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The effect of fluorine and titanium on the vapour-absent melting of phlogopite and quartz

Introduction

THE reaction biotite + quartz = orthopyroxene + K-feldspar + V or orthopyroxene + L, has been considered as one of the important model reactions applicable to the melting of common crustal rock types (Clemens and Wall, 1981; Grant, 1986). An end-member equivalent of this reaction $ph + qtz = en + L$ was studied by several working groups, but with lack of consensus on the P – T location of the melting curve (Bohlen *et al.*, 1983; Peterson and Newton, 1989a; Montana and Brearley, 1989; Vielzeuf and Clemens, 1992 and Clemens, 1983). Synthesised phlogopite was used as the starting material in all these studies and results have been used to discuss P – T conditions of anatexis and melt compositions, although a synthetic end-member phlogopite is not quite comparable to a natural biotite from high-grade terrain, which contains substantial fluorine substituting for hydroxyl ion and significant amounts of Ti.

This suggests that melting equilibria involving F- and Ti-bearing micas may be closer analogues to melting at lower crustal levels. Peterson *et al.* (1991) made the first study of this reaction using synthetic fluor phlogopite with 60 mole % of F substituting for OH. They found an increase in the incongruent melting temperatures by about 170°C as compared to the average temperatures reported earlier for the same reaction with F-free hydroxy phlogopite. In this communication we report the incongruent melting equilibria in the system phlogopite + quartz, where a natural phlogopite, containing both F and Ti, has been used.

Experimental conditions

Experiments were performed in a 1.25 cm diameter piston cylinder apparatus using talc and pyrex cell. Both piston-in and piston-out techniques were used

and a 13 % pressure correction was made based on the comparative values obtained in the gas bomb. Temperature was measured using Pt/PtRh₁₃ thermocouples and is within 10°C of the reported values. None of the runs were reversed. The starting mixture contained natural phlogopite (supplied by M/S Wards) and natural quartz in equal mass proportion, ground in acetone for 20 minutes. About 40 mg of this mixture was sealed in platinum capsules (2.5mm diameter and 4.5mm long). At P – T points where unseeded experiments yielded phlogopite + melt and phlogopite + enstatite + melt, runs were repeated using starting material seeded with 10 wt.% synthetic enstatite. Phases in starting materials and run products were identified with X-ray powder diffraction, polarising microscope and beginning of melting and extent of reaction were determined using BSE imaging. Sanidine was not identified in any of the runs. Quantitative analysis of starting phlogopite and phases in run products were obtained on CAMECA SX-50 electron microprobe using WDS method (Tables 1 and 3) with 15 kV accelerating voltage and 15 nA beam current. The counting time for each element was 10s. Major element counts were calibrated against a set of synthetic and natural mineral standards (courtesy of Ian Steele, University of Chicago). Fluorine analyses were obtained for phlogopite and melt phases using a TAP crystal. Fluorite (48.66 wt.% F) was used as standard and the concentration of F was determined by collecting counts over 60s time intervals. Beam size was 2 µm in all cases. The starting phlogopite analysis was recalculated using the program GEO/ML to determine H₂O.

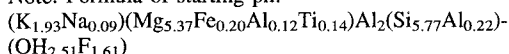
Results and discussion

The experimental results are given in Table 2 and the melting curve obtained is plotted in Fig 1. The fluid-

TABLE 1. Composition of the starting phlogopite and run product phases

	Starting ph (n = 10)	Unreacted ph (n = 5)	en (n = 10)
SiO ₂	40.42	41.65	59.90
TiO ₂	1.31	1.30	—
Al ₂ O ₃	13.89	13.82	0.28
Cr ₂ O ₃	0.02	0.01	0.02
MgO	25.20	24.92	38.08
FeO	1.66	1.41	0.58
MnO	0.04	0.01	—
CaO	0.01	0.01	0.14
Na ₂ O	0.33	0.28	0.01
K ₂ O	10.59	10.05	0.14
F	3.57	3.05	—
H ₂ O	2.63	—	—

Note: Formula of starting ph:



