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Fluorine and chlorine contents of phlogopites crystallized from ultrapotassic rock compositions in high pressure experiments: implication for halogen reservoirs in source regions

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Abstract

Phlogopite crystallized in suprasolidus high pressure experiments between 10 and 40 kbar from four ultrapotassic mafic–ultramafic rock compositions shows wide variations in F content (0.13 to 2.41 wt.%) and Cl below the detection limits (<0.03 wt.%). The rock compositions range from 0.02 to 1.59 wt.% F, with K/(K + Na) ratios of 0.41 to 0.94. For compositions in which phlogopite is the only F-bearing mineral, the F contents of phlogopite are higher than those of the rocks from which they crystallize and F in phlogopite increases with decreasing temperature and is not appreciably affected by pressure. These data suggest that F is preferentially incorporated in the phlogopite rather than in the liquid and that increasing F contents in phlogopite with decreasing temperatures are primarily a result of increasing crystal/liquid ratios. In one rock composition with coexisting apatite and phlogopite, F in the phlogopite appears to decrease with decreasing temperature and is slightly lower than in the rock composition. This suggests that in the presence of both F-bearing minerals, F is partitioned between them. Average F content of phlogopite in this study is about twice that of F in "primary" phlogopite from garnet lherzolite nodules in kimberlities although the range of F values is similar.

A compilation of F and K_2O contents in ultrapotassic rocks indicates higher K_2O and F and slightly greater F/K_2O ratios than in other basaltic rocks. A higher F/K_2O and greater abundance of phlogopite relative to apatite in the source regions for ultrapotassic magmas may account for this higher ratio. The higher ratio also implies that phlogopite rather than apatite may be the main reservoir for F in such regions.

Introduction

Analyses of F and Cl in mantle-derived rocks and their xenoliths, and in phlogopites, amphiboles and apatites in these rocks (Aoki and Kanisawa, 1979; Boettcher and O'Neil, 1980; Ishikawa et al., 1980; Dawson and Fuge, 1980; Aoki et al., 1981; Smith, 1981; Smith et al., 1981; Jones et al., 1982) indicate that these minerals may be the main reservoirs for halogens in the source regions for mantle-derived magmas. Phlogopites in mantle-derived xenoliths contain large amounts of F and lesser Cl in their (OH) sites (Aoki and Kanisawa, 1979; Boettcher and O'Neil, 1980; Aoki et al., 1981; Smith et al., 1981; Jones et al., 1982). Apatite in these xenoliths also contains high F and Cl contents and Smith (1981) proposed that apatite may be the primary source of the halogens in the mantle, with phlogopite being a secondary source. Excepting MORB-type basalts, the positive correlation between K_2O and F led Aoki et al. (1981) and Smith et al. (1981) to suggest that phlogopite is the main K_2O and F reservoir in the source regions for basaltic magmas. Except for kaersutite megacrysts, Smith et al. (1981) found that F values are substantial in phlogopites, amphiboles and apatites, whereas Cl is low in most phlogopites and in all amphiboles but variable in apatite.

As there are no high-pressure experimental studies on the halogen contents of these minerals, the role of pressure, temperature, and bulk compositions on the partitioning of F and Cl between these minerals is unknown (Smith et al., 1981). In this study we have analyzed phlogopites for F and Cl in suprasolidus experiments on bulk compositions of four potassic-rich mafic volcanic rocks (wolgidite, katungite, cedricite, olivine ugandite) to assess the effects of pressure, temperature and bulk composition on the amounts of F and Cl in the phlogopites. Compositions of the starting materials are given in Table 1.

Results of the experiments on the olivine ugandite were published by Edgar et al. (1980); those of the katungite and wolgidite by Arima and Edgar (1983a, b). Experiments on the cedricite are unpublished. In all cases, experiments were done in a 1.27 cm diameter piston-cylinder apparatus in which temperatures and pressures were calibrated at the kyanite–sillimanite transition at 22 kbar and 1300°C (Richardson et al., 1968) and at the albite = jadeite + quartz transition at 16.3 kbar and 600°C (Johannes et al., 1971). Both pressures and temperatures were well within accepted values. No frictional correction was applied to pressure and no pressure correction to the e.m.f. of the Pt-$Pt_{90}Rh_{10}$ thermocouples was used. Quoted pressures are considered

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Table 1. Compositions of starting materials

