Fluorine in igneous rocks and minerals with emphasis on ultrapotassic mafic and ultramafic magmas and their mantle source regions

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Abstract

In reviewing the distribution of fluorine in igneous rocks it is clear that F abundance is related to alkalinity and to some extent to volatile contents. Two important F-bearing series are recognized: (1) the alkali basalt—ultrapotassic rocks in which F increases with increasing K_2O and decreasing SiO_2 contents; and (2) the alkali basalt—phonolite—rhyolite series with F showing positive correlation with both total alkalis and SiO_2. Detailed studies of series (1) show that F abundance in ultrapotassic magmas (lamproite, kamafugite, lamprophyre) occurs in descending order in the sequence phlogopite>apatite>amphibole>glass. Fluorine contents in the same minerals from fresh and altered mantle xenoliths may be several orders of magnitude less than those in the host kamafugite. For many lamproites, F contents correlate with higher mg# suggesting that F is highest in the more primitive magmas.

  Experiments at mantle conditions (20 kbar, 900—1400°C) on simplified F-bearing mineral systems containing phlogopite, apatite, K-richterite, and melt show that F is generally a compatible element. Additionally, low F abundance in minerals from mantle xenoliths suggests that F may not be available in mantle source regions and hence is unlikely to partition into the melt phase on partial melting. Melting experiments on the compositions of F-free and F-bearing model phlogopite harzburgite indicate that even small variations in F content produce melts similar in composition to those of lamproite.

KEYWORDS: fluorine, igneous rocks, mafic magmas, ultramafic magmas.

Introduction

FLUORINE is important in igneous rocks ranging from SiO_2-rich granitic pegmatites to SiO_2-poor alkali-rich kimberlite, lamproite, lamprophyre, kamafugite, and carbonatite. At a meeting of the Mineralogical Society in 1994 on 'Halogens in geological processes', only 2 of 10 papers dealt with halogens in igneous rocks. This reflects our knowledge of the abundance of halogens in these rocks but does not reflect our knowledge of the potential, particularly of F, in controlling the conditions involving partial

melting to produce some of these rocks. Many magmatic processes are governed by the effects of halogens in silicate glasses (Dingwall, 1988).

The understanding of the role of F in magmatism is hindered by: (1) Few data on the abundance of F in igneous rocks, partly due to difficulties of F analysis; (2) Scarcity of F data in micas, amphiboles and apatites found in SiO_2-poor, alkali-rich mafic and ultramafic rocks, and in their mantle-derived xenoliths. Such mineral data, easily obtained by modern electron microprobe, are often more important than whole rock data; (3) Poor understanding of the differences between the role of F and Cl, the only other important halogen in igneous processes.

This paper restricts discussion of halogens (F, C, Br, I) in igneous rocks to F because; (1) It is most abundant in magmatic processes; with Cl being more restricted to more SiO_2-rich rocks; and Br and I abundances restricted to very low ppm ranges to negligible (Schilling *et al.*, 1980; Unni and Schilling, 1978); (2) There is no indication that F is geochemically similar to the other halogens (Schilling *et al.*, 1980). Studies of halogens in oceanic regions suggest that Cl, Br and I are lost during degassing from the fluid phase whereas F remains in the melt according to these authors. Both Unni and Schilling (1978) and Schilling *et al.* (1980) relate the halogen contents in the lavas in the North Atlantic to models involving metasomatism by migrating fluids in the underlying mantle regions.

One reason for our lack of knowledge of F in igneous processes is that analyses have not been done. Fluorine often occurs in trace amounts that require special analytical methods and hence are often not analysed routinely. Fluorine contents of common important mineral reservoirs are also sparse; for example no F contents of micas, amphiboles and apatites in lamproites are given in Mitchell and Bergman (1991). Data for F distribution in magmatic rocks (Wedepohl, 1978) suggest that F is most abundant in alkaline rocks rather than in those with calcalkaline or tholeiitic affinities. For the purposes of F abundance, and hence importance to magmatic process, alkaline rocks of both SiO_2-rich and SiO_2-poor series are most significant (Fig. 1). This paper describes the abundance and behaviour of F in the SiO_2-poor alkaline (potassic) mafic ultramafic trend (Fig. 1).

Distribution trends for fluorine

Figure 1 is a scbematic 'cartoon' showing the distribution of fluorine into 4 igneous trends:-(1) An SiO_2-rich alkaline and peralkaline trend occurs with increasing F in the sequence of alkali basalt–trachyte–phonolite or rhyolite and their
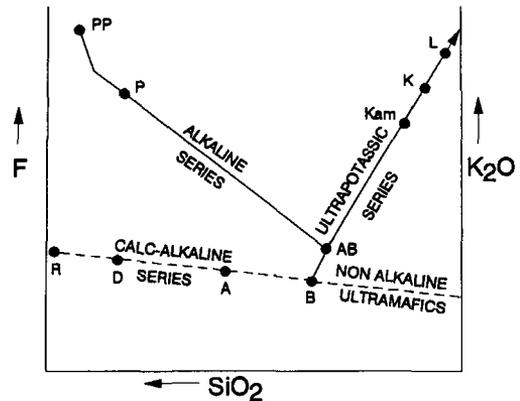

FIG. 1. Schematic diagram showing relationship between F, K_2O and SiO_2 contents in igneous rock trends. Axes are qualitative and therefore dimensionless. Abbreviations: A = andesite, AB = alkali basalt, B = basalt, D = dacite, K = kimberlite, KAM = kamafugite, L = lamproite, P = phonolite, PP = peralkaline phonolite, R = rhyolite.

peralkaline varieties. In these rocks, F occurs in mica, amphibole (particularly alkali amphibole), apatite, and rarer minerals such as villiaumite (NaF) occasionally found as a late-stage magmatic mineral, and sometimes as fluorite. (2) The SiO_2-poor alkali-enriched mafic–ultramafic trend with very high F/Cl. Fluorine is particularly abundant in the potassic-ultrapotassic rocks of this series where $K_2O \gg Na_2O$ (Foley *et al.*, 1987) and in which F increases with increasing K_2O as shown by Aoki *et al.* (1981). Figure 2 shows that the amount of F increases relative to K_2O in the sequence alkali basalt–kamafugite–kimberlite–lamprophyre–lamproite. In these rocks, the main F reservoirs are phlogopite, apatite and amphibole (often K-richterite). (3) An unenriched trend in mafic–ultramafic rocks from basalt to picritic compositions with F in low abundance and F-bearing minerals absent. (4) Rocks of the calc-alkaline trend (basalt–andesite–dacite–rhyolite) generally have lower F abundance than those of the alkaline and peralkaline trend (Wedepohl, 1978). Some of these, however, may exhibit a systematic increase in F with increasing SiO_2; the F is mainly in fluorite. The amounts of F in mica and amphiboles are not well known.

