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# Four-Phase Curve in the System $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$ between 1 and 10 Kilobars\*)

By *David B. Stewart* (Washington)\*\*)

With 8 figures in the text and 3 tables

## Abstract

The  $\text{CaAl}_2\text{Si}_2\text{O}_8(\text{An})\text{-SiO}_2(\text{Qz})$  system has a eutectic at  $\text{SiO}_2$  49.5 weight per cent (SCHAIRER and BOWEN, 1947); the ternary system  $\text{An-Qz-H}_2\text{O}$  projected from  $\text{H}_2\text{O}$  is also of eutectic type. Anorthite, quartz, liquid, and gas coexist under the following conditions:

$P_{\text{H}_2\text{O}} = P_{\text{total}}$ (bars)	Temperature °C	$\text{CaAl}_2\text{Si}_2\text{O}_8\text{:SiO}_2$	
		in liquid (weight per cent)	$\text{H}_2\text{O}$ in liquid (weight per cent)
1000	$1040 \pm 10$	32 : 68	?
2000	$922 \pm 3$	37 : 63	~ 6
5000	$815 \pm 5$	42 : 58	~10
10000	$757 \pm 7$	48 : 52	> 12

The  $\text{H}_2\text{O}$ -saturated  $\text{Qz-H}_2\text{O}$  liquidus lies at  $1130 \pm 5^\circ\text{C}$  at 2000 bars,  $1065 \pm 5^\circ\text{C}$  at 5000 bars, and  $1055 \pm 10^\circ\text{C}$  at 10,000 bars. The  $\text{H}_2\text{O}$ -saturated  $\text{An-H}_2\text{O}$  liquidus determined by YODER (1954) was confirmed to 5000 bars and extended to 10,000 bars at  $1110 \pm 10^\circ\text{C}$ . The unit-cell parameters are given for four samples of anorthite synthesized from various compositions, temperatures, and pressures but only small differences were found, the most significant being for the cell volume and inter-axial angle  $\alpha$ . An indexed powder-diffraction pattern is given for primitive anorthite.

Petrologic applications suggested include explanation of differentiation paths of magmas containing quartz and feldspar, a geobarometer for  $\text{H}_2\text{O}$  pressure, and explanation for resorbed quartz crystals in volcanic rocks.

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\*) Publication authorized by the Director, U.S. Geological Survey.

\*\*) U.S. Geological Survey, Washington, D. C. 20242.

## INTRODUCTION

Rocks consisting largely of quartz, plagioclase, and alkali feldspar are abundant, and the phase relations between silica and feldspar components have been the subject of intensive experimental study (TUTTLE and BOWEN, 1958; STEWART, 1957, 1958; YODER, STEWART, and SMITH, 1957; SHAW, 1963; LUTH, JAHNS, and TUTTLE, 1964; and by WINKLER and VON PLATEN, summarized by WINKLER, 1965, p. 178—199). This study of the system  $\text{CaAl}_2\text{Si}_2\text{O}_8$  (hereafter called An)- $\text{SiO}_2$  (called Qz)- $\text{H}_2\text{O}$  supplements these investigations, and is of interest because discussion of the phase relations of quartz and feldspars over a wide range of temperatures and pressures requires this information. The data are applicable strictly to few rocks because anorthite-quartz assemblages are very rare (BIRKELAND, 1958, p. 351—352), but they do offer further evidence of the nature of silicate-water systems over a wide range of pressures that can be combined with similar results by others (DOLIVO-DOBROVOL'SKIY, 1961; ORLOVA, 1964; KADIK and KHITAROV, 1963; KHITAROV, KADIK and LEBEDEV, 1963; SHAW, 1964).

Professor LAVES has contributed much to our knowledge of many of the complexities of the structures of plagioclase feldspars. His discussions of the polymorphism of  $\text{NaAlSi}_3\text{O}_8$  and  $\text{CaAl}_2\text{Si}_2\text{O}_8$  have stimulated the author to investigate these compounds further, and his contributions to the study of unmixing in peristerites and labradorites suggest many experiments. In the present paper the unit-cell parameters of anorthites synthesized under various conditions will be presented, as will an indexed powder diffraction pattern of anorthite supplementing the partial indexing of GOLDSMITH and LAVES (1956, p. 399) and BROWN (1960) p. 315). Reviews of the crystallographic complexities of anorthite are given by GAY (1962, p. 42—45) and MEGAW (1962, p. 121—124) for those unfamiliar with past research.

## EXPERIMENTAL METHODS

*Starting materials*

Glasses prepared by SCHAIRER and BOWEN (1947, p. 70—72) were used for starting materials. For some experiments the crystalline equivalents of these glasses were prepared either by anhydrous crystallization

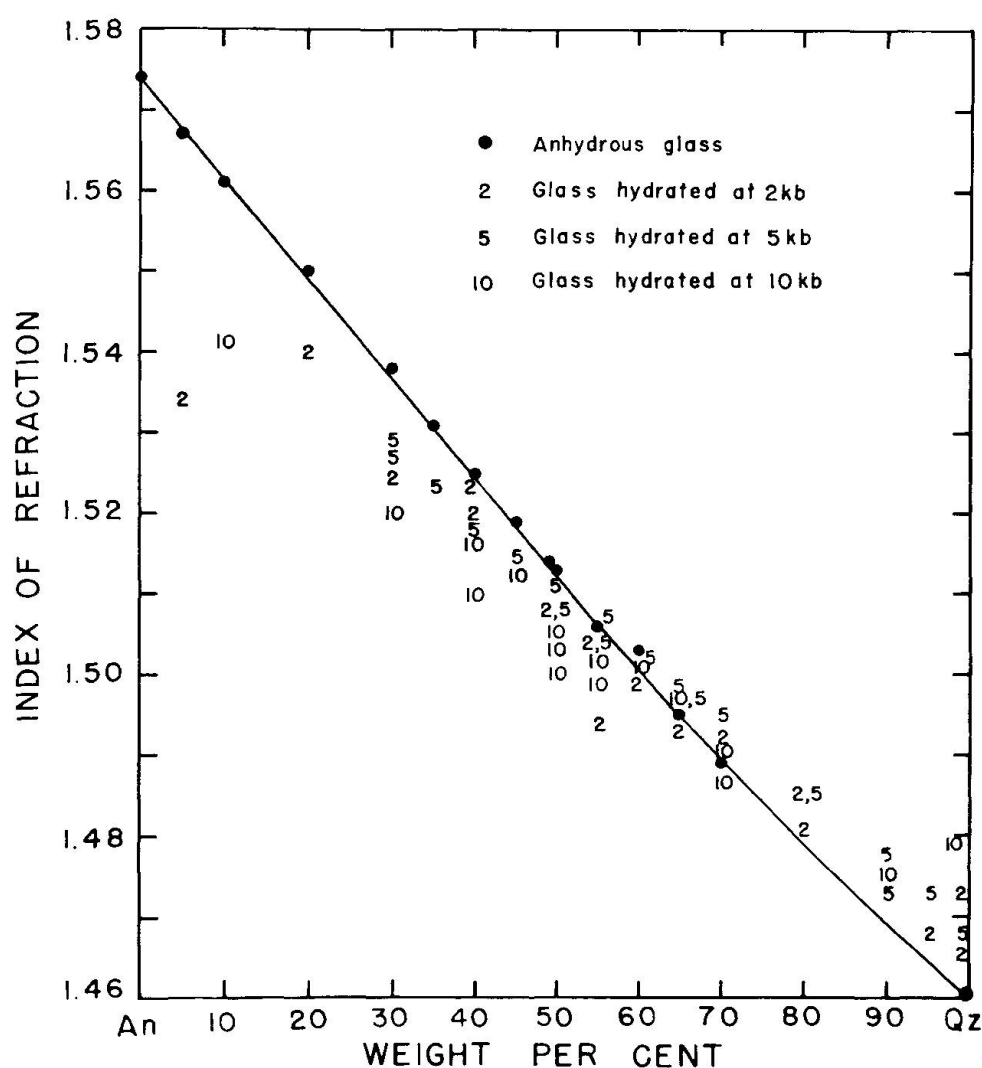


Fig. 1. Index of refraction of anhydrous glasses in the system An-Qz at room temperature, and of hydrous glasses quenched to room temperature at the pressures shown by the numbers. Data for glasses containing less than 5% crystals are plotted, but most samples contained less than 2% crystals and the small correction involved was not applied.

Hydrous An-rich glass has a lower index of refraction than the anhydrous composition, and Qz-rich hydrous glass has a higher index of refraction than its anhydrous equivalent. The effect is enhanced the higher the pressure during quenching. Other factors than the  $\text{H}_2\text{O}$  content of the glass may be responsible in part for the effect, such as pressure densification of the glass at constant  $\text{H}_2\text{O}$  content, or the presence of residual stresses in the initial anhydrous glass that affected its original index of refraction.



to anorthite and cristobalite by SCHAIRER and BOWEN or by hydrothermal crystallization to anorthite and quartz at 750—800°C at 2 kb for several hundred hours. Where necessary, new batches and additional compositions were prepared under the direction of J. F. Schairer. The index of refraction of each glass was measured with freshly calibrated oils in sodium light, and the results (Figure 1) plot as a curve at slightly lower values than previously reported by SCHAIRER and BOWEN (1947, Table 1).

Glass of  $\text{CaAl}_2\text{Si}_2\text{O}_8$  composition was very carefully prepared from  $\text{CaCO}_3$  (BAKER's lot 51735),  $\text{Al}_2\text{O}_3$  (T 61 grade), and  $\text{SiO}_2$  (Lisbon, Maryland, quartz inverted to cristobalite at 1500°C), and was crystallized at 1200°C for 12 hours. The index of refraction of the glass in sodium light was  $1.574 \pm 0.0005$  at 25°C. The melting point of this crystalline anorthite was determined with great care under J. F. Schairer's direction to be  $1551.0^\circ\text{C} \pm 1.5^\circ\text{C}$ ; the melting interval (first sintering to all glass) was 4°C. A Pt-Pt90Rh10 thermocouple calibrated against the melting point of diopside, 1391.5°C, and pseudowollastonite, 1544°C, was used, and a linear extrapolation was assumed.

