

Experimentally determined solidi in the Ca-bearing granite system NaAlSi₃O₈-CaAl₂Si₂O₈-KAlSi₃O₈-SiO₂-H₂O-CO₂

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ABSTRACT

We have determined the phase relationships of melting of synthetic granite (two ternary feldspars + quartz) in the presence of an H₂O-CO₂ fluid. Synthesis and reversed experiments were conducted in a piston-cylinder apparatus over the range 650–900 °C and 6–15 kbar. At $X_{\text{H}_2\text{O}} = 0.75$, melting occurred between 670 and 680 °C (15 kbar), 700 and 710 °C (10 kbar), and 710 and 720 °C (7.4 kbar). At $X_{\text{H}_2\text{O}} = 0.5$, melting occurred between 760 and 770 °C (15 kbar), 780 and 790 °C (10 kbar), and 800 and 820 °C (6–7.4 kbar). At $X_{\text{H}_2\text{O}} = 0.25$, melting occurred between 830 and 840 °C (15 kbar), 830 and 840 °C (10 kbar), and 860 and 870 °C (6–7.4 kbar).

These results provide important constraints on the maximum temperatures of regional metamorphism attainable in vapor-saturated metapelitic and quartzofeldspathic rocks that escaped widespread melting. At pressures below 10 kbar, a fluid phase of $X_{\text{H}_2\text{O}} = 0.75$, 0.5, and 0.25 limits temperatures to below ~700–725, ~800–825, and ~850–875 °C, respectively. As a consequence, the formation of granulite does not require CO₂ concentrations in a coexisting fluid to exceed an X_{CO_2} of 0.25–0.5, a range that may include dilution of the H₂O component of the fluid through internal buffering by devolatilization reactions. Therefore, the formation of granulites by the influx of CO₂ may be a less common phenomenon than previously thought.

INTRODUCTION

The relationships among pressure, temperature, and fluid composition have been a focus of research in metamorphic petrology for the past two decades, especially with respect to the formation of granulites and other high-grade metamorphic rocks. Yet despite the intense interest in the conditions attending high-grade metamorphism, relatively little has been done to elucidate the stability of granitoid rocks in the presence of an H₂O-CO₂ fluid. The stability of felsic assemblages in the presence of such a fluid should provide first-order limits on the maximum temperatures to which felsic rocks could have been subjected during regional metamorphism and still have escaped widespread melting. Conversely, the *P*-*T*-*X* relations of melting in granitoids could limit fluid compositions given independent knowledge of pressure and temperature conditions.

At the inferred *P*-*T* conditions attending metamorphism of lower crustal rocks, relatively low activities of H₂O are required for felsic assemblages to be stable. Knowledge of these H₂O activities and whether or not a fluid was present at all is required for a complete understanding of metamorphism in the lower crust. In this paper we present data that constrain melting relationships in the system NaAlSi₃O₈-CaAl₂Si₂O₈-KAlSi₃O₈-SiO₂-H₂O-CO₂. These data bear directly on the critical issues of the presence and nature of fluid attending high-grade metamorphism.

PREVIOUS WORK

The study of melting in granite systems has had an illustrious history beginning with the seminal work of Bowen and coworkers (Schairer and Bowen, 1935, 1947; Tuttle and Bowen, 1958) and continuing with work by Luth et al. (1964) and Huang and Wyllie (1975). However, these studies addressed melting only in the haplogranite system, and the lack of Ca in the experiments limits their useful application to rocks.

Previous work on Ca-bearing granitoid systems is also somewhat limited because only H₂O-saturated or vapor-absent conditions were investigated. The melting of H₂O-saturated graywacke was investigated by Winkler and von Platen (1961). The H₂O-saturated solidi in synthetic Ca-bearing granite systems were investigated by von Platen (1965) and subsequently constrained in detail by Johannes (1984). Von Platen (1965) noted an increase in the solidus temperature of 35 °C for a granite containing a plagioclase of An₃₅ composition in comparison with haplogranite. This and other studies led to similar conclusions about the effect of Ca on the H₂O-saturated solidus of granite and were summarized by Winkler (1979). Johannes (1984) reported the first systematic, internally consistent study of the effect of Ca on the solidus of haplogranite. These data indicated a much smaller effect than that indicated by previous experiments, only ~10 °C for plagioclase of An₄₀ composition.

