

A phase equilibrium study in the system $\text{KAlSi}_3\text{O}_8\text{-NaAlSi}_3\text{O}_8\text{-SiO}_2\text{-Al}_2\text{SiO}_5\text{-H}_2\text{O}$ and petrogenetic implications

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ABSTRACT

The effect of saturating haplogranitic melts with sillimanite at 2 kbar was examined by determining near-eutectic or near-minimum melt phase relations in the sillimanite-free and sillimanite-saturated haplogranite systems. Three series of compositions were studied with $\text{Ab}/(\text{Ab} + \text{Sa})$ ratios of 0, 0.545, and 1.0. The solubilities of sillimanite in these melts were nearly indistinguishable from each other (3.5 ± 0.5 , 3.7 ± 0.3 , and 3.7 ± 0.5 wt%, respectively). Under sillimanite-saturated conditions, the eutectic or minimum-melt temperatures were lowered by 15–29 °C, and the melt compositions were shifted to more quartz-rich compositions by 1.5–2.5 wt%.

At 2 kbar, the temperatures and compositions (on an anhydrous, sillimanite-free basis) of the four- and five-phase points are

Ab + Qz + Liq + V	748 ± 5 °C	36 ± 1.0 wt% Qz
Ab + Qz + Sill + Liq + V	736 ± 5 °C	38 ± 1.0 wt% Qz
Sa + Qz + Liq + V	767 ± 7 °C	42 ± 1.0 wt% Qz
Sa + Qz + Sill + Liq + V	737 ± 5 °C	43.5 ± 1.0 wt% Qz
Fsp + Qz + Liq + V	685 ± 7 °C	33.5 ± 2 wt% Qz
Fsp + Qz + Sill + Liq + V	656 ± 10 °C	36.0 ± 2 wt% Qz.

The solubility of sillimanite in these melts was found to be insensitive to P and T over the range studied, 2.0 and 6.0 kbar, 680–900 °C, but preliminary experiments indicate that it is increased by the presence of mafic components. This lowering of the minimum-melt temperature may explain the observation of apparently primary magmatic andalusite in some granitic rocks.

INTRODUCTION

Partial melting of aluminous metasedimentary rocks is commonly hypothesized to produce large masses of granitic magmas. A prominent feature of S-type granites is their peraluminous nature (Chappell and White, 1974). Aluminum silicate minerals are found in some high-level peraluminous granites (Clarke et al., 1976; de Albuquerque, 1971, 1973; Price, 1983), and sillimanite is a common constituent of metapelites at the high grades of metamorphism corresponding to beginning of melting. The present study was undertaken to determine the effect of excess alumina in the form of sillimanite (Sill) on the phase relations in the haplogranite system.

Experiments were performed first to measure the solubility of sillimanite in near-eutectic melts. Subsequently, the phase relations near the eutectic or minimum melt in sillimanite-absent systems were determined more precisely than had been done previously. Finally, to evaluate

the melting point depressions of feldspars and quartz due to the dissolution of sillimanite into the melt, the phase relations near the eutectic point were redetermined in the presence of excess sillimanite. The experiments focused primarily on the phase relations near the eutectic points in the binary systems, and near the minimum-melt composition in the haplogranite system at 2.0 kbar.

PREVIOUS WORK

The Ab-Qz-H₂O system was studied by Tuttle and Bowen (1958) up to 4.0 kbar. The best estimate of the H₂O-saturated eutectic point at 2.0 kbar from their data is 752 ± 10 °C, 62 ± 2.0 wt% albite. Shaw (1963) determined the H₂O-saturated eutectic point in the Sa-Qz-H₂O system. At 2 kbar he found the eutectic point to be at 58 wt% sanidine, 767 ± 7 °C. Chatterjee (1974) determined the solidus temperature as a function of pressure in the Ab-Qz-aluminum silicate-H₂O system. In that study, the

solidus temperature at 2.0 kbar lies at 730 ± 15 °C. The compositions of the melts were not determined.

There are very few experimental data on the solubilities of aluminous minerals in granitic melts. Dimitriadis (1978) determined, by microprobe analysis, the Al contents of corundum-bearing synthetic glasses in the peraluminous haplogranite system at 2.0 kbar, 760 °C, and at 5.0 kbar, 680 °C. The compositions had from 2.11 to 3.56 wt% sillimanite (corresponding to 1.33–2.24 wt% normative corundum), with no apparent systematic variation with pressure or composition of the glass.

Solubility data can be obtained from studies in natural systems. Winkler and von Platen (1961) melted paragneisses made from graywackes. Two of these compositions contained sillimanite at the highest metamorphic grade before melting. Comparison of the modes of these gneisses to those of the crystalline residues 85 °C above the solidus (~70% melt) indicates a solubility of sillimanite between 2.9 and 4.1 wt%. Also, Winkler (1979) synthesized a gneiss containing 3.0 wt% sillimanite. At 2.0 kbar, 770 °C (H_2O -saturated), this material was 80% molten. All the sillimanite had dissolved, resulting in ~3.75 wt% sillimanite in the melt. The average sillimanite content of these three natural melts was about 3.6 wt% (corresponding to 2.27 wt% normative corundum).

Clemens and Wall (1981) seeded two peraluminous granitic glasses with finely ground sillimanite and quartz, and partially crystallized them at 5 kbar and 800 and 850 °C, with a variety of H_2O - CO_2 fluid compositions. They analyzed the residual glasses by electron microprobe analysis. The values ranged from 4.1 to 7.5 wt% sillimanite, corresponding to 2.6–4.7 wt% normative corundum. No estimate of error was given. These compositions included ferromagnesian components, which preliminary experiments have shown to increase the solubility of sillimanite.

Recently, Holtz et al. (1992a, 1992b) investigated the effects of excess Al_2O_3 on the phase relations in the Qz-Ab-Or system at 2 kbar with $a_{H_2O} = 0.5$. They reported a solubility of mullite equivalent to 2.38–3.66 wt% sillimanite (corresponding to 1.5–2.3 wt% normative corundum), and a shift in the composition of the boundary between quartz and feldspar to more quartz-rich compositions (3 ± 1 wt% more quartz-rich) in the peraluminous system.

