies the gen-

**TABLE 1.** Chemical analysis of fluorspessartine crystal used for X-ray study

Oxide	Wt%	Atoms per 12 anions
SiO <sub>2</sub>	32.55	2.704
Al <sub>2</sub> O <sub>3</sub>	20.13	1.970
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.000
TiO <sub>2</sub>	0.06	0.007
FeO	4.79	0.333
MnO	37.98	2.673
MgO	0.00	0.000
CaO	0.60	0.053
BaO	0.00	0.000
Na <sub>2</sub> O	0.00	0.000
SO <sub>3</sub>	0.00	0.000
F	3.68	0.967
H <sub>2</sub> O*	0.64	0.355
	100.43	
-F (= O)	1.55	
Total	98.88	
(F + OH)/4		0.330
3 - Si		0.296

\* H<sub>2</sub>O content estimated from IR spectra of a second crystal. Other values from microprobe analysis.

eral position (multiplicity 96). There are three kinds of cation coordination polyhedra in the structure. The X cation (point symmetry 222) is coordinated by eight O in a triangular dodecahedron or highly distorted cube. The Y cation (point symmetry 3) is coordinated by six O in a fairly regular octahedron. The Z cation (point symmetry 4) is coordinated by four O in a distorted tetrahedron, or more accurately, a tetragonal disphenoid. Because the location of the Z site is fixed by symmetry at the special position with point symmetry,  $\bar{4}$ , it is straightforward to compute a mean Z-O distance even if the Z site is completely vacant as in katoite (Lager et al., 1987).

The ZO<sub>4</sub> tetrahedra and YO<sub>6</sub> octahedra are linked such that tetrahedra share each corner with adjacent octahedra and vice versa. Because no two tetrahedra share a common corner, the structure is classified as an orthosilicate. The linkage between the tetrahedra and the triangular dodecahedra, in which opposite edges of each tetrahedron are shared with dodecahedra, forms chains parallel to the major axes. The octahedron shares six of its twelve edges with adjacent dodecahedra.

Each oxygen is coordinated by two X, one Y, and one Z cations in a near-tetrahedral configuration. There is fairly efficient packing of O brought about by the lack of tetrahedral polymerization and the relatively large number of shared polyhedral edges.

## EXPERIMENTAL PROCEDURES AND RESULTS

### Microprobe chemical analysis

Electron-microprobe analysis of the crystal used for the X-ray study is reported in Table 1. This analysis is the average of seven spots on the crystal and indicates a composition of Mn<sub>2.67</sub>Fe<sub>0.33</sub>Ca<sub>0.05</sub>Al<sub>1.97</sub>Si<sub>2.70</sub>O<sub>10.7</sub>F<sub>1.0</sub>(OH)<sub>0.36</sub> (Sps<sub>87</sub>Alm<sub>11</sub>Gr<sub>02</sub>). Standard deviations of the oxide wt% indicate a slight variation in Fe-Mn ratio, but minimal

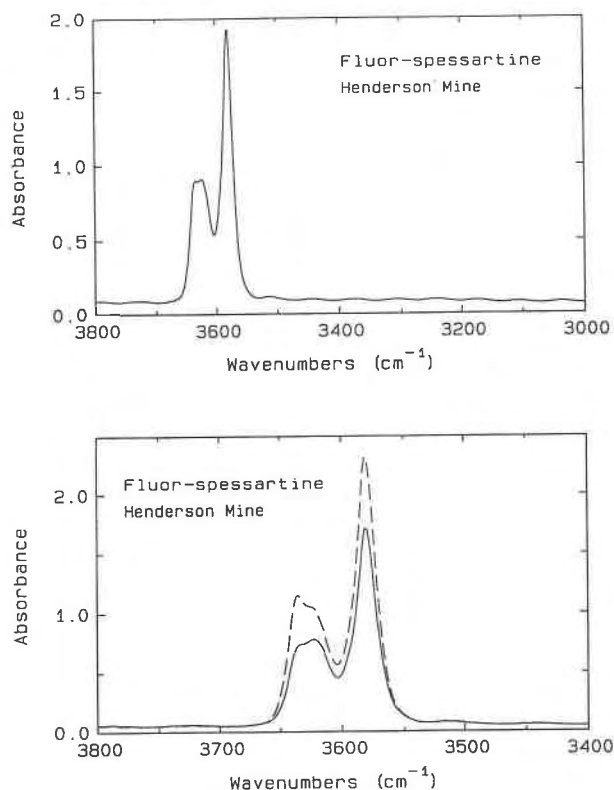


Fig. 1. Infrared absorption spectra of F-bearing spessartine. (a, upper) Unpolarized spectrum taken with 200  $\mu\text{m}$  aperture on interior of crystal 44  $\mu\text{m}$  in thickness. (b, lower) Polarized spectra showing effect of birefringence on hydroxyl absorption bands.

variation in other components. Chemical analyses of other grains from the same sample showed from 3.2 to 4.3 wt% F.

