THE FOUR-PHASE CURVE SANIDINE-QUARTZ-LIQUID-GAS BETWEEN 500 AND 4000 BARS[1]

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ABSTRACT

The four-phase curve sanidine+quartz+liquid+gas in the system $KAlSi_3O_8$-SiO_2-H_2O has been determined at the following points:

P(bars)	T(°C)	$[KAlSi_3O_8/(KAlSi_3O_8+SiO_2)]\times100$ (weight per cent)	H_2O in liquid (weight per cent)
500	825 ± 7	54 ± 2	~2.8
1000	795 ± 7	57 ± 1	~4.3
2000	767 ± 7	58 ± 1	~5.1
4000	735 ± 7	58.5 ± 1	~6.3

These results are similar in form to those obtained by Tuttle and Bowen (1958) for the systems $KAlSi_3O_8$-SiO_2-H_2O and $NaAlSi_3O_8$-SiO_2-H_2O, and by Stewart (1957, 1958) for the system $CaAl_2Si_2O_8$-SiO_2-H_2O.

INTRODUCTION

The present study was made as a part of more extensive investigations of solid-liquid-gas phase relations in silicate-H_2O systems of interest in consideration of problems of the evolution of granites and granitic pegmatites. The subsystem $KAlSi_3O_8$-SiO_2-H_2O obviously is of importance in these investigations and for this reason it was necessary to follow up with additional data the work on the liquidus in this system initiated by Tuttle and Bowen (1958). The data given by Tuttle and Bowen (1958, Table 8) are few and are not sufficient to define the four-phase curve sanidine-quartz-liquid-gas.

The classic work by Schairer and Bowen (1955) on the system K_2O-Al_2O_3-SiO_2 provides data on melting relations at atmospheric pressure for the eutectic or three-phase point sanidine-tridymite-liquid at atmospheric pressure. Because of the extreme viscosity and slow rates of crystallization from liquids on the join leucite-silica they were unable to determine closely the position of the eutectic on this join. Working in the ternary K_2O-Al_2O_3-SiO_2, however, made it possible for them to define the liquidus surface for compositions more potassic than the leucite-silica join because of much lower viscosity and much higher crystallization rates, and also for more aluminous compositions than those on the leucite-silica join because of the much higher temperatures involved. Thus, by approaching the join from two sides, relations on the binary were refined. The three-phase point sanidine-tridymite-liquid (neglecting the gas phase at 1 atm) was found to lie at $990\pm20°$ C. and

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a composition of 58.2 per cent sanidine, 41.8 per cent tridymite by weight (Schairer and Bowen, 1955, p. 718).

Preparation and Properties of "Gel" Starting Materials

Preparation of anhydrous silicate glasses by simple fusion is a tedious and time-consuming operation although excellent results can be obtained (Schairer and Bowen, 1955). In the present study a "gel" method was used that differs somewhat from that described by Roy (1956). Ammonia-stabilized colloidal silica solution, "Ludox," was used rather than ethyl orthosilicate as the source of SiO_2.

The general procedure used was to prepare standardized solutions of KNO_3 and $Al(NO_3)_3 \cdot 9H_2O$ and add these in the desired proportions to standardized Ludox, which has sufficiently low viscosity so that it can be measured using a pipette or burette. It was found necessary to mix the solutions at a pH less than 3, adjusted with HNO_3, to avoid precipitation of $Al(OH)_3$. The resulting mixture was slowly dehydrated over a steam bath until a gelatinous residue remained. This residue was then slowly heated at increasing temperatures until ammonia was driven off and the nitrates were decomposed. When the "gel" was heated at 1000° C. nearly all of the H_2O was removed and the index of refraction corresponded to the index of glass prepared by anhydrous fusion (Schairer and Bowen, 1955, Fig. 5).

The KNO_3 and $Al(NO_3)_3 \cdot 9H_2O$ used were ACS grade. A dehydrated portion of the Ludox used was quantitatively analyzed by a spectrographic method by Harry Bastron of the U. S. Geological Survey. Impurities present in amounts of 0.01 per cent or more were: Fe(0.03), Al(0.05), Ti(0.01), Zr(0.03), Mg(0.02), Ca(0.02), and Na(0.07), equivalent to 0.09 per cent Na_2O. The amount of sodium was checked by W. W. Brannock of the U. S. Geological Survey using a flame spectrophotometer and reported to be 0.14 per cent Na_2O. No K_2O was detected by either method.

