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LETTER

An appraisal of the stability of phlogopite in the crust and in the mantle*

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ABSTRACT

Experimental and theoretical investigations of phlogopite at high pressures serve as a guide to the role of water in the melting of crustal and mantle rocks. We propose that the geometrical arrangement of phase relationships of phlogopite-bearing olivine-normative assemblages characteristic of the upper mantle is similar to that of crustal, quartz-normative assemblages. Despite differences in interpretation of some experimental data on the stability of phlogopite, nearly all of the results—including some new ones that are presented here—are consistent with these proposed phase relationships, which provide a sound basis for future research.

INTRODUCTION

A significant proportion of the H_2O component in the crust and in the upper several hundred kilometers of the mantle of the Earth is sequestered in phyllosilicates, particularly biotite and phlogopite. Thus, it is desirable to understand the behavior of these minerals under conditions of high pressures and temperatures and in a variety of chemical and mineral environments. To investigate the role of mica in the mantle, Modreski and Boettcher (1972, 1973) determined the stability of phlogopite to 35 kbar for olivine-normative compositions for both vapor-absent and H_2O-saturated conditions, building on the low-pressure, vapor-saturated experiments of Luth (1967). Bohlen et al. (1983) made similar studies to 20 kbar for quartz-normative compositions as a model for melting in the crust. Based on these experimental and theoretical studies and our new experimental results, coupled with the theoretical analysis of Grant (1986), we propose that the phase relationships for micas under crustal and mantle conditions are approximately as depicted in Figures 1 and 2, respectively, using phlogopite to proxy for micas, enstatite for pyroxenes, forsterite for olivine, and sanidine for potassic feldspars.

Grant (1986) correctly perceived that the avilable data for quartz-normative conditions require at least one singular point for the equilibria that include the phases quartz (Qz), phlogopite (Ph), enstatite (En), and liquid (L). It is of interest that this singular point (S^1 in Fig. 1) is chemographically analogous to the singular point discussed by Modreski and Boettcher (1972) for those assemblages that contain forsterite (Fo), Ph, En, and L, shown in Figure 2 as S^3. Singular points of this type, originally described by Schreinemakers (1916a, p. 1539), can be conceived as the *P*-*T* projection of the locus in *P*-*T*-*X* space where *C*-component assemblages intersect (C + 1)-component assemblages—e.g., S^1 in Figure 1, where the ternary reaction Ph + Qz ⇌ En + L tangentially joins the two quaternary reactions Ph + Qz + V ⇌ En + L and Ph + Qz ⇌ En + L + V, where V is vapor. At pressures below the singular point S^1, the quaternary liquid forms a plane with En and V that is pierced by the Ph-Qz tieline (Fig. 3). At the pressure of S^1, the quaternary liquid lies on the Ph-Qz-En plane (these four phases are coplanar), and the vapor is an indifferent phase (Schreinemakers, 1916b, p. 514). At higher pressures, the quaternary liquid becomes progressively enriched in H_2O, causing the En-L tieline to pass through the Ph-Qz-V plane. Singular point S^2 in Figure 1 is required at some pressure below 5 kbar (Grant, 1986), because Bohlen et al. (1983) determined experimentally that the quaternary reaction at that pressure is Ph + Qz ⇌ Sa + En + L; i.e., the En-L tieline crosses the Ph-Qz tieline (these four phases become coplanar) at S^2, and at higher pressures, the Ph-Qz tieline intersects the Sa-En-L plane. It appears that lower activities of H_2O raise the pressure of S^2, because Wendlandt (1981) added CO_2 component to this system and followed the quinary

