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Fluorphlogopite and fluortremolite in Adirondack marbles and calculated C–O–H–F fluid compositions[1]

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Abstract

Fluorphlogopites (up to XF = 0.96) and fluortremolites (up to XF = 0.82) have been found in Grenville marbles near Balmat, New York. In these minerals high fluorine contents correlate inversely with iron solid solution, but do not appear to affect the stable isotope fractionation of hydrogen.

The substitution of fluorine for hydroxyl in micas and amphiboles is partly responsible for stabilizing hydrous minerals in the granulite facies marbles of the Adirondacks. The importance of this effect can be calculated from thermochemical data and a knowledge of F/OH distribution in natural assemblages. Phlogopite concentrates fluorine relative to tremolite. The F/OH distribution coefficient does not vary with metamorphic grade but differs significantly in the most F-rich sample from the other samples. Application of volatilization equilibria in marbles without consideration of possible fluorine substitution can lead to large errors in estimated pressures, temperatures and fluid compositions.

The fugacities of eight C–O–H–F fluid components are restricted by the assemblage fluorphlogopite + calcite + quartz + graphite. At 650°C, 6 kbar, the estimated range in these values is: log $f\mathrm{H_2O}$ = 2.47 to 3.37, log $f\mathrm{CO_2}$ = 4.52 to 4.22, log $f\mathrm{CH_4}$ = 0.25 to 2.35, log $f\mathrm{CO}$ = 2.07 to 1.92, log $f\mathrm{H_2}$ = 0.34 to 1.39, log $f\mathrm{O_2}$ = −18.01 to −18.31, log fHF = −1.27 to −0.37 and log $f\mathrm{F_2}$ = −34.19 to −33.43. H_2O and CO_2 were the dominant fluid components in these graphitic marbles and CH_4 was minor. Calculations of many oxidation–fluoridation equilibria ($f\mathrm{F_2}$ *vs.* $f\mathrm{O_2}$) for common calcsilicate minerals support these values of $f\mathrm{F_2}$ and $f\mathrm{O_2}$. The inferred $f\mathrm{O_2}$ is within 0.5 log unit of the QFM buffer, near that commonly inferred for other Adirondacks marbles. Minimum values of log $f\mathrm{F_2}$ are −35.0 for end-member fluorphlogopite, −34.4 for end-member fluortremolite and −34.1 for norbergite plus fluortremolite in calcite marbles at these P and T. Such values of $f\mathrm{F_2}$ may not be unusual suggesting that fluorphlogopite and fluortremolite could be relatively common rock-forming minerals in iron-poor marbles.

The mineral assemblage fluortremolite + fluorphlogopite + diopside + calcite + quartz + graphite and fluortremolite + calcite + graphite + norbergite restrict ΔG°_{f923} (fluortremolite) to −10,378±11 kjoules relative to available free energy data for the other phases.

Introduction

Fluorine-rich micas and amphiboles may be more common than is generally recognized (Petersen *et al.*, 1982). Vast amounts of chemical data on micas and amphiboles have been produced by electron microprobe, but many have not included fluorine because of the relative difficulty of analysis. Recent advances in crystal spectrometers (curved TAP analyzer crystals, ultra thin detector windows, and

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a high operating vacuum) make fluorine analysis routine by microprobe, although longer counting periods are still required and fluorine is not accessible by most energy dispersive systems.

In this paper we report analyses of fluorphlogopites (up to Fph_{96}) and fluortremolites (up to Ftr_{82}) from siliceous marbles of the Adirondack Mountains, New York. We have calculated the composition of metamorphic fluids that were buffered by assemblages containing these minerals in order to determine whether unusual fluid conditions are required for their stability and formation, or conversely, whether these minerals might actually be relatively common but as yet unrecognized.

Occurrence and associations

The N.W. Adirondack Lowlands of New York were metamorphosed to upper amphibolite facies (Buddington, 1939) during the 1.0 b.y. Grenville Orogeny. Recent estimates yield 6.5±1 kbar and 650±30°C for the peak of metamorphism at Balmat (Brown *et al.*, 1978; Bohlen *et al.*, 1980). Because metamorphic grade varies gradually in the Adirondacks (Bohlen *et al.*, 1980) all samples for this study were collected from within 12 km of Balmat and are believed to have been metamorphosed near these conditions.

The samples for this study are from siliceous marbles which are common in the Adirondack Lowlands (Engel and Engel, 1953). Sample GOV 50-2 is from Hammond Quadrangle, 3.6 km ENE of Somerville on Rt. 11 (12 km W. of Balmat). It consists of fluorphlogopite, tremolite, diopside, calcite, quartz, graphite, scapolite, plagioclase, pyrite, pyrrhotite, chalcopyrite, and fluorapatite. A second generation of tremolite occurs as rims on diopside and minor dolomite is concentrated at calcite grain boundaries. These last two minerals are inferred to be retrograde by Valley and Essene (1980a) for chemical and textural reasons. Sample BMT-1 is from the 900-foot level of the Balmat No. 3 mine (Lower Gleason Orebody). It consists of fluorphlogopite, fluortremolite, calcite and norbergite. Minor graphite, pyrite, fluorapatite and sphalerite are also present as well as minor retrograde dolomite concentrated at calcite grain boundaries.

Chemical analyses

Fluorphlogopite, fluortremolite and norbergite were analyzed for 12 major and minor elements by electron microprobe (Table 1) as described in Petersen *et al.* (1982). Because total iron amounted to less than 0.54 weight percent (calculated as FeO) in all minerals analyzed in this study, the ferric/ferrous ratio was not determined directly, but was inferred from normalization about cations (Valley and Essene, 1980a).

Hydrogen was directly determined in four samples using the extraction lines at the University of Utah light stable isotope laboratory. Between 80 and 300 mg of mineral separate were thermally decomposed *in vacuo* at 1500°C and evolved gases were converted to H_2 by reaction with uranium at 800°C. Contaminants were condensed with a liquid N_2 trap and H_2 was measured manometrically. The purity and stable isotope ratio of the evolved H_2 was measured using a standard gas-ratio mass spectrometer. The calculated values for H_2O agree very well with the measured values (Table 1) except in GOV 50-2 where it was impossible to obtain a pure separate of fluortremolite and the sample contained approximately 10% of anhydrous impurity making the measured H_2O content low, but not affecting the stable isotope ratio.

