

# Reversed determination of the reaction: Phlogopite + quartz = enstatite + potassium feldspar + H<sub>2</sub>O in the ranges 750–875 °C and 2–12 kbar at low H<sub>2</sub>O activity with concentrated KCl solutions

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## ABSTRACT

The reaction of phlogopite plus quartz to enstatite, potassium feldspar, and aqueous fluid in the system KMASH-KCl was reversed at 2–12 kbar and 750–875 °C and at low H<sub>2</sub>O activities by reversal of the H<sub>2</sub>O content of concentrated KCl solutions equilibrated with product and reactant assemblages. Synthetic 1M phlogopite [KMg<sub>3</sub>AlSi<sub>5</sub>O<sub>10</sub>(OH)<sub>2</sub>] and enstatite (MgSiO<sub>3</sub>) maintained end-member stoichiometry throughout, and the potassium feldspar (KAlSi<sub>3</sub>O<sub>8</sub>) was a high sanidine, based on unit-cell refinements. The broad *P-T-X<sub>H<sub>2</sub>O</sub>* and narrow reversal ranges of this investigation were possible because of the low and well-defined H<sub>2</sub>O activity, yet powerful fluxing action, of concentrated KCl solutions. Solubility experiments on quartz and potassium feldspar in our *P-T-X<sub>H<sub>2</sub>O</sub>* range showed that fluid-phase solution of silicate constituents was too small to have affected the H<sub>2</sub>O activity in the experiments. The new determinations are more definitive than previous work done at very low pressures with pure H<sub>2</sub>O or in CO<sub>2</sub>-H<sub>2</sub>O mixtures. They establish the standard free energy of the reaction in the experimental range with an uncertainty of about 1 kJ and indicate that the synthetic phlogopite has maximal (Al-Si) disorder under our experimental conditions. The standard enthalpy of reaction at 298 K is 106.54 ± 2.0 kJ (2σ) based on our reversals, a value 6 kJ less positive than that currently used by many workers in calculations of biotite stability and H<sub>2</sub>O activity in the petrogenesis of high-grade metamorphic rocks. The lower thermal stability that we find for phlogopite requires revision in estimates of H<sub>2</sub>O activity of granulite facies metamorphism: typical values for the natural assemblage orthopyroxene-biotite-garnet-potassium feldspar-plagioclase-quartz at deep-crustal metamorphic conditions (750–850 °C, 5–10 kbar) are *a<sub>H<sub>2</sub>O</sub>* = 0.4–0.6 compared with values of 0.15–0.30 which would have been estimated with previously available data on phlogopite stability. An important consequence of the expanded H<sub>2</sub>O activity range of granulites is that alkali chloride solutions of only moderate concentration [*X<sub>H<sub>2</sub>O</sub>* = 0.5–0.7], which are the values observed in actual fluid inclusions in many kinds of igneous and metamorphic rocks, are a feasible alternative to the vapor-absent conditions considered necessary by many workers based on previous low estimates of *a<sub>H<sub>2</sub>O</sub>*. Participation of concentrated brines in deep-crust/upper mantle metamorphic processes enables alkali metasomatism and other kinds of chemical transport in an aqueous fluid without large-scale melting of the crust.

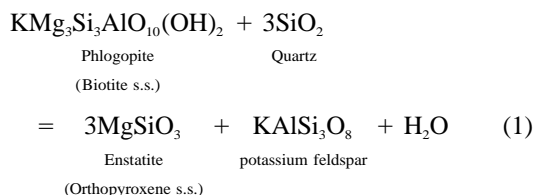
## INTRODUCTION AND PREVIOUS WORK

Biotite is, with amphibole, one of the two most important refractory hydrate minerals of the crust and upper mantle, and, as a major reservoir of alkalis and volatile components, plays a crucial role in generation of magmas. In ultramafic upper mantle assemblages, magnesian biotite is a stable primary phase (Dawson and Smith 1975). Biotite-rich ultramafic rocks comprise the glimmerite and MARID suites of incompatible-element-enriched mantle rocks (Dawson and Smith 1977). In some of these rocks, biotite approaches the composition of ideal

phlogopite, KMg<sub>3</sub>(AlSi<sub>3</sub>)O<sub>10</sub>(OH)<sub>2</sub>. Partial substitution of Ti for octahedral cations (Mg and Fe) and partial replacement of OH<sup>-</sup> by F<sup>-</sup> are typical of refractory phlogopitic biotites.

Typical biotites of crustal rocks, except for those of high-grade marbles, are generally more Fe- and Al-rich than their ultramafic counterparts. Nevertheless, the phlogopite end-member is commonly the most convenient basis for thermodynamic analysis of biotite stability; effects of other substituents may be assessed with solid solution models. In the granulite facies, the presence of biotite is particularly important as a possible indicator of H<sub>2</sub>O activity by means of such simple-system reactions as:

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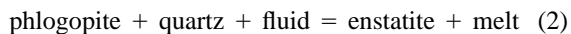


Biotite commonly coexists with orthopyroxene and garnet, even in the highest-grade rocks of the granulite facies, such as those of Enderby Land, Antarctica (Grew 1980). Calculations based on reaction 1 have yielded very low  $\text{H}_2\text{O}$  activity values for these granulites, on the order of 0.1–0.2 (Aranovich 1984; Bhattacharya and Sen 1986; Moecher and Essene 1991), regardless of the differences in the solid-solution models accepted by the authors for the minerals involved.

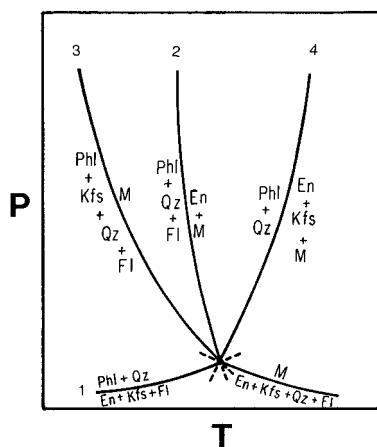
The extremely refractory nature of phlogopite, in the absence of quartz, at high pressures was demonstrated in pioneering studies by Luth (1967) and Yoder and Kushiro (1969). These studies showed that phlogopite is stable to temperatures of at least 1300 °C on its own composition at pressures above 10 kbar and stable to temperatures in excess of 1200 °C in the presence of hydrous fluids at 30 kbar. The upper temperature of phlogopite stability is limited by incongruent melting reactions that produce forsterite. Especially significant is the high-temperature stability of phlogopite in fluids of low  $\text{H}_2\text{O}$  activity, as in  $\text{CO}_2$ -rich fluids (Wendlandt and Egglar 1980).

Forbes and Flower (1974) showed that Ti substitution in phlogopite has a substantial stabilizing effect, increasing the melting temperature by more than 100 °C. Fluorine substitution for (OH) also has a large stabilizing effect (Munoz and Ludington 1974).

A nearly comprehensive topology of phlogopite stability in the system  $\text{K}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  (KMASH) was worked out to 3.5 kbar by Luth (1967). His  $P$ - $T$  net included subsolidus univariant reactions in silica-saturated compositions as well as melting reactions. Experimental data constraining the  $P$ - $T$  positions of univariant equilibria was provided by synthesis from gels. No reversals of reactions were presented. Subsequent workers (Grant 1986; Vielzeuf and Clemens 1992; Clemens 1995) elaborated on Luth's arrangement of univariant equilibria in the  $\text{SiO}_2$ -saturated part of the KMASH system (Fig. 1). The phlogopite-quartz dehydration reaction is confined to very low pressures for  $\text{H}_2\text{O}$  activities of unity (pure  $\text{H}_2\text{O}$ ) and is terminated in the vicinity of 800 °C by hydrous melting, according to the reaction:

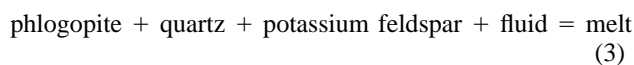


Wood (1976) produced the first reversal data for the reaction of phlogopite and quartz, reaction 1. His data include two reversals in mixtures of synthetic phases, at 750 °C between 0.29 and 0.36 kbar and at 790 °C between 0.40 and 0.47 kbar. The slow reactions required experiment durations of several weeks to detect reaction direction by X-ray diffraction (XRD) of quenched charges. Critical details of the experimental techniques and reac-



