

The significance of metamorphic fluorite in the Adirondacks*

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(Received 20 January 1978; accepted in revised form 5 July 1978)

Abstract—Thermodynamic calculations for selected silicate-oxide-fluorite assemblages indicate that several commonly occurring fluorite-bearing assemblages are restricted to relatively narrow f_{O_2} - f_{F_2} fields at constant P - T . The presence of fayalite-ferrohedenbergite-fluorite-quartz \pm magnetite and ferrosalite-fluorite-quartz-magnetite assemblages in orthogneisses from Au Sable Forks, Wanakena and Lake Pleasant, New York, buffered fluorine and oxygen fugacities during the granulite facies metamorphism in the Adirondack Highlands. These buffering assemblages restrict f_{F_2} to $10^{-29 \pm 1}$ bar and f_{O_2} to $10^{-16 \pm 1}$ bar at the estimated metamorphic temperature of 1000 K and pressure of 7 kbar. The assemblage biotite-magnetite-ilmenite-K-feldspar, found in the same Au Sable Forks outcrop as the fayalite-fluorite-ferrohedenbergite-quartz-magnetite assemblage, restricts H_2O fugacities to less than $10^{3.3}$ bar. These fugacities limit H_2 and HF fugacities to less than 10^1 bar for the Au Sable outcrop. The data indicate that relative to H_2O , O_2 , H_2 , F_2 and HF are not major species in the fluid equilibrated with Adirondack orthogneisses. The calculated F_2 fugacities are similar to the upper limits possible for plagioclase-bearing rocks and probably represent the upper f_{F_2} limit for metamorphism in the Adirondacks and in other granulite facies terranes.

INTRODUCTION

OF THE three most common fluoride minerals known in terrestrial igneous and metamorphic rocks [fluorite (CaF_2), villiaumite (NaF) and cryolite (Na_3AlF_6)], fluorite is the most abundant (STORMER and CARMICHAEL, 1970). Fluorite is a typical accessory phase in hypersolvus granites, fayalite granites, syenites and nepheline syenites. It is also a common mineral in skarns and hydrothermal veins. Villiaumite and cryolite are best known as rare accessory phases in quartz-saturated and undersaturated rocks, although cryolite occurs in minable quantities at Ivigtut, Greenland. Because of the rarity of these sodium fluorides, one must turn to fluorite reactions and hence reactions involving Ca-silicates in order to evaluate f_{F_2} and f_{HF} in many igneous and metamorphic rocks.

Despite the frequent occurrence of fluorite as an accessory phase, there are little experimental data on fluorite stability or the relative stability of other fluoride minerals. STORMER and CARMICHAEL (1970) calculated the relative stabilities of villiaumite, cryolite and fluorite coexisting with acmite-plagioclase-magnetite \pm nepheline \pm quartz as a function of f_{O_2} - f_{F_2} - T . MUNOZ and EUGSTER (1969) investigated three fluorine-oxygen buffering reactions involving wollastonite-fluorite-quartz, anorthite-fluorite-sillimanite-quartz and calcite-fluorite-graphite. Using these buffers Munoz and Eugster established experimentally that phlogopites efficiently scavenge fluorine from the fluid phase. They concluded that the pres-

ence of HF in the fluid phase can profoundly affect mica compositions even though HF concentration in equilibrium with the three buffers studied is extremely low.

The MUNOZ-EUGSTER (1969) and the STORMER-CARMICHAEL (1970) studies estimate fluorite stabilities in a few assemblages. However, the stability of fluorite in equilibrium with iron-rich ortho- and clinopyroxenes, fayalite, quartz and iron oxides has not yet been carefully evaluated. Reactions among the minerals in these fluorite-bearing assemblages buffer f_{O_2} and f_{F_2} , and the presence of these assemblages in Adirondack metamorphics allow a calculation of f_{O_2} - f_{F_2} fugacities in a few orthogneisses. These data coupled with estimates of f_{H_2O} allow restriction of values for f_{H_2} and f_{HF} . We have considered F_2 and O_2 as variables rather than HF and H_2O because f_{F_2} and f_{O_2} directly control the reactions of interest; this eliminates the need for accurate knowledge of f_{H_2O} and f_{H_2} in calculations of mineral stabilities using f_{HF} and f_{H_2O} as variables. Use of f_{F_2} and f_{O_2} is to be preferred in application to any rocks where f_{H_2O} is uncertain, i.e. most igneous and many metamorphic rocks. Evaluation of gas fugacities is necessary to understand more fully the composition and role of fluids during the Grenville granulite facies metamorphism in the Adirondack Highlands.

ADIRONDACK FLUORITE ASSEMBLAGES

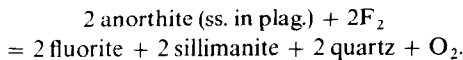
Fluorite is a widespread accessory phase in skarns and gneisses in the Adirondack Highlands. LEONARD and BUDDINGTON (1964) describe fluorite in a number of magnetite-rich gneisses and skarns in the NW

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Adirondacks. Assemblages include:

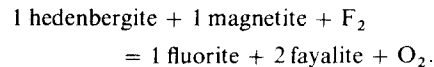
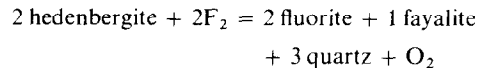
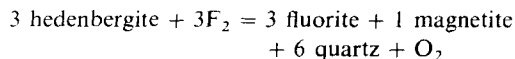
ferrosalite–scapolite–microcline–sphene–fluorite
 ± calcite ± andradite
 biotite–sphene–fluorite ± magnetite ± sulfides
 biotite–quartz–K–feldspar–magnetite ± spessartine
 ± fluorite
 biotite–quartz–K–feldspar–sillimanite–fluorite (tr)–
 plagioclase (tr).