Fe–F avoidance

The principle of Fe^{2+}–F avoidance, that Fe-rich silicates require higher fF_2 to stabilize a given XF than Mg-rich silicates, has been demonstrated in studies of mineral compositions (Ekström, 1972; Allen, 1976; Zaw and Clark, 1978; Valley and Essene, 1980a), examined by structural analyses (Cameron, 1971; Hazen and Burnham, 1973), and investigated experimentally (Troll and Gilbert, 1972; Munoz and Ludington, 1974). These observations have been accounted for by stronger Mg–F bonds than Fe^{2+}–F bonds (Ramberg, 1952) and more recently by crystal field theory (Rosenberg and Foit, 1977). Our fluorine-rich minerals have little or no iron (Table 1) which may in part account for their high XF. Analyses of other fluorine end-member micas and amphiboles usually show high magnesium, although hastingsites, arfvedsonites and biotites with high iron may also contain high fluorine (Petersen *et al.*, 1982).

Hydrogen isotopes

The δD values of three hydrous silicates from this study vary from −62 to −87 permil (SMOW) (Table 1), consistent with previous analyses of hydrous minerals from the Adirondacks (Valley and O'Neil, 1981). As there can only have been negligible

Table 1. Chemical and isotopic analyses of fluorphlogopite, fluortremolite, and norbergite

	F phlog GOV 50-2	F phlog BMT 1	Trem GOV 50-2	Trem (rim) GOV 50-2	F trem BMT 1	Norb BMT 1
SiO_2	41.68	44.34	57.05	59.12	59.30	29.78
TiO_2	0.68	≤0.05	0.14	≤0.05	≤0.05	0.10
Al_2O_3	12.34	11.47	2.27	0.70	0.26	≤0.05
Fe_2O_3*	0.00	0.00	0.00	0.41	0.00	0.00
FeO*	0.54	0.07	0.46	0.00	≤0.05	≤0.05
MnO	0.09	≤0.05	0.07	0.08	≤0.05	≤0.05
MgO	27.41	27.36	24.16	24.40	24.58	59.75
CaO	≤0.05	0.07	13.48	13.60	12.03	0.17
Na_2O	0.39	0.45	0.95	0.27	2.07	*nd*
K_2O	10.73	10.44	0.43	0.09	0.61	*nd*
BaO	*nd*	1.58	*nd*	*nd*	≤0.05	*nd*
H_2O*	1.80	0.25	1.37	1.51	0.40	0.41
H_2O**	1.89	*nd*	1.09†††	*nd*	0.50	0.36
F	5.06	8.53	1.83	1.54	3.84	17.86
Cl	0.06	0.05	0.03	≤0.02	≤0.02	≤0.02
SUM†	98.64	100.94	101.47	101.07	101.47	101.55
Si	2.973	3.145	7.761	7.932	8.010	1.000
Al	1.027	0.855	0.239	0.068	0.000	0.000
Al	0.011	0.104	0.135	0.043	0.041	≤0.005
Ti	0.036	≤0.005	0.014	≤.005	≤0.005	0.006
Fe^{3+}*	0.000	0.000	0.000	0.041	0.000	0.000
Fe^{2+}*	0.032	0.004	0.051	0.000	≤0.003	≤.003
Mn	0.005	≤0.005	0.008	0.009	≤0.005	≤.005
Mg	2.915	2.891	4.801	4.880	4.948	2.990
Ca	≤.003	0.005	1.965	1.955	1.741	0.006
Na	0.054	0.061	0.255	0.070	0.543	*nd*
K	0.977	0.945	0.076	0.015	0.105	*nd*
Ba	*nd*	0.010	*nd*	*nd*	≤0.005	*nd*
F	1.141	1.914	0.784	0.652	1.638	1.897
OH*	0.859	0.084	1.216	1.348	0.352	0.091
Cl	0.007	0.002	0.008	≤.005	0.005	*nd*
O	*nd*	*nd*	*nd*	*nd*	*nd*	0.012*
F/(F+OH)††	0.57	0.96	0.39	0.33	0.82	0.96
δD (SMOW)	-62‰	*nd*	-67‰	*nd*	-87‰	*nd*

**calculated; **measured; †adjusted for F, Cl, OH, Fe³⁺; ††using calculated values; †††samples included 10% anhydrous impurity; nd-not determined.*

amounts of CH_4, H_2 or HF in equilibrium with these samples (see the following sections and Table 2) H_2O was the dominant H-bearing fluid component and its isotopic ratio is reflected by these analyses. These values provide no clear evidence as to the source of the metamorphic fluids in these few samples, but hydrogen isotopic values may provide a basis for mass-balance calculations of the magnitude and direction of fluid flow.

The five permil difference in δD between coexisting fluortremolite and fluorphlogopite in sample GOV 50-2 (ΔFtr − Fph = −5‰) is consistent with the hydrogen isotope fractionation predicted from OH end-member minerals by Suzuoki and Epstein

Table 2. The range in C–O–H–F fluid fugacities (in bars) buffered by the assemblage fluorphlogopite ($XF = 0.57$) + calcite + quartz + graphite at 650°C, 6.0 kbar (specimen GOV 50-2)

XH_2O	0.07	0.54
log fH_2O	2.47	3.37
log fCO_2	4.52	4.22
log fCH_4	0.25	2.35
log fCO	2.07	1.92
log fH_2	0.34	1.39
log fO_2	-18.01	-18.31
log fHF	- 1.27	- 0.37
log fF_2	-34.19	-33.43
log fSO_2	- 2.33	- 2.63
log fH_2S	1.87	2.92

(1976). This supports their conclusion that hydrogen isotope fractionation is controlled by octahedral cation substitutions, especially Fe. It further suggests that H/D fractionation is independent of XF in these minerals.

