

## The effects of fluorine on the vapor-absent melting of phlogopite + quartz: Implications for deep-crustal processes

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### ABSTRACT

The vapor-absent partial melting of biotite-bearing quartzofeldspathic assemblages may play an important role in the petrogenesis of high-temperature granitoid rocks. F-bearing biotite has been reported in high-grade terranes; therefore, melting equilibria involving fluorhydroxy micas may be better models for lower-crustal anatexis than those involving the hydroxy end-member. In order to make an initial assessment of the effect of F on vapor-absent melting, the reaction fluorhydroxy phlogopite + quartz = enstatite + liquid has been investigated experimentally near 8 and 15 kbar, using a synthetic phlogopite of  $F/(F + OH) = 0.58 (\pm 0.12)$ . Near 15 kbar, melting occurs between 1020 and 1050 °C; at 8 kbar, melting occurs between 950 and 1000 °C. The equilibrium was reversed at 15 kbar by a two-stage experiment between 1100 and 1000 °C, and it was reversed at 8 kbar by a two-stage experiment between 1050 and 950 °C. Reversal criteria included textural evidence for mica regrowth from melt. Results of this study indicate that ~60 mol% substitution of F for OH in phlogopite stabilizes the phlogopite + quartz assemblage by as much as 175 °C relative to enstatite and liquid. This significant stabilizing effect indicates that vapor-absent partial melting of rocks containing high fluorine micas may be restricted to temperatures in excess of 950 °C, leaving a residual unmelted micaceous assemblage of higher F content. The stabilizing effect of F in this system is broadly consistent with current models for the petrogenesis of A-type granites. Quantitative analyses of quenched liquid generated from the vapor-absent fluorhydroxy phlogopite + quartz assemblage, however, indicate melts are lamproitic in composition, not granitic.

### INTRODUCTION

Initial melting of most quartzofeldspathic crustal rocks occurs at the solidi of constituent mica-bearing assemblages. Because the stability of biotite exceeds that of muscovite in quartzofeldspathic rocks (Brown and Fyfe, 1970), biotite is the mica applicable to the modeling of lower-crustal anatexis. To a first approximation, the vapor-absent melting of biotite + quartz represents a limit to the beginning of melting in crustal rocks and is consequently an important constraint on the process of granitoid genesis.

The vapor-absent melting temperature of the biotite + quartz assemblage has been determined for an end-member hydroxy phlogopite in the system  $K_2O$ -MgO- $Al_2O_3$ - $SiO_2$ - $H_2O$  (KMASH) (Peterson and Newton, 1989a); however, many biotite samples from high-grade terrains contain substantial fluorine (F<sup>-</sup>) in place of hydroxyl (OH<sup>-</sup>)

(Guidotti, 1984), which indicates that the KMASH-F system may be a closer analogue to rocks. It has been demonstrated experimentally that the  $F/(F + OH)$  ratio of phlogopite increases with increasing temperature upon equilibration with a fluid of constant  $f_{HF}$  (Munoz and Luddington, 1974, 1977). Therefore, it is presumed that F substitution for OH increases the decomposition temperature of phlogopite at low pressures. No quantitative data exist, however, for the vapor-absent partial melting of fluorhydroxy phlogopite + quartz at pressures applicable to the middle and lower crust. To obtain this information, we have conducted an experimental investigation of the vapor-absent melting of fluorhydroxy phlogopite + quartz in the system  $K_2O$ -MgO- $Al_2O_3$ - $SiO_2$ - $H_2O$ -F. The principal objective of the study was to obtain reversed experimental  $P$ - $T$  determinations of the solidus of the reaction fluorhydroxy phlogopite + quartz = enstatite + liquid. This information provides an initial quantification of the stabilizing effect of F in biotite, and thereby places further constraints on the partial melting processes responsible for the genesis of magmas in the lower crust.