These assemblages do not buffer f_{F_2} and f_{O_2} by simple reactions except for the last which carries both products and reactants of the reaction



If these phases are in equilibrium and the composition of the plagioclase is determined, the univariant curve can be calculated in f_{F_2} – f_{O_2} space at constant P – T . BUDDINGTON and LEONARD (1962) report fluorite in alaskites near South Russell, Fine, Parishville and Oswegatchie in the NW Adirondacks. Typical mineral assemblages are quartz–microcline–plagioclase–amphibole–fluorite ± sphene ± zircon ± biotite ± iron oxides. They also report the assemblage quartz–micropertite–plagioclase–ferrohedenbergite–fayalite–hornblende–ilmenite–zircon–fluorite in fayalite granites near Wanakena, New York. At this locality fluorite occurs in association with fayalite–ferrohedenbergite–amphibole clots (see Fig. 1), and it is nearly always juxtaposed to these other mafic minerals. KEMP and ALLING (1925) have reported fluorite-bearing assemblages in the Au Sable Quadrangle. Fluorite occurs in a fayalite granite near Au Sable Forks and in a granite on Palmer Hill, north of Au Sable Forks. In addition to these localities investigated by the writers, a new fluorite occurrence was also discovered near Lake Pleasant. Fine-grained fluorite (25 μm) occurs in a quartz mangerite together with clinopyroxene (Hd_{70}), orthopyroxene (Fs_{82}), quartz, microcline perthite (Ab_{30}), plagioclase (An_{23}) and magnetite ($\text{Uv}_{2,1}$). The occurrence of such small grains of primary fluorite in a typical Adirondack orthogneiss is significant; fluorite might be a more common primary phase than reported. Careful microscopic examination of nearly 200 thin sections of charnockite and mangerite has failed to reveal additional fluorite-bearing assemblages. However, small grains (<25 μm) could easily go undetected despite extensive searching, especially in a partially altered rock.

The fluorite-bearing assemblages in the Adirondacks may have buffered oxygen and fluorine fugacities. The buffering reactions are:



A knowledge of pressures and temperatures of metamorphism will allow calculation of oxygen and fluorine fugacities if experimental calibration of these reactions or the Gibbs free energy of the solid phases is available.

ANALYTICAL METHODS

Most of the free energy data for thermodynamic calculations were taken from JANAF (1971, 1974, 1975) tables and ROBIE and WALDBAUM (1968) with adjustments as given in HEMINGWAY and ROBIE (1977) and CODATA (1976). The ΔG_T^0 data for FeF_2 were obtained from SCHAEFER (1975). Free energy data for hedenbergite and andradite were calculated from experimental curves of LIU (1974). The free energy obtained for hedenbergite (–554.151 cal/mol) agrees well with estimates of NAVROTSKY and COONS (1976) at 1350 K. When estimates of hedenbergite entropy are made ($S_T^0 \text{ Hd} \approx S_T^0 \text{ Di} + 1/2 S_T^0 \text{ Fa} - 1/2 S_T^0 \text{ Fo}$), one may calculate $\Delta G_{1000}^0 \text{ Hd} = -553.160$ cal/mol from their ΔG_{350}^0 estimate. KURCHAKOVA and AVETISYAN (1974) also estimated the free energy for hedenbergite, obtaining $\Delta G_{1000}^0 \text{ Hd} = -550.504$ cal/mol, a fortuitously good agreement in view of their reliance on unreversed experimental data not in agreement with Liou's reversals. The free energy for sphene was calculated from HUNT and KERRICK'S (1977) experiments. Table 1 contains the ΔG_{1000}^0 data used in construction of Figs. 2 and 3. Molar volumes of the minerals were obtained from ROBIE and WALDBAUM (1968) and CLARK for V^0 (Hd) which was taken from LINDSLEY *et al.* (1968).^{*} The V^0 of FeF_2 , TiF_4 and ZrF_4 were calculated from reported densities, and the V^0 for K_3AlF_6 was calculated from ASTM cell volume data. The f_{O_2} – f_{F_2} phase diagram was calculated using the equation

$$\Delta G(P, T) = \Delta G_T^0 + \frac{\Delta V_s^0 \Delta P}{41.84} + RT \ln f_{O_2}^n / f_{F_2}^m,$$

where n and m are the numerical coefficients for O_2 and F_2 respectively in a given equation with n moles of O_2 on the right-hand side and m moles of F_2 on the left. The assumption that $\Delta V_s^0(P, T) \approx \Delta V_s^0(1 \text{ atm.}, 298 \text{ K})$ produces negligible errors for these calculations. Figure 2 has been constructed at constant P of 7 kbar and T of 1000 K, the estimated conditions in the Adirondacks (BOHLEN and ESSENE, 1977a). For comparison we have calculated the F_2 – O_2 buffers used by MUNOZ and EUGSTER (1969) as well as some other simple reactions in Figs. 2 and 3. BURT (1972) schematically constructed a diagram similar to Fig. 2 in the system CaO – FeO – SiO_2 – O_2 – F_2 plotting μ_{F_2, O_2} vs μ_{O_2} . We consider the variable F_2O_{-1} to be an unnecessary artifice, and Burt gives no magnitude or specific values for his variables. Nevertheless, the hedenbergite- and andradite-bearing reactions in Figs. 2 and 3 are topologically consistent with Burt's diagram.