Stability of fluorine-rich phlogopite and tremolite

P–T–XCO₂

Reactions that restrict the stabilities of hydroxyphlogopite and tremolite in marbles have been experimentally calibrated (Skippen, 1971; Hoschek, 1973; Hewitt, 1975; Slaughter *et al.*, 1975; Metz, 1976; Kase and Metz, 1977; Metz *et al.*, 1977; and Puhan, 1978). In quartz-saturated calcitic marbles such as are common in the Adirondacks (including GOV 50-2), the upper stabilities of phlogopite and tremolite are controlled by the reactions:

5 phlogopite + 6 calcite + 24 quartz =
3 tremolite + 5 K-feldspar + 2 H_2O + 6 CO_2 (a)

tremolite + 3 calcite + 2 quartz
= 5 diopside + H_2O + 3 CO_2 (b)

In the absence of quartz the upper stability of tremolite is controlled by reaction with carbonate alone:

tremolite + 5 calcite =
2 forsterite + 11 diopside + 3 H_2O + 5 CO_2 (c)

tremolite + 3 calcite =
dolomite + 4 diopside + H_2O + CO_2 (d)

tremolite + 11 dolomite =
8 forsterite + 13 calcite + H_2O + 9 CO_2 (e)

4 tremolite + 5 dolomite =
13 diopside + 6 forsterite + 4 H_2O + 10 CO_2 (f)

In reactions such as (b) through (f) where fluorine substitutes into only one reactant mineral, it extends the stability of that mineral (*i.e.*, tremolite) to higher temperatures. However, in reactions such as (a), where fluorine can substitute into both reactants and products, equilibrium will be shifted to higher or to lower temperatures depending on the partitioning of fluorine between the two minerals. Quantitative estimates of the magnitude of this shift are made by Valley and Essene (1980a) for buffered Adirondack assemblages including GOV 50-2.

For very fluorine-rich minerals such calculations are presently hampered by the lack of calibrated activity *versus* composition data. Valley and Essene (1980a) estimated activities by an ideal ionic model, noting the possible uncertainties:

$$a_{\text{Trem}} = (XCa^{M4})^2 \cdot (XMg^{M1,2,3})^5 \cdot (XOH)^2$$

$$a_{\text{Phlog}} = (XK) \cdot (XMg)^3 \cdot (XOH)^2$$

Using these estimated activities, the direction and importance of the shift in hydrous-mineral stability due to fluorine substitution can be approximated from a general knowledge of the fluorine distribution between reactants and products. A more accurate calculation of this effect will be possible once *a–X* relations are experimentally calibrated for these minerals.

The distribution of F/OH has been studied in natural amphibole-mica assemblages (Godfrey, 1962; Carmichael, 1970; Ekström, 1972; Berg, 1975; Parry and Jacobs, 1975; Allen, 1976; Rice, 1980; Valley and Essene, 1980a; Kearns *et al.*, 1980) and in experimental products (Munoz and Eugster, 1969; Munoz and Ludington, 1974, 1977; Ludington and Munoz, 1975; Westrich, 1977, 1978; Duffy and Greenwood, 1979). For twelve tremolite–phlogopite assemblages from Grenville marbles (Berg, 1975; Allen, 1976; Valley and Essene, 1980a) it is found that $K_{D_{Tr/Ph}}^{F/OH} = 0.39$ to 0.68 (mean = 0.53) (Figure 1).

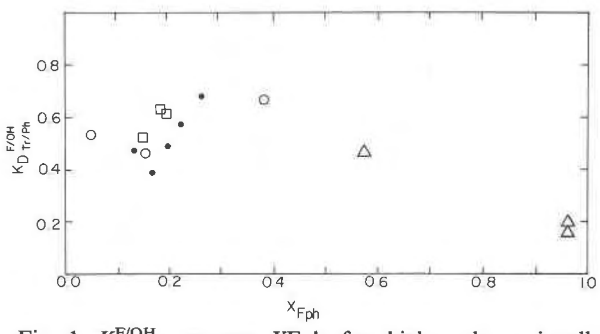

Fig. 1. $K_{DTr/PH}^{F/OH}$ *versus* $XFph$ for high-grade regionally metamorphosed minerals from Grenville marbles. Data are taken from △ this study, □ Valley and Essene (1980a), ● Allen (1976), and ○ Berg (1975).

This is slightly lower than the more variable results of Ekström (1972) who found $K_D = 0.30$–1.20 (mean $= 0.67$) for 40 Ca-amphiboles and biotites.

Ekström showed that the distribution coefficient, $K^{F/OH}_{D_{Am/Bi}} = (XF/XOH)_{Amph}/(XF/XOH)_{Biot}$, correlated positively with metamorphic grade. However, it appears that cation substitutions are a more important controlling factor on K_D than temperature. Rice (1980) showed such a compositional effect on 16 Ca amphibole–phlogopite assemblages where the distribution coefficient correlates strongly with Al^{IV} substitution in amphiboles. This effect may not actually be controlled by tetrahedral cations, but rather it may be the result of the coupled octahedral substitutions that are required to charge balance Al^{IV}. In both mica and amphibole the hydroxyl site is bonded directly to octahedral sites making such an effect plausible.

The likelihood of a compositional effect on the F/OH distribution coefficient makes the near end-member, Grenville tremolite–phlogopite assemblages more significant as they show very little solid solution other than fluorine for hydroxyl. In these assemblages no correlation of K_D is found with metamorphic grade which is estimated to vary from 4 kbar, 475°C in the Southern Hastings–Haliburton Basin to 8 kbar, 750°C in the Central Adirondacks (Allen, 1976; Valley and Essene, 1980b).

The K_D determined for BMT-1 is significantly lower than that for less fluorine-rich assemblages. This is shown in Figure 1 where K_D is plotted against XF in phlogopite for Grenville mineral pairs with less than 0.5 Al^{VI} per 8 Si^{IV} in tremolite (the possible effect on K_D due to this amount of Al^{VI} variation is inferred to be less than ± 0.05). The Grenville K_D's range from 0.39 to 0.67 except for BMT-1 which is 0.16 (from the measured OH value for fluortremolite) or .20 (using the OH value inferred by probe analysis). No direct measurement of the OH content in fluorphlogopite in BMT-1 could be made because of the small grain size and the scarcity of crystals which made separation of the necessary 200–400 mg of sample difficult.

Rice (1980) reports K_D's for six tremolite–phlogopite pairs with Al^{IV} less than 0.5 from the Marysville aureole. These K_D's range from 0.45 to 0.50 for phlogopites with 0.5 to 1.5 wt.% F (Rice's K_D's are inverted to correspond to those used here). These contact metamorphic values fall within the zone of Grenville K_D's in Figure 1 further supporting the premise that mineral chemistry and not metamorphic grade is the dominant control of F/OH partitioning.