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## EXPERIMENTAL PROCEDURES

### Apparatus

Experiments were performed at  $\sim 8$  and  $\sim 15$ – $16$  kbar in a solid-medium piston-cylinder apparatus. All experiments were conducted at the University of Chicago, except the 8-kbar reversal experiment (F18), which was performed at the University of Alberta. Two types of salt (NaCl) pressure media were used in the experiments. In one type, the sample was surrounded by NaCl cylinders inside a cylindrical graphite furnace. The furnace assembly was jacketed by a 1.905 cm (o.d.) NaCl outer sleeve. In a second type, the sample was placed between two soft-glass cylinders (Ca-Na glass, Corning no. 47057), inside a graphite furnace that was separated from the NaCl outer sleeve by a 1-mm thick soft-glass sheath. The assembly containing soft-glass internal parts was necessary for high-temperature experiments in which the melting temperature of NaCl was exceeded. Pressure was applied to the all-NaCl assembly 3–4 kbar below the desired pressure at room temperature. A precalibrated amount of thermal expansion allowed final pressures to be attained within 200 bars of the desired value upon heating. For the soft-glass assembly, a cold pressure of 4–5 kbar was initially applied to the assembly. The temperature was then raised to approximately 520 °C, at which point the soft glass relaxed enough to allow the desired pressure to be applied to the assembly without shattering it. The temperature was then raised to the appropriate conditions. No pressure correction was applied to either of the NaCl pressure media. A third type of assembly was used for the reversal experiment at 8 kbar. The assembly consisted of talc, pyrex, and alumina. A  $-10\%$  friction correction was applied to this assembly, based on delineation of the reaction fayalite + quartz = ferrosillite (R.W. Luth, personal communication). Nominal pressures were measured with a Heise bourdon tube gauge. Measured pressures for all assemblies are considered accurate to within 500 bars, and precise to within 100 bars.

Temperatures were measured with W-WRe thermocouples situated directly above the encapsulated sample. The cold junction of the thermocouple was laboratory temperature. Temperature was controlled to within a degree with an electronic, solid-state controller. No correction was made for pressure-induced emf. Temperature gradients were measured for the graphite furnaces used in this study. Reported temperatures are considered accurate to within 10 °C.

Starting material was synthesized in an internally heated Ar pressure vessel (design after Holloway, 1971). Pressure was measured with an Astra bourdon tube gauge, and temperature was measured with two Inconel-sheathed, chromel-alumel thermocouples.

### Starting materials

The fluorhydroxy phlogopite used in this study was synthesized hydrothermally from a combination of  $\text{KF} \cdot 2\text{H}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$ . A homogenized mixture

of the components was loaded into an Pt capsule with an outside diameter of 8 mm and reacted at 1.5 kbar and 750 °C for 5 d. Optical examination, as well as the absence of nonmica reflections on X-ray diffractograms, indicated a successful synthesis. Natural quartz from Lisbon, Maryland, was used as the  $\text{SiO}_2$  phase in the experiments.

Starting materials of fluorhydroxy phlogopite + quartz (2:3 by weight) were ground in an agate mortar under distilled  $\text{H}_2\text{O}$  to a fine-grained homogeneous mixture. Samples were dried under a heat lamp at  $\sim 80$  °C for 1 h, then loaded in 4–7 mg amounts into Pt capsules with an outside diameter of 1.5 mm. The encapsulated samples were then dried for a minimum of 1.5 h at 110 °C before sealing of the capsules.

### Analytical methods

Starting fluorhydroxy phlogopite was characterized by powder X-ray diffraction and electron microprobe techniques. X-ray diffraction unit-cell refinements, using Ni-filtered  $\text{CuK}\alpha$  radiation, were obtained by scanning at a rate of  $\frac{1}{4}^\circ 2-\theta/\text{min}$  with an internal standard of synthetic corundum. Refinements were facilitated by the least squares refinement program of Appleman and Evans (1973), for *1M* (*C2/m*) mica polytype. The F content of the phlogopite was determined by the refinement equation for F-OH substitution in phlogopite of Noda and Ushio (1964). Unit-cell parameters and an  $\text{F}/(\text{F} + \text{OH})$  value for starting mica are shown in Table 1. According to the X-ray characterization,  $\text{F}/(\text{F} + \text{OH}) = 0.58 (\pm 0.12)$  for the synthetic phlogopite.