Very pure quartz (0.03% residue on evaporation with HF and  $\text{H}_2\text{SO}_4$ ) from Lisbon, Maryland, and a silica glass prepared by C. N. Fenner were used as sources of silica.

In a few experiments finely ground mixtures of crystalline synthetic anorthite plus silica glass were used as starting materials.

A sample of lawsonite from Panoche Pass, California, supplied by W. G. Ernst was used for a few experiments at 10 kb.

### *Procedure*

The experiments were performed at the Geophysical Laboratory, Carnegie Institution of Washington, in internally heated high pressure apparatus designed by H. S. YODER, Jr. (1950). Samples were sealed in platinum tubes with  $\text{H}_2\text{O}$  present in excess of saturation requirements. The temperature given is the highest temperature measured during an experiment; the lowest temperature during an experiment was less than 15°C below the specified temperature of the experiment. Pressure oscillations resulting from temperature regulation normally were about 2% of the total pressure of the experiment. The total pressure was measured with calibrated gauges, and is accurate to within 1% of the stated pressure. Quenching to 500°C took place in 2 to 3 minutes following the shutting off of power to the furnace, and the samples were quenched isobarically by pumping during the quench.

## CRYSTALLINE PHASES

## Anorthite

Anorthite crystallized readily as euhedral crystals tabular on (010) (Figure 2) or as sub-parallel aggregates in experiments made in the presence of silicate liquid. Albite-twinning crystals were common, and occasionally twinning on other laws was observed. Experiments as short as one hour yielded crystals as large as those produced in the longest experiments, 45 hours. Liquids quenched from as much as  $75^\circ\text{C}$  above the anorthite plus liquid field yielded distinctive radiating fibrous aggregates of anorthite (Figure 3) formed during the quenching.

LAVES and GOLDSMITH (1955) and GOLDSMITH and LAVES (1956) have shown how strongly the polymorphism of anorthite as observed at room temperature is affected by the thermal history of the sample, and that the presence of lines with  $h+k$  even,  $l$  odd ("c-reflections") in the powder diffraction pattern indicates that the lattice is primitive with a  $c$  axis of  $\sim 14 \text{ \AA}$ . As observed at room temperature on x-ray photographs a weak  $\bar{1}\bar{1}1$  diffraction line appeared from anorthite synthesized from glass after as little as one hour under the temperature and pressure of the experiment, and this line was strong after as little as two hours under many experimental conditions. Geiger-counter diffractometer traces were only slightly less sensitive for detecting the  $\bar{1}\bar{1}1$  line. The qualitative data at hand are inadequate to ascertain any temperature dependence on the rate of development of the phenomenon responsible for the change. BROWN, HOFFMAN, and LAVES (1963) have shown that the "c-reflections" disappear continuously on heating between  $25^\circ\text{C}$  and  $350^\circ\text{C}$  in a sample of natural anorthite from Vesuvius and reappear on cooling, and BLOSS (1964) has indicated other rapidly reversible optical changes at higher temperatures. The presence or absence of c-reflections at  $25^\circ\text{C}$  apparently indicates the structural state the crystal attained both under the experimental conditions and during the cooling from these temperatures to room temperature. The presence of "c-reflections" in either synthetic or natural crystals therefore lacks significance as either a geothermometer or geobarometer.

LAVES and GOLDSMITH (1955, p. 233) noted "... no major change in lattice constants can be correlated with the various thermal states. Some small changes are observable, however, that can be correlated with the degree of diffuseness of the type (c) reflections ..." and on p. 234 they said "The size of the 'out-of-step' domains thus has a small but definite influence on the lattice constants". To investigate this problem further,

the unit-cell dimensions were determined for four anorthites synthesized under a variety of experimental conditions yielding  $\bar{1}\bar{1}1$  reflections varying in intensity from very weak to very distinct. (Sample ANS-26 has the weakest  $\bar{1}\bar{1}1$  reflection, and sample ANS-305 the most distinct.) The results are given in Table 1, together with other reported measurements for anorthite. Comparisons between data collected in different ways mean little, but comparisons of the changes shown by the natural and heated samples from Salem, India (with sharp and very diffuse "c-reflections", respectively), with the new data and with the sample from Monte Somma which has strong "c-reflections" all indicate that the primitive cell has a smaller volume, a distinctly smaller value of  $\alpha$ , possibly smaller values for  $a$  and  $c$ , and possibly larger value of  $\gamma$ . Only a few differences are apparent by inspection of the powder-diffraction patterns, the most notable being the larger separation of the  $\bar{2}42$  and  $\bar{2}\bar{4}\bar{2}$  reflections ( $0.37^\circ 2\theta$  CuK  $\alpha_1$  in ANS 305 with distinct "c-reflections", and  $0.30^\circ$  in ANS-26 with very weak "c-reflections"), and smaller separation of  $\bar{1}34$  and  $\bar{1}\bar{3}4$  in ANS 305 ( $1.81^\circ$  vs.  $1.86^\circ$ ). Anorthite produced in the presence of excess silica was indistinguishable from that formed from pure An glass. An indexed x-ray powder-diffraction pattern of primitive anorthite obtained by least-squares methods using the latest version of the EVANS, APPLEMAN, and HANDWERKER (1963) computer program (D. E. APPLEMAN, written communication, 1966) is given in Table 2. Nine distinctive "c-reflections" were observed in this pattern, which was

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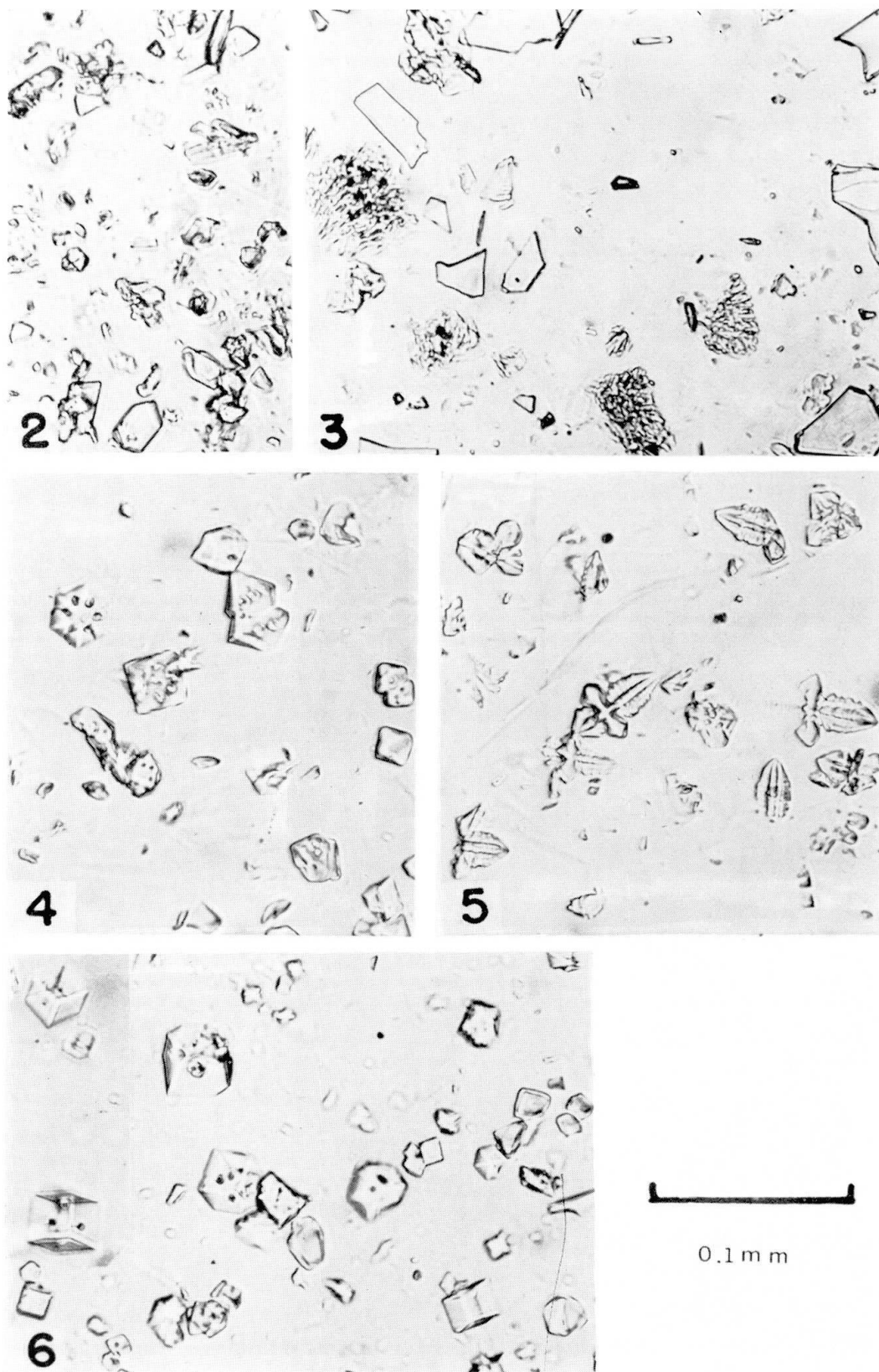
Fig. 2. Anorthite crystals with the tabular habit commonly found in experiments near the liquidus. Starting material  $An_{50}Qz_{50}$  glass, 10 kb,  $765^\circ\text{C}$ , 4 hours, run ANS-348. Glass nearly matching the index of refraction of the oil is present in this photomicrograph and in Figures 3 to 6.