A "gel" of composition $KAlSi_3O_8$ was analyzed by M. K. Carron of the U. S. Geological Survey for all major constituents except alkalies, which were determined by flame photometer by W. W. Brannock (Table 1). Minor elements were determined spectrographically by Harry Bastron and found to be about the same as those reported in Ludox alone. Ideally $KAlSi_3O_8$ contains 16.9 weight per cent[1] K_2O, 18.3 per cent Al_2O_3, and 64.8 per cent SiO_2. The $K_2O + Al_2O_3 + SiO_2$ in the analysis recalculated to 100 per cent gives 16.8 K_2O, 18.3 Al_2O_3, 64.9 SiO_2, demonstrating the efficacy of the method. The impurities are

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[1] Weight per cent is used throughout this paper unless stated otherwise.

TABLE 1. CHEMICAL ANALYSIS OF KALSI$_3$O$_8$ "GEL" THAT HAD BEEN
HEATED IN AIR AT 700° C.

	Per cent by weight
SiO$_2$	61.02
Al$_2$O$_3$	17.19
Fe$_2$O$_3$	.10
CaO	.13
MgO	.05
K$_2$O	15.8
Na$_2$O	.17
H$_2$O[1]	5.06
	99.52

Analysts: M. K. Carron and W. W. Brannock.

[1] The sample was exposed to the atmosphere at room temperature before this analysis was performed and therefore the result does not represent the state of hydration of the "gel" at 700° C.

slightly more than would be desired, especially Na$_2$O, but are not considered serious limitations of the technique. It is of interest to compare these results with those for the anhydrous fusion technique. Schairer and Bowen (1955, p. 688) compare a chemical analysis of an anhydrous glass with its theoretical composition. The recalculated analysis of a glass they prepared to have the weight ratio 9.3 K$_2$O, 7.0 Al$_2$O$_3$, 83.7 SiO$_2$ was 9.5 K$_2$O, 7.1 Al$_2$O$_3$, and 83.4 SiO$_2$. The method used in the present work gives at least as good compositional control. The amount of Na$_2$O in Schairer and Bowen's (1955) glasses is apparently less than would be expected in the "gel" preparations although some amount must be present in the glasses, judging from their discussion (p. 682). The amounts of CaO, MgO and Fe$_2$O$_3$ are not stated.

EXPERIMENTAL METHOD

All data were obtained using cold seal bombs. Pressure was externally controlled using H$_2$O as the pressure medium. The charge was contained in sealed gold tubes.

Temperature measurement and control. Temperature was measured by means of a calibrated thermocouple inserted into the end of the bomb so that the junction was approximately in the middle of the segment of bomb in which the charge is positioned and approximately $\frac{1}{4}$ inch away from the charge. The charge was approximately $\frac{3}{4}$ inch long and the temperature gradient over this interval was approximately 3° C. The accuracy of temperature measurements is believed to be ±5° C. Temper-

ature was controlled automatically by motor driven variable trans-
formers.

Pressure measurement and control. Pressures were measured by means of
a manganin gauge and a bourdon gauge was also in the system at all
times as an additional check. Pressure measurement is believed to be
accurate to ± 500 psi. Pressure was not maintained automatically and
therefore each bomb was equilibrated with the system, at the appropri-
ate pressure, several times during a run. Leaks were detected by a drop
in gauge pressure when the valve was opened.

Procedure. The charge of 40 mg "gel," or either glass or crystalline
material previously made from a "gel," was placed in a gold tube with
distilled water in excess (10–15 mg H_2O). The tubes were weighed before
and after welding to check that no H_2O was lost during the welding.
After each run the tube was again weighed. Most runs checked within
± 0.1 mg, and differences greater than 0.2 or 0.3 mg indicated a leak
and the results were considered questionable.

After the run the presence or absence of a water phase in the products
was carefully noted. The charge was examined by means of a binocular
and petrographic microscope and by x-rays.