Assemblages of phlogopite + calcite + quartz and tremolite + calcite + quartz are common in the amphibolite and granulite facies terranes of the Adirondacks (Valley and Essene, 1980a) and the Hudson Highlands (Kearns *et al.*, 1980). Independent geothermometry in both areas indicates that hydroxyl phlogopite and tremolite should be unstable in these assemblages relative to the high-temperature assemblages in reactions (a) and (b). Both sets of authors attribute this to fluorine substitution, but there is significant disagreement as to the magnitude of this effect. Valley and Essene's calculated shifts for analyzed buffering assemblages are all less than +30°C for reaction (b) ($XF_{Amph} \leq 0.44$), but Kearns *et al.*, (p. 562) propose shifts of "about 100°C" for amphiboles of similar composition even though, as they point out, this is greatly in excess of calculated results of Moore and Kerrick (1976). Kearns *et al.* base their arguments on geothermometry that yields 836°C for their rocks. In fact, our calculation of reaction (b) using the computer program EQUILI (Valley and Essene, 1980a) and experimental data (Skippen, 1971; Slaughter *et al.*, 1975) produces an even larger discrepancy yielding a value for the upper stability of tremolite ($XF = 0$) + calcite + quartz at 685°C, 8 kbar, over 150°C below Kearns *et al.*'s postulated metamorphic temperature of 836°C. Much of this discrepancy may be due to errors in geothermometry. Kearns *et al.* (1980) report temperatures from calcite-dolomite solvus geothermometry using bulk chemical analysis of calcite (Kearns, 1977). The analysis may have been affected by primary dolomite with calcite resulting in erroneously high temperatures. Thus we believe that field evidence favors a more moderate influence of fluorine, extending the stabilities of hydrous phases in accord with our calculations.

C–O–H–F fluid compositions

The presence of graphite in GOV 50-2 allows fluid buffering equilibria to be calculated defining the fugacities of the fluid components in the system C–O–H. Four independent reactions can be written relating the six most significant fluid components:

$$C + O_2 = CO_2 \qquad (g)$$

$$CO + 0.5\ O_2 = CO_2 \qquad (h)$$

$$H_2 + 0.5\ O_2 = H_2O \qquad (i)$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O \qquad (j)$$

At fixed pressure and temperature the equilibrium constants for these reactions can be calculated from knowledge of the Gibbs energies of each fluid (Robie *et al.*, 1979) thus defining the fugacity ratios of the fluid components. Simultaneous solution of the four reactions (g–j) in six unknowns yields a divariant system (French, 1966; Ohmoto and Kerrick, 1977). This system becomes univariant if it is additionally assumed that:

$$P_{Total} = P_{H_2O} + P_{CO_2} + P_{CH_4} + P_{CO} + P_{H_2} + P_{O_2} \quad (k)$$

and fugacity coefficients can be estimated for each fluid. The stability of the assemblage phlogopite + calcite + quartz + tremolite + K-feldspar removes the last degree of freedom through reaction (a) making the graphite-bearing assemblage invariant.

Sample GOV 50-2 does not contain K-feldspar, but the product $(fH_2O)(fCO_2)^3$ is still tightly restricted at 650°C and 6 kbar. When the effect of mineral solid solutions in GOV 50-2 are modelled for reaction (a), equilibrium is shifted to higher temperature slightly relaxing these restrictions on fCO_2 and fH_2O, but even when a large upwards shift of +40°C is assumed, the ratio $(H_2O)/(H_2O + CO_2)$ must still lie between 0.54 and 0.07. These limits are calculated from the experimental reversal of Hoschek (1973) at 6 kbar 620°, $XH_2O = 0.44$, $XCO_2 = 0.56$ in the presence of a binary H_2O–CO_2 fluid. The use of an experimental reversal at intermediate XH_2O minimizes any possible error due to non-ideal mixing of H_2O and CO_2. Thus, if hydrostatic pressures are 6 kbar, if a shift in equilibria of +40°C is assumed and if no restriction is placed on the presence of additional C–O–H fluid components, then these experiments yield:

$$\log ((fH_2O)^2(fCO_2)^6) = 32.07 \quad (1)$$

at 650°C, 6 kbar. The equality sign becomes "greater than" for the assemblage in GOV 50-2. If a smaller shift in equilibria is assumed or if calculations are based on the experiments of Hewitt (1975), then XH_2O is even more tightly constrained.

At 650°C, 6 kbar reactions (g) through (k) yield:

$$6000 = P_{H_2O} + P_{CO_2} + P_{CH_4} + P_{CO} + P_{H_2} + P_{O_2} \quad (m)$$

$$\log \frac{fCO_2}{fO_2} = 22.53 \quad (n)$$

$$\log \frac{fCO_2}{fCO(fO_2)^{1/2}} = 11.45 \quad (o)$$

$$\log \frac{fH_2O}{fH_2(fO_2)^{1/2}} = 11.13 \quad (p)$$

$$\log \frac{fCO_2(fH_2O)^2}{fCH_4(fO_2)^2} = 45.29 \quad (q)$$

Fugacity coefficients used in our calculations are: $\gamma_{H_2O} = 0.760$ (Burnham *et al.*, 1969), $\gamma_{CO_2} = 5.89$ (Ryzhenko and Volkov, 1971; Wall and Burnham, unpublished) and $\gamma_{CH_4} = 8.66$ (Ryzhenko and Volkov, 1971) relative to a 1 bar, T standard state. Although fugacity coefficients for CO, H_2 and O_2 are estimated by Ryzhenko and Volkov (1971) we have simplified this calculation by assuming ideality ($\gamma = 1$) for these components in reaction (m). The results of these calculations show low $P(CO)$, $P(H_2)$ and $P(O_2)$ justifying this simplification. It will be shown that other fluid components such as HF and H_2S, not in the C–O–H system, diluted the metamorphic fluids in these rocks, but that their partial pressures were insignificant (even if $\gamma \ll 1$) relative to 6000 bars in equation (m) and thus they may be safely disregarded in this calculation. The ΔG°_{923} (formation) for H_2O, CO_2, CH_4 and CO are from Robie *et al.* (1979) and compressibility of graphite is from Birch (1966). The equilibrium constants thus calculated for equations (n) through (q) are in excellent agreement with those of Ohmoto and Kerrick (1977). The simultaneous solution of equations (1) through (q) yields two values for each gas fugacity, when an inequality is substituted in equation (1). These values define the permissible ranges in fugacity (Table 2, Figs. 2 and 3) for the metamorphic fluid buffered by GOV 50-2.

Although the limits on XH_2O set by reaction (a) and GOV 50-2 are broad, they allow a range in fluid fugacities to be calculated that is quite restrictive when expressed in log units (Table 2). The log of oxygen fugacity ranges only from −18.01 to −18.31, at or slightly below, the quartz–magnetite–fayalite buffer, similar to values of fO_2 estimated by Bohlen and Essene (1977) for Adirondack orthogneisses from coexisting magnetite + ilmenite.