Quantitative chemical analyses of starting mica were obtained from polished sections on a JEOL 733 Superprobe with Tracor Northern software at the University of Washington in Seattle. Two different electron microprobe techniques were employed. In the first technique (method 1, Table 1), major element oxides were analyzed by EDS using 15 keV accelerating voltage and 10 nA beam current, and results are considered accurate to within 2% of the amount present. Quantitative F analyses were obtained through WDS methods using a TAP crystal. A calibration curve of counts vs. concentration was constructed using a natural fluorite (48.7 wt% F) and synthetic fluorphlogopite (9.02 wt% F) as standards. Concentration of F in the starting mica was determined from the calibration curve by collecting counts over 60 s time intervals. Representative analyses are shown in Table 1 and indicate an  $\text{F}/(\text{F} + \text{OH}) = 0.52 (\pm 0.03)$  for the starting mica. In the second technique (method 2, Table 1), all elements were analyzed by WDS, including F with a synthetic LDE 1 crystal. Analytical data were collected at 15 keV accelerating voltage and a 5 nA beam current. Maximum counting time for each element was 40 s. Major element counts were calibrated against a natural biotite standard, and F was calibrated against an end-member fluorphlogopite. The average  $\text{F}/(\text{F} + \text{OH})$  from this technique is  $0.54 (\pm 0.03)$ . Because of the small grain size ( $< 5 \mu\text{m}$ ) of the starting material, only those grains with

**TABLE 1.** Representative characterizations of starting mica (X-ray diffraction and electron microprobe techniques)

	wt% (method 1)			wt% (method 2)			Unit-cell parameters
SiO <sub>2</sub>	44.50	45.26	46.73	40.64	41.66	42.40	$a = 5.328 (\pm 0.001)$
Al <sub>2</sub> O <sub>3</sub>	12.39	12.65	12.74	11.12	10.76	11.22	$b = 9.194 (\pm 0.002)$
MgO	30.16	30.58	29.94	27.47	27.24	27.74	$c = 10.209 (\pm 0.001)$
K <sub>2</sub> O	12.65	11.26	10.54	10.76	10.55	11.14	$\beta = 99.95^\circ (\pm 0.02)$
F	4.57	4.58	4.53	5.11	4.65	5.09	$V = 492.57 \text{ \AA}^3 (\pm 0.13)$
	counts/min*						
F	2200	2205	2178				
	average F/(F + OH) = 0.52 ( $\pm 0.03$ )			average F/(F + OH) = 0.54 ( $\pm 0.03$ )			F/(F + OH) = 0.58 ( $\pm 0.12$ )**

Note: Method 1—Major elements analyzed with EDS and normalized to 100%. F analyzed with WDS, see text. Method 2—All elements analyzed on WDS. See text for details.  
\* Standardization method described in text. Fluorite (48.7 wt% F) yields 23409 counts/min and full fluorphlogopite (9.02 wt% F) yields 4340 counts/min.  
\*\* Derived from empirical calibration of Noda and Ushio (1964).

a basal surface normal to the beam could be analyzed. X-ray and electron probe results are in good agreement. In this study, we consider the X-ray determination to be a more accurate indication of F content because of the uncertainties associated with analyzing grains smaller than 5  $\mu\text{m}$ .

Experimental products were examined optically in refractive index (RI) oil mounts of RI  $\sim 1.540$ – $1.542$ . Quartz was identified by its low positive relief and colorless appearance in plane light. Enstatite was identified by high positive relief, weak birefringence, and straight extinction, if prismatic in habit. Enstatite occurred as abundant granules ( $\sim 5 \mu\text{m}$  diameter) forming a wormlike intergrowth with glass and quartz, and also as a small number of relatively large prisms ( $\sim 100 \mu\text{m}$  long) at temperatures well above the solidus. Two types of mica were observed, both with positive relief. Residual starting mica occurred as highly birefringent recrystallized mats of variable and irregular habit. Mica grown in reversal experiments occurred as euhedral crystals, commonly as hexagonal plates,

several times larger than residual mica grains. Glass (quenched melt) was observed as clusters of low-index beadlets intimately associated with enstatite in near-solidus experiments, and larger angular fragments containing enstatite and quartz at temperatures well above the solidus.