On the basis of experiments on the effects of H₂O-CO₂

fluids on the melting of S-type granite (Clemens and Wall, 1981) and on the melting of albite-H₂O-CO₂ (Bohlen et al., 1982) and sanidine-quartz-H₂O-CO₂ (Bohlen et al., 1983), Newton (1987) calculated *PTX* relationships for melting in the system granite-H₂O-CO₂. Subsequently, solidus curves for the haplogranite-H₂O-CO₂ system were constrained experimentally by Keppler (1989). Solidi and minimum-melt compositions in this system were determined by Ebadi and Johannes (1991). The limited effect on the solidus of adding plagioclase as calcic as An₄₀ in the H₂O-saturated system (Johannes, 1984) led Ebadi and Johannes (1991) to postulate that Ca would have the same limited effect in the system haplogranite-H₂O-CO₂. However, the experiments conducted by Keppler and Ebadi and Johannes only place upper temperature limits on the stability of haplogranite. The duration of the experiments in both studies was relatively short (1–24 h, mostly 4–8 h in Keppler, 1989; 1–7 d in the melting determinations of Ebadi and Johannes, 1991), and a potentially insensitive method (quartz disappearance on X-ray powder patterns) was used in both studies to identify the initiation of melting. None of the melting curves was reversed. Thus, the melting curves determined in these studies may have been located at temperatures higher than the true equilibrium boundaries, especially for H₂O-rich conditions. In addition, the assumption that Ca-bearing granite in the presence of a CO₂-bearing fluid will respond in the same manner as Ca-bearing granite under H₂O-saturated conditions (Ebadi and Johannes, 1991) requires direct investigation, especially since no obvious explanation is evident for the discrepancy between the results of Johannes (1984) and those summarized by Winkler (1979).

EXPERIMENTAL METHODS

Starting materials

Synthetic alkali feldspars of the compositions Ca_{0.03}Na_{0.25}K_{0.72}Al_{1.03}Si_{2.97}O₈, Ca_{0.03}Na_{0.29}K_{0.68}Al_{1.03}Si_{2.97}O₈, and Ca_{0.05}Na_{0.33}K_{0.62}Al_{1.05}Si_{2.95}O₈, and plagioclase feldspar of the composition Ca_{0.3}Na_{0.6}K_{0.1}Al_{1.3}Si_{2.7}O₈ were crystallized hydrothermally (1–2 wt% H₂O, 625–650 °C, 7 kbar for 4 d) from glasses of the same compositions. The glasses were prepared by grinding the appropriate amounts of reagent-grade CaCO₃, K₂CO₃, Na₂CO₃, γ-Al₂O₃, and natural Brazilian quartz together in an agate mortar. The mixture was heated to 850–900 °C for a period of several hours and then melted at 1450 °C and 1 atm for 30 min. The resultant glasses were reground and melted again at 1450 °C. After three cycles of melting and grinding, the glasses contained no visible evidence of any of the starting materials and were homogeneous and stoichiometric as determined by electron probe analyses, using conditions chosen to avoid the volatilization of alkalis. Hydrothermal crystallization of the glasses yielded feldspars that were very fine grained (3–10 μm in maximum dimension) and difficult, if not impossible, to analyze with the electron probe. Optical examination of the products of the syntheses revealed only feldspar and traces of quenched

vapor. Both careful examination of the feldspars in immersion oils and powder diffraction patterns showing very sharp, narrow reflections support the meager data from the microprobe indicating that the synthetic feldspars were homogeneous and stoichiometric. The diffraction data also indicate that the alkali feldspars were disordered.

