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Reversed determination of the reaction: Phlogopite + quartz = enstatite + potassium feldspar + H_2O in the ranges 750–875 °C and 2–12 kbar at low H_2O activity with concentrated KCl solutions

L.Y. ARANOVICH* AND R.C. NEWTON

Department of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Avenue, Chicago, Illinois 60637, U.S.A.

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_2O activities by reversal of the H_2O content of concentrated KCl solutions equilibrated with product and reactant assemblages. Synthetic 1M phlogopite [$KMg_3AlSi_3O_{10}(OH)_2$] and enstatite ($MgSiO_3$) maintained end-member stoichiometry throughout, and the potassium feldspar ($KAlSi_3O_8$) was a high sanidine, based on unit-cell refinements. The broad P-T-X_{H_2O} and narrow reversal ranges of this investigation were possible because of the low and well-defined H_2O activity, yet powerful fluxing action, of concentrated KCl solutions. Solubility experiments on quartz and potassium feldspar in our P-T-X_{H_2O} range showed that fluid-phase solution of silicate constituents was too small to have affected the H_2O activity in the experiments. The new determinations are more definitive than previous work done at very low pressures with pure H_2O or in CO_2-H_2O 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_2O activity in the petrogenesis of high-grade metamorphic rocks. The lower thermal stability that we find for phlogopite requires revision in estimates of H_2O 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 $a_{H_2O} = 0.4$–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_2O activity range of granulites is that alkali chloride solutions of only moderate concentration [$X_{H_2O} = 0.5$–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_{H_2O}. 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, $KMg_3(AlSi_3)O_{10}(OH)_2$. Partial substitution of Ti for octahedral cations (Mg and Fe) and partial replacement of OH^- by F^- 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_2O activity by means of such simple-system reactions as:

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* E-mail: lyaranov@midway.uchicago.edu

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$$\underset{\substack{\text{Phlogopite}\\ \text{(Biotite s.s.)}}}{KMg_3Si_3AlO_{10}(OH)_2} + \underset{\text{Quartz}}{3SiO_2}$$

$$= \underset{\substack{\text{Enstatite}\\ \text{(Orthopyroxene s.s.)}}}{3MgSiO_3} + \underset{\text{potassium feldspar}}{KAlSi_3O_8} + H_2O \qquad (1)$$

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 H_2O 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 H_2O activity, as in CO_2-rich fluids (Wendlandt and Eggler 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 K_2O-MgO-Al_2O_3-SiO_2-H_2O (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 SiO_2-saturated part of the KMASH system (Fig. 1). The phlogopite-quartz dehydration reaction is confined to very low pressures for H_2O activities of unity (pure H_2O) and is terminated in the vicinity of 800 °C by hydrous melting, according to the reaction:

$$\text{phlogopite} + \text{quartz} + \text{fluid} = \text{enstatite} + \text{melt} \quad (2)$$

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 reaction 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 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 H_2O-CO_2 fluids with X_{H_2O} = 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:

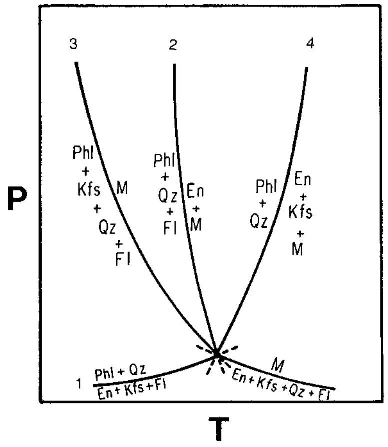

FIGURE 1. Schematic univariant equilibria involving phlogopite-quartz reactions in the SiO_2-saturated portion of the system K_2O-MgO-Al_2O_3-SiO_2-H_2O (KMASH) (after Luth 1967). The univariant reactions are labeled as in the text. (Phl = phlogopite, $KMg_3AlSi_3O_{10}(OH)_2$; En = orthoenstatite, $MgSiO_3$; Kfs = sanidine, $KAlSi_3O_8$; Qz = quartz, SiO_2; Fl = aqueous fluid; M = silicate melt.)

$$\text{phlogopite} + \text{quartz} + \text{potassium feldspar} + \text{fluid} = \text{melt} \quad (3)$$

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 H_2O-CO_2 fluid with X_{H_2O} = 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 H_2O-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:

$$\text{phlogopite + quartz = enstatite + potassium feldspar + melt} \quad (4)$$

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 $Pb_2B_2O_4$ at 714 °C. These measurements take into account the enthalpy of solution of H_2O in the calorimenter 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, ΔH^0_f, of phlogopite from the elements of -6215.33 ± 6.28 kJ (2σ) 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 ΔH^0_f 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 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 H_2O and between 760 and 768 °C at 1.74 kbar in an equimolar H_2O-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 Vielzuf and Clemens (1992). Correspondingly, the H_2O 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 H_2O activities than inferred by several previous interpretations. A single datum on reaction 1 reported by Clemens (1995) (between 0.51 and 0.62 ± 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 H_2O, 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 prefered orientation of phlogopite and enstatite. Another source of discrepancy is that all three experimental studies in which reversals on reaction 1 in pure H_2O 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 H_2O-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 H_2O activity is a new possibility for investigating the stabilities of refractory hydrate minerals over extended *P-T* ranges. Aranovich and Newton (1996, 1997) determined H_2O 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 H_2O activity and found that the 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 H_2O-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 H_2O or H_2O-CO_2 mixtures.