EXPERIMENTAL TECHNIQUE

Starting material

Adularia (OR-1), quartz, sillimanite, and Amelia albite, as well as glasses made from mixtures of these minerals, were used in the Ab-Qz and haplogranite parts of this study (Table 1). Sillimanite and glassy and crystalline material prepared from gels were also used in all parts of this study. In addition, the solubility of sillimanite in haplogranitic melts was initially determined using a glass donated by G. Fine and E. Stolper (Table 1).

Brazilian quartz was ground to <400 mesh and rinsed

TABLE 1. Analysis of albite, adularia (OR-1), and minimum-melt glass starting materials (wt%), with the compositions expressed as mole percent end-member minerals

Oxide	Amelia albite*	OR-1**	Min. melt†
SiO ₂	67.5	61.00	86.06
Al ₂ O ₃	18.9	18.20	7.72
CaO	0.09	0.00	0.00
Na ₂ O	11.3	1.03	2.43
K ₂ O	0.14	14.73	3.33
L.O.I.	2.70	na	na
Total	100.6	94.96	100.0
Calculated mole percent of end-member minerals			
NaAlSi ₃ O ₈	97.62	9.1	20.7
KAlSi ₃ O ₈	0.80	90.9	19.8
CaAl ₂ Si ₂ O ₈	0.43	0.0	0.0
Si ₄ O ₈	1.16	0.0	59.5
Total	100.01	100.0	100.0

* Analyst H. Gong. Sample no. 83-246.

** By electron microprobe.

† Analysis supplied by G. Fine: includes 0.46% Sb₂O₃.

in HCl and HNO₃. The sillimanite, from Williamstown, Australia, was donated by J. G. Blencoe. For the Sa-Qz part of this study, it was ground to a size <5 μm, and the very fine material was removed by flotation. For the Ab-Qz and haplogranite parts of this study, the sillimanite was ground and sieved for the <80 and >200 mesh. X-ray powder diffraction (XRD) analysis revealed only sillimanite. The Amelia albite was prepared by crushing, hand-picking, grinding, and sieving for the fraction <80 and >200 mesh and then performing density separations in bromoform + acetone liquids. Optical and XRD examination revealed pure albite only. The albite was analyzed spectrochemically at the Mineral Constitution Laboratory, Pennsylvania State University (H. Gong, analyst); this analysis and the calculated composition of the albite are presented in Table 1. Adularia (OR-1) was used to make glasses in the haplogranite part of the study and was analyzed by electron microprobe (Table 1). An approximate minimum-melt composition glass, donated by G. Fine and E. Stolper, was used to make a preliminary determination of sillimanite solubility. An analysis of this glass is also presented in Table 1.

For the Sa-Qz part of this study, mixtures of crystalline sanidine and quartz were used as the starting material. The sanidine starting material was crystallized from a gel prepared according to the procedure outlined by Luth and Ingamells (1965). The gel had a calculated Na₂O content of 0.1 wt%. It was crystallized with excess H₂O at 5.0 kbar, 800 °C, in an IHPV for one week. The resulting material was identified as sanidine by XRD. Microscopic examination showed no signs of residual gel. Gels of compositions Ab₆₂Qz₃₈ and Ab₃₀Sa₅₀ were prepared using the same technique. The Ab₆₂Qz₃₈ gel was fired to a glass, which was used in the initial determination of sillimanite solubility in the Ab-Qz system. The Ab₃₀Sa₅₀ gel was hydrothermally crystallized and used as seeds in the haplogranite part of this study.

Glasses of compositions spanning the Ab + Qz eutectic or granite minimum-melt composition were made by

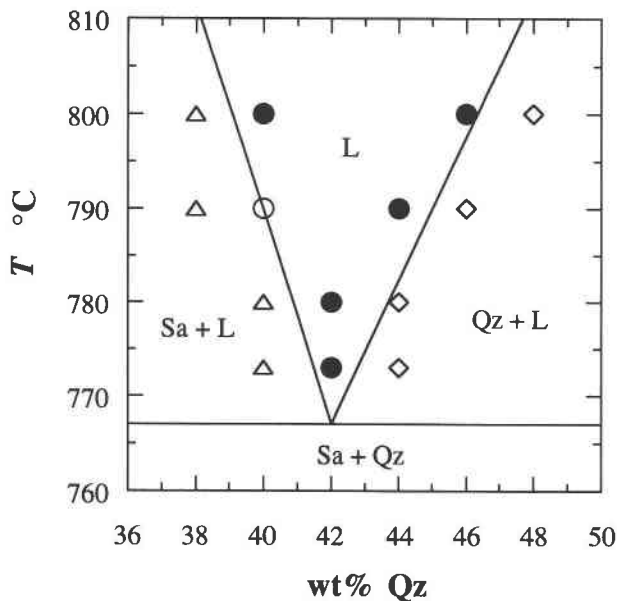


Fig. 1. The phase relations near the H_2O -saturated eutectic in the $KAlSi_3O_8$ - SiO_2 - H_2O system at 2.0 kbar, projected onto the anhydrous sanidine-quartz binary. Solid circles = liquid stable. Open triangles = sanidine stable. Open diamonds = quartz stable. Open circle indicates indeterminate phase relations that are interpreted to lie close to a phase boundary.

weighing out appropriate amounts of albite, orthoclase, and quartz, mixing them in an agate mortar, and melting them hydrothermally. Microprobe analyses of these hydrous glasses confirmed their compositional homogeneity, but, because of low probe totals, the gravimetrically determined compositions were considered more accurate.

In the Ab-Qz part of the study, glasses were made from mixtures of 52–70 wt% albite in 2 wt% intervals. Total amounts of each composition ranged from 400 to 840 mg. Each composition was ground in an agate mortar for 30 min and then split in half. Between 3.7 and 3.45 wt% sillimanite was added to one of the splits of each composition. These compositions were melted hydrothermally at 2.5 kbar, 900 °C, for 6 d. The resulting glasses were finely ground, and the sillimanite-free glasses were seeded with 0.5–4.0 wt% crystalline albite and quartz, the bulk composition of the seed material being the same as that of glass. The sillimanite-containing compositions were seeded with sillimanite and, in some cases, albite or quartz as well. In experiments with glasses containing only sillimanite seeds, it was found that the stable phase nucleated heterogeneously on the sillimanite crystals.