Experimental procedures

For each experiment equal weight fractions of alkali feldspar, ternary plagioclase, and quartz were mixed together by grinding in an agate mortar for roughly 1–2 min and loaded into Pt capsules 3 mm in diameter. To minimize potential complications for metastable melting that may result from inappropriate feldspar compositions in the starting materials (Johannes, 1983), equilibrium compositions were calculated for the chosen experimental conditions using the data of Fuhrman and Lindsley (1988). With these estimates of alkali feldspar compositions in equilibrium with a plagioclase of composition Ca_{0.3}Na_{0.6}K_{0.1}Al_{1.3}Si_{2.7}O₈, initial alkali feldspar compositions in our experiments were selected from one of the following compositions that came closest to the estimated equilibrium composition: Ca_{0.03}Na_{0.25}K_{0.72}Al_{1.03}Si_{2.97}O₈, Ca_{0.03}Na_{0.29}K_{0.68}Al_{1.03}Si_{2.97}O₈, and Ca_{0.05}Na_{0.33}K_{0.62}Al_{1.05}Si_{2.95}O₈. Volatile components were weighed into the capsule prior to loading solid phases. Solid phases were combined with sufficient H₂O and silver oxalate to saturate the system in a fluid phase (10–15 wt% volatiles).

Experiments were conducted in a piston-cylinder apparatus with NaCl furnace assemblies and pistons 2.54 cm in diameter. The furnace assemblies were calibrated against the melting of alkali halides (Bohlen, 1984). Temperature was measured using Pt₁₀₀-Pt₉₀Rh₁₀ (type-S) thermocouples, and temperature was not corrected for the effects of pressure and temperature gradients on emf. Capsules were positioned horizontally so as to be located within the isothermal portion of the furnace assembly (thermal gradient <5 °C, Bohlen, 1984) and packed with sintered hematite in order to maintain a high *f*_{O₂} so that the CO₂ would not reduce to C + CO or C + O₂. We used the piston-in technique by bringing pressure to 20% below that of the final value, increasing temperature to that desired for the experiment, and then increasing pressure to the final value. The precision of *P* and *T* is ±0.1 kbar and ±2 °C. Accuracy of *P* and *T* is estimated to be better than ±0.5 kbar and ±10 °C.

Experimental products

After completion of most experiments, the capsule was cleaned, weighed, and placed in a freezer for 10–15 min. It was then punctured, weighed again, placed in a drying oven for 15 min, and weighed a third time. The three weights allow calculation of the moles of CO₂ and H₂O released. With the exception of experiments during which extensive melting had occurred, the H₂O-CO₂ ratio was always within 2 mol% of the intended value and usually within 1 mol%. After this process, the experimental prod-