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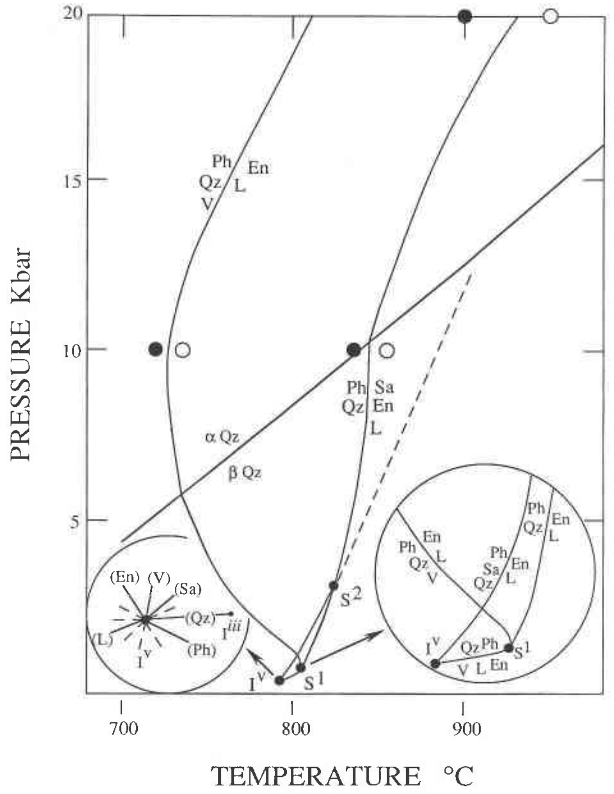

Fig. 1. Pressure-temperature projection of Qz + Ph phase relationships in the system $KAlSiO_4$-Mg_2SiO_4-SiO_2-H_2O, modified from Luth (1967), Bohlen et al. (1983), and Grant (1986). Quaternary invariant points I^v and I^{iii} (see Fig. 2) are from Luth (1967); singular points S^1 and S^2 are after Grant (1986, Fig. 3). The dashed curve extending above S^2 is the metastable extension of Ph + Qz ⇌ En + L. The insets show the schematic geometry near I^v and S^1. The open and closed circles at 10 and 20 kbar are hypersolidus and subsolidus runs, respectively (Table 1).

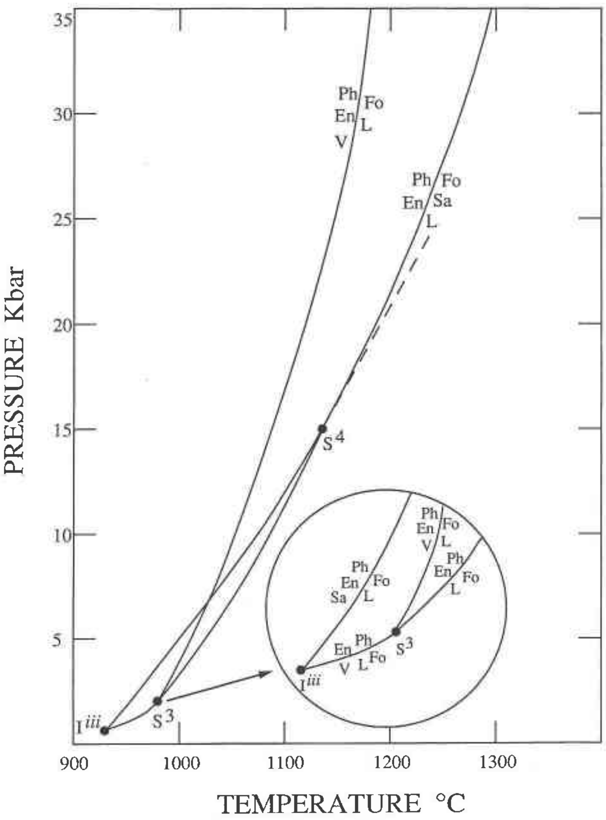

Fig. 2. Pressure-temperature projection of Fo + Ph phase relationships in the system $KAlSiO_4$-Mg_2SiO_4-SiO_2-H_2O, modified from Modreski and Boettcher (1972). Invariant point I^{iii} is after Luth (1967). The inset shows some of the schematic geometry at S^3 and I^{iii}. The existence of singular point S^4 is speculative. The dashed curve extending above S^4 is the metastable extension of Ph + En ⇌ Fo + L.

reaction Ph + Sa + Qz + V ⇌ En + L to at least 15 kbar (see Grant, 1986, p. 1073).