Crystallization of "gels." Determination of the solidus, the temperature
of the first appearance of liquid (glass), requires entirely crystalline start-
ing material. Thus, portions of the "gels" were hydrothermally crystal-
lized completely to mixtures of quartz and sanidine at approximately
700° C. and 2000 bars.

The time required for complete crystallization depended partly on the
grain size of the "gel" fragments and apparently also on their initial
H_2O content. "Gels" which, during preparation, were heated in air to
about 700° C. and were exposed to the atmosphere at room temperature
after preparation, may contain about 5 per cent H_2O (see Table 2).
These "gels" required several days for virtually complete hydrothermal
crystallization of finely ground material, whereas finely ground "gels"
heated at 1000° C. and stored in a desiccator before use required less
than two days to obtain the same result at the same temperature and
H_2O pressure. Therefore, all "gels" of each composition to be used to
obtain mixtures of quartz and sanidine were heated in air at 1000° C.
and stored in desiccators.

The effect of grain size is probably related to diffusion rates in the
framework of the "gel." Within the larger grains crystals grow to larger
size, thus forming inhomogeneities which require greater migration
distances for complete crystallization. Very finely ground "gels" rapidly

produced a crystalline aggregate of fairly uniform grain size with individual grains averaging roughly one or two microns in diameter.

It was found that granular "gel" containing 5 per cent or so H_2O can fuse together into a glass slug containing crystals at temperatures well below that at which melting is found in crystallized charges of the same composition. This suggests that metastable liquid forms more readily from the hydrous "gels" than does the stable crystalline assemblage for these conditions. Metastable liquid was observed to occur as much as

TABLE 2. H_2O CONTENT OF QUENCHED GLASS

Run	Composition (Per cent Or)[1]	Pressure (bars)	Temperature (°C)	Time (hrs.)	Starting material	Products[2]	Density (g/cc)	Index of refraction[3] (±0.002)	H_2O (Wt. per cent)
192	50	500	890	160	gel[4]	Gl+Q(1)	2.0	1.480	2.7
193	55	500	890	160	gel	Gl+(Q+S)(1)	2.2	1.479	2.6 (2.23, 2.49)[5]
194	60	500	890	160	gel	Gl+S(1)	2.1	1.480	3.1
151	50	1000	880	120	gel	Gl	2.2	1.480	4.2
152	55	1000	880	120	gel	Gl	2.2	1.480	4.3 (3.59)[5]
153	60	1000	880	120	gel	Gl	2.3	1.479	4.4
116	50	2000	855	120	gel	Gl	2.2	1.480	5.1
110	55	2000	840	190	gel	Gl	2.2	1.480	5.3 (5.65)[5]
111	60	2000	840	190	gel	Gl	2.2	1.480	5.0
221c	60	4000	750	16	Gl+S(2)	Gl+S(2)	—	1.483	5.8
223a	55	4000	750	18	gel	Gl+(Q+S)(5)	2.2	1.482	6.9
223b	60	4000	750	18	gel	Gl+S(2)	2.2	1.483	6.3

[1] Composition is expressed in weight per cent $KAlSi_3O_8$ on an anhydrous basis.

[2] Q=quartz, S=sanidine, Gl=glass. Numbers in parentheses represent visual estimates of abundance in per cent (r=rare).

[3] These values represent averages of measurements on glasses from two or more different runs.

[4] Finely ground "gel" heated in air at 1000° C.

[5] Values in parentheses are those obtained by Tuttle and Bowen (1958, Table 9, p. 57) for the composition 56 per cent Or under similar conditions.

50° C. below the temperature at which a mixture of sanidine and quartz begins to melt, but no detailed study of this phenomenon was made.

Determination of the liquidus. The preliminary work on the system $KAlSi_3O_8$-SiO_2-H_2O by Tuttle and Bowen (1958) indicated that at 500, 1000 and 2000 kg/cm² H_2O pressure the isobaric four-phase point, sanidine-quartz-liquid-gas, lies at a composition between 50 and 60 per cent $KAlSi_3O_8$. Three capsules could be run in the same bomb under nearly identical conditions in the present study and therefore three compositions containing, respectively, 50, 55, and 60 per cent $KAlSi_3O_8$ were chosen for early runs. These proved to bracket the isobaric four-phase point for all conditions studied. Determination of the liquidus at both more felspathic and more siliceous compositions was prohibited by the strength limitations of the pressure vessels.

