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Hydrothermal melting behavior of $KAlSi_3O_8$ as microcline and sanidine

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ABSTRACT

The hydrothermal melting of $KAlSi_3O_8$ has been investigated from 1–28 kbar, using microcline and sanidine as starting materials. Both polymorphs melted at the same P-T conditions, and no metastable melting was observed; unlike albite, the inversion temperature from ordered to disordered structures is well below the P-T region of melting; thus sanidine cannot melt in the field of microcline, and microcline invariably inverts to sanidine before melting. The melting curve is drawn through points at 950 °C at 2 kbar, 900 °C at 4 kbar, 820 °C at 10 kbar, 800 °C at 12 kbar, 780 °C at 15 kbar, 765 °C at 18 kbar, and 700 °C at 28 kbar. A flattening of the dP/dT slope at higher pressures, although present, is less pronounced and occurs at higher pressures (>20 kbar) than that for albite (>14 kbar), and the effect of pressure on H_2O solubility in the melt is less than for albite. The melting of $KAlSi_3O_8$ was reversed by two-step reversal experiments that consisted of melting microcline, followed by crystallization of sanidine from the quenched melt. Above 15 kbar coherent glass was not produced by quenching, but a granular incoherent brownish isotropic substance (GIBIS) was observed in the quench product. Abundant quenched vapor precipitate, not readily distinguished from quenched melt, was also observed in experiments above 15 kbar. Vapor solubility of potassium feldspar components is greater than that of albite components at these pressures, and the univariant nature of the melting curve may be lost at $P_{H_2O} > 15$ kbar because of incongruent solubility in the vapor phase. The lack of metastable melting of microcline suggests that disordering, as in the case of albite, always precedes melting. No incongruent melting to leucite was observed in experiments as low as 1.8 kbar, suggesting that metastability may have played a role in earlier low-pressure experimentation of others, and a field of leucite + liquid must exist only at lower H_2O pressures than previously thought.

INTRODUCTION

Experimental studies on alkali feldspars have furthered our understanding of a broad range of mineralogic and geologic phenomena. Much work has been done on hydrothermal melting, but it has been for the most part concentrated in albite. The rather few studies on $KAlSi_3O_8$ have been at low pressures or on a portion of a more complex system (e.g., Goranson, 1938; Shaw, 1963; Lambert et al., 1969; Bohlen et al., 1983). The earliest work on the system $KAlSi_3O_8$-H_2O was that of Goranson (1938), which was restricted to a pressure range from 0.5 to 3.7 kbar. Goranson's data indicated that the incongruent melting of potassium feldspar to leucite and liquid was eliminated at H_2O pressures greater than 2.6 kbar. The only investigation of the hydrous melting of $KAlSi_3O_8$ over a sizeable range of P_{H_2O} is that of Lambert et al. (1969), but this study used the composition $Or_{95}Ab_5$, not pure $KAlSi_3O_8$. In the present study, we present P-T data for the melting of pure $KAlSi_3O_8$ from 1–28 kbar P_{H_2O}.

Some aspects of hydrous albite melting may be suggestive of alkali feldspar melting in general and warrant further examination of $KAlSi_3O_8$. The melting behavior of ordered vs. disordered albite was reported by Goldsmith and Jenkins (1985b). It was found that the melting temperature of low albite exceeds that of high albite by 75 °C at pressures near 15 kbar. All investigations to date have used disordered sanidine as starting material, not ordered microcline. In the albite system, H_2O-saturated melts quenched from pressures greater than 14 kbar do not quench to a coherent glass as in lower-pressure experiments, but rather to a granular, unconsolidated powder. This texture is suggestive of a highly hydrated and depolymerized melt, perhaps tending toward a critical state. In addition to presenting melting temperatures for $KAlSi_3O_8$ over a large range of pressures, this work also uses both microcline and sanidine as starting material and touches on the physical characteristics of high-pressure $KAlSi_3O_8$ melts.

EXPERIMENTAL METHODS

The experimental apparatus and techniques (piston-cylinder apparatus and internally heated Ar pressure vessels) are essentially the same as those described by Goldsmith and Jenkins (1985a, 1985b). NaCl pressure cells were used in the piston-cylinder experiments, with the charges sealed in Pt capsules. Enough H_2O was loaded into each capsule with the solid sample to ensure that the

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melt formed would be vapor-saturated. Exceptions were experiments MC-189a and MC-189b at 1 kbar, which were H_2O-unsaturated to avoid bursting of the capsule. Temperatures in piston-cylinder experiments were controlled and measured with chromel-alumel thermocouples, situated above and perpendicular to the horizontally oriented capsules. Temperatures are considered accurate to within 10 °C. The lower-pressure experiments (<10 kbar) were made in the gas apparatus, with the capsule placed between two chromel-alumel thermocouples. The temperature difference between the two thermocouples did not exceed 3 °C. Temperature accuracy in these experiments is considered to be better than ±2 °C. Ar pressure was measured with a bourdon-type gauge and independently checked against a manganin cell. Both the gauge and the manganin cell were checked against a 100 000-psi Heise gauge, calibrated by the manufacturer. Pressure was read and controlled to a conservatively estimated ±50 bars. Experiments were conducted with NaCl furnace assemblies using the piston-out technique, and no pressure correction was applied.

