Mineralogical Magazine, June 1998, Vol. 62(3), pp. 373–380

Stability of F-Ti-phlogopite in the system phlogopite–sillimanite–quartz: an experimental study of dehydration melting in H_2O-saturated and undersaturated conditions

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ABSTRACT

Melt generation during granulite-grade metamorphism is believed to be controlled by the stability temperatures of biotite, whose breakdown provides H_2O and controls fluid-absent melting in the lower crust. In a simple KMASH system, the restite minerals crystallising due to incongruent melting of phlogopite depend upon the bulk composition. In an alumina-poor and silica-rich portion of the system (Phl + Qtz), enstatite appears with the melt, while in an alumina-rich system (Phl + Sil + Qtz) cordierite appears first instead of enstatite. Since the temperature of biotite stability is believed to be strongly controlled by its F and Ti content, it will have significant effect on the fluid-absent melting reactions during granulite-grade metamorphism of mica-containing granites as well as pelitic rocks in the deeper crust.

To understand such effects in an aluminous portion of the KMASH system, experiments were performed (between 850 and 1100°C and at 7, 10 and 12 kbar) with bulk composition containing 2Phl - 6Sil - 9Qtz, where natural phlogopite with F/(F+OH) = 0.39 and Mg/(Mg+Fe) = 0.96 was used. In runs with this charge and containing 5 wt.% of excess water, cordierite appeared around 920°C at 7 kbar and 990°C at 12 kbar, and it disappeared at about 1080°C with the appearance of 221 sapphirine. In fluid-absent runs, these boundaries marginally shift to higher temperatures (30–50°C). The enstatite which was distinctly absent in H_2O-saturated runs, crystallises in the high-temperature sapphirine field with up to 12 wt.% Al_2O_3 in H_2O-undersaturated runs. The enstatite formation with cordierite is perhaps inhibited due to the Al consumption by cordierite and instability of Al-free enstatite at temperatures of cordierite stability. Re-equilibrated phlogopite persists in both the cordierite and sapphirine fields. The temperatures of the beginning of phlogopite breakdown are about 100–140°C above those reported for reaction Phl + Qtz $\rightarrow$ En + Sa + L (Vielzeuf and Clemens, 1992) with F and Ti-free phlogopite, but are $\approx$50–100°C lower than the temperatures reported (Tareen *et al.*, 1995; Dooley and Patino Douce, 1996) for the same reaction containing F- and Ti- bearing phlogopite. The combined effect of the F and Ti content in phlogopite on its stability temperatures in the KMASH system has been found to be additive in relation to those containing only F or Ti. H_2O-saturated runs produced per-aluminous melts with $\approx$27 wt.% Al_2O_3 in the cordierite field and $\approx$23% Al_2O_3 in the sapphirine field. The H_2O-undersaturated runs produced melts rich in K_2O ($\approx$ 10 wt.%), SiO_2 (72.5 wt.%) and relatively poor Al_2O_3 (12 wt.%).

KEYWORDS: fluorine, titanium, sillimanite, dehydration melting.

Introduction

THE presence of F and Ti in natural biotite has significanct effects on the temperature of fluid-absent melting reactions associated with granulite-facies metamorphism of crustal rocks. There has been an increasing interest in the experimental study of the effects on the stability of micas and mica-bearing reactions. The increase in the thermal stability of F-bearing over OH mica was reported by Munoz and Luddington (1974), Peterson *et al.* (1991) and Valley *et al.* (1992), and a similar effect for Ti-bearing micas has been reported by Tronnes *et al.* (1985) and Patino Douce (1993). The combined effect of these two in the fluid-absent melting boundary for the reaction

$$\text{Phl} + \text{Qtz} \rightarrow \text{En} + (\text{Kfs}) + \text{L} \qquad (1)$$