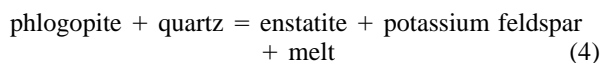
**FIGURE 1.** Schematic univariant equilibria involving phlogopite-quartz reactions in the  $\text{SiO}_2$ -saturated portion of the system  $\text{K}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  (KMASH) (after Luth 1967). The univariant reactions are labeled as in the text. (Phl = phlogopite,  $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ ; En = orthoenstatite,  $\text{MgSiO}_3$ ; Kfs = sanidine,  $\text{KAlSi}_3\text{O}_8$ ; Qz = quartz,  $\text{SiO}_2$ ; Fl = aqueous fluid; M = silicate melt.)

tion progress were not given. Wones and Dodge (1977) presented data on the low-pressure melting reactions that support an invariant point around 0.5 kbar and 820 °C, in agreement with the results of Wood (1976). Peterson and Newton (1989) studied experimental dehydration reactions near Wood's invariant point in mixtures of synthetic phlogopite and quartz, but were unable to reverse reaction 1 in experiments of several weeks duration. Bohlen et al. (1983) made an extensive experimental study of subsolidus and melting reactions in the  $\text{SiO}_2$ -saturated portion of the KMASH system. They presented a very comprehensive data set on melting up to 15 kbar pressure of sanidine + quartz in the presence of  $\text{H}_2\text{O}-\text{CO}_2$  fluids with  $X_{\text{H}_2\text{O}} = 1.0, 0.7, 0.5, 0.3, 0.1,$  and 0.0. The melting points are virtually unchanged if phlogopite is added to the reactants:



Therefore the component MgO enters only negligibly into the liquid at 700–800 °C. This inference was later confirmed by microprobe analyses of quenched glasses by Puziewicz and Johannes (1990) and Clemens (1995) in their studies of model phlogopite granite systems.

Bohlen et al. (1983) obtained one reversed bracket on reaction 1 in the presence of an  $\text{H}_2\text{O}-\text{CO}_2$  fluid with  $X_{\text{H}_2\text{O}} = 0.35$ . Their bracket at 5 kbar lies between 780 and 800 °C, and appears to require a considerably less stable phlogopite than given by the brackets of Wood (1976), if the  $\text{H}_2\text{O}-\text{CO}_2$  mixing properties of Kerrick and Jacobs (1981) are applied. Bohlen et al. (1983) also presented numerous data on the melting reactions 2 and 3 and on the fluid-absent melting reaction at higher temperatures:



Their  $P$ - $T$  location of equilibrium 4 was unreversed and later challenged as being too high in temperature in the higher pressure range by Montana and Brearley (1989) and Peterson and Newton (1989). Both of these studies obtained reversals of the dehydration melting curve based on textural evidence of mica growth from previously melted charges; however, neither one produced tight reversal brackets for the vapor-absent melting curve, and it may be suspected that their determinations underestimated the temperature of the equilibrium curve. Clemens et al. (1987) measured the enthalpy of solution of synthetic phlogopite in molten  $\text{Pb}_2\text{B}_2\text{O}_4$  at 714 °C. These measurements take into account the enthalpy of solution of  $\text{H}_2\text{O}$  in the calorimeter solvent, which quantity was assumed to be a constant independent of the small amount of hydroxide dissolved. The calorimetric cycle involved five reaction steps with accrued uncertainties. Their measurements yielded an enthalpy of formation,  $\Delta H_f^\circ$ , of phlogopite from the elements of  $-6215.33 \pm 6.28$  kJ ( $2\sigma$ ) per mol at 298 K. From this result they deduced that synthetic phlogopite must have maximal (Al-Si) disordering entropy,  $S(\text{dis}) = -4R(\frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4}) = 18.70$  J/K, for the measured  $\Delta H_f^\circ$  to be compatible with existing phase equilibrium determinations, principally those of Wood (1976).

Vielzeuf and Clemens (1992) gave an exhaustive review of phlogopite stability in the  $\text{SiO}_2$ -rich portion of the KMASH system, with extensive topological and thermodynamic analysis and some new experimental data that favor the low-pressure determination of Wood (1976) of reaction 1. Their reconstruction requires a very stable phlogopite with the maximum amount of (Al-Si) disordering entropy.

Recently, Berman et al. (1995) and Clemens (1995) presented reversed brackets on reaction 1 at low pressures. The results of Berman et al. (1995) suggest a considerably less stable phlogopite. Their data indicate equilibrium of reaction 1 between 752 and 774 °C at 0.48 kbar with pure  $\text{H}_2\text{O}$  and between 760 and 768 °C at 1.74 kbar in an equimolar  $\text{H}_2\text{O}$ - $\text{CO}_2$  fluid. The standard free energy of the reaction in this temperature range must be about 6 kJ more negative than indicated by the thermodynamic data tabulated by Vielzeuf and Clemens (1992). Correspondingly, the  $\text{H}_2\text{O}$  isoactivity curves of reaction 1 must be shifted to substantially higher pressures and lower temperatures than those shown by Vielzeuf and Clemens (1992), which suggests that in quartzo-feldspathic systems orthopyroxene can be stable, at any given temperature, at considerably higher  $\text{H}_2\text{O}$  activities than inferred by several previous interpretations. A single datum on reaction 1 reported by Clemens (1995) (between 0.51 and  $0.62 \pm 0.06$  kbar at 800 °C) appears to support the early results of Wood (1976), although only traces of phlogopite and no quartz were observed in the phlogopite+quartz producing half-bracket (Clemens 1995, Table 2, experiment K-37).

Several factors might be responsible for the current disagreement about phlogopite+quartz stability. Reaction 1 is extremely sluggish, particularly at the very low pressures in pure  $\text{H}_2\text{O}$ , so that an appreciable reaction yield can be detected only in experiments of at least one month duration (Wood 1976; Berman et al. 1995). Maintaining steady experimental conditions is therefore an important consideration that was not addressed adequately in the earlier study. Moreover, small amounts of reaction progress are difficult to establish by powder XRD because of strong preferred orientation of phlogopite and enstatite. Another source of discrepancy is that all three experimental studies in which reversals on reaction 1 in pure  $\text{H}_2\text{O}$  have been obtained (Wood 1976; Berman et al. 1995; Clemens 1995), employed cold-seal externally heated apparatus and measured experiment temperature with external thermocouples. Calibration experiments (Boettcher and Kerrick 1971; Kapustin et al. 1982) have demonstrated that there is typically a temperature gradient across the vessel walls due to the convection of the fluid within the vessel. Depending on the specific  $P$ - $T$  conditions, thickness of the vessel, and nature of the pressure medium (water, nitrogen, methane, etc.), the outer thermocouple readings may exceed the actual sample temperatures within the vessel by up to 40 °C. This problem was minimized in the experiments of Berman et al. (1995) by the use of filler rods that impede fluid convection within the vessels (Boettcher and Kerrick 1971). Finally, existing theoretical estimates of  $\text{H}_2\text{O}$ - $\text{CO}_2$  mixing properties at elevated  $T$  and  $P$  cannot yet be considered as definitive (Anovitz et al. 1996).

Use of concentrated chloride solutions to create hydrothermal fluid media of low  $\text{H}_2\text{O}$  activity is a new possibility for investigating the stabilities of refractory hydrate minerals over extended  $P$ - $T$  ranges. Aranovich and Newton (1996, 1997) determined  $\text{H}_2\text{O}$  activities in concentrated NaCl and KCl solutions over large ranges of state parameters (1–15 kbar, 550–900 °C, and concentrations up to salt saturation). They used depression of the brucite-periclase equilibrium to monitor  $\text{H}_2\text{O}$  activity and found that the  $\text{MgO}$  solubility in the concentrated salt solutions was negligibly small because of a “salting-out” effect produced by the much more soluble chlorides; low solubility of other silicate constituents in concentrated chloride solutions is also likely. Such salt solutions were also found to be more effective than  $\text{H}_2\text{O}$ - $\text{CO}_2$  in suppressing melting in quartzofeldspathic systems at high pressure (Shmulovich and Graham 1996; Newton and Aranovich 1996). Concentrated KCl solutions may, therefore, be a logical medium for investigation of phlogopite-quartz stability to much higher temperatures and pressures than can be achieved in pure  $\text{H}_2\text{O}$  or  $\text{H}_2\text{O}$ - $\text{CO}_2$  mixtures.