For the olivine-normative reactions (Fig. 2), if we assume that Modreski and Boettcher's singular point (S^3 in Fig. 2) and Luth's (1967) invariant points I^v (i.e., Reaction 26) and I^{iii} are correct, and if we also make the reasonable assumption that the liquid associated with the reaction Ph + En + Sa ⇌ Fo + L dissolves more H_2O component with increasing pressure, then the Fo-L tieline may eventually cross that for Ph-En, occasioning the singular point S^4, analogous to S^2 in Figure 1. Modreski and Boettcher (1972) did not infer a singular point S^4, but their compositions of the liquid in the reaction Ph + En ⇌ Fo + L change from quartz-normative at pressures of ~15 kbar or less to leucite-normative at higher pressures (Modreski and Boettcher, 1973, Fig. 1), which is consistent with a point S^4. It is conceivable that they overlooked sanidine in their run products, but we re-examined them and found no evidence of this. It is also conceivable that S^4 exists below 30 kbar but that Modreski and Boettcher (1972) were determining and reversing the metastable equilibrium Ph + En ⇌ Fo + L at pressures above S^4 (see Fig. 2). Much more work is required to establish which situation prevails, but the available evidence favors the configuration in Figure 2.

PHLOGOPITE IN THE CRUST

One of the major points of this communication is to re-examine the reactions determining the stability of phlogopite (biotite) in the crust. We investigated the melting of Ph + Qz and Ph + Qz + V(H_2O) (Fig. 1) at 10 kbar, using far longer run durations than did Bohlen et al. (1983). Our new results are in Table 1. The experimental procedures were similar to those used by Bohlen et al., except that the interiors of our furnace assemblies were the same as the original design of Boettcher et al. (1981), using BN and MgO. We used Pt-$Pt_{90}Rh_{10}$ thermocouples. We used the hematite-magnetite (HM) buffer in a double-capsule configuration in all experiments with excess H_2O and in some of the vapor-absent experiments (Table 1).

For the reaction Ph + Qz + V ⇌ En + L, our ~200-

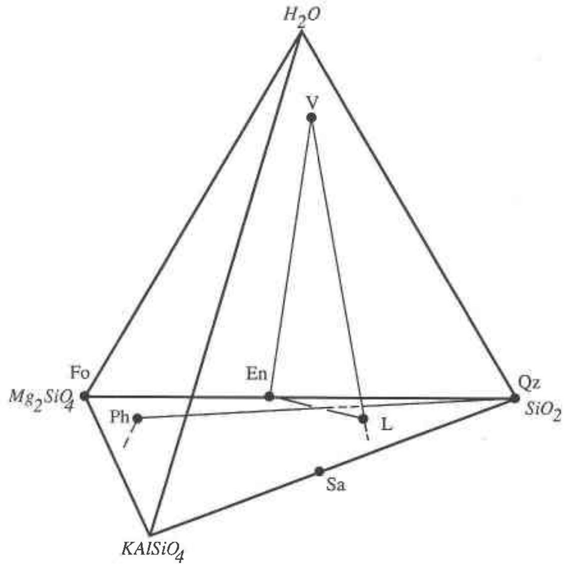

Fig. 3. Schematic representation of pertinent phases in the system $KAlSiO_4$-Mg_2SiO_4-SiO_2-H_2O. As an example, we show the composition of the liquid (L) for the reaction Ph + Qz ⇌ En + L + V at a pressure just below that of singular point S^1 (see Fig. 1).

h, unbuffered experiments yielded a temperature of 720–730 °C at 10 kbar, in agreement with the ~710 °C in the ~24-h experiments of Bohlen et al. (1983). All of these results from 30 to 5 kbar are consonant with those of Wones and Dodge (1977) up to 4 kbar. In our unbuffered experiments (run 182), melting begins at least 30 °C higher because of the higher f_{H_2} (i.e., lower f_{H_2O}; see Luth and Boettcher, 1986), which *increases* the temperature of the solidus at pressures above S^1 (Yoder and Kushiro, 1969). Bohlen et al. also obtained higher temperatures when they lowered f_{H_2O} by adding CO_2 to the vapor.