TABLE 1. Experimental conditions and results

Expt.	T (°C)	P*	X _{H₂O}	X _{Ab}	t (h)	Results
1096	710	7.4	0.75	25	66	S
1093	720	7.4	0.75	25	88	Tr. M
1089	690	10	0.75	25	64	S
1091	700	10	0.75	25	66	S
1084	710	10	0.75	25	71	2% M
1135Ra	720	10	0.75	25	72	see Expt. 1084
	695	10	0.75	25	151	1% M
1135Rb	720	10	0.75	33	72	see Expt. 1084
	695	10	0.75	33	151	Tr. M
1137Ra	720	10	0.75	25	72	see Expt. 1084
	695	10	0.75	25	268	Tr. M
1137Rb	720	10	0.75	33	72	see Expt. 1084
	695	10	0.75	33	268	S
1081	750	10	0.75	25	76	30% M
1106	670	15	0.75	25	70	S
1097	680	15	0.75	25	93	Tr. M
1095	690	15	0.75	25	67	Tr. M
1085	700	15	0.75	25	69	5% M
1099	800	6	0.5	25	90	S
1105	810	7.4	0.5	25	71	S
1103	820	7.4	0.5	25	51	1% M
1066	750	10	0.5	25	94	S
1068	780	10	0.5	25	92	S
1109	780	10	0.5	29	70	S
1127	780	10	0.5	29	160	S
1075	790	10	0.5	25	71	3% M
1071	800	10	0.5	29	92	5% M
1063	800	10	0.5	25	141	3% M
1121Ra	800	10	0.5	25	75	see Expt. 1075
	775	10	0.5	25	144	S
1121Rb	800	10	0.5	33	75	see Expt. 1071
	775	10	0.5	33	144	S
1098	760	15	0.5	25	91	S
1104	770	15	0.5	25	71	1% M
1102	780	15	0.5	25	53	<1% M
1130Ra	780	15	0.5	25	76	see Expt. 1102
	750	15	0.5	25	223	S
1130Rb	780	15	0.5	33	76	see Expt. 1102
	750	15	0.5	33	223	S
1100	860	6	0.25	25	73	S
1126	870	7.4	0.25		116	M
1114	880	7.4	0.25	33	87	15% M
1117	880	7.4	0.25	25	93	15% M
1119	880	7.4	0.25	29	78	20% M
1065	830	10	0.25	29	118	S
1067	840	10	0.25	25	163	5% M
1079	840	10	0.25	33	95	2% M
1143	840	10	0.25	33	70	1% M
1146Ra	840	10	0.25	25	120	see Expt. 1067
	825	10	0.25	25	336	S
1146Rb	840	10	0.25	33	120	see Expt. 1079
	825	10	0.25	33	336	S
1054	850	10	0.25	29	113	5% M
1062	850	10	0.25	33	123	5% M
1060	900	10	0.25	33	94	30% M
1090	830	15	0.25	25	63	S
1094	840	15	0.25	25	65	Tr. M
1092	850	15	0.25	25	56	5% M
1160a	880	1 atm		25	243	S
1160b	880	1 atm		33	243	S
1133a	900	1 atm		25	255	Tr. M
1133b	900	1 atm		33	255	2% M
1123a	910	1 atm		25	146	15% M
1123b	910	1 atm		33	146	15% M

Note: X_{Ab} refers to the molar fraction of albite in the alkali feldspar. The a and b refer to two capsules used in a single experiment. R = a two-stage reversal experiment during which the temperature was lowered after the interval indicated and held at the lower temperature for the period indicated. S = subsolidus, no glass (quenched liquid) present. M = melted (contains glass), percentages indicate the proportion of glass in the experimental product. Tr. = trace amounts (<0.1%).

* Unless otherwise indicated, the unit is kilobars.

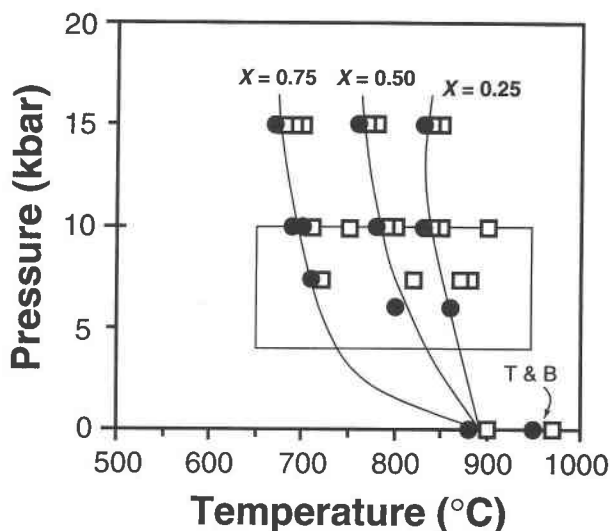


Fig. 1. Experimentally determined solidi for the melting of synthetic granite in the presence of H₂O-CO₂ vapor. Circles indicate the stability of solids + vapor, squares indicate the stability of solids + silicate liquid + vapor. The melting of haplogranite at 1 atm (T & B) by Tuttle and Bowen (1958) is shown for comparison. The box indicates the general range of the P-T conditions for granulites (from Newton, 1987).

ucts were analyzed optically and with X-ray powder diffraction techniques.