Glass fragments from a sample quenched at 14.7 kbar and 1100  $^\circ\text{C}$  (experiment F5, Table 2) were analyzed by electron microprobe WDS techniques, using a synthetic LDE 1 crystal for F. More than ten individual glass fragments were analyzed within the sample. Analytical data were collected at 15 keV accelerating voltage and a 5 nA beam current. Maximum counting time for each element was 40 s. Major element counts were calibrated against a natural biotite standard and F against an end-member fluorphlogopite (method 2 above). It was determined that a surface beam size greater than 1  $\mu\text{m}$  diameter would incorporate adjacent quartz and enstatite in the analysis of glass. Therefore, beam diameter for glass analyses was maintained to  $< 1 \mu\text{m}$ . H<sub>2</sub>O content was determined by difference from a 100% total. Representative analyses are given in Table 3.

**TABLE 2.** Experimental data for synthetic Ph + Qz starting assemblage (F/F + OH = 0.58)

Experiment no.	P kbar	T $^\circ\text{C}$	Time (h)	Product assemblage
F11*	8.0**	1030	432	Qz + En + Gl + (Ph)
F12	8.4	1075	231	Qz + En + Gl + (Ph)
F13	8.5	1000	336	Qz + En + Gl + (Ph)
F18	8.0	1050	51	
	-8.0	-950	162	Ph + Qz + (En) + (Gl?)
F1	14.8	950	48	Ph + Qz
F2	15.5	1000	50	Ph + Qz + (En?) + (Gl?)
F3	16.0	1020	47	Ph + Qz
F4	15.7	1020	142	Ph + Qz + (En) + (Gl?)
F6	15.5	1020	289	Ph + Qz + (En) + (Gl?)
F8	15.2	1050	68	Qz + En + Gl + (Ph)
F5	14.7	1100	218	Qz + En + Gl + (Ph)
F7	14.9	1100	237	
	-14.8	-1000	319	Ph + Qz + (Gl)

Note: Ph = fluor-hydroxy phlogopite, Qz = quartz, En = enstatite, Gl = glass (quenched melt), ( ) = small to trace amounts, ? = presence of phase uncertain,  $\rightarrow$  = second stage.

\* Temperature measurement within 20 $^\circ\text{C}$  on this experiment.

\*\* Pressure measurement precision is  $\pm 100$  bars, accuracy is  $\pm 500$  bars.

## EXPERIMENTAL RESULTS

Experimental data for the reaction fluorhydroxy phlogopite + quartz = enstatite + liquid are listed in Table 2 and illustrated in Figure 1. At 8.0–8.5 kbar, melting of the starting assemblage occurs between 950 and 1000  $^\circ\text{C}$ . In the pressure range of 15.2–16.0 kbar, melting occurs between 1020 and 1050  $^\circ\text{C}$ . Note that the slope of the reaction changes from undefined in the KMAH system to approximately 140 bars/ $^\circ\text{C}$  in the F-bearing system. Trace amounts of glass and enstatite in products quenched from 15.5 kbar and 1000  $^\circ\text{C}$  (experiment F2) may be the result of trace amounts of moisture remaining in the sample before sealing.

The vapor-absent melting reaction was reversed at  $\sim 8$  and  $\sim 15$  kbar by two-stage experiments, as illustrated by brackets in Figure 1. For example, the first stage of the reversal experiment at 14.9 kbar (experiment F7, Table 2) consisted of holding a sample of fluorhydroxy phlogopite + quartz at 1100  $^\circ\text{C}$  for 237 h, a temperature at

which a previous experiment (F5) had produced abundant enstatite + melt. In the second stage of the experiment, the temperature was lowered nearly isobarically to 1000 °C in the same experiment and held for 319 h. Reversal of the melting reaction near 8 and 15 kbar was indicated by the absence of enstatite and textural evidence for pronounced mica regrowth. This mica regrowth included ~50- $\mu$ m diameter crystals as well as finer grained mica textures similar to those reported for vapor-absent melting in the pure-H<sub>2</sub>O system (Peterson and Newton, 1989a). The reader is referred to the sketches in the last reference for textural details.

