Fluorine-bearing garnets in Adirondack calc-silicates[1]

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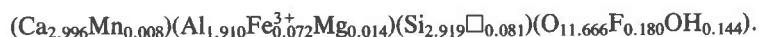
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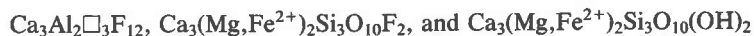*Ann Arbor, Michigan 48109*

Abstract

Several grossulars from Adirondack calc-silicates have been found to contain up to 0.76 weight percent fluorine substituted in the structure, equivalent to a 1.5 mole percent substitution of fluorine for oxygen. These garnets occur with secondary prehnite and form through retrogradation of wollastonite after the peak of Grenville regional metamorphism. Normalization of a microprobe analysis for one garnet yields an inferred formula of:

$$(Ca_{2.996}Mn_{0.008})(Al_{1.910}Fe^{3+}_{0.072}Mg_{0.014})(Si_{2.919}\square_{0.081})(O_{11.666}F_{0.180}OH_{0.144}).$$

The unit cell parameter, $a = 11.858(5)$Å, and the refractive index, $n = 1.726(3)$, are compatible with the presence of both OH and F in solid solution. The analytical data may be explained by several coupled substitutions:

$$\{\square \cdot (F,OH)_4\}^{4-} = \{SiO_4\}^{4-}, \qquad Al^{3+} \cdot O^{2-} = (Mg,Fe)^{2+} \cdot (F,OH)^{1-}.$$

The new hypothetical garnet endmembers:

$$Ca_3Al_2\square_3F_{12}, \quad Ca_3(Mg,Fe^{2+})_2Si_3O_{10}F_2, \text{ and } Ca_3(Mg,Fe^{2+})_2Si_3O_{10}(OH)_2$$

may be derived from these substitutions.

Introduction

Fluorine has been detected in garnets from Adirondack calc-silicates during electron microprobe analyses performed to chemically characterize and distinguish primary and secondary metamorphic minerals (Valley and Essene, 1980a). Three samples with retrograde textures contained garnets with detectable fluorine ranging from 0.15 to 0.76 wt.%. Six other garnet samples with texturally primary garnets contained no detectable fluorine. This implies that the presence of fluorine may serve as a criterion for identification of secondary garnet in these quartz-saturated rocks.

Occasional analyses of fluorine in garnets are reported in the literature. Eckermann (1922) analyzed garnet with 0.63 wt.% fluorine from the Mansjo Mountain pegmatite, Sweden, but contamination by fluorine-bearing inclusions may

have been difficult to avoid in a wet-chemical analysis. Gunow *et al.* (1980) report spessartine with 0-3 wt.% fluorine along with fluorite and topaz in the Henderson Deposit, Colorado, but no other details are given. Smith (1982) reports mass 19 peaks in ion microprobe analyses of anhydrous mantle minerals and suggests that such minerals may represent a previously unrecognized reservoir of fluorine in the mantle. We report chemical, optical and X-ray data on one Adirondack garnet to document the unusual nature of the fluorine solid solution.

Fluorine partitions preferentially into hydroxysilicates even at very low ratios of the fugacities of fluorine to oxygen. The minerals fluorphlogopite ($X_F = 0.96$) and fluortremolite ($X_F = 0.82$) formed in nearby Adirondack marbles, during amphibolite facies metamorphism at $\log_{10} fF_2 = -33.4$ to -34.2, $T = 650°C$, $P = 6$ kbar (Valley *et al.*, 1982). However, in these minerals the substitution is via the simple substitution exchange reaction $F^- = OH^-$. This does not, by itself, explain fluorine substitution in garnet which requires some coupled substitution involving cations for charge balance. For example, cryolithion-

ite ($Na_3Li_3Al_2F_{12}$) has a garnet structure (Strunz, 1970) and its formula clearly indicates the kind of charge adjustment required on cation sites in garnet which has fluorine substituted for oxygen.