$X_{Mg} = 0.97$; $X_F = 0.39$

Analyses of the unreacted ph are from run PC 79

en analyses are from run PC 126

n = number of points analysed

absent melting curves reported by other workers are shown for comparison. At 8.7 kbar and 1000°C (PC 76), there was clearly no melting even with runs extending to 200 hours. In the run with unseeded starting material, although melting was encountered at 1025°C (PC 79), enstatite was not identified by XRD. The BSE image (Fig. 2a) showed small amounts of melt in the form of isolated globules as well as fine beadlets around phlogopite and quartz (Fig. 2a). Analyses of this phlogopite (Table 1) indicated it to be unreacted rather than re-equilibrated phlogopite, as there was no enrichment in Ti, Mg or Al. However, enstatite was clearly detected by XRD at 1050°C (PC 82). The lack of enstatite along with initial melt was considered to be due to the absence of enstatite seeding in the starting mixture and the extremely sluggish nature of the reaction in those systems with natural phases. In order to verify this, starting material with 10 wt.% synthetic enstatite seeds was used in runs at 1000, 1025 and 1050°C at 6.1 kbar and 1025, 1050 and 1100°C at 8.7 kbar. In runs closer to the solidus, phlogopite continued to persist in traces and in the rest of the runs, the reaction was complete with total elimination of phlogopite, extensive melting and well developed prisms (10–50 µm) of enstatite (Fig. 2b).

TABLE 2. Results of the piston cylinder runs

Run No.	P# (kbar)	T (°C)	Duration (h)	Assemblage
PC102	6.1	950	220	ph + qtz
PC104	6.1	975	220	ph + qtz
PC101	6.1	1000	200	ph + qtz + L
PC121*	6.1	1000	180	en + L + (ph)
PC105	6.1	1025	200	ph + en + L
PC122*	6.1	1025	180	en + L
PC106	6.1	1050	200	ph + en + L
PC123*	6.1	1050	180	en + L
PC77	8.7	950	200	ph + qtz
PC76	8.7	1000	200	ph + qtz
PC79	8.7	1025	200	ph + qtz + L
PC124*	8.7	1025	180	en + L + (ph)
PC82	8.7	1050	200	ph + en + L
PC125*	8.7	1050	180	en + L
PC80	8.7	1100	200	ph + en + L
PC126*	8.7	1100	180	en + L
PC110	13.0	1000	180	ph + qtz
PC112	13.0	1025	180	ph + qtz
PC113	13.0	1050	180	ph + qtz
PC114	13.0	1100	180	en + L + (ph)

* denotes piston-in runs seeded with en; () = trace

pressure values are after 13% friction correction

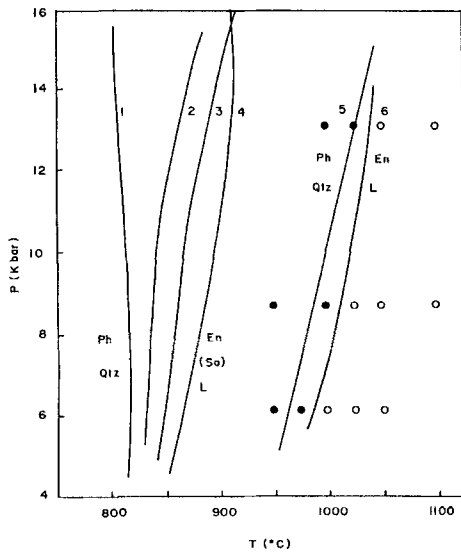


Fig. 1. The P - T location of the reaction: $ph + Qtz = en + L$ using F- and Ti-bearing natural phlogopite (curve 6). Melting curves for the same reaction in the system KMASH (curves 1 to 4) and KMASH-F (curve 5) are shown for comparison. Curve 1 — Peterson and Newton, (1989); 2 — Montana and Brearley, (1989); 3 — Vielzeuf and Clemens, (1992); 4 — Bohlen *et al.*, (1983); 5 — Peterson *et al.*, (1991). Symbols: Filled circles — $ph + Qtz$; Open circles — $en + L$.