Haplogranitic glasses were made from mixtures prepared by weighing out appropriate amounts of OR-1, Amelia albite, and Brazilian quartz to produce compositions at 31.5, 34.5, 37.5, and 41.0 wt% quartz, with the balance being feldspar. The ratio of albite to sanidine in these compositions was constant at 1.2, with the albite content of the OR-1 adularia and the sanidine content of the Amelia albite taken into account. These mixtures were hydrothermally melted at 2 kbar, 800 °C, for 4 d. A small

amount of crystalline material was still present in most cases. These glasses were finely ground, and splits were taken of each. Between 6.7 and 8.0 wt%, sillimanite was added to one split of each composition. These compositions were then reloaded and hydrothermally remelted at 2 kbar, 750–780 °C—approximately 50 °C above the liquidus temperature. Seeds of composition $Ab_{50}Sa_{50}$ were prepared by hydrothermally crystallizing a gel. Sillimanite-free compositions were seeded with 0.4–0.5 wt% feldspar, quartz, or both.

Equipment

The Sa-Qz and Ab-Qz parts of this study were conducted in large-volume internally heated pressure vessels (IHPV) (Holloway, 1971). Experiments with haplogranitic compositions were conducted in cold-seal vessels. Phase boundaries were commonly bracketed by capsules placed in the same vessel and were thus reacted at nearly identical conditions. IHPV experiments were quenched by turning off the power to the furnace, and cold-seal experiments were quenched by holding the vessel under a jet of air. Isobaric conditions usually were maintained until the temperature had fallen to at least 400 °C.

Manganin cells (Harwood Engineering, Walpole, Massachusetts) were used to monitor the pressure in the IHPV, and a Bourdon-tube gauge was used to monitor the pressure in the cold-seal system. The pressure determinations are considered accurate to ± 50 bars.

Temperature was measured by sheathed Chromel-Alumel (type K) thermocouples. The maximum fluctuation of the temperature from the set point was always <2.0 °C and usually <1.0 °C. The thermocouples were calibrated against a NBS standard K-type thermocouple, the melting points of H_2O and Al, and the boiling point of H_2O . Temperatures are considered accurate to ± 10 °C.

Samples were made by loading 30–70 mg of material into Pt capsules with a 5-mm o.d. with 10–20 wt% H_2O . This H_2O content was sufficient to produce a H_2O -saturated sample at experiment conditions.

Experiment times varied from 4 to 14 d. In experiments with seeded samples, this length of time was sufficient for the small amount of seeds to react in the melt (dissolve completely, or show significant growth). Two experiments (AQLS-11 and AQLS-16) were reacted at the same temperature, but for 10 and 14 d, respectively. There were no detectable differences in the kind, texture, or amounts of the various phases in equivalent samples between these two experiments. When crystalline, micronized starting material was used, the samples were heated for 10–14 d to promote the growth of larger crystals.

Identification of phases

Crystalline phases were distributed uniformly throughout the quenched glasses after the experiments and were identified optically with a petrographic microscope in all samples. Certain samples, including all haplogranitic compositions, were analyzed by XRD, verifying the op-

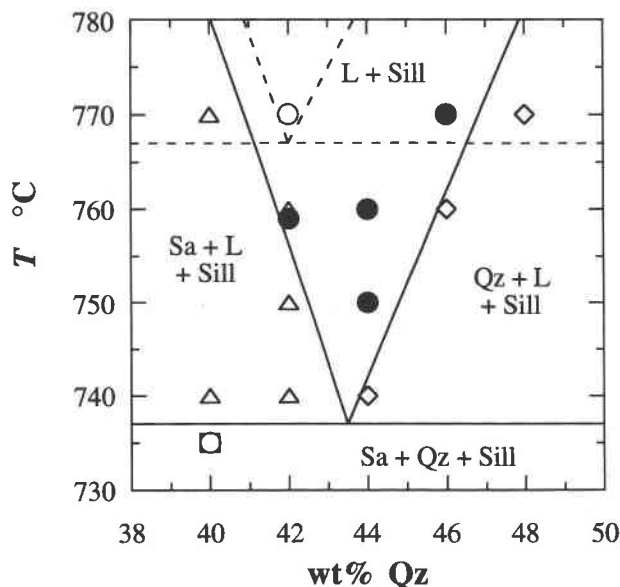


Fig. 2. The phase relations near the H_2O - and sillimanite-saturated eutectic in the $KAlSi_3O_8-SiO_2-Al_2SiO_5-H_2O$ system at 2.0 kbar, projected onto the anhydrous sanidine-quartz binary. Solid circles = liquid stable. Open triangles = sanidine stable. Open diamonds = quartz stable. Open square = sanidine and quartz stable. Open circles indicate indeterminate phase relations that are interpreted to lie close to a phase boundary. The dashed lines are the phase boundaries from the sillimanite-free system, superimposed for comparison.

tical identifications of sillimanite, quartz, and feldspars. In several cases, the XRD patterns constrained the Ab/Sa ratios of the alkali feldspars, in accordance with the method of Tuttle and Bowen (1958). Sillimanite had a distinctive fibrous, needlelike habit, high relief, and parallel extinction. Sanidine and alkali feldspar formed equant, euhedral crystals, which facilitated identification. Albite usually formed rectangular laths with inclined extinction. The morphology of quartz ranged from anhedral blebs to subhedral doubly terminated bipyramids.

SILLIMANITE SOLUBILITY

The solubility of sillimanite in near-minimum or near-eutectic melts was determined by heating samples with various amounts of sillimanite and noting its disappearance in undersaturated samples and its persistence in oversaturated samples. This technique is considered more robust for these hydrous alkali glasses than electron microprobe analysis because of the problem of alkali volatility and because oversaturated samples generally contained extremely fine-grained, dispersed needles of sillimanite, making it difficult to analyze only the glass.