#### EXPERIMENTAL METHOD

Experiments on reaction 1 were carried out in internally heated gas pressure apparatus at 2 kbar and in  $\frac{3}{4}$ "-diameter piston-cylinder apparatus with NaCl pressure medium at 7, 10, and 12 kbar. The experimental tech-

**TABLE 1.** Representative microprobe analyses of experimental products

Phase Exp. no	Phlogopite		Enstatite		Potassium feldspar	
	PQ-16	PQ-17	PQ-16	PQ-17	PQ-16	PQ-17
SiO <sub>2</sub>	42.07	41.88	60.01	59.58	66.09	65.03
Al <sub>2</sub> O <sub>3</sub>	11.61	11.22	0.24	0.35	18.14	18.04
MgO	28.16	27.02	39.71	39.58		
K <sub>2</sub> O	9.83	10.15			16.08	16.14
Cl	0.13	0.10				
Total	91.80	90.38	99.96	99.51	100.31	99.21
Si	3.00	3.02	1.002	1.000	3.03	3.02
Al	1.04	0.98	0.005	0.007	0.98	0.99
Mg	3.01	3.02	0.988	0.990		
K	0.91	0.93			0.94	0.96

Notes: Compositions in weight percent; formula proportions based on 8 O atoms for feldspar, 3 O atoms for enstatite, and 11 O atoms for phlogopite.

niques were identical to those of Aranovich and Newton (1996, 1997). Temperature uncertainty in individual experiments, in both kinds of apparatus, is  $\pm 2$  °C; pressure uncertainty is  $\pm 200$  bars in the piston-cylinder apparatus and only  $\pm 7$  bars in the gas pressure apparatus. Starting materials were intimate powder mixtures of synthetic crystalline products and reactants of reaction 1. Product and reactant assemblages were present in equal proportions. The synthetic phlogopite was crystallized from a gel at 2 kbar and 800 °C for 166 hours. Sanidine was crystallized from reagent-grade KNO<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and silica glass with 10% H<sub>2</sub>O at 2 kbar and 800 °C for 72 hours. Enstatite was crystallized hydrothermally from MgO and silica glass at 2 kbar and 800 °C for 48 hours. Quartz was a natural material from Lisbon, Maryland. Synthetic phlogopite and enstatite were too fine grained for reliable microprobe analysis, but some experimental charges showing nearly complete reactions to phlogopite or enstatite contained material that yielded good analyses. The phlogopite totals are slightly low, which we believe is caused by difficulty obtaining good polish of phlogopite in the mounts. However, the analyses are stoichiometric and reveal essentially no Cl. The enstatite has a very low Al<sub>2</sub>O<sub>3</sub> content. Unit-cell parameters were determined by XRD, scanning with CuK $\alpha$  radiation at  $\frac{1}{8}^\circ$  2 $\theta$  per minute. The phlogopite is a well-crystallized 1M polytype, and the potassium feldspar is a high sanidine, based on the determinative charts of Wright and Stewart (1968).

Chemical compositions and unit-cell parameters are given in Tables 1 and 2.

Weighed amounts of starting mix, distilled H<sub>2</sub>O introduced with a microsyringe, and reagent KCl were sealed without significant weight loss in platinum tube segments of 1 mm bore, 0.13 mm wall thickness, and 6 mm length. Typical amounts of mix, H<sub>2</sub>O, and KCl were 5, 1, and 4 mg, respectively. Two capsules, each with somewhat different H<sub>2</sub>O/(H<sub>2</sub>O+KCl) mole fraction,  $X_{\text{H}_2\text{O}}$ , were placed side by side in the experimental assemblies. During an experiment, the H<sub>2</sub>O mole fraction either increased or decreased, depending on whether phlogopite grew or broke down. After a certain amount of reconnaissance, it was generally possible to bracket the equilibrium at a given  $P$  and  $T$  by demonstrating reaction in opposite directions in a single experiment. Reaction progress was monitored in three ways. The major signal was growth or decline of XRD peak heights of the phases in quenched charges in comparison with the diffractograms of the starting mix. It was usually possible to monitor the reaction direction by weight loss-on-drying of punctured capsules. This signal was not as pronounced as with the brucite-periclase reaction because the vapor-phase H<sub>2</sub>O changes in growth or breakdown of phlogopite were quite small. A third method was microscopic observation of textural changes in the solid phases of quenched charges in which corrosion textures signify dissolution of phases whereas geometrical overgrowths signify growth of phases. Large changes in amounts of reactants or products were often visually evident. The photomicrographs in Figure 2 of a typical two-capsule experiment show nearly complete reactions in opposite directions at the same  $P$ - $T$  conditions.

## RESULTS OF EXPERIMENTS

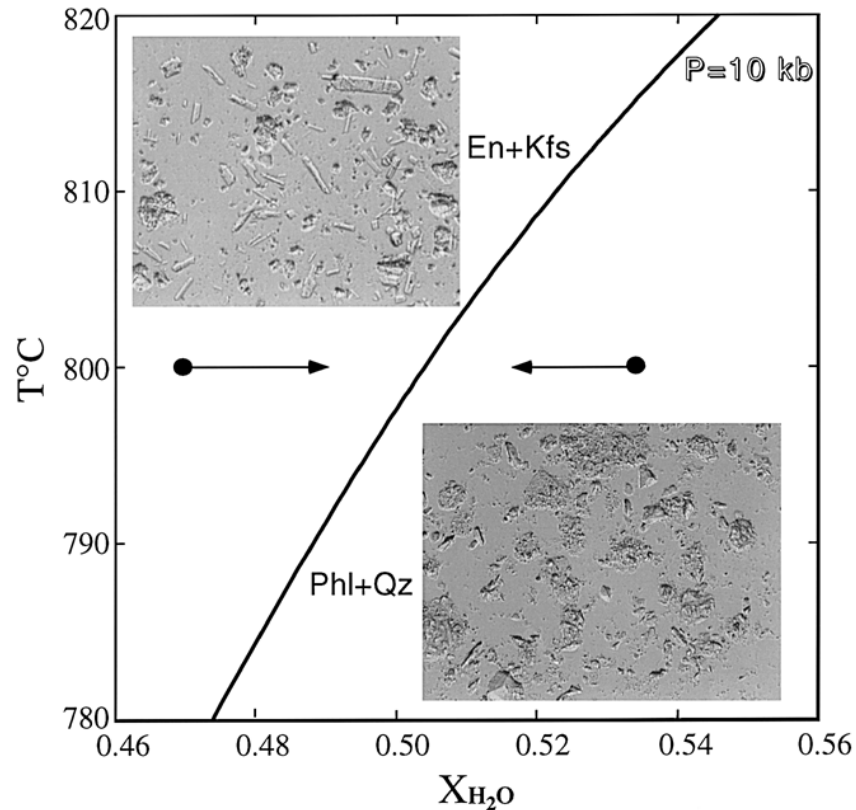
Table 3 gives data for the eight reversed brackets at varying  $T$ ,  $P$ , and fluid composition. The  $P$ - $T$  ranges over which reversals could be secured were limited by three factors: the advent of sylvite saturation below 750 °C at the high solute concentrations necessary to bracket reaction 1; the onset of partial melting at temperatures above 850–875 °C; and the slow reaction kinetics at the lowest pressures and temperatures. The H<sub>2</sub>O activities,  $a_{\text{H}_2\text{O}}$ , corresponding to the final reversed fluid compositions were calculated from the equations of Aranovich and Newton (1997) that summarized their experimental

**TABLE 2.** Unit-cell parameters of synthetic starting material

	$a$	$b$	$c$	$\gamma$	$V$
Phlogopite	5.315	9.204	10.304	99.913	14.952
KMg <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	(0.005)	(0.004)	(0.003)	(0.030)	(0.011)
Enstatite	18.232	8.818	5.176		3.132
MgSiO <sub>3</sub>	(0.002)	(0.001)	(0.001)		(0.001)
K-feldspar	8.602	13.013	7.179	116.08	10.867
KAlSi <sub>3</sub> O <sub>8</sub>	(0.005)	(0.003)	(0.003)	(0.02)	(0.011)

Note: Numbers in parentheses are standard deviations of the corresponding parameters ( $1\sigma$ ).  $a$ ,  $b$ ,  $c$  in nanometers,  $\gamma$  in degrees, and  $V$  in Joules/bar.