In many runs it was desirable to start with material consisting partly or wholly of glass. In trial runs at 2000 bars starting with water and dry glass, prepared from "gel" at 1200° C., it was found that a few per cent of the charge crystallized in the time required to reach a temperature of about 800° C. On the other hand using glasses containing several per cent H_2O, that is, glass obtained by quenching liquids produced at 2000 bars, trial runs at 2000 bars showed little or no evidence of crystallization during the time required to reach 800° C. or higher (30 to 60 minutes).

Thus, in this system, it is possible to obtain experimental results which are not complicated by reactions that occur in attaining the conditions of the experiment or during the quench. Although this is useful, it is indicative of the sluggish reaction rates in the system. While it is possible to obtain readily the minimum melting temperature, it is exceedingly difficult to obtain complete equilibrium between crystals and liquid. Runs which begin entirely as mixtures of crystals and produce all liquid or liquid plus a trace of crystals lie on or above the liquidus. In order to bracket the liquidus it is desired to produce crystallization at a somewhat lower temperature from material that was entirely liquid. Runs in this system at 2000 bars and lower showed that when a charge was cooled from the liquid state undercooling of several tens of degrees produced little or no crystallization in periods of as much as a few days. Thus, the hope of closely bracketing the liquidus by noting the first appearance of crystals could not be realized.

In view of this difficulty it was necessary to use a technique similar to that employed by Schairer in dry liquidus work (Schairer and Bowen, 1955, p. 684–686). Glasses were prepared hydrothermally, mainly at 2000 bars, which contain approximately one per cent of crystals of sanidine or of quartz. The crystals distributed in the glass were up to 10 microns in size and were subhedral to anhedral in outline. Using these starting materials it was possible in many cases over a period of a week or more to detect either crystal growth, indicating a temperature below the liquidus, or crystal resorption indicating a temperature near or above the liquidus. Crystal growth was recognized by a general increase in the number of crystals and in more nearly euhedral morphology. The liquidus was taken to lie at a temperature between that where crystals were all resorbed and that where crystals grew.

Identification of crystalline phases. Crystals distributed in glass were optically identified by habit, index of refraction relative to the glass, birefringence and optic orientation. Quartz usually formed as doubly terminated crystals lacking prism faces. Since the conditions of all runs

were in the stability field of β-quartz (see Yoder, 1950) the morphology observed was of this form. The sanidine crystals formed in thin plates and laths which were generally easily distinguished from quartz.

X-ray diffractometer patterns were useful for recognition of quartz in amounts greater than about 2 per cent and sanidine in amounts greater than about 5 per cent. Diffractometer patterns of pure synthetic sanidine grown at 700° C. and 2000 bars correspond closely to the high-temperature sanidine indexed by Donnay and Donnay (1952). In all cases in the present work where the sanidine pattern is clearly resolved the strong reflections (220), (20$\bar{2}$), (040), and (002) were clearly distinguished and their intensities were usually in the order (220) > (002) > (20$\bar{2}$) > (040).

Properties of the hydrous glasses. Quenched liquids in this system have the form of a small glass slug or bead having the shape of the container and with a smooth meniscus at the interface with the H_2O-rich gas phase. A part of the small silicate content of the gas phase condenses to minute glass beads which are found in the upper part of the tube and on the meniscus surface of the glass slug. These beads have a distinctly lower index of refraction (1.472–1.475) than the quenched liquid, for liquid compositions near the isobaric four-phase points, which suggests that material dissolved in the gas is more silica-rich than the liquid (see Schairer and Bowen, 1955, Fig. 5 for the effect of silica content on indexes of refraction of glasses in the system $K_2O\text{-}Al_2O_3\text{-}SiO_2$). During the formation of silicate liquid from crystals or "gel," bubbles of gas are trapped and the viscosity of the liquid is so great that bubbles may remain in the quenched liquid after runs of several weeks duration at 500, 1000 and 2000 bars. Glasses formed at 4000 bars contain fewer bubbles than those formed at lower pressures.

