

THE FOUR-PHASE CURVE SANIDINE-QUARTZ-LIQUID-GAS  
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## ABSTRACT

The four-phase curve sanidine+quartz+liquid+gas in the system  $\text{KAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$  has been determined at the following points:

P(bars)	T(°C)	$[\text{KAlSi}_3\text{O}_8/(\text{KAlSi}_3\text{O}_8+\text{SiO}_2)]\times 100$ (weight per cent)	H <sub>2</sub> O 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  $\text{KAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$  and  $\text{NaAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$ , and by Stewart (1957, 1958) for the system  $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$ .

## INTRODUCTION

The present study was made as a part of more extensive investigations of solid-liquid-gas phase relations in silicate-H<sub>2</sub>O systems of interest in consideration of problems of the evolution of granites and granitic pegmatites. The subsystem  $\text{KAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$  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  $\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$  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  $\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ , 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  $990 \pm 20^\circ \text{C}$ . and

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

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  $\text{SiO}_2$ .

The general procedure used was to prepare standardized solutions of  $\text{KNO}_3$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  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  $\text{HNO}_3$ , to avoid precipitation of  $\text{Al}(\text{OH})_3$ . 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  $1000^\circ\text{C}$ . nearly all of the  $\text{H}_2\text{O}$  was removed and the index of refraction corresponded to the index of glass prepared by anhydrous fusion (Schairer and Bowen, 1955, Fig. 5).

The  $\text{KNO}_3$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  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  $\text{Na}_2\text{O}$ . 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  $\text{Na}_2\text{O}$ . No  $\text{K}_2\text{O}$  was detected by either method.

A "gel" of composition  $\text{KAlSi}_3\text{O}_8$  was analyzed by M. K. Carron of the U. S. Geological Survey for all major constituents except alkalis, 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  $\text{KAlSi}_3\text{O}_8$  contains 16.9 weight per cent<sup>1</sup>  $\text{K}_2\text{O}$ , 18.3 per cent  $\text{Al}_2\text{O}_3$ , and 64.8 per cent  $\text{SiO}_2$ . The  $\text{K}_2\text{O} + \text{Al}_2\text{O}_3 + \text{SiO}_2$  in the analysis recalculated to 100 per cent gives 16.8  $\text{K}_2\text{O}$ , 18.3  $\text{Al}_2\text{O}_3$ , 64.9  $\text{SiO}_2$ , demonstrating the efficacy of the method. The impurities are

<sup>1</sup> Weight per cent is used throughout this paper unless stated otherwise.

TABLE 1. CHEMICAL ANALYSIS OF  $KAlSi_3O_8$  "GEL" THAT HAD BEEN HEATED IN AIR AT 700° C.

	Per cent by weight
SiO <sub>2</sub>	61.02
Al <sub>2</sub> O <sub>3</sub>	17.19
Fe <sub>2</sub> O <sub>3</sub>	.10
CaO	.13
MgO	.05
K <sub>2</sub> O	15.8
Na <sub>2</sub> O	.17
H <sub>2</sub> O <sup>1</sup>	5.06
	99.52

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

<sup>1</sup> 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<sub>2</sub>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<sub>2</sub>O, 7.0 Al<sub>2</sub>O<sub>3</sub>, 83.7 SiO<sub>2</sub> was 9.5 K<sub>2</sub>O, 7.1 Al<sub>2</sub>O<sub>3</sub>, and 83.4 SiO<sub>2</sub>. The method used in the present work gives at least as good compositional control. The amount of Na<sub>2</sub>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<sub>2</sub>O<sub>3</sub> are not stated.

#### EXPERIMENTAL METHOD

All data were obtained using cold seal bombs. Pressure was externally controlled using H<sub>2</sub>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  $\pm 5^\circ$  C. Temper-

ature was controlled automatically by motor driven variable transformers.

*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  $\pm 500$  psi. Pressure was not maintained automatically and therefore each bomb was equilibrated with the system, at the appropriate 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<sub>2</sub>O). The tubes were weighed before and after welding to check that no H<sub>2</sub>O was lost during the welding. After each run the tube was again weighed. Most runs checked within  $\pm 0.1$  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 starting material. Thus, portions of the "gels" were hydrothermally crystallized 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<sub>2</sub>O 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<sub>2</sub>O (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<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub>O CONTENT OF QUENCHED GLASS

Run	Composi- tion (Per cent Or) <sup>1</sup>	Pressure (bars)	Tempera- ture (°C)	Time (hrs.)	Starting material	Products <sup>2</sup>	Density (g/cc)	Index of refrac- tion <sup>3</sup> (± 0.002)	H <sub>2</sub> O (Wt. per cent)
192	50	500	890	160	gel <sup>4</sup>	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) <sup>5</sup>
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) <sup>5</sup>
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) <sup>5</sup>
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

<sup>1</sup> Composition is expressed in weight per cent KAlSi<sub>3</sub>O<sub>8</sub> on an anhydrous basis.