Sample	Katungite*	Ol-Ugandite**	Cedricite***	Wolgidite****
SiO_2	38.05	43.73	49.80	44.65
TiO_2	3.84	1.84	4.45	6.92
Al_2O_3	7.54	9.85	6.65	2.75
Fe_2O_3	8.41	3.04	5.59	6.94
FeO	2.80	8.03	1.04	1.36
MnO	0.21	0.17	0.037	0.078
MgO	13.55	20.18	9.62	14.39
CaO	13.90	8.70	7.01	3.81
Na_2O	1.31	1.54	0.34	0.83
K_2O	3.02	1.73	7.84	6.80
P_2O_5	0.95	0.37	0.92	1.41
F	0.27	0.02	0.268	0.590
Cl	0.02	0.02	0.16	0.12
H_2O^+	2.27	0.47	2.54	3.22
H_2O^-	3.00	0.08	1.66	2.18
CO_2	0.53	n.d.	0.64	0.93
BaO	0.25	0.03	1.08	2.62
Total (Less O = F.Cl)	99.56	99.71	99.54	99.30
$Mg/Mg+Fe_T$	0.70	0.77	0.74	0.77
K/K+Na	0.60	0.41	0.94	0.84

* From Arima and Edgar (1983a)
** From Holmes and Harwood (1937)
*** Analyst - K. Ramlal
**** From Arima and Edgar (1983b)

to be precise to ±0.5 kbar or less and temperatures to ±5°C. All experiments were done in sealed $Ag_{50}Pd_{50}$ capsules. In most experiments 15% H_2O was added to the starting materials (Table 2). At the pressures used these experiments represent vapor-absent conditions. The f_{H_2} was buffered by the graphite furnace and hence f_{O_2} is approximately >NNO external buffer (Brey and Green, 1977). For all compositions, selected runs were reversed over phase boundaries by holding the charge above the temperature of the boundary and reducing the temperature isobarically by 25°C to below the boundary. For the wolgidite composition, the reversal runs at 25 kbar and 1075°C gave comparable values to the original run under the same *P–T* conditions for fluorine, chlorine and major elements in the phlogopite (Table 2). Similar comparable analyses for orthopyroxene in this run (see Arima and Edgar, 1983b, Table 2) suggest that run times were sufficient to establish melt-crystal equilibria.

Based on these experiments, the role of phlogopite in the source regions from which these magmas were derived has already been discussed (Edgar et al., 1980; Arima and Edgar, 1983a,b). Amphibole does not occur in any of these experiments and apatite is present in only minor amounts (1–3%) in runs on the katungite composition (Arima and

Table 2. Averages and ranges of phlogopite. All analyses recalculated to 100%

	Wolgidite							
P(Kbar)	40	30	30	30	25	25**	22	20
$\overline{T}$(°C)	1150	1050	1025	1000	1075	1075	1075	1150
$\Delta\overline{T}$(°C)*	15	80	106	130	37	37	30	50
H_2O(wt.%) added	15	15	15	15	15	15	15	3
Time(min.)	10	30	40	45	30	20	30	25
Number of analyses	2	2	2	3	3	3	2	2
SiO_2	43.69 (43.42-43.95)	45.18 (44.86-45.50)	44.98 (44.84-45.12)	42.75 (42.32-43.48)	44.30 (43.93-44.60)	44.61 (44.03-45.10)	42.27 (42.20-42.33)	43.26 (43.07-43.45)
TiO_2	2.87 (2.83-2.90)	2.69 (2.35-3.03)	2.61 (2.41-2.80)	4.49 (3.24-5.94)	2.88 (2.79-2.90)	2.72 (2.65-2.81)	7.27 (6.84-7.69)	5.69 (5.58-5.79)
Al_2O_3	11.29 (11.25-11.32)	11.01 (10.88-11.13)	10.93 (10.58-11.27)	11.44 (11.41-11.49)	12.02 (11.42-12.51)	11.16 (10.90-11.30)	9.87 (9.81-9.92)	12.12 (12.11-12.13)
FeO***	6.31 (6.05-6.56)	5.37 (5.16-5.58)	6.26 (5.77-6.74)	5.66 (5.33-6.23)	4.89 (4.84-4.91)	4.44 (4.17-4.83)	5.96 (5.83-6.09)	4.15 (4.03-4.26)
MnO	0.00	0.00	0.00	0.13 (0.00-0.22)	0.00	0.00	0.00	0.00
MgO	23.33 (23.25-23.41)	24.50 (24.07-24.93)	24.10 (23.85-24.35)	22.87 (22.33-23.22)	25.26 (24.84-25.85)	25.56 (25.14-26.00)	22.68 (22.44-22.91)	22.85 (22.78-22.91)
CaO	0.00	0.00	0.07 (0.00-0.14)	0.14 (0.12-0.16)	0.05 (0.00-0.14)	0.00	0.15 (0.13-0.17)	0.00
Na_2O	0.27 (0.0-0.54)	0.00	0.00	0.33 (0.00-0.56)	0.12 (0.00-0.38)	0.00	0.39 (0.37-0.41)	0.00
K_2O	10.99 (10.78-11.20)	10.10 (9.32-10.87)	9.77 (9.10-10.43)	10.72 (10.12-11.40)	9.57 (8.97-9.87)	10.39 (10.17-10.58)	10.34 (10.27-10.40)	10.32 (10.20-10.44)
F	1.27 (1.23-1.31)	1.16 (1.13-1.18)	1.30 (1.25-1.34)	1.46 (1.29-1.58)	0.89 (0.72-1.04)	1.13 (1.07-1.17)	1.11 (1.03-0.18)	1.61 (1.59-1.66)
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Original Total	96.39	94.60	96.30	97.05	96.17	95.25	97.97	96.14
Mg/Mg+Fe***	0.87	0.89	0.87	0.88	0.90	0.91	0.87	0.91

Edgar, 1983a). We have also analyzed phlogopites from unpublished experiments on a cedricite composition. The bulk compositions of these potassic-rich mafic volcanic rocks (Table 1) are very suitable for determination of the relationship of F and, to a lesser extent, Cl in phlogopites to pressure, temperature and bulk composition as these rocks have very high K_2O, F and Cl contents.

Data sources

Fluorine and chlorine analyses of phlogopites crystallized from 16 runs on these bulk compositions form the basis of this study. Phlogopites in these runs have been reanalyzed for major oxides as well as for fluorine and chlorine. Only primary phlogopites as opposed to "quench" varieties were used (see Arima and Edgar, 1983b). Nine of these runs are from a wolgidite from the West Kimberley area, Western Australia. In this composition (Table 1), phlogopites crystallized between 950 and 1150°C, and between 10 and 40 kbar represent suprasolidus conditions but do not occur on the liquidus (Arima and Edgar, 1983b, Fig. 1). Orthopyroxene, clinopyroxene and minor rutile are coexisting minerals. In a single run at 950°C and 10 kbar, phlogopite coexists with clinopyroxene, armalcolite and priderite [$(K,Ba)_{1.33}(Mg,Fe,Ti)_{8-x}O_{16}$]; the latter mineral being the only K-bearing mineral other than phlogopite.

Three phlogopites crystallized from a katungite (Table 1) from Southwest Uganda (Arima and Edgar, 1983a), were also analyzed. These samples, crystallized between 1050 and 1150°C, and between 15 and 25 kbar, coexist with clinopyroxene, minor titanomagnetite and minor apatite. In this composition, phlogopite, although also a suprasolidus phase, occurs farther from the liquidus than the phlogopite in the wolgidite (Arima and Edgar, 1983a, Fig. 1).

Two samples of phlogopite crystallized from an olivine ugandite composition (Table 1) from Southwest Uganda (Edgar et al., 1980) were analyzed. In this composition, phlogopite is restricted to just above the solidus between 1000 and 1100°C and 10 and 20 kbar (Edgar et al., 1980, Fig. 1) where it coexists with olivine, clinopyroxene, and minor chromite.

Two phlogopite analyses were also used from unpublished experiments on a cedricite from the West Kimberley area, Western Australia (Table 1). For this composition, phlogopite occurs along with clinopyroxene and very minor rutile as a liquidus phase at about 27 kbar. The phlogopites analyzed were crystallized at 20 and 30 kbar at 1025 and 1100°C respectively.

Table 2. (Cont.)

	Wolgidite	Cedricite		Katungite			Olivine-ugandite	
P(Kbar)	10	30	20	25	20	15	20	10
T(°C)	950	1100	1025	1070	1150	1050	1100	1000
T(°C)*	116	40	74	106	91	85	40	96
H_2O(wt.%) added	15	15	15	15	3	15	25	15
Time(min.)	60	15	45	45	30	130	30	25
Number of analyses	2	1	3	3	1	3	4	2
SiO_2	41.75 (41.45-42.05)	46.64	44.68 (44.42-44.85)	42.30 (42.21-42.48)	39.97	41.61 (41.29-41.96)	42.56 (42.06-42.89)	41.46 (41.06-41.85)
TiO_2	6.42 (6.27-6.57)	2.51	3.57 (3.53-3.62)	1.46 (1.35-1.62)	2.15	2.11 (1.88-2.30)	2.22 (1.86-2.59)	2.85 (2.84-2.85)
Al_2O_3	11.40 (11.32-11.47)	9.49	11.21 (11.01-11.49)	14.01 (13.85-14.18)	15.05	14.48 (14.32-14.59)	16.20 (15.91-16.42)	16.05 (15.73-16.36)
FeO***	4.42 (4.33-4.51)	4.99	5.55 (5.34-5.75)	5.11 (4.61-5.41)	5.85	5.09 (4.75-5.48)	6.97 (6.61-7.18)	8.28 (8.26-8.30)
MnO	0.00	0.09	0.00	0.00	0.00	0.10 (0.00-0.30)	0.00	0.00
MgO	22.91 (22.60-23.22)	24.71	23.64 (23.39-23.79)	26.42 (26.24-26.67)	25.19	26.03 (25.49-26.42)	23.16 (22.79-23.51)	21.88 (21.77-21.99)
CaO	0.07 (0.00-0.13)	0.00	0.00	0.00	0.20	0.20 (0.00-0.30)	0.00	0.15 (0.00-0.30)
Na_2O	0.00	0.00	0.00	0.00	0.65	0.00	0.00	0.76 (0.69-0.83)
K_2O	10.63 (10.48-10.77)	11.02	10.56 (10.52-10.59)	10.57 (10.46-10.69)	10.68	10.18 (10.00-10.32)	8.71 (8.04-9.22)	8.39 (7.69-9.09)
F	2.41 (2.33-2.51)	0.54	0.69 (0.65-0.72)	0.13 (0.11-0.14)	0.25	0.17 (0.16-0.18)	0.19 (0.12-0.28)	0.21 (0.18-0.23)
Cl	0.00	0.00	0.12 (0.00-0.17)	0.00	0.00	0.00	0.00	0.00
Original Total	98.30	94.08	95.15	93.48	98.13	93.51	94.49	96.62
Mg/Mg+Fe***	0.90	0.90	0.88	0.90	0.89	0.90	0.86	0.82

* Differences between liquidus temperature and crystallization temperature at given P

** This represents a reversal run (see Arima and Edgar, 1983b)

*** All iron as FeO or Fe^{2+}

Within the spectrum of ultrapotassic mafic rocks, the bulk compositions used appear to have primitive chemistry based on their $Mg/(Mg + Fe_T)$ values (0.70-0.77). They also represent a wide range of K-enrichment, ranging from the mildly K-enriched olivine ugandite ($K/(K + Na) = 0.41$) to the extreme K-enriched cedricite ($K/(K + Na) = 0.94$). Edgar et al., (1980) and Arima and Edgar (1983a,b) suggest that these rocks are partial melts of mantle sources, K-enriched relative to lherzolite.

Analytical methods

Phlogopites were analyzed for F, Cl and major elements using an automated CAMECA Camebax electron microprobe at the University of Manchester fitted with two wavelength-dispersive spectrometers (WDS) and a Link Systems 860–500 energy dispersive spectrometer (EDS). Specimens were coated with a 20 nm carbon film. Major elements and Cl were done on the E.D.S. system and F on the W.D.S. system. This instrument has a 40° take off angle and analyses were done with an accelerating potential of 15 kV, beam current of 14.5 nA and counting time of 100 sec. Data corrections were made using a ZAF-4/FLS (Statham, 1977) program with fluorite and halite as standards for F and Cl respectively. Because many phlogopite grains were <10 μm and the probe beam size was approximately 2–3 μm, accurate analysis for most samples was severely restricted with 2–4 spots being analyzed for each sample. Using these procedures, detection limits (2σ) for F and Cl were 0.04 and 0.03 wt.% respectively (T. Hopkins, written comm.).

Averages and ranges of major element analyses of the phlogopites, given in Table 2, were very comparable to those previously published for phlogopites in the wolgidite (Arima and Edgar, 1983b, Table 4), in the katungite (Arima and Edgar, 1983a, Table 6), in the olivine ugandite (Edgar et al., 1980, Table 8) and in unpublished analyses for the cedricite composition, using a MAC-400 microprobe.

Results

Table 2 lists the physical conditions of the experiments for each rock composition and the F and Cl contents of the phlogopites. Chlorine in all phlogopites except one ($Cl = 0.12$ wt.%) crystallized from the cedricite composition were below the detection limits and are not further considered. All analyses were recalculated to 100% to avoid slight error in F and K_2O contents caused by the variable totals (Table 2). This procedure results in slightly higher average values of F (<0.06) and K_2O (<0.65) but does not affect the conclusions. Similarly, most experiments were done with 15 wt.% H_2O added to the bulk compositions, therefore the F and Cl contents of these starting materials will be slightly lower than those listed (Table 1).

Fluorine in phlogopites and bulk compositions

Average analysis of F in all phlogopites (Table 2) is 0.91 wt.% (range 0.13–2.41) or 0.81 wt.% (range 0.13–1.61) if the extremely high value of 2.41 wt.% is ignored. Reasons for ignoring this analysis are discussed later. These averages and ranges are higher than those quoted by Smith et al., (1981) for primary phlogopites in garnet lherzolite xenoliths in kimberlites (average $F = 0.43$, range 0.15–0.73). Except for katungite, the average F analysis in phlogopites is higher than that of the bulk compositions from which they crystallize. Fluorine in phlogopites in the wolgidite ($F = 0.59$) are 1.38 (0.89–2.41) or 1.25 (ignoring the high value), in the cedricite ($F = 0.27$) are 0.62 (0.54–0.69), in the katungite ($F = 0.27$) are 0.19 (0.13–0.25) and in the olivine ungandite ($F = 0.02$) are 0.20 (0.19–0.21). The higher F in the phlogopites in the experiments indicates that F preferentially enters the phlogopite relative to the coexisting liquid (see Discussion). For the katungite composition, which has comparable F in the phlogopites and the bulk rock, both apatite and phlogopite occur in the experimental run. The average F content in the phlogopite from the wolgidite composition is higher than that from kimberlites and their nodules (Smith et al., 1981).

Chlorine in phlogopites and bulk compositions

Smith et al. (1981, Table 1) found higher Cl in primary phlogopites (average $Cl = 0.08$ wt.%) from peridotite nodules in kimberlites than those of phlogopites in the present study, in which with one exception Cl is below the detection limits (0.03 wt.%). In secondary phlogopites, Smith et al. (1981) report Cl contents (average 0.03 wt.%) less than those of primary phlogopites and close to the detection limits in this study. In the ultrapotassic rocks used in this study, the average Cl is 0.08 wt.% (range 0.02–0.16) which is higher than that for kimberlites (approximately 0.03 wt.%) given by Smith et al. (1981, Fig. 3).

Discussion

Relationships of F in phlogopites to crystallization temperatures

In Figure 1, the F contents of phlogopites from each bulk composition are plotted against the crystallization temperature below the liquidus (ΔT). This parameter was used in preference to actual crystallization temperatures as it accounts for the effect of increasing crystal/liquid ratios with decreasing temperatures. For the wolgidite, olivine ugandite and cedricite compositions, phlogopite is the only mineral in the experiments in which F is likely to occur. The data in Figure 1 suggest an increase of F in the phlogopites with increasing ΔT for the wolgidite composition. Based on two analyses for each of the cedricite and olivine ugandite compositions, a similar relationship may exist for these compositions. As increasing ΔT represents an increase in the proportion of all crystalline phases, the data suggest that F in successive residual liquids increases. In contrast, the katungite composition appears to have the opposite trend (Fig. 1), which may be due to this composition being the only one with apatite, which probably also contains F. The presence of F in apatite could not be verified by microprobe due to the fine grain size of the apatite. As apatite crystallizes at virtually the same temperature as phlogopite (Arima and Edgar, 1983a, Fig. 1a), residual liquids from this composition may not be as enriched in F as temperature decreases as those for the other bulk compositions.

For the wolgidite composition, two analyses do not conform to the overall trend (Fig. 1). The phlogopite with 2.41 wt.% F and ΔT of 116°C was crystallized at 10 kbar,

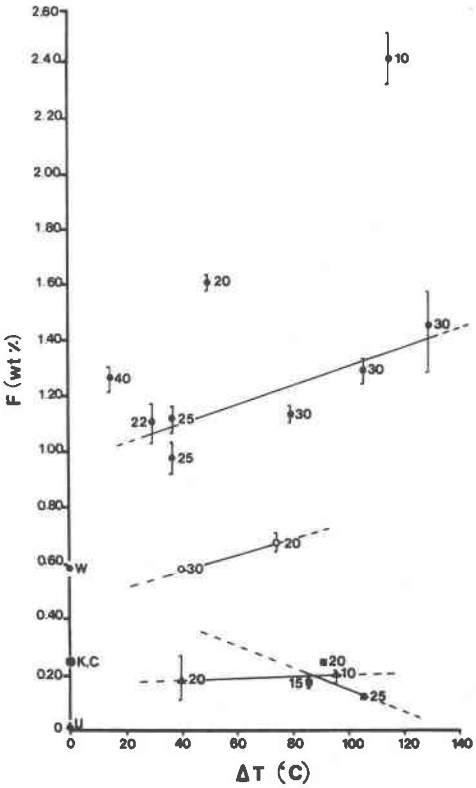

Fig. 1. Average F in phlogopites plotted against temperature below the liquidus (ΔT) for phlogopites crystallized from wolgidite (closed circles), cedricite (open circles), katungite (squares) and olivine ugandite (triangles), Vertical bars indicate ranges of F analyses for each sample. Numbers are the pressures used. F contents of rock compositions are shown on vertical axis.

950°C and coexists with priderite (the only K-bearing mineral in addition to phlogopite crystallized from any of the compositions). As shown by Arima and Edgar (1983b, Fig. 1a), this run crystallizes about 116°C below the liquidus temperature of wolgidite at 10 kbar but is only approximately 60°C below the appearance of phlogopite, in contrast to runs at higher pressure where phlogopite occurs much closer to liquidus temperatures. This implies that residual liquids at 10 kbar between liquidus temperatures and the appearance of phlogopite are more enriched in both K_2O and F than comparable liquids at higher pressures. At 950°C, K_2O in such liquids crystallizes as both priderite and phlogopite with F partitioning into the latter resulting in a very high F content relative to other phlogopites in the wolgidite and other compositions.

The second data point for the wolgidite composition which does not conform with the trend in Figure 1 is for the phlogopite with 1.61 wt.% F at ΔT of 50°C and 20 kbar. This is the only phlogopite in all of the experiments using wolgidite that was crystallized with 3 wt.% H_2O, (Arima and Edgar, 1983b). Two possible explanations may account for the higher F content in this sample. The lower H_2O content in the bulk composition will produce an enrichment of F relative to H_2O in residual liquids and hence F may be higher in the phlogopite when it crystallized about 50°C below the liquidus. Additionally, phlogopite in the 3 wt.% H_2O run at 20 kbar crystallizes about 25°C farther from the liquidus than in the 15 wt.% H_2O experiments (Arima and Edgar, 1983b, Fig. 1a) resulting in a higher proportion of F and K_2O in the liquid of the 3 wt.% H_2O runs than in that of the 15 wt.% H_2O runs. In future discussion, both runs not conforming to the trend are eliminated.

The relations shown in Figure 1 suggest that the F contents in phlogopites could be related to increased F in residual liquids with decreasing temperature. The possibility that partitioning of F between liquid and phlogopite is temperature dependent may affect this relationship but cannot be assessed.

Relationship of F in phlogopites to crystallization pressure

The relationship of pressure to the F contents of phlogopites is uncertain. For the wolgidite composition, phlogopites crystallized at 22, 25, 30, and 40 kbar ($\Delta T < 80$°C) have similar F contents (Fig. 1). Similarly, phlogopites crystallized at 15–25 kbar in the katungite, at 10 and 20 kbar in the olivine ugandite, and at 20 and 30 kbar in the cedricite compositions have very similar F contents (Fig. 1). This may suggest that F in phlogopites is not as dependent on pressure as on the dilution effects indicated by the ΔT–F relationship. The possibility of pressure influencing the partitioning of F between liquid and phlogopite cannot be determined but appears to be minimal.

Possible relationship of F and Cl in natural phlogopites to those in the experimental studies and correlation of F to major elements

A comparison of F and Cl contents of phlogopites in the rock starting compositions with those crystallized in the experimental products would be interesting. Unfortunately only the wolgidite and the cedricite contain phlogopite and analyses of phlogopites in both of these rocks (Mitchell, 1981) do not include F or Cl. Mitchell (1981, p. 243) indicates further geochemistry of the minerals in these rocks will be done. Absence of phlogopite in the katungite may be due to its reacting out to form olivine and liquid. This is supported by the experiments in which phlogopite does not appear below 10 kbar (Arima and Edgar, 1983a, Fig. 1). The relatively low K_2O and F contents in the olivine ugandite (Table 1) and the presence of groundmass olivine, leucite and glass (Edgar and Arima, 1981) suggest that phlogopite present at 10 kbar in the experiments could also have reacted out at lower pressure to produce these groundmass minerals.

Table 2 indicates no clear correlation between F and other elements in the phlogopite analyses. If halogen fractionation in these rocks is affected by crystal/liquid ratios, some correlation might be expected between F and Mg/(Mg + Fe) in phlogopite. The small variations in Mg/(Mg + Fe) for phlogopite (0.04 for each bulk composition) appears not to show systematic correlation with F contents (Table 2). However, if more data were available and if the Mg/(Mg + Fe) ratios in phlogopite were not controlled by other crystallizing minerals, then the possibility that such a correlation might occur cannot be ruled out.

Phlogopite as a reservoir for F in mantle source regions of ultrapotassic magmas

In high-pressure experiments on ultrapotassic mafic to ultramafic rock compositions, phlogopite is a liquidus or near liquidus mineral (Edgar et al., 1976; Arima and Edgar, 1983a,b) suggesting that phlogopite is present in the source regions for these magmas. On partial melting of such sources, the early liquid may contain high K_2O and H_2O, essential constituents of phlogopite (Arima and Edgar, 1983b). Smith et al. (1981) conclude that mica must be an early melting phase in a garnet lherzolite mantle source. If such phlogopites are the only reservoir for K_2O and F in the source region, a compatible relationship between K_2O and F in both the rocks and in the near liquidus phlogopites crystallized from these rock compositions might be expected. Figure 2 shows that for all compositions containing only phlogopite, there is a positive correlation between the F and K_2O contents of the rocks with those of the phlogopites crystallized closest to the liquidus. In contrast, for the katungite with both phlogopite and apatite, the correlation is negative implying that F may reside in both phlogopite and apatite.

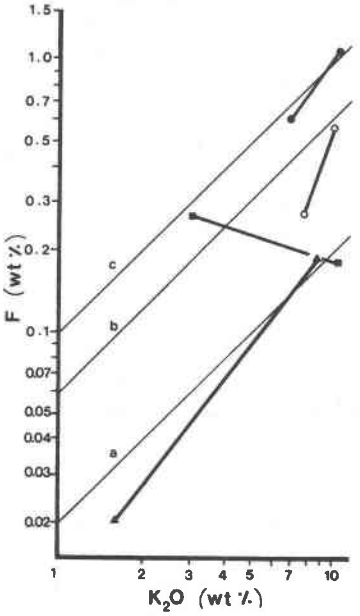

Fig. 2. Fluorine plotted against K_2O for rock compositions and phlogopites crystallized closest to the liquidus temperatures. Left hand point on each tie-line represents rock composition and right hand point phlogopite composition. Symbols are given in Fig. 1. Lines a, b and c are taken from Aoki et al. (1981, Figs. 1, 2) and show constant F/K_2O ratios of 0.02, 0.06 and 0.10 respectively.

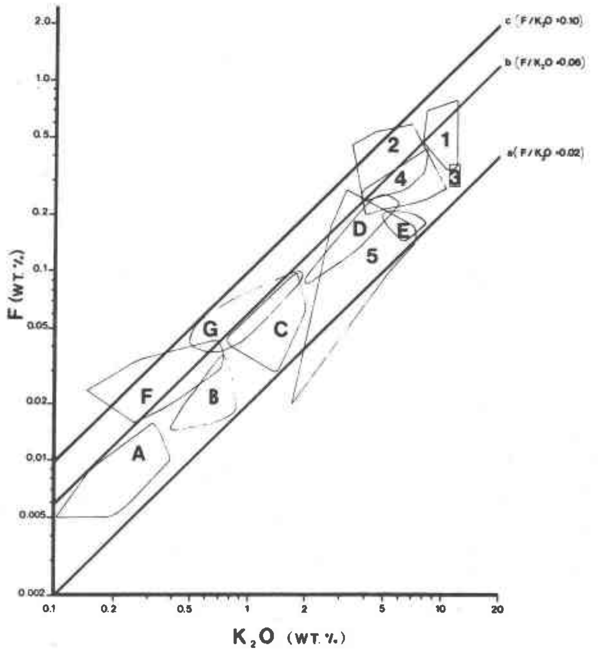

Fig. 3. Fluorine versus K_2O for ultrapotassic rocks compared to other mafic rocks indicating ranges of compositions; 1. Leucite Hills, Wyoming; 2. West Kimberley, Western Australia, 3. Gaussberg, Antarctica; 4. Somma, Italy; 5. Southwest Uganda. Lettered areas from Aoki et al. (1981, Figs. 1, 2). A. island arc tholeiites, B. continental olivine tholeiites, C. nephelinites and alkali basalts. D. nephelinites and leucitites, E. minettes, F. Hawaiian tholeiite series, G. Hawaiian alkali series. Lines a, b and c from Aoki et al. (1981, Figs. 1, 2) showing constant F/K_2O ratios.

Aoki et al. (1981, Fig. 1) showed a continuous trend of increasing F and K_2O in the sequence island arc tholeiites, continental olivine tholeiites, nepheline-bearing alkali basalts, nephelinites and a few ultrapotassic rocks that have a narrow range of F/K_2O ratios lying between lines a and b in Figure 2. These authors also showed a trend for the Hawaiian tholeiites and alkali basalt series with higher F/K_2O ratios lying between lines b and c in Figure 2. The tie-lines between rock and phlogopite compositions lie within, or close to, the limits of the island arc tholeiite, continental olivine tholeiite, alkali basalt, ultrapotassic series (Fig. 2 between lines a and b) and the Hawaiian basalts (Fig. 2, between lines b and c) of Aoki et al. (1981, Figs. 1 and 2). This relationship appears to support Aoki et al.'s (1981) conclusion that phlogopite may be the principal reservoir for F in mantle sources for ultrapotassic magmas but the absence of apatite in most of the starting compositions does not permit distinction between apatite and phlogopite as the primary F reservoirs (cf. Aoki et al., 1981; Smith et al., 1981).

As shown in Figure 3, we have supplemented Aoki et al.'s (1981) data for ultrapotassic rocks to include additional data from Leucite Hills, Wyoming (Yagi and Matsumoto, 1966; Carmichael, 1967; Kuehner et al., 1981), Gaussberg, Antarctica (Sheraton and Cundari, 1980) West

Kimberley, Western Australia (Arima and Edgar, 1983b; Jaques et al 1984), Somma, Italy (Savelli, 1967) and the lavas of Southwest Uganda (Higazy, 1954; Bell and Powell, 1969; Arima and Edgar, 1983a; Lloyd, unpublished data).

Although there is an overall concordance between the trend shown by Aoki et al. (1981) and the trend of Figure 3, in that the ultrapotassic rocks have the highest F and K_2O, there is a wider spread in these rocks, both in total and between different localities, than for the rock divisions of Aoki et al. (1981). The ultrapotassic rock localities richest in K_2O (Leucite Hills, West Kimberley, Gaussberg and Somma) tend to have higher F than those of the Southwest Ugandan province. The overall trend in ultrapotassic rocks ranges from the "a" line ($F/K_2O = 0.02$) to above the "c" line ($F/K_2O = 0.1$), which may imply that some of the source regions for these magmas have a F/K_2O ratio slightly greater than Aoki et al.'s (1981) trend for island arc tholeiite to ultrapotassic rocks ($F/K_2O = 0.02$–0.06). As shown on Figure 3, F/K_2O ratios for ultrapotassic magma sources may be relatively high. Such F/K_2O values for ultrapotassic rocks might be expected if these rocks are derived from an anomalous mantle source such as that represented by the clinopyroxenite type nodules with abundant phlogopite (Lloyd and Bailey, 1975, Fig. 1). If such phlogopite-rich nodules represent the source materials for ultrapotassic magmas, and if phlogopite is the only reservoir for F, then F/K_2O ratios in the phlogopites and hence in the source regions for such magmas might be higher than sources for less extreme alkali magmas.

Although F analyses in mantle-derived nodules in ultrapotassic rocks are very sparse, the average modal analyses of 84 nodules from ultrapotassic rocks of South West Uganda (Lloyd et al., ms.) give 35 wt.% phlogopite and 2 wt.% apatite. Assuming this nodule composition represents the source for the ultrapotassic magmas of the region, the higher proportion of phlogopite relative to that of apatite in these nodules suggests phlogopite as the most likely F reservoir. In comparison, the average of 10 garnet lherzolite nodules in kimberlites (Dawson, 1981) contains only 1% phlogopite and no apatite.

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