Location of the solidi requires a determination of the temperature at which the first glass (quenched liquid) is formed. The glass has a refractive index of >1.50 and is isotropic, whereas the quenched vapor has a refractive index of <1.47 and is slightly anisotropic. Therefore, it was an easy matter to distinguish quenched vapor and quenched liquid, and we saw no evidence that the silicate liquid quenched to solid phases. Locally, the quenched liquid contained vapor inclusions of sufficient size to reveal two phases, an H₂O-rich liquid and a CO₂-rich gas. No carbonate phase was detected in any of the products.

Experimental results

All pertinent experimental data are listed in Table 1, and the results of the experiments are shown graphically in Figure 1. The solidi are constrained by synthesis experiments that were conducted for relatively long periods in the hope that equilibrium would be attained. The curves were reversed at a pressure of 10 kbar by first holding a sample at conditions known from previous experiments to yield significant amounts of glass (quenched liquid). In the second stage of the reversal experiment, the temperature was lowered to a value thought to be just below the solidus. The absence of glass in the products of such experiments demonstrates that the equilibrium solidus must lie between the two temperatures. It is satisfying that the reversal experiments confirm the location of the solidi based on the synthesis experiments. This suggests that the duration of our experiments (2–7 d) was sufficient to obtain equilibrium.

It is also interesting that the solidus temperatures were not much affected by the composition of the alkali feldspar. One interpretation of these results is that the feldspars equilibrated chemically during the experiments, and therefore equilibrium melting relations were deduced regardless of the composition of the initial alkali feldspar. Unfortunately, the feathery intergrowth of the feldspars and quartz and glass coatings of the grains, combined with the very fine grain size of the feldspars, made quantitative analyses of the products impossible.

DISCUSSION

In Figure 2 our experimental results are compared with the experimental results of Clemens and Wall (1981), Keppler (1989), and Ebadi and Johannes (1991) for the system (haplo)granite-H₂O-CO₂. It is clear and not very surprising that Ca has a significant effect on the locations of the solidi in comparison with the haplogranite system, although the magnitude of the effect is not easily ascertained because the slopes of the solidi inferred in our study are somewhat shallower. Contrasts in slopes are sufficient to cause the solidi in Keppler's study at 15 kbar to cross the corresponding solidi of our study, something that cannot be attributed to the effect of plagioclase composition (e.g., note parallelism of solidi for different anorthite contents in Johannes, 1984). This disagreement implies that Keppler may have overestimated the inferred equilibrium temperatures of the various solidi at high *P*. The relatively short duration of the experiments and the technique used to deduce the beginning of melting would both contribute to the displacement of the inferred solidi to higher temperatures. In contrast, the solidi of Ebadi and Johannes (1991), determined in experiments with durations similar to those used in our experiments, do not cross our curves.

The shallower slopes of our solidi imply a lower entropy of fusion than that implied by previous work. The dP/dT slopes for roughly linear segments of these solidi can be used to derive differences in the entropy of melting (ΔS_m). Using our data in the interval 10–15 kbar over which the dP/dT slopes of the solidi can be approximated by a straight line, we calculate an entropy of fusion of ~200–400 J/(mol·K) for the range $X_{H_2O} = 0.75$ –0.25. These estimates are considerably less than values calculated from the experimental data on the haplogranite system by as much as a factor of eight. Our inferred values of the entropy of melting are much closer to those calculated from the data of Johannes for H₂O-saturated granite melting.