Measurements of the index of refraction and density were made on glasses produced at all pressures studied, and the H_2O content was determined as carefully as possible. The measurements of the index of refraction were made in ordinary light using oils calibrated at intervals of approximately 0.005. This permitted estimates only to ± 0.002. The values obtained for the compositions studied were all in the range 1.478–1.483. These measurements are too rough to indicate the separate effects of changing the $KAlSi_3O_8/SiO_2$ ratio and H_2O, in the interval studied, on the indexes of refraction except that these effects are small.

Considering the difficulties in obtaining bubble-free glass from the viscous liquids in this system it is apparent that precise measurements of density and H_2O content are difficult. Present methods of making these measurements leave much to be desired and it is difficult to assign uncertainties to the methods used. The density measurements were made

on glass slugs using a Berman density balance with calibrated toluene. The weights of these slugs ranged from 15 to 70 mg. In the worst cases bubbles occupy on the order of 10 per cent of the volume of a glass slug. If these were unoccupied by "quenched gas" the density would be low by this factor. The bubbles contain two phases (liquid plus gas), however, and the density error is somewhat less, probably falling between 5 and 10 per cent low. Glasses formed at 500 bars would give low results by the greatest factor. A few per cent crystals present in a glass would increase the measured density only to a small extent since the densities of quartz and sanidine are less than 0.5 g/cc higher than those of the glass. Measured densities together with H_2O content and index of refraction are given in Table 3. The approximate H_2O contents given in the abstract represent averages for each set of determinations at each pressure.

The H_2O content of the quenched liquids (glasses) is thought to represent the content in the liquid in equilibrium with the H_2O-rich gas phase under the conditions of the run. Exsolution of appreciable H_2O from the glass slug during the quench is considered unlikely because quenching is carried out isobarically.

The H_2O content of the glasses was determined on crushed glass with grains averaging on the order of a few tenths of a millimeter in diameter. The crushed glasses were placed in platinum envelopes and held at 110° C. to essentially constant weight which required about two hours. On the assumption that H_2O in bubbles represents trapped gas, crushing results in a smaller positive error in the determination by freeing some of this H_2O at 110° C. The envelopes were then taken to 1000° C. for about an hour, and the weight loss was used to calculate the per cent H_2O. To check on the completeness of dehydration at 1000° C. a group of three envelopes was heated at 1000° C. for ten minutes, cooled, weighed, reheated at 1350° C. for about 15 minutes and reweighed. The weight difference between the two heatings was less than the uncertainty in the individual weights.

Data obtained in the H_2O determinations are given in Table 2. The glass labeled 192 is an average obtained from weight loss of two platinum envelopes which adhered together during the heating. The glass labeled 194 was ground very fine in an agate mortar before the H_2O determination.

The temperatures at which the glasses were formed were generally several tens of degrees above the liquidus. Thus the measured H_2O contents must differ somewhat from the amount in the liquid at the isobaric four-phase points. The magnitude of this effect is not known accurately. The effect on H_2O content of changing the weight ratio of

TABLE 3. EXPERIMENTS USED TO DEFINE THE UNIVARIANT CURVE
SANIDINE-QUARTZ-LIQUID-GAS[1]