**FIGURE 2.** Reversal criteria of a typical experiment, no. PQ 26-27, Table 3, (800 °C, 10 kbar). Reaction 1 is bracketed by demonstration of nearly complete reaction to either enstatite + potassium feldspar or phlogopite + quartz, as shown in the photomicrographs of immersion oil ( $n=1.598$ ) mounts of quenched charges. The charge pictured at the lower right contains large crystals of phlogopite (textured clots) and faceted quartz, but no enstatite prisms, whereas the other charge is almost entirely enstatite + potassium feldspar. Quenched KCl was leached from the charge, using water, before mounting. The circles show the initial fluid compositions of the experiments. The arrowheads indicate the final  $\text{H}_2\text{O}$  contents of the fluid phases as determined by loss-on-drying. (Widths of photos are 500  $\mu\text{m}$ .)



work on the brucite-periclase equilibrium in the presence of concentrated KCl solutions:

$$a_{\text{H}_2\text{O}} = \frac{\gamma X_{\text{H}_2\text{O}}}{1 + \alpha X_{\text{H}_2\text{O}}} \quad (5)$$

**TABLE 3.** Experimental data on the reaction  $\text{Phl} + 3\text{Qz} = 3\text{En} + \text{Kfs} + \text{H}_2\text{O}$  in the presence of  $\text{H}_2\text{O}$ -KCl solutions

Exper. no.	<i>P</i> (kbar)	<i>T</i> (°C)	Dura-tion (h)	$X_{\text{H}_2\text{O}}$ (st.)	$X_{\text{H}_2\text{O}}$ (fin.)	Phases grown
PQ-43	12	875	264	0.626	0.642	En+Kfs
PQ-42	12	875	264	0.663	0.655	Phl+Qz
PQ-39	12	875	193	0.685	0.672	Phl+Qz
PQ-16	10	850	119	0.594	0.613	En+Kfs
PQ-17	10	850	119	0.640	0.633	Phl+Qz
PQ-27	10	800	217	0.534	0.522	Phl+Qz
PQ-26	10	800	217	0.469	0.485	En+Kfs
PQ-20	10	800	196	0.505	0.510	n/r
PQ-51	10	750	432	0.416	0.428	En+Kfs
PQ-52	10	750	432	0.465	0.455	Phl+Qz
PQ-22	7	850	163	0.632	0.641	En+Kfs
PQ-23	7	850	163	0.672	0.663	Phl+Qz
PQ-19	7	850	128	0.647	0.648	n/r
PQ-18	7	850	128	0.604	0.626	En+Kfs
PQ-28	7	800	285	0.551	0.562	En+Kfs
PQ-29	7	800	285	0.591	0.582	Phl+Qz
PQ-53	7	750	402	0.499	0.484	Phl+Qz
PQ-48	7	750	239	0.452	0.463	n/r
PQ-47	7	750	239	0.398	0.412	En+Kfs
PQ-37	2	800	312	0.656	0.661	En+Kfs
PQ-21	2	800	312	0.708	0.698	Phl+Qz
PQ-40	2	800	396	0.680	0.684	n/r

Note: n/r = no clear reaction progress detected by the combination of the  $\text{H}_2\text{O}$  weight change, optics, and X-ray methods.

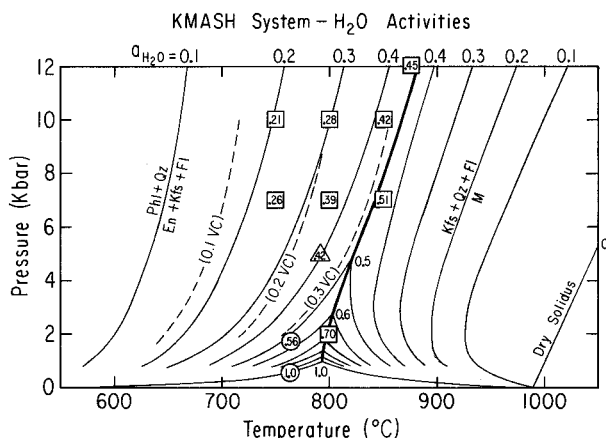
where  $\alpha$  is a degree of dissociation parameter that quantifies pressure-induced ionic dissociation of KCl (leading to low  $\text{H}_2\text{O}$  activities at pressures above 4 kbar) and  $\gamma$  is an activity coefficient that accounts mainly for non-ideality from such factors as solvation of ions. The parameters  $\alpha$  and  $\gamma$  were evaluated from the brucite-periclase equilibrium data:

$$\alpha = \exp(4.166 - 2.709/\rho) - 212.1P/T$$

$$\gamma = \exp[X^2(\text{KCl})(-589.6 - 23.1P)/T] \quad (6)$$

with  $P$  in kbar,  $T$  in K, and  $\rho$  (the density of pure  $\text{H}_2\text{O}$  at  $P$  and  $T$ ) in  $\text{g}/\text{cm}^3$ . Densities of  $\text{H}_2\text{O}$  were calculated from the specific volume tables of Burnham et al. (1969), with a small linear extrapolation (at 875 °C) to 12 kbar. The calculated  $\text{H}_2\text{O}$  activity values at each experimental  $T$  and  $P$  are shown in Figure 3, along with activity values calculated from previous work on reaction 1 in  $\text{CO}_2$ - $\text{H}_2\text{O}$  fluids (Bohlen et al. 1983; Berman et al. 1995).

Determination of  $\text{H}_2\text{O}$  activity by our method is subject to the assumptions that the two Equations 6 describing  $a_{\text{H}_2\text{O}}$  are accurate and that they are applicable to systems containing silicate minerals, i.e., that solution of the silicate components is negligible. The first assumption is



**FIGURE 3.** Mean  $\text{H}_2\text{O}$  activity data for the eight reversals of reaction 1 in  $\text{H}_2\text{O}$ -KCl solutions from the present study (squares), two reversed determinations in  $\text{H}_2\text{O}$ - $\text{CO}_2$  solutions of Berman et al. (1995) (circles), and one reversal of Bohlen et al. (1983) in  $\text{H}_2\text{O}$ - $\text{CO}_2$  solutions (triangle). The  $\text{H}_2\text{O}$  activities in  $\text{CO}_2$  solutions were based on the results of Kerrick and Jacobs (1981).  $\text{H}_2\text{O}$  isoactivity lines of reaction 1 were fit to the reversal data by a least-squares method using the measured thermophysical data of Table 4. The dashed lines are corresponding isoactivity curves according to Vielzeuf and Clemens (1992) shown for comparison. The  $\text{H}_2\text{O}$  isoactivity solidus curves were taken from the latter reference. Their intersections with corresponding isoactivity lines of reaction 1 define the dehydration melting reaction 4 (text and Fig. 1), shown by the bold line.