Representative analyses of quenched liquid produced by the melting of fluorhydroxy phlogopite + quartz at 1100 °C and 15 kbar are given in Table 3. Melts are 50.8–62.4% SiO<sub>2</sub>, 10.6–13.8% Al<sub>2</sub>O<sub>3</sub>, 11.9–19.1% MgO, and 9.4–12.7% K<sub>2</sub>O by weight. The average melt lacks normative quartz and has a normative olivine to orthopyroxene ratio of 6.6:1. The compositions are similar to those tabulated for lamproites by Bergman (1987).

## DISCUSSION

### Stabilization of phlogopite

The data of this investigation indicate that ~60 mol% substitution of F for OH in phlogopite stabilizes the phlogopite + quartz assemblage relative to enstatite + liquid by 125 °C at ~8 kbar and by 175 °C at ~15 kbar (Fig. 1). Because F represents an additional component relative to the pure-H<sub>2</sub>O system, the melting equilibrium is divariant with respect to the KMASH curve. This is manifested by the presence of recrystallized, presumably more F-rich, phlogopite in experimental products from supersolidus conditions.

It has been known that F substitution for hydroxyl increases the thermal stability of phlogopite (see Munoz, 1984). Hydroxy phlogopite decomposes at less than 905 °C at pressures lower than 100 bars (Wones, 1967) as compared to the melting temperature of pure fluorphlogopite, which is between ~1345 and 1390 °C at 1 bar (Van Valkenburg and Pike, 1952; Shell and Ivey, 1969). The decomposition temperatures of intermediate fluorhydroxy phlogopites are unknown, however, as is the nature of the breakdown reactions with respect to dehydration, defluorination, or melting. Likewise, no experimental data exist on the subsolidus breakdown of fluorhydroxy phlogopite in the presence of quartz; therefore, further comparison of fluorhydroxy phlogopite melting to the pure-H<sub>2</sub>O system (Peterson and Newton, 1989a) is not possible.

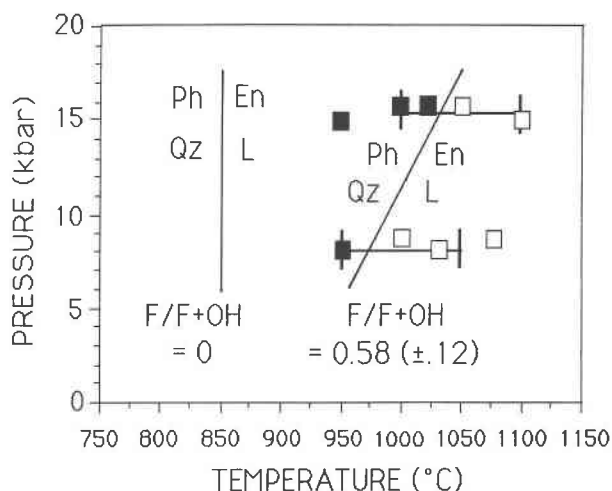


Fig. 1. *P-T* diagram illustrating key experimental data from Table 2. Results are compared to the vapor-absent melting of stoichiometric hydroxy-phlogopite + quartz in the F-free KMASH system (Peterson and Newton, 1989a).  $F/(F + OH)$  values refer to phlogopite. Open boxes represent experiments with products of abundant enstatite and glass (quenched liquid). Brackets indicate two-stage reversal experiments as described in text. Notice that the slope of the reaction changes from undefined in the KMASH system to approximately 140 bars/°C in the F-bearing system. Ph = phlogopite, Qz = quartz, En = enstatite, L = liquid.

Results similar to those of this study were observed for the vapor-absent melting of pargasite [NaCa<sub>2</sub>Mg<sub>4</sub>Al(Al<sub>2</sub>Si<sub>6</sub>)O<sub>22</sub>(OH,F)<sub>2</sub>]. Holloway and Ford (1975) reported that 43 mol% substitution of F for OH<sup>-</sup> increased the solidus of pargasite by 70–100 °C at 15 kbar. Combined with our results, this indicates that F is partitioned preferentially into phlogopite and pargasite relative to the vapor-undersaturated liquids produced upon melting of the respective minerals.