Fig. 3. Radiating, fibrous aggregates of anorthite, formed on quenching, and plates of " $\beta$ -alumina", believed to have been present during the experiment. Starting material  $An_{90}Qz_{10}$  glass, 10 kb,  $1100^\circ\text{C}$ , 2 hours, run ANS-315.

Fig. 4. Hexagonal dipyrarnidal crystals of quartz with six-fold layers of fluid inclusions, interpreted to have been  $\beta$ -quartz under experimental conditions. Starting material  $An_{30}Qz_{70}$  glass, 2 kb,  $975^\circ\text{C}$ , 22 hours, run ANS-37.

Fig. 5. Crystals of quartz showing the rapid axial growth that results in the entrapment of fluid inclusions. Sample interpreted to have been hexagonal under experimental conditions because of six-fold symmetry. Starting material  $An_{30}Qz_{70}$  glass, 2 kb,  $925^\circ\text{C}$ , 2 hours, run ANS-9.

Fig. 6. Composite photomicrograph of quartz crystals with  $\alpha$ -quartz morphology and three-fold layers of fluid inclusions. Starting material  $An_{40}Qz_{60}$  glass, 10 kb,  $765^\circ\text{C}$ , 4 hours, run ANS-351.



obtained with a diffractometer equipped with a pulse height analyser for  $\text{CuK}\alpha$  radiation. The lines at  $d \sim 3.74$  and  $\sim 2.49$  Å reported by LAVES and GOLDSMITH (1955, p. 233) to show spacing changes with variation in intensity of "c-reflections" seem to involve splitting of overlapping "a-reflections".

#### Silica polymorphs

Quartz most commonly formed sharp hexagonal dipyrramids typical of  $\beta$ -quartz (Figure 4), though it all transformed to  $\alpha$ -quartz on cooling. Many of these crystals contained inclusions arranged in two layers of six inclusions, one layer located above the girdle of the crystal and the other below it, with the inclusions in crystallographic register with each other. Such inclusions are entrapped by rapid initial growth along the axial directions (Figure 5). In some experiments at 10 kb the quartz plus liquid field occurs at temperatures below  $815^\circ\text{C}$  so that  $\alpha$ -quartz is stable on the liquidus (YODER, 1950), and rhombohedral crystals of quartz grew with two layers of inclusions with the three inclusions in each layer displaced  $60^\circ$  relative to the other layer (Figure 6).

No evidence was obtained for solid solution in the quartz.

The products of some experiments at 1 kb contained tridymite and cristobalite. Most cristobalite originated from crystalline starting materials and all presumably was metastable. Tridymite occurred at  $1040^\circ\text{C}$  and quartz was obtained abundantly at  $1025^\circ\text{C}$ , thus confirming the temperature of  $1040^\circ\text{C}$  of the quartz-tridymite transition reported for 1 kb by TUTTLE and BOWEN (1958, p. 30).

#### Other phases

An-rich compositions held near the liquidus at high pressures contained from traces to 10% of thin hexagonal plates of " $\beta$ -alumina" of unknown composition (Figure 3). The " $\beta$ -alumina" arose from the incongruent solubility of anorthite in the gas, which was enriched in silica. The effect was pressure sensitive, being extensive at 10 kb, much less so at 5 kb, and not observable at lower pressures, in parallel with the decreased solubility in the gas at low pressures. On quenching, the gas condensed to liquid water and hydrous silicate glass balls, which represented the dissolved solids.

The surfaces of charges of silica-rich compositions ( $\text{An}_{45}\text{Qz}_{55}$ - $\text{An}_{30}\text{Qz}_{70}$ ) in many cases showed isolated clots of small euhedral bladed crystals deposited from the gas during the quench interval. The crystals were biaxial (+), with moderate  $2V$ ,  $\alpha \sim 1.493$ ,  $\gamma \sim 1.51$ , and an extinction



angle of  $38^\circ$ . The amount was always insufficient to be detected by x-ray examination by routine methods. The mineral was not identified, but presumably was a zeolite.

#### HYDROUS GLASSES

In many experiments the hydrous silicate liquid quenched to bubble-free hydrous glass on which the index of refraction, specific gravity, and  $\text{H}_2\text{O}$  content were measured. Such data are potentially useful in evaluating the structure of the melts and the role of  $\text{H}_2\text{O}$  in them, and will be discussed elsewhere. The trends of the variation of index of refraction with  $\text{H}_2\text{O}$  content are shown in Figure 1. Some of these data are given in Table 3, along with the  $\text{H}_2\text{O}$  content determined by the weight loss of glass slugs after drying to constant weight at  $110^\circ\text{C}$  and then slowly heating to  $1200^\circ\text{C}$ .

Hydrous liquids produced at 5 kb and below can be quenched without loss of  $\text{H}_2\text{O}$ , and their  $\text{H}_2\text{O}$  content can be found by the weight loss technique, but the hydrous liquids produced at 10 kb cannot be quenched without loss of  $\text{H}_2\text{O}$  from the liquid. The system  $\text{SiO}_2\text{-H}_2\text{O}$  at 10 kb as studied by the author by a static equilibrium method yields hydrous silicate liquid containing 22%  $\text{H}_2\text{O}$  by weight at  $1055^\circ\text{C}$ . The following observations by my colleague EDWIN ROEDDER (written communication, 1963) on fluid inclusions in  $\alpha$ -quartz synthesized at 10 kb (Figure 6) (sample ANS 351,  $\text{An}_{40}\text{Qz}_{60}$  glass = 78.63%,  $\text{H}_2\text{O}$  = 21.37%,  $765^\circ\text{C}$ , 4 hours) indicate that the hydrous silicate liquid near the four-phase point at 10 kb contains more  $\text{H}_2\text{O}$  than the  $\sim 12\%$  found in the quenched glasses. During growth the quartz crystal engulfed a portion of hydrous silicate liquid, and subsequently the quartz served as an impermeable container. The inclusions now consist of rounded bodies of hydrous silicate glass and a spherical drop of water with a bubble of gas. Under the conditions of formation the liquid that was trapped was homogeneous and in equilibrium with quartz and gas, but during quenching has become heterogeneous principally by exsolution of  $\text{H}_2\text{O}$ , probably initially in the form of gas. The gas has later condensed to hydrous liquid plus water vapor. Measured at 1250 X with a micrometer ocular, two such inclusions were found to contain 7.9, 6.2% water by volume, and 0.5, 0.3% vapor. Assuming that the hydrous silicate glass has properties similar to those produced by quenching other samples of the same composition, the volumetric relations observed in the inclusions indicate that the initial homogeneous liquid contained 14.6, 15.3%  $\text{H}_2\text{O}$  by weight. The accuracy

of the measurements is less than the precision of the two measurements reported. Optical measurements on such small objects with spherical shapes are very difficult, and the errors caused by the negative lenses of the spherical objects normally tend toward significant underestimation of the size of the water drop in the spherical glass inclusion. It is uncertain if the  $\text{H}_2\text{O}$  content of the original liquid in the sample studied ever was as high as the  $\text{H}_2\text{O}$  content of the charge, but it was higher than is now found in liquids free to exsolve  $\text{H}_2\text{O}$  in the capsule during quenching. The figure obtained by weight loss methods thus sets a lower limit on the  $\text{H}_2\text{O}$  content.

Under isobaric conditions the  $\text{H}_2\text{O}$  content of a  $\text{H}_2\text{O}$ -saturated liquid of fixed An : Qz ratio decreases as the temperature is raised. The  $\text{H}_2\text{O}$  content may vary isothermally with variation of the An : Qz ratio, decreasing as the content of An increases. In such a case the effects are probably not greater than the uncertainty of the individual measurements, about 10% of the amount of  $\text{H}_2\text{O}$  reported at that pressure.

The hydrous An-rich melts have such low viscosity that anorthite crystals settled 2 to 3 mm in times averaging a few hours; anorthite settling was observed in compositions richer in Qz as the  $\text{H}_2\text{O}$  pressure increased. No evidence was seen of settling of quartz.

## PHASE RELATIONS

### System An- $\text{H}_2\text{O}$

The  $\text{H}_2\text{O}$ -saturated An- $\text{H}_2\text{O}$  liquidus was reported by YODER (1954, p. 107; oral communication, 1957) to be  $1343 \pm 5^\circ\text{C}$  at 2 kb, and  $1235 \pm 5^\circ\text{C}$  at 5 kb. These points are consistent with the data given in Table 3, and the liquidus at 10 kb is shown to lie at  $1110 \pm 10^\circ\text{C}$ . This point has also been determined as  $1115 \pm 5^\circ\text{C}$  by YODER (1965, p. 85—88). The presence of  $\beta$ -alumina has been ignored in interpreting the liquidus relations, and the solubility in the gas has not been determined.

Under some conditions of temperature and pressure anorthite reacts with gas to form hydrous phases (zeolites), assemblages including one or more phases with aluminum in six-fold coordination (grossularite, corundum, aluminosilicates) and free silica, or to hydrous phases that contain aluminum in six-fold coordination (lawsonite, zoisite, pumpellyite, prehnite) (P. LE COMTE, written communication, 1959; D. H. LINDSLEY, oral communication, 1963; NEWTON and KENNEDY, 1963; CRAWFORD and FYFE, 1965; and NEWTON, 1966). None of these phases or assem-

blages were synthesized stably in the present research, and none would be expected in the pressure-temperature range studied on the basis of all information available to the author to date. The natural lawsonite held at 10 kb decomposed at 940°C and 750°C to clinozoisite, epidote, and gas, and the clinozoisite was in turn decomposing to anorthite when the experiments were terminated. It was concluded that anorthite was the stable calcium-bearing silicate at the  $\text{H}_2\text{O}$ -saturated liquidus throughout this investigation.