Runs	Composition Per cent Or[2]	Starting Material[3]	T (°C.)	Time (hrs)	Products[3]
		P = 500 bars			
172, 173, 174	50, 55, 60	Q+S	820	16	Q+S
206, 207	50, 60	Q+S	830	116	Gl+Q+S
184	50	Gl+Q(<1)	860	192	Gl+Q(<1, eu)
185	55	Gl+(Q+S)(3)	860	192	Gl+S(1)
186	60	Gl+S(1)	860	192	Gl+S(2, eu)
196	50	Gl+Q(1)	870	112	Gl+Q(r, eu)
197	60	Gl+S(1)	870	112	Gl+S(1)
187	50	Gl+Q(1)	880	126	Gl
188	55	Gl+(Q+S)(3)	880	126	Gl
189	60	Gl+S(1)	880	126	Gl+S(1)
181	50	Q+S	885	172	Gl+Q(10)
182	55	Q+S	885	172	Gl+Q(1−2)+S(1−2)
183	60	Q+S	885	172	Gl+S(10)
202	50	Gl+Q(<1)	890	124	Gl
203	60	Gl+S(2)	890	124	Gl+S(<1)
208	60	Gl+S(5)	900	115	Gl
		P = 1000 bars			
166, 167	50, 60	Q+S	790	43	Q+S
131	50	Q+S	800	16	Q+S+Gl
135, 136	55, 60	Q+S	800	186	G+S+Gl
163	50	Gl+Q(10)	820	430	Gl+Q(10, eu)
164	55	Gl+Q(1)	820	430	Gl+Q(2, eu)
165	60	Gl+S(1)	820	430	Gl+S(5, eu)
154	50	Q+S	840	168	Gl+Q(10)
155	55	Q+S	840	168	Gl+(Q+S)(1−2, an)
159	60	Q+S	840	284	Gl+S(2)
160	50	Gl+Q(1)	840	384	Gl+Q(1, eu)
161	55	Gl+(Q+S)(2)	840	384	Gl
162	60	Gl+S(<1)	840	384	Gl+S(1, eu)
168	50	Gl+Q(<1)	850	404	Gl+Q(<1, eu)
169	60	Gl+S(1)	850	404	Gl
140	50	Q+S	860	184	Gl+Q(10, an)
141	55	Q+S	860	184	Gl
151, 152, 153	50, 55, 60	gel	880	120	Gl

[1] In all of these experiments a gas phase was present which consisted of H_2O saturated with the silicate components.

[2] Composition is expressed in weight per cent $KAlSi_3O_8$ on an anhydrous basis.

[3] Q=quartz, S=sanidine, Gl=glass. Numbers in parentheses represent visual estimates of abundance, in per cent, to be taken only as indications of an observable difference in amount when two samples were compared (r=rare). The symbol "eu" indicates improved crystal form and the symbol "an" indicates rounding and resorption. Runs which produced both euhedral and anhedral forms in indeterminate proportions are not labeled.

TABLE 3—(continued)

Runs	Composition Per cent Or[2]	Starting Material[3]	T (°C.)	Time (hrs)	Products[3]
		P = 2000 bars			
113b	55	Q+S	763	147	Q+S
124	55	Q+S	770	24	Q+S+Gl
86	55	Q+S	775	505	Gl+(Q>S)(5)
87	60	Q+S	775	505	Gl+(Q+S)(10)
50	50	Q+S	780	17	Gl+Q+S
76	55	Q+S	790	211	Gl+Q(2)
77	60	Q+S	790	211	Gl+S(5)
68	50	Q+S	800	68	Gl+Q(10)
146	50	Gl+Q(1)	800	41	Gl+Q(2, eu)
211	55	Gl+(Q+S)(2)	800	771	Gl
212	60	Gl+(Q+S)(2)	800	771	Gl
205	60	Gl+S(2)	810	144	Gl
200	50	Gl	820	190	Gl+Q(r, eu)
201	60	Gl+S(2)	820	190	Gl
69	50	Q+S	830	89	Gl+Q(3)
70	55	gel	835	137	Gl
93	60	gel	850	143	Gl
116	50	gel	855	120	Gl
		P = 4000 bars			
216a, c	50, 60	Q+S	730	16	Q+S
214a, b, c	50, 55, 60	Q+S	740	27	Q+S+Gl
221a	50	Gl+Q(r)	750	16	Gl+Q(10, eu)
221b	55	Gl+Q(1)	750	16	Gl+Q(5, eu)
221c	60	Gl+S(2)	750	16	Gl+S(2)
219a	50	Q+S	760	68	Gl+Q(10)
219b	55	Q+S	760	68	Gl+Q(3)
219c	60	Q+S	760	68	Gl

$KAlSi_3O_8 : SiO_2$ from 50:50 to 60:40 is too small to be reflected in the H_2O determinations.

PHASE RELATIONS NEAR THE ISOBARIC FOUR-PHASE POINTS

The temperature of the isobaric four-phase point was established by the first appearance of glass in initially completely crystalline material. Small amounts of glass are readily recognized by the fritted appearance of the charge when the capsule is opened and by optical examination of the crushed material in oils.