justified by the precision of the equations of Aranovich and Newton (1997), which reproduce mole fraction midpoints on the brucite dehydration to  $\pm 0.012$ , i.e., well within the experimental brackets; these equations also reproduce almost exactly the very precise DTA measurements on the hydrous melting of KCl at pressure up to 2 kbar, obtained by Chou et al. (1992). The second assumption, that of insignificant vapor solubility of silicate constituents, required additional experiments in the present study. Although a "salting out" effect is anticipated,

the relatively coarse crystal growth observed in our highest temperature experiments indicates at least moderate solubility of the minerals in the concentrated brines. To test for major solubility of silicates, we made experiments with capsules containing 1 mg  $\text{H}_2\text{O}$ , 4 mg KCl, and 0.15 mg of either quartz or sanidine. The experiments were at 10 kbar and 800 °C for 48 hours. Had the entire amount of quartz dissolved, the maximum contribution to the vapor phase would have been 2.2 mol%. In fact, most of the original quartz was recovered in the form of doubly terminated euhedral crystals. No evidence could be found of an  $\text{SiO}_2$ -rich vapor quench precipitate. The potassium feldspar also was recovered mostly in the form of well-faceted crystals, but some chalky quench precipitate was observed. These experiments indicate that the amount of solute silicate components was too small to have influenced our activity measurements appreciably. Independent support for this conclusion is afforded by the recent work of Shmulovich and Graham (1996). These authors used depression of the low albite melting temperature in concentrated  $\text{H}_2\text{O}$ -NaCl solutions relative to that in  $\text{H}_2\text{O}$ - $\text{CO}_2$  to constrain  $a_{\text{H}_2\text{O}}$  in the brine. At 9.2 kbar and 800 °C they observed melting in the  $\text{H}_2\text{O}$ -NaCl fluid of composition  $X_{\text{H}_2\text{O}} = 0.82$ , and in the  $\text{H}_2\text{O}$ - $\text{CO}_2$  fluid at  $X_{\text{H}_2\text{O}} = 0.59$  (Shmulovich and Graham 1996, Fig. 1); this is their only datum that allows direct comparison of the  $\text{H}_2\text{O}$  activity in the two systems. Neglecting the effect of minor amounts of Cl and  $\text{CO}_2$  dissolved in the corresponding melts,  $\text{H}_2\text{O}$  activity must be the same in both systems under these conditions. For the  $\text{H}_2\text{O}$ -NaCl system, equations analogous to Equation 6 give  $a_{\text{H}_2\text{O}} = 0.72$  (Aranovich and Newton 1996); for the system  $\text{H}_2\text{O}$ - $\text{CO}_2$ , the equation of state of Kerrick and Jacobs (1981) also predicts  $a_{\text{H}_2\text{O}} = 0.72$ . The exactness of the agreement may be fortuitous, given all the experimental uncertainties involved, but it appears to indicate that the equations for  $\text{H}_2\text{O}$  activity, derived from experimental data in the simple system  $\text{MgO}$ - $\text{H}_2\text{O}$ -(K,Na)Cl (Aranovich and Newton 1996, 1997), may be applied with confidence to more complex

**TABLE 4.** Thermodynamic data for phlogopite and related minerals

	$-\Delta H_f^\circ$ (kJ)	$S^\circ$ (J/K)	$a$	$b$	$c$	$d$	$e$
Phlogopite $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$	6212.35	334.60	372.13	-0.077 25	357 500	0	-8600.6
Enstatite $\text{MgSiO}_3$	1545.52	66.27	350.70	-0.147 30	1 679 000	$5.826 \times 10^{-5}$	-4296.0
Sanidine $\text{KAlSi}_3\text{O}_8$	3959.56	232.90	693.37	-0.171 70	3 462 200	$4.9188 \times 10^{-5}$	-8305.4
$\alpha$ -Quartz $\text{SiO}_2$	910.70	41.46	81.119	0.018 283	-180 990	$5.406 \times 10^{-6}$	-698.46
$\beta$ -Quartz $\text{SiO}_2$			57.959	0.009 330	1 834 710	0	0
Steam $\text{H}_2\text{O}$	241.81	188.83	7.368	0.027 468	-223 160	$-4.8117 \times 10^{-6}$	341.74

Notes:  $C_p = a + bT + c/T^2 + dT^2 + e/(T)^{1/2}$ .  $V = V_{298} + \alpha V(T - 298) - \beta VP$ . References are 1 = Present work; 2 = Robie and Hemingway (1984) (disorder entropy of 18.70 J/K assigned to phlogopite); 3 = Koziol and Newton (1995) ( $\Delta H_f^\circ$ , enstatite); 4 = Krupka et al. (1985a, 1985b); 5 = Robie et al. (1978) (disorder entropy of 18.70 J/K assigned to sanidine); 6 = Hemingway (1987) ( $\Delta H_f^\circ(\alpha - \beta\text{Qz}) = 0.625$  kJ at 848 K); 7 = Holland and Powell (1990).

systems with a small amount of dissolved silicate material.

Standard Gibbs free energy changes at each experimental temperature and standard enthalpy changes of reaction 1 at 298 K were calculated from each experimental half-bracket with the measured thermophysical data of Table 4. The relevant equations are:

$$\begin{aligned} \Delta G_T^0 &= -RT \ln f^0(\text{H}_2\text{O}) - RT \ln a_{\text{H}_2\text{O}} \\ &\quad - (P - 1)\Delta V^*298 \\ \Delta H_{298}^0 &= \Delta G_T^0 - \int \Delta S_T^0 dT + 298\Delta S_{298}^0 T \end{aligned} \quad (7)$$

where  $\Delta G_T^0$  is the standard Gibbs free energy change at  $T$  and one bar,  $\Delta H_{298}^0$  is the standard enthalpy change at 298 K,  $a_{\text{H}_2\text{O}}$  is the derived activity value for  $\text{H}_2\text{O}$  at each experimental point,  $f_{\text{H}_2\text{O}}^0$  is the corresponding fugacity of pure  $\text{H}_2\text{O}$ , and  $\Delta V^*$  is the solid volume change of the reaction evaluated at  $T$  and  $P/2$ . The  $\Delta G_T^0$  values derived from our 16 experimental data points are given in Table 5. The calculations make use of the  $\text{H}_2\text{O}$  fugacities interpolated from the tables of Burnham et al. (1969). A logarithmic extrapolation was made to derive the  $\text{H}_2\text{O}$  fugacity at 12 kbar and 875 °C. Also included in Table 5 are the  $\Delta G_T^0$  values derived from the reaction 1 bracketing points of Bohlen et al. (1983), which define the equilibrium between 780 and 800 °C at 5 kbar in the presence of a  $\text{H}_2\text{O}$ - $\text{CO}_2$  fluid with  $X_{\text{H}_2\text{O}} = 0.35$ ; the similar data of Berman et al. (1995) with  $X_{\text{H}_2\text{O}} = 0.51$  at conditions of  $1.74 \pm 0.1$  kbar and  $764 \pm 5$  °C; and a reversed point by the latter authors at  $0.48 \pm 0.02$  kbar and  $763 \pm 11$  °C with pure  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}$  activities in the experimental fluids with  $\text{CO}_2$  were taken from Kerrick and Jacobs (1981). Our tentative conclusion is that the experimental reaction points in  $\text{H}_2\text{O}$ - $\text{CO}_2$  fluids, and the  $\text{H}_2\text{O}$  activity in the mixtures of Kerrick and Jacobs (1981) are consistent with our results in the  $\text{KCl}$ - $\text{H}_2\text{O}$  solutions.

In calculating the standard enthalpy change, it is necessary to determine the standard entropy change,  $\Delta S_T^0$ , at

some temperature. This quantity differs from the Third Law entropy change, which is well determined by low-temperature heat capacity measurements for all of the phases, by entropy increments added to sanidine and phlogopite to account for (Al-Si) disorder. The enlarged temperature range covered by experiments of this study allows  $\Delta S_T^0$  to be evaluated independently from the temperature change of the derived  $\Delta G_T^0$  values. The 22  $\Delta G_T^0$  values given in Table 5 were fitted by least-squares regression as a linear function of temperature, yielding:

$$\Delta G_T^0 \text{ (kJ)} = 95.447 - 0.14373 T \text{ (K)}$$

with  $r^2 = 0.973$ . The temperature coefficient, 143.73 J/K, is the average  $\Delta S_T^0$  over the range 1023–1148 K. This value is almost exactly the Third Law entropy change at the mean temperature, 1073 K, and indicates that the disorder entropy of phlogopite is very nearly equal to that of sanidine, so that the two increments cancel in reaction 1. This conclusion is in accord with Clemens et al. (1987) and Vielzeuf and Clemens (1992), who adopted the maximum disorder entropy for phlogopite. Accordingly, the entropy of phlogopite at 298 K is taken as the sum of the Third Law entropy (315.9 J/K) and the configurational entropy, totaling 334.6 J/K.