IMPLICATIONS FOR REGIONAL METAMORPHISM

Our data do not provide unique constraints on *P*-*T* conditions of high-grade metamorphic rocks, but several implications may be derived from Figure 1 for areas in which metamorphism occurred in the presence of a fluid phase. These include upper limits on the temperatures of regional metamorphism attainable in metapelitic to quartzofeldspathic rocks that escaped widespread melt-

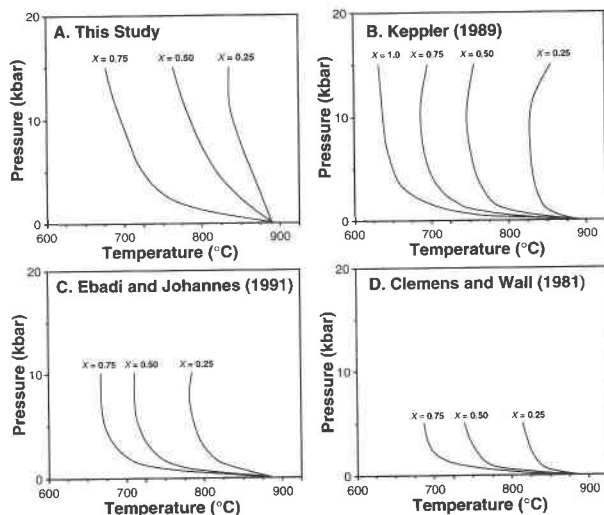


Fig. 2. Comparison of solidus curves for melting in the system granite-H₂O-CO₂. (A) Solidi constrained by the experimental results of this study. (B) Solidi of Keppler (1989); curves constructed from his reported experimental data. (C) Solidi of Ebadi and Johannes (1991); curves constructed from their reported experimental data. (D) Solidi of Clemens and Wall (1981); curves constructed from their experimental data. Data as a function of *P* and *T* were extracted from their plots of *T* vs. X_{H_2O} at 1, 2, and 5 kbar (Figs. 1–3 in Clemens and Wall, 1981).

ing. At pressures below 10 kbar, a fluid phase of $X_{H_2O} = 0.75$ limits temperatures to below ~700–725 °C; at this temperature, only incipient granulite formation is likely as additional heating would result in widespread melting. For a fluid with equimolar H₂O and CO₂, maximum temperatures are constrained to below ~800–825 °C, temperatures wholly consistent with granulite-facies metamorphism. A vapor phase with 25 mol% H₂O would permit metamorphic temperatures as high as 850 °C with little melting. Hence, these results indicate that formation of granulite-facies assemblages does not require CO₂ concentrations in a pervasive metamorphic fluid to exceed an X_{CO_2} of 0.25–0.5, a range that may result from dilution of the H₂O component through internal buffering by devolatilization and melting reactions. We emphasize that these limiting temperatures deduced from the experimental data are higher for Ca-bearing granite than for haplogranite. Thus, metamorphism at a given temperature need not require as high a CO₂ concentration as that required by calculations with haplogranite (Newton, 1987) or by experiments on haplogranite (Keppler, 1989; Ebadi and Johannes, 1991). At $X_{H_2O} = 0.5$ and in the absence of widespread melting, our results limit temperature to below 800 °C, whereas the equivalent curve for the haplogranite system implies a temperature limit of only ~715 °C (Newton, 1987), ~720 °C (Ebadi and Johannes, 1991), or ~750 °C (Keppler, 1989). Thus, attainment of granulite-facies metamorphism without wholesale melting of supracrustal rocks can occur with CO₂ concentrations in the vapor phase of only 25–50 mol%, or X_{H_2O} of 0.75–

0.5. As a consequence, the influx of CO₂ deduced by some as the cause of granulite-facies metamorphism in certain terranes may be less extreme than previously thought.

ACKNOWLEDGMENTS

This research was supported by the Deep Continental Studies and the Geothermal Resource Programs of the U.S. Geological Survey. J.O.E. was funded by an N.R.C. postdoctoral award. Lewis Calk is thanked for his help in our attempts to obtain microprobe analyses of the fine-grained starting materials and experimental products. The manuscript was improved by the reviews of Guy Hovis, Jake Lowenstern, and Craig Manning.

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MANUSCRIPT RECEIVED SEPTEMBER 8, 1994

MANUSCRIPT ACCEPTED MARCH 18, 1995