The amount of OH in the structure is poorly constrained from microprobe analyses but may be estimated by several different methods. Assuming no OH in the structure we can compute the numbers of cations per 24 anions (O + F). This indicates a F content of 1.003 fluorines per 12 anions, which is slightly less than four times the calculated Si deficiency. Also, there are more than 2.000 Al atoms per 12 anions, and the weight percent oxide total is less than 100%, both indicating the possible presence of OH.

### OH content

In order to constrain the OH content of the sample, infrared spectral measurements were obtained on a Nicolet 60SX FTIR operating at 2-cm<sup>-1</sup> resolution. A twinned crystal approximately 650  $\times$  800  $\mu\text{m}$  doubly polished to a thickness of 44  $\mu\text{m}$  was mounted over circular steel apertures (200 and 50  $\mu\text{m}$  diameter), which defined the region of study. Spectra in the range of 3000 to 3800 cm<sup>-1</sup> were measured from several regions of the sample and representative polarized and unpolarized spectra are pre-

sented in Figure 1. Polarized spectra were obtained with a  $\text{LiIO}_3$  crystal polarizer.

The OH content was determined from the intensity of the OH bands in the infrared spectrum. The overall spectrum was broadly similar to published spectra of OH in spessartine garnets (Aines and Rossman, 1984). It consists of a prominent band at  $3580\text{ cm}^{-1}$  and two less intense, overlapping bands at  $3634$  and  $3624\text{ cm}^{-1}$  (Fig. 1). The OH content determination was based on the spessartine calibration from the integrated area of the OH absorptions presented by Rossman et al. (1988). The core of the sample contained 0.64 wt%  $\text{H}_2\text{O}$  and the rim 0.50 wt%. Their calibration was derived with garnets which extended only up to 0.12 wt%  $\text{H}_2\text{O}$ , so this determination represents a significant extrapolation beyond the region of direct calibration.

The OH content estimated from the IR spectra is added to the microprobe chemical analysis in Table 1 and the F equivalent of O subtracted from the total. Cation ratios computed on the basis of a total of 12 anions (O plus F plus OH) in a manner similar to that employed by Flohr and Ross (1989), except that we use the OH content determined from IR and assume that the difference from the 100% total is a random analytical error plus some possible  $\text{Fe}^{3+}$  content. Based on these assumptions we do see a small amount of  $\text{Fe}^{3+}$  reflected in the total Mn + Fe + Ca (3.059) and the total Al (1.976). Also, the sum (F + OH)/4 (0.330) is in relatively good agreement with the deficiency in Si atoms (0.296).

#### Unit-cell and space-group determination

The F-bearing garnets in this study are strikingly birefringent, with  $N - n$  estimated at up to 0.008, similar to hydrogarnets. The OH absorption bands in the IR spectrum are similarly anisotropic (Fig. 1b). The obvious anisotropy of OH ions in an isometric host is reminiscent of the same phenomenon observed in birefringence grossular garnets (Rossman and Aines, 1986; Allen and Buseck, 1988). For the rim sections, the stronger OH absorption occurs when the electric vector is oriented parallel to a dodecahedral face.

The optical and infrared anisotropy both indicate that true local symmetry may be lower than isometric. In order to check the space-group symmetry of this material, a crystal of approximately  $400\text{ }\mu\text{m}$  in mean dimension was examined by long-exposure X-ray precession photography. Twenty-four-hour exposures of the zero-level and ( $h = 1$ )-level photographs were taken, and the reflections indexed to determine if any violations of the extinction conditions existed. No reflections violating the extinction conditions of space group  $Ia\bar{3}d$  were observed.