Analytical technique

At the completion of each experiment the capsule was opened, dried at 110 °C, and analyzed with the petrographic microscope and by X-ray powder diffraction. Selected experimental products were also examined with a JEOL scanning electron microscope (SEM). Best estimates by eye of relative proportions of crystals and amorphous material were made where pertinent, and whenever possible the estimate was also based on the intensities of the X-ray diffraction pattern relative to scans of crystalline sanidine.

Starting materials

Nine samples of potassium feldspar were used for the experiments: four triclinic microcline feldspar samples, four monoclinic sanidine samples, and one orthoclase sample. All were essentially pure $KAlSi_3O_8$, as follows: Microcline A: K-exchanged Amelia albite, Hovis 71104 (Hovis, 1986). Microcline B: K-exchanged Amelia albite (Rutherford Mine, USNM C5390), using 400 mg in 13 g KCl, 850 °C, 23.5 h. Reexchanged in 8 g KCl for 9 h. Microcline C: Essentially Na-free microcline, Jeffrey Mine, Asbestos, Quebec (Olsen, 1961; Goldsmith, 1988b). Microcline D: Microcline perthite from Deponiestollen, Palagnedra, Tessin, Switzerland, K-exchanged at 850 °C. Sanidine A: Crystallized from $KAlSi_3O_8$ gel, 800 °C, P_{H_2O} = 1 kbar, 46 h. Sanidine B: Crystallized from K_2CO_3, Al_2O_3, SiO_2, 750 °C, P_{H_2O} = 1 kbar, 4 d. Sanidine C: Amelia albite (USNM C5390), converted to high albite at 1150 °C, 20 kbar, 5 h, K-exchanged at 850 °C, 24 h. Sanidine D: K-exchanged Amelia albite, heat-treated at 1077 °C, 32 d, then K-exchanged (supplied by H. T. Haselton). Orthoclase: K-exchanged orthoclase from Betroka, Madagascar, Hovis 7053 (Hovis, 1974).

The four microcline feldspar samples all had values of triclinicity or obliquity equivalent to maximally observed Al/Si order, i.e., $\Delta \sim 1.0$, where $\Delta = [d(131) - d(1\bar{3}1)] \times 12.5$ (Goldsmith and Laves, 1954).

EXPERIMENTAL RESULTS

Table 1 contains the data on the hydrothermal melting of $KAlSi_3O_8$ and the behavior of the starting materials. Because interpretations of what appears to be complex behavior are not always straightforward or obvious, discussion of the textures observed is in order.

Identification of quenched phases

At pressures greater than 15 kbar, melts do not quench to a coherent glass, but to a fine-grained (granular) brownish isotropic substance, which is soft and pulverulent, not crunchy in the mortar and pestle. Similar behavior of $NaAlSi_3O_8$ was noted in the references given above and in Goldsmith and Jenkins (1985b). The characteristics of this amorphous substance are in part also dependent on temperature and the degree of H_2O saturation, but these factors have only been examined in this study with several exploratory experiments. Some experiments, noted in Table 1, show tiny sparkles under the microscope, reminiscent of a starry night sky. The birefringent substance is probably mica. In some experiments the basal peaks of a mica are present (weakly) on diffraction scans. It is not known if some or all of the mica is formed during the quench, although larger crystals might be expected if mica were a liquidus phase. It is our impression that the sparkles are more apparent when sanidine rather than microcline is the starting material.

In Table 1 the isotropic material of the higher pressure experiments is identified as GIBIS (granular isotropic brownish incoherent substance). Boettcher and Wyllie (1968) investigated the hydrothermal melting of granite to 32 kbar and noted that at pressures greater than 15 kbar a (presumed) vapor-phase deposit was abundant and formed brown aggregates of isotropic or slightly birefringent material. Mica was also present. Difficulty in unequivocal identification of this material leads to uncertainty not only in the precise location of the melting curve at higher pressures, but also about its character. Hydrothermal melting curves of many phases are considered to be univariant, but if the substance is incongruently soluble in the vapor, melting will not be univariant, and a detectable melting interval or region will be present. Tuttle and Bowen (1958) reported that albite melts over a temperature range of 10 °C or more and ascribed the melting interval to several possibilities, one of which was that the liquid or the vapor had compositions off the binary join albite-H_2O. Goldsmith and Jenkins (1985b) noted similar melting behavior and pointed out that there is no compelling argument for congruent solubility of multicomponent phases.