A possible substitution of F in garnet would parallel the well-known OH substitution in hydrogarnet ($\square \cdot (OH)_4 = SiO_4$), as in grossular (Pabst, 1942), andradite (Peters, 1965), and some other minerals. The substitution would then be more generally written as $4(OH,F)^- = SiO_4^{4-}$ where the OH/F ratio would presumably in part depend on the ratios of the fugacities of H_2O/HF in the fluid phase. However, a second series of coupled substitutions of the form $(R^{3+VI}O) = (R^{2+VI}F)$ and $(R^{3+VI}O) = (R^{2+VI}OH)$ cannot be ruled out. Hydroxyl ion has also been shown to occur in silicates in other ways, such as substitution for O^- coordinated to Si (Wilkins and Sabine, 1973), but only in trace amounts not seen with electron microprobe analysis. Hydrogarnet-type substitutions are known to exist in orthosilicates, but the analogous substitution for fluorine, $\square \cdot F_4 = SiO_4$, has not hitherto been considered and complex $F = O$ solid solutions may occur in some garnets and in other phases.

Sample description

Fine-grained fluorine-bearing garnets are found as secondary rims associated with alteration of primary metamorphic minerals in calc-silicate rocks (Fig. 1) near the contact of Grenville marble and syenite south of Lake Bonaparte in Lake Bonaparte Quadrangle, New York (GOV 25-4) and east of Port Leyden in Port Leyden Quadrangle, (PL 1197, PL 1271-283). Primary coexisting minerals in GOV 25-4 include wollastonite, pale-green diopside, sphene, calcite, K-feldspar and quartz (Valley and Essene, 1980a). In hand sample this rock is composed of coarse-grained (up to 15 mm) wollastonite-rich and finer grained (1–3 mm) diopside-rich domains, each several centimeters thick. Primary minerals in PL 1197 include wollastonite, deep-green clinopyroxene, sphene, calcite, quartz, and apatite and in PL 1271-283 they include deep-green clinopyroxene, sphene, calcite, quartz and K-feldspar.

The conditions of upper amphibolite facies metamorphism in the vicinity of Lake Bonaparte have been estimated at 650°C, 6 kbar from assemblages of K-feldspar + plagioclase (Bohlen *et al.*, 1980) and sphalerite + pyrite + pyrrhotite (Brown *et al.*, 1978). Port Leyden is located just within the granulite facies and reached somewhat higher pressures and temperatures than at Lake Bonaparte.

Wollastonite was commonly stable during regional metamorphism in parts of the Adirondacks (Valley and Essene, 1977). It was stabilized during granulite facies metamorphism by low fCO_2 at Cascade Slide in the Adirondack Highlands (Valley and Essene, 1977, 1980b; Tracy *et al.*, 1978). The presence of wollastonite in GOV 25-4 and PL 1197 likewise requires metamorphism at low fCO_2 either due to dilution of the metamorphic fluid
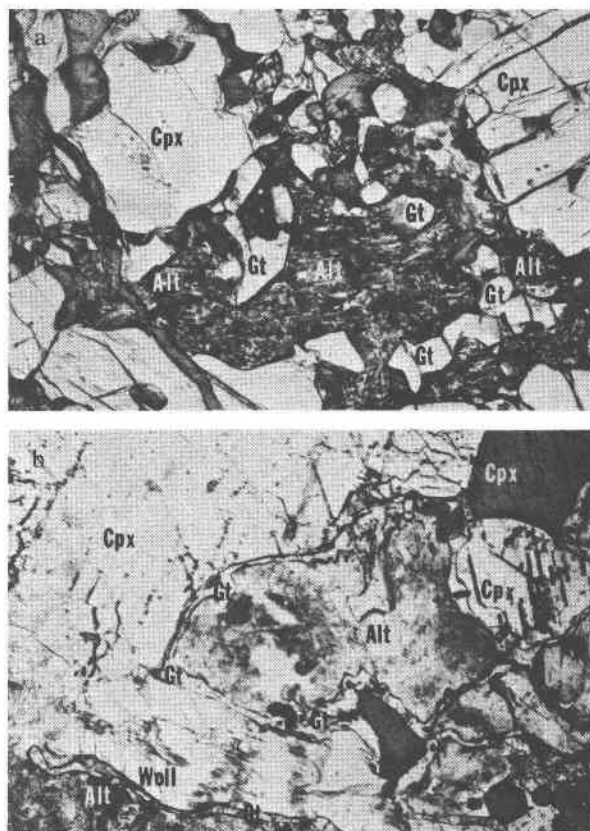