To further check for reflections violating space group  $Ia\bar{3}d$ , a second crystal measuring approximately  $300\text{ }\mu\text{m}$  in diameter was mounted on a Picker automated four-circle X-ray diffractometer. The unit-cell parameters of this crystal refined from centering parameters of five strong reflections ( $2\theta = 38^\circ$ ) in each of eight octants of reciprocal space were  $a = 11.618(2)\text{ }\text{\AA}$ ,  $b = 11.616(2)\text{ }\text{\AA}$ ,  $c =$

$11.619(2)\text{ }\text{\AA}$ ,  $\alpha = 90.00(1)^\circ$ ,  $\beta = 89.97(3)^\circ$ ,  $\gamma = 90.02(3)^\circ$ , so the cell is dimensionally isometric within one standard deviation. Using Zr-filtered MoK-series radiation, one thousand X-ray intensities were measured with  $5 < 2\theta < 25^\circ$  without constraint on  $h$ ,  $k$ , and  $l$ . In this data set, three intensities violating  $Ia\bar{3}d$  and greater than four times the standard deviation of the background were observed, corresponding to (003), (103), and (446). Of these, the first two appeared to be due to weak  $K\beta$  radiation, and the last to double diffraction, as the intensity disappeared on rotation about  $\psi$ .

A smaller crystal measuring approximately  $150\text{ }\mu\text{m}$  in diameter was mounted on a Nicolet automated four-circle diffractometer, and the unit-cell lengths obtained by least-squares refinement from centering parameters of 12 strong reflections of  $2\theta$  greater than  $50^\circ$  (MoK $\alpha$  radiation). The unit-cell parameters thus determined were  $a = 11.628(1)\text{ }\text{\AA}$ ,  $b = 11.629(1)\text{ }\text{\AA}$ ,  $c = 11.628(1)\text{ }\text{\AA}$ ,  $\alpha = 90.04(5)^\circ$ ,  $\beta = 90.04(5)^\circ$ ,  $\gamma = 90.05(5)^\circ$ , so this crystal is also dimensionally isometric within one standard deviation. The slight variation in cell edge between it and the first crystal is most likely due to a slight variation in the Fe-Mn ratio or the F and OH contents. We conclude from these data that insofar as it is detectable by X-rays, the space group is  $Ia\bar{3}d$ .

#### Intensity measurement

X-ray-diffraction intensity data were measured on the second smaller crystal using a Nicolet automated four-circle diffractometer. With a maximum  $2\theta$  of  $80^\circ$ , a total of 2682 intensities were measured. An absorption correction was applied to the collected data (absorption coefficient =  $57.4\text{ cm}^{-1}$ ) based on an ellipsoidal approximation of the crystal shape. After the data were corrected for absorption and for Lorentz and polarization effects, the symmetrically equivalent data were averaged, resulting in 550 symmetry-independent intensities with a discrepancy index,  $R_{\text{avg}}$ , of 0.012. Of the 550 measured intensities, 493 were greater than  $3\sigma$ .

#### Structure refinements

The atomic coordinates and temperature factors were refined using a locally modified version of RFINE, a program for crystal-structure refinement (Finger and Prince, 1975). The refinement was done in five steps, each step composed of several refinement cycles. In the first step, only the scale factor was refined. In the next step, the scale plus positional parameters for oxygen only were refined. Step three included refinement of positional parameters for oxygen plus isotropic temperature factors for all four atoms. Step four included everything in step three with a change to anisotropic rather than isotropic temperature factors. Finally, step 5 was a refinement of the occupancy of Si. The Si content of 2.70 atoms per formula unit is consistent with Si occupancy determined from diffraction data, as reported in Table 2. Final positional and anisotropic thermal parameters are reported in Table 2. The unweighted discrepancy index for all reflections,

**TABLE 2.** Atom coordinates and anisotropic temperature factors ( $\beta \times 10^5$ )

	Mn	Al	Si	O
<i>x</i>	1/8	0	3/8	0.0336(1)
<i>y</i>	0	0	0	0.0481(1)
<i>z</i>	1/4	0	1/4	0.6520(1)
Occ.	1.0	1.0	0.90(1)	1.0
$\beta_{11}$	6.6(2)	7.6(3)	8.3(6)	13.2(7)
$\beta_{22}$	12.4(2)	= $\beta_{11}$	6.1(3)	11.4(7)
$\beta_{33}$	= $\beta_{22}$	= $\beta_{11}$	= $\beta_{22}$	9.6(7)
$\beta_{12}$	0	-0.76(3)	0	-0.2(6)
$\beta_{13}$	0	= $\beta_{12}$	0	-0.4(6)
$\beta_{23}$	2.2(2)	= $\beta_{12}$	0	-1.4(5)

Note: Estimated standard deviations in parentheses.