The most significant result of the present investigation is that for any  $T$  and  $P$  where the assemblage represented by reaction 1 is in equilibrium, the  $\text{H}_2\text{O}$  activity is substantially higher than given by previous estimates, including that of Vielzeuf and Clemens (1992), shown in Figure 3. The higher  $a_{\text{H}_2\text{O}}$  in turn requires a substantially smaller  $\Delta H_{298}^0$ . The mean value of the derived  $\Delta H_{298}^0$  from the 22 data points of Table 5 is 106.54 kJ, with a standard deviation ( $2\sigma$ ) of 2.00 kJ. The data in Table 5 reveal also that the  $\Delta H_{298}^0$  values yielded by the determinations in  $\text{H}_2\text{O}$ - $\text{CO}_2$  fluids of Bohlen et al. (1983) and Berman et al. (1995) are in good agreement with the present results. The present average value is 6 kJ smaller than that estimated by Vielzeuf and Clemens (1992) using the same entropy of disorder assumptions and other input data. The latter authors do not give any uncertainties on their tabulated values of  $\Delta G^0$  of the minerals (Vielzeuf and Clemens 1992, Table 4), which prevents a closer comparison with their results. The reason for the discrepancy is, however, evident: They based their calculations on the experimental data of Wood (1976) on reaction 1, which have been shown to be at odds with some other phase equilibrium studies (see detailed discussion in Clemens et al. 1987) as well as with the results of the present study. The enthalpy of formation from the elements of phlogopite at 298 K, which is consistent with the measured data of Table 4 and the present average  $\Delta H_{298}^0$  of reaction 1, is  $-6212.35 \pm 4.62$  kJ ( $2\sigma$  uncertainty, which includes the  $\pm 2$  kJ uncertainty in  $\Delta H_{298}^0$  of reaction 1 and the sum of the corresponding uncertainties for quartz, sanidine, and enstatite, and is therefore a maximal value).

Using the present mean  $\Delta H_{298}^0$ , the entropy change of the reaction,  $\Delta S_{298}^0 = 161.56$  J/K, which assumes maximal disordering entropy in phlogopite and sanidine and the

TABLE 4—Extended

	$V_{298}^0$ (J/bar)	$\alpha V$ (J/barK)	$\beta V$ (J/bar <sup>2</sup> )	Refs.
Phlogopite $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$	14.964	$39.0 \times 10^{-5}$	$24.5 \times 10^{-6}$	1, 2, 7
Enstatite $\text{MgSiO}_3$	3.131	$9.0 \times 10^{-5}$	$2.3 \times 10^{-6}$	3, 4, 7
Sanidine $\text{KAlSi}_3\text{O}_8$	10.892	$20.6 \times 10^{-5}$	$20.0 \times 10^{-6}$	5, 7
$\alpha$ -Quartz $\text{SiO}_2$	2.269	$8.0 \times 10^{-5}$	$5.9 \times 10^{-6}$	6, 7
$\beta$ -Quartz $\text{SiO}_2$	2.367	0	$2.6 \times 10^{-6}$	6, 7
Steam $\text{H}_2\text{O}$				5

thermophysical data from Table 4, the isoactivity lines of Figure 3 were constructed. Figure 3 shows that enstatite and sanidine can be stable together relative to phlogopite and quartz at  $\text{H}_2\text{O}$  activities approaching 0.5 in the mid-crustal pressure range.

Subsolidus phlogopite + quartz stability is limited at high temperatures by fluid-absent melting (dehydration melting) according to reaction 4. The amount of potassium feldspar that appears on the right-hand side is small and was discounted by Peterson and Newton (1989) but was confirmed by Vielzeuf and Clemens (1992). The  $P$ - $T$  position of the fluid-absent melting reaction can be located accurately from our data for reaction 1 together with a description of the  $\text{H}_2\text{O}$  isoactivity curves of the sanidine-phlogopite-quartz-fluid melting reaction 3. The sanidine-quartz melting curves can be constructed with the experimental data in  $\text{CO}_2$ - $\text{H}_2\text{O}$  fluids of Bohlen et al. (1983), imposing an activity model of mixing, and assuming that the  $\text{MgO}$  and  $\text{CO}_2$  contents of the liquids are negligible. A very similar isoactivity set is provided by the theoretical hydrous silicate liquid activity model of H. Nekvasil and C. W. Burnham used by Vielzeuf and Clemens (1992). Adopting the latter  $\text{H}_2\text{O}$  activity model, the dehydration melting reaction curve, shown in Figure 3, is defined by the intersections of corresponding  $\text{H}_2\text{O}$  isoactivity curves of the subsolidus reaction 1 and those of the hydrous melting reaction 3. The resulting dehydration melting curve lies at somewhat lower temperatures than shown by Vielzeuf and Clemens (1992), but at considerably higher temperatures than estimated by Montana and Brearley (1989) and Peterson and Newton (1989). One of our reversed  $\text{H}_2\text{O}$  activity data points, at 850 °C

and 7 kbar, is in slight violation of the dehydration melting curve, which should place absolute upper temperature limits on possible reversals of reaction 1. The discrepancy probably results from slight temperature uncertainty of the isoactivity sanidine-quartz solidus lines by the Nekvasil-Burnham model. The discrepancy is removed if the solidus curves are raised by a few degrees in the vicinity of dehydration melting.

#### PETROLOGICAL INTERPRETATION

The most important result for petrology of the present revision of phlogopite stability is that  $\text{H}_2\text{O}$  activity may be considerably higher in charnockitic metamorphic and magmatic processes than assumed by most previous workers. This principle is illustrated in Figure 3 and can be made somewhat more directly applicable to nature by extension of the present results to a simple granite system that includes the component  $\text{Na}_2\text{O}$  and in which the additional feldspar albite participates (or, at supersolvus conditions, in which the feldspar is an intermediate alkali feldspar). In this reconstruction, it is necessary to assign a bulk K/Na ratio appropriate for a granite, which we take as unity. The alkali feldspar solvus is reconstructed from the subregular mixing parameters of Fuhrman and Lindsley (1988). The boundary between subsolvus and supersolvus feldspars is shown in Figure 4. The  $\text{H}_2\text{O}$  isoactivity solidus curves are taken from Johannes (1985) and based on the Nekvasil-Burnham model.

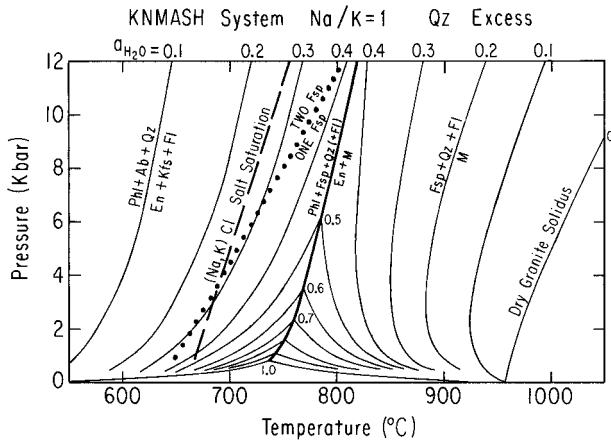
Figure 4 shows that the dehydration melting reaction of phlogopite and quartz in a simple granite system lies at low temperatures, below 800 °C at pressures to 8 kbar. This result confirms the recent experimental work of

**TABLE 5.** Results of the calculations of  $\Delta G_{\text{T}}^{\circ}$  and  $\Delta H_{298}^{\circ}$  of the reaction  $\text{Phl} + 3\text{Qz} = 3\text{En} + \text{Kfs} + \text{H}_2\text{O}$  from experiments in  $\text{H}_2\text{O}$ -KCl  $\text{H}_2\text{O}$ - $\text{CO}_2$