was reported by Tareen *et al.* (1995). They showed an increase in the reaction boundary temperature by about 140°C relative to an F-Ti-free system (Vielzeuf and Clemens, 1992) with their natural phlogopite containing 1.31 wt.% TiO_2 and 3.5 wt.% F ($X_{Mg} = 0.97$ and $X_F = 0.39$). The study of Dooley and Patino Douce (1996) in the system Phl–En–Rt shows an increase in the thermal stability of F-Ti phlogopite in the assemblage Phl-En-Rt-L by nearly 300°C. Steven *et al.* (1997) in their experimental study of melt production from primitive metasedimentary protoliths found ilmenite as a product of the Ti-bearing systems (brought to the authors' notice by the referee).

While reaction 1 has been considered useful as a model for the melting of crustal rocks close to granitic composition (Bohlen *et al.*, 1983; Peterson and Newton, 1989; Montana and Brearly, 1989; Vielzeuf and Clemens, 1992), another simplified reaction that better represents the beginning of granulite-grade metamorphism in aluminous rocks is:

$$2\text{Phl} + 6\text{Sil} + 9\text{Qtz} \rightarrow 3\text{Mg} - \text{Crd} + 2\text{Kfs} + H_2O \ (2)$$

Reaction 2 using the Fe-bearing biotite instead of pure phlogopite was reported by Hoffer (1976) and Holdaway and Lee (1977). The Fe-free system has been recently studied by Tareen *et al.* (1997) between 3 and 10 kbar and up to 850°C; they reported the phase boundaries for the subsolidus reaction 1 as well as the melting reaction:

$$\text{Phl} + \text{Sil} + \text{Qtz} \rightarrow \text{Crd} + \text{L} \qquad (3)$$

The stability of cordierite has been studied by Newton (1972) and Bertrand *et al.* (1991) where cordierite breaks down to En + Sil + Qtz at high pressures (13 kbar) and to Spr + Qtz at high temperatures (>1050°C). Carrington and Harley (1995) have reported the phase relations in high-grade metapelites in KFMASH system. Based on the experimetnal data of Vielzeuf and Holloway (1988) and Patino Douce and Johnston (1991), they showed that the higher stability temperatures for biotite directly correlate with their F and Ti-content. However, the temperature interval of melting of biotite was shown to be inversely related to the X_{Mg} value of the biotite and at very high X_{Mg} values of >0.74, the melting interval for biotite reduced to zero. Considering the significant increase in the thermal stability of mica due to F and Ti content observed in reaction (1), it becomes equally important to study experimentally such an effect in pelitic compositions subjected to extreme granulite metamorphism, where sapphirine–enstatite assemblages are encountered along with partial melting. In this communication we report the fluid-absent melting and stability of F-Ti-bearing phlogopite in the KMASHTiF system with a bulk composition corresponding to 2Phl + 6Sil + 9Qtz under H_2O-saturated and H_2O-undersaturated conditions.

Experimental and analytical procedures

The starting mixture contained natural F and Ti-bearing phlogopite, natural sillimanite (both supplied by Wards) and quartz in the molar ratio 2:6:9. Analyses of starting phlogopite and the bulk chemical composition of starting material is given in Table 1. The finely ground mixture was dried in an air oven at 100°C before sealing in Pt capsules. Five wt.% of water was added to the charge as a flux. However, in order to compare the run products in a H_2O-undersaturated systems, runs were also carried out at selected $P-T$ points without adding excess water to the charges. Here, the only H_2O available for the reaction was from the breakdown of phlogopite which was about 1.5 wt.% of the bulk composition. Leaks in the capsules were checked for by measuring any weight loss through extended heating before the runs. Experiments were carried out at 7, 10 and 12 kbar (13% friction correction applied to nominal pressures), using a talc pyrex cell in a half-inch piston-cylinder (procured from the Grant Institute, Edinburgh, UK). The pressures are believed to be accurate to ±100 bar and temperatures ±10°C. The products were identified by X-ray diffraction and some selected run products were analysed on a CAMECA SX-50 EPMA, using a WDS spectrometer with a beam current of 15nA and an accelerating voltage of 15 kV. Calibration was carried out employing both synthetic and natural mineral standards and the counting time for each element was 10 s. The fluorine counts of phlogopite and melt were determined using a TAP crystal with a fluorite standard (48.66 wt.% F) and a counting time of 60 s.