#### System Qz- $\text{H}_2\text{O}$

The  $\text{H}_2\text{O}$ -saturated Qz- $\text{H}_2\text{O}$  liquidus has been studied by TUTTLE and ENGLAND (1955), OSTROVSKIY, MISHINA, and POVILAITIS (1959), KENNEDY, WASSERBURG, HEARD, and NEWTON (1962) and STEWART (unpublished data). There is general agreement that the  $\text{H}_2\text{O}$ -saturated liquidus at 2 kb is  $1130 \pm 5^\circ\text{C}$ . This liquidus at 5 kb is  $1065 \pm 5^\circ\text{C}$  and at 10 kb is  $1055 \pm 5^\circ\text{C}$  according to the present work; OSTROVSKIY and others (1959) and KENNEDY and others (1962) report temperatures  $15^\circ$  to  $25^\circ\text{C}$  higher at 5 kb, which seem incompatible with data of Table 3 for the  $\text{H}_2\text{O}$ -saturated liquidus for quartz in the system Qz-An- $\text{H}_2\text{O}$ . KENNEDY and others (1962) claim the upper critical end point lies at  $1080^\circ\text{C}$  and 9.7 kb; the results of the author based on the distribution of stable phase assemblages on an isobaric T-X section indicate that the liquid on the three-phase curve at 10 kb contains  $22 \pm 2\%$   $\text{H}_2\text{O}$ , and the gas contains  $38 \pm 2.0\%$  Qz. These results indicate that the upper critical end point lies at some pressure higher than 10 kb, and probably at a temperature lower than  $1055^\circ\text{C}$ , although it is possible for the temperature to be either lower or higher with increasing pressure (KADIK and KHITAROV, 1963).

The steep slope of the univariant curve representing stable assemblages of  $\beta$ -quartz + liquid + gas in the  $\text{H}_2\text{O}$ -saturated Qz- $\text{H}_2\text{O}$  system (see Figure 7) is probably caused by a change in the structure of the hydrous melt. On a plot of density against index of refraction such glasses plot on the line between quartz and water. A similarity of the structures of quartz and the melt could account for the observed slope.

#### System An-Qz- $\text{H}_2\text{O}$

The data of Table 3 locate the saturated liquidus at several pressures. The ternary system projected from the  $\text{H}_2\text{O}$  apex to the An-Qz sideline yields a diagram of eutectic type (Figure 8). Gas coexists with the phases



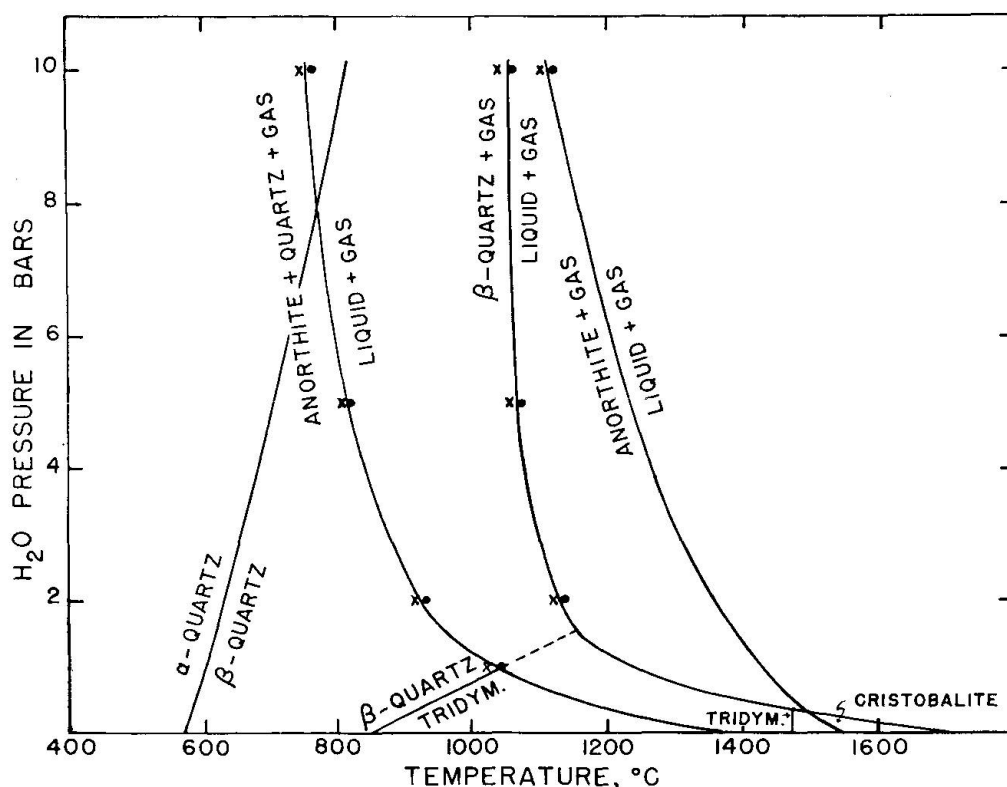


Fig. 7. P-T projection of the  $\text{H}_2\text{O}$ -saturated liquidus in the systems Qz- $\text{H}_2\text{O}$ , An- $\text{H}_2\text{O}$ , and An-Qz- $\text{H}_2\text{O}$ . The curve for the  $\alpha$ - $\beta$  quartz inversion is from YODER (1950) and for the quartz-tridymite transition from TUTTLE and BOWEN (1958); An- $\text{H}_2\text{O}$  liquidus at 2 and 5 kb is from YODER (1954; oral communication, 1957).

Dots represent liquid plus gas, and crosses represent crystals plus gas.

shown on the diagram, and only the An : Qz ratios of the liquids are shown. The amount of  $\text{H}_2\text{O}$  contained in the glasses (liquids) are shown in Table 3 where known. Four phases coexist at the "eutectic": anorthite, a silica polymorph, hydrous silicate liquid, and gas. The composition of the liquid at the four phase point varies with pressure, as does the temperature of the point:

$P_{\text{H}_2\text{O}} = P_{\text{total}}$ (bars)	Temperature °C	$\text{CaAl}_2\text{Si}_2\text{O}_8 : \text{SiO}_2$	
		in liquid (weight per cent)	$\text{H}_2\text{O}$ in liquid (weight per cent)
1000	$1040 \pm 10$	32 : 68	?
2000	$922 \pm 3$	37 : 63	$\sim 6$
5000	$815 \pm 5$	42 : 58	$\sim 10$
10000	$575 \pm 7$	48 : 52	$> 12$

The relations are also summarized graphically in Figure 8. The lowering of liquidus temperatures with increasing  $\text{H}_2\text{O}$  pressure is common to all

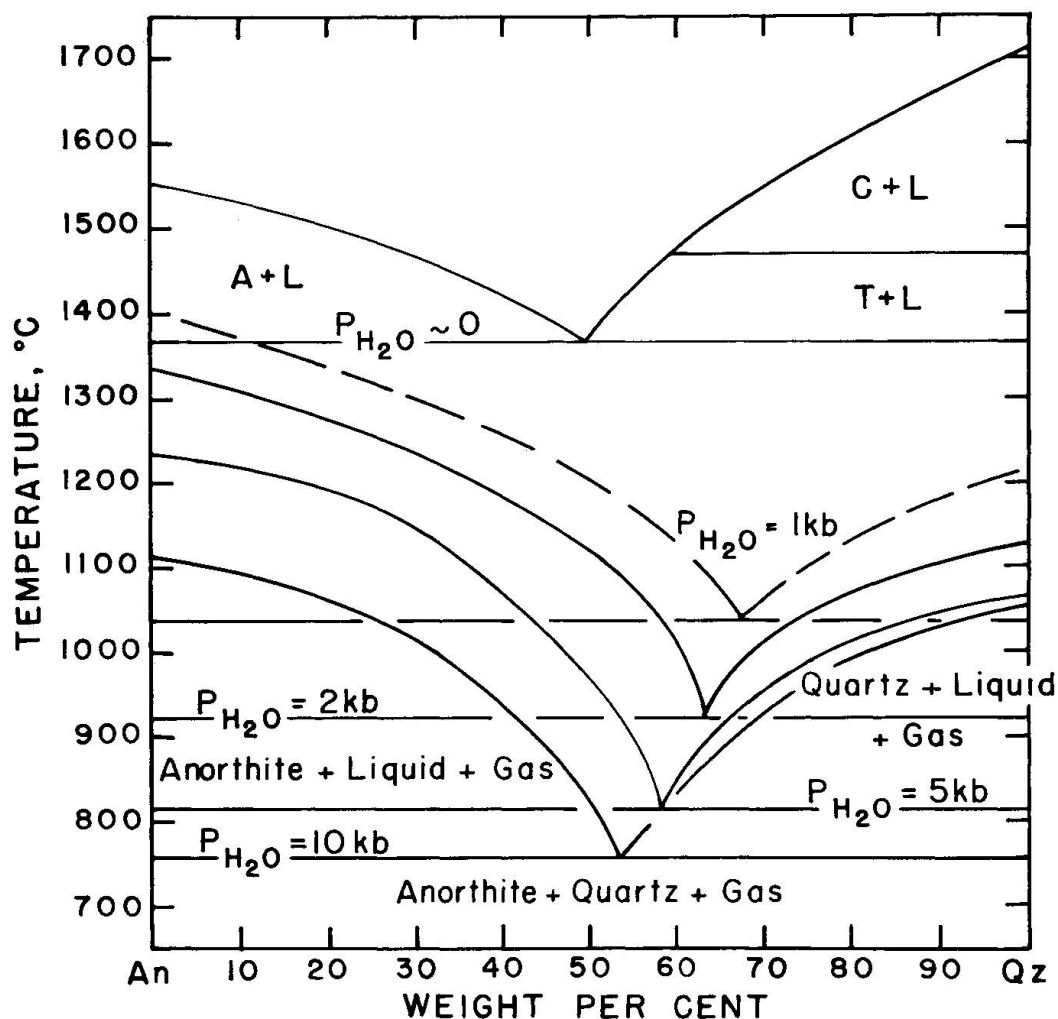


Fig. 8. Projections of the liquidus for  $\text{H}_2\text{O}$ -saturated melts at 1, 2, 5, and 10 kb in the system An-Qz- $\text{H}_2\text{O}$  to the join An-Qz. A = anorthite, C = cristobalite, L = liquid, T = tridymite. Data for the anhydrous join were taken SCHAIRER and BOWEN (1947). The silica polymorph stable on the liquidus at 1 kb is tridymite; the four-phase point on this projection is experimentally indistinguishable from the invariant point quartz-tridymite-anorthite-liquid-gas, and quartz is the stable phase of silica at temperatures below this four-phase point. At higher pressures, quartz is the stable silica phase at all temperatures studied.

feldspar-silica systems, as is the variation with rising  $\text{H}_2\text{O}$  pressure of the feldspar-silica ratio in the liquid toward lower feldspar-silica ratios while cristobalite and tridymite are stable on the liquidus, and toward higher feldspar-silica ratios when quartz is stable at liquidus temperatures. The effect is more pronounced in the An-Qz- $\text{H}_2\text{O}$  system than in the other feldspar-silica systems because the temperatures in the anhy-

drous binary system are high and cristobalite and tridymite occur over a long temperature interval.