EXPERIMENTAL METHOD

Experiments on reaction 1 were carried out in internally heated gas pressure apparatus at 2 kbar and in ¾''-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_2	42.07	41.88	60.01	59.58	66.09	65.03
Al_2O_3	11.61	11.22	0.24	0.35	18.14	18.04
MgO	28.16	27.02	39.71	39.58		
K_2O	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 ±2 °C; pressure uncertainty is ±200 bars in the piston-cylinder apparatus and only ±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_3, γ-Al_2O_3, and silica glass with 10% H_2O 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_2O_3 content. Unit-cell parameters were determined by XRD, scanning with Cu$K\alpha$ radiation at ⅛° 2θ 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_2O 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_2O, and KCl were 5, 1, and 4 mg, respectively. Two capsules, each with somewhat different $H_2O/(H_2O+KCl)$ mole fraction, X_{H_2O}, were placed side by side in the experimental assemblies. During an experiment, the H_2O 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_2O 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_2O activities, a_{H_2O}, 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*	γ	*V*
Phlogopite	5.315	9.204	10.304	99.913	14.952
$KMg_3AlSi_3O_{10}(OH)_2$	(0.005)	(0.004)	(0.003)	(0.030)	(0.011)
Enstatite	18.232	8.818	5.176		3.132
$MgSiO_3$	(0.002)	(0.001)	(0.001)		(0.001)
K-feldspar	8.602	13.013	7.179	116.08	10.867
$KAlSi_3O_8$	(0.005)	(0.003)	(0.003)	(0.02)	(0.011)

Note: Numbers in parentheses are standard deviations of the corresponding parameters (1σ). *a, b, c* in nanometers, γ in degrees, and *V* in Joules/bar.

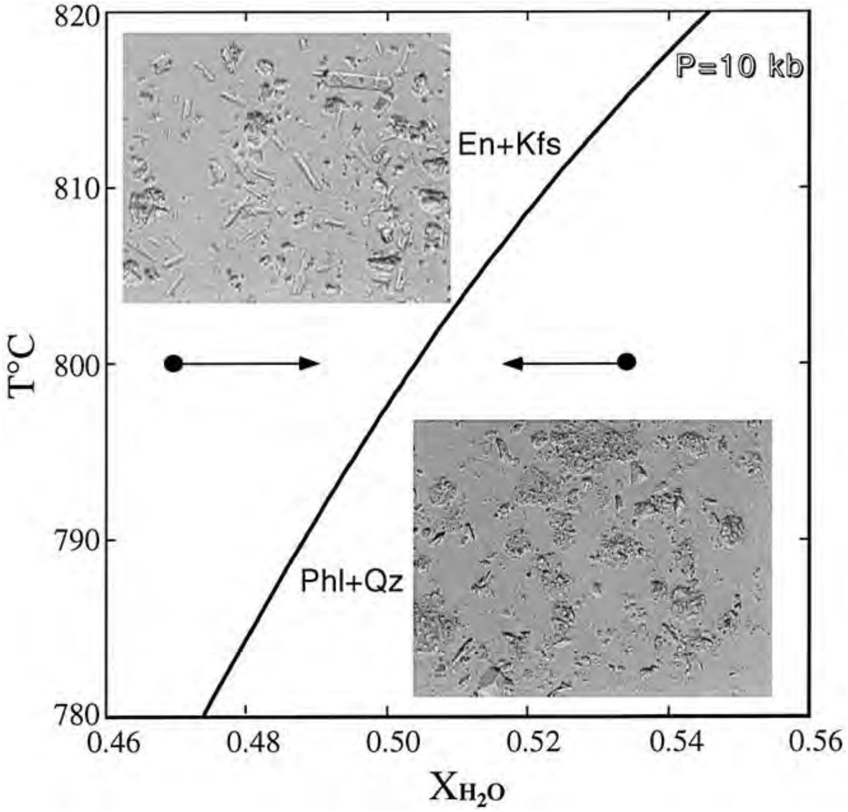

FIGURE 2. Reversal criteria of a typical experiment, no. PQ 26-27, Table 3, (800 °C, 10 kbar). Reaction 1 is bracketed by demonstration of nearly complete reaction to either enstatite + potassium feldspar or phlogopite + quartz, as shown in the photomicrographs of immersion oil (n = 1.598) mounts of 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 H_2O contents of the fluid phases as determined by loss-on-drying. (Widths of photos are 500 mm.)

TABLE 3. Experimental data on the reaction Phl + 3Qz = 3En + Kfs + H_2O in the presence of H_2O-KCl solutions

Exper. no.	*P* (kbar)	*T* (°C)	Duration (h)	X_{H_2O} (st.)	X_{H_2O} (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 H_2O weight change, optics, and X-ray methods.