Solubility considerations, textures, and the nature of the melting curve

The data of Table 1 are plotted in Figure 1. The melting curve of $KAlSi_3O_8$ is depressed less with increased P_{H_2O}

TABLE 1. Hydrothermal melting data

Experiment number MC-	Starting material	T (°C)	P (kbar)	Time (h)	Results
155a	microcline A	675	28	6.5	xls (~1/3) in GIBIS*
b	sanidine B	675	28	6.5	xls (>1/3) in GIBIS
158a	microcline B	699	28	24	all GIBIS, some sparkles
b	sanidine B	699	28	24	xls in GIBIS (50-50?), some sparkles
157a	microcline A	700	28	5	sparse euhedral xls in GIBIS
b	sanidine B	700	28	5	rare xls in GIBIS with sparkles**
154a	microcline A	675	27	5.5	crystals in GIBIS
b	sanidine B	675	27	5.5	crystals in GIBIS with sparkles
153a	microcline A	700	26	5.2	sparse xls in GIBIS
b	sanidine B	700	26	5.2	sparse xls (more than a?) in GIBIS
159a	microcline A	725	26	22	capsule cracked
b	sanidine C	725	26	22	all GIBIS with sparkles; (weak) mica X-ray pattern
176a	microcline B	770	26	23	GIBIS (fine bubbly glass?); No sparkles
b	sanidine D	770	26	23	as above
129a	sanidine A	750	25	26	GIBIS + sparkles
b	microcline A	750	25	26	GIBIS; (weak) mica pattern?
147a	sanidine A	650	25	72	xls in GIBIS with sparkles
b	microcline D	650	25	72	xls in GIBIS (<a)
146a	microcline A	675	25	23	xls + GIBIS
b	sanidine B	675	25	23	xls in GIBIS with sparkles
163a†	microcline A	650	24	93	sanidine + GIBIS
b	sanidine D	650	24	93	sanidine + GIBIS
c	microcline B	650	24	93	sanidine + GIBIS
142a	microcline A	700	24	5	xls (euhedral?) and GIBIS (50-50?), sparkles
b	sanidine A	700	24	5	GIBIS with some xls, sparkles
152a	microcline A	725	24	5.5	leaked
b	sanidine B	725	24	5.5	GIBIS, some xls (<50%)
160a	microcline A	735	23	22.5	xls, some GIBIS
b	sanidine C	735	23	22.5	xls with GIBIS (>50% xls)
162a	sanidine A	745	23	26	GIBIS, with sparkles
b	sanidine C	745	23	26	GIBIS, with sparkles
151a	microcline A	725	22	25.5	all xln (leaked?)
b	sanidine B	725	22	25.5	xls, some GIBIS
140a	microcline A	726	20.3	5	xls (>50%) in GIBIS
b	sanidine A	726	20.3	5	xls (<50%?) in GIBIS
128	microcline A	750	20	23	xls in GIBIS
139a	microcline A	750	20	6	all GIBIS with sparkles
b	sanidine A	750	20	6	all GIBIS with sparkles
174a	microcline B	750	20	18	xls in GIBIS
b	sanidine D	750	20	18	xls only (capsule leaked)
137a	microcline A	775	20	5	all GIBIS, some sparkles
b	microcline D	775	20	5	all GIBIS, less sparkle
173a	microcline B	750	19	27	xls + GIBIS (~50-50)
b	sanidine D	750	19	27	xls + GIBIS with glass (?) (some bubbles)
145a	microcline A	750	18	4.2	xls + GIBIS (>50% xls)
b	sanidine B	750	18	4.2	xls + GIBIS (>50% xls)
166a	microcline B	760	18	71.5	xls in GIBIS (>50% GIBIS)
b	sanidine D	760	18	71.5	xls in GIBIS (>50% GIBIS)
131	microcline A	775	18	23.5	xls in GIBIS (>50% xls)
172a	microcline B	775	18	23	all GIBIS (some bubbly regions) with some sparkles
b	sanidine D	775	18	23	all GIBIS (some tiny bubbles)
171a	microcline B	775	17	48	xls + bubbly glass
b	Orth #7053	775	17	48	xls + bubbly glass + some sparkles
170a	microcline B	785	16.2	23	all GIBIS + sparkles
b	Orth #7053	785	16.2	23	all glass
161a	microcline A	775	16	23	xls + quench globules + some GIBIS
b	sanidine C	775	16	23	xls + quench globules + some GIBIS
127	microcline A	750	15	27	all xls
130	microcline A	775	15	23.5	all xls (mcl + trace residual triclinic material)
132b	microcline C	775	15	19.5	all xls
165a	microcline A	786	15	22	all xls
b	sanidine D	786	15	22	xls + quench globules + some GIBIS
168a	microcline B	795	15	27	glass, bubbly, but not coherent mass
b	sanidine D	795	15	27	glass, as above
134a	microcline A	800	15	5.2	GIBIS + sparkles
b	sanidine A	800	15	5.2	GIBIS + sparkles
136a	microcline A	800	13.2	4	glass, bubbly, some xls (residual?)
b	sanidine A	800	13.2	4	all glass, bubbly
185a	microcline B	815	12	23	all glass, but incoherent powder + some quench globules
b	microcline B	815	12	23	unopened—used for 186a
186a	capsule 185b	790	12	72	large euhedral xls + quench globules
b	microcline B	790	12	72	all xln, angular starting material + quench globules
135a	microcline A	850	11	4.7	all glass (bubbly) + quench globules
b	microcline D	850	11	4.7	all glass (bubbly) + quench globules