Deviation of phlogopite-quartz incongruent melting temperatures obtained by various workers increase with pressure. Comparing our curve with that of Vielzeuf and Clemens (1992), curve 3, Fig. 1, the melting temperatures drift by nearly 140°C at 15 kbar and 120°C at 7 kbar. This increase in the

temperature of the solidus is attributed essentially to the presence of 1.61 mole F and 0.14 mole of Ti in the natural phlogopite used, though the role of the Tschermak molecule cannot be ruled out. Interestingly the phlogopite-quartz melting curve (curve 5, Fig. 1) in the system KMASH-F (Peterson *et al.*, 1991) with 60 mole % of F in phlogopite is close to the one reported in this study (curve 6, Fig. 1). It has been shown experimentally that a high Ti content (Forbes and Flowers, 1974) as well as substitution of F for (OH) in phlogopite (Shell and Ivey, 1969) leads to a drastic increase in the melting temperature of phlogopite. However, the full extent of the bulk effect of F and Ti combined on the phlogopite-quartz melting is not precisely known.

Although biotites from most of the granulite terranes have higher concentrations of F and Ti than the phlogopite used in this study, they are quite substantial compared to the pure KMASH system investigated by previous workers, to cause the observed positive shift in the fluid-absent melting temperatures in the present study.

The reluctance of Ti to enter pyroxenes at high pressures (Forbes and Flower, 1974) has resulted in its complete partitioning into melt. The stabilising effects of F (Peterson *et al.*, 1991) and F and Ti (this study) suggest that vapour-absent melting during granulite-grade metamorphism may exceed 1000°C . There are cases of granulite terranes preserving temperatures of 900 – 1000°C (Harley, 1989) and this is not unlikely because biotites from most granulite terranes contain high Ti and F.

Goldman and Albee (1977) and Essene (1982) have discussed the effects of various substitutions in biotites on the Mg/Fe ratios and Mg = Fe exchange sites available. But most of the studies using biotite containing pairs for thermometric calculations ignore these constraints. In view of this, the values from such thermometry may represent the lower temperature limits of metamorphism at least in some

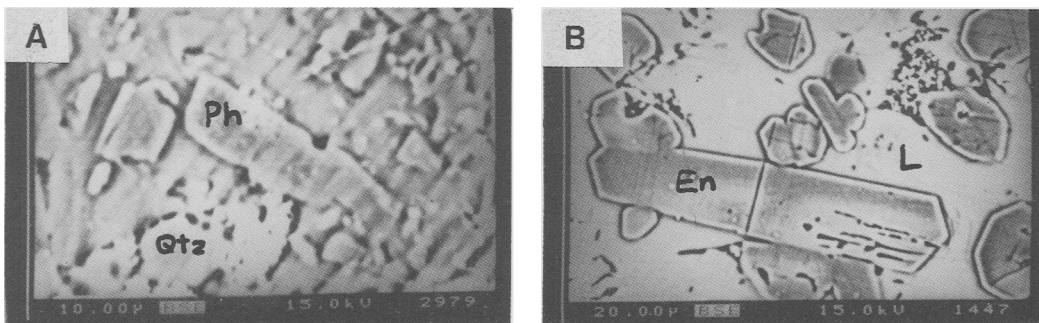


Fig. 2. Back-scattered electron (BSE) images of the run products. [A] Unreacted phlogopite and quartz with quenched melt at the grain boundaries from the unseeded run at 8.7 kbar and 1025°C [run no. PC 70]; [B] Well developed enstatite crystals in melt from a seeded run at 8.7 kbar and 1100°C [run no. PC 126].

TABLE 3. Analyses of melt at 8.7 kbar and 1100°C (85°C above solidus)

	1	2	3	4	5	6	7	8	9	10
SiO ₂	72.14	72.71	73.22	71.56	70.87	73.13	73.90	75.75	72.49	75.76
TiO ₂	0.47	0.37	0.25	0.32	0.50	0.49	0.51	0.66	0.73	0.66
Al ₂ O ₃	9.08	9.43	10.19	10.11	9.18	9.39	9.50	9.52	9.54	9.43
Cr ₂ O ₃	0.05	—	—	—	—	0.02	0.01	0.02	—	0.01
MgO	4.17	3.98	3.83	3.72	4.17	4.22	4.07	3.99	4.10	4.17
FeO	0.02	—	—	0.08	0.05	0.08	0.03	—	0.10	0.01
MnO	0.02	0.05	0.02	0.02	—	—	—	0.21	—	0.12
CaO	0.26	0.26	0.18	0.26	0.27	0.24	0.19	—	0.14	—
Na ₂ O	0.82	0.63	0.76	0.83	0.79	0.78	0.89	0.23	0.71	0.39
K ₂ O	9.24	9.06	8.30	9.40	9.10	8.10	7.30	5.90	8.31	5.92
F	1.89	1.74	1.55	1.63	1.92	1.07	0.95	1.85	1.04	1.58