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

$$a_{H_2O} = \frac{\gamma X_{H_2O}}{1 + \alpha X_{H_2O}} \qquad (5)$$

where α is a degree of dissociation parameter that quantifies pressure-induced ionic dissociation of KCl (leading to low H_2O activities at pressures above 4 kbar) and γ is an activity coefficient that accounts mainly for non-ideality from such factors as solvation of ions. The parameters α and γ were evaluated from the brucite-periclase equilibrium data:

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

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

with P in kbar, T in K, and ρ (the density of pure H_2O at P and T) in g/cm^3. Densities of H_2O 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 H_2O 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 CO_2-H_2O fluids (Bohlen et al. 1983; Berman et al. 1995).

Determination of H_2O activity by our method is subject to the assumptions that the two Equations 6 describing a_{H_2O} 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

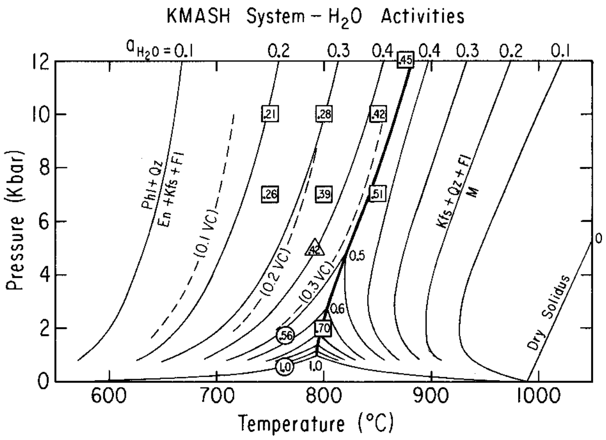

FIGURE 3. Mean H_2O activity data for the eight reversals of reaction 1 in H_2O-KCl solutions from the present study (squares), two reversed determinations in H_2O-CO_2 solutions of Berman et al. (1995) (circles), and one reversal of Bohlen et al. (1983) in H_2O-CO_2 solutions (triangle). The H_2O activities in CO_2 solutions were based on the results of Kerrick and Jacobs (1981). H_2O 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 H_2O 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 ±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 H_2O, 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 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 H_2O-NaCl solutions relative to that in H_2O-CO_2 to constrain a_{H_2O} in the brine. At 9.2 kbar and 800 °C they observed melting in the H_2O-NaCl fluid of composition $X_{H_2O} = 0.82$, and in the H_2O-CO_2 fluid at $X_{H_2O} = 0.59$ (Shmulovich and Graham 1996, Fig. 1); this is their only datum that allows direct comparison of the H_2O activity in the two systems. Neglecting the effect of minor amounts of Cl and CO_2 dissolved in the corresponding melts, H_2O activity must be the same in both systems under these conditions. For the H_2O-NaCl system, equations analogous to Equation 6 give $a_{H_2O} = 0.72$ (Aranovich and Newton 1996); for the system H_2O-CO_2, the equation of state of Kerrick and Jacobs (1981) also predicts $a_{H_2O} = 0.72$. The exactness of the agreement may be fortuitous, given all the experimental uncertainties involved, but it appears to indicate that the equations for H_2O activity, derived from experimental data in the simple system MgO-H_2O-(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

	$-\Delta H^0_f$ (kJ)	S^0 (J/K)	*a*	*b*	*c*	*d*	*e*
Phlogopite $KMg_3AlSi_3O_{10}(OH)_2$	6212.35	334.60	372.13	−0.077 25	357 500	0	−8600.6
Enstatite $MgSiO_3$	1545.52	66.27	350.70	−0.147 30	1 679 000	5.826×10^{-5}	−4296.0
Sanidine $KAlSi_3O_8$	3959.56	232.90	693.37	−0.171 70	3 462 200	4.9188×10^{-5}	−8305.4
α-Quartz SiO_2	910.70	41.46	81.119	0.018 283	−180 990	5.406×10^{-6}	−698.46
β-Quartz SiO_2			57.959	0.009 330	1 834 710	0	0
Steam H_2O	241.81	188.83	7.368	0.027 468	−223 160	-4.8117×10^{-6}	341.74

Notes: $C_p = a + bT + c/T^2 + dT^2 + e/(T)^{1/2}$. $V = V^0_{298} + \alpha V(T - 298) - \beta VP$. 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) (ΔH^0_f, 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) ($\Delta H(\alpha - \beta Qz) = 0.625$ 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:

$$\Delta G^0_T = -RT \ln f^0(H_2O) - RT \ln a_{H_2O} - (P - 1)\Delta V^*298$$

$$\Delta H^0_{298} = \Delta G^0_T - \int \Delta S^0_T \, dT + 298\Delta S^0_{298}T \qquad (7)$$

where ΔG^0_T is the standard Gibbs free energy change at T and one bar, ΔH^0_{298} is the standard enthalpy change at 298 K, a_{H_2O} is the derived activity value for H_2O at each experimental point, $f^0_{H_2O}$ is the corresponding fugacity of pure H_2O, and ΔV^* is the solid volume change of the reaction evaluated at T and $P/2$. The ΔG^0_T values derived from our 16 experimental data points are given in Table 5. The calculations make use of the H_2O fugacities interpolated from the tables of Burnham et al. (1969). A logarithmic extrapolation was made to derive the H_2O fugacity at 12 kbar and 875 °C. Also included in Table 5 are the ΔG^0_T 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 H_2O-CO_2 fluid with $X_{H_2O} = 0.35$; the similar data of Berman et al. (1995) with $X_{H_2O} = 0.51$ at conditions of 1.74 ± 0.1 kbar and 764 ± 5 °C; and a reversed point by the latter authors at 0.48 ± 0.02 kbar and 763 ± 11 °C with pure H_2O. H_2O activities in the experimental fluids with CO_2 were taken from Kerrick and Jacobs (1981). Our tentative conclusion is that the experimental reaction points in H_2O-CO_2 fluids, and the H_2O activity in the mixtures of Kerrick and Jacobs (1981) are consistent with our results in the KCl-H_2O solutions.