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

<sup>3</sup> These values represent averages of measurements on glasses from two or more different runs.

<sup>4</sup> Finely ground "gel" heated in air at 1000° C.

<sup>5</sup> 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<sub>3</sub>O<sub>8</sub>-SiO<sub>2</sub>-H<sub>2</sub>O by Tuttle and Bowen (1958) indicated that at 500, 1000 and 2000 kg/cm<sup>2</sup> H<sub>2</sub>O pressure the isobaric four-phase point, sanidine-quartz-liquid-gas, lies at a composition between 50 and 60 per cent KAlSi<sub>3</sub>O<sub>8</sub>. 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<sub>3</sub>O<sub>8</sub> 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<sub>2</sub>O, 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  $\beta$ -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<sub>2</sub>O-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<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>). 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<sub>2</sub>O 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  $\pm 0.002$ . 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<sub>3</sub>O<sub>8</sub>/SiO<sub>2</sub> ratio and H<sub>2</sub>O, 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<sub>2</sub>O 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<sub>2</sub>O content and index of refraction are given in Table 3. The approximate H<sub>2</sub>O contents given in the abstract represent averages for each set of determinations at each pressure.

The H<sub>2</sub>O content of the quenched liquids (glasses) is thought to represent the content in the liquid in equilibrium with the H<sub>2</sub>O-rich gas phase under the conditions of the run. Exsolution of appreciable H<sub>2</sub>O from the glass slug during the quench is considered unlikely because quenching is carried out isobarically.

The H<sub>2</sub>O 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<sub>2</sub>O in bubbles represents trapped gas, crushing results in a smaller positive error in the determination by freeing some of this H<sub>2</sub>O 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<sub>2</sub>O. 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<sub>2</sub>O 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<sub>2</sub>O determination.

The temperatures at which the glasses were formed were generally several tens of degrees above the liquidus. Thus the measured H<sub>2</sub>O 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<sub>2</sub>O content of changing the weight ratio of



TABLE 3. EXPERIMENTS USED TO DEFINE THE UNIVARIANT CURVE  
SANIDINE-QUARTZ-LIQUID-GAS<sup>1</sup>

Runs	Composition Per cent Or <sup>2</sup>	Starting Material <sup>3</sup>	T (°C.)	Time (hrs)	Products <sup>3</sup>
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

<sup>1</sup> In all of these experiments a gas phase was present which consisted of H<sub>2</sub>O saturated with the silicate components.

<sup>2</sup> Composition is expressed in weight per cent KAlSi<sub>3</sub>O<sub>8</sub> on an anhydrous basis.

<sup>3</sup> 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 <sup>2</sup>	Starting Material <sup>3</sup>	T (°C.)	Time (hrs)	Products <sup>3</sup>
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

$\text{KAlSi}_3\text{O}_8:\text{SiO}_2$  from 50:50 to 60:40 is too small to be reflected in the  $\text{H}_2\text{O}$  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