The relationships between F and alkalinity (Fig. 1) also apply to volatile abundances that are associated with both SiO_2-poor and SiO_2-rich alkali magmas. The principal volatile species appear to be H_2O and CO_2 (Foley, 1988; Foley *et al.*, 1987); both are important to the genesis and variability of alkaline and carbonatite magmas.
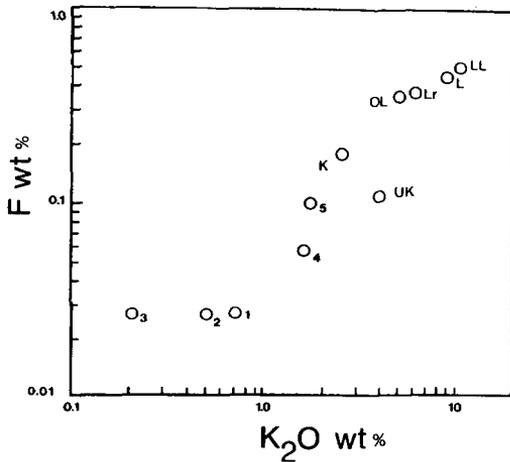
FIG. 2. Plot of K_2O vs. F for rocks of the basalt-ultrapotassic rock trend in Fig. 1: Modified from Aoki *et al.* (1981). Abbreviations: LL = leucite lamproite, L = all lamproites, Lr = lamprophyre, OL = olivine lamproite, K = kimberlite, UK = kamafugite, 5 = Hawaiian alkali basalts, 4 = continental alkali basalts, 3 = mid atlantic ridge tholeiites, 2 = hawaiian tholeiites, 1 = average continental tholeiites.

Many studies indicate potential roles for F in magmatic processes (see Fitton and Upton, 1987, and references therein) In some cases, hypotheses for the genesis of magmas have been proposed without researchers knowing whether the abundances of F are sufficient to support such hypothesis. One example is the role of F in redox melting (Foley, 1988) discussed later in this paper.

Early experimental studies of Kuellner *et al.* (1966) indicated that F had a large effect in lowering liquidus and solidus temperatures in volatile-rich alkali-silicate and carbonate systems, thus indicating that the onset of final crystallization in magmas that could be modelled by these simple systems might occur at lower temperature. The relative effectiveness of the volatiles in lowering temperatures was $F > Cl > H_2O \approx CO_2$.

The stability of phlogopite at high P, T, conditions indicates that fluor phlogopite is stable to a much higher temperature than hydroxy-phlogopite (Kushiro *et al.*, 1967), thus increasing the potential depth range and hence the importance of phlogopite as a F reservoir in the mantle. The increased stability of phlogopite in the presence of F results in changes in the topology of phlogopite-bearing systems such as $KAlSiO_4$–Mg_2SiO_4–SiO_2–H_2O–F (Foley *et al.*, 1986*a,b*) and fluor phlogopite–fluor apatite (Vukadinovic and Edgar, 1993). This change has important petrological implications (see later).

Most of the results of experimental studies can be related to the effect of F on silicate melt structures that have been the subject of intense study (Dingwall, 1988). The results of these experiments predict the behaviour of many physical parameters such as viscosity and density, important to many magmatic processes.

Fluorine and Cl also differ in their partitioning behaviour in a silicate melt–vapour–apatite system where Cl partitions into the vapour phase, whereas F remains in the solid (Candela, 1986; see also Schilling *et al.*, 1980). More recently Vukadinovic and Edgar (1993) and Edgar and Pizzolato (1995) have shown that F generally partitions into solids at mantle pressures in the systems hydroxy-fluor phlogopite–fluor apatite (Vukadinovic and Edgar, 1993) and in hydroxy-fluor phlogopite–hydroxy-fluor K-richterite, and hydroxy-fluor K-richterite–fluor apatite (Edgar and Pizzolato, 1995).

Studies of the abundance and relative distribution of F have been complemented in experiments that model the partitioning of F between the main mineralogical reservoirs and silicate-rich melts under upper mantle conditions. From these results the abundance of F in partial melts of probable mantle sources for kamafugitic magmas has been determined. These results can be used to consider the role of F in the genesis of magmas of ultrapotassic mafic-ultramafic affinities (Fig. 2).

Fluorine in the alkali basalt-lamproite magma series (the ultrapotassic trend)

Early work on F in these rocks was restricted to bulk rock analyses rather than minerals. Aoki *et al.* (1981) showed that continental alkaline rocks from the south-west USA, Deccan and South Africa, as well as those from the oceanic environment (Hawaii and the mid Atlantic ridge), showed good positive correlation between K_2O and F (Fig. 2) relative to other oxides. This relationship and correlation implied that these magmas were derived as partial melts from phlogopite-bearing mantle sources that were also the main F reservoir. For abyssal tholeiitic magmas, Aoki *et al.* (1981) suggested a pargasite-bearing mantle source, although a K-rich amphibole-bearing source might also be consistent with their results. Aoki *et al.* (1981) assumed that the upper mantle contains 1% modal phlogopite with 0.4 wt.% F. On partial melting, all of this phlogopite would be consumed and the amount of F that would be available for continental basaltic magmas would average 0.04 wt.%. Fluorine in abyssal tholeiitic magmas would come from amphibole and be slightly less.

As shown in Fig. 2, the F content of highly alkaline lamproitic and lamprophyric magmas with even

higher proportions of K_2O is 6–8 times greater than that of tholeiites and alkali basalts. Hence, if the same argument can be made that the relationship between K_2O and F indicates a phlogopite mantle source for F, the F in the mantle must be: (1) 6–8 times more than that of the source for continental alkali basalts, (2) 6–8 times richer in F but have the same abundance, or (3) stored in other hydrous minerals stable in the mantle or in minerals stable only at very high pressures in mantle material such as those reported by Edgar *et al.* (1994*b*). These arguments assume that F is present only in phlogopitic mica or pargasitic or K-richteritic amphiboles in the mantle source regions of magmas, because these minerals are known to be stable under appropriate $P-T$ conditions for partial melting in the mantle (Modreski and Boettcher, 1973; Foley, 1991). Apatite is also a likely mantle mineral host for F although the relationship between P_2O_5 and F in highly K-enriched rocks (Fig. 3) is not as pronounced as that of K_2O *vs.* F (Fig. 2).

There have been few systematic studies of F contents in minerals in igneous rocks. Aoki and Kanisawa (1979) found low F contents (100–400 ppm) in pargasites from websterites and from a lherzolite from Ittamone-gata Japan, consistent with their calc-alkaline trend (see Fig. 1). In contrast, phlogopite and K-richterite from various mantle rocks including peridotites, micaceous xenoliths and eclogites from South African kimberlite have F values up to 8000 ppm; still relatively low compared to phlogopite in ultrapotassic and related volcanic rocks.

Although no mineral analyses for halogens are given by Schilling *et al.* (1980) or Unni and Schilling (1978) for the rocks from Iceland and the Azores, they noted that the small F ions are associated with Sr and P whereas the large Cl and Br ions correlated with the larger cations Rb, Cs and Ba implying that F was unlikely to reside in phlogopite.