The temperature of the invariant point quartz + tridymite + anorthite + liquid + gas can be estimated from a P-T projection (Figure 7) of the four-phase univariant curve and the quartz-tridymite univariant curve (TUTTLE and BOWEN, 1958) to be 1040°C, at a pressure of 1 kb, indistinguishable from the values of the four-phase point tridymite + anorthite + liquid + gas.

#### PETROLOGIC APPLICATIONS

The boundary surface in the quinary system Or-Ab-An-Qz-H<sub>2</sub>O at constant pressure along which liquids crystallize to quartz and feldspar (or feldspars) is of great petrologic interest, for the composition of the liquid once on this surface cannot leave it under equilibrium conditions. It follows that the differentiation paths of many magmas proceed away from the primary phase (commonly a plagioclase) toward the boundary surface, and on reaching it, change course to stay on the surface. One example of an application of these relationships is given by BATEMAN and others (1963, p. D 33-D 38). A reverse course would be obtained on partial melting of pre-existing rocks.

The ratio of feldspar to quartz forming from the liquid when it reaches the boundary surface has been shown by TUTTLE and BOWEN (1958), SHAW (1963), and LUTH, JAHNS, and TUTTLE (1964), and this study to be sensitive to H<sub>2</sub>O pressure. STEWART (1957) suggested this variation as the basis for a geologic barometer, and attempted an application to zones in granitic pegmatites. Another application to the problem of the depth of differentiation of rhyolitic magma was made by WHITE, THOMPSON, and SANDBERG (1964, p. B 38-B 39).

Another application of these relationships concerns an explanation for the resorption of phenocrysts in lavas, most commonly quartz phenocrysts, but sometimes feldspar phenocrysts instead. Rarely are both kinds of phenocrysts attacked. This problem is not at all as enigmatic as described by FOSTER (1960).

The basic premise of the argument is that the phenocrysts of most lavas form by growth deep within a magma chamber, and not during or following extrusion. Once feldspar and a silica polymorph have begun to crystallize (the liquid has reached the boundary surface), any process that results in movement of the boundary surface necessitates a change

in the composition of the liquid in equilibrium with the quartz and feldspar phenocrysts. The liquid changes composition by dissolving one of the phenocrysts. The phase resorbed during small deviations from equilibrium will be the phase toward which the boundary surface moves. The explanation sought thus involves consideration of what processes can move the boundary surface toward quartz. It is a characteristic of the feldspar-silica system that the boundary surface moves toward Qz as the  $\text{H}_2\text{O}$  pressure is increased from below one bar to a maximum of 1 kb. However, the stable silica phase crystallizing under such conditions is tridymite, rarely found as phenocrysts. At higher pressures where quartz is stable on the liquidus the boundary surface moves toward feldspar with increasing pressure. A sudden drastic reduction in the  $\text{H}_2\text{O}$  pressure such as might accompany the early stage of an eruption would normally result in a change in the position of the boundary surface toward Qz and in disequilibrium in the composition of the liquid. If the silica polymorph crystallizing with feldspar was tridymite, decrease in  $\text{H}_2\text{O}$  pressure would result in resorption of feldspar in all compositions except those on the feldspar side of the new four-phase point at the reduced pressure. In the usual geologic case where quartz is the stable silica polymorph, partial decrease in pressure would enlarge the feldspar plus liquid field and result in the resorption of quartz crystals in compositions except those on the silica side of the new four-phase point. When equilibrium was reestablished normal growth of all phases would continue, and the appearance of resorptions of inner zones followed by normal growth would be observed.

If the phenocrysts have always coexisted, the ratio of phenocrysts of feldspars to those of silica minerals can vary only from 2.0 to 0.5 under geologically reasonable variations of  $\text{H}_2\text{O}$  pressure ( $< 10$  kb). A ratio outside this range indicates that the more abundant mineral crystallized first. Judging from geologic evidence of the ratio of feldspar and silica phenocrysts, it is unusual when silica minerals crystallize first.

The system Ab ( $\text{NaAlSi}_3\text{O}_8$ )-An-Di ( $\text{CaMgSi}_2\text{O}_6$ ) is commonly used for teaching purposes as an example of a ternary system with one solid solution. However, there are complications introduced by solid solution in the pyroxene, and a more useful example is the tetrahedron with Ab, An, Qz, and  $\text{H}_2\text{O}$  as apices as projected from the  $\text{H}_2\text{O}$  apex onto the base of silicate components. The boundary curve between the plagioclase and silica polymorph fields can be readily sketched from the data for An-Qz- $\text{H}_2\text{O}$  given above and from data for Ab-Qz- $\text{H}_2\text{O}$  given in TUTTLE and BOWEN (1958, p. 50—53). The boundary curve between these points can

be readily estimated by analogy to the anhydrous Ab-An-Qz system given by SCHAIRER (1957, Figure 35). The resulting diagram is applicable to many rocks, and its interpretation involves the same principles as are involved in the system Ab-An-Di.

### Acknowledgments

The author wishes to thank J. F. Schairer for many of the starting materials used in this investigation, and for guidance in preparing others, W. G. Ernst for the sample of lawsonite, and Mrs. Daphne Ross and Mrs. Dora von Limbach, who gathered and measured some of the x-ray diffraction data used in this study. This investigation was performed with Dr. H. S. Yoder's apparatus, and the author is grateful to him for the privilege of using this equipment. E. Roedder kindly contributed data on the nature of the fluid inclusions. Reviews by E. Roedder, E. H. Roseboom Jr., H. S. Yoder, Jr., and J. J. Papike were very helpful.

Table 1. *Cell dimensions of anorthite*

a, Å	b, Å	c, Å	$\alpha$	$\beta$	$\gamma$	Volume Å <sup>3</sup>	
8.1768 0.0005	12.8768 0.0005	14.1690 0.0005	93° 10.0' 1.0'	115° 50.8' 1.0'	91° 13.3' 1.0'	1338.84	Monte Somma, Italy. COLE, SORUM, TAYLOR (1951)
8.16 <sub>15</sub>	12.87 <sub>79</sub>	14.16 <sub>70</sub>	93° 6.9'	115° 48'	91° 10.2'	1336.96	Salem, India. LAVES and GOLDSMITH (1955)
8.17 <sub>52</sub>	12.87 <sub>19</sub>	14.17 <sub>07</sub>	93° 14.8'	115° 46'	91° 14.1'	1339.06	Salem, India heated 1 hour at 1425°C. LAVES and GOLDSMITH (1955)
8.17	12.87	14.14	93° 16'	115° 48'	91° 16'	1334.6	"Synthetic". GOLDSMITH and LAVES (1955, p. 215)
8.18 <sub>15</sub> 0.0026	12.87 <sub>33</sub> 0.0024	14.17 <sub>76</sub> 0.0027	93° 12.4' 1.1'	115° 50.1' 1.4'	91° 8.2' 1.2'	1340.25 0.39	Hydrothermal synthesis from An 90 Qz 10 glass, 1300°C, 2 kb, 1 hour, ANS-26, 32 lines, $\sigma =$ 0.0166° 2 $\theta$
8.18 <sub>25</sub> 0.0022	12.87 <sub>16</sub> 0.0022	14.18 <sub>13</sub> 0.0025	93° 7.3' 1.2'	115° 53.3' 1.1'	91° 15.0' 1.1'	1340.02 0.33	From An 100 glass crys- tallized at 1200°C, 12 hours, then hydrother- mally at 1060°C, 10 kb, 2 hours, ANS-304, 33 lines, $\sigma = 0.0151^\circ 2 \theta$
8.17 <sub>37</sub> 0.0024	12.87 <sub>53</sub> 0.0025	14.16 <sub>74</sub> 0.0027	93° 6.2' 1.2'	115° 50.4' 1.1'	91° 18.3' 1.2'	1338.13 0.38	Hydrothermal synthesis from An 95 Qz 5 glass, 750°C, 10 kb, 3 hours, ANS-324, 28 lines, $\sigma =$ 0.0151° 2 $\theta$
8.17 <sub>93</sub> 0.0019	12.86 <sub>87</sub> 0.0020	14.17 <sub>38</sub> 0.0021	93° 6.9' 1.0'	115° 53.2' 0.9'	91° 14.1' 0.9'	1338.52 0.28	Hydrothermal synthesis from An 100 glass, 1060°C, 10 kb, 2 hours, ANS-305. See Table 2 for indexed pattern. 33 lines, $\sigma =$ 0.0130° 2 $\theta$

Table 2. *Indexed powder-diffraction pattern for primitive anorthite synthesized at 10 kb, 1060°C, 2 hours from  $\text{CaAl}_2\text{Si}_2\text{O}_8$  glass in the presence of steam*

Triclinic  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ;  $P\bar{1}$ ,  $a = 8.179 \pm 0.002$  Å,  $b = 12.869 \pm 0.002$ ,  $c = 14.174 \pm 0.002$ ,  $\alpha = 93^\circ 6.9' \pm 1.0'$ ,  $\beta = 115^\circ 53.2' \pm 0.9'$ ,  $\gamma = 91^\circ 14.1' \pm 0.9'$ , cell volume  $1338.5 \pm 0.3$  Å<sup>3</sup> as determined by least squares refinement of measured data italicized. No unique reflections with  $h+k$  odd and  $l$  even were observed, and all calculated reflections of this type have been omitted from the tabulated data.