The solubility of sillimanite in the near-eutectic melts in the Sa-Qz system was determined for the $Sa_{38}Qz_{42}$ composition at a temperature of 790 °C by analyzing samples with 2.0, 3.0, 4.0, 5.0, 10.0, 15.0, and 20.0 wt%

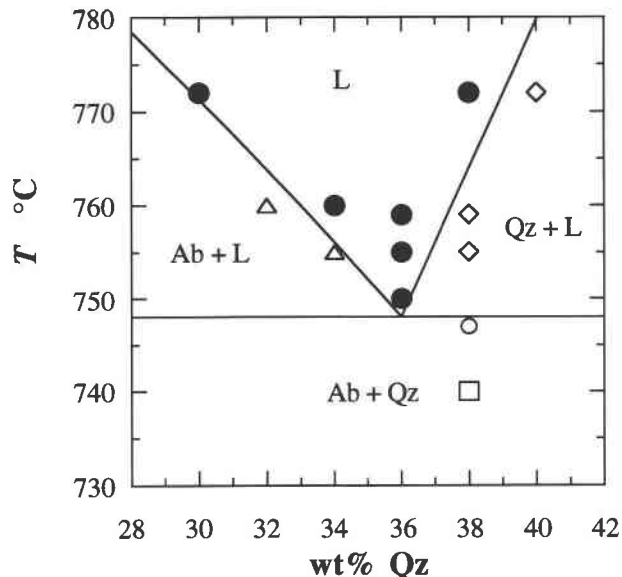


Fig. 3. The phase relations near the H_2O -saturated eutectic in the $NaAlSi_3O_8-SiO_2-H_2O$ system at 2.0 kbar, projected onto the anhydrous albite-quartz binary. Solid circles = liquid stable. Open triangles = albite stable. Open diamonds = quartz stable. Open square = albite and quartz stable. Open circle indicates indeterminate phase relations that are interpreted to lie close to a phase boundary.

sillimanite. Sillimanite was visible optically in the sample that contained 4.0 wt% sillimanite, but not in the sample that contained 3.0 wt% sillimanite. Therefore, the solubility is taken to be 3.5 ± 0.5 wt% sillimanite.

The solubility of sillimanite in Ab-Qz melts was determined first for a glass made from a gel of composition $Ab_{62}Qz_{38}$ by heating samples with 2.0, 3.0, 4.0, 5.0, 10.0, and 15.0 wt% added sillimanite, with excess H_2O at 2.0 kbar and 740 °C for 13 d. No sillimanite was observed in the 2.0 or 3.0 wt% sillimanite compositions, but a trace was present in the 4.0 wt% sample. The 5, 10, and 15 wt% compositions contained abundant sillimanite. The 2.0 wt% sample also had nucleated albite and quartz. In contrast, the 3.0 wt% sample contained albite, but not quartz—qualitative evidence that the eutectic shifts to more quartz-rich compositions with the addition of sillimanite. The 4, 5, 10, and 15 wt% samples contained only sillimanite and glass.

To ensure that equilibrium was attained, the samples with 3.0 and 4.0 wt% sillimanite were reground, reloaded into capsules, and held at 2.0 kbar and 750 °C for another 14 d. No changes were observed. A glass (from crystals) of $Ab_{38}Qz_{42}$ containing 3.39 wt% crystalline sillimanite was also heated to 750 °C at 2.0 kbar. No sillimanite was observed in this glass at the end of the experiment. Thus, the solubility is taken to lie at 3.7 ± 0.3 wt% sillimanite at the Ab + Qz + Sill + Liq + H_2O eutectic.

The solubility of sillimanite seems to be independent

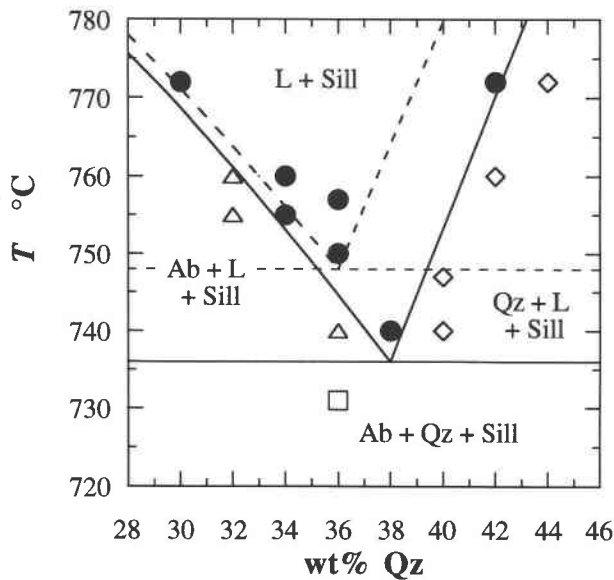


Fig. 4. The phase relations near the H_2O - and sillimanite-saturated eutectic in the $NaAlSi_3O_8$ - SiO_2 - Al_2SiO_5 - H_2O system at 2.0 kbar, projected onto the anhydrous albite-quartz binary. Solid circles = liquid stable. Open triangles = albite stable. Open diamonds = quartz stable. Open square = albite and quartz stable. The dashed lines are the phase boundaries from the sillimanite-free system, superimposed for comparison.

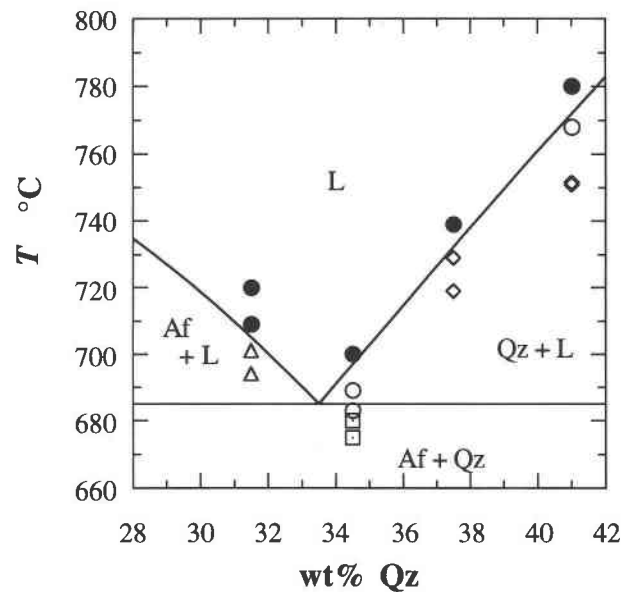


Fig. 5. The phase relations near the H_2O -saturated minimum melt in the $NaAlSi_3O_8$ - $KAlSi_3O_8$ - SiO_2 - H_2O system at 2.0 kbar, projected onto the anhydrous $Ab_{34.5}Sa_{45.5}$ -quartz join. Solid circles = liquid stable. Open triangles = alkali feldspar ($\sim Ab_{33}Sa_{47}$) stable. Open diamonds = quartz stable. Open squares = alkali feldspar and quartz stable. Open circles indicate indeterminate phase relations that are interpreted to lie close to a phase boundary.