TABLE 1.—*Continued*

Experiment number MC-	Starting material	T (°C)	P (kbar)	Time (h)	Results
164a	microcline A	835	10	24	all glass, bubbly
b	sanidine D	835	10	24	all glass, bubbly
167a	microcline B	820	10	24	xls + glass (>50% xls) + quench globules
b	sanidine D	820	10	24	glass (bubbly) + xls (~50-50)
179a	microcline G	950	5.0	22.5	all glass (bubbly)
b	microcline A	950	5.0	22.5	all glass (bubbly)
c	sanidine D	950	5.0	22.5	all glass (bubbly)
180a	microcline B	950	4.0	21.5	all glass (bubbly)
b	microcline A	950	4.0	21.5	all glass (bubbly)
c	sanidine D	950	4.0	21.5	all glass (bubbly)
183a	microcline B	900	4.0 → 3.5‡	16	glass + large euhedral xls
b	microcline B	900	4.0 → 3.5‡	16	not opened — rerun as 184a
181a	microcline B	951	3.03	23	all glass (bubbly)
b	microcline A	951	3.03	23	all glass (bubbly)
c	sanidine D	951	3.03	23	all glass (bubbly)
184a	capsule 183b	903	3.0	74	relict melt spheres + loose powder, all large euhedral xls
b	microcline B	903	3.0	74	all xls, angular starting material
182a	microcline B	950	2.0	24.5	mostly glass (clear), some xls (no leucite)
b	microcline A	950	2.0	24.5	glass + xls (no leucite)
c	sanidine D	950	2.0	24.5	mostly glass (clear), sparse xls (no leucite)
187a	microcline B	975	1.8	47	clear glass (no leucite)
b	sanidine D	975	1.8	47	clear glass (no leucite)
189a§	microcline B	970	1.0	20	sanidine (recrystallized), small amount glass (no leucite)
b	sanidine D	970	1.0	20	sanidine (texturally unchanged) small amount glass (no leucite)

Note: The notation xls refers to monoclinic $KAlSi_3O_8$ (sanidine).

* Granular isotropic brownish incoherent substance.

** Starry night appearance—probably mica.

† Other experiments below liquidus not included in table (made for structural state determinations).

‡ Leaked overnight.

§ Experiments 189a and 189b were H_2O-undersaturated to avoid bursting of capsule. Both used ~5 mg feldspar, 189a with 0.00096 g H_2O, 189b with 0.00238 g H_2O.

than is that for $NaAlSi_3O_8$, indicating that the effect of pressure on the solubility of H_2O is less in $KAlSi_3O_8$ melt than in $NaAlSi_3O_8$ melt. Although solubility data for H_2O in melts are meager, as they also are for solubilities in supercritical fluid, the data available indicate that H_2O solubility in the albite melt indeed in greater than that of $KAlSi_3O_8$ (Goranson, 1938; Oxtoby and Hamilton, 1978). This fact, however, does not imply that the solubility of $NaAlSi_3O_8$ in the vapor is greater than that of $KAlSi_3O_8$; all evidence points to the contrary. The greater solubility of K-containing components in the vapor is clearly indicated in the work on the hydrous melting of granite by Boettcher and Wyllie (1968). A granite with 29 modal % orthoclase was reacted with 30% H_2O at 600 °C and 20 kbar. No orthoclase remained after experiments of only 6 h, and all K_2O (4.6% in the rock) had been transferred to the vapor, producing a solution with about 10.8 g K_2O/100 g H_2O, in addition to the other dissolved components. Ryabchikov and Boettcher (1980) presented data for the solubility of K in aqueous vapor in equilibrium with assemblages, including phlogopite with one or more of forsterite, orthopyroxene, and spinel at 1100 °C. The results in grams of K_2O per 100 g H_2O were 4 at 11 kbar, 7 at 20 kbar, and 25 at 32 kbar. They estimated that total dissolved solute amounted to about 25% at 20 kbar and 50% at 30 kbar.