In calculating the standard enthalpy change, it is necessary to determine the standard entropy change, ΔS^0_T, 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 ΔS^0_T to be evaluated independently from the temperature change of the derived ΔG^0_T values. The 22 ΔG^0_T values given in Table 5 were fitted by least-squares regression as a linear function of temperature, yielding:

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

with $r^2 = 0.973$. The temperature coefficient, 143.73 J/K, is the average ΔS^0_T 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.

Table 4—*Extended*

	V^0_{298} (J/bar)	αV (J/barK)	βV (J/bar^2)	Refs.
Phlogopite $KMg_3AlSi_3O_{10}(OH)_2$	14.964	39.0×10^{-5}	24.5×10^{-6}	1, 2, 7
Enstatite $MgSiO_3$	3.131	9.0×10^{-5}	2.3×10^{-6}	3, 4, 7
Sanidine $KAlSi_3O_8$	10.892	20.6×10^{-5}	20.0×10^{-6}	5, 7
α-Quartz SiO_2	2.269	8.0×10^{-5}	5.9×10^{-6}	6, 7
β-Quartz SiO_2	2.367	0	2.6×10^{-6}	6, 7
Steam H_2O				5

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 H_2O activity is substantially higher than given by previous estimates, including that of Vielzeuf and Clemens (1992), shown in Figure 3. The higher a_{H_2O} in turn requires a substantially smaller ΔH^0_{298}. The mean value of the derived ΔH^0_{298} from the 22 data points of Table 5 is 106.54 kJ, with a standard deviation (2σ) of 2.00 kJ. The data in Table 5 reveal also that the ΔH^0_{298} values yielded by the determinations in H_2O-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 ΔG^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 at 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 ΔH^0_{298} of reaction 1, is -6212.35 ± 4.62 kJ (2σ uncertainty, which includes the ± 2 kJ uncertainty in ΔH^0_{298} 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 ΔH^0_{298}, the entropy change of the reaction, $\Delta S^0_{298} = 161.56$ J/K, which assumes maximal disordering entropy in phlogopite and sanidine and the 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 H_2O 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 H_2O isoactivity curves of the sanidine-phlogopite-quartz-fluid melting reaction 3. The sanidine-quartz melting curves can be constructed with the experimental data in CO_2-H_2O fluids of Bohlen et al. (1983), imposing an activity model of mixing, and assuming that the MgO and 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 H_2O activity model, the dehydration melting reaction curve, shown in Figure 3, is defined by the intersections of corresponding H_2O 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 H_2O 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 H_2O 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 Na_2O 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 H_2O 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 ΔG^0_T and ΔH^0_{298} of the reaction Phl + 3Qz = 3En + Kfs + H_2O from experiments in H_2O-KCl H_2O-CO_2

P (kb)	*T* (K)	ρ_{H_2O} (g/cm³)	$f^0_{H_2O}$ (bar)	X_{H_2O}	Soln.	a_{H_2O}	$-\Delta V_s$ (J/bar)	$-(\Delta)G^0_T$ (kJ)	ΔH^0_{298} (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	CO_2	0.421	1.701	58.91	106.39	1
	1053		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	CO_2	0.562	1.712	54.34	106.51	2
	1032		1313	0.510		0.558		53.62	105.80	
0.48	1047	—	431	1.000	H_2O	1.000	1.715	51.98	109.59	2
	1025		425	1.000		1.000		50.75	107.66	
									avg. 106.54 ± 2.00 (2σ)	

Note: $\Delta G^0_T = 95.447 - 0.14373T(K)$ (1023–1148 K) $r^2 = 0.973$. References are 1 = Bohlen et al. 1983; 2 = Berman et al. 1995; 3 = present study.