TABLE 1: Chemical analyses of the starting phlogopite and run products

									H_2O-saturated				H_2O-under saturated
									L_1		L_2		L_3
	Bulk	Phl$_1$	Phl$_2$	Phl$_3$	Phl$_4$	Crd	Spr	En	Expt.	Calc.	Expt.	Calc.	Expt.
SiO_2	52.70	40.42	41.30	40.20	41.34	49.64	15.46	55.60	60.70	53.93	68.23	64.79	72.50
TiO_2	0.47	1.31	0.60	1.25	0.93	0.50	0.23	–	0.25	–	0.42	–	0.40
Al_2O_3	30.88	13.89	13.00	14.34	14.99	32.48	59.94	12.52	26.89	30.51	19.54	23.32	12.50
FeO	0.61	1.66	3.10	0.72	0.72	2.13	0.03	0.98	0.41	–	0.03	–	0.01
MgO	9.14	25.20	25.30	24.42	24.61	13.92	20.77	30.16	0.41	–	1.24	–	0.43
Na_2O	0.12	0.33	0.40	0.13	0.22	0.09	0.02	–	0.02	–	0.12	–	0.01
K_2O	3.84	10.59	10.30	10.33	10.15	0.14	0.05	–	3.58	4.02	4.46	3.07	10.10
F	1.29	3.57	3.80	2.98	3.39	–	–	–	0.18	–	0.51	–	0.61
H_2O	0.95	2.63	1.00	–	–	–	–	–	–	11.53	–	8.81	–
Total	99.99	99.60	98.80	94.37	96.35	98.90	96.50	99.26	92.44	99.99	94.55	99.99	96.55

Note: Bulk-starting mixture of Phl$_1$ + Sil + Qtz in the ratio 2:6:9
Phl$_1$: Natural phlogopite in starting material (present study);
Phl2-Natural phlogopite in starting material of Dooley and Patino Douce (1996);
Phl$_3$ and L_1-Phlogopite and melt in field II [Expt.No. PC41; *P–T*: 7 kbar/1000°C);
Phl$_4$, Spr and L_2: Phlogopite, sapphirine and melt in field III (Expt.No. PC36; *P–T*:10 kbar/1100°C);
En and L_3: Enstatite and melt in field III in water undersaturated run (Expt. No. PC70; *P–T*: 10 kbar/1100°C);
Crd-Cordierite from field II (Expt.No. PC41; *P–T*: 7 kbar/1000°C)

Results and discussion

H_2O-saturated runs

The experimental results for the F- and Ti-containing system are given in Table 2 and plotted in Fig. 1. Three distinct mineral assemblages with characteristic presence or absence of cordierite and sapphirine were encountered. They are; Field I : Phl-Sil-Qtz, Field II: Crd-Phl-L and Field III: Spr-Phl-(Sil)-L. There is evidently a positive slope in the boundary between Fields I and II around 920°C at 7 kbar and 990°C at 12 kbar. The Crd-out, Spr-in boundary is nearly parallel to the *P* axis around 1080°C. The chemical analyses of the run products in Fields II and III are given in Table 1. The Al-content of phlogopite in the cordierite and sapphirine fields was slightly higher, while the Ti content was lower than in the starting phlogopite. There is an increase in F in phlogopite with increasing temperature. The sapphirine was of 2:2:1 type and cordierite of 2:4:5 type. Since the solid product in fields II and III indicated a near total consumption of quartz and sillimanite, we did not attempt to calculate the stoichiometry of the reactions across the cordierite-in and sapphirine-in boundaries. However, on the basis of analyses of the associated melts in these fields and the presence of phlogopite, we assumed at least about 1.5Crd:1Phl and 1.5Spr:1Phl as solids at the beginning of fields II and III respectively, leaving the rest of the starting charge to form melts. The analysis of melts from runs closer to the phase boundaries (PC41 and PC36) have been compared with composition of melts calculated based on these assumed ratios of Crd and Spr with respect to phlogopite in field II and III (Table 1). This ratio of cordierite and sapphirine to phlogopite however, is bound to increase with increasing temperature and corresponding change in the composition and an increase in the quantity of partial melt. The absence of enstatite or other potassic minerals, such as osumilite, in Field III is attributed to water saturation and the stability of phlogopite with respect to these minerals.