It is significant that in this fO_2 range, H_2O and CO_2 are the only major fluid components. Although the log fCH_4 ranges from 0.25 to 2.35 this corresponds to a maximum partial pressure of methane of 26 bars due to its large non-ideality ($\gamma = 8.66$). Thus, methane that might be expected to be dominant in a graphite-bearing rock accounts for less than 0.5 percent of the fluid phase. Similar estimates are derived from other phlogopite + calcite +

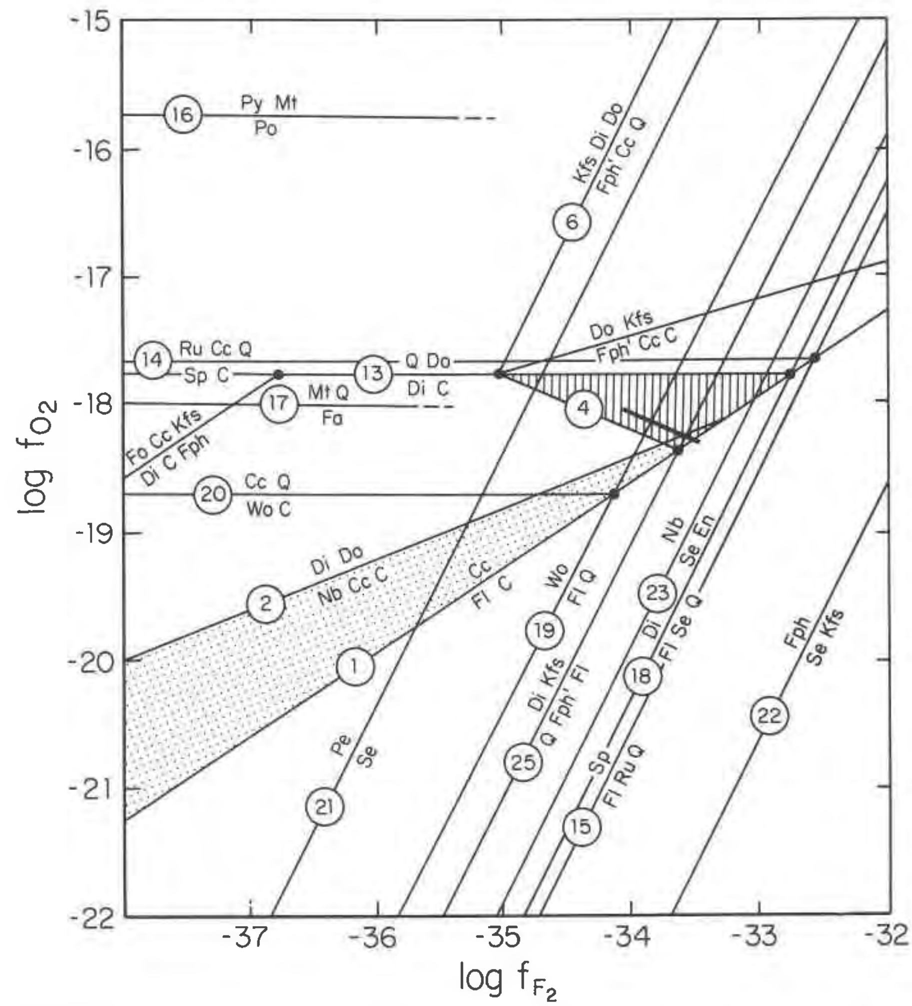

Fig. 2. $fO_2 - fF_2$ diagram for selected silicate–oxide–fluoride reactions at 650°C and 6 kbar. Mineral abbreviations, free energy and volume data are given in Table 4. The abbreviation Fph′ indicates a reduced activity of Fph with $XF = 0.57$. Numbers next to mineral abbreviations refer to reactions in Table 3. The heavy bar is the range of C–O–H–F fluid compositions shown in Table 2. The striped area is the stability field of the GOV 50-2 assemblage and the heavy stipple is the stability field of the BMT-1 assemblage.

quartz + graphite assemblages (Valley and Essene, 1980a) in both the amphibolite and granulite facies of the Adirondacks. The common assumption that in marbles P (lithostatic) = P (H_2O) + P (CO_2) is supported as approximately correct for these assemblages, but this assumption should still always be evaluated in graphitic samples.

The fugacity of HF and F_2 can also be estimated for sample GOV 50-2 (Table 2). Fluorine-hydroxyl exchange experiments (Munoz and Ludington, 1974; Luddington and Munoz, 1975) allow the ratio fH_2O/fHF to be fixed at a given P, T through the exchange reaction:

$$.5 \text{ hydroxyphlogopite} + \text{HF} = 0.5 \text{ fluorphlogopite} + H_2O \qquad \text{(r)}$$

if the activity of each phlogopite component is well approximated by the mole fraction. Values of fF_2 can then be calculated through the reaction:

$$2\,\text{HF} = H_2 + F_2 \qquad \text{(s)}$$

using ΔG_f°(HF) data (Stull and Prophet, 1971) and the calculated values of fH_2O and fH_2 (Table 2).

Pyrite and pyrrhotite in GOV 50-2 fix fS_2 at $10^{-2.06}$ bars (Table 4) and permit the calculation of fSO_2 and fH_2S through the relations

$$0.5\,S_2 + O_2 = SO_2 \quad \log \frac{fSO_2}{fO_2(fS_2)^{1/2}} = 16.71 \qquad \text{(t)}$$

$$0.5\,S_2 + H_2 = 0.5\,H_2S \quad \log \frac{(fH_2S)^{1/2}}{fH_2(fS_2)^{1/2}} = 2.57 \qquad \text{(u)}$$

giving the results shown in Table 2.