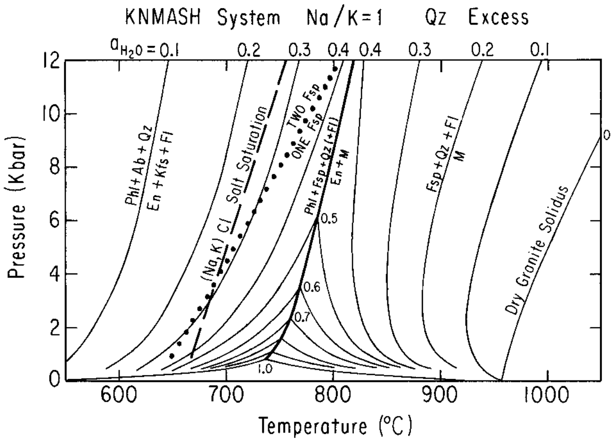

FIGURE 4. H_2O isoactivity lines of reaction 1 in a simple granitic system (K_2O-Na_2O-MgO-Al_2O_3-SiO_2-H_2O: KNMASH) with equimolar Na and K and quartz in excess. The curves are from Figure 3 with a correction for the $NaAlSi_3O_8$ content of alkali feldspar according to the feldspar solid solution properties of Fuhrman and Lindsley (1988). The bold dotted line is their solvus temperature as a function of pressure for Na/K = 1.0. Shown also are simple granite solidus curves for a_{H_2O} 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 (Na,K)Cl solutions of variable concentrations and Na/(K+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_{H_2O} 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 (Na,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 H_2O 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_{H_2O} values should lie in the range 0.10–0.25. The present results suggest that H_2O 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_{H_2O} range over which biotite and orthopyroxene can coexist in quartzofeldspathic systems (cf. Patiño-Douce 1993).

The magnitude of H_2O 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 H_2O activities in the range 0.4–0.6. Figure 5 shows two examples of South Indian granulites. H_2O 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 KMASH system probably extend somewhat the H_2O 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 H_2O activity. It is noteworthy that the a_{H_2O} range inferred for the South Indian samples corresponds to only moderately concentrated alkali chloride solutions at the inferred P-T conditions. The appropriate (Na,K)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 CO_2-bearing systems at high-grade metamorphic conditions would be immiscible with a CO_2-rich phase (Duan et al. 1995). This could account for the apparently coeval suites of dense 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 CO_2 (Watson and Brenan 1987). The importance of CO_2 infiltration has probably been overestimated from the fluid inclusion evidence.

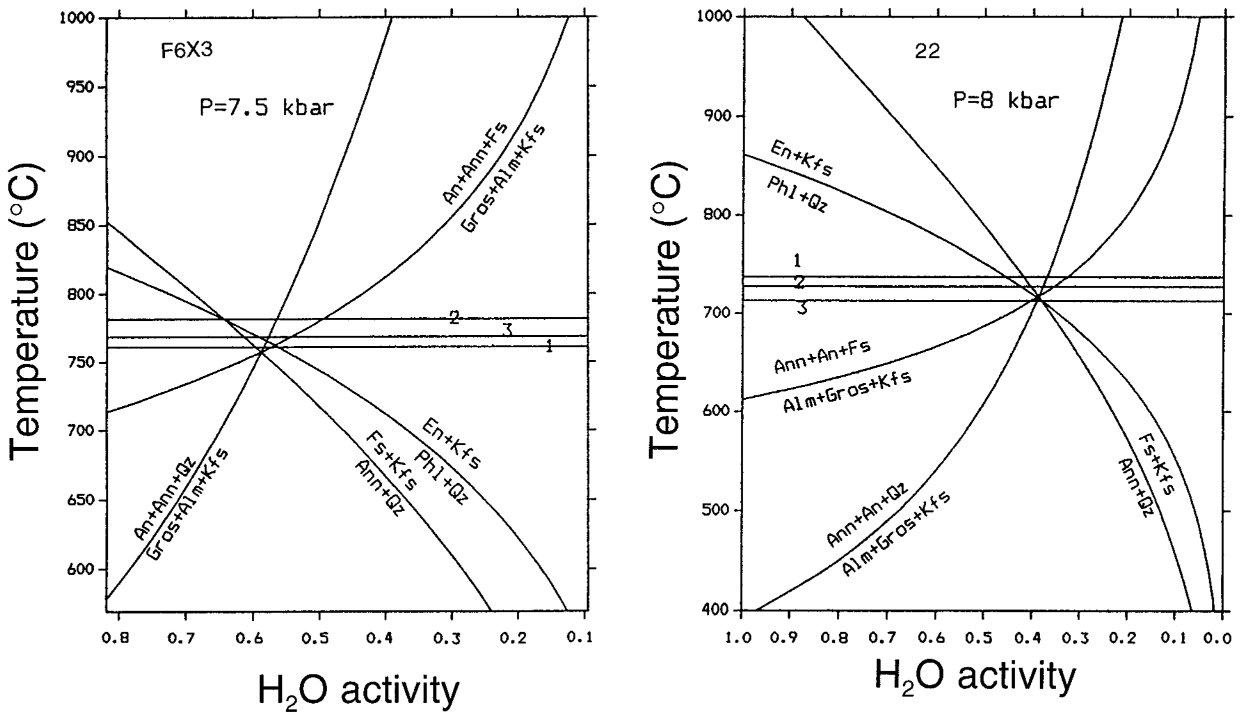

FIGURE 5. H_2O activity-T relations of two South Indian charnockites, no. F6X3 from the Shevaroy Hills, Tamil Nadu (Hansen et al. 1995) and no. 22 from the Nilgiri Hills, Tamil Nadu (Raith et al. 1990), based on their mineral compositions. Seven independent univariant reactions yield highly consistent temperatures, pressures, and H_2O 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 H_2O activities are substantially higher (0.4–0.6) than estimated by these authors. (Abbreviations: En = enstatite, $MgSiO_3$; Fs = ferrosilite, $FeSiO_3$; Phl = phlogopite, $KMg_3AlSi_3O_{10}(OH)_2$; Ann = annite, $KFe_3AlSi_3O_{10}(OH)_2$; Alm = almandine, $Fe_3Al_2Si_3O_{12}$; Py = pyrope, $Mg_3Al_2Si_3O_{12}$; Gros = grossular, $Ca_3Al_2Si_3O_{12}$; Kfs = potassium feldspar, $KAlSi_3O_8$; An = anorthite, $CaAl_2Si_2O_8$; Qz = quartz, SiO_2. Reaction 1: Alm + En = Py + Fs; reaction 2: Alm +Phl = Py + Ann; reaction 3: Fs + Phl = En + 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 K/(K+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 reinterpreted as the univariant melting equilibrium in the presence of (Na,K)Cl brines of suitably low H_2O activity:

