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THE SYSTEMS $NaAlSi_3O_8$–SiO_2 AND $KAlSi_3O_8$–SiO_2 TO 20 kb AND THE RELATIONSHIP BETWEEN H_2O CONTENT, P_{H_2O}, AND P_{total} IN GRANITIC MAGMAS

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ABSTRACT. Liquidus relations in the binary systems $NaAlSi_3O_8$–SiO_2 and $KAlSi_3O_8$–SiO_2 at pressures between 8 and 20 kb were determined. In both systems the eutectic liquid is enriched in the feldspar component with increasing pressure. The observed shift in eutectic composition with increasing pressure is similar in direction to that previously found for the eutectic liquids in the systems $NaAlSi_3O_8$–SiO_2–H_2O and $KAlSi_3O_8$–SiO_2–H_2O at pressures to 10 kb.

This information is used in conjunction with available data in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O to demonstrate that P_{total} and P_{H_2O} must be treated as independent variables in the quaternary system.

Consequently the implicit assumption employed by some investigators in the application of experimental studies to specific granites, that pressure affects the equilibria only through the variable P_{H_2O}, is invalid.

INTRODUCTION

The quaternary system $NaAlSiO_4$–$KAlSiO_4$–SiO_2–H_2O has received a great deal of attention from experimental petrologists. Much of this attention has been due to the interest generated by the fundamental studies of J. F. Schairer and N. L. Bowen. A preliminary report on melting relations in the anhydrous ternary system (Schairer and Bowen, 1935) was followed by a brief report on equilibria in the ternary systems Na_2O–Al_2O_3–SiO_2 and K_2O–Al_2O_3–SiO_2 (Schairer and Bowen, 1947). Schairer (1950) presented more detail on the alkali feldspar join and a revised equilibrium diagram for the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2. Detailed reports on the systems K_2O–Al_2O_3–SiO_2 and Na_2O–Al_2O_3–SiO_2 were presented by Schairer and Bowen (1955, 1956). These studies were concerned with equilibria in the dry systems at atmospheric pressure. Evaluation of hydrous melting relations in this system include major contributions by Goranson (1938), Bowen and Tuttle (1950), Tuttle and Bowen (1958), Yoder, Stewart, and Smith (1957), and a great many other workers. In dealing with the hydrous systems, nearly all investigators other than Yoder, Stewart, and Smith (1957) and Burnham and Jahns (1962) were concerned exclusively with equilibria involving H_2O-saturated liquids. The experimental study reported in this paper represents an attempt to provide limitations on possible liquidus equilibria in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O in the absence of a free vapor phase, based on liquidus equilibria in the systems $NaAlSi_3O_8$–SiO_2 and $KAlSi_3O_8$–SiO_2 at high pressure. These results, with those of Boyd and England (1963), Bell and Roseboom (1966), and Lindsley (1966, 1967), permit analysis of possible phase relations in one of the cases where P_{H_2O} in the silicate melt is less than P_{total}.

EXPERIMENTAL TECHNIQUES AND APPARATUS

These experiments were performed in solid-media, single-stage, piston-cylinder apparatus (Boyd and England, 1963). The techniques employed were very similar to those described by Bell and Roseboom (1965) and Lindsley (1966). Boyd and others (1967) have discussed difficulties in pressure measurement using the single-stage apparatus. In view of their discussion and the purposes of these experiments, all runs reported were performed using the "piston-out" technique (over-pressure $\approx$ 5 kb) and are not corrected for friction. A new pressure vessel was used for all of the experiments in the system $NaAlSi_3O_8$–SiO_2 and most of those in the system $KAlSi_3O_8$–SiO_2. Examination of the pressure vessel during and after the study revealed no cracks or chips in the carbide bore. A different vessel, also with no cracks or chips in the carbide bore, was used for the remainder of the experiments in the system $KAlSi_3O_8$–SiO_2. Precision of pressure and temperature measurements reported in tables 1 and 2 is estimated to be $\pm$ 0.2 kb and $\pm$ 10°C. Thus the isobars are believed to be isobaric to $\pm$ 0.2 kb, although the accuracy of the pressure measurements may be subject to errors as large as 5 percent.

Starting materials used in this study were the same as those used by Luth, Jahns, and Tuttle (1964), prepared as described by Luth and Ingamells (1963). Crystalline starting materials were used for the determination of the solidus, and either glass or fired gel was used in the determination of the liquidus. The starting materials were placed in carbon or platinum capsules and dried carefully at 900°C (crystalline) or 1100°C (glass or gel) for 40 minutes. After drying, the platinum capsules were sealed by electric arc welding. Upon completion of the experiment the charge was examined using standard immersion techniques and the petrographic microscope. The criterion used for the determination of the solidus reaction was the presence or absence of glass in the initially crystalline starting material. The determination of the liquidus was based on the appearance and abundance of a crystalline phase in the initial glass or gel.

EXPERIMENTAL RESULTS: $NaAlSi_3O_8$–SiO_2

The experimental data are given in table 1. The temperature of the eutectic reaction (Ab + Q = L) was determined over the pressure interval 