of pressure. Two samples with the $Ab_{62}Qz_{38}$ composition held at 6 kbar, 760 °C, bracketed the solubility of sillimanite between 3.5 and 4.0%, indicating a solubility of 6 kbar of $3.7\% \pm 0.3\%$ sillimanite, indistinguishable from the solubility at 2.0 kbar.

The solubility of sillimanite in haplogranitic minimum-melt was determined at 2 kbar and 900 °C, using a glass donated by E. Stolper and G. Fine (Table 1). Mixtures of glass with 1.5, 2.5, 3.5, and 4.5 wt% sillimanite were held at 900 °C for a total of 100 h. Optical examination of the products showed that only the 4.5 wt% sillimanite mixture contained sillimanite. This sample contained abundant sillimanite. Accordingly, the solubility of sillimanite is estimated to be 3.7 ± 0.5 wt%.

A reconnaissance study of the Ab-Sill- H_2O system was undertaken wherein crystalline Amelia albite was mixed with 0.5, 1.0, 3.0, and 4.0 wt% sillimanite and held at 840 °C, 2.0 kbar, for 4 d. The 0.5 and 1.0 wt% sillimanite experiments contained albite and glass. The 3.0 and 4.0 wt% experiments contained albite, sillimanite, and glass. The percentage of glass in the samples increased perceptibly with increasing sillimanite content. Because the assemblage liquid + H_2O -rich fluid + albite + sillimanite is an isothermal, isobaric invariant point, the assemblages in the 3.0 and 4.0 wt% experiments represent disequilibrium. The data indicate that the minimum solubility of sillimanite in Ab-Sill melts is >1 wt% at these conditions.

THE EFFECT OF SILLIMANITE ON THE FELDSPAR AND QUARTZ LIQUIDI AND SOLIDI

The Sa-Qz system

In the Sa-Qz system, the effect of sillimanite on the liquidus and solidus temperatures was determined using crystalline starting material, owing to problems with nucleation and growth from the melt in this very viscous system. Mixtures of sanidine + quartz were prepared in large quantities of nearly a gram to decrease the relative error associated with a fixed weighing error. Mixtures of compositions 52, 54, 56, 58, 60, and 62 wt% sanidine were prepared. Each composition was homogenized by mixing it dry in a mortar for 15 min. The error in these compositions is estimated to be ± 1.0 wt%.

The liquidus was located by noting the presence of crystalline phases of larger size and more euhedral character than in the starting material, indicating crystal growth in a solid \pm liquid field, or an absence of crystals, indicating melting in the all-liquid field. The eutectic was located at the intersection of the quartz and sanidine liquidi.

Four wt% sillimanite was added to the mixtures, and the liquidi were then redetermined. The sillimanite acted as seeds for heterogeneous nucleation, and some determinations were made by soaking the samples for 48–72 h at 800 °C, where all compositions were in the liquid +

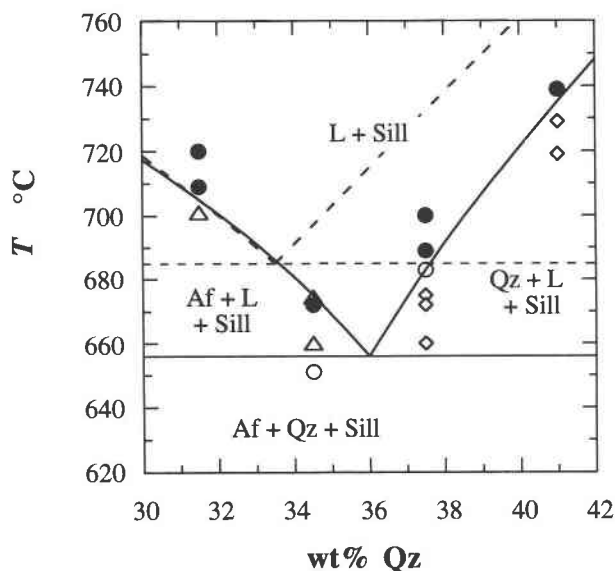


Fig. 6. The phase relations near the H_2O - and sillimanite-saturated minimum melt in the $NaAlSi_3O_8$ - $KAlSi_3O_8$ - SiO_2 - H_2O system at 2.0 kbar, projected onto the anhydrous $Ab_{50}Sa_{50}$ -quartz join. Solid circles = liquid stable. Open triangles = alkali feldspar ($\sim Ab_{33}Or_{47}$) stable. Open diamonds = quartz stable. Open circles indicate indeterminate phase relations that are interpreted to lie close to a phase boundary. The dashed lines are the phase boundaries from the sillimanite-free system, superimposed for comparison.

sillimanite field, and then lowering the temperature to the final experimental conditions. The compositions that were in a liquid + solid + sillimanite field then showed growth of large euhedral crystals of the stable phase, whereas compositions below the solidus contained sanidine, quartz, and sillimanite. The solidus was again located at the intersection of the liquidus curves and was confirmed through bracketing, by noting the first presence of melt in experiments performed without prior soaking at 800 °C.