$hkl$	Reflection type <sup>1)</sup>	Calculated <sup>2)</sup>		Measured <sup>3)</sup>	
		$d_{hkl}$ (Å)	$2\theta$ Cu K $\alpha_1$	$2\theta$ K $\alpha_1$	$I_0/I_{100}$
001	c	12.720	6.943		
0 $\bar{1}$ 1	b	9.372	9.428		
011	b	8.730	10.124		
$\bar{1}$ 01	b	8.081	10.939		
$\bar{1}$ 11	c	6.870	12.874	12.850	2
$\bar{1}\bar{1}$ 1	c	6.806	12.996	12.960	4
$\bar{1}$ 10	a	6.521	13.567	13.542	10
020	a	6.417	13.789	13.770	5
002	a	6.360	13.912		
110	a	6.244	14.173		
0 $\bar{2}$ 1	c	5.899	15.005	15.000	3
$\bar{1}$ 12	a	5.785	15.302		
$\bar{1}\bar{1}$ 2	a	5.660	15.643		
021	c	5.572	15.890	15.870	1
101	b	5.417	16.349		
$\bar{1}\bar{1}$ 1	c	5.116	17.320	17.310	3
$\bar{1}$ 21	b	5.051	17.544		
$\bar{1}\bar{2}$ 1	b	5.000	17.724	17.700	1
111	c	4.875	18.183		
0 $\bar{2}$ 2	a	4.686	18.921	18.914	25
103	b	4.663	19.017		
$\bar{1}\bar{1}$ 3	c	4.448	19.942		
022	a	4.365	20.327		
$\bar{1}\bar{1}$ 3	c	4.319	20.546		
$\bar{1}$ 21	b	4.284	20.716		
003	c	4.240	20.934	20.950	3
031	b	4.144	21.422		
0 $\bar{1}$ 3	b	4.114	21.584		
$\bar{2}$ 02	a	4.040	21.980	21.282	50
201	c	4.033	22.020		
121	b	4.008	22.158		
031	b	3.971	22.372		
013	b	3.943	22.527		
$\bar{1}\bar{1}$ 2	a	3.914	22.698	22.689	15
$\bar{2}$ 11	b	3.884	22.875		
$\bar{1}\bar{2}$ 3	b	3.857	23.038		
$\bar{2}$ 11	b	3.812	23.315		
$\bar{1}$ 31	c	3.797	23.408		

<sup>1)</sup> GOLDSMITH and LAVES (1956, p. 397).

<sup>2)</sup> Calculated spacings are shown for  $d \geq 2.500$  Å — calculated spacings less than 2.100 Å are listed only when they correspond to an indexed observed reflection.

<sup>3)</sup> Average of three observations with annealed  $\text{CaF}_2$  as internal standard,  $a = 5.4622$  Å at 25°C. Ni-filtered CuK  $\alpha_1$  radiation ( $\lambda = 1.54050$  Å). Lower limit of  $2\theta$  measured = 6° (14.72 Å). Pattern obtained at 25°C.

$hkl$	Reflection type <sup>1)</sup>	Calculated <sup>2)</sup>		Measured <sup>3)</sup>	
		$d_{hkl}$ (Å)	$2\theta$ Cu K $\alpha_1$	$2\theta$ K $\alpha_1$	$I_0/I_{100}$
$\overline{1}30$	a	3.781	23.510	23.512	45
$\overline{1}31$	c	3.765	23.613		
$\overline{1}12$	a	3.756	23.666	23.650	25
$\overline{1}23$	b	3.692	24.083		
$\overline{2}03$	c	3.691	24.089		
$\overline{2}00$	a	3.675	24.199		
$\overline{0}23$	c	3.659	24.307		
$\overline{1}30$	a	3.619	24.579	24.591	50
$\overline{1}32$	a	3.601	24.702		
$\overline{2}13$	b	3.558	25.006		
$\overline{2}13$	b	3.537	25.156		
$\overline{1}32$	a	3.511	25.346	25.290	5
$\overline{1}31$	c	3.473	25.628		
$\overline{2}21$	c	3.466	25.677		
$\overline{1}14$	a	3.460	25.728	25.723	25
$\overline{2}22$	a	3.435	25.914	25.890	3
$\overline{0}23$	c	3.427	25.974		
$\overline{2}22$	a	3.403	26.162	26.200	5
$\overline{2}21$	c	3.365	26.463		
$\overline{1}14$	a	3.364	26.472	26.475	45
$\overline{2}20$	a	3.280	27.330	27.336	70
$\overline{1}31$	c	3.252	27.398		
$\overline{1}33$	c	3.227	27.619		
$\overline{2}23$	c	3.215	27.724		
$\overline{0}40$	a	3.208	27.782	27.940	100
$\overline{2}04$	a	3.196	27.891		
$\overline{2}23$	c	3.184	27.996		
$\overline{0}04$	a	3.180	28.036		
$\overline{2}01$	c	3.178	28.051		
$\overline{0}41$	c	3.165	28.175		
$\overline{2}11$	b	3.130	28.491		
$\overline{1}03$	b	3.127	28.523		
$\overline{0}33$	b	3.124	28.547		
$\overline{2}20$	a	3.122	28.570	28.581	50
$\overline{1}13$	c	3.091	28.862		
$\overline{1}33$	c	3.082	28.942		
$\overline{0}41$	c	3.060	29.159		
$\overline{2}11$	b	3.042	29.337		
$\overline{1}32$	a	3.040	29.358	29.347	30
$\overline{1}41$	c	2.993	29.830		
$\overline{1}13$	c	2.988	29.881		
$\overline{2}31$	b	2.984	29.919		
$\overline{1}41$	b	2.971	30.048		
$\overline{0}42$	a	2.950	30.273	30.267	50
$\overline{0}24$	a	2.933	30.449	30.437	35
$\overline{2}21$	c	2.920	30.589	30.550	10
$\overline{0}33$	b	2.910	30.697		
$\overline{1}23$	b	2.896	30.848		
$\overline{2}24$	a	2.893	30.886	30.897	10
$\overline{2}31$	b	2.888	30.941		
$\overline{1}41$	b	2.846	31.407		
$\overline{2}24$	a	2.830	31.587	31.616	35
$\overline{1}32$	a	2.828	31.614		
$\overline{1}05$	b	2.816	31.751		
$\overline{2}33$	b	2.810	31.817		
$\overline{1}34$	a	2.803	31.904	31.910	10
$\overline{0}42$	a	2.786	32.097		

$hkl$	Reflection type <sup>1)</sup>	Calculated <sup>2)</sup>		Measured <sup>3)</sup>	
		$d_{hkl}$ (Å)	$2\theta$ Cu K $\alpha_1$	$2\theta$ K $\alpha_1$	$I_0/I_{100}$
$\overline{115}$	c	2.785	32.111		
$\overline{221}$	c	2.781	32.159		
$\overline{233}$	b	2.779	32.177		
$\overline{024}$	a	2.772	32.264		
$\overline{123}$	b	2.733	32.744		
$\overline{205}$	c	2.724	32.850	32.850	2
$\overline{115}$	c	2.717	32.939		
$\overline{202}$	a	2.708	33.043		
$\overline{143}$	b	2.702	33.130		
$\overline{303}$	b	2.694	33.231		
$\overline{215}$	b	2.686	33.332		
$\overline{141}$	b	2.682	33.374		
$\overline{312}$	a	2.676	33.459	33.460	2
$\overline{134}$	a	2.656	33.715	33.722	20
$\overline{043}$	b	2.650	33.790		
$\overline{312}$	a	2.648	33.820		
$\overline{215}$	b	2.644	33.873		
$\overline{313}$	c	2.642	33.904		
$\overline{125}$	b	2.636	33.974		
$\overline{313}$	c	2.631	34.050		
$\overline{231}$	b	2.629	34.067		
$\overline{301}$	b	2.629	34.071		
$\overline{133}$	c	2.618	34.222	34.20	3
$\overline{311}$	b	2.596	34.521		
$\overline{143}$	b	2.588	34.628		
$\overline{222}$	a	2.558	35.052	35.079	5
$\overline{311}$	c	2.556	35.078		
$\overline{241}$	c	2.552	35.134		
$\overline{051}$	b	2.551	35.145		
$\overline{005}$	c	2.544	35.249		
$\overline{225}$	c	2.543	35.264		
$\overline{015}$	b	2.530	35.453		
$\overline{114}$	a	2.528	35.478		
$\overline{242}$	a	2.525	35.517	35.509	25
$\overline{125}$	b	2.524	35.536		
$\overline{314}$	a	2.510	35.744		
$\overline{314}$	a	2.506	35.806		
$\overline{242}$	a	2.500	35.890	35.902	30
$\overline{222}$	a	2.437	36.846	36.850	5
$\overline{310}$	a	2.429	36.977	36.950	3
$\overline{152}$	a	2.405	37.363	37.360	3
$\overline{321}$	b	2.399	37.441	37.450	2
$\overline{150}$	a	2.386	37.667	37.679	3
$\overline{310}$	a	2.384	37.695		
$\overline{152}$	a	2.360	38.105	38.095	4
$\overline{240}$	a	2.359	38.121		
$\overline{332}$	a	2.323	38.725	38.725	5
$\overline{244}$	a	2.296	39.204	39.210	3
$\overline{116}$	a	2.265	39.765	39.755	10
$\overline{152}$	a	2.237	40.274	40.296	5
$\overline{244}$	a	2.234	40.339	40.340	3
$\overline{334}$	a	2.191	41.173	40.150	2
$\overline{226}$	a	2.160	41.792	41.821	3
$\overline{242}$	a	2.142	42.151	42.153	20
$\overline{060}$	a	2.139	42.215		
$\overline{006}$	a	2.120	42.611	42.650	3
$\overline{152}$	a	2.095	43.141	43.135	15