Giese (1984) and Munoz (1984) discuss the stabilizing solubility mechanism of F substitution for hydroxyl in mica. In trioctahedral phlogopite, the mechanism is based on the fact that the H<sup>+</sup> proton of the (OH<sup>-</sup>) radical is directed toward the interlayer K<sup>+</sup> cation by the Mg atoms. The substitution of F<sup>-</sup> for OH<sup>-</sup> is a means by which the interlayer cation K<sup>+</sup>-H<sup>+</sup> repulsion can be removed, with consequent stabilization of the structure.

The data presented here show that F substitution increases vapor-absent melting temperatures of assem-

TABLE 3. Representative analysis of glass quenched from 14.7 kbar and 1100 °C in equilibrium with quartz and enstatite

SiO <sub>2</sub>	57.76	52.93	56.37	60.02	59.90	55.24	50.77	56.01	62.37	57.14	55.42
Al <sub>2</sub> O <sub>3</sub>	12.63	12.03	13.06	12.86	13.17	13.82	12.14	12.49	10.56	13.42	13.01
MgO	12.52	19.13	13.59	13.66	12.02	11.90	17.50	16.31	12.77	13.37	14.44
K <sub>2</sub> O	12.64	10.47	12.18	12.06	12.09	13.61	11.00	11.43	9.36	12.32	11.54
F	3.32	2.74	2.32	0.98	1.88	4.15	3.84	3.00	1.00	2.79	3.86
Total	98.87	97.30	97.52	99.58	99.06	98.72	95.25	99.24	96.06	99.04	98.27

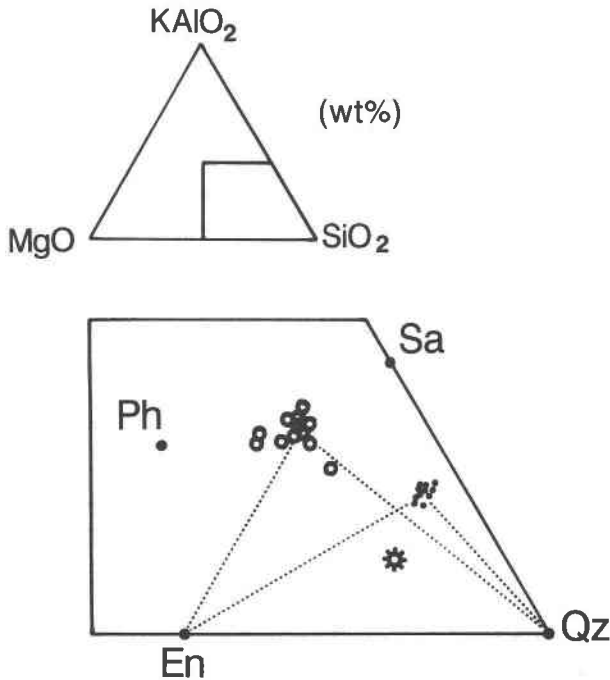


Fig. 2. Diagram comparing nonvolatile compositions (wt%) of quenched melt (glass) from the KMAH and KMAH-F system. Large open circles represent F-bearing melts quenched from 14.7 kbar and 1100 °C (~75 °C above solidus). See Table 3. Small solid circles represent F-free melts quenched from 10.0 kbar and 950 °C (~100 °C above solidus) (Peterson and Newton, 1989a). Sun symbol represents H<sub>2</sub>O and F-free bulk compositions for both systems. Dotted lines are tie lines for three-phase triangle enstatite-melt-quartz. Sa = sanidine. Other abbreviations are same as in Figure 1. See text for discussion.

blages in which micas and amphibole are key constituents. The effect of F on the H<sub>2</sub>O-saturated melting of mica or amphibole has not been investigated systematically. In the H<sub>2</sub>O-saturated haplogranite system, Manning (1981) demonstrated experimentally that the liquidus is lowered by 100 °C at 1 kbar upon addition of 4 wt% F to the system. Similarly, the vapor-saturated solidus is lowered by more than 165 °C.