H_2O-undersaturated runs

The experimental details of H_2O-undersaturated runs are given in Table 2. The results differ from those of H_2O-saturated experiments in that the stability of Phl-Sil-Qtz field extends further by 20–30°C for the cordierite-in reaction. Similarly, there is an increase in temperature by 50°C in the

TABLE 2: Details of experimental runs in the system 2Phl-6Sil-9Qtz

Run no.	Pressure (kbar)	Temp. (°C)	Duration (Hours)	Product
H_2O-Saturated runs				
PC225	7	850	275	Phl-Sil-Qtz
PC226	7	900	250	Phl-Sil-Qtz
PC51	7	950	150	Phl-Sil-Qtz-Crd-L
PC41*	7	1000	150	Crd-Phl-L
PC43	7	1050	150	Crd-Phl-L
PC39	7	1100	150	Spr-Phl-Sil-L
PC57	8.5	1000	150	Crd-Phl-L
PC55	8.5	1050	150	Crd-Phl-L
PC30	10	875	250	Phl-Sil-Qtz
PC32	10	900	175	Phl-Sil-Qtz
PC87	10	950	160	Phl-Sil-Qtz
PC37	10	1000	160	Crd-Phl-L
PC53	10	1050	160	Crd-Phl-L
PC36*	10	1100	160	Spr-Phl-Sil-L
PC225	12	900	200	Phl-Sil-Qtz
PC229	12	950	200	Phl-Sil-Qtz
PC59	12	1000	160	Crd-Phl-L
PC58	12	1050	160	Crd-Phl-L
PC45	12	1100	160	Spr-Phl-Sil-L
H_2O-undersaturated runs				
PC155	7	950	300	Phl-Sil-Qtz
PC156	7	975	300	Crd-Phl-L
PC66	7	1075	250	Crd-Phl-L
PC157	7	1100	200	Spr-En-Phl(tr)-Sil-Qtz-L
PC71	10	975	250	Phl-Sil-Qtz
PC67	10	1025	250	Crd-Phl-L
PC164	10	1075	200	Crd-Phl-L
PC70	10	1100	180	Spr-En-Phl(tr)-Sil-Qtz-L

* Experiments where run product phases were analysed

cordierite-out and sapphirine-in boundaries. There is no difference in the mineral assemblage in Field II, as cordierite and phlogopite persist along with the melt. However, the mineral assemblage in Field III contains free enstatite, sillimanite and quartz in addition to sapphirine, phlogopite and melt. The sapphirine has 2:2:1 composition and the Al_2O_3 in enstatite ranges between 10 and 14 wt.%. The composition of the melt (L3) in field III (Expt. No.70) is given in Table 1.