Ab-Qz and haplogranite

The method used in the Ab-Qz and haplogranite parts of this study to determine the liquidus and the solidus involved seeding a glass of known composition, conducting the experiment at the desired temperature, and examining the experiment products to determine which of the seed phases had grown and which had dissolved. The small amounts of crystalline seeds thus acted as a probe of the equilibrium phase assemblage. The disappearance of seed crystals of both phases indicated that the charge was in the all-liquid field. The seeds overcame the problem of requiring homogeneous nucleation of feldspars or quartz in these viscous melts. Previously made glasses (both with and without sillimanite) were seeded with crystalline material ranging in amounts from a few tenths of a percent to a few percent. In each case, the seed material either was of the same composition as the glass, or was present in such small quantities that the bulk composition was essentially the same as that of the glass.

TABLE 2. Diagnostic results: Sa-Qz-Sill- H_2O

Expt.	t (h)	T (°C)	Composition*	Products**
5/18-1	240	800	Sa ₅₂	Qz + L
5/18-2	240	800	Sa ₅₄	L
5/18-5	240	800	Sa ₆₀	L
5/18-6	240	800	Sa ₆₂	Sa + L
3/4-2	168	790	Sa ₅₄	Qz + L
3/4-3	168	790	Sa ₅₆	L
3/4-5	168	790	Sa ₆₀	L
7/31-3	336	790	Sa ₆₀	Sa + L
3/4-6	168	790	Sa ₆₂	Sa + L
3/14-9	168	780	Sa ₅₆	Qz + L
3/14-10	168	780	Sa ₅₈	L
3/14-11	168	780	Sa ₆₀	Sa + L
5/19-3	240	773	Sa ₅₆	Qz + L
5/19-4	240	773	Sa ₅₈	L
5/19-5	240	773	Sa ₆₀	Sa + L
10/19-1	336	770	Sa ₅₂ + 4% Sill	Qz + L + Sill
10/19-2	336	770	Sa ₅₄ + 4% Sill	L + Sill
9/3-4	240	770	Sa ₅₈ + 5% Sill	L + Sill
9/3-2	240	770	Sa ₅₈ + 5% Sill	Sa + L + Sill
9/3-3	240	770	Sa ₆₀ + 5% Sill	Sa + L + Sill
10/12-1	240	760	Sa ₅₈ + 4% Sill	Sa + L + Sill
10/21-11	336	760	Sa ₅₆ + 4% Sill	L + Sill
10/21-12	336	760	Sa ₅₄ + 4% Sill	Qz + L + Sill
9/10-4	552	759	Sa ₅₈ + 4% Sill	Sill + L
9/10-8	552	759	Sa ₅₈ + 3% Sill	L
9/10-9	552	759	Sa ₅₈ + 2% Sill	L
10/21-8	336	750	Sa ₅₈ + 4% Sill	Sa + L + Sill
11/4-15	336	750	Sa ₅₆ + 4% Sill	Sill + L
11/4-13	336	740†	Sa ₅₆ + 4% Sill	Qz + L + Sill
1/14-2	336	740†	Sa ₅₈ + 4% Sill	Sa + L + Sill
2/1-4	168	740‡	Sa ₆₀ + 4% Sill	Sa + L + Sill
10/21-10	168	735†	Sa ₆₀ + 4% Sill	Sa + Qz + Sill + L
2/1-5	168	735‡	Sa ₆₀ + 4% Sill	Sa + Qz + Sill

* Subscript represents wt% Sa on an anhydrous, sillimanite-free basis. Wt% Sill on an anhydrous basis.

** L = melt (silicate liquid), Sill = sillimanite, Sa = sanidine, and Qz = quartz. All experiments are H_2O -saturated.

† Held at 800 °C for 24 h, then lowered to experiment temperature.

‡ Brought up temperature to experiment conditions.

The determination of the stable phases depended on the assemblage observed after quenching, as well as on the textures observed. In a few cases, grain mounts of the unreacted glasses + seeds were used for comparison. The textural criteria for determining that an observed phase is stable were (1) the presence of euhedral crystals, distinct from the irregular, fractured grains added as seeds, (2) the presence of crystals much larger than the restricted size range of the seed fragments, (3) overgrowths on optically homogeneous but irregularly shaped grains, indicating homogeneous growth on seeds, and (4) heterogeneous nucleation and growth of the phases on sillimanite seeds.

Several charges yielded ambiguous results. The crystalline phase observed in these charges after the experiment was present in smaller amounts than what was loaded and appeared as rounded or embayed subhedral to anhedral blebs. These same compositions had been held at very similar temperatures (within 5 °C) and had shown unambiguous results (growth or complete dissolution). Also, in some of those cases, experiments adjacent in composition at the same temperatures showed consistent, unambiguous results. Therefore, the ambiguous experi-