Jones *et al.* (1982) analysed micas from metasomatised mantle rocks (MARID) from Bultfontein kimberlite with F ranging from zero to 1.36 wt.% (usually 1.0 wt.% with an average of 0.63 wt.%).
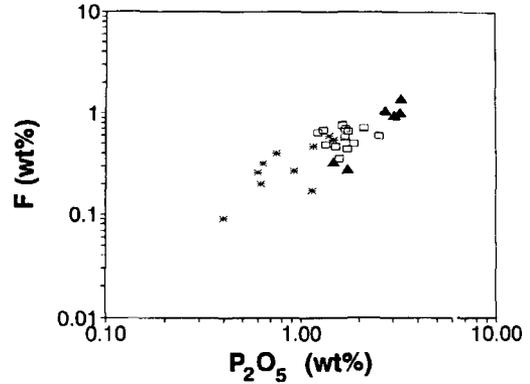

FIG. 3. Plot of log F *vs.* log P_2O_5 for rocks from lamproites from various localities. Key-filled triangles = Gaussberg, Antarctica; open squares = Leucite Hills, Wyoming; star = West Kimberley, Western Australia.

Smith *et al.* (1981) found F was 'substantial' in phlogopite, amphibole (excepting kaersutite) and apatite in peridotite xenoliths (Table 1). Good correlation between F and P in apatite (Smith *et al.*, 1981) led them to suggest that apatite was an additional source for F in oceanic basalts. They speculated that the F in kimberlitic magmas was derived from partial melting leading to the consumption of mica and apatite in the mantle peridotite source. These authors assumed that the partitioning of F was such that the amounts in the source regions were sufficient to account for the amounts in primary magmatic products such as kimberlites.

Experiments to constrain the distribution of F between melt and ultrapotassic ultramafic kamafugitic rock compositions by Edgar and Arima (1985) showed that F in phlogopite was independent of pressure but increased with decreasing temperature below the liquidus. They concluded that if phlogopite was the only F-bearing mineral, it preferentially entered phlogopite. However, in a single set of

TABLE 1. Fluorine contents of minerals in the upper mantle (after Smith *et al.*, 1981)

F-bearing Mineral	No. of analysis	Fluorine (wt.%)		Host rocks
		Average	Range	
Phlogopite (primary)	20	0.43	(0.15–2.75)	
Phlogopite (secondary)	21	0.20	(0.05–0.24)	peridotites
Phlogopite (total)	41	0.63	(0.01–2.94)	
Amphibole	8	0.59	(0.44–0.94)	MARID suite
Apatite	3	1.22	(0.45–1.88)	Kimberlite
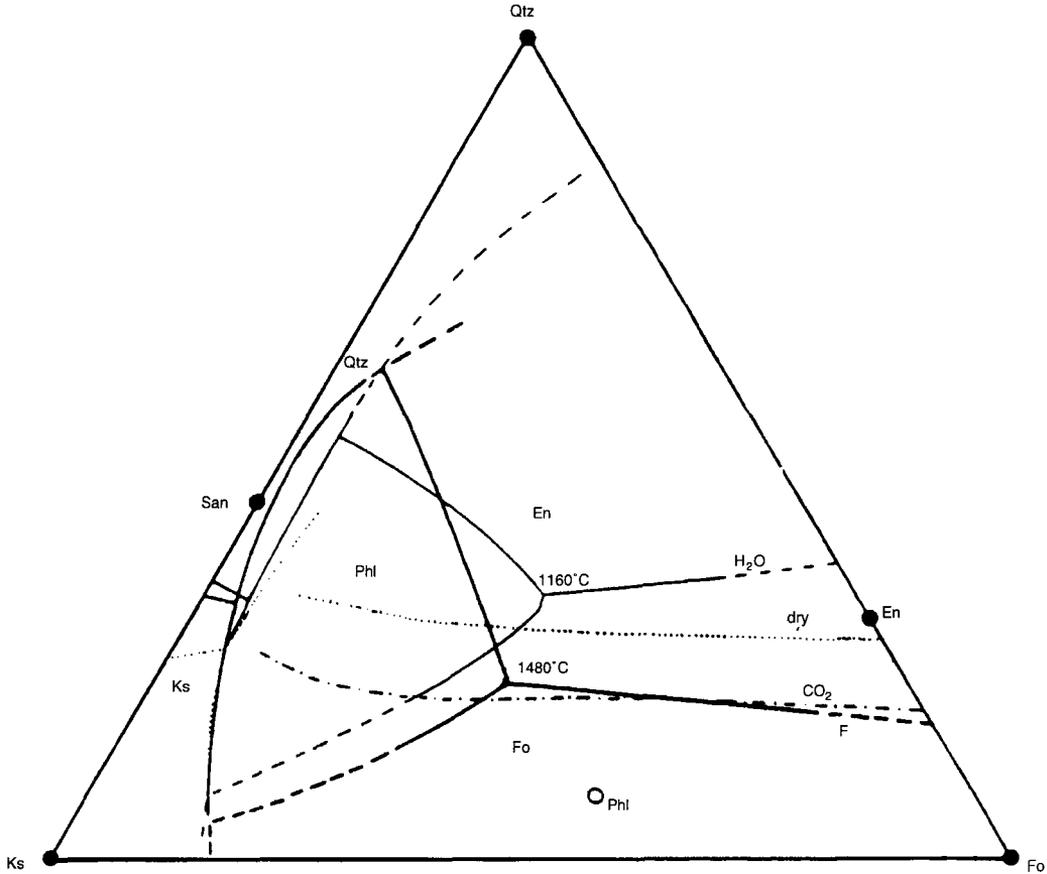
FIG. 4. Phase relations in the KAlSiO$_4$(Ks)–Mg$_2$SiO$_4$(Fo)–SiO$_2$(Qtz) system (without H$_2$O = dotted lines, H$_2$O saturated = full lines, CO$_2$ saturated = dotted and dashed line, and with 4 wt.% F = thick full line). Abbreviations San = sanidine, En = enstatite, Phl = phlogopite, Modified from Foley et al. (1986a).

experiments with both phlogopite and apatite as F reservoirs, F was partitioned in slightly greater amounts in phlogopite relative to apatite. The amounts of F in both minerals in the rocks used in these experiments was considerably higher than that in basalts and slightly higher than that in kimberlite (see Fig. 2). Edgar and Arima (1985) noted that F and K$_2$O contents in phlogopite from kamafugite, as well as the F/K$_2$O ratios were greater than F and K$_2$O and slightly greater F/K$_2$O than in phlogopite from basalt. They suggested that this higher ratio and greater abundance of F in phlogopite relative to apatite might suggest that mica was a more likely mantle reservoir for F.

  Foley et al. (1986a) investigated the Mg$_2$SiO$_4$–KAlSiO$_4$–SiO$_2$ system at 28 kbar with 4 wt.% F$_2^{0-1}$ added. This amount of F is much greater than the F

values in minerals in the mantle as established in later studies (Edgar and Charbonneau, 1991; Edgar et al., 1994a). Figure 4 shows the phase relations in the KAlSiO$_4$–Mg$_2$SiO$_4$–SiO$_2$ system without added volatiles, under H$_2$O- and CO$_2$-saturated conditions and with 4 wt.% F. The much larger field of phlogopite in the 4 wt.% F system, relative to that in the H$_2$O-saturated system, indicated an extended possible range of source compositions for K-rich magmas that can be generated in this system.