The reaction Ph + Qz ⇌ Sa + En + L proceeds slowly under experimental conditions because of the absence of a hydrous vapor. For most of their definitive experiments on this reaction, Bohlen et al. (1983) used run durations of about 24 h, although an experiment at 890 °C and 10 kbar for 123 h produced no melting. Using durations in most runs of at least 600 h (Table 1), we obtained at 10 kbar a bracket of 835–850 °C, compared to 890–900 °C in the unbuffered experiments of Bohlen et al., and at 20 kbar a bracket of 925–950 °C, compared to their value of ~920 °C. In the experiments of Bohlen et al. using H_2O-CO_2 vapor with $X^V_{H_2O} = 0.50$, the bracket at 10 kbar is 870–880 °C. This result is consonant with their vapor-absent experiments, which must be at a higher temperature (see Bohlen et al., 1983, p. 274), but it is higher than our vapor-absent results, which is inconsistent. As their experiments and ours are buffered with HM, the explanation for their somewhat higher temperatures at 10 kbar probably lies in their shorter run durations. Note in Table 1 that our run 126 at 860 °C for 214 h did not melt, but that run 216 at 850 °C for 600 h did.

Table 1. Experimental results for the melting of phlogopite + quartz

Run*	*P* (kbar)	*T* (°C)	*t* (h)	Results
		Ph + Qz ⇌ Sa + En + L		
211	10	825	624	Ph + Qz
237	10	835	600	Ph + Qz
216	10	850	600	Ph + Qz + En + L
118	10	850	205	Ph + Qz + (L?)
126	10	860	214	Ph + Qz
179	10	890	600	(Ph) + Qz + En + L
119	10	925	212	Ph + Qz + En + (Sa?) + L
243	20	900	600	Ph + Qz
244	20	950	600	Ph + Qz + En + L
		Ph + Qz + V(H_2O) ⇌ En + L		
215	10	720	201	Ph + Qz + V
238	10	730	200	Ph + Qz + (En) + L + V
212	10	750	213	Ph + Qz + En + L + V
182	10	750	200	Ph + Qz + V

Note: Parentheses indicate trace or minor proportions of a phase.
* All experiments run with HM buffer except runs 215, 238, and 212.

More recently, Peterson and Newton (1988) redetermined the vapor-absent reaction Ph + Qz ⇌ Sa + En + L at 10 kbar in unbuffered runs. They proposed that melting begins at 815 °C, with a divariant melting interval extending from 815 to 850 °C.

Peterson and Newton reversed the reaction by holding the charge at 950 °C (10 kbar) for ~90 h (which would substantially melt the charge according to everyone's results) and then lowering the temperature to the desired value for ~200 h. We propose that their "reversals" are valid to the extent that they are consistent with our curve, but they do not establish the beginning of melting at 815 °C. Their textural criteria of mica regrowth from liquid are what we would expect because mica should have grown at 815 °C (and below 835 or possibly 850 °C according to our bracket) after being held at 950 °C, according to our results. That mica did not grow above 850 °C in their "reversals" is also consistent with our results. The coexistence of phlogopite and liquid in their experiments between 815 and 850 °C can simply be explained by the metastable persistence of liquid after the temperature is dropped from 950 °C. In short, their published results are not dissonant with our present values or those of Bohlen et al. (1983).

We agree with Peterson and Newton that K-feldspar is a minor or an unnecessary phase in this reaction; this may simply imply that the two curves above the singular point S^2 are at similar temperatures. It is conceivable that the higher temperatures of Bohlen et al. were obtained on the metastable extension of the ternary reaction Ph + Qz ⇌ En + L at pressures above S^2 (see Fig. 1). The interested reader can demonstrate that neither of the quaternary reactions at S^2 extend metastably beyond this singular point.

Conclusions

We propose that all of the pertinent, published experimental results on the melting of the phlogopite-bearing assemblages are in accord with those in Figures 1 and 2. Applicability of these results will be improved by adding other components, for example, FeO, to the micas, pyroxenes, and olivines and by examining other values of a_{H_2O}. As Grant (1986) pointed out, Wendlandt's (1981) addition of CO_2 to the quartz-normative system raised the pressure of the singular point S^2 to at least 15 kbar. The f_{H_2} is an important variable, particularly in the vapor-absent reactions (Luth and Boettcher, 1986) or when using multicomponent vapors (Luth et al., 1987). An equally serious limitation is the uncertainty in the degree to which Al and Si are ordered in synthetic and natural micas (Bohlen et al., 1983). Phase relationships in these phlogopite-bearing systems are now sufficiently well known to investigate these other variables.

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