granulite terranes. However, addition of Fe and Na particularly under vapour-saturated conditions should have a substantial counter effect, depressing the melting temperatures to account for the generally

retrieved P - T range of 5–12 kbar and 700–1000°C for granulite metamorphism.

The composition of melt was obtained from a seeded run (PC 126) at 8.7 kbar and 1100°C where the sole product was enstatite and liquid in equilibrium, and the peritectic reaction was complete. The average melt had normative enstatite and quartz. The normative quartz:orthoclase ratio was 1 : 1.4. The solubility of Mg in melt averaged 4.04 by weight percent. Melt analyses from KMASH (Peterson and Newton, 1989) and KMASH-F systems (Peterson *et al.*, 1991) compared on a non-volatile basis to analyses from this study (Fig. 3). In the KMASH-F system, Peterson *et al.*, have shown that 60 mole % of F for OH in phlogopite shifts the liquid composition from the SiO₂-rich side to the SiO₂-poor side across the enstatite-sanidine join to make it more lamproitic. This effect was not observed in the melt compositions of the present study, which only cautions on the more complex nature of the mechanism involved during melting in natural mineral systems. However, on a first approximation, the differences in the melt compositions observed by Peterson *et al.*, 1991, and the present study can be explained in two ways: (a) the dissolved Mg in the melt would be reduced when the peritectic reaction is complete and magnesium is consumed by the enstatite in equilibrium with the liquid; (b) the melt is likely to be richer in magnesium at the beginning of melting and at temperatures closer to the melting curve where the enstatite crystallisation is kinetically hindered, which results in a metastable melt closer to lamproitic compositions as observed by Peterson *et al.*, 1991. However, in such a situation, the effect should be visible even in the fluorine-free KMASH system. It is also not experimentally established if F and Ti in the melt would inhibit enstatite crystallization (thereby increasing the solubility of

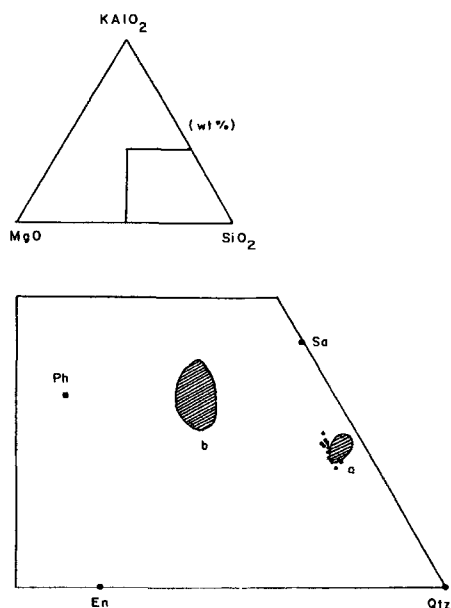


FIG. 3. Diagram showing non-volatile compositions [wt.%] of melt quenched from 8.7 kbar and 1100°C [85°C above solidus]. Regions [shaded] 'a' and 'b' indicate respectively, melt compositions in systems KMASH [Peterson and Newton, 1989] and KMASH-F [Peterson *et al.*, 1991]. Observe the near overlapping of melt compositions in the system KMASH and the present study.

magnesium in the melt) in the reaction $ph + qtz = en + L$ by some polymerising effects. Further work on the likely elements whose enrichment in KMASH melts inhibit enstatite formation, will throw light on the generation of melts closer to lamproitic compositions from the KMASH system.

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Erratum

A table published by Bowell (1992; Table 3) failed to cite all four sources of the given data which were: a compilation by Groen *et al.* (1990) with additional information from Puddephatt (1978; 1987) and

Bjerrum (1971), and calculations by this author based on reported values of Gibbs free energies. The last group were incorrectly calculated and should be ignored. The literature sources are, in turn, compila-