The location of the An–Fl–Si–Q (AFSQ) curve relative to the Wo–Fl–Q (WFQ) curve has been a matter of some dispute. MUNOZ and LUDINGTON (1974) concluded that the AFSQ buffer was incorrectly located relative to WFQ by MUNOZ and EUGSTER (1969). Munoz and Ludington recalculated the two curves using ROBIE and WALDBAUM'S (1968) data and still inferred a discrepancy with their experimental data. They considered that errors were to be found in the free energy of the aluminosilicates and adjusted the AFSQ curve to be consistent with their experiments. The more recent thermochemical data (Table 1)

^{*} The cell volume of synthetic hedenbergite (450.04 \AA^3) reported by KURCHAKOVA and AVETISYAN (1974) disagrees with their cell dimensions and should read 450.44 \AA^3 which converts to 67.83 cm^3/mol and is in good agreement with the volume (67.88 cm^3/mol) of LINDSLEY *et al.* (1968).

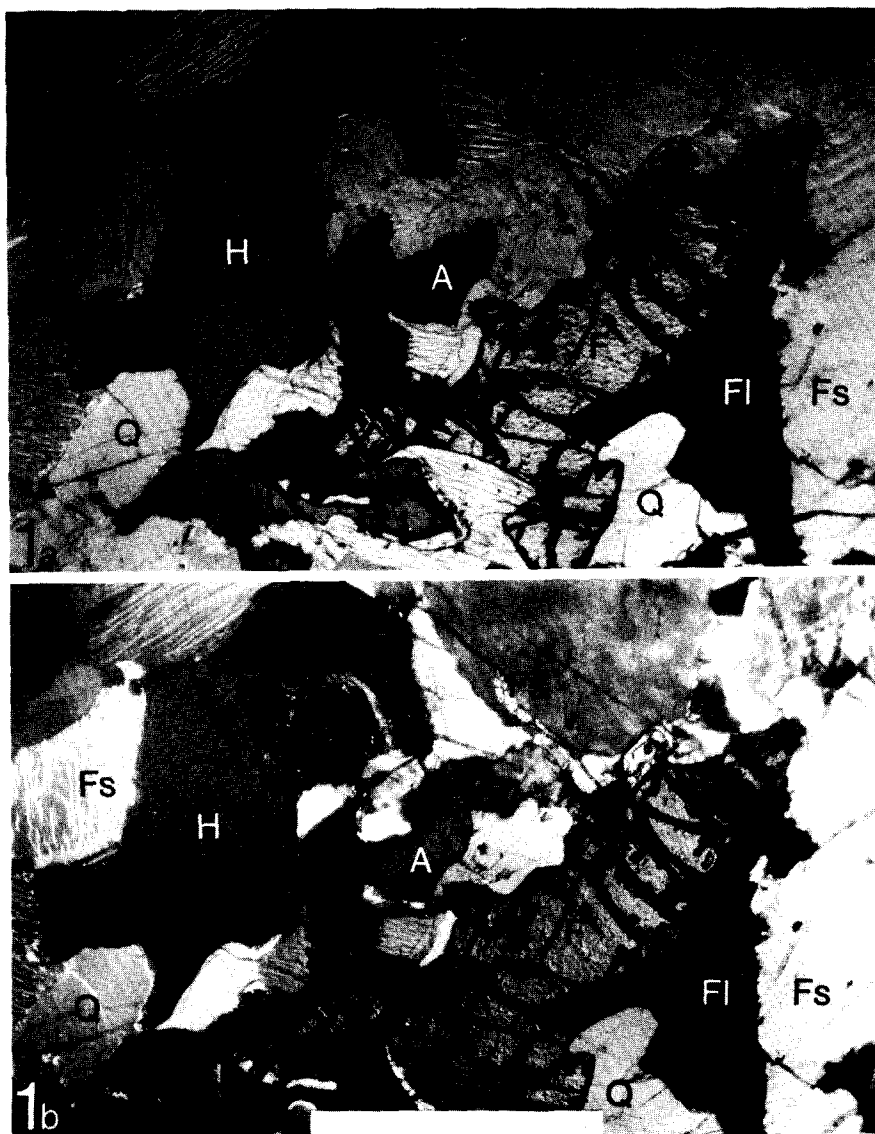


Fig. 1a. Clot of fayalite (F), ferrohedenbergite (H), ferrofluorendenite (A), fluorite (stained) (Fl), quartz (Q), and alkali feldspar (Fs) in fayalite granite near Wanakena, New York.

