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Four-Phase Curve in the System $CaAl_2Si_2O_8-SiO_2-H_2O$ between ¹ and 10 Kilobars*)

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With ⁸ figures in the text and ³ tables

Abstract

The $CaAl_2Si_2O_8(An)$ -Si $O_2(Qz)$ system has a eutectic at SiO₂ 49.5 weight per cent (SCHAIRER and BOWEN, 1947); the ternary system An-Qz-H₂O projected from H2O is also of euteetic type. Anorthite, quartz, liquid, and gas coexist under the following conditions:

The H₂O-saturated Qz-H₂O liquidus lies at $1130 \pm 5^{\circ}$ C at 2000 bars, $1065 \pm 5^{\circ}$ C at 5000 bars, and $1055 \pm 10^{\circ}$ C at 10,000 bars. The H₂O-saturated An-H₂O liquidus determined by YODER (1954) was confirmed to 5000 bars and extended to $10,000$ bars at $1110 \pm 10^{\circ}$ 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 interaxial angle α . 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 H_2O pressure, and explanation for resorbed quartz crystals in volcanic rocks.

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INTRODUCTION

Rocks consisting largely of quartz, plagioclase, and alkali feldspar are abundant, and the phase relations between silica and feldspar compohave 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 $CaAl₂Si₂O₈$ (hereafter called An)-SiO₂ (called Qz)-H₂O supplements these investigations, and is of interest because discussion of the phase relations of quartz and feldspars over ^a wide range of peratures 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 valents of these glasses were prepared either by anhydrous crystallization

Fig. 1. Index of refraction of anhydrous glasses in the system An-Qz at room perature, 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 compoand 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 H_2O content of the glass may be responsible in part for the effect, such as pressure densification of the glass at constant H2O 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 $CaAl₂Si₂O₈$ composition was very carefully prepared from CaCO₃ (BAKER's lot 51735), Al_2O_3 (T 61 grade), and SiO₂ (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 ± 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° C + 1.5° C; the melting interval (first sintering to all glass) was 4° C. A Pt-Pt90Rh 10 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 H_2SO_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 $H₂O$ 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 sence of silicate liquid. Albite-twinned 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° ^C above the anorthite plus liquid field yielded distinctive radiating fibrous aggregates gates 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 Å. As observed at room temperature on x-ray photographs a weak 111 diffraction line appeared from anorthite synthesized from glass after as little as one hour under the temperature and pressure of the experiand 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 $\overline{11}1$ 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° ^C and 350° ^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° ^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 $\overline{11}1$ reflections varying in intensity from very weak to very distinct. (Sample ANS-26 has the weakest $\overline{11}1$ reflection, and sample ANS-305 the most distinct.) The results are given in Table 1, together with other reported measurefor 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 α , possibly smaller values for a and c, and possibly larger value of γ . Only a few differences are apparent by inspection of the powder-diffraction patterns, the most notable being the larger separation of the $\overline{2}42$ and $\overline{24}2$ reflections $(0.37^\circ 2 \theta \text{ CuK}\alpha_1 \text{ in ANS } 305 \text{ with distinct "c-reflections",}$ and 0.30° in ANS-26 with very weak "c-reflections"), and smaller separation of $\overline{134}$ and $\overline{134}$ in ANS 305 (1.81° vs. 1.86°). 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

Fig. 4. Hexagonal dipyramidal crystals of quartz with six-fold layers of fluid inclusions, interpreted to have been β -quartz under experimental conditions. Starting material An₃₀Qz₇₀ glass, 2 kb, 975[°]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 $\text{Ang}_0\text{Qz}_{70}$ glass, ² kb, 925°C, ² hours, run ANS-9.'

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

Fig. 2. Anorthite crystals with the tabular habit commonly found in experiments near the liquidus. Starting material $\text{An}_{50}\text{Qz}_{50}$ glass, 10 kb, 765°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 " β -alumina", believed to have been present during the experiment. Starting material An₉₀Qz₁₀ glass, 10 kb, 1100 $^{\circ}$ C, 2 hours, run ANS-315.