$$\begin{aligned}&\text{phlogopite} + \text{alkali feldspar} + \text{quartz}\\&\quad + \text{fluid} = \text{enstatite} + \text{melt}\end{aligned} \tag{8}$$

The brine-present univariant melting curve is identical in *P-T* position to the dehydration melting curve, inasmuch as the single parameter a_{H_2O} 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 anatectic melting is not limited by the H_2O 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 H_2O 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 H_2O 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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REFERENCES CITED

Andersson, U.B., Carsson, L., and Wikström, A. (1992) Charnockites, pyroxene granulites, and garnet-cordierite gneisses at a boundary between svecofennian and Småland-Värmland granitoids, Karlskoga, southern Sweden. Geologiska Föreningens i Stockholm Förhandlingar, 114, 1–5.

Anovitz, L.M., Blencoe, J.G., Joyce, D.B., and Horita, J. (1996) Activity/composition relations of H_2O-N_2 and H_2O-CO_2 fluids at 500 °C, 500 bars. Geological Society of America Abstracts with Programs, 28, A-159.

Aranovich, L.Y. (1984) Biotite-garnet equilibria in metapelites: II. Calculation of T, P and water fugacity. Contributions to Physico-Chemical Petrology, 12, 92–103 (in Russian).

Aranovich, L.Y. and Newton, R.C. (1996) H_2O activity in concentrated NaCl solutions at high pressures and temperatures measured by the brucite-periclase equilibrium. Contributions to Mineralogy and Petrology, 125, 200–212.

——— (1997) H_2O activity in concentrated KCl and KCl-NaCl solutions at high temperatures and pressures measured by the brucite-periclase equilibrium. Contributions to Mineralogy and Petrology, 127, 261–271.

Berman, R.G. and Aranovich, L.Y. (1996) Optimized standard and solution properties of minerals: Part I. Model calibration for olivine, orthopyroxene, cordierite, garnet, and ilmenite in the system FeO-MgO-CaO-Al_2O_3-TiO_2-SiO_2. Contributions to Mineralogy and Petrology, 126, 1–24.

Berman, R.G., Aranovich, L.Y., Genkin, M., and Mäder, U.K. (1995) Phase equilibrium constraints on the stability of biotite: Part 1. Mg-Al biotite in the system K_2O-MgO-Al_2O_3-SiO_2-H_2O-CO_2. Current Research (Geological Survey of Canada), 1995-E, 253–261.

Bhattacharya, A. and Sen, S.K. (1986) Granulite metamorphism, fluid buffering, and dehydration melting in the Madras charnockites and metapelites. Journal of Petrology, 27, 1119–1141.

Boettcher, A.L. and Kerrick, D.M. (1971) Temperature calibration in cold-seal pressure vessels. In G.C. Ulmer, Ed., Research Techniques for High Pressure and High Temperature, p. 179–194. Springer Verlag, New York.

Bohlen, S.R., Boettcher, A.L., Wall, V.I., and Clemens, J.D. (1983) Stability of phlogopite-quartz and sanidine-quartz: A model for melting in the lower crust. Contributions to Mineralogy and Petrology, 83, 270–277.

Burnham, C.W., Holloway, J.R., and Davis, N.F. (1969) Thermodynamic properties of water to 1,000 °C and 10,000 bars. Geological Society of America Special Paper 132, 1–96.

Chou, I.-M., Sterner, S.M., and Pitzer, K.S. (1992) Phase relations in the system NaCl-KCl-H_2O: IV. Differential thermal analysis of the sylvite liquidus in the KCl-H_2O binary, the liquidus in the NaCl-KCl-H_2O ternary, and the solidus in the NaCl-KCl binary to 2 kb pressure, and a summary of experimental data for thermodynamic-PTX analysis of solid-liquid equilibria at elevated *P-T* conditions. Geochimica et Cosmochimica Acta, 56, 2281–2293.

Clemens, J.D. (1995) Phlogopite stability in the silica-saturated portion of the system $KAlO_2$-MgO-SiO_2-H_2O: New data and a reappraisal of phase relations to 1.5 GPa. American Mineralogist, 80, 982–997.

Clemens, J.D., Circone, S., Navrotsky, A., and McMillan, P.F. (1987) Phlogopite: High-temperature solution calorimetry, thermodynamic properties, Al-Si and stacking disorder, and phase equilibria. Geochimica et Cosmochimica Acta, 51, 2569–2578.

Crawford, M.L. and Hollister, L.S. (1986) Metamorphic fluids: The evidence from fluid inclusions. In J.V. Walther and B.J. Wood, Eds., Fluid-Rock Interactions During Metamorphism, p. 1–35. Springer, New York.