Fig. 1b. Same view under crossed polars. Bar scale is 0.5 mm.

Table 1. Free energy and volume data used for calculation of Figs. 2 and 3

Phase	Formula	Abbrev.	$\Delta G^0_{1000^{\circ}\text{K}}$	Reference	$V^0_{298^{\circ}\text{K}}$	Reference
Albite, high	$\text{NaAlSi}_3\text{O}_8$	Ab	- 763 408	(8)	100.43	(10)
Andradite	$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$	Ad	- 1 117 638	(6)	131.65	(10)
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	An	- 833 596	(8)	100.79	(10)
Calcite	CaCO_3	Cc	- 227 411	(9)	36.93	(10)
Cryolite	Na_3AlF_6	Cry	- 659 283	(1)	70.81	(10)
Fayalite	Fe_2SiO_4	Fa	- 275 030	(8)	46.39	(10)
Fluorite	CaF_2	F1	- 252 638	(1)	24.54	(10)
HF, ideal gas	HF	HF	- 66 723	(7)	0	-
H ₂ O, ideal gas	H ₂ O	H ₂ O	- 46 040	(1)	0	-
Hedenbergite	$\text{CaFeSi}_2\text{O}_6$	Hd	- 554 151	(6)	67.88	(11)
Hematite	Fe_2O_3	H	- 134 363	(1)	30.27	(10)
Ilmenite	FeTiO_3	Ilm	- 234 400	(3)	31.69	(10)
Iron Fluoride	FeF_2	IF	- 138 112	(4)	22.92	(12)
K-cryolite	K_3AlF_6	Kcry	- 664 818	(1)	92.14	(13)
Lime	CaO	Lm	- 126 942	(2)	16.76	(10)
Magnetite	Fe_3O_4	M	- 189 541	(1)	44.52	(10)
Periclase	MgO	Pe	- 117 886	(7)	11.25	(10)
Quartz	SiO_2	Q	- 174 526	(7)	22.69	(10)
Rutile	TiO_2	Ru	- 182 303	(2)	18.82	(10)
Sanidine	KAlSi_3O_8	Or	- 770 290	(8)	109.05	(10)
Sellaite	MgF_2	Se	- 227 066	(1)	19.61	(10)
Sillimanite	Al_2SiO_5	Si	- 501 051	(1)	49.90	(10)
Sphene	CaTiSiO_5	Sph	- 508 885	(5)	55.65	(10)
Titanium Fluoride	TiF_4	TF	- 326 378	(1)	44.28	(12)
Wollastonite	CaSiO_3	Wo	- 323 107	(8)	39.93	(10)
Wustite	$\text{Fe}_{.947}\text{O}$	W	- 47 686	(1)	12.04	(10)
Zircon	ZrSiO_4	Zc	- 392 935	(1)	39.26	(10)
Zirconium Fluoride	ZrF_4	ZF	- 378 237	(1)	37.75	(12)

References: (1) JANAF (1972); (2) JANAF (1975); (3) ROBIE and WALDBAUM (1968); (4) SCHAEFER (1975); (5) calc. from HUNT and KERRICK (1977); (6) calc. from LIU (1974); (7) CODATA (1976); (8) HEMINGWAY and ROBIE (1977); (9) STAVELY and LINFORD (1969); (10) ROBIE *et al.* (1967); (11) LINDSLEY *et al.* (1968); (12) calc. from density; (13) calc. from ASTM cell dimensions.

have substantially different ΔG^0_7 values than ROBIE and WALDBAUM (1968) for anorthite, sillimanite and fluorite. The inferred f_{Fe_2} for the two curves at f_{O_2} fixed by NNO ($-\log f_{\text{O}_2} = 15.68$) at 1000 K are listed in Table 2. The WFQ curve has shifted by $-0.6 \log f_{\text{Fe}_2}$ units relative to that obtained from Robie and Waldbaum's data largely because of a -3 kcal/mol change in ΔG^0_7 for fluorite. This value for fluorite has been confirmed by recent solubility, EMF and calorimetric measurements summarized in NORDSTROM and JENNE (1977). MUNOZ and LUDINGTON'S (1974) experiments imply a $1.9 \log f_{\text{Fe}_2}$ difference between AFSQ and WFQ curves, close to the value (2.1) calculated for this paper. Considering the errors, it is concluded that the writers' calculated curves are consistent with Munoz and Ludington's experiments but require a small shift to lower f_{Fe_2} and f_{HF} in both curves from their calculated values.