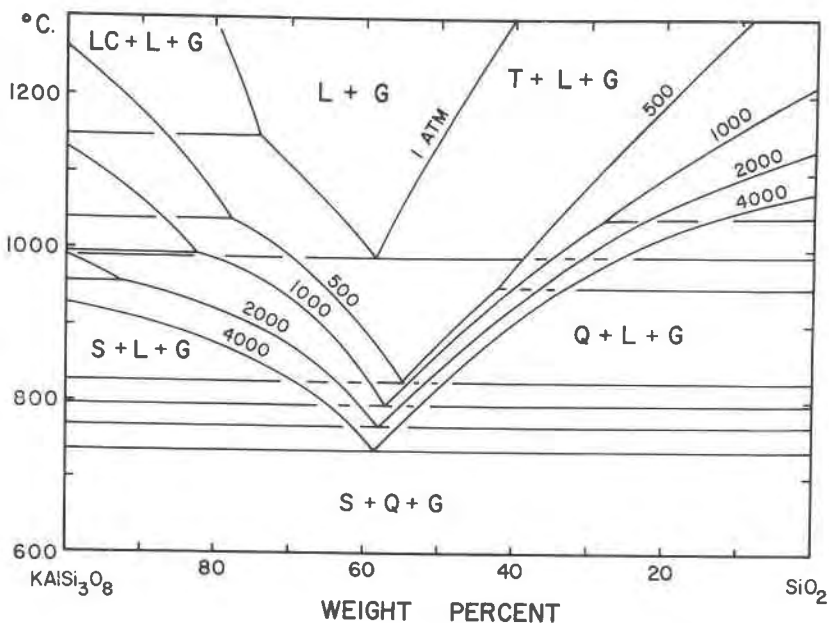


FIG. 1. Projections of the saturated liquidus at 500, 1000, 2000 and 4000 bars in the system  $\text{KAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$  to the join  $\text{KAlSi}_3\text{O}_8\text{-SiO}_2$ . S= sanidine, LC=luecite, Q= quartz, T= tridymite, L= liquid, and G= gas. Data at 1 atm were taken from Schairer and Bowen (1955). Data for  $\text{KAlSi}_3\text{O}_8\text{-H}_2\text{O}$  were taken from Goranson (1938), and for  $\text{SiO}_2\text{-H}_2\text{O}$  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  $\text{KAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$  in which condensed phases coexist with an  $\text{H}_2\text{O}$ -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  $\text{H}_2\text{O}$  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  $820^\circ$  and  $830^\circ$  C. The position is believed to lie at a little less than  $\text{Or}_{55}$  (55 per cent  $\text{KAlSi}_3\text{O}_8$ )<sup>1</sup> but cannot be stated with assurance closer than  $54 \pm 2$  per cent  $\text{KAlSi}_3\text{O}_8$ . The four-phase

<sup>1</sup> The symbol Or is used for the component  $\text{KAlSi}_3\text{O}_8$  and its percentage in the sum of the components  $\text{SiO}_2 + \text{KAlSi}_3\text{O}_8$  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  $\text{H}_2\text{O}$  in the liquid.

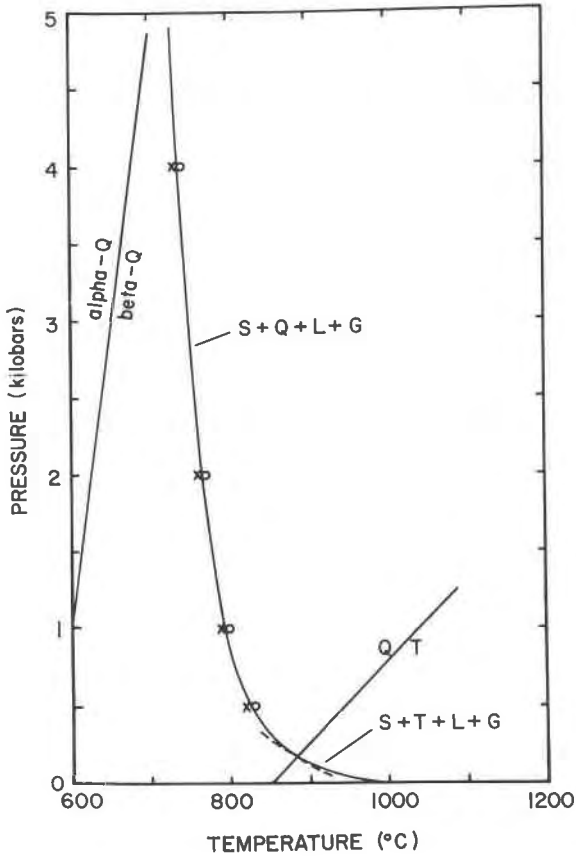


FIG. 2. P-T projections of the univariant curves sanidine+quartz+liquid+gas and sanidine+tridymite+liquid+gas in the system  $\text{KAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$ . Crosses represent the presence of crystals only and circles the presence of liquid+crystals. The curve for the alpha-beta quartz inversion is after Yoder (1950) and for the quartz-tridymite transition is after Tuttle and England (1955).

point at 1000 bars lies between  $790^\circ$  and  $800^\circ$  C. and the composition is believed to be  $\text{Or}_{57\pm 1}$ . At 2000 bars the temperature of the four-phase point was bracketed between  $763^\circ$  and  $770^\circ$  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  $\text{Or}_{58\pm 1}$ . The temperature of the four-phase point at 4000 bars lies between  $730^\circ$  and  $740^\circ$  C. The saturated liquidus could be investigated only to about  $25^\circ$  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  $Or_{58.5\pm 1}$ .

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  $T=885^\circ$  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/cm<sup>2</sup> (~980 bars) and 500 kg/cm<sup>2</sup> (~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/cm<sup>2</sup> 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/cm<sup>2</sup> and above are very close to those given by this paper at comparable pressures.

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