*R*, for the final cycle of refinement was 0.054 with  $R_{wt} = 0.038$ , and with weighting based on counting statistics for unrejected reflections. Cation-anion distances, together with polyhedral volumes and distortion parameters, are reported in Table 3, and thermal vibration ellipsoids and equivalent isotropic temperature factors for F-bearing spessartine are reported in Table 4. Observed and calculated structure factors are available as Table 5.<sup>1</sup>

## DISCUSSION

This study was undertaken to determine if the F is indeed present in the structure, and if so, with which crystal chemical mechanism does it substitute. The lack of any extra diffracted intensities in the long-exposure precession photographs indicate that the F is indeed substituting in the garnet structure. This evidence is further supported by the agreement of the Si deficiency with one fourth of the F plus OH in the chemical analysis. The mean Z-O distance in the structure is significantly longer than those in nonsilica-deficient spessartine (Table 3). Therefore, it appears that the mechanism of fluorine substitution in garnet is similar to well-known OH substitution in hydrogarnet.

Direct refinement of the occupancy of the Z site indicates approximately 10% vacancies, and would require a 10% substitution of O by F plus OH to maintain charge balance. The microprobe analysis of the actual crystal used in the X-ray study shows about 8.1% substitution of O by F, whereas infrared spectroscopy of a second crystal shows about 3.0% substitution of O by OH corresponding to a Si deficiency of about 11.1%. The amount of F plus OH observed in the chemical analysis thus appears to be consistent with both the amount required to compensate the Si deficiency observed in the chemical analysis and the site occupancy refinement.

Substitution of OH in the garnet structure results in a substantial increase in the Z-O distance, which may also

**TABLE 3.** Interatomic distances (Å), angles (°), and cation-site parameters

	F-bearing spessartine*	Spessartine†	Katoite‡ (hydrogrossular)
<b>Tetrahedron</b>			
<b>Distances</b>			
Si-O	1.656(1)	1.636	1.962(1)
2 O(1)-O(2)	2.539(1)	2.518	3.076(1)
4 O(1)-O(3)	2.806(1)	2.821	3.267(1)
<b>Angles</b>			
O(1)-Si-O(2)	100.06(5)	100.67	103.19(4)
O(1)-Si-O(3)	114.37(4)	114.04	112.70(3)
Polyhedral <i>V</i> (Å <sup>3</sup> )	2.286	2.206	3.839
Quadratic elongation	1.0134	1.0117	1.0060
Occupancy	Si <sub>0.90</sub> □ <sub>0.10</sub>	Si <sub>1.0</sub>	□ <sub>1.0</sub>
<b>Octahedron</b>			
<b>Distances</b>			
Al-O	1.894(1)	1.901	1.907(1)
6 O(1)-O(4)	2.648(1)	2.676	2.578(1)
6 O(1)-O(5)	2.709(1)	2.700	2.810(1)
<b>Angles</b>			
O(1)-Al-O(4)	88.69(4)	89.48	85.80(3)
O(1)-Al-O(5)	91.31(4)	90.52	94.92(3)
Polyhedral <i>V</i> (Å <sup>3</sup> )	9.0455	9.155	9.149
Quadratic elongation	1.0005	1.0001	1.0070
Occupancy	Al <sub>1.0</sub>	Al <sub>1.0</sub>	Al <sub>1.0</sub>
<b>Dodecahedron</b>			
<b>Distances</b>			
Mn-O(4)	2.238(1)	2.245	2.461(1)
Mn-O(4)	2.400(1)	2.406	2.512(1)
2 O(1)-O(2)	2.539(1)	2.518	3.076(1)
4 O(1)-O(4)	2.648(1)	2.676	2.578(1)
4 O(4)-O(6)	3.369(1)	3.364	3.738(1)
2 O(4)-O(7)	2.784(1)	2.744	3.059(1)
4 O(1)-O(7)	2.839(1)	2.820	3.031(1)
2 O(8)-O(7)	3.921(1)	3.952	4.023(1)
<b>Angles</b>			
O(1)-Mn(2)-O(2)	69.11(4)	68.21	77.33(2)
O(1)-Mn(2)-O(4)	69.53(4)	70.14	62.45(2)
O(4)-Mn(2)-O(6)	93.10(4)	92.58	97.46(2)
O(4)-Mn(2)-O(7)	74.36(4)	74.59	75.91(2)
O(1)-Mn(2)-O(7)	72.52(4)	71.76	74.27(2)
O(8)-Mn(2)-O(7)	109.54(4)	110.40	106.36(2)
Polyhedral <i>V</i> (Å <sup>3</sup> )	21.49	21.65	25.76
Occupancy	Mn <sub>0.85</sub> Fe <sub>0.13</sub> Ca <sub>0.02</sub>	Mn <sub>0.88</sub> Fe <sub>0.10</sub> Ca <sub>0.02</sub>	Ca <sub>1.0</sub>