Quantitative electron microprobe analyses of the Adirondack minerals were obtained in order to adjust the calculated phase equilibria for solid solutions. Major and minor element analyses were obtained using an ARL-EMX electron microprobe analyzer with wavelength dispersive PET, LiF and TAP crystal spectrometers. Spectrometer data were corrected for atomic number, fluorescence, absorption, continuous background and machine drift effects using the FORTRAN program EMPADR VII written by RUCKLIDGE and GASPARRINI (1969). Details of

microprobe techniques are described in BOHLEN and ESSENE (1977a). For fluorite analyses the electron beam was spread out to approx 25–30 μm and the beam energy reduced to 10 keV in order to minimize volatilization. Thousand second energy dispersive analyses failed to reveal any elements besides Ca, although care was taken to look for rare earth elements. The writers conclude that the fluorite in Adirondack orthogneisses is $>99.5\%$ pure CaF_2 . For all minerals ferric iron has been inferred by normalization about the cations with adjustment of ferrous-ferric ratio to maintain stoichiometry. For pyroxenes, fayalites and magnetites, the formulae were normalized so that the sum of tetrahedral and octahedral cations = 4, 3 and 3 respectively; for amphiboles the sum of M_1 , M_2 , M_3 and tetrahedral cations was taken as 13 for Fe, Mn, Mg, Al, Ti, Si. This technique is critically dependent on careful elemental analyses, especially for Si and Al, and assumes stoichiometric phases; however, errors as large as 50% in the estimated Fe^{3+} of the silicates will not significantly affect the calculations and conclusions which follow.

ANALYTICAL RESULTS AND DISCUSSION

The calculated phase relations for hedenbergite–andradite–fluorite–quartz–iron oxide in f_{O_2} – f_{Fe_2} space

Table 2. Comparison of estimated f_{F_2} for the AFSQ and WFQ buffers at f_{O_2} fixed by NNO for $P_s = 2$ kbar

Reference	WFQ(NNO)		A-B
	A=-log f_{F_2}	B=-log f_{F_2}	
Munoz and Eugster (1969) calc.	30.1	27.1	3.0
Munoz and Ludington (1974) exptl.	(30.0)	(28.1)	1.9
Calc. from Robie and Waldbaum (1968)	30.0	28.8	1.2
Calc. from table 1 (this paper)	30.6	28.5	2.1

at constant P - T ($P = 7$ kbar, $T = 1000$ K) are shown in Fig. 2. The P - T were chosen so that the diagram would apply to wide areas of the Adirondacks. Temperatures of 700–800°C for the Adirondacks Highlands have been determined by BOHLEN and ESSENE (1977a) using magnetite-ilmenite and feldspar thermometry (BUDDINGTON and LINDSLEY, 1964; STORMER, 1975). Pressures in the Adirondacks can be estimated by sphalerite-pyrite-pyrrhotite barometry (BROWN *et al.*, 1978), by the occurrence of ferrosilite-rich orthopyroxenes, by the assemblage fayalite-quartz and by the ubiquitous presence of sillimanite. If impurities in the olivine-orthopyroxene-quartz system are considered (BOHLEN and ESSENE, 1977b), the sulfide, pyroxene and Al_2SiO_5 systems restrict Adirondack pressures to 6 ± 1 kbar in the Lowlands to 8 ± 1 kbar in the Highlands.

The topology (Fig. 2) shows that fluorite-bearing assemblages significantly restrict fluorine fugacities. The upper f_{F_2} limit in terrestrial rocks is apparently represented by the fluoridation of iron oxide to iron fluoride since iron fluoride (a relatively soluble phase) is unknown as a mineral. Other reactions such as the fluoridation of zircon and rutile lie to the fluorine-rich side of the iron fluoride curve (Fig. 3). These reactions presumably restrict maximum fluorine fuga-

Table 3. Analyses of coexisting amphibole, fayalite, ferrohedenbergite (with ilmenite, fluorite, quartz) from Wanakena, New York

	NF-4 Amphibole	NF-4 Fayalite	NF-4 Ferrohedenbergite
SiO ₂	39.83	29.44	48.79
TiO ₂	1.74	0.00	0.24
Al ₂ O ₃	8.49	0.00	0.89
FeO*	32.06	68.23	30.57
MnO	0.83	1.58	0.73
MgO	0.79	0.56	1.08
CaO	9.57	0.04	16.22
Na ₂ O	1.56	nd	1.19
K ₂ O	1.75	nd	0.00
Cl	0.62	nd	nd
F	1.71	nd	nd
TOTAL	98.95	98.85	99.71
O = Cl, F	0.86	0.00	0.00
TOTAL	98.09	99.85	99.71
TOTAL**	98.71	99.88	99.82
Si	6.491	0.996	2.002
Al	1.509	---	0.000
Al	0.120	---	0.043
Ti	0.213	---	0.007
Fe ³⁺	0.768	0.008	0.035
Mg	0.192	0.028	0.066
Fe ²⁺	3.593	1.922	1.014
Mn	0.115	0.045	0.025
Ca	0.669	0.001	0.713
Na	0.492	---	0.094
K	0.363	---	0.000
F	0.878	---	---
Cl	0.171	---	---
OH	0.951	---	---

* Total iron as FeO.