Dawson, J.B. and Smith, J.V. (1975) Chemistry and origin of phlogopite megacrysts in kimberlite. Nature, 253, 336–338.

——— (1977) The MARID (mica-amphibole-rutile-ilmenite-diopside) suite of xenoliths in kimberlite. Geochimica et Cosmochimica Acta, 41, 309–323.

Duan, Z., Moller, N., and Weare, J.H. (1995) Equation of state for the NaCl-H_2O-CO_2 system: Prediction of phase equilibria and volumetric properties. Geochimica et Cosmochimica Acta, 59, 2869–2882.

Dunbar, N.W., Campbell, A.R., and Candela, P.A. (1996) Physical, chemical, and mineralogical evidence for magmatic fluid migration within the Capitan pluton, southeastern New Mexico. Geological Society of America Bulletin, 108, 318–333.

Forbes, W.C. and Flower, M.F.J. (1974) Phase relations of titan-phlogopite, $K_2Mg_4TiAl_2Si_6O_{20}(OH)_4$: A refractory phase in the upper mantle? Earth and Planetary Science Letters, 22, 60–66.

Fuhrman, M.L. and Lindsley, D.H. (1988) Ternary-feldspar modeling and thermometry. American Mineralogist, 73, 201–215.

Grant, J.A. (1986) Quartz-phlogopite-liquid equilibria and origins of charnockites. American Mineralogist, 71, 1071–1075.

Grew, E.S. (1980) Sapphirine + quartz associations from Archean rocks in Enderby Land, Antarctica. American Mineralogist, 65, 821–836.

Hansen, E.C., Newton, R.C., Janardhan, A.S., and Lindenberg, S. (1995) Differentiation of Late Archean crust in the eastern Dharwar Craton, Krishnagiri-Salem area, South India. Journal of Geology, 103, 629–651.

Hemingway, B.S. (1987) Quartz: Heat capacities from 340 to 1000 K and revised values for the thermodynamic properties. American Mineralogist, 72, 273–279.

Holland, T.J.B. and Powell, R. (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations:

The system K_2O-Na_2O-CaO-MgO-MnO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2-C-H_2-O_2. Journal of Metamorphic Geology, 8, 89–124.

Iiyama, J.T. (1965) Influence des anions sur les équilibres d'échange d'ions Na-K dans les feldspaths alcalins à 600 °C sous une pression de 1000 bars. Bulletin de la Societé francaise de Minéralogie et Cristalogie, 88, 618–622.

Johannes, W. (1985) The significance of experimental studies for the formation of migmatites. In J.A. Ashworth, Ed., Migmatites, p. 36–85. Blackie, Glasgow.

Kapustin, N.V., Fonarev, V.I., and Litvinov, A.V. (1982) Measurements of the temperature field in externally heated pressure vessels. In V.A. Zharikov, Ed., Problems of Experiment in Solid-Medium and Hydrothermal High-Pressure Apparati, p. 187–190. Nauka Press, Moscow (in Russian).

Kerrick, D.M. and Jacobs, G.K. (1981) A modified Redlich-Kwong equation for H_2O, CO_2, and H_2O-CO_2 mixtures at elevated pressures and temperatures. American Journal of Science, 281, 735–767.

Koziol, A.M. and Newton, R.C. (1995) Experimental determination of the reactions magnesite + quartz = enstatite + CO_2 and magnesite = periclase + CO_2, and enthalpies of formation of enstatite and magnesite. American Mineralogist, 80, 1252–1260.

Krupka, K.M., Robie, R.A., Hemingway, B.S., Kerrick, D.M., and Ito, J. (1985a) Low-temperature heat capacities and derived thermodynamic properties of anthophyllite, diopside, enstatite, bronzite, and wollastonite. American Mineralogist, 70, 249–260.

Krupka, K.M., Hemingway, B.S., Robie, R.A., and Kerrick, D.M. (1985b) High-temperature heat capacities and derived thermodynamic properties of anthophyllite, diopside, dolomite, enstatite, bronzite, talc, tremolite, and wollastonite. American Mineralogist, 70, 261–271.

Lamb, W.M. and Valley, J.W. (1988) Granulite facies amphibole and biotite equilibria, and calculated peak-metamorphic water activities. Contributions to Mineralogy and Petrology, 100, 349–360.

Luth, W.C. (1967) Studies in the system $KAlSiO_4$-Mg_2SiO_4-SiO_2-H_2O: I. Inferred phase relations and petrologic applications. Journal of Petrology, 8, 372–416.

Metrich, N. and Rutherford, M.J. (1992) Experimental study of chlorine behavior in hydrous silicic melts. Geochimica et Cosmochimica Acta, 56, 607–616.

Moecher, D.P. and Essene, E.J. (1991) Calculation of CO_2 activity using scapolite equilibria: Constraints on the presence and composition of a fluid phase during high grade metamorphism. Contributions to Mineralogy and Petrology, 108, 219–240.

Montana, A. and Brearley, M. (1989) An appraisal of the stability of phlogopite in the crust and in the mantle. American Mineralogist, 74, 1–4.