TABLE 3. Diagnostic results: Ab-Qz-Sill-H₂O

Expt.	t (h)	P (kbar)	T (°C)	Composition* Glass + (seeds)	Results**
AQS-2	312	2.0	740	Ab ₆₂ + (2% Sill)	L + Ab + (Qz)
	312	2.0	740	Ab ₆₂ + (3% Sill)	L + Ab
	312	2.0	740	Ab ₆₂ + (4% Sill)	L + Sill
	312	2.0	740	Ab ₆₂ + (4% Sill)	L + Sill
	312	2.0	740	Ab ₆₂ + (Ab + Qz)	growth of Ab + Qz
AQ-5	142	2.0	755	Ab ₆₂ †	L + Ab + Qz
AQL-9	360	2.0	759	Ab ₆₂ + (Ab + Qz)	L + Qz
	360	2.0	759	Ab ₆₂ + (Ab + Qz)	L
AQSL-10	312	2.0	750	Ab ₆₄ + (Sill)	L + Sill
AQSL-11	336	2.0	740	Ab ₆₄ + (Sill)	L + Ab + Sill
	336	2.0	740	Ab ₆₂ + (Sill)	L + Sill
	336	2.0	740	Ab ₆₀ + (Sill)	L + Qz + Sill
AQSL-15	192	2.0	747	Ab ₆₀ + (Sill)	L + Qz + Sill
	192	2.0	747	Ab ₆₂ + (Ab + Qz)	L = Ab + Qz
	192	2.0	747	Ab ₆₄ + (Sill)	L + Sill
AQSL-17	168	2.0	755	Ab ₆₈ + (Ab + Qz)	L + Ab
	168	2.0	755	Ab ₆₆ + (Ab + Qz)	L + Ab (trace)
	168	2.0	755	Ab ₆₄ + (Ab + Qz)	L
	168	2.0	755	Ab ₆₂ + (Ab + Qz)	L + Qz
	168	2.0	755	Ab ₆₈ + (Ab + Qz + Sill)	L + Ab + Sill
	168	2.0	755	Ab ₆₆ + (Ab + Qz + Sill)	L + Sill
	168	2.0	755	Ab ₆₈ + (Ab)	L + Ab
AQSL-19	240	2.0	760	Ab ₆₆ + (Ab + Qz)	L
	240	2.0	760	Ab ₆₈ + (Ab + Qz + Sill)	L + Ab + Sill
	240	2.0	760	Ab ₆₆ + (Ab + Qz + Sill)	L + Sill
	240	2.0	760	Ab ₅₈ + (Ab + Qz + Sill)	L + Qz + Sill
	240	2.0	760	Ab ₁₀₀ †	Ab
AQSLM-20	96	2.0	840	Ab ₁₀₀ + 0.5% Sill†	L + Ab
	96	2.0	840	Ab ₁₀₀ + 1% Sill†	L + Ab
	96	2.0	840	Ab ₁₀₀ + 3% Sill†	L + Ab + Sill
	96	2.0	840	Ab ₁₀₀ + 4% Sill†	L + Ab + Sill
	96	2.0	840	Ab ₇₀ + (Ab + Qz + Sill)	L + Sill
AQSL-21	168	2.0	772	Ab ₅₈ + (Qz + Sill)	L + Sill
	168	2.0	772	Ab ₅₆ + (Qz + Sill)	L + Qz + Sill
	168	2.0	772	Ab ₆₂ + (Ab + Qz)	L
	168	2.0	772	Ab ₆₀ + (Ab + Qz)	L + Qz (trace)
	168	2.0	772	Ab ₇₀ + (Ab)	L
	168	2.0	772	Ab ₈₄ + 6% Sill†	Ab + Qz + Sill
AQSS-23	48	2.0	731	Ab ₈₀ + 4% Sill†	L + Sill
AAQS-5-7	316	6.0	765	Ab ₈₂ + 3.5% Sill†	L
AAQS-5-6	316	6.0	765	Ab ₈₂ + 3.5% Sill†	L

* Subscript represents wt% Ab on an anhydrous, sillimanite-free basis. Wt% Sill on an anhydrous basis.

** L = melt (silicate liquid), Sill = sillimanite, Sa = sanidine, and Qz = quartz. All experiments are H₂O-saturated.

† Purely crystalline starting material.

ments are interpreted to lie virtually on the phase boundaries and are plotted as open circles in Figures 1–6.

Results

Results from experiments in the Sa-Qz subsystem are listed in Table 2 and shown graphically in Figures 1 and 2. The location of the 2-kbar four-phase point Sa + Q + Liq + H₂O at Sa₅₈ (anhydrous basis) and at 767 ± 5 °C compares very well with Shaw's (1963) determination at Sa₅₈ and 767 ± 7 °C.

The effect of saturating the near-eutectic Sa-Qz melts with sillimanite is shown in Figure 2, where the curves are projected from Al₂SiO₅ and H₂O onto the KAlSi₃O₈-SiO₂ binary join. Also shown for comparison are the liquidus and solidus in the sillimanite-free system, from Figure 1. The eutectic point has shifted to 737 ± 5 °C at a projected composition of Sa_{56.5} on an anhydrous, sillimanite-free basis. Although the position of the sanidine liquidus is relatively unaffected, the quartz liquidus is depressed significantly.

Results of all experiments in the Ab-Qz subsystem are presented in Table 3. The best estimates of the liquidus near the eutectic in the Ab-Qz-H₂O system are presented graphically in Figure 3 and those for the Ab-Qz-Sill-H₂O system in Figure 4. The eutectic compositions in the sillimanite-saturated and the sillimanite-free systems were found at the intersections of the liquidus for quartz and albite at 62 and 64 ± 1 wt% albite, respectively (anhydrous, sillimanite-free basis). The composition of the Tuttle and Bowen (1958) Ab + Qz + H₂O eutectic at 2.0 kbar is 62 ± 2 wt% albite. The differences between these eutectic determinations are less than the combined uncertainties of the two studies.

Results from the haplogranite system are presented in Table 4 and plotted in Figures 5 and 6 for the sillimanite-free and sillimanite-saturated systems, respectively. The best estimate of the eutectic points are at 687 ± 7 °C, 33.5 ± 2 wt% quartz (sillimanite-free), and at 653 ± 10 °C, 36.0 ± 2 wt% quartz (sillimanite-saturated). The effect of sillimanite in this subsystem is similar to the effect in the Sa-Qz system, resulting in a depression of the eu-

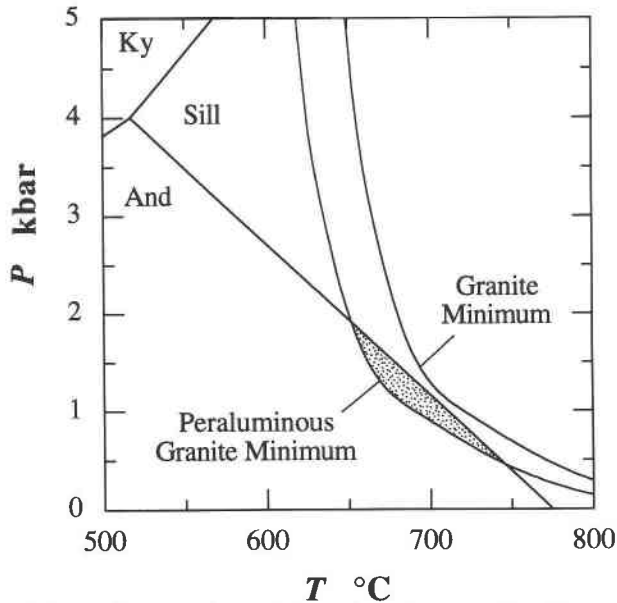


Fig. 7. The aluminum silicate phase diagram of Robie and Hemingway (1984), plotted with the granite minimum melting curve (Tuttle and Bowen, 1958; Luth et al., 1964), and a hypothetical peraluminous granite minimum melting curve depressed 30 °C by the dissolution of an aluminum silicate mineral. The stippled area represents the P , T region where andalusite could precipitate from a peraluminous, granitic magma.

tectic temperature by ~ 29 °C, and shifting it to more quartz-rich compositions by ~ 3 wt%.