$hkl$	Reflection type <sup>1)</sup>	Calculated <sup>2)</sup>		Measured <sup>3)</sup>	
		$d_{hkl}$ (Å)	$2\theta$ Cu K $\alpha_1$	$2\theta$ K $\alpha_1$	$I_0/I_{100}$
$\overline{404}$	a	2.020	44.825	44.870	5
$\overline{402}$	a	2.017	44.910		
062	a	1.985	45.659	45.610	3
224	a	1.878	48.426	48.419	5
$\overline{246}$	a	1.846	49.321	49.356	5
406	a	1.846	49.334		
$\overline{064}$	a	1.836	49.608	49.596	15
260	a	1.809	50.391	50.401	5
116	a	1.797	50.761	50.772	10
208	a	1.769	51.621	51.623	15

Table 3. *Experiments in the system An-Qz-H<sub>2</sub>O used to define the liquidus and solidus at several pressures, and H<sub>2</sub>O content of quenched glasses*

Run number ANS-	Tem- perature °C	Time hours	% H <sub>2</sub> O in capsule	An : Qz	Products <sup>1)</sup> , estimated weight percent
<i>Experiments at 1 kb H<sub>2</sub>O pressure</i>					
404	1040	2	23.8	40 : 60*	A = 30, (C) = 40, G = 30 (1.494)
400	1025	3	16.7	40 : 60*	A = 40, (C) = 10, Q = 50
405	1040	2	20.9	35 : 65	A = 20, (C) = 5, G = 75 (1.494)
401	1025	3	17.9	35 : 65	A = 25, (C) = 35, (G) = 35 (1.494), Q = 5
406	1040	2	34.9	30 : 70	(C) = 12, G = 85 (1.492), Q = 3
402	1025	3	16.9	30 : 70	A = 20, (C) = 45, (G) = 30 (1.494), Q = 5
407	1040	2	44.4	20 : 80*	A = 19, (G) = 1, Q = 70, T = 10
403	1025	3	24.0	20 : 80*	A = 20, Q = 80
<i>Experiments at 2 kb H<sub>2</sub>O pressure</i>					
HSY	1350	1	?	100 : 0*	(A), (B), G
HSY	1320	1	?	100 : 0*	A = 100, (B)
53	1330	1	15.7	95 : 5	(A) = 1; G = 99 (1.534), 5.9 % H <sub>2</sub> O
62	920	36	16.8	95 : 5*	A = 95, Q = 5
26	1300	1	16.8	90 : 10	A = 90, G = 10 (1.531)
27	1300	1	15.1	80 : 20	(A) = 1, G = 99 (1.540)
21	1250	1	13.0	80 : 20	A = 85, G = 15 (1.513)
22	1250	1	10.9	70 : 30	(A) = 1; G = 99 (1.524), 5.1 % H <sub>2</sub> O
30	1200	1	14.8	65 : 30	A = 20, G = 80 (1.524)
67	1320	0.5	18.1	60 : 40	G = 100 (1.520), 4.8 % H <sub>2</sub> O
23	1250	1	12.2	60 : 40	G = 100 (1.523), 4.4 % H <sub>2</sub> O
31	1200	1	17.4	60 : 40	G = 100 (1.517)
32	1200	1	14.0	51 : 49	(A) = < 1; G = 100 (1.510), 6.2 % H <sub>2</sub> O
28	1300	1	15.3	50 : 50	G = 100 (1.509), 5.5 % H <sub>2</sub> O
15	1100	4	19.8	50 : 50	A = 20, G = 80 (1.501)
46	1100	6	19.1	45 : 55	(A) = < 1; G = 100 (1.504), 5.1 % H <sub>2</sub> O
43	1050	7	16.9	45 : 55	A = 1; G = 99 (1.503), 6.1 % H <sub>2</sub> O
34	975	22	17.2	45 : 55	A = 5; G = 95 (1.494), 5.7 % H <sub>2</sub> O
38	915	45	14.6	45 : 55	A = 45, Q = 55
63	920	36	15.3	45 : 55*	A = 45, (G) = < 1, Q = 55
47	1100	6	18.7	40 : 60*	G = 100 (1.499), 4.8 % H <sub>2</sub> O
44	1050	7	23.1	40 : 60*	(A) = < 1; G = 100 (1.499), 5.3 % H <sub>2</sub> O
60	1000	8	18.5	40 : 60	A = 10; G = 90 (1.499), 5.9 % H <sub>2</sub> O
35	975	22	19.3	40 : 60*	A = 10; G = 90 (1.494), 6.2 % H <sub>2</sub> O
11	925	2	45.3	40 : 60	A = 25, G = 70, (Q) = 5

Run number ANS-	Tem- perature °C	Time hours	% $\text{H}_2\text{O}$ in capsule	An : Qz	Products <sup>1)</sup> , estimated weight percent
<i>Experiments at 2 kb <math>\text{H}_2\text{O}</math> pressure — continued</i>					
39	915	45	17.4	40 : 60*	A = 40, Q = 60
1	1150	1	18.0	35 : 65	G = 100 (1.494), 6.0 % $\text{H}_2\text{O}$
61	1000	8	18.5	35 : 65	G = 100 (1.494), 5.3 % $\text{H}_2\text{O}$ ; (Q) = < 1
36	975	22	17.9	35 : 65	(A) = < 1; G = 100 (1.493), 5.9 % $\text{H}_2\text{O}$ ; (Q) = < 1
10	925	2	22.1	35 : 65	G = 80 (1.495), Q = 20
64	920	36	19.2	35 : 65*	A = 35, (G) = < 1, Q = 65
66	1320	0.5	19.9	30 : 70	G = 100 (1.492), 4.7 % $\text{H}_2\text{O}$
2	1100	1	16.0	30 : 70	G = 100 (1.493), 6.5 % $\text{H}_2\text{O}$
3	1050	1	19.0	30 : 70	G = 100 (1.493), 5.5 % $\text{H}_2\text{O}$ ; (Q) = < 1
19	1000	6	24.1	30 : 70	G = 95 (1.493), 6.2 % $\text{H}_2\text{O}$ ; Q = 5
8	925	2	16.9	30 : 70*	(A) = 25, G = 10 (1.495), Q = 65
9	925	2	25.4	30 : 70	(A) = < 1, G = 70 (1.495), Q = 30
41	915	45	18.3	30 : 70	A = 30, Q = 70
29	1300	1	22.4	20 : 80*	G = 100 (1.481), 4.3 % $\text{H}_2\text{O}$
45	1050	7	28.1	20 : 80*	G = 95 (1.485), 4.9 % $\text{H}_2\text{O}$ ; Q = 5
70	1125	5	20.9	10 : 90*	G = 100 (1.486), 3.6 % $\text{H}_2\text{O}$
48	1100	6	17.6	10 : 90*	G = 85 (1.475), 4.3 % $\text{H}_2\text{O}$ ; Q = 15
71	1125	5	27.9	5 : 95*	G = 100 (1.468), 4.1 % $\text{H}_2\text{O}$
79	1115	4	22.8	5 : 95*	G = 90 (1.473), 4.0 % $\text{H}_2\text{O}$ ; Q = 10
65	920	36	24.0	5 : 95*	A = 5, Q = 95
54	1330	1	20.6	0 : 100	G = 100 (1.465), 3.6 % $\text{H}_2\text{O}$
57	1135	7	19.6	0 : 100	G = 100 (1.472), 4.5 % $\text{H}_2\text{O}$
58	1135	7	14.4	0 : 100*	G = 45 (1.468), (Q) = 55
75	1130	3	17.5	0 : 100	G = 96 (1.466), 3.5 % $\text{H}_2\text{O}$ ; Q = 4
72	1125	5	18.4	0 : 100	G = 5 (1.468), Q = 95
73	1125	5	14.2	0 : 100*	G = 8 (1.468), Q = 92
81	1115	4	28.0	0 : 100	Q = 100
<i>Experiments at 5 kb pressure</i>					
145	810	41	16.3	95 : 5	A = 95, Q = 5
131	1190	1	16.3	80 : 20	A = 25, G = 75 (1.535)
132	1190	1	14.9	70 : 30	(A) < 1; G = 99 (1.529), 7.7 % $\text{H}_2\text{O}$
134	1140	2	14.3	70 : 30	A = 2; G = 98 (1.527), 8.6 % $\text{H}_2\text{O}$
135	1140	2	16.8	65 : 35	G = 100 (1.523), 8.4 % $\text{H}_2\text{O}$
136	1140	2	16.5	60 : 40	(A) < 1; G = 100 (1.518), 9.8 % $\text{H}_2\text{O}$
118	1050	4	19.6	60 : 40	A = 5, G = 95 (1.519), 8.9 % $\text{H}_2\text{O}$
117	1050	4	15.5	55 : 45	G = 100 (1.515), 9.5 % $\text{H}_2\text{O}$
160	1010	4	14.6	55 : 45	A = 1; G = 99 (1.514), 9.9 % $\text{H}_2\text{O}$ , S. G. = $2.324 \pm 4$
146	1000	5	15.2	55 : 45	A = 5; G = 95 (1.514), 8.2 % $\text{H}_2\text{O}$
147	1000	5	14.7	50 : 50	G = 100 (1.511), 8.8 % $\text{H}_2\text{O}$
128	950	5	18.8	50 : 50	A = 5; G = 95 (1.508), 9.2 % $\text{H}_2\text{O}$
124	900	17	15.7	50 : 50	A = 10; G = 90 (1.504), 10.0 % $\text{H}_2\text{O}$
161	1010	4	15.0	45 : 55	G = 100 (1.506), 8.8 % $\text{H}_2\text{O}$ , S. G. = $2.294 \pm 4$
166	950	4	16.2	45 : 55	G = 100 (1.504), 9.6 % $\text{H}_2\text{O}$ , S. G. = 2.286
141	920	6	17.1	45 : 55	(A) = 1; G = 99 (1.507), 10.0 % $\text{H}_2\text{O}$
159	900	14	13.8	45 : 55	A = 2; G = 98 (1.504), 8.9 % $\text{H}_2\text{O}$
138	850	17	12.9	45 : 55	A = 5, (A) = 2; G = 93 (1.504), 9.5 % $\text{H}_2\text{O}$
104	820	25	17.0	45 : 55	A = 45, G = 5, Q = 50
144	810	41	16.5	45 : 55*	A = 45, Q = 55
123	900	17	22.2	40 : 60	G = 100 (1.501), 10.2 % $\text{H}_2\text{O}$
156	875	5	16.2	40 : 60	(A) = 1; G = 99 (1.503), S. G. = $2.285 \pm 4$ ; (Q) < 1
139	850	17	17.4	40 : 60	G = 99 (1.502), 9.3 % $\text{H}_2\text{O}$ ; (Q) = 1
164	835	16	16.4	40 : 60	G = 90 (1.503), 9.8 % $\text{H}_2\text{O}$ ; Q = 10
101	820	25	18.0	40 : 60	(A) = 2, G = 60 (1.499), Q = 38