The high solubility of potassic compositions in the vapor is also indicated in the current study, based upon the amount of noncrystalline material observed in experiments quenched from above, as well as from well below, the liquidus. We have been unable to distinguish material quenched from the vapor at pressures greater than 15 kbar from melts quenched from above the liquidus. As a

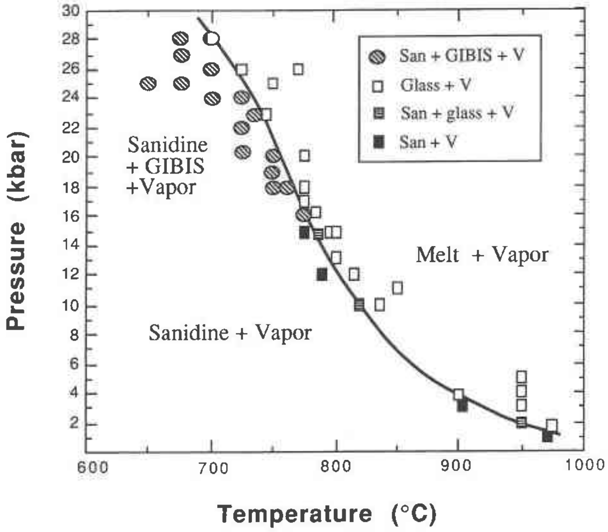

Fig. 1. The liquidus curve for H_2O-saturated melts in the system $KAlSi_3O_8$-H_2O. As discussed in the text, no field containing leucite was observed. The distinction in the symbols in the lower-pressure and high-pressure regions is also discussed in the text.