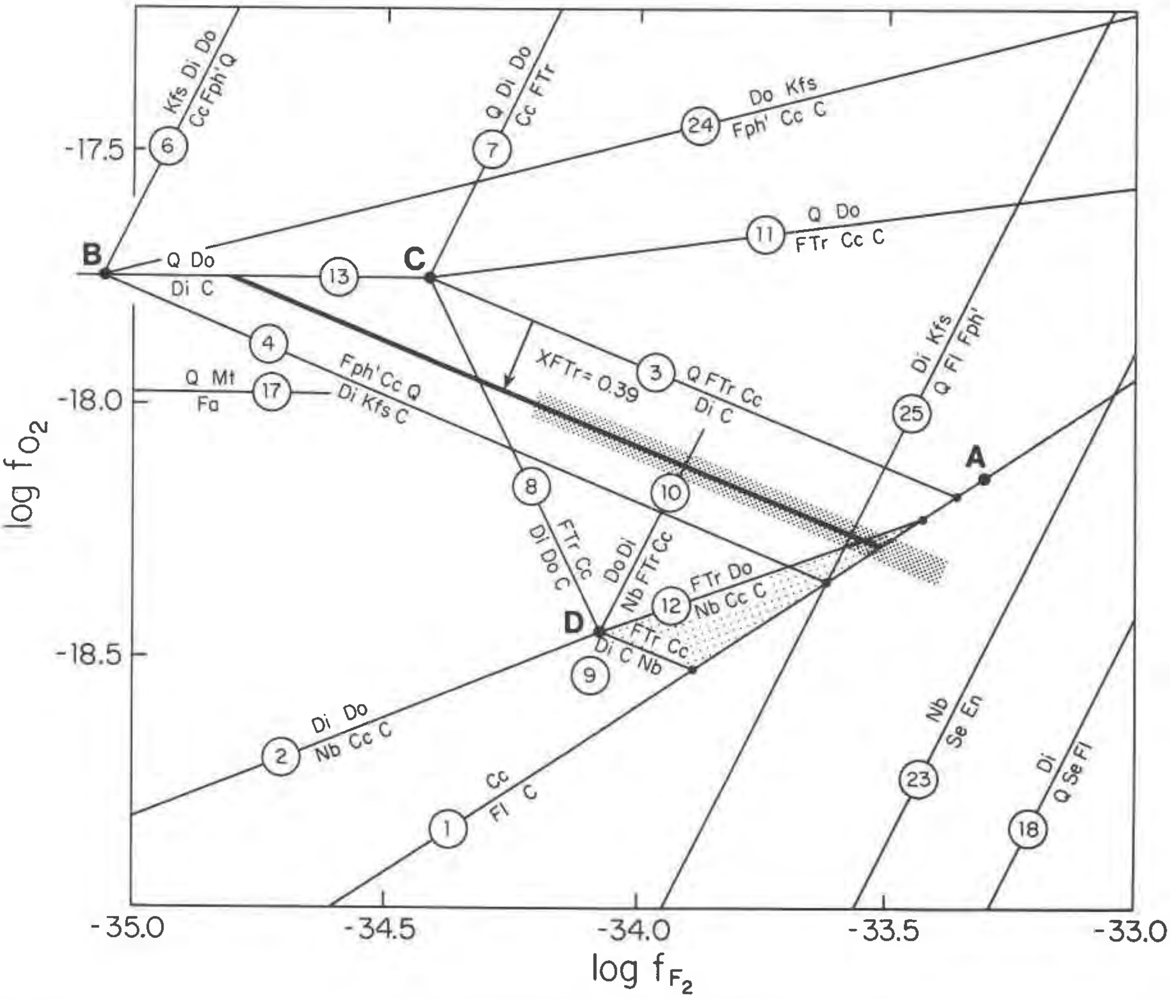

Fig. 3. $fO_2 - fF_2$ diagram, enlargement of a portion of Figure 2, showing fluortremolite-bearing reactions. Reactions 14, 15, 19 are omitted from the diagram for clarity. The stippled bar is the range of C–O–H–F fluid compositions shown in Table 2 and the open stipple is the stability field of BMT-1 assemblage.

fO_2 *versus* fF_2

An alternate, independent check on the values of fO_2 and fF_2 of Table 2 is provided by the calculation of fluoridation-oxidation equilibria involving calcsilicate minerals. Important reactions and those involving the minerals in this study are listed in Table 3, and the relevant thermodynamic data are given in Table 4. The position of these reactions in $fO_2 - fF_2$ space (Figures 2 and 3) are calculated from the relation:

$$\Delta G_T^P = \Delta G_T^\circ + \Delta V_s \Delta P + RT \ln K$$

where ΔG is the Gibbs free energy and ΔV_s is volume change of reaction (for solid phases only) and K is the equilibrium constant. The assumption $V_{298}^\circ = V_{923}^{6000}$ has negligible effect on the placement of equilibria. Uncertainties quoted by Robie *et al.* (1979) for ΔG (formation) generally correspond to uncertainties in equilibria of less than one-half log unit.

The heavy line in Figure 2 and stippled band in Figure 3 outline the range in the fO_2 and fF_2 given in Table 2 for GOV 50-2. To avoid crowding, all the fluorphlogopite (Fph′) reactions are for reduced activities (XF = 0.57, GOV 50-2). The range of values predicted by fluoridation-oxidation equilibria are consistent (Figure 2) with the values given by fluid composition calculations. In the absence of fluortremolite only upper limits of fO_2 and fF_2 can be fixed for the norbergite bearing assemblage (BMT-1) (Figure 2). The range of values permitted lies within the wedge (stippled field) bounded by the calcite fluoridation reaction (1) and the dolomite + diopside fluoridation reaction (2).

Table 3. Fluoridation-oxidation reactions

(1)	Fl + C + 1.5 O_2 = Cc + F_2
(2)	2 Nb + 6 Cc + 4 C + 5 O_2 = Di + 5 Do + 2 F_2
(3)	Ftr + 3 Cc + 2 Q = 5 Di + 3 C + 2.5 O_2 + F_2
(4)	3 Di + 3 C + Kfs + 2.5 O_2 + F_2 = Fph + 3 Cc + 6 Q
(5)	Po + 0.5 S_2 = Py
(6)	6 Q + 2 Fph + 6 Cc + O_2 = 3 Di + 3 Do + 2 Kfs + 2 F_2
(7)	2 Ftr + 6 Cc + O_2 = 2 Q + 7 Di + 3 Do + 2 F_2
(8)	4 Di + C + Do + 0.5 O_2 + F_2 = Ftr + 3 Cc
(9)	19 Di + 9 C + 2 Nb + 7.5 O_2 + 3 F_2 = 5 Ftr + 9 Cc
(10)	2 Nb + 4 Ftr + 18 Cc + 3 O_2 = 17 Di + 9 Do + 6 F_2
(11)	Ftr + 3 Cc + 7 C + 7.5 O_2 = 8 Q + 5 Do + F_2
(12)	8 Nb + 21 Cc + 17 C + 20.5 O_2 = Ftr + 19 Do + 7 F_2
(13)	Di + 2 C + 2 O_2 = 2 Q + Do
(14)	Sp + C + O_2 = Ru + Cc + Q
(15)	Fl + Ru + Q + 0.5 O_2 = Sp + F_2
(16)	3 Py + Mt = 6 Po + 2 O_2
(17)	3 Fa + O_2 = 3 Q + 2 Mt
(18)	2 Q + Fl + Se + O_2 = Di + 2 F_2
(19)	Q + Fl + 0.5 O_2 = Wo + F_2
(20)	Wo + C + O_2 = Q + Cc
(21)	Se + 0.5 O_2 = Pe + F_2
(22)	Kfs + 3 Se + O_2 = Fph + 2 F_2
(23)	En + 2 Se + 0.5 O_2 = Nb + F_2
(24)	Fph + 3 Cc + 3 C + 3.5 O_2 = Kfs + 3 Do + F_2
(25)	6 Q + Fph + 3 Fl + 2 O_2 = 3 Di + Kfs + 4 F_2
(26)	Di + C + Fph + 1.5 O_2 = 2 Fo + Cc + Kfs + F_2