Run number ANS-	Tem- perature °C	Time hours	% H <sub>2</sub> O in capsule	An : Qz	Products <sup>1)</sup> , estimated weight percent
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*Experiments at 5 kb pressure — continued*

143	810	41	21.1	40 : 60*	A = 40, Q = 60
167	950	4	16.1	35 : 65	G = 100 (1.499), 10.6 % H <sub>2</sub> O; (Q) < 1
151	920	8	17.5	35 : 65	G = 99 (1.497), 9.2 % H <sub>2</sub> O; Q = 1
158	900	14	17.0	35 : 65	G = 95 (1.498), 9.2 % H <sub>2</sub> O; Q = 5
162	1010	4	15.2	30 : 70	G = 100 (1.495), 9.9 % H <sub>2</sub> O, S.G. = 2.250
168	950	4	16.4	30 : 70	G = 99 (1.494), 8.5 % H <sub>2</sub> O, S.G. = 2.23; Q = 1
150	920	8	11.9	30 : 70	G = 90 (1.493), 7.43 % H <sub>2</sub> O; Q = 10
163	1010	4	17.0	20 : 80*	G = 97 (1.486), 7.3 % H <sub>2</sub> O; (Q) = 3
148	1000	5	18.6	20 : 80*	G = 93 (1.485), 7.8 % H <sub>2</sub> O; Q = 7
109	1070	4	18.5	10 : 90*	G = 100 (1.473) with liquid inclusions, 10.9 % H <sub>2</sub> O
116	1055	4	18.3	10 : 90*	G = 100 (1.475), 11.0 % H <sub>2</sub> O (bubbles in glass)
105	1040	5	18.1	10 : 90*	G = 98 (1.477), 11.9 % H <sub>2</sub> O (bubbles); Q = 2
110	1070	4	20.0	5 : 95*	G = 100 (1.473), 9.5 % H <sub>2</sub> O
115	1055	4	22.7	5 : 95*	G = 70 (1.473), Q = 30
142	810	41	26.0	5 : 95*	A = 5, Q = 95
111	1070	5	19.6	0 : 100	G = 100 (1.468), 11.2 % H <sub>2</sub> O (bubbles)
112	1070	5	12.9	0 : 100*	G = 75 (1.468), (Q) = 25
113	1055	4	20.1	0 : 100	Q = 100
114	1055	4	16.1	0 : 100*	Q = 100

*Experiments at 10 kb H<sub>2</sub>O pressure*

333	1120	1	16.8	100 : 0	(A) = 25, (B) = 25, G = 50 (1.553)
332	1120	1	26.1	100 : 0*	(A) = 40, (B) = 10, G = 50 (1.551)
312	1100	2	22.3	100 : 0*	A = 95, (B) = 5, G < 1 (1.544)
305	1060	2	19.3	100 : 0	A = 100
304	1060	2	17.9	100 : 0*	A = 99, (B) = 1
334	1120	1	16.9	95 : 5	(A) = 4, (B) = 11, G = 85 (1.548)
314	1100	2	18.7	95 : 5	A = 40, (B) = 5, G = 55 (1.545)
324	750	3	15.0	95 : 5*	A = 95, Q = 5
315	1100	2	12.5	90 : 10	(A) = 2, (B) = 3, G = 95 (1.541)
307	1060	2	19.3	90 : 10	A = 50, (B) = 1, G = 49 (1.521)
364	1050	2	14.0	80 : 20	A = 23, (B) = 2, G = 75 (1.530)
343	1040	2	17.8	70 : 30	G = 100 (1.520), 12.5 % H <sub>2</sub> O, S.G. = 2.324
362	940	2	17.0	60 : 40	G = 100 (1.510), 11.7 % H <sub>2</sub> O, S.G. = 2.280
355	920	2	16.7	60 : 40	A = 3; G = 97 (1.516), 12.6 % H <sub>2</sub> O, S.G. = 2.26
354	920	2	16.0	55 : 45	G = 100 (1.513), 11.9 % H <sub>2</sub> O, S.G. = 2.26
339	900	3	19.2	55 : 45	A = 1; G = 99 (1.513), 12.6 % H <sub>2</sub> O, S.G. = 2.285 ± 5
359	850	2	12.1	51 : 49	G = 100 (1.504), 12.1 % H <sub>2</sub> O, S.G. = 2.232
361	940	2	20.4	50 : 50	G = 100 (1.505), 11.2 % H <sub>2</sub> O, S.G. = 2.247
358	850	2	19.6	50 : 50	G = 100 (1.503), 12.0 % H <sub>2</sub> O, S.G. = 2.245
318	800	3	29.7	50 : 50	A = 2; G = 98 (1.506), 11.9 % H <sub>2</sub> O, S.G. = 2.26 ± 2
345	780	3	17.8	50 : 50	A = 3; G = 97 (1.504), 10.0 % H <sub>2</sub> O
348	765	4	17.9	50 : 50	A = 4; G = 96 (1.500), 12.8 % H <sub>2</sub> O, S.G. = 2.250
367	1050	2	18.0	45 : 55	G = 100 (1.503), 11.3 % H <sub>2</sub> O, S.G. = 2.224
328	900	3	25.3	45 : 55	G = 100 (1.504), 12.5 % H <sub>2</sub> O, S.G. = 2.207 ± 2
357	850	2	18.1	45 : 55	G = 100 (1.499), 11.2 % H <sub>2</sub> O, S.G. = 2.232
319	800	3	14.9	45 : 55	G = 98 (1.506), 11.8 % H <sub>2</sub> O, S.G. = 2.265 ± 7; (Q) = 2
349	765	4	26.4	45 : 55	(A) < 1; G = 97 (1.498), 11.8 % H <sub>2</sub> O; Q = 3
350	765	4	18.2	45 : 55*	G = 93 (1.499), 10.4 % H <sub>2</sub> O; Q = 7
329	900	3	17.8	40 : 60	G = 100 (1.500), 12.3 % H <sub>2</sub> O, S.G. = 2.200 ± 4
356	850	2	18.0	40 : 60	G = 100 (1.498), 11.6 % H <sub>2</sub> O, S.G. = 2.21 ± 1
351	765	4	21.4	40 : 60	G = 90 (1.498), Q = 10
325	750	3	17.6	40 : 60*	A = 40, Q = 60
353	920	2	16.1	35 : 65*	G = 100 (1.495), 10.6 % H <sub>2</sub> O, S.G. = 2.26

Run number ANS.	Tem- perature °C	Time hours	% $\text{H}_2\text{O}$ in capsule	An: Qz	Products <sup>1)</sup> , estimated weight percent
<i>Experiments at 10 kb <math>\text{H}_2\text{O}</math> pressure — continued</i>					
330	900	3	19.8	35:65	G = 99 (1.497), 12.2 % $\text{H}_2\text{O}$ , S.G. = $2.21 \pm 1$ ; Q = 1
360	940	2	18.6	30:70*	G = 100 (1.486), 12.0 % $\text{H}_2\text{O}$
352	920	2	18.6	30:70*	G = 97 (1.490), 11.2 % $\text{H}_2\text{O}$ , S.G. = 2.22; Q = 3
331	900	3	22.9	30:70	G = 95 (1.490), 11.8 % $\text{H}_2\text{O}$ ; Q = 5
323	1032	2	21.0	10:90*	G = 95 (1.475), Q = 5
326	750	3	20.1	5:95*	A = 5, Q = 95
371	1060	2	39.5	0:100	G = 100 (1.479)
376	1060	2	23.1	0:100*	G = 100
365	1050	2	20.6	0:100	G = 15 (1.475), Q = 85
366	1050	2	14.9	0:100*	G = 10, Q = 90
380	1040	2	35.0	0:100*	Q = 100

<sup>1)</sup> A = anorthite, B = " $\beta$ -alumina", C = cristobalite, G = glass (index of refraction in parentheses), Q = quartz, T = tridymite. Abbreviations in parentheses indicate quench or metastable phase.

\* Crystalline starting materials used.

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