Fig. 1. Photomicrographs of GOV 25-4 (1a) and PL 1197 (1b) showing secondary fluorine-bearing garnet (Gt) with fine-grained alteration (Alt) and primary wollastonite (Woll) and clinopyroxene (Cpx). The field of view is 4 mm.

(possibly by water passing along marble contacts with syenite) or to the absence of a metamorphic fluid phase.

Post-metamorphic alteration affected many of the wollastonite-bearing samples. In GOV 25-4 these alteration products are primarily fine-grained and chemically heterogeneous at the scale of electron microprobe analysis, but homogeneous zones of prehnite (<1 mm in diameter, Fig. 1), pumpellyite, veinlets of calcite, and rims of fluorine-bearing garnet are found. The garnet rims show pale yellow cathodoluminescence upon excitation by a 15 kV electron beam, unusual in comparison with ordinary garnets. These secondary minerals have formed partly at the expense of wollastonite which may either be fresh, or fractured and highly altered. Nearby wollastonite is sometimes also altered to pectolite.

A small amount of fine-grained quartz is sometimes seen with the garnet rims in GOV 25-4 suggesting that the retrograde reaction may be idealized as wollastonite + anorthite = grossular + quartz. This reaction has also been noted as common in wollastonite-bearing marbles from near the Morin anorthosite massif in Quebec (J. Martignole, personal communication, 1977). The absence of primary plagioclase or scapolite in GOV 25-4 would

require that either a small amount of plagioclase or scapolite was originally present and was exhausted upon back-reaction, that Al was derived from a small Tschermak's component in the clinopyroxene, or that Al was introduced in solution to form garnet.

Chemical analysis

Garnets were chemically analyzed by electron microprobe for nine major and minor elements. Standard operating conditions were observed (Valley and Essene, 1980a) with 15 kV accelerating potential, 0.015 μa specimen current and 1–2 μm beam spot diameter. Fluorine and chlorine were run at a lower potential of 12 kV to decrease possible volatilization. Wavelength-dispersive spectrometers were employed with TAP, PET and LiF crystals. Pulse height analysis was used to optimize the peak/background ratio and to minimize interferences. Crystalline silicate standards were used to minimize the ZAF matrix correction (EMPADR VII), except F which was analyzed with synthetic fluorphlogopite and natural fluorapatite, and Cl which was analyzed with synthetic chlorapatite. In addition, 500 second counts were made on each grain with a Li-doped Si energy-dispersive detector. This allowed detection of all elements ($Z \geq 11$) present at levels of 0.1 element wt.% or greater.

Because of the unusual nature of fluorine in a garnet, special care was taken to increase the reliability of the analyses for this element. On each of six grains that were analyzed from three samples (GOV 25-4, PL 1197 and PL 1271-283) data were obtained on five different points for 50 seconds each. The range of values for each grain deviated from the mean by less than three standard deviations (1 S.D. = $\sqrt{N}$) indicating very little if any heterogeneity in fluorine. This clearly implies that fluorine is present in the garnet structure and not as inclusions of another phase. For GOV 25-4 and PL 1197 with 0.70 to 0.76 wt.% F the peak values were 15 standard deviations above background with peak/background ratios greater than three. By contrast, PL 1271-283 with 0.15 wt.% F has peak values only 4 standard deviations above background and peak/background equal to 1.4. Garnets that texturally appear primary from six other quartz-bearing Adirondack marbles were also analyzed for fluorine at the same time as these samples. Each of these six garnets registered peak fluorine counts corresponding to less than 0.05 wt.% F. Values of fluorine below 0.1 wt.% are not statistically significant under these operating conditions, but the values in the 0.7 wt.% range are clearly significant.