### Melt compositions

Glass analyses from the F-free KMAH system are compared on a nonvolatile basis to analyses from this study in Figure 2. Although compositions of the F-bearing glasses are more variable than the F-free glasses, Figure 2 demonstrates clearly that quenched melt from this study contains significantly less SiO<sub>2</sub> than KMAH melts. The presence of 1–4 wt% F in the melt increases the proportions of quartz to other phases, relative to the F-free system. This is apparent if the two three-phase triangles, enstatite-quartz-melt, are examined with reference to the nearly identical nonvolatile bulk composition for both systems. The liquid composition shifts from the SiO<sub>2</sub>-rich side of the enstatite-sanidine join to the SiO<sub>2</sub>-poor side.

Consequently, in the simplified system, the melts change from granitic to lamproitic.

It can be seen in Figure 2 that melts become significantly richer in MgO and KAIO<sub>2</sub> upon addition of F to the KMAH system. F-bearing melts contain an average of 10 wt% more MgO, 4 wt% more K<sub>2</sub>O, and 3 wt% more Al<sub>2</sub>O<sub>3</sub> than the F-free melts (Peterson and Newton, 1989a). A trajectory from the cluster of analyses of KMAH glass, through the cluster of analyses from this study, to the MgO-KAIO<sub>2</sub> sideline yields the nonvolatile compositional control on the liquid variation. Accordingly, F enhances the solubility of a fictive mafic-alkali component with a MgO/KAIO<sub>2</sub> ratio of 55/45 by weight, or 2/1 on a molar basis.

The observed change in quenched liquid compositions is broadly consistent with the results of studies on other F-bearing systems. In F-bearing, H<sub>2</sub>O-free systems, spectroscopic and phase equilibrium data suggest that F preferentially complexes with network-modifying or charge-balancing cations (e.g., K and Mg) in the melt. This complexing results in an expansion of the stability fields of the more polymerized (Si-rich) phases (Foley et al., 1986; Luth, 1988a, 1988b). This is evidenced in the kalsilite-forsterite-quartz system in which the addition of F expands the stability field of enstatite relative to that of forsterite (Foley et al., 1986) and in the diopside-albite system in which the stability field of albite expands relative to that of diopside (Luth, 1988b). In H<sub>2</sub>O-F systems, there is an overall depolymerization of the melt structure (caused by H<sub>2</sub>O), but an expansion of the stability fields of the polymerized phases (caused by F) (Foley et al., 1986) compared to stability fields of polymerized phases in the pure-H<sub>2</sub>O system. This is apparent in the H<sub>2</sub>O-saturated haplogranite system, in which the addition of F expands the liquidus phase field of quartz relative to those of the feldspars (Wyllie and Tuttle, 1961; Manning and Pichavant, 1983). The above findings are consistent with the observation in this study that F expands the stability field of quartz relative to other phases, resulting in a more mafic-alkalic melt.

### Implications for biotite + quartz assemblages in granulite terranes

It is clear from our results that, under vapor-absent conditions, F-rich micas are stable to high temperatures in quartzofeldspathic rocks. Quartzofeldspathic rocks containing biotite with 1–5 wt% F have been reported from many granulite terranes including southern India (Leenanandam, 1969; Janardhan et al., 1982; Chacko et al., 1987), the Grenville Province of Canada (Lonker, 1979), and Namaqualand, South Africa (Waters, 1988). The higher F contents tend to be associated with the metasedimentary lithologies, although orthogneisses are also included in the references mentioned. The significant stabilizing effect of F indicates that vapor-absent partial melting during granulite grade metamorphism may be restricted to temperatures exceeding 950 °C, if the rock

contains F-rich micas. Furthermore, the residual micas will be progressively F rich.