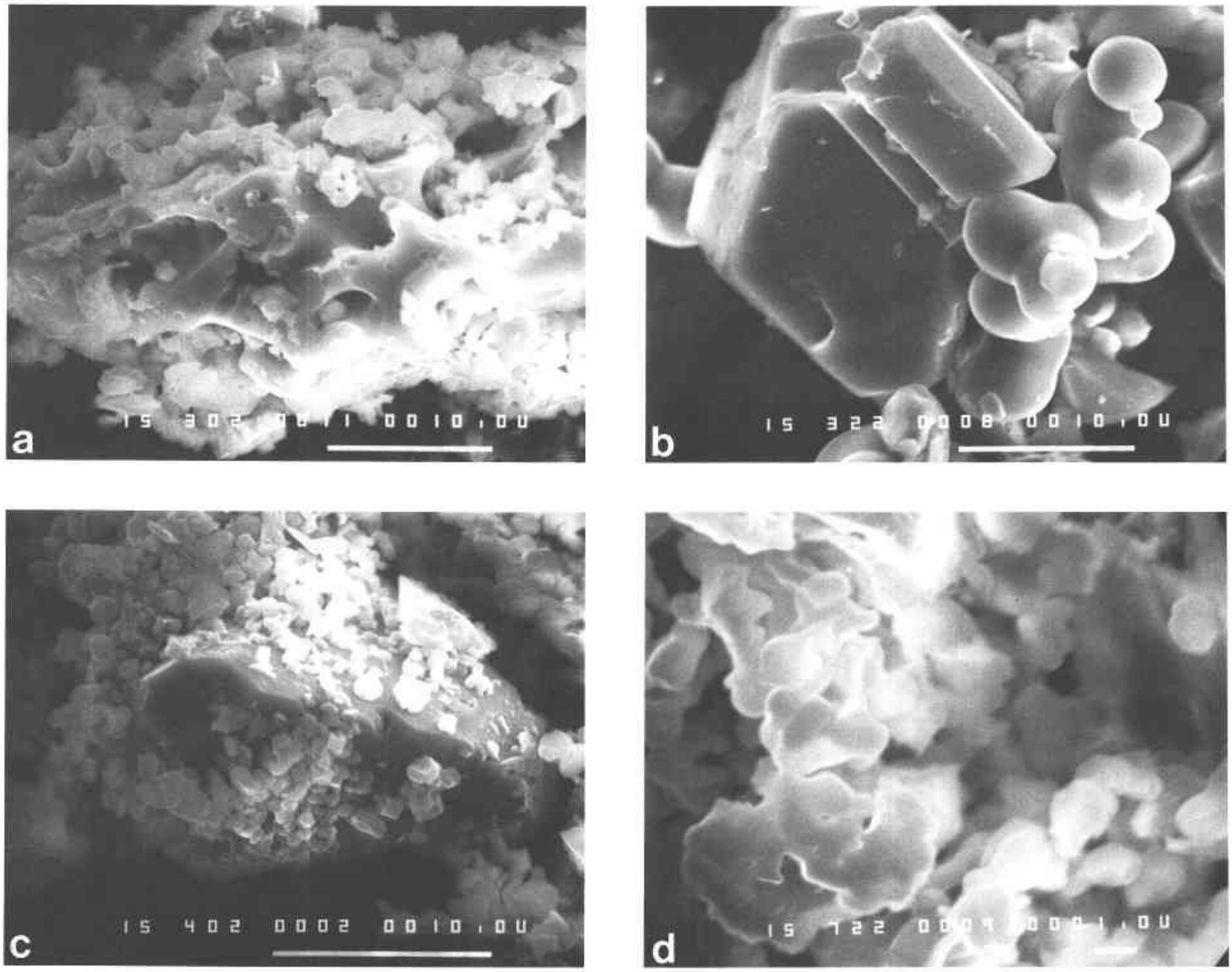

Fig. 2. SEM photograph of selected experiments. (**a**) MC-162a, sanidine held at 745 °C, 23 kbar, 26 h. Scale bar is 10 μm. Under optical microscope, GIBIS with sparkles observed. Here fragments of what appears to be vesiculated glass are also seen. Experiment is on or near liquidus curve. (**b**) MC-161a, microcline held at 775 °C, 16 kbar, 23 h. Crystals, quench globules, and GIBIS observed with optical microscope. The microcline has recrystallized to sanidine. Scale bar is 10 μm. (**c**) MC-163b, sanidine, held at 650 °C, 24 kbar, 93 h. Approximately 60 °C below liquidus. Crystals + GIBIS. Scale bar is 10 μm. (**d**) Also MC-163b, at greater magnification. Scale bar is 1 μm.

consequence, we cannot define a solidus curve at the higher pressures. The brownish aggregates of isotropic or slightly birefringent matter described by Boettcher and Wyllie (1968) from experiments quenched at greater than 15 kbar and interpreted as a vapor-phase deposit are probably this same ambiguous material. Figure 2 shows SEM photographs of two experiments at or near the melting curve of Figure 1 and one at a considerably lower temperature. The melting curve drawn in Figure 1 is our best estimate of the liquidus curve, above which feldspar is not stable in the presence of H_2O. The single point at 5 kbar for the melting of $KAlSi_3O_8$ determined by Yoder et al. (1957) falls on the curve of Figure 1. The liquidus curve shows a less-pronounced flattening of the dP/dT slope at higher pressures than does that of albite (Goldsmith and Jenkins, 1985b), but the reversed curvature and inflection point are present, as in the case of albite. The more pronounced reverse bend in the albite melting curves was discussed in the above reference, and it was suggested that the flattening of the solidi might indicate an approach to maxima on the three-phase curves, as observed in $K_2Si_2O_5$ (Morey and Fenner, 1917).

This approach to critical behavior could be complicated by incongruent solubility relations; a rather large multiphase region (melting band) could separate the liquidus from the solidus curve. Much of the higher-pressure region of Figure 1 indicated by shaded symbols (sanidine + GIBIS + vapor) can be considered to represent this multiphase region, and an approach to a maximum may well exist on a solidus curve (as yet undetermined).

No measure has been made of the H_2O content of either $NaAlSi_3O_8$ or $KAlSi_3O_8$ melts at the high pressures from which the incoherent melt phases are quenched, and it would be difficult to do so. Determination of this as well as the high-pressure solubility in the vapors awaits the development of apparatus in which these phases can be isolated and directly analyzed. It is most unlikely that ambient conditions of the experiments can be maintained in a quenched liquid. The melts are certainly highly depolymerized (Burnham, 1975; Goldsmith and Jenkins, 1985b), and the textures observed probably represent those resulting after H_2O is exsolved from a melt too tenuous to form a coherent glass upon quenching.

Reversals

Reversals of melting equilibria are usually not attempted. The presumption is generally made that under the conditions that produce melting, equilibrium is readily attained. As a precautionary measure, two-stage reversal experiments were made at 790 °C and 900 °C (experiments MC-186 and 184). In addition, what amounted to a single-stage reversal was made in experiment MC-183. In the two-stage reversals, the sample in one of two capsules was observed to have melted to glass. The other (unopened) capsule was brought again to a lower temperature (MC-186a) or a lower pressure (MC-184a). In both experiments the glass produced large crystals, many euhedral, along with relict spheres of what was once melt, now recrystallized. In experiment MC-183, the pressure in the gas vessel inadvertently dropped (because of leakage) from 4.0 to 3.5 kbar. The experiment (183a) contained glass and large euhedral crystals, almost certainly produced by the decreased pressure. These experiments clearly indicate the equilibrium nature of the lower-pressure portion of the liquidus curve.

No reversals were made at pressures greater than 15 kbar. The difficulty in elucidating the nature of the phases in the region where GIBIS is present would cloud reversal criteria.

CONVERSION OF MICROCLINE TO SANIDINE—NO METASTABLE MELTING

Significantly different melting curves were obtained when low and high albite were used as starting materials in an earlier study (Goldsmith and Jenkins, 1985b). At temperatures below ~760 °C, the melting curve for high-albite starting material deviates increasingly from that of the low-albite starting material. At this temperature and above (at ~18 kbar) albite is largely disordered, with a $\Delta 2\theta(131)$ value of 1.85 and greater (Goldsmith and Jenkins, 1985a). At 15 kbar, high albite melts at 600 °C, whereas the melting curve for low albite is at 675 °C; at 12 kbar the two curves are only about 20° apart. On the other hand, no metastable melting of low albite was observed; a single melting curve was produced by both low and high albite starting materials. It was apparent that at temperatures >760 °C the hydrothermal conversion of low albite to high albite is rapid enough that the melting of high albite determined the liquidus, even if residual low albite remains. The absence of a detectable metastable extension of the low-albite melting curve beneath the high-albite curve may be because disordering is a necessary precursor to melting. The melting of low albite may require that the enthalpy of disordering be added to that of melting, resulting in either a two-stage process or one requiring superheating.