** Total corrected for calculated ferric iron.

Table 4. Analyses of coexisting fayalite, ferrohedenbergite, magnetite (with fluorite, quartz) from Au Sable, New York (AS) and coexisting ferrosalite, magnetite (with fluorite, orthopyroxene, quartz) from Lake Pleasant, New York (LP)

	As Faya- lite	As Ferro- heden- bergite	As Magne- tite	LP Ferro- salite	LP Magne- tite
SiO ₂	29.64	47.93	0.00	48.60	0.00
TiO ₂	0.00	0.19	0.09	0.14	0.26
Al ₂ O ₃	0.00	1.21	0.46	1.23	0.47
FeO*	67.45	29.76	92.89	23.47	91.87
MnO	1.45	1.97	0.00	0.53	0.00
MgO	1.09	0.73	0.02	4.06	0.00
CaO	0.05	17.24	nd	20.40	nd
Na ₂ O	nd	0.78	nd	0.41	nd
K ₂ O	nd	0.02	nd	0.00	nd
TOTAL	99.68	99.81	93.46	98.84	92.60
TOTAL**	99.68	99.95	100.24	98.95	99.23
Si	1.000	1.973	0.000	1.965	0.000
Al	0.000	0.027	0.021	0.035	0.025
Al	0.000	0.032	---	0.023	---
Ti	0.000	0.006	0.002	0.004	0.021
Fe ³⁺	0.000	0.045	1.975	0.004	1.935
Mg	0.055	0.045	0.001	0.245	0.000
Fe ²⁺	1.902	0.980	1.001	0.790	1.018
Mn	0.041	0.069	0.000	0.018	0.000
Ca	0.002	0.761	---	0.884	---
Na	0.000	0.062	---	0.032	---
K	0.000	0.000	---	0.000	---
K	0.000	0.000	---	0.000	---

* Total iron as FeO.

** Total corrected for calculated ferric iron.

cities in most crustal rocks. The writers have also calculated andradite reactions which arise from invariant points involving hedenbergite, so that the diagram might be more widely applicable to skarns and other rocks of the granulite facies. It is shown in Fig. 2 that andradite-bearing assemblages restrict the lower f_{F_2} limit of fluorite-hedenbergite stability. A number of typical skarn assemblages such as andradite-wollastonite-hedenbergite-fluorite and andradite-hedenbergite-magnetite-fluorite are univariant for the end-member compositions. Discovery of fluorite in iron-rich skarns containing garnet-clinopyroxene-wollastonite-quartz and garnet-clinopyroxene-magnetite-quartz described by HOLTZ and WILLDEN (1964), LEONARD and BUDDINGTON (1964) and BURT (1971) would make these assemblages invariant, fixing f_{O_2} - f_{F_2} . Hence, one must be careful not to overlook even minor amounts of fluorite in Fe-rich rocks when evaluating f_{F_2} . Figure 2 and similar relations at various other P - T conditions will be useful in estimating fluorine and oxygen fugacities in a number of skarn assemblages if adjustments in the equilibria are made for mineral impurities.

Although fluorites in Adirondack gneisses are probably igneous in origin, their stability in the subsequently metamorphosed charnockites, mangerites and granites is important since the fluorite-bearing assemblages buffered f_{O_2} and f_{F_2} during metamorphism. Most of the fluorite-bearing assemblages in granitic rocks are divariant (at constant P - T) and do not uniquely restrict fluorine fugacities. However, the fayalite-granite assemblages near Wanakena and Au

Sable Forks, New York, tightly constrain fluorine and oxygen fugacities. The Wanakena assemblage of fayalite-ferrohedenbergite-amphibole-ilmenite-fluorite-quartz is univariant (at constant P - T and for the end-member system). Oxygen fugacities can be approximated from a fayalite-magnetite (U_{V29})-ilmenite (Hm_6)-quartz assemblage found in the same rock body less than 0.5 miles away. Applying the Buddington-Lindsley oxygen barometer, this assemblage requires oxygen fugacities of 10^{-17} bar at 700°C. One cannot assume the oxygen fugacity will be the same throughout the rock body, and indeed slight local variations in f_{O_2} , probably account for the sporadic occurrence of magnetite in the Wanakena fayalite granite. Nevertheless, justification for using 10^{-17} as an approximate f_{O_2} is supported by the data of BOHLEN and ESSENE (1977a) which indicates that a number of different orthogneisses throughout the Adirondacks have oxygen fugacities within $10^{\pm 1}$ of the quartz-magnetite-fayalite buffer as determined by magnetite-ilmenite (BUDDINGTON and LINDSLEY, 1964). If oxygen fugacities in the Wanakena fayalite granite are $10^{-17 \pm 1}$ bar, then fluorine fugacities can be restricted to $10^{-28.6 \pm 0.3}$ bar when impurities in the fayalite and ferrohedenbergite are considered (Fig. 3).

The effect of additional components on the calculated equilibria can be corrected for by the equation:

$$f_{O_2}/f_{F_2} = (f'_{O_2}/f'_{F_2}) \cdot \frac{a_i^b \cdot a_j^c \dots}{a_x^m \cdot a_y^n \dots}$$

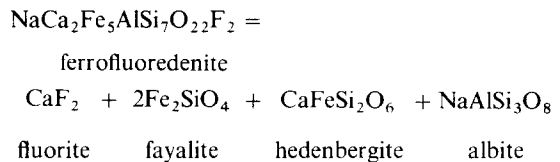
where f'_{O_2} and f'_{F_2} are the calculated fugacities for the end-member minerals at the P - T of interest and where a_i^b , a_j^c are the activities of product phases i and j raised to their respective numerical reaction coefficients (b , c , ...). Similarly a_x^m , a_y^n are the activities of the reactant phases x , y , etc., raised to their numerical reactant coefficients m , n , etc. When the necessary activity data are not available, the substitution of mole fraction X_i for a_i allows calculation of an approximate shift of end-member reactions due to additional components.