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obtained with a diffractometer equipped with a pulse height analyser for CuK α 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 dipyramids typical of β -quartz (Figure 4), though it all transformed to α -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° C so that α -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° 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° C and quartz was obtained abundantly at 1025° C, thus confirming the temperature of 1040° ^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 " β -alumina" of unknown composition (Figure 3). The " β -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 sented the dissolved solids.

The surfaces of charges of silica-rich compositions $(An_{45}Qz_{55}-An_{30}Qz_{70})$ 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°. 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 bubblefree hydrous glass on which the index of refraction, specific gravity, and $H₂O$ content were measured. Such data are potentially useful in evaluating the structure of the melts and the role of $H₂O$ in them, and will be discussed elsewhere. The trends of the variation of index of refraction with $H₂O$ content are shown in Figure 1. Some of these data are given in Table 3, along with the H_2O content determined by the weight loss of glass slugs after drying to constant weight at 110°C and then slowly heating to 1200° C.

Hydrous liquids produced at ⁵ kh and below can be quenched without loss of H_2O , and their H_2O content can be found by the weight loss technique, but the hydrous liquids produced at 10 kb cannot be quenched without loss of H_2O from the liquid. The system SiO_2-H_2O at 10 kb as studied by the author by a static equilibrium method yields hydrous silicate liquid containing 22% H₂O by weight at $1055\degree$ C. The following observations by my colleague EDWIN ROEDDER (written communication, 1963) on fluid inclusions in α -quartz synthesized at 10 kb (Figure 6) (sample ANS 351, $An_{40}Qz_{60}$ glass = 78.63%, $H_2O = 21.37\%$, 765°C, ⁴ hours) indicate that the hydrous silicate liquid near the four-phase point at 10 kb contains more H_2O 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 $H₂O$, 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% H_2O 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 $H₂O$ content of the original liquid in the sample studied ever was as high as the H_2O content of the charge, but it was higher than is now found in liquids free to exsolve H_2O in the capsule during quenching. The figure obtained by weight loss methods thus sets ^a lower limit on the $H₂O$ content.

Under isobaric conditions the $H₂O$ content of a $H₂O$ -saturated liquid of fixed An : Qz ratio decreases as the temperature is raised. The H_2O 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 H_2O 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 H_2O pressure increased. No evidence was seen of settling of quartz.

PHASE RELATIONS

System $An - H₂O$

The $H₂O$ -saturated An- $H₂O$ liquidus was reported by YODER (1954, p. 107; oral communication, 1957) to be $1343 \pm 5^{\circ}$ C at 2 kb, and $1235 \pm$ \pm 5°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 $1110 \pm 10^{\circ}$ C. This point has also been determined as $1115 \pm 5^{\circ}$ C by YODER (1965, p. 85—88). The presence of β -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 Fyee, 1965; and Newton, 1966). None of these phases or assemblages 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 $H₂O$ -saturated liquidus throughout this investigation.

System QZ-H2O

The $H₂O$ -saturated $Qz-H₂O$ 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 $H₂O$ -saturated liquidus at 2 kb is $1130 \pm 5^{\circ}$ C. This liquidus at 5 kb is $1065 \pm 5^{\circ}$ C and at 10 kb is $1055 \pm 5^{\circ}$ C according to the present work; OSTROVSKIY and others (1959) and KENNEDY and others (1962) report temperatures 15° to 25° ^C higher at ⁵ kb, which seem incompatible with data of Table ³ for the $H₂O$ -saturated liquidus for quartz in the system $Qz-An-H₂O$. Kennedy and others (1962) claim the upper critical end point lies at 1080°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 $22 \pm 2\%$ H₂O, 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° 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 β -quartz + liquid + gas in the H₂O-saturated Qz-H₂O 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 $An-0z-H_2O$