Although not directly comparable, the results of this study are in overall good agreement with the results of Holtz et al. (1992a, 1992b). The present experiments were carried out with $a_{\text{H}_2\text{O}} = 1.0$, and the aluminum silicate phase was sillimanite, whereas the experiments of Holtz et al. were carried out at $a_{\text{H}_2\text{O}} = 0.5$, and the aluminum silicate phase was mullite. In that study, the haplogranite minimum-melt temperature was depressed 25 ± 10 °C upon the addition of an aluminum silicate phase, vs. 29 ± 10 °C in this study. This small difference may be insignificant, or it may be due to the lower $a_{\text{H}_2\text{O}}$, indicating a possible effect of $a_{\text{H}_2\text{O}}$ on the solubility of Al_2O_3 in these melts. Holtz et al. (1992a, 1992b) reported a solubility of mullite equivalent to 1.9 ± 0.4 wt% normative corundum. The solubility of sillimanite in haplogranite melts observed in this study corresponds to 2.3 ± 0.3 wt% normative corundum. With structural equilibrium in the melt, less dissolved alumina produces a concomitantly smaller depression of the minimum-melt temperature. Therefore, the difference in melting point depression may be due to different amounts of alumina being dissolved in the melts in these two cases. Mullite, being metastable, should have a higher solubility than sillimanite, all other factors being equal. The factors that were different were $a_{\text{H}_2\text{O}}$ and, to a lesser extent, temperature and composition. Thus, the results obtained by Holtz et al. (1992a, 1992b) may indicate an effect of H_2O activity, temperature, or composition on the solubility of mullite.

TABLE 4. Results in the haplogranite system

Expt.	t (h)	T (°C)	Products*
31.5 wt% Qz			
5,4a	200	720	L
4,2a	384	709	L
3,2a	168	701	L + Fsp
1,3	112	694	L + Fsp
6,3b	156	680	Fsp + Qz
34.5 wt% Qz			
1,2	112	675	Qz + Sa _{46.5}
3,1b	168	683	Xls + L
4,5a	90	689	Xls + L
5,3a	200	700	L
6,3a	156	680	Qz + Fsp
37.5 wt% Qz			
5,2b	200	739	L
4,3b	384	729	Qz + L
2,2b	165	719	Qz + L
1,1	112	709	Qz + L
41.0 wt% Qz			
2,1	165	751.5	Qz + L
4,1	384	768	L + Qz (trace)
5,1	200	780	L
31.5 wt% Qz + Sill			
5,4b	200	720	L + Sill
4,2b	384	709	L + Sill
3,2b	168	701	L + Sill + Fsp (trace)
34.5 wt% Qz + Sill			
4,4b	384	672	L + Sill
2,4	165	651	Sill + Qz + Fsp + L
1,4	112	674.5	Sill + Fsp + L
6,2a	156	660	Sill + Fsp + L
37.5 wt% Qz + Sill			
1,5	112	675	Qz + L + Sill
2,3	165	689	Sill + L
3,1a	168	683	Sill + L
4,4a	384	672	Qz + Sill + L
5,3b	200	700	L + Sill
6,2b	156	660	L + Sill + Qz (trace)
41.0 wt% Qz + Sill			
5,2a	200	739	L + Sill
4,3a	384	729	Sill + L + Qz
2,2	165	719	Sill + L + Qz

* L = melt (silicate liquid), Sill = sillimanite, Fsp = alkali feldspar, Xls = unidentified crystalline phases, and Qz = quartz. All experiments are H_2O saturated.

PETROLOGICAL IMPLICATIONS

Formation of peraluminous melts

The results of this and other studies (Voigt, 1983; Joyce, 1986; Voigt and Joyce, 1991; Holtz et al., 1992a, 1992b) imply that compositions in the Al_2SiO_5 -saturated haplogranite system begin to melt at temperatures 15–30 °C lower than in the Al_2SiO_5 -free system, to produce peraluminous, quartz-enriched melts containing ~ 2.3 wt% normative corundum.

However, the results of this study probably do not represent the upper limit of the alumina content of natural melts. Preliminary experiments on the solubility of garnet in Ab-Qz melts indicates that the dissolution of 9 wt% garnet will increase the solubility of sillimanite from 3.7 to 4.5 wt% (resulting in a total of 4.8 wt% normative corundum). Clemens and Wall (1981) determined the normative corundum content of a natural garnet + cordierite + biotite granite melt saturated with sillimanite at 800 °C. Aside from the mafic components, the com-

position of their starting material is very similar to the one used in this study. Their results (4.7% normative corundum) also suggest that mafic components increase the peraluminous nature of melts in equilibrium with an aluminum silicate mineral.

Al₂SiO₅ in granitic rocks

Although aluminum silicate minerals in granitic rocks are often interpreted to be restite phases, some petrographers have observed andalusite in granitic rocks and, on the basis of textural or chemical evidence, have interpreted it as magmatic (Clarke et al., 1976; de Albuquerque, 1971, 1973; Price, 1983). However, the aluminum silicate phase diagram (Holdaway, 1971; Robie and Hemingway, 1984) shows no overlap between the andalusite stability field and the granite minimum-melting curve (Luth et al., 1964; Tuttle and Bowen, 1958), as shown in Figure 7. Price (1983) discussed this discrepancy and noted that the addition of B, Li, and F lowered the granite solidus (Wyllie and Tuttle, 1961, 1964; Chorlton and Martin, 1978; Manning, 1981). However, the results of this study suggest that one large effect in lowering the haplogranite minimum-melting temperature is due to andalusite saturation itself. The peraluminous granite minimum is plotted as the curve 30 °C lower than the simple granite minimum in Figure 7, representing a haplogranite composition saturated in an aluminum silicate mineral. This depression of the granite minimum results in a region of overlap (the stippled area in Fig. 7), where andalusite can crystallize directly from a peraluminous granitic magma.

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