  For lamproitic magmas, Foley et al. (1986b) considered the effects of H$_2$O, CO$_2$, CH$_4$ and HF on partial melting of a phlogopite harzburgite source at different depths. According to Foley (pers. comm., 1992) F has a polymerizing effect in the aluminosilicate part of the melt produced from F-bearing systems. Hence the presence of large amounts of F

relative to H_2O in the model experimental system moves invariant points involving forsterite + enstatite + phlogopite + liquid to less SiO_2-rich compositions. Foley *et al.* (1986*b*) suggested that F-rich conditions result in high f_{O_2}. Based on the results of these experiments, Foley *et al.* (1986*b*) proposed a genetic distinction between what were later referred to as Group I (lamproites) and Group II (kamafugites) magmas (Foley *et al.*, 1987). In this model lamproite is a product of partial melting of a phlogopite harzburgite mantle formed at different depths under reduced f_{O_2} from volatiles in the H_2O–CH_4–HF-saturated conditions. In contrast, kamafugitic magmas formed at higher pressures and higher f_{O_2} with higher CO_2 and H_2O conditions such that $CO_2/(CO_2+H_2O)$ is high (Edgar, 1987). According to Foley *et al.* (1986*b*), the kamafugitic magmas in areas such as the West African Rift form from H_2O-poor conditions but with sufficient F that initial melts from the phlogopite harzburgite are characteristically MgO-rich and SiO_2-poor.

If the hypothesis of Foley *et al.* (1986*b*) is correct and lamproites are products of partial melting under more F-rich conditions than those required for kamafugites, the phlogopite harzburgite source for lamproites must have elevated F contents compared with that for kamafugite source regions. Furthermore, this hypothesis is based on the assumption that F must partition preferentially into the melt during partial melting of source rocks.

Foley (1988) used the concept of redox melting to model the genesis of leucite and olivine lamproitic and kimberlitic magmas. He proposed that kimberlites are a result of early stages of melting from a fertile oxidized zone at the base of the continental lithosphere. Later episodic melts of both olivine and leucite-bearing lamproitic compositions would be depleted in CO_2, Ca, Na, and Al. The efficiency of the redox melting model is in part dependent on the availability of F in the subcontinental mantle although it does not necessitate the excessive F used in Foley *et al.*'s (1986*a*) experiments.

Foley (1989*a,b*) showed that the chemistry of phlogopite in lamproites varied depending on the f_{O_2} and H_2O/CH_4 conditions. At constant pressure and temperature, Ba and Al increase whereas F, K and Si decrease as H_2O/CH_4 and f_{O_2} increase. From these experiments, Foley (1989*a,b*) proposed that phlogopite in the source regions of perpotassic (K/Al>1) melts must be F-rich and form under low f_{O_2} (Foley, 1989*a*).

Experiments on the stability of other F-bearing reservoirs at mantle conditions are few. Foley (1991) compared the stability of fluor K-richterite, hydroxy-K-richterite and fluor pargasite up to 50 kbar. He showed that both K-richterites were stable at 50 kbar whereas fluor pargasite broke down at $\geqslant 35$ kbar.

Based on experiments on F-rich armalcolite–phlogopite lamproite from 8–60 kbar (Edgar *et al.*, 1992; Edgar and Vukadinovic, 1993), Edgar *et al.* (1992) proposed that the F/H_2O ratio in the bulk composition affects the P–T conditions at which phlogopite first appears.

Abundance of F in mineral reservoirs in ultrapotassic magmas

The role of F in ultrapotassic magma genesis can only be resolved when the amounts of F in these rocks and their source regions, as determined from cogenetic, entrained mantle-derived xenoliths, are established. Additionally, F partitioning between partial melts and crystallizing solids must be known. Edgar and Charbonneau (1991) and Edgar *et al.* (1994*a*) have compiled data for F in phlogopite, amphibole, apatite, and glass in lamproites, kamafugites, and lamprophyres. In addition, these minerals and glass were determined from mantle-derived xenoliths, believed to include mantle source materials for the kamafugites of southwest Uganda and the West Eifel, Germany (Lloyd, 1987).

Figure 5 shows the relative distribution and abundance of F in minerals and glass in lamproite from five localities. The F in lamproite minerals usually occurs in the sequence F(phlogopite) > F(apatite) > F(amphibole) > F(glass). Edgar and Charbonneau (1991, Fig. 4) discuss the significance of the F distribution with respect to the number of F-bearing phases. Four of the 5 lamproite suites, have glass, with highest F in the glassy rocks of Gaussberg; but F was below detection limits in all Smoky Butte lamproite glass and some of the West Kimberley and Leucite Hills glass in lamproite (Fig. 5). The low F in some lamproite glass may be due to physical constraints such as cooling rates (Edgar and Charbonneau, 1991). Edgar *et al.* (1994*a*) found that the abundance and distribution of F in the same minerals in kamafugite and lamprophyre were comparable to those of lamproites. However, the average F between F-reservoirs in different rock types varies considerably (Table 2). The highest average F values in phlogopite, apatite and amphibole in kamafugite are significantly greater than those of lamproite with the minerals of lamprophyre being lowest. In all cases the F contents of glasses are much lower than those of mineral phases.