The analysis of the fluorine-bearing grossular of GOV 25-4 is reported in Table 1. If the formula is calculated about Ca + Mn + Mg + Al + Fe + Si = 8 (our usual procedure when lacking Fe^{2+}/Fe^{3+} data), one obtains R^{2+} = 3.048 assuming all iron as ferric, Al + Fe^{3+} = 2.002, and Si = 2.950. The latter value is consistent with hydrogarnet type substitutions but inconsistent with the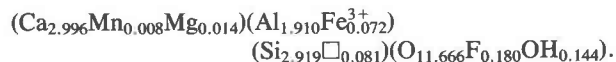 preliminary assumption that the tetrahedral site would be filled with ordinary cations. Barring a direct determination of FeO/Fe_2O_3 and H_2O, that is made difficult by the fine grain size (<100 μm) of these garnets, the only recourse is to normalize Ca + Mn + Mg + Al + Fe to 5 (VIII + VI) coordinated cations, obtaining:

$$(Ca_{2.996}Mn_{0.008}Mg_{0.014})(Al_{1.910}Fe^{3+}_{0.072})$$
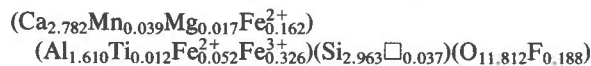$$(Si_{2.919}\square_{0.081})(O_{11.666}F_{0.180}OH_{0.144}).$$

This normalization requires that no Al replaces Si, a reasonable assumption for natural hydrogarnets (e.g., Pabst, 1942; Meagher, 1980). The Fe^{3+} content is then inferred by filling the VI-coordinated site and the OH content by filling the matching vacancy of the tetrahedral site with (F + OH)/4. This calculation suggests that the GOV 25-4 garnet has 0.3% spessartine, 0.5% pyrope, 3.6% andradite, 1.2% hydrogrossular ($Ca_3Al_2H_{12}O_{12}$) and 1.5% fluorgrossular ($Ca_3Al_2F_{12}$), with the remainder as grossular. However, the possibility of yet another substitution of the sort $R^{3+} \cdot O = R^{2+} \cdot (F,OH)$, yielding garnets with solid solution of $Ca_3R^{2+}_2Si_3O_{10}F_2$, cannot be ruled out. This substitution would be maximized if all the iron is ferrous and magnesium is placed in the octahedral site:

$$(Ca_{2.996}Mn_{0.008})(Al_{1.910}Mg_{0.014}Fe^{2+}_{0.072})$$
$$(Si_{2.919}\square_{0.081})(O_{1.630}F_{0.180}OH_{0.144}).$$
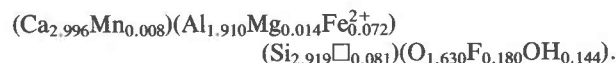
The occupancy of the VIII and VI sites is closer to the expected stoichiometry if the magnesium is shifted to the octahedral site. In either case, 1.5% of the oxygen is replaced by fluorine in the GOV 25-4 garnet.

Table 1. Electron microprobe analysis of fluorine-bearing garnet, GOV 25-4

SiO_2	38.99	38.99	Si	2.919	3.000
			$\square$	0.081	
TiO_2	<0.05	<0.05	Ti	<0.003	
Al_2O_3	21.64	21.64	Al	1.910	1.996
Fe_2O_3**		1.29	Fe^{3+}	0.072	
FeO	1.16	0.00	Fe^{2+}	0.000	
MgO	0.13	0.13	Mg	0.014	
MnO	0.13	0.13	Mn	0.008	3.004
CaO	37.33	37.33	Ca	2.996	
Cl	<0.05	<0.05	Cl	<0.002	
F	0.76	0.76	F	0.180	11.990
H_2O**		0.58	OH	0.144	
Sum*	99.82	100.53	O	11.666	