A much more restricted range for fO_2 and fF_2 may be defined for the norbergite assemblage using fluortremolite-bearing reactions. Although the free energy of fluortremolite is not well known, it can be estimated from the mineral assemblage in our rocks. In Figure 3 it can be seen that reaction (3),

$$\text{fluortremolite} + 3\ \text{calcite} + 2\ \text{quartz} = 5\ \text{diopside} + 3\ \text{graphite} + 2.5\ O_2 + F_2 \qquad (3)$$

(for GOV 50-2) lies on the high fO_2-high fF_2 side of reaction (4),

$$\text{fluorphlogopite} + 3\ \text{calcite} + 6\ \text{quartz} = 3\ \text{diopside} + \text{K-feldspar} + 3\ \text{graphite} + 2.5\ O_2 + F_2 \qquad (4)$$

and within the shaded band when corrected for OH substitution. For a given value of fO_2 and fF_2 within this band, a free energy for fluortremolite may be calculated. The value for ΔG°_{923} (fluortremolite) is −10,382 kjoules. Using this value we have calculated the position of other fluortremolite-bearing reactions (Figure 3). These reactions further restrict the range in values of fF_2 and fO_2 for both GOV 50-2 and BMT-1, and permit one to determine the minimum and maximum values of ΔG°_{T} (fluortremolite) which would still yield a phase diagram consistent with observed mineral assemblages.

The minimum value of the free energy of fluortremolite consistent with oxidation-fluoridation equilibria in sample GOV 50-2 is obtained when reactions (3) and (4) coincide after correction for OH substitution. This value is −10,387 kjoules which is only 5 kjoules lower than the value derived above using fluid composition calculations and slightly expands the limits of fF_2 and fO_2 for both rock assemblages. A maximum possible value for the free energy can be calculated on the basis of the assemblage in BMT-1. For the maximum value of −10,366 kjoules the range in fF_2 and fO_2 defined by the mineral assemblage (stippled area in Figure 3) in BMT-1 becomes vanishingly small and shifts to point A (Figure 3). The range defined by the mineral assemblage in GOV 50-2 contracts considerably and is shifted slightly towards higher fF_2 values; *i.e.*, a band whose endpoints are −17.75, −33.89 and −18.07, −33.21 (log fO_2, log fF_2).

The free energy of the fluortremolite determined here is lower than the free energy of hydroxytremolite. This is consistent with the observation in other micas, amphiboles, and apatites that the F end-

Table 4. Thermodynamic data for the calculation of Figures 2 and 3

Mineral	Symbol	Formula	$-\Delta G^{\circ}_{923}$ Kjoules	Reference	ΔV°_{298} joules/bar	Reference
calcite	Cc	$CaCO_3$	969.4	1	3.6934	1
chondrodite	Ch	$MgF_2 \cdot 2Mg_2SiO_4$	4,588.4	2	10.732	2
diopside	Di	$CaMgSi_2O_6$	2,667.4	3, 4	6.609	1
dolomite	Do	$CaMg(CO_3)_2$	1,827.8	1	6.434	1
enstatite	En	$MgSiO_3$	1,279.3	5, 1	3.147	1
fayalite	Fa	Fe_2SiO_4	1,175.5	1	4.6390	1
fluorite	Fl	CaF_2	1,072.8	1	2.4542	1
f-phlogopite	Fph	$KMg_3AlSi_3O_{10}(F)_2$	5,340.2	1	14.637	1
f-tremolite	Ftr	$Ca_2Mg_5Si_8O_{22}(F)_2$	10,382.4	5	27.048	6
forsterite	Fo	Mg_2SiO_4	1,801.8	7, 1	4.379	1
graphite	C	C	0	1	0.5298	1
lime	Lm	CaO	538.9	1	1.6764	1
magnetite	Mt	Fe_3O_4	812.2	1	4.4524	1
norbergite	Nb	$MgF_2 \cdot Mg_2SiO_4$	2,776.5	2	6.3466	2
periclase	Pe	MgO	501.8	1	1.1248	1
pyrite	Py	FeS_2	116.4	1	2.3940	1
pyrrhotite	Po	FeS	101.7	1	1.8200	1
quartz	Q	SiO_2	743.5	1	2.2688	1
rutile	Ru	TiO_2	775.5	1	1.8820	1
sanidine	Kfs	$KAlSi_3O_8$	3,265.0	1	10.872	1
sellaite	Se	MgF_2	963.5	1	1.961	1
sphene	Sp	$CaTiSiO_5$	2,167.6	1	5.5650	1
tremolite	Tr	$Ca_2Mg_5Si_8O_{22}(OH)_2$	10,114.7	1	27.292	1
wollastonite	Wo	$CaSiO_3$	1,373.6	8, 1	3.993	1

1 *Robie et al. (1979)*
2 *Duffy and Greenwood (1979)*
3 *Navrotsky and Coons (1976)*
4 *Charlu et al. (1978)*
5 *Krupka et al. (1979)*
6 *This paper*
7 *Comeforo and Kohn (1954)*
8 *Robie, unpbd. (1980)*
9 *Krupka et al. (1980)*

member of a OH–F solid solution series also has a lower free energy (relative to the elements).