The results in Table 2 may be compared to the average F contents in the corresponding rock types (Fig. 2) in which the average F values in both olivine and leucite lamproites are ≈ 0.5 wt.%, with average F in lamprophyre <0.5 wt.%, and kamafugite at ≈ 0.1 wt.%. The higher F contents in the minerals of kamafugite relative to those of lamproite primarily
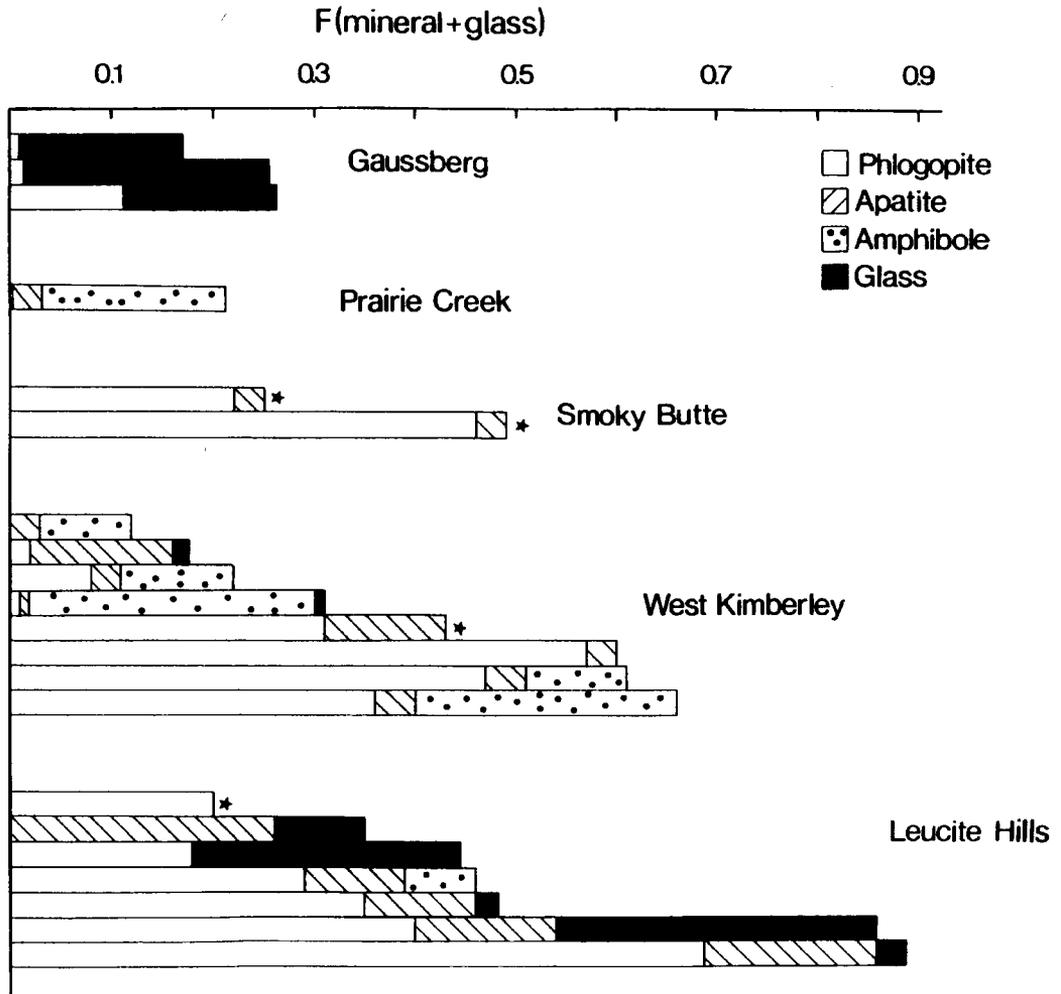
FIG. 5. Distribution of F between minerals and glass in lamproites from variou~s localities. Length of each motif indicates relative amounts (wt.% F × vol.% in rock) of F in each sample. Star indicates glass contains no detectable F (modified from Edgar and Charboneau, 1991).

TABLE 2. Average F (wt.%) values for different F reservoirs in various ultrapotassic rocks and mantle xenoliths

Rocks (# of rocks)	Phlogopite		Apatite		Amphibole		Glass	
	Average	Range	Average	Range	Average	Range	Average	Range
Lamproite (27)	2.18	(0.01−4.58)	2.82	(0.00−6.40)	1.98	(0.63−3.20)	0.52	(0.00−4.45)
Kamafugite (24)	3.50	(0.00−7.19)	3.37	(3.31−6.22)	2.40	(0.98−3.82)	0.35	(0.00−2.96)
Lamprophyre (8)	1.70	(0.48−3.49)	2.07	(0.96−2.81)	—	—	0.04	(0.00−0.16)
Mantle (21) xenoliths in kamafugites	0.26	(0.00−0.55)	1.74	(0.80−2.65)	0.22	(0.16−−0.28)	0.20	(0.00−1.80)

reflect the higher modal proportions of phlogopite (and occasionally apatite) in the lamproite. The differences may also be due to variable a_{H_2O}, a_F in the melts from which these minerals crystallized, and to different $D_F^{(mineral/melt)}$ (Foley, 1992a; Edgar and Pizzolato, 1995) Edgar and Charbonneau (1991) and Edgar *et al.* (1994a) also found a general decrease in F with decrease in mg# for phlogopite (Fig. 6a,b), amphibole (Fig. 6c) and glass. Occasionally F increases with decreasing mg# such as in the core-rim relationships of phlogopite in the lamproites from Leucite Hills (Fig. 6d). The relations shown in Fig. 6 indicate that, in general, F in minerals of ultra-potassic rocks decreases with increasing degrees of evolution as indicated by decreasing mg#. For apatite in ultrapotassic rocks there is some tendency for F to decrease from core to rim (Edgar, 1989) thus supporting the data from silicate minerals (Fig. 6).

Figure 7 shows the antipathetic relationship between BaO and F in apatite from West Kimberley lamproite (Edgar, 1989). This relationship may indicate that F is fractionated from apatite causing a resultant increase in Ba. Similar relations are not as pronounced in apatites in other ultra-potassic magmas (Edgar and Charbonneau, 1991; Edgar *et al.* 1994a), nor do they occur in other Ba-enriched phlogopite in some kamafugites (Edgar, 1992). Distinctive relationships between F and other elements are not obvious. Fluorine substitutes for OH in all mica, amphibole, and apatite structures and hence a relationship between F/(F+OH) in different minerals might give an estimate of the preference for F. Results from some of the lamproite localities (see Edgar and Charbonneau, 1991, Fig. 8) show no clear trends. Wagner and Velde (1986) suggested that F might be equally distributed between phlogopite and
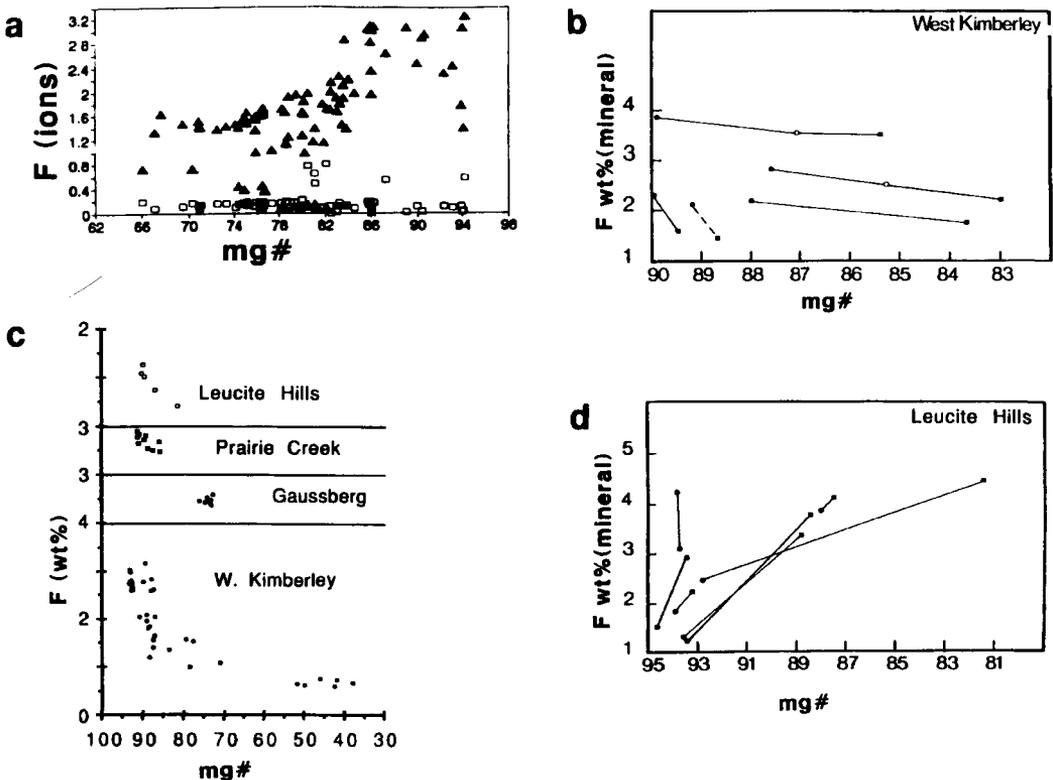
Fig. 6. Distribution of F in minerals with respect to mg# for ultrapotassic magmas and xenoliths. (a) F *vs.* mg# for phlogopites in kamafugites (closed triangles) and mantle-derived xenoliths (open squares) from southwest Uganda (modified from Edgar *et al.*, (1994a). (b) F *vs.* mg# for core-rim analyses of phlogopite and amphibole for lamproites from West Kimberley, Western Australia. Heavy full line = phlogopite, dashed line = amphibole, c = core, I = intermediate, r = rim (from Edgar and Charbonneau, 1991). (c) F *vs.* mg# for amphiboles from various lamproites (from Edgar and Charbonneau, 1991). (d) F *vs.* mg# for core-rim analyses of phlogopite from Leucite Hills lamproites. For abbreviations see Fig. 6b (modified from Edgar and Charbonneau, 1991).
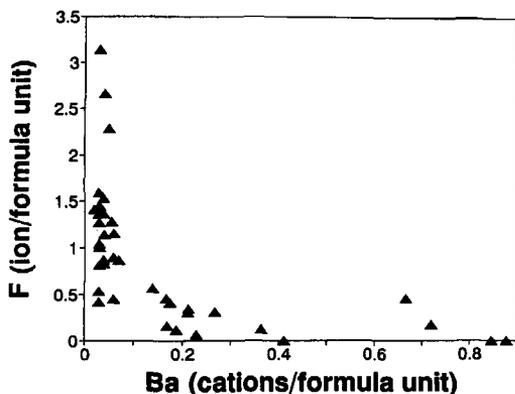
FIG. 7. F(ions/formula unit) vs. Ba(cations/formula unit) for apatites from West Kimberley lamproites.