$P$ (kb)	$T$ (K)	$\rho_{\text{H}_2\text{O}}$ (g/cm <sup>3</sup> )	$f_{\text{H}_2\text{O}}^0$ (bar)	$X_{\text{H}_2\text{O}}$	Soln.	$a_{\text{H}_2\text{O}}$	$-\Delta V_{\text{e}}$ (J/bar)	$-(\Delta)G_{\text{T}}^{\circ}$ (kJ)	$\Delta H_{298}^{\circ}$ (kJ)	Ref.
12.0	1148	0.897	25861	0.642	KCl	0.437	1.675	68.98	107.15	3
				0.655		0.453		69.32	106.81	
10.0	1123	0.866	16953	0.613	KCl	0.404	1.682	65.64	106.87	3
				0.633		0.427		66.16	106.35	
10.0	1073	0.885	16214	0.485	KCl	0.258	1.686	57.57	107.77	3
				0.522		0.293		58.67	106.63	
10.0	1023	0.905	15331	0.428	KCl	0.198	1.691	51.37	106.76	3
				0.455		0.220		52.27	105.86	
7.0	1123	0.760	8323	0.641	KCl	0.498	1.690	65.94	106.57	3
				0.663		0.525		66.43	106.08	
7.0	1073	0.783	7847	0.562	KCl	0.383	1.695	59.67	105.63	3
				0.582		0.406		60.19	105.11	
7.0	1023	0.806	7299	0.412	KCl	0.219	1.699	50.65	107.48	3
				0.484		0.275		52.59	105.54	
5.0	1073	—	4545	0.350	$\text{CO}_2$	0.421	1.701	58.91	106.39	1
			4396	0.350		0.427		57.49	104.92	
2.0	1073	0.425	1576	0.656	KCl	0.678	1.708	58.80	106.50	3
				0.708		0.734		59.51	105.79	
1.74	1042	—	1329	0.510	$\text{CO}_2$	0.562	1.712	54.34	106.51	2
			1313	0.510		0.558		53.62	105.80	
0.48	1047	—	431	1.000	$\text{H}_2\text{O}$	1.000	1.715	51.98	109.59	2
			425	1.000		1.000		50.75	107.66	
									avg.	
									106.54 ± 2.00	
									(2σ)	

Note:  $\Delta G_{\text{T}}^{\circ} = 95.447 - 0.14373T(\text{K})$  (1023–1148 K)  $r^2 = 0.973$ . References are 1 = Bohlen et al. 1983; 2 = Berman et al. 1995; 3 = present study.





**FIGURE 4.**  $\text{H}_2\text{O}$  isoactivity lines of reaction 1 in a simple granitic system ( $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ : KNMASH) with equimolar Na and K and quartz in excess. The curves are from Figure 3 with a correction for the  $\text{NaAlSi}_3\text{O}_8$  content of alkali feldspar according to the feldspar solid solution properties of Fuhrman and Lindsley (1988). The bold dotted line is their solvus temperature as a function of pressure for  $\text{Na}/\text{K} = 1.0$ . Shown also are simple granite solidus curves for  $a_{\text{H}_2\text{O}}$  of various values, reproduced from Johannes (1985). The two sets of isoactivity curves intersect in the dehydration melting curve. The curves apply equally well to a vapor-absent system or a system with  $(\text{Na},\text{K})\text{Cl}$  solutions of variable concentrations and  $\text{Na}/(\text{K}+\text{Na}) = 0.8$ . The lower temperature limit at which such solutions could coexist with enstatite + potassium feldspar before salt saturation occurs is shown by the bold dashed line. The interval between the salt saturation and fluid-absent melting is the  $P$ - $T$ - $a_{\text{H}_2\text{O}}$  space in which charnockitic assemblages (containing orthopyroxene) could coexist with an alkali chloride solution without melting. (Phase abbreviations as in Figure 1; Ab = Na-rich feldspar, Fsp = supersolvus  $(\text{Na},\text{K})$ -rich feldspar.)

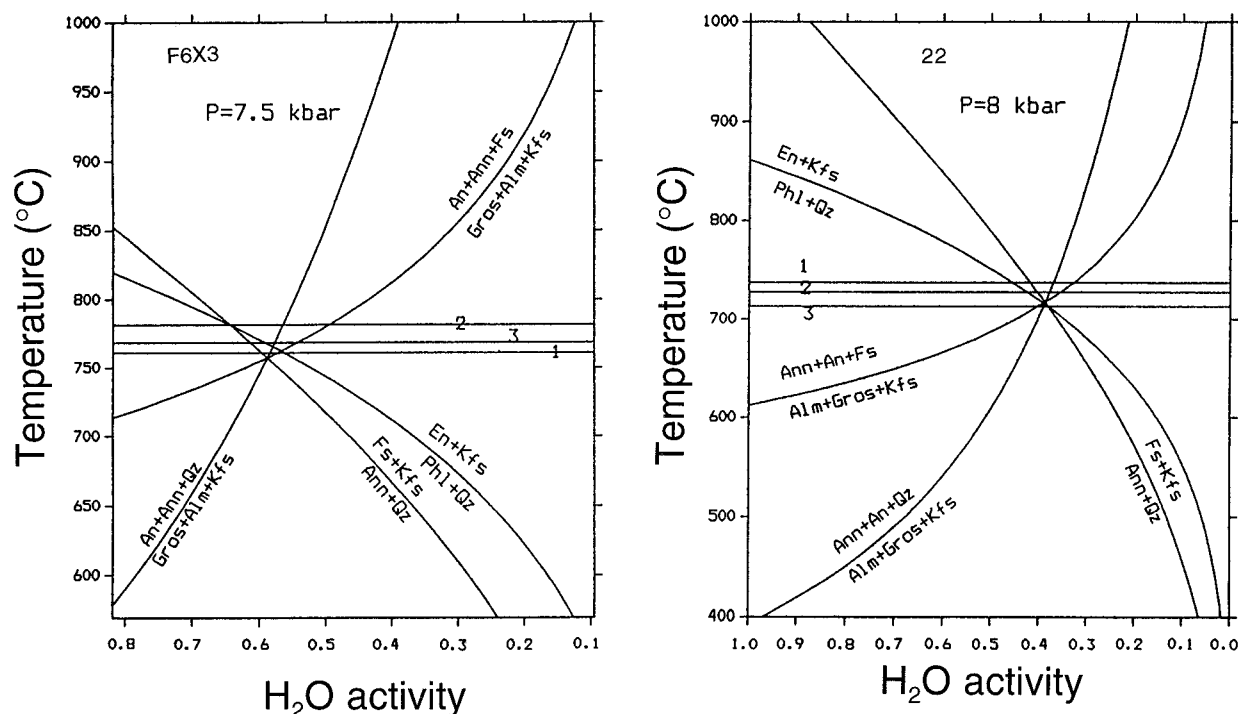
Singh and Johannes (1996) for dehydration melting of a plagioclase An 45 with phlogopite and quartz to 12 kbar. Their  $P$ - $T$  curve for the first melting departs from the present analogous curve to considerably lower temperatures in the pressure range above 7 kbar, presumably because of the appearance of the dense Ca-bearing phases clinopyroxene, amphibole, and zoisite, along with melt, which drives melting to lower temperatures at higher pressures.

Figure 4 shows that orthopyroxene can form in quartzofeldspathic systems at substantially higher  $\text{H}_2\text{O}$  activities than estimated by most previous workers. These include Aranovich (1984), Bhattacharya and Sen (1986), Lamb and Valley (1988), Moecher and Essene (1991), and Newton (1995). These studies concluded that, for the temperature range of 700–800 °C and pressure range 6–10 kbar considered by some workers to be characteristic for granulite metamorphism, the corresponding  $a_{\text{H}_2\text{O}}$  values should lie in the range 0.10–0.25. The present results suggest that  $\text{H}_2\text{O}$  activities as high as 0.5 may be appropriate for charnockitic (orthopyroxene-feldspar-quartz-biotite) magmatic and metamorphic processes at crustal pressures. Substitution of additional Al and Ti in biotite

extends the temperature- $a_{\text{H}_2\text{O}}$  range over which biotite and orthopyroxene can coexist in quartzofeldspathic systems (cf. Patiño-Douce 1993).