Our determination of the Gibbs free energy for fluortremolite is 31 kjoules lower than that given by Westrich (in press). If the error bars on Westrich's values (±25 kjoules) and our error bars (−10,378±11 kjoules) are included in the comparison there is actually a small range of overlap for the likely value of fluortremolite. Reasonable errors in activity coefficients could perhaps explain a difference of up to ten kjoules/mole. Because HF is a minor gas component, errors in its activity coefficient will not affect the properties of the other gas species nor the inferred fO_2 and fF_2. Substantial disequilibrium in these rocks is not likely to be the cause for reasons already stated and because the incompatibilities required are apparently even more profound than such well known examples as quartz-corundum or quartz-forsterite. Westrich (1978) does not discuss his heat of solution measurements for fluortremolite and we are unable to further evaluate his errors. We have used our calculated value for ΔG°_f(Ftr) in our calculations for the phase diagram given in Figure 3 because it generates topologies that are in better agreement with the observed assemblages in these rocks and with other assemblages common in marbles (Valley and Essene, 1980a).

Many common assemblages restrict fO_2 and fF_2 to within one log unit of the tightly constrained values calculated here for GOV 50-2 and BMT-1 (Figures 2, 3). Calcite + quartz ± graphite is an ubiquitous Adirondack assemblage and although more than 30 granulite or amphibolite facies wollastonite occurrences have been examined (Valley and Essene, 1977), wollastonite has never been found with graphite. This limits fO_2 to above reaction (20) at $\log fO_2 = -18.7$ in Figure 2. In the wollastonite + calcite + quartz assemblages low fF_2 is also indicated by reaction (19) in Figure 2. Sphene and diopside are likewise very common in Adirondack marbles. Either mineral in a graphitic calcite marble is restricted by reactions (15), (18), (14), (13), and the fluoridation of calcite, reaction (1). Pyrrhotite with or without pyrite is also common in Adirondack marbles, but magnetite is only found in calc-silicate skarns at meta-igneous contacts. At the value of fS_2 buffered by pyrite + pyrrhotite, magnetite can only be stable at higher fO_2 than is calculated here (reaction 16). Thus magnetite is generally not stable with pyrite because fO_2 is too low.

The close agreement between fluid compositions calculated in two independent ways (C–O–H–F fluid equilibria and fluoridation-oxidation equilibria) supports results of each calculation and indicates that the assumptions made here are reasonable and that the calculated value for the free energy of fluortremolite is consistent with natural mineral assemblages.

Discussion

The reactions in Figure 3 place minimum values on fF_2 in many marbles. The presence of end-member fluorphlogopite in siliceous marbles requires fF_2 values greater than $10^{-35.0}$ bars at 6 kbar, 650°C (invariant point B). End-member fluortremolite in calcitic marbles requires that fF_2 be greater than $10^{-34.4}$ bars (invariant point C). Norbergite in fluortremolite-bearing calcite marbles require fF_2 values greater than $10^{-34.1}$ bars (invariant point D). To the extent that the activities of fluorine end-member minerals can be modeled in tremolite, phlogopite and norbergite, the occurrence of these common minerals in calcite marbles permit minimum fluorine fugacities to be quantified. At present there are too few analyses for fluorine of hydrous minerals from iron-poor metasediments to determine if the values of fF_2 in our rocks are anomalous or not. If not then fluorphlogopite and fluortremolite should be relatively common rock-forming minerals in many marbles.

The fO_2 defined by the mineral assemblage in GOV 50-2 is essentially identical to that defined by the mineral assemblage in BMT-1 (Figure 3) and both are at or just below the QFM buffer. The presence of commonly occurring graphite in fluortremolite + calcite assemblages restricts fO_2 values (by reactions (1), (8), (9), and (11)) to within 0.5 log units of QFM. The assemblage norbergite + fluortremolite + graphite in calcitic marbles restricts fO_2 to slightly below QFM (Figure 3; stippled area) similar to values of fO_2 found in Adirondack orthogneisses (Bohlen and Essene, 1977).

The availability of fluorine in marine sediments is ample to account for the compositions of the minerals analyzed in this study without necessarily requiring large-scale metasomatism. Limestones typically average 200 ppm F and may contain up to 1200 ppm, shales average 900 ppm F and phosphatic sandstones can contain 28,600 ppm F (Allmann and Kortnig, 1972). Most Adirondack marbles are actually metamorphosed marls with several percent of apatite and thus a pre-metamorphic composition of 1000 ppm F would seem normal. This would correspond to a rock with 1% fluorphlogopite (XF = 1.0) if no metamorphic concentration occurred. However, rocks with much higher concentrations of fluorine may also be accounted for by localized small-scale movements of metamorphic fluids containing HF.

The most fluorine-rich calc-silicate rock that we know of in the Adirondacks contains up to 5 wt.% F, but still a mass balance calculation of F is consistent with concentration by small scale fluid movements. The rock forms a 1 m thick zone at the contact of the marble xenolith at Cascade Slide with surrounding anorthosite and is comprised of up to 50% cuspidine ($Ca_4Si_2O_7F_2$) with 10.1 wt.% F coexisting with akermanite, monticellite, wollastonite, diopside and garnet (Valley and Essene, 1980b). No other F-bearing minerals of any quantitative importance occur in the 30 × 200 m xenolith. The average content of the body is well below 1000 ppm if outcrop areas are in any way indicative of actual rock volumes. We do not favor this model to account for *all* fluorine-bearing minerals in the Adirondacks, but we wish to stress that the presence of the fluorine-rich minerals described here does not necessarily suggest that massive amounts of fluids have pervasively migrated through the terrane.

The calcite breakdown reaction in Figure 2 shows that the value of fF_2 could not have been higher than $10^{-33.1}$ in a carbonate-bearing rock at 6 kbar, 650°C, and QFM. The values of fF_2 calculated by Bohlen and Essene (1978) that are several orders of magnitude higher than this are for fluorite-bearing orthogneisses in the Adirondacks and thus could not be sustained in a calcite marble. The presence of such high fF_2 locally in Adirondack orthogneisses and the absence of fluorite-rich calc-silicate skarn replacing marble demonstrates complex fluid heterogeneities during amphibolite and granulite facies metamorphism. This argues against massive, pervasive fluid migration during metamorphism as large amounts of HF-bearing fluid movement across lithologic boundaries would tend to erase heterogeneities.

Note added in proof:

Imeokparia (1981, Chemical Geology, 32, 247–254) has reported partial analyses for F and Sn in biotites from tin-bearing granites including 10 biotites with $0.5 < XF \leq 0.98$. Although lack of complete analyses preclude proper ZAF corrections, these data indicate high fluorine concentrations in iron-rich micas and suggest fF_2 values higher than those calculated for Adirondack marbles. This further supports the petrologic importance of fluorine solid solutions.

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