apatite. Their F contents are much lower than those reported by Edgar and Charbonneau (1991) for minerals in similar rocks.

Fluorine contents of minerals in mantle xenoliths in ultrapotassic rocks

The role of F in the generation of magmas of ultrapotassic mafic–ultramafic affinities may begin with initial partial melting in the mantle (see previous section). This necessitates that F be sufficiently abundant in the source regions of these magmas. Such sources of ultrapotassic magmas may be sampled and transported by the magma as xenoliths. Ultrapotassic magmas are considered to ascend rapidly from their sites of generation, ranging from 70 to 100 km down to the base of the continental lithosphere. Such magmas generated at shallower levels are kamafugite and lamprophyre and often contain a wide spectrum of metasomatically enriched mantle xenoliths, some of which are likely source material of these magmas. In contrast, xenoliths from the deeper derived lamproite magmas are much more restricted in compositions and are often refractory (dunite) or only slightly incompatible and LIL enriched types.

The alkali-enriched clinopyroxenite mantle xenoliths hosted by the kamafugite of southwest Uganda and West Eifel, Germany, are believed to represent metasomatized mantle sources for their host magmas (Lloyd and Bailey, 1975; Lloyd, 1987). In partial melting experiments of a composition typical of the alkali clinopyroxenite, Lloyd et al. (1985) found that the initial melts have a composition very comparable to that of the most predominant lava in the southwest Ugandan area; this supports the concept that such xenoliths are parental to these kamafugite magmas.

Foley (1988, 1991) considered phlogopite harzburgite as the likely source of lamproite magmas based upon near liquidus assemblages in high $P-T$ experiments on olivine and leucite lamproites. Xenoliths of this composition are uncommon in lamproites for reasons not fully understood.

Edgar et al. (1994a) determined F contents of phlogopite, amphibole, apatite and glass in xenoliths from the West Eifel and southwest Uganda kamafugite lavas (Table 2). Based on average values from 21 xenoliths, the amount of F in phlogopite in these xenoliths is about 7 times less than the average F in phlogopite in the lavas. Average F in amphiboles in the xenoliths is also more than 3 times lower than the average amphibole in the kamafugite. Apatite in these xenoliths has the highest average F contents of any F-reservoir in these rocks (Table 2). The differences in F-enrichment for phlogopite and amphibole in the lavas relative to the same minerals in the mantle-derived xenoliths (Fig. 6a,c), indicate that the F in kamafugite magmas in both West Eifel and southwest Uganda is unlikely to have come directly from partial melting of these xenoliths. Additionally, these mantle xenoliths have much lower F than the 4 wt.% F used by Foley et al. (1986a) in experiments on the $KAlSiO_4–Mg_2SiO_4–SiO_2$ system used to model ultrapotassic magma generation.

Although it seems unlikely that the mantle-derived xenoliths are the source of the F in the kamafugitic magmas, the magmas themselves are likely partial melts of these xenoliths based upon detailed petrographic, chemical and experimental studies (Lloyd and Bailey, 1975; Lloyd et al., 1985; Lloyd, 1987, 1990; Edgar and Vukadinovic, 1992). The possibility that the minerals in these particular mantle xenoliths have anomalously low F contents also seems unlikely as these values (Table 2) are higher than those for the same minerals that occur in less metasomatized xenoliths (Jones et al., 1982; Smith et al., 1981). Only if F is a highly incompatible element $(K_D \ll 1)$ will partial melts of early melting mantle assemblages containing phlogopite $\pm$ amphibole $\pm$ apatite enrich melts in F sufficiently to produce the observed values in ultrapotassic rocks. Fluorine partitioning in simple model mantle systems (see below) does not suggest that F behaves incompatibly.

Experimental determination of F distributions for principal mantle reservoirs

Experimental studies have not been done on the distribution of F between the main F-reservoirs (phlogopite, apatite, amphibole). Such determinations are essential before any hypothesis for the mechanisms of F enrichment in ultrapotassic magmas can be made. Vukadinovic and Edgar (1993)

determined phase relations at 20 kbar in the Fe- and Ti-free systems hydroxy-phlogopite–hydroxy-apatite and hydroxy-fluor phlogopite–hydroxy-fluor apatite. In the F-absent system, the minimum melting temperature is 1225°C at 85 wt.% phlogopite, 15 wt.% apatite, whereas in the F-bearing system the comparable temperature at which melt first appears is 1260°C at about 66 wt.% phlogopite, 34 wt.% apatite (Vukadinovic and Edgar, 1993). Thus the presence of F enhances the initial melt composition in CaO and depletes it in SiO_2, K_2O, MgO, Al_2O_3, and H_2O relative to the melt in the F-absent system. This study showed that the $D_F^{Phlgopite/liquid}$ ranged from 2 to 1.25 depending on temperature and bulk composition whereas the $D_F^{apatite/liquid}$ is about 1. These results constrain the possible mechanism of enrichment of F during partial melting in this model mantle system because under the conditions of the experiments F tends to remain in the solid phases (phlogopite and apatite). Hence, the major source of F enrichment in ultrapotassic magmas cannot come directly from early melting of phlogopite and/or apatite in the upper mantle.