\* Fluorspessartine—this study (esd in parentheses).

† Spessartine (Novak and Gibbs, 1971; Smyth and Bish, 1988).

‡ Synthetic katoite (Lager et al., 1987) (300K, X-ray data).

be affected by the size of the X-site cation, but to a much smaller degree. The cation-oxygen distances observed in this structure are compared with those of anhydrous spessartine (Novak and Gibbs, 1971; Smyth and Bish, 1988) and pure synthetic katoite (hydrogrossular) [Ca<sub>3</sub>Al<sub>2</sub>(O<sub>4</sub>H<sub>4</sub>)<sub>3</sub>] (Lager et al., 1987) in Table 3. It appears that the tetrahedral site is significantly expanded in the F-bearing spessartine relative to pure spessartine, consistent with 8 to 12% vacancies in the Si site. However, without structure data for hydro-spessartines, it would be difficult to estimate precisely the proportion of Si vacancies or F or OH content of the tetrahedra from these distances or from polyhedral volumes.

This study raises an interesting question as to the de-

<sup>1</sup> A copy of Table 5 may be ordered as Document AM-90-429 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 4. Thermal-vibration ellipsoids for F-bearing spessartine

Site	Axis	RMS amplitude A	Angle with a (°)	Angle with b (°)	Angle with c (°)	Equivalent isotropic B
Mn	1	0.067(3)	0	90	90	0.57
	2	0.084(3)	90	45	135	
	3	0.100(3)	90	45	45	
Al	1	0.064(4)	55	55	55	0.41
	2	0.076(4)	114	114	35	
	3	0.076(4)	114	114	35	
Si	1	0.065(4)	90	90	0	0.37
	2	0.065(4)	90	90	180	
	3	0.076(4)	0	90	90	
O	1	0.078(4)	84	60	30	0.62
	2	0.091(4)	95	30	119	
	3	0.095(4)	7	89	97	

gree of short-range order of F that cannot be addressed from the current data. The cell shape, lack of reflections violating  $Ia\bar{3}d$ , and the apparent isometric distribution of intensities are all consistent with space group  $Ia\bar{3}d$ . The obvious optical anisotropy, however, indicates that the symmetry is not isometric so that the refined structure parameters must represent an average structure. The small  $R_{avg}$ , however, indicates that refinement of structure parameters in a lower symmetry would be unlikely to yield significant results, as have been obtained for grossulars (Allen and Buseck, 1988).

Because there are no known mineral structures in which OH or F bond directly to tetrahedral Si, it seems likely that there is a high degree of short-range order associating Si vacancy with F substitution. That is, it is unlikely that F is randomly distributed throughout the O sites in the structure, but rather are preferentially located adjacent to Si vacancies, which, themselves, may be distributed randomly. It might be possible to address this question using X-ray absorption fine-structure spectroscopy (XAFS) on F, but unless there were some long-range order that caused a lowering of symmetry, i.e., ordering of the vacancies, it would not be possible to detect the short-range order by X-ray diffraction.

### CONCLUSIONS

Hydrogarnets typically display several structural and chemical characteristics resulting from substitution of OH, e.g., a lower Si content (less than 3.0 atoms of Si per formula unit), a longer Z-O distance, and a larger unit cell. Each of these characteristics also is present in the F-bearing spessartine structure. We therefore conclude that F is indeed present within the garnet structure and not in submicroscopic inclusions or exsolution-derived grains of other F-bearing minerals such as fluorite. The substitution mechanism is therefore similar to that of OH in hydrogrossular. This conclusion raises the possibility that garnets may preserve a record of variations in the F activity of aqueous fluids during metamorphism or hydrothermal alteration and suggests that garnets obtained from these environments should be routinely analyzed for F.

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