Curves 1 and 2 in Fig. 1 are after Tareen *et al.* (1995) and Dooley and Patino Douce (1996) respectively, for the breakdown of Ti-F containing phlogopite to form enstatite in reaction 1. Curve 3 is after Peterson *et al.* (1991) who used only the F-phlogopite in reaction 1. A comparison of our experimental results with those reported earlier (Fig. 1), shows that the phlogopite breakdown in an aluminous KMASH system (Phl-Sil-Qtz) begins at temperatures lower by 50°C in a H_2O-saturated system and about 25°C in an H_2O-undersaturated system, relative to its breakdown in the silica-saturated Phl-Qtz system. This difference doubles when compared with the Phl-Qtz melting curve of Dooley and Patino Douce (1996). This variation is attributed to the differences in starting phlogopite composition and experimental conditions in the studies of Tareen *et al.* (1995) and Dooley and Patino Douce (1996). The fluorine content of the starting phlogopite was similar in both studies. However, in the latter, the starting charge was higher in titanium because a_{TiO_2} was buffered using rutile as one of the phases.

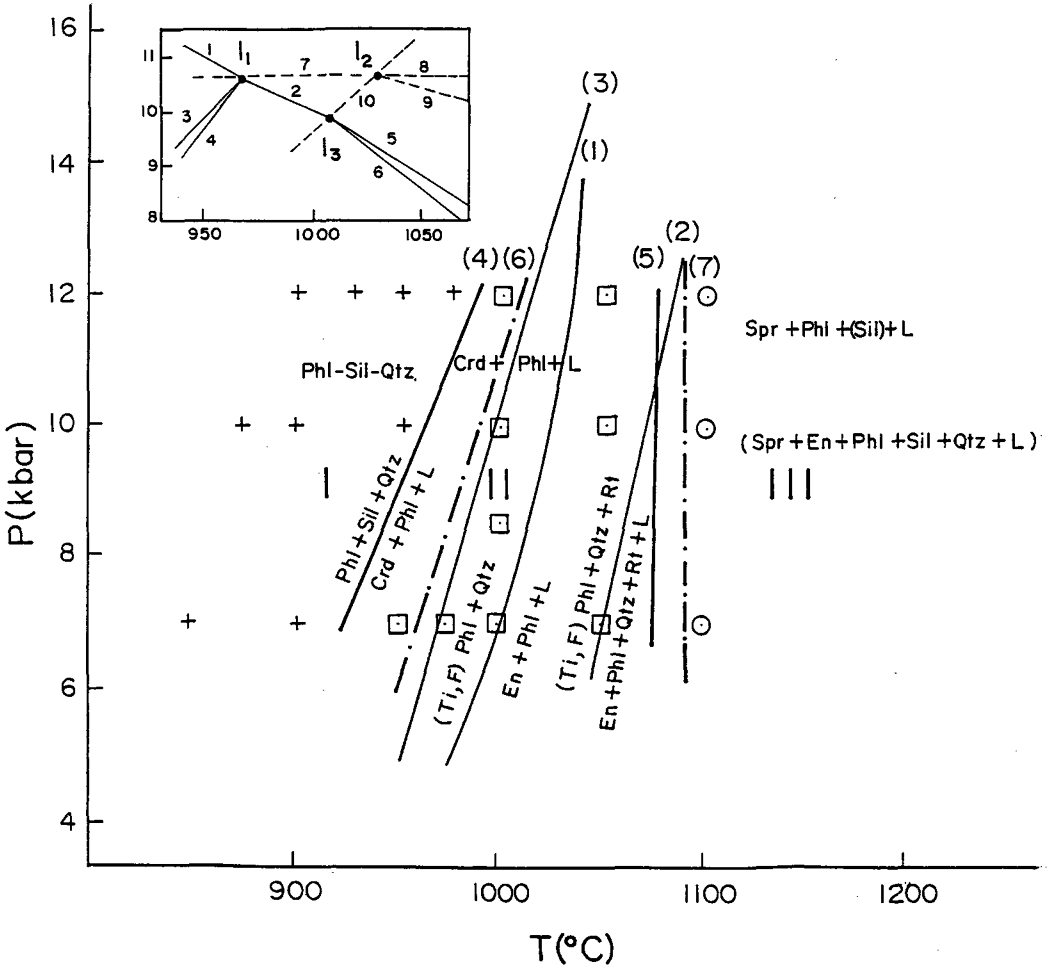

FIG. 1. Experimental points in the system KMASHTiF with bulk composition 2Phl-6Sil-9Qtz and the phase boundaries for Crd-in, Crd-out and Spr-in reactions. Lines 1 and 2 are after Tareen *et al.* (1995) and Dooley and Patino Douce (1996) respectively for the reaction Phl+Qtz = En+(Kfs)+L using F-Ti bearing phlogopite and curve 3 is after Peterson *et al.* (1991) for the same reaction with phlogopite containing only F. Lines 4 and 5 define the Crd-in and Spr-in reactions respectively with 5 wt% excess H_2O in the charge. Broken lines 6 and 7 represent the shift for Crd-in and Spr-in reaction respectively under H_2O-undersaturated runs. Experimental points for H_2O-undersaturated runs are not shown. Note the presence of phlogopite in field I,II and III in both H_2O-saturated and undersaturated runs. Assemblage in parantheses in field III is for H_2O-undersaturated runs.

Inset shows the existence of three invariant points I_1[Bt,Spr,Grt], I_2[Bt,Crd,Grt] and I_3 [Bt, Kfs,Grt] between the $P-T$ range 8–11 kbar and 950–1050°C. Curves 1-6 are after Carrington and Harley (1995) in the system KMASH [(1) Crd+Kfs = En+Sil+L, (2) Os+Crd = En+Sil+L, (3) Crd+En+Kfs = Os+L, (4) Crd+Kfs = Os+Sil+L, (5) Os+Crd = En+Spr+L and (6) Os+Crd+Sil = Spr+L]. Curves 7-9 are after Carrington and Harley (1995) in the system KMAS. [(7) Os = En+Sil+Kfs, (8) Os = En+Spr+Kfs and (9) Os+Sil = Spr+Kfs] and the curve 10 (En+Sil = Spr+Qtz) is from Chatterjee and Schreyer (1972) in the MAS system.