Studies of the systems hydroxy-fluor K-richterite–hydroxy-fluor apatite, and hydroxy-fluor phlogopite–hydroxy-fluor K-richterite have also been investigated at 20 kbar (Edgar and Pizzolato, 1995) to complement the study of Vukadinovic and Edgar (1993). Chemically, these systems are more complex than the hydroxy-fluor phlogopite–hydroxy-fluor apatite system. Results from both studies showed: (1) The minimum melting temperature occurs in systems with hydroxy-fluor K-richterite; hydroxy-fluor phlogopite is most effective in altering minimum melt compositions. (2) The minimum liquid compositions are controlled by bulk compositions of the end-member components in the systems, and possibly by buffering by non F-bearing minerals due to dissociation of phlogopite and K-richterite in these systems. (3) Distribution coefficients between F-bearing K-richterite, phlogopite, apatite and coexisting melts are ⩾1 to slightly <1, and are functions of temperature and bulk compositions. Fluorine, therefore, generally behaves as a compatible element in these simple systems. These distribution coefficients are in general agreement with the sequences of F distribution in these minerals in ultrapotassic rocks (Edgar and Charbonneau, 1991; Edgar *et al.*, 1994*a*). The compatible nature of F precludes F-enrichment in ultrapotassic magmas being derived directly from partial melting of mantle xenolithic material because insufficient F is likely to enter melts from minerals that have low F contents. At depths corresponding to 20 kbar, phlogopite, apatite and amphibole may not be the source of the F enrichment in such magmas, nor can F be effective in redox processes in the mantle

(Foley, 1988). Preliminary results at 30 kbar suggest that pressure has no significant influence on F partitioning in using these systems. This is in agreement with results of Edgar and Arima (1985) involving more complex F distribution between phlogopite and melt.

Effect of F and other volatiles on the composition of partial melts of model mantle sources of ultrapotassic magmas

The source materials and volatile conditions present at partial melting to produce the major varieties of ultrapotassic magmas are variable. Few experiments have been done to determine the compositions of partial melts under different volatile conditions as discussed by Foley *et al.* (1987). Kamafugitic magmas in southwest Uganda contain mantle xenoliths of alkali clinopyroxenite and appear to be partial melts of this source. Using this alkali clinopyroxenite as a model mantle source, experiments at 30 kbar by Lloyd *et al.* (1985) indicated that small degrees of partial melting resulted in compositions comparable to kamafugites. Although this model source composition contained both F and H_2O, CO_2 was the principal volatile. These authors determined that at 25% partial melting, the melt composition was very similar to that of the most abundant kamafugitic volcanic rock in the southwest Ugandan area. In contrast, at lower pressure (20 kbar), Lloyd *et al.* (1985) showed that the composition of the minimum partial melt did not correspond to that of a kamafugitic magma. This suggested that the source regions might be restricted to a minimum depth or that the sources of such magmas vary with depth.

For lamproitic magmas, Foley (1990) suggested that phlogopite harzburgite is a likely source with H_2O and HF producing redox melting conditions. The low F found in potential mantle source assemblages (Edgar *et al.*, 1994*a*) casts doubt on redox conditions but does not disqualify a phlogopite harzburgite source. Although phlogopite harzburgite xenoliths are rarely found in lamproites (Mitchell and Bergman, 1991) in contrast to the common occurrence of phlogopite-bearing clinopyroxenites in kamafugite, phlogopite harzburgites are sufficiently enriched in K and other LIL and incompatible elements to produce lamproite magmas.

In order to assess whether a model phlogopite harzburgite with and without minor F is a reasonable source for lamproitic magmas, experiments were done to determine compositions of partial melts of the model phlogopite harzburgite under F-poor (F = 0.02 wt.%) and F-present (F = 0.12 wt.%) conditions at 30 kbar. Phases between liquidus and solidus and the composition of melts at low degrees of melting of

TABLE 3. Experiments on a model phlogopite harzburgite composition

| | Starting material phlogopite harzburgite | | Observed glass composition (recalculated to 100%) | | Olivine lamproites (after Sobolev et al.,1989) | |
	(0.02 wt.% F)	(0.l2 wt.% F)	8% melt	10% melt	1	2
SiO_2	47.64	46.35	49.51	39.38	42.85	41.52
TiO_2	0.38	0.38	1.18	2.14	2.76	2.68
Al_2O_3	2.81	2.77	9.83	9.50	3.92	3.54
Cr_2O_3	0.16	0.15	0.46	0.00	0.14	0.00
FeO_T	7.15	6.97	5.04	5.76	8.20	8.01
MnO	0.12	0.12	0.07	0.06	0.18	0.13
MgO	38.96	37.94	28.46	32.30	26.19	26.90
CaO	1.39	2.62	0.68	2.07	5.12	4.38
BaO	0.04	0.04	0.00	0.08	0.00	0.00
K_2O	0.81	0.81	4.61	6.50	1.59	4.10
Na_2O	0.09	0.08	0.11	0.08	0.40	0.36
H_2O^+	0.30	0.30	0.00	0.00	3.50	4.13
H_2O^-	–	–	–	–	–	1.60
CO_2	–	–	–	–	0.20	0.19
P_2O_5	0.00	1.20	0.00	1.44	1.48	0.62
F	0.02	0.12	0.09	1.05	0.60	0.20
Cl	0.00	0.01	0.00	0.08	0.00	0.00
Total	99.87	99.86	100.04	100.46	97.13	98.36
O = F+Cl	0.01	0.05	0.04	0.46	0.25	0.08
Total	99.86	99.81	100.00	100.00	96.88	98.28

both F-poor and F-rich starting compositions are shown in Table 3 and Fig. 8. The difference in the F and K_2O contents in each melt caused by differences in the amounts of phlogopite and apatite crystallized from each bulk composition are given in Table 3. Also included in Table 3 are the compositions typical of olivine lamproite considered by Sobolev et al. (1989) to have formed as partial melts at 55 kbar.

Figures 8a,b and Table 3, show that about 8–10% partial melting of a phlogopite harzburgite can produce a melt whose composition is comparable to that of olivine lamproite, excepting for lower Al_2O_3 (Fig. 8a) and K_2O, and higher FeO (Fig. 8a), and CaO. In the presence of even a small percentage of F, partial melts occur at similar temperatures ($\approx 1175°C$) but have lower SiO_2 and higher MgO and K_2O. The sequence of crystallization of this type of melt (in which the F was added as fluor apatite) is slightly different (Fig. 8a,b).

These preliminary results show that lamproitic melts can form in the absence of appreciable F by relatively low degrees of partial melting at shallower mantle depths than postulated for a phlogopite harzburgite source (Foley, 1990). Recently, Foley (1992a,b) suggested that a more complex genesis for lamproites in his veined mantle–wall rock interaction model.

Alternate mechanisms for F-enrichment

The low F contents in minerals of mantle source regions relative to those in lavas, and the experimentally determined compatible nature of F in model mantle systems, suggest that alternate hypotheses to partial melting of F-enriched sources in the mantle may be required to explain the enrichment in F in ultrapotassic magmas. Alternatively, a different mantle source for F than the ones considered here, and of F-enrichment processes post-partial melting must be considered.