Table 3 gives the runs from which the liquidus was determined. For simplicity pseudobinary diagrams of 500, 1000, 2000 and 4000 bars, together with the eutectic at 1 atm determined by Schairer and Bowen (1955), have been compiled in Fig. 1. These have the appearance of
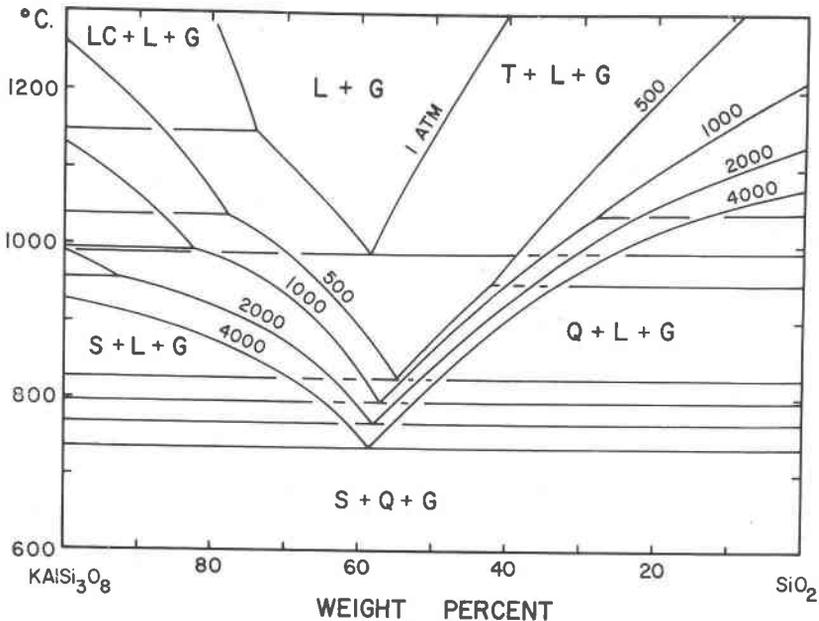
Fɪɢ. 1. Projections of the saturated liquidus at 500, 1000, 2000 and 4000 bars in the system KAlSi₃O₈-SiO₂-H₂O to the join KAlSi₃O₈-SiO₂. S=sanidine, LC=luecite, Q= quartz, T=tridymite, L=liquid, and G=gas. Data at 1 atm were taken from Schairer and Bowen (1955). Data for KAlSi₃O₈-H₂O were taken from Goranson (1938), and for SiO₂-H₂O from Stewart (1958) and Tuttle and England (1955). There are no experimental data for the composition coordinates of the points S+LC+L+G and Q+T+L+G.

binary diagrams but represent the surfaces in the ternary system KAlSi₃O₈-SiO₂-H₂O in which condensed phases coexist with an H₂O-rich gas. The P-T curve representing the beginning of melting in this system, or the curve through the isobaric four-phase points, projected to the P-T plane, is shown in Fig. 2. The H₂O contents are not shown graphically as the data are not isothermal.

The temperature of the four-phase point sanidine-quartz-liquid-gas at 500 bars lies between 820° and 830° C. The position is believed to lie at a little less than Or_{55} (55 per cent KAlSi₃O₈)[1] but cannot be stated with assurance closer than 54 ± 2 per cent KAlSi₃O₈. The four-phase