A review of all these experimental studies suggests that there is an uncertainty about the systematic effect of titanium substitution on the dehydration melting of phlogopite in KMASHTiF system. A comparison of the results of Peterson *et al.* (1991) and Tareen *et al.* (1995) indicates that the combined effect of F and Ti is additive on the thermal stability of phlogopite. The flourine content of (3.5 wt.%) in natural phlogopite used by Tareen *et al.*, (1995) produced an enstatite-in boundary at temperatures higher by 50°C than that of Peterson *et al.* (1991) who used synthetic phlogopite with a higher flourine content of 5.09 wt.%. This discrepancy may be due to the presence of 1.31 wt.% of TiO_2 in the natural phlogopite used by the former. This also supports the studies of Dooley and Patino Douce (1996). However, in the studies of Skjerlie and Johnston (1993) and Dooley and Patino Douce (1996), there is no systematic variation of Ti content with either pressure or temperature, while an increase in F content of phlogopite with temperature is conspicuous. Dooley and Patino Douce (1996) suggest an inverse correlation between F and Ti contents of phlogopite at high temperatures (>1250°C) . The wide divariant field of dehydration melting of phlogopite in their experiments may be attributed to the combined effects of MgO and $Al^{(VI)}$ in phlogopite and continued buffering of Ti in their reaction. This is evident from the earlier report of Tareen *et al.* (1995) in which the Ti content of phlogopite in the Phl-Qtz system was un-buffered and as a result, phlogopite did not persist for more than 50°C above the enstatite-in boundary and it disappeared when the runs were seeded with enstatite.

The experimentally observed coexistence of Ti-F phlogopites with cordierite and sapphirine at high temperature are not really comparable to the known natural rocks. However, it is certain that the flourine–titanium substiution in phlogopite, expands the stability field of Phl-Sil-Qtz to higher temperatures and thus squeezes down the temperature range over which the cordierite-melt assemblages exist.