Mantle sources of F might involve veined–wall rock mantle melting as suggested most recently by Foley (1992a,b). The validity of this concept is difficult to assess experimentally but the presence of veins of metasomatized mantle material is common in mantle xenoliths (Nixon, 1987). The metasomatized material may be altered to an assemblage largely consisting of phlogopite (glimmerite). The F contents of phlogopite in such glimmerite are poorly known. Preliminary results (Edgar, unpublished) of mica analyses from glimmerites from southwest Uganda and the Christopher Island Formation, N.W.T. Canada (Peterson et al., 1994) show F contents are not significantly higher than those of phlogopite from unaltered mantle xenoliths that
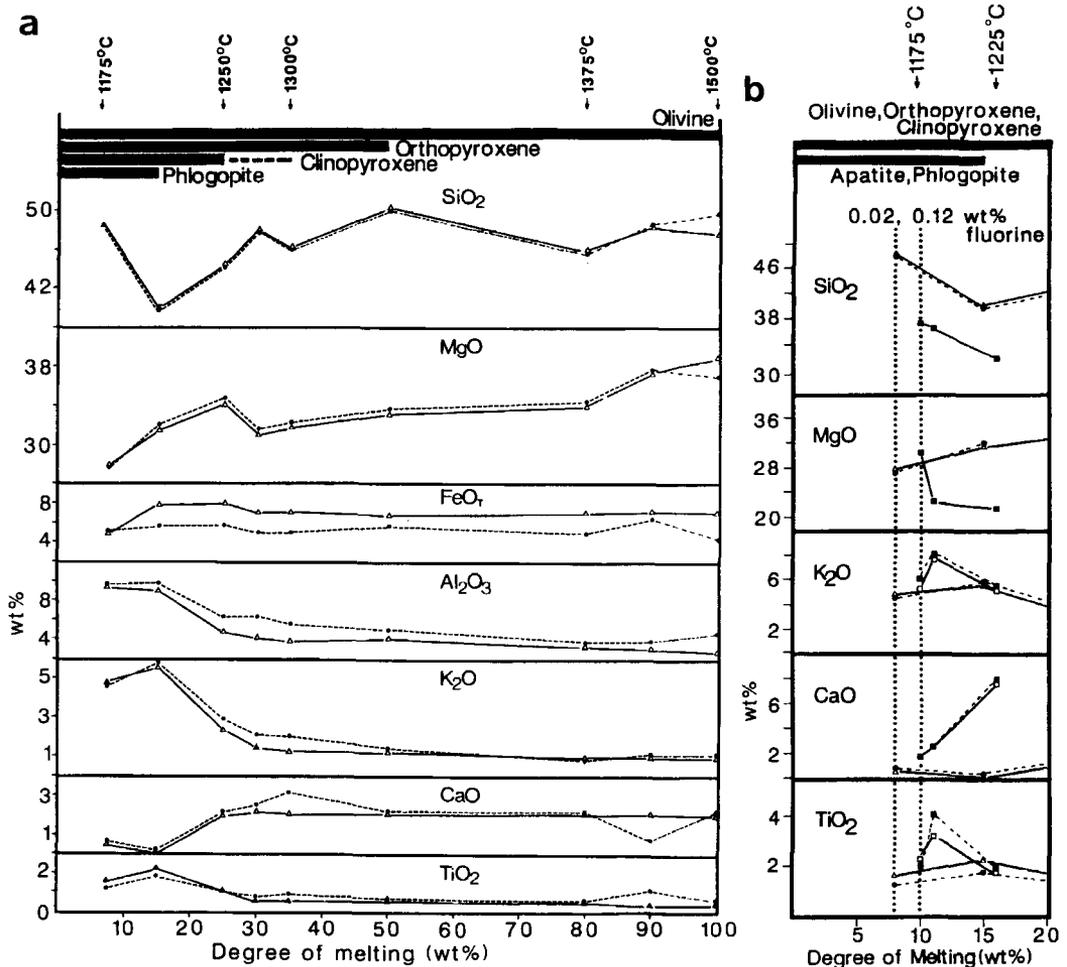
FIG. 8. Phase relations and melt compositions for partial melts determined at 30 kbar of a model phlogopite harzburgite composition (Table 3); (*a*) with F = 0.02 wt.% (*b*) with F = 0.02 and 0.12 wt.%. Abbreviations: heavy full lines = limit of stabilities of different crystallizing minerals, full lines = calculated values of glass compositions based on least squares mass balance calculations, dashed lines = analysed compositions of glass determined by electron microprobe, FeO_T = total iron as FeO, temperatures as °C are given along the top edge of figure and degrees of partial melting (wt.%) along the lower edge. Vertical dotted lines represent first glass compositions for phlogopite harzburgite with 0.02 and 0.12 wt.% F.

otherwise have the same chemistry (see Table 4). The distribution of F between phlogopite and apatite in these altered rocks (Table 4) does not necessarily indicate that the F-bearing minerals are in disequilibrium because the conditions of alteration may be dissimilar.

Potential enrichment in F from either a vein-wall-rock source (eg. Foley, 1992,*a,b*) or during ascent is difficult as long as F partitions preferentially into solids. The F contents of many potential wall rocks is

quite large, particularly for alkaline country rocks (Wedepohl, 1978). However, under large scale melting conditions of such rocks the ascending ultrapotassic magma may be significantly enhanced in F.

Another possible mechanism to explain F-enrichment in ultrapotassic magmas would be the presence of a very F-enriched source material other than the 'standard' mica, amphibole and apatite. Edgar and Pizzolato (1995) detected a mineral of approximate

TABLE 4. Fluorine contents of minerals in altered mantle xenoliths (glimmerite) from (a) Christopher Island Formation, NWT, Canada lamproites and (b) Southwest Ugandan kamafugites

	Average F (phlogopite)	Average F (apatite)
(a) lamproite hosted xenoliths–Christopher Island Formation NWT		
	0.52 (17)*	2.21 (26)
(b) kamafugite hosted xenoliths–Southwest Uganda		
	0.27 (17)	0.19 (2)

* bracketed figures indicate number of analyses

composition $(K_6Na_2)Mg_9F_{26}$ $(F\sim42$ wt.%) in the products of experiments at 20 kbar and 900–1000°C in the system hydroxy-fluor phlogopite–hydroxy-fluor K-richterite. The stability of this unnamed phase is currently under investigation but, even if stable in only trace amounts, might provide an adequate mechanism for F enrichment, provided such a compound was consumed at an early stage of the partial melting process.

Degassing occurs in alkaline mafic magmas during ascent from mantle depths, therefore, based upon limited data in simple systems (Candela, 1986), Cl may be lost to the vapour phase during such a process (see also Schilling *et al.*, 1980) whereas F will remain primarily in solid phases. Loss of Cl and retention of F during degassing will subsequently enrich the residual magma in F. The enhancement of F in ultrapotassic magmas is likely a consequence of a combination of processes described above rather than to a single process.

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