The calculated equilibria in Fig. 3 show that fayalite-ferrohedenbergite-fluorite granites require relatively high f_{F_2} values, above the stability of most plagioclase compositions. Preliminary examination of other fayalite granites suggest the assemblage fayalite-ferrohedenbergite-fluorite-quartz is common and deserves more attention. Rocks containing cryolite-quartz at Ivigtut, Greenland and cryolite-topaz-quartz at Pikes Peak, Colorado (HURLBUT, 1971) may require similar or slightly higher fluorine fugacities than fayalite-hedenbergite-fluorite granites, although the phase relations have not yet been considered in detail.

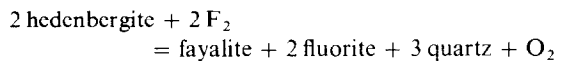
Rocks not containing fluorite may well have formed under lower f_{F_2} conditions than those discussed in this paper. Rocks containing sphene (which is very common in the Adirondacks) appears to require at least an order of magnitude lower f_{F_2} at

the same f_{O_2} compared to the assemblage Hd-F1-Q-Fa (Fig. 3). In fluorite-free rocks reactions involving F/OH exchange between coexisting micas, amphiboles, mica-amphibole or mica/amphibole-apatite must then be sought to estimate f_{F_2} . For these assemblages f_{H_2O} and f_{O_2} will first need to be estimated before f_{F_2} and f_{HF} can be evaluated.

The Wanakena fayalite granite is special in that the assemblage fluorite-fayalite-ferrohedenbergite-amphibole is found as clots in a matrix of quartz and feldspar with minor amounts of ilmenite, zircon and apatite (see Fig. 1). There is textural evidence for the reaction:



This reaction can be approximately balanced using analyzed mineral compositions (Table 3) if ilmenite, plagioclase, and a fluid (containing H_2O , Cl_2 , F_2 , O_2) are considered as additional phases. If the complex decomposition of ferrofluorendenite occurs in this rock, the reaction (for the non-end-member phases) must intersect the univariant reaction:



at an invariant point in f_{O_2} - f_{F_2} space (at constant P , T , f_{Cl_2} , f_{H_2O}).

In the Au Sable Forks fayalite granite the assemblage fayalite-ferrohedenbergite-fluorite-magnetite-quartz (Table 4) is invariant in f_{O_2} - f_{F_2} space at constant P - T . For this rock, f_{F_2} and f_{O_2} are $10^{-28.9 \pm 0.3}$ and $10^{-16.4 \pm 0.2}$ bar respectively (Fig. 3). Elsewhere in the outcrop fayalite-magnetite-ilmenite-quartz fixes f_{O_2} - T at 10^{-17} bar and 710°C (BOHLEN and ESSENE, 1977a). Within the same outcrop, another rock type contains the assemblage magnetite-ilmenite-biotite-K-feldspar. This assemblage fixes f_{O_2} - f_{H_2O} and T (725°C) using data from BUDDINGTON and LINDSLEY (1964) and WONES (1972). This assemblage and other assemblages around the Adirondack Highlands restrict water fugacities to $<10^{3.3 \pm 0.2}$ bar (BOHLEN and ESSENE, in prep.). There is a substantial uncertainty in f_{H_2O} determination because of the problem of calculating the annite component in micas with significant amounts of impurities (halogens, Mn, Ti, Al^{VI} , Fe^{3+} , interlayer and octahedral site deficiencies, etc.). If an annite component is calculated as $X(\text{annite}) = Fe^{2+}/(Fe^{2+} + Mg)$, the water fugacity for the Au Sable assemblage magnetite(U_{V32})-ilmenite(Hm_5)-biotite(Ann_{56})-perthite(Or_{67}) is $10^{3.3}$. However, this f_{H_2O} value represents an upper limit as other schemes for calculating annite components from complicated biotite formulae (WONES, 1972; CZAMANSKE and WONES, 1973) yield much lower annite mole fractions and hence lower water fugaci-

ties. Indeed WONES (1972) inferred water fugacities on the order of 10^1 for orthogneisses in the NW Adirondacks. Nevertheless for the Au Sable outcrop an upper limit on $f_{\text{H}_2\text{O}}$ will allow calculation of limiting values for f_{HF} and f_{H_2} , assuming no large gradients in $f_{\text{H}_2\text{O}}$ in the Au Sable outcrop and assuming ideal mixing of gases. The calculated results are $f_{\text{H}_2} \leq 10^{1.4}$ bar and $f_{\text{HF}} \leq 10^{0.3}$ bar for 727°C , $f_{\text{F}_2} \approx 10^{-28.9}$ bar, $f_{\text{O}_2} \approx 10^{-16.4}$ bar and $f_{\text{H}_2\text{O}} \leq 10^{3.3}$ bar. Taking into account the errors in our analysis, it can be seen that H_2 and HF fugacities are on the order of 10^1 . If the limiting $f_{\text{H}_2\text{O}}$ value of $10^{3.3}$ is too high, the magnitude of HF and H_2 decrease somewhat. For $f_{\text{H}_2\text{O}} = 10^2$ bar at $f_{\text{O}_2} \approx 10^{-16.4}$ bar and $f_{\text{F}_2} \approx 10^{-28.9}$ bar, $f_{\text{H}_2} \approx 10^{0.2}$ bar and $f_{\text{HF}} \approx 10^{0.1}$ bar.