Munoz, J.L. and Ludington, S.D. (1974) Fluoride-hydroxyl exchange in biotite. American Journal of Science, 274, 396–413.

Newton, R.C. (1995) Simple-system mineral reactions and high-grade metamorphic fluids. European Journal of Mineralogy, 7, 861–881.

Newton, R.C. and Aranovich, L.Y. (1996) Simple granite melting in concentrated NaCl-KCl solutions at deep crustal conditions. Geological Society of America Abstracts with Programs, 28, A–158.

Nozhkin, A.D. and Turkina, O.M. (1994) Radiogeochemistry of the charnockite-granulite complex, Sharyzhalgay Window, Siberian Platform. Geochemistry International, 32, 62–78.

Orville, P.M. (1963) Alkali ion exchange between vapor and feldspar phases. American Journal of Science, 261, 201–237.

Patiño-Douce, A.E. (1993) Titanium substitution in biotite: An empirical model with applications to thermometry, O_2 and H_2O barometries, and consequences for biotite stability. Chemical Geology, 108, 133–162.

Percival, J.A. (1991) Granulite-facies metamorphism and crustal magmatism in the Ashuanipi complex, Quebec-Labrador, Canada. Journal of Petrology, 32, 1261–1297.

Peterson, J.W. and Newton, R.C. (1989) Reversed experiments on biotite-quartz melting in the system KMASH: Implications for crustal anatexis. Journal of Geology, 97, 465–485.

Puziewicz, J. and Johannes, W. (1990) Experimental study of a biotite-bearing granitic system under water-saturated and water-undersaturated conditions. Contributions to Mineralogy and Petrology, 104, 397–406.

Raith, M., Srikantappa, C., Ashamanjari, K.G., and Spiering, B. (1990) The granulite terrane of the Nilgiri Hills (Southern India): Characterization of high-grade metamorphism. In D. Vielzeuf and P. Vidal, Eds., Granulites and Crustal Evolution, p. 339–365. Kluwer Academic Publishers, Dordrecht.

Robie, R.A. and Hemingway, B.S. (1984) Heat capacities and entropies of phlogopite ($KMg_3[AlSi_3O_{10}](OH)_2$) and paragonite ($NaAl_2[AlSi_3O_{10}](OH)_2$) between 5 and 900 K and estimates of the entropies and Gibbs free energies of formation. American Mineralogist, 69, 858–868.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978) Thermodynamic properties of minerals and related substances at 298.15° K and 1 bar (10^5 pascals) pressure and at higher temperatures. United States Geological Survey Bulletin, 1452, 1–456.

Shmulovich, K.I. (1988) Carbon dioxide in high-temperature processes of mineral formation, 232 p. Nauka Press, Moscow (in Russian).

Shmulovich, K.I. and Graham, C.M. (1996) Melting of albite and dehydration of brucite in H_2O-NaCl fluids to 9 kbars and 700–900 °C: Implications for partial melting and water activities during high pressure metamorphism. Contributions to Mineralogy and Petrology, 124, 370–382.

Singh, J. and Johannes, W. (1996) Dehydration melting of tonalites: Part I. Beginning of melting. Contributions to Mineralogy and Petrology, 125, 16–25.

Smit, C.A. and Van Reenen, D.D. (1997) Deep crustal shear zones, high-grade tectonites, and associated metasomatic alteration in the Limpopo Belt, South Africa: Implications for deep crustal processes. Journal of Geology, 105, 37–58.

Touret, J.L.R. (1985) Fluid regime in southern Norway: The record of fluid inclusions. In A.C. Tobi and J.L.R. Touret, Eds., The Deep Proterozoic Crust in the North Atlantic Provinces, p. 517–549. Reidel, Dordrecht.

Vielzeuf, D. and Clemens, J.D. (1992) The fluid-absent melting of phlogopite + quartz: Experiments and models. American Mineralogist, 77, 1206–1222.

Watson, E.B. and Brenan, J.M. (1987) Fluids in the lithosphere: 1. Experimentally determined wetting characteristics of CO_2-H_2O fluids and their implications for fluid transport, host-rock physical properties, and fluid inclusion formation. Earth and Planetary Science Letters, 85, 497–515.

Wendlandt, R.F. and Eggler, D.H. (1980) The origins of potassic magmas: 2. Stability of phlogopite in natural spinel lherzolite and in the system $KAlSiO_4$-MgO-SiO_2-H_2O-CO_2 at high pressures and high temperatures. American Journal of Science, 280, 421–458.

Wones, D.R. and Dodge, F.C.W. (1977) The stability of phlogopite in the presence of quartz and diopside. In D.G. Fraser, Ed., Thermodynamics in Geology, p. 229–247. Reidel, Dordrecht.

Wood, B.J. (1976) The reaction phlogopite + quartz = enstatite + sanidine + H_2O. Third Science Report, Department of Research, National Environment Research Council (U.K.) Publications Series, D-6, p. 17–20.

Wright, T.L. and Stewart, D.B. (1968) X-ray and optical study of alkali feldspar: I. Determination of composition and structural state from refined unit-cell parameters and 2V. American Mineralogist, 53, 38–87.

Yoder, H.S. and Kushiro, I. (1969) Melting of a hydrous phase: Phlogopite. American Journal of Science, 267-A, 558–582.

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