*Adjusted for $F = 0$

**Calculated from normalized formula (see text).

Analytical totals were consistently low (92–96 wt.%) for the two PL samples, possibly due to the poor polish of these samples. The amount of H_2O required to raise the totals to acceptable levels (>98%) is in excess of that indicated by the deficiency on the tetrahedral site. For instance the analysis of PL 1197 (with anhydrous totals of 95.4 wt.%) yielded the formula:

$(Ca_{2.782}Mn_{0.039}Mg_{0.017}Fe^{2+}_{0.162})$
$(Al_{1.610}Ti_{0.012}Fe^{2+}_{0.052}Fe^{3+}_{0.326})(Si_{2.963}\square_{0.037})(O_{11.812}F_{0.188})$

where the ferrous iron on the octahedral site was calculated as $(Fe^{2+})^{VI} = Ti^{4+} + F - 4\square^{IV}$. By this normalization the vacancy on the tetrahedral site is exceeded by the fluorine and no room is left for $(OH)^{4-}_4$ substitution for SiO^{4-}_4. Alternatively, all $(Fe^{3+})^{VI}$ could be reduced to Fe^{2+} with concomitant replacement of O by OH. This would yield 1.3 wt.% H_2O, raising the analytical total to 96.8 wt.%, still low and requiring that all the iron be ferrous.

Clearly, complete analyses for Fe^{2+}/Fe^{3+} and H_2O are needed to better evaluate the minor element substitutions of these grossulars. It is difficult to infer the substitutional mechanism of the minor species in complex silicates from a microprobe analysis alone.

X-ray diffraction and optics

In order to further evaluate possible substitutions in the garnet structure, the value of the cell edge for GOV 25-4 was refined by X-ray diffraction. Values for twenty-three reflections were measured from a photograph obtained *in vacuo* from a 100 micron-diameter crystal with a 114.6 mm diameter Gandolfi Camera and $CuK\alpha$ radiation, resulting in the lattice parameter $a = 11.858(5)$Å. Using lattice parameters of Meagher (1980) and independently using the equation of Novak and Gibbs (1971), a cell edge of 11.85(1)Å for GOV 25-4 is predicted if F and OH are discounted. Thus, the measured lattice parameter is slightly larger than the predicted value calculated for an anhydrous and fluorine-free formula, but the difference is within the standard errors. Whatever the mechanism of charge compensation, the fluorine is probably replacing oxygen in the garnet structure. Because the radius of F^- is approximately 0.07Å less than that of $O^=$ (Shannon and Prewitt, 1969), such a substitution should result in some decrease in the lattice parameter. However any contraction of the lattice by fluorine substitution may be offset by the expansion due to hydroxyl and loss of silicon (Shoji, 1974).

The refractive index of the garnet GOV 25-4 was measured on a gelatin slide using the same 100 μm sized crystal as was used for X-ray diffraction. Cargille immersion oils were calibrated by refractometer and after small temperature corrections were made, a value of 1.726(3) was obtained. This is 0.014 less than the value of 1.739 predicted from linear combinations of values given by Meagher (1980) for the garnet end-members neglecting F and OH. The reduction is consistent with some substitu-

tion by hydrogrossular ($n = 1.605$, Flint *et al.*, 1941) and by fluorgrossular (index unknown but presumably less than grossular due to loss of heavy elements). We conclude that all observed data are consistent with the presence of limited amounts of both F^- and $(OH)^-$ in GOV 25-4.

Note added in proof:

In a recent volume of *Economic Geology* (77:4, 1982), S. Yun and M. T. Einandi (p. 1013–1032) and D. C. Dobson (p. 1033–1052) have described grossular-andra-dites from skarns with 0.1–0.9 wt.% F_2. While noting in passing that Dobson misnormalized his garnets assuming all iron as ferrous, the analyses require up to 2 mole percent substitution of fluorine for oxygen.

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