Unlike albite, both microcline and sanidine produce a single hydrothermal melting curve. No metastable melting of either polymorph is observed. There is no melting of the high-temperature (disordered) form at temperatures below the inversion temperature because, unlike in the case of albite, this temperature or temperature range is well below that of any hydrothermal melting. Although the triclinic-monoclinic inversion temperature is not known, it is presumed to be in the range 450–500 °C (Goldsmith and Laves, 1954; Hovis, 1974; Senderov and Yas'kin, 1975; Bambauer et al., 1989), and any presumed crossover of melting curves at the inversion temperature would occur in a *P-T* region far below that of melting of either polymorph. As in albite, the low-temperature (ordered) form does not melt as such. The temperature is high enough and the conversion to the stable (disordered) sanidine rapid enough that disordering precedes melting. It is possible that rapid superheating of dry microcline would produce melting before disordering, but no sign of metastable hydrothermal melting of the ordered polymorphs has been seen for either $NaAlSi_3O_8$ or $KAlSi_3O_8$. In all of the experiments in Table 1 in which microcline was used as the starting material, conversion to monoclinic potassium feldspar took place before melting was observed. Structural state variation (degree of Al/Si order, to be considered) in the monoclinic form had no apparent effect on the melting relations.

In conjunction with disordering prior to melting, it was observed that when capsules of both microcline and sanidine were held at conditions close to the liquidus curve, recrystallization took place in the microcline starting material, but not in the sanidine. This is well shown in experiments MC-189a and MC-189b, at 1 kbar and 970 °C. Under these conditions, disordering takes place by a solution-reprecipitation process, or regrowth of the feldspar. The crystals of sanidine, the stable phase, retain their original form during the process.

STRUCTURAL STATE

In conjunction with the melting experiments, some preliminary experimental data are at hand on the equilibrium state of Al-Si order as a function of temperature in monoclinic potassium feldspar (Goldsmith, 1988a). The rate of Al-Si interchange is extremely slow in the range of several kilobars in which most hydrothermal experimentation takes place; reversals of degree of order have not been feasible and structural state-temperature relations of $KAlSi_3O_8$ are not known. Because of the preliminary nature of the data, the information is not included in Table 1, but observable reversal of the degree of order is seen in experiments of several days at 15–25 kbar, in hydrothermal experiments and in experiments containing carbonate flux but lacking H_2O (as in Goldsmith and Jenkins, 1985a). Longer times are necessary to establish equilibrium, but it is apparent that the degree of order is variable and reversible with temperature over at least this interval. The state of order is determined by a simple X-ray powder diffraction technique (three-line spacings) developed by Hovis (1989), using feldspars ranging from monoclinic adularia to high sanidine.

Microcline is converted to monoclinic $KAlSi_3O_8$ at high pressures by a nucleation and growth (two-phase) process, with little or no change in the triclinic geometry (triclinicity or obliquity) during conversion. The unobserved phase change to triclinic geometry takes place well below 600 °C. These results are similar to those observed in anhydrous conversion at high pressures (Goldsmith, 1988b); it is suggested that the triclinic-monoclinic transformation may be a first-order phase change.

THE LEUCITE PROBLEM

Leucite was not observed in any of the experimental products, although no special effort was made to locate a field of leucite along the lower pressure and higher temperature portion of the liquidus curve. Goranson (1938) showed a field of leucite + liquid + vapor that appears at pressures below 2.6 kbar at 950 °C and enlarges at lower pressures and higher temperatures. In this study only sanidine, and no leucite, was observed in an experiment at 1 kbar and 970 °C, and only glass was observed at 1.8 kbar and 975 °C.

It is possible that Goranson's reported temperatures and pressures differ somewhat from ours, but our data indicate that Goranson's value of 2.6 kbar for the maximum pressure stability of leucite is too high.

The diagram of Bowen and Tuttle (1950) of the system $KAlSi_3O_8$-$NaAlSi_3O_8$ at pressures of 1 bar (dry) and at P_{H_2O} of 1000 kg/cm^2 and at 2000 kg/cm^2 (essentially 1 and 2 kbar) are widely known. In the dry system a liquidus curve delimiting the field of leucite + liquid is shown from the data of Schairer and Bowen (1935) and Schairer (1950). A smaller field with leucite is shown at 1000 kg/cm^2, and the field is almost nonexistent at 2000 kg/cm^2. The data of Bowen and Tuttle showed only five leucite-containing experiments at three different compositions, all at 1000 kg/cm^2 and all between 980 °C and 1000 °C. At 2000 kg/cm^2, no compositions containing less than 20% $NaAlSi_3O_8$ were used, and no leucite was observed. No liquidus-determining experiments were made at either pressure. Only two experiments were made with pure $KAlSi_3O_8$. At 1000 kg/cm^2, a 4-h experiment at 1000 °C yielded glass + leucite, and at 980 °C all feldspar. Neither result disagrees with our data, as plotted in Figure 1. The leucite-containing fields shown by Bowen and Tuttle (1950) were for the most part based on the published data of Goranson (1938). Bowen and Tuttle's (1950) principal concern, however, was with the solvus, not the liquidus or solidus curves.