[1] The symbol Or is used for the component KAlSi₃O₈ and its percentage in the sum of the components SiO₂+KAlSi₃O₈ is given as a subscript. Thus the compositions given represent only the ratio of the silicate components and not the amount of these components in the hydrous liquid. The composition is given in this way because the ratio of the silicate components is known with more accuracy than the amount of H₂O in the liquid.
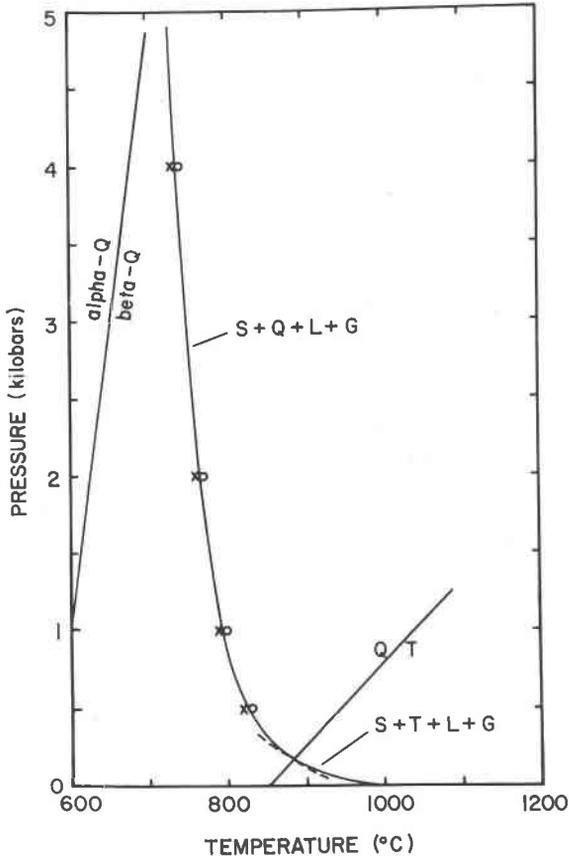
Fig. 2. P-T projections of the univariant curves sanidine+quartz+liquid+gas and sanidine+tridymite+liquid+gas in the system $KAlSi_3O_8$-SiO_2-H_2O. Crosses represent the presence of crystals only and circles the presence of liquid+crystals. The curve for the alpha-beta quartz inversion is after Yoder (1950) and for the quartz-tridymite transition is after Tuttle and England (1955).

point at 1000 bars lies between 790° and 800° C. and the composition is believed to be $Or_{57\pm1}$. At 2000 bars the temperature of the four-phase point was bracketed between 763° and 770° C. The shift in composition for the four-phase point must be small between 1000 and 2000 bars and the composition for this point at 2000 bars is in the range $Or_{58\pm1}$. The temperature of the four-phase point at 4000 bars lies between 730° and 740° C. The saturated liquidus could be investigated only to about 25° C. above the temperature of the four-phase point at 4000 bars because the life of the pressure vessels is short at this pressure for tempera-

tures near 750° C. The results of runs in this interval, however, were clear. The composition at the four-phase point is given as $Or_{58.5\pm1}$.

Thus the four-phase curve shifts toward Or only to a small extent between 1000 and 4000 bars. The magnitude of the shift appears to be greater below 1000 bars.

The positions of the four-phase curves quartz+tridymite+liquid+gas and sanidine+leucite+liquid+gas within the system $KAlSi_3O_8$-SiO_2-H_2O are unknown except for their P-T coordinates which are taken from the data on the system $KAlSi_3O_8$-H_2O by Goranson (1938) and from data on the system SiO_2-H_2O by Tuttle and England (1955).

Discussion

A rough estimate for the invariant point quartz+tridymite+sanidine +liquid+gas (Fig. 2) can be obtained by extrapolating the P-T projection and compositions along the four-phase curve Q+S+L+G. This procedure gives T=885° C.; P=175 bars; anhydrous composition, Or_{52}; and H_2O content, 1.3 per cent. The latitude possible in this extrapolation is considerable and therefore no estimate of accuracy can be given. It is evident that from this invariant point, with decreasing pressure and increasing temperature, the four-phase curve tridymite+sanidine+liquid +gas must shift to higher ratios of $KAlSi_3O_8/SiO_2$ in order to coincide with the eutectic composition at atmospheric pressure ($Or_{58.2}$) given by Schairer and Bowen (1955).

A detailed comparison of the present results for the four-phase curve Q+S+L+G with those of Tuttle and Bowen (1958) is difficult owing to the paucity of their data (their Table 8, p. 53). Values for the ratio $KAlSi_3O_8/SiO_2$ indicated by them on the join Or-SiO_2 in their figures 22 through 25 (Tuttle and Bowen, 1958, p. 54–56) are quite similar to those found in the present work although they show the ratio to be a little smaller at 1000 kg/cm² (~980 bars) and 500 kg/cm² (~490 bars). The main differences lie in the temperatures implied by figures 22 and 23 for the four-phase curve Q+S+L+G at 500 and 1000 kg/cm² which are approximately 25 and 35° C. lower than those found in the present work at 500 and 1000 bars respectively. The implied temperatures at 2000 kg/cm² and above are very close to those given by this paper at comparable pressures.

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