The vapor-absent solidus temperatures of fluorhydroxy mica-bearing natural rocks may be different than those given by our experimental work. First and most importantly, a relatively sodic plagioclase becomes an additional reactant phase in the melting reaction. By analogy with the pure H<sub>2</sub>O system, this may lower the solidus by 20–50 °C (e.g., Thompson and Tracy, 1979; Waters, 1988). Secondly, the significant Fe content of natural biotite is likely to mitigate somewhat the stabilizing effect of F because of Fe-F avoidance in micas (Rosenberg and Foit, 1977; Valley et al., 1982). On the other hand, many biotite samples from granulites have high Ti contents, and it has been demonstrated that Ti stabilizes biotite to higher temperatures (Forbes and Flower, 1974; Tronnes et al., 1985). The cumulative effect of additional components is difficult to ascertain.

### Implications for the origin of A-type granites

Our experimental data also bear on models that have been proposed for the origin of A-type granites (Loiselle and Wones, 1979; Collins et al., 1982). A-type, or anorogenic granites, were originally thought to be restricted to rift-related tectonic settings (Bailey, 1978; Loiselle and Wones, 1979). However, recent studies indicate that they may be found in a variety of tectonic settings, including transcurrent faulting zones, continent-continent collision zones or even subduction zones (Whalen et al., 1987; Sylvester, 1989). Geochemically, A-type granites are characterized by high contents of Si, Na + K, Ga, Zr, Nb, and F, and low contents of Ca, Mg, Ba, and Sr relative to S- and I-type granites (Collins et al., 1982; Whalen et al., 1987). Petrographic and experimental studies indicate that these granites were emplaced in an almost completely molten state at temperatures possibly exceeding 900 °C (Collins et al., 1982; Clemens et al., 1986), significantly higher than temperatures of many other granitoid magmas.

To account for their high-temperature character and also for the fact that they commonly postdate the intrusion of other spatially associated granitoids, one currently popular model maintains that A-type granites were derived by the high-temperature, fluid-absent partial melting of previously melt-depleted source regions that contained halogen-enriched micas and amphibole (Collins et al., 1982; Clemens et al., 1986). Our experimental data are broadly consistent with this model, in that the substitution of F<sup>-</sup> for OH<sup>-</sup> in phlogopite does indeed stabilize the mica + quartz assemblage, thereby forcing the melting of any residual F-rich biotite to occur at relatively high temperatures. The gross inconsistency is, however, the somewhat surprising result that the melts generated are lamproitic in composition, not granitic as may have been predicted. It is probable that less mafic, more granite-like melts are produced by the melting of micas with lower F contents.

Considering the vapor-undersaturated melts generated

in the H<sub>2</sub>O and H<sub>2</sub>O-F systems (Fig. 2), a genetic connection between granitic melts and lamproitic melts may involve heterogeneities in the F contents of the lower crust. These heterogeneities could arise because of primary lithologic variations in the lower crust or because of the spatially variable influx of halogen-rich mantle-derived fluids (e.g., Bailey, 1978; Harris and Marriner, 1980). Whatever the cause of the heterogeneities, under vapor-absent conditions, F-rich pockets would remain melt-free or melt-poor during the lower-temperature melting events that produced granitic melts in adjacent F-poor rocks. A subsequent higher-temperature melting event could then generate melts of lamproitic composition from these F-rich regions. The potential genetic relationship between granitic and lamproitic-lamprophyric rocks (see Rock, 1987) warrants further investigation in light of the results of this study.

We have considered the melting of fluorhydroxy phlogopite + quartz, and the resultant magmas, only in the context of vapor-absent melting; alternate scenarios are possible. Several workers have suggested that a CO<sub>2</sub>-rich fluid may play an important role in the evolution of anorogenic granites, granulites, and associated rocks (Taylor et al., 1980; Wendlandt, 1981; Santosh and Drury, 1988). Data from recent experiments indicate that the addition of a 1:1 molar, CO<sub>2</sub>-H<sub>2</sub>O fluid significantly lowers the solidus of phlogopite + quartz assemblages relative to the vapor-absent and pure H<sub>2</sub>O-saturated solidi (Peterson and Newton, 1989b), with attendant melts ranging from granitic to lamprophyric in composition. The effect of this carbonic fluid on melting temperatures in the F-bearing system remains to be evaluated.

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