Goranson's original data are of interest. His tables of experiments list pressure and temperature, but not the duration of the experiments. The only comment made as to length of the experiments was: "For a particular run pressure and then temperature are raised to the desired amounts and held at these values for a length of time sufficient for attainment of equilibrium. Although these silicates are very sluggish in crystallizing from an anhydrous melt they crystallize very readily from hydrous solutions, in fact relatively large crystals have been grown in half an hour" (Goranson, 1938, p. 73). Goranson gave no indication whatsoever of the time he felt was required to establish equilibrium, and in 1938 reversing of equilibria was not done. Goranson's experiments used glasses as the starting material, and Goranson, as most who followed him, perhaps felt than in hydrothermal experiments the promotion of a reaction implied equilibrium. More recently, experimenters have realized that melting equilibria can be quite sluggish, as shown by Peterson and Newton (1989b). It is quite possible that the field containing leucite shown by Goranson is at least in part metastable.

In the dry system, Schairer and Bowen (1935) and Schairer (1950) have shown that the field of leucite produced by incongruent melting of potassium feldspar on the join $KAlSi_3O_8$-$NaAlSi_3O_8$ is very large, extending to 51% albite along the join. As mentioned by Goranson (1938), the sluggishness of the feldspar-containing systems is well known, and the system K_2O-Al_2O_3-SiO_2 at the composition of $KAlSi_3O_8$ may well be the most sluggish and intractable, even at the melting temperature, of any system known. Schairer (1950) said: "All alkali-feldspar compositions and particularly those with more than 50 per cent of potash feldspar give viscous melts that are difficult to crystallize dry, and in these crystalline or partly crystalline melts equilibrium between crystals and liquid is attained very slowly. It was possible to determine liquidus temperatures within narrow temperature limits by observing temperatures at which a small amount of tiny crystals grew in the melt and above which they were dissolving. On the other hand, it was not possible to determine the beginning of melting, since none of these alkali-feldspar compositions could be completely crystallized dry and since, even if crystallized hydrothermally, no accurate value for beginning of melting can be obtained because the crystals must be heated above their temperature of beginning of melting for a week or several weeks before observable melting (glass under the microscope) can be recognized."

The elimination at H_2O pressures of several kilobars or less of the field of leucite + liquid that was outlined by Schairer (1950) at 1 atm is impressive. It might be produced by the lowering of the hydrothermal melting point of $KAlSi_3O_8$ to a temperature below that of the metastable congruent melting point of $KAlSi_3O_8$. Schairer (1950) showed the incongruent melting point to be at 1150 ± 20 °C, and a metastable congruent melting point at 1 bar could be at a lower temperature. Although extrapolation of the liquidus of Figure 1 to 1 bar is uncertain because of the flatness of the curve, it would appear to be below 1150 °C. Goranson (1938) extrapolated the curve orthoclase + vapor to ~1110 °C at $P_{H_2O} = 1$ bar. If the quaternary point for orthoclase, leucite, liquid, and vapor shown by Goranson at 2.6 kbar and 950 °C could be dropped to 1 bar, the field of leucite + liquid would disappear at ~1110 °C, and $KAlSi_3O_8$ would melt congruently at all pressures of H_2O. Thus hydrous congruent melting might produce the realization of the metastable congruent melting point. If equilibrium reactions prove to be sluggish at low H_2O pressures, metastability might be a factor, and the true disappearance of leucite might be below 1 kbar. Although this study has not been aimed at this problem, it would appear that investigation of possible metastable behavior in this system, both dry and hydrothermally at low pressures, should be considered.

MELT BEHAVIOR

The possibility exists that a tenuous, alkali-rich, near-critical fluid could be formed at pressures corresponding to the lowermost crust. The inability to quench melted $KAlSi_3O_8$ to glass in the higher-pressure experiments is indicative of a fluid with much lower viscosity than other silicate melts. Because of its greater mobility, a fluid of this nature may greatly enhance heat transfer and element distribution, as well as alkali metasomatism in the lower crust. In the KMASH-CO_2 system, Peterson and Newton (1989a) found that volatile, alkali-rich melts were not quenchable to glass at temperatures as low as 700 °C at pressures in the range 6–10 kbar. The presence of these ultravolatile-rich liquids (or fluids rich in alkalis and silica) at moderate *P-T* conditions in feldspathic and granite-analogue systems is just beginning to be recognized. Further examination is needed to evaluate their petrologic potential.

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