Of course errors in the calculated phase diagram will generate uncertainty in the estimated f_{O_2} and f_{F_2} . However, for the fayalite-magnetite-quartz bearing assemblages, the errors in f_{O_2} will be small since the inferred f_{O_2} has been confirmed by magnetite-ilmenite analysis in nearby rocks (BOHLEN and ESSENE, 1977a). Uncertainties in f_{F_2} are generated by errors in ΔG_T^0 for reactants and products of a given reaction. The ΔG_T^0 for hedenbergite probably has a relatively large error as it was calculated simultaneously with andradite from two experimental curves. A change of ± 3 kcal in ΔG_T^0 (Hd) will shift the calculated f_{F_2} in the hedenbergite reactions by about $10^{\pm 0.5}$. Errors of 1–2 kcal must still be anticipated for many of the other phases in Table 1, producing errors of approximately $10^{\pm 0.3}$ in the calculated curves.

The estimated f_{F_2} and f_{O_2} in the fayalite granites are generally consistent with the calculated stabilities of other minerals such as zircon, ilmenite, albite, K-feldspar and sphene. The writers did not find the assemblage, ferrohedenbergite-fayalite-fluorite-quartz-sphene in rocks from Wanakena consistent with sphene's instability as calculated in Fig. 3. However, LEONARD and BUDDINGTON (1964) do report sphene in the Wanakena fayalite-ferrohedenbergite granite, posing a problem if it is in equilibrium with fayalite-ferrohedenbergite-quartz-fluorite. This deserves further study particularly in analyzing the sphene to see if additional components can extend the sphene stability field. The relatively large error in the ΔG_T^0 of sphene (HUNT and KERRICK, 1977) may also explain the inconsistency. The stability of albite may be contracted by a more stable reaction involving topaz instead of sillimanite, but no ΔG_T^0 data are available for the topaz calculation.* The calculations suggest that cryolite may be stable instead of albite in some fayalite granites, and it should be considered as a possible phase in such rocks. The effect of solid solution on plagioclase stability was calculated using ORVILLE'S (1972) activity coefficients for albite and

anorthite components. It can be seen that the hedenbergite reactions are close to the upper stability of intermediate plagioclases, and plagioclase-bearing rocks in the Adirondacks must have equilibrated at lower f_{F_2} for comparable f_{O_2} (assuming the same P - T).

ADIRONDACK METAMORPHIC FLUIDS

Even though f_{O_2} and f_{F_2} directly govern the reactions considered in Figs. 2 and 3 and other reactions generating fluorite-bearing assemblages, their values are insignificant compared to f_{H_2} , f_{HF} and $f_{\text{H}_2\text{O}}$. Even f_{H_2} and f_{HF} have low values: if a fluid phase equilibrated with these granites, the mole fraction of H_2 and HF would each be less than 0.001. Preliminary data on $f_{\text{H}_2\text{O}}$ indicate that water pressures in the Adirondacks are substantially less than solid pressure. This is not altogether surprising since substantial melting would be required for many charnockites and granites containing microcline-albite-quartz at Adirondack P - T if water pressures approximated solid pressures. Since there is little evidence of extensive partial melting in the Adirondack Highlands (such as migmatites or restites), it must be concluded that water pressures are much less than solid pressures for granulite facies metamorphism in the Adirondacks. The writers suspect that this may be a general condition of granulite facies metamorphism elsewhere, and it should not be assumed that $P_{\text{H}_2\text{O}} \approx P_s$ in high-grade metamorphic rocks. As might be expected, it appears that O_2 , H_2 , F_2 and HF do not play a significant role in maintaining high fluid pressures in the Adirondacks. We conclude that $P_{\text{H}_2\text{O}}$ is $\leq 0.25 P_{\text{solid}}$ and that $P_{\text{fluid}} \ll P_{\text{solid}}$ unless other gas species such as CO_2 or Ar are present in quantities sufficient to maintain high fluid pressures.

Acknowledgements—The writers are thankful for the support of National Science Foundation Grant No. 014573 to EJE, Geological Society of America Grant No. 2003-75 to SRB and the Turner Fund of The University of Michigan. The electron microprobe facilities at The University of Michigan are supervised by Professor WILBUR C. BIGELOW of the Department of Metallurgy and Material Science whose cooperation made this study possible. Several members of this staff, particularly L. F. ALLARD, P. J. HOLLINGSWORTH and A. J. MARDINGLY, gave valuable assistance during data collection. The writers wish to thank Dr. D. R. PEACOR and Dr. W. C. KELLY of the Department of Geology and Mineralogy, The University of Michigan, for the reviews of the manuscript. Dr. D. R. WONES and Dr. L. G. LIU are also thanked for their manuscript reviews. Mr. DERWIN BELL drafted the line drawings which appear in this paper.

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* The AFSQ buffer itself may become metastable with respect to topaz; carefully reversed experiments or accurate thermochemical data for topaz are necessary to evaluate this possibility.

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