The magnitude of  $\text{H}_2\text{O}$  activity appropriate to the crystallization of natural deep crustal assemblages containing orthopyroxene and biotite can be assessed by incorporating the present derived enthalpy and entropy of phlogopite into the systematic data sets of Berman et al. (1995) and Berman and Aranovich (1996). Calculations were performed on garnet-biotite granulite assemblages from two Archean granulite terranes in southern India where complete mineral chemistry documentation exists for many orthopyroxene-bearing rocks. The areas chosen are the Nilgiri Hills (Raith et al. 1990) and the Shevaroy Hills (Hansen et al. 1995), both in northern Tamil Nadu. Paleopressures near 8 kbar have been well characterized for both terranes and were verified by the present calculations. All of the assemblages for which calculations were performed yielded  $\text{H}_2\text{O}$  activities in the range 0.4–0.6. Figure 5 shows two examples of South Indian granulites.  $\text{H}_2\text{O}$  activity and temperature of recrystallization are determined simultaneously as the intersections of seven univariant exchange and net transfer reactions involving garnet, plagioclase, orthopyroxene, biotite, potassium feldspar, and quartz. The consistency of the determinations for individual rocks is evident. The indicated paleotemperatures are in excellent agreement with those inferred by the authors of the analytical data. The calculations show that components additional to the KNMASH system probably extend somewhat the  $\text{H}_2\text{O}$  activity range over which orthopyroxene may be stable in quartzofeldspathic rocks (charnockites) at deep crustal conditions.

Concentrated aqueous solutions of strong electrolytes have been suggested (e.g., Shmulovich 1988; Aranovich and Newton 1996; 1997; Shmulovich and Graham 1996) as a possible model of metamorphic fluid with a low  $\text{H}_2\text{O}$  activity. It is noteworthy that the  $a_{\text{H}_2\text{O}}$  range inferred for the South Indian samples corresponds to only moderately concentrated alkali chloride solutions at the inferred  $P$ - $T$  conditions. The appropriate  $(\text{Na},\text{K})\text{Cl}$  concentrations are far from salt saturation and, in fact, are similar to the concentrations of brine inclusions estimated microscopically by Touret (1985) for the Bamble, S. Norway, granulites (40–80 wt% NaCl equivalent). Concentrated brines in  $\text{CO}_2$ -bearing systems at high-grade metamorphic conditions would be immiscible with a  $\text{CO}_2$ -rich phase (Duan et al. 1995). This could account for the apparently coeval suites of dense  $\text{CO}_2$  inclusions and brine inclusions observed in the Bamble rocks and in other granulites (Crawford and Hollister 1986). The brine suite of fluids is likely to have been the more important in its geochemical effects because of its capacity for alkali exchange and the much greater infiltration ability of concentrated salt solutions in quartzofeldspathic rocks than dense  $\text{CO}_2$  (Watson and Brenan 1987). The importance of  $\text{CO}_2$  infiltration has probably been overestimated from the fluid inclusion evidence.

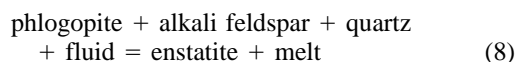


**FIGURE 5.**  $\text{H}_2\text{O}$  activity- $T$  relations of two South Indian charnockites, no. F6X3 from the Shevaroy Hills, Tamil Nadu (Hansen et al. 1995) and no. 22 from the Nilgiri Hills, Tamil Nadu (Raith et al. 1990), based on their mineral compositions. Seven independent univariant reactions yield highly consistent temperatures, pressures, and  $\text{H}_2\text{O}$  activities by intersection using the Berman et al. (1995) and Berman and Aranovich (1996) thermodynamic data sets with the properties of phlogopite derived from the present study. The indicated temperatures and pressures are quite close to those advocated by Hansen et al. (1995) and Raith et al. (1990), but the  $\text{H}_2\text{O}$  activities are substantially higher (0.4–0.6) than estimated by these authors. (Abbreviations: En = enstatite,  $\text{MgSiO}_3$ ; Fs = ferrosilite,  $\text{FeSiO}_3$ ; Phl = phlogopite,  $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ ; Ann = annite,  $\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ ; Alm = almandine,  $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ; Py = pyrope,  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ; Gros = grossular,  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ; Kfs = potassium feldspar,  $\text{KAlSi}_3\text{O}_8$ ; An = anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ; Qz = quartz,  $\text{SiO}_2$ . Reaction 1:  $\text{Alm} + \text{En} = \text{Py} + \text{Fs}$ ; reaction 2:  $\text{Alm} + \text{Phl} = \text{Py} + \text{Ann}$ ; reaction 3:  $\text{Fs} + \text{Phl} = \text{En} + \text{Ann}$ .)

Crystallization of some felsic magmas in the presence of concentrated brines is suggested by recent observations of hypersaline fluid inclusions in granitic rocks (for example, Dunbar et al. 1996). It is of interest to determine the  $P$ - $T$  range over which orthopyroxene and potassium feldspar could coexist in the crystallization of a granite magma in the presence of an alkali chloride brine. The bold dashed line of Figure 4 shows the lower temperature limit of orthopyroxene-potassium feldspar stability in the model brine-present granite system before salt saturation occurs. It is assumed that the  $\text{K}/(\text{K}+\text{Na})$  ratio of 0.2 of aqueous chloride solutions that coexist with both potassium feldspar and albite at lower pressures and dilute solutions (Orville 1963; Iiyama 1965) continues to apply to near-solidus granite systems at higher pressures and with more concentrated solutions. The assumption is also made in Figure 4 that Cl contents of the granitic liquids under these conditions are negligible, in accord with the experimental data at both low (Metrich and Rutherford 1992) and high (Shmulovich and Graham 1996; Newton and Aranovich 1996) pressure.

The continuous bold curve of Figure 4 can be reinter-

preted as the univariant melting equilibrium in the presence of (Na,K)Cl brines of suitably low  $\text{H}_2\text{O}$  activity:



The brine-present univariant melting curve is identical in  $P$ - $T$  position to the dehydration melting curve, inasmuch as the single parameter  $a_{\text{H}_2\text{O}}$  determines its temperature at any pressure, under the assumption of negligible Cl in the silicate melt. The behavior of biotite granites in the concentrated brine-present system is, however, different from that in the fluid-absent system in two important ways. First, a substantial  $P$ - $T$  range exists over which subsolidus dehydration to orthopyroxene may occur. The lower temperature bound of the subsolidus charnockite region is limited by salt saturation of the fluids, shown in Figure 4. In a fluid-absent system, in contrast, orthopyroxene in a biotite granite cannot form unless partial melting takes place at the fluid-absent melting line. The extended window of orthopyroxene stability in granitic systems with concentrated brines may help to explain the charnockitic metamorphism in certain areas, which seem to occur

without the intervention of melting, as in southwestern Sweden (Andersson et al. 1992), and the recent identification of concentrated brine inclusions in quartz associated with granulite metamorphism and alkali metasomatism (Smit and Van Reenen 1997). Second, the amount of anatexis melting is not limited by the  $\text{H}_2\text{O}$  contained in biotite, as it is in dehydration melting, but may be much larger at near-solidus temperatures in brine-present melting processes that generate orthopyroxene. This feature in part may account for the enigma of large amounts of charnockitic migmatization found in some terranes, as in the Ashuanipi diatexites of northern Labrador, where the amount of leucosome approaches 50% of the rock volume, thus implying extremely high temperatures of anatexis, for which there is no independent evidence under the dehydration melting hypothesis (Percival 1991). Also, many high-grade migmatite restites are rich in biotite, the supposed source of  $\text{H}_2\text{O}$  for melting, which seems contradictory to the large amount of leucosome commonly observed, but is consistent with the melting in presence of a fluid phase. Other geochemical features of high-grade terranes, such as local extreme mobility of thorium in some charnockitic complexes, are better explained by fluid-transport processes (with or without melting), quite plausibly as halide species, than by magmatic processes alone (Nozhkin and Turkina 1994).

The present use of concentrated aqueous salt solutions in determining the stability of phlogopite may be applicable also to the study of other refractory hydrate minerals at lowered  $\text{H}_2\text{O}$  activity. Pargasite, alkali amphibole, and white micas are examples of hydrous silicates that have proven difficult to define thermochemically in experimental systems, but which may be amenable to investigation in concentrated chloride solutions.

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