The data of Table ³ locate the saturated liquidus at several pressures. The ternary system projected from the $H₂O$ 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 H₂O-saturated liquidus in the systems $Qz-H_2O$, An-H₂O, and An-Qz-H₂O. The curve for the α - β quartz inversion is from YODER (1950) and for the quartz-tridymite transition from TUTTLE and Bowen (1958) ; An-H₂O 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 $H₂O$ 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 perature of the point:

The relations are also summarized graphically in Figure 8. The lowering of liquidus temperatures with increasing $H₂O$ pressure is common to all

Fig. 8. Projections of the liquidus for H20-saturated melts at 1, 2, 5, and ¹⁰ kb in the system An-Qz-H₂O to the join An-Qz. A = anorthite, C = cristobalite, L = liquid, $T = \text{tridymite}$. 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 $H₂O$ 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 $An-Qz-H₂O$ system than in the other feldspar-silica systems because the temperatures in the anhydrous 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.

PETROLOG1C APPLICATIONS

The boundary surface in the quinary system $Or-Ab-An-Qz-H₂O$ 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. D33-D38). 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 $H₂O$ 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. B38-B39).

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 H₂O 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 $H₂O$ 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 $H₂O$ 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 H_2O 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 (NaAl Si_3O_8)-An-Di (CaMg Si_2O_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 $H₂O$ as apices as projected from the $H₂O$ 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- $H₂O$ given above and from data for Ab-Qz- $H₂O$ given in Tuttle and Bowen (1958, p. 50—53). The boundary curve between these points can

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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.

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Table 1. Cell dimensions of anorthite

Table 2. Indexed powder-diffraction pattern for primitive anorthite synthesized at 10 kb, 1060°C, 2 hours from $CaAl₂Si₂O₈$ glass in the presence of steam

Triclinic CaAl₂Si₂O.; P₁, a = 8.179 \pm 0.002 Å, b = 12.869 \pm 0.002, c = 14.174 \pm 0.002, α = 93° 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 ± 0.3 Å³ 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.

¹) GOLDSMITH and LAVES (1956, p. 397).

²) Calculated spacings are shown for $d \ge 2.500 \text{ Å}$ — calculated spacings less than 2.100 Å are listed only when they correspond to an indexed observed reflection.

³) Average of three observations with annealed CaF₂ as internal standard, $a = 5.4622 \text{ Å}$ at 25°C. Ni-filtered CuK α_1 radiation ($\lambda = 1.54050$ Å). Lower limit of 2 θ measured = 6° (14.72 Å). Pattern obtained at 25°C.

 \sim μ

 $\label{eq:1} \begin{array}{c} \mathbf{a} \\ \mathbf{b} \end{array}$

 $\hat{\mathcal{A}}$

 ~ 6

Four-Phase Curve in the System $\rm CaAl_2Si_2O_8-SiO_2-H_2O$

 $\tilde{\mathcal{S}}_i$

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hkl	Reflection type ¹	$Calculated2$)		Measured ³	
		d_{hkl} (A)	2θ Cu K α_1	$2 \theta K \alpha_1$	I_0/I_{100}
404	\mathbf{a}	2.020	44.825	44.870	5
$\overline{4}02$ 062	\mathbf{a} a	2.017 1.985	44.910 45.659	45.610	3
224	a	1.878	48.426	48.419	5
246 $\overline{4}06$	\mathbf{a} \mathbf{a}	1.846 1.846	49.321 49.334	49.356	$\bf{5}$
$0\overline{6}$ 4	a.	1.836	49.608	49.596	15
260	a	1.809	50.391	50.401	$\rm 5$
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-H₂O used to define the liquidus and solidus at several pressures, and $H_{2}O$ content of quenched glasses

 \mathcal{Q}

353 920 2 16.1 35:65* $G = 100$ (1.495), 10.6% H₂O, S.G. = 2.26

¹) A = anorthite, B = " β -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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