Comparison of H_2O-saturated and H_2O-undersaturated experiments suggest a limited influence of H_2O-saturation on cordierite-in, cordierite-out and sapphirine-in phase boundaries. However, H_2O-saturation has a significant effect on the stability of sillimanite, enstatite and quartz, since these phases go into the melt. In H_2O-undersaturated runs, the crystallization of sapphirine, Al-enstatite along with traces of phlogopite, sillimanite and quartz can significantly reduce the quantity of melt and also effect the Al_2O_3, K2O and SiO_2 contents of the melt (see Table 1). The melt L_3 from field III in H_2O-undersaturated runs showed enrichment of K_2O and SiO_2 and decrease in Al_2O_3 compared with the melts L_1 and L_2 from fields II and III from H_2O-saturated runs. Fig. 2 shows the compositional trends of liquids produced in the cordierite- and sapphirine-bearing fields.

The petrogenetic grids for the H_2O-undersaturated KMASH system developed, based on limited experimental data (Motoyoshi *et al.*, 1993; Carrington and Harley, 1995), require the total disappearance of phlogopite at about 950°C. In studies using natural pelitic compositions (Vielzeuf and Holloway, 1988; Patino Douce and Johnston, 1991; Skjerlie and Johnston, 1993), the fluid-absent reactions of biotite were complete between 850 and 950°C. However, the experimental studies of Skjerlie and Johnston (1993) on natural tonalitic gneisses showed that an incongruent melting of F-bearing biotite occurs between 950 and 975°C producing nearly 20 wt.% of F-rich granitic melt. The three important invariant points [Bt, Spr, Grt], [Bt, Crd, Grt] and [Bt, Kfs, Grt] in the petrogenetic grid for the KFMASH system, are qualitatively located between 10 and 11 kbar and in the temperature range of 950–1050°C (Carrington and Harley, 1995). The osumilite-, sapphirine-

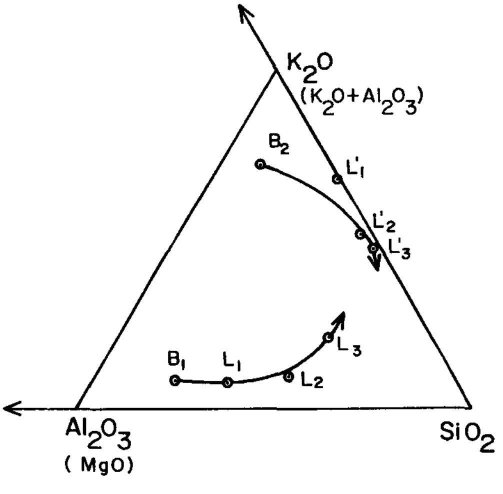

FIG. 2. Plot of the bulk composition and the liquids produced in cordierite and sapphirine fields of Fig. 1. B_1, L_1, L_2 and L_3 are on K_2O-Al_2O_3-SiO_2 variation and B_2, L'_1, L'_2 and L'_3 are for (K_2O-Al_2O_3)-MgO-SiO_2 variation. L_1 and L_2 are liquids from H_2O-saturated runs of fields II and III respectively and L_3 is the liquid from H_2O-undersaturated run in field III. Note the change of liquid composition with mineral assembalge as well as the H_2O-saturation.

and enstatite-forming reactions emerge from these invariant points (Fig. 1, inset), with total absence of phlogopite. The observed divariant stability of F-Ti phlogopite extending into the cordierite as well as sapphirine–ensatite fields beyond 1100°C, therefore warrants a careful constraining of the KMASH and KFMASH petrogenetic grids through experimental study of these systems appropriately buffered with F and Ti.

Acknowledgements

This work was supported by the Department of Science and Technology, New Delhi [No.24-(6P-24)84 - STP.II ES]. We thank the refree J.D. Clemens for his critical review and suggestions on the manuscript. AVKP and AVG thank DST for fellowships.

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[*Manuscript received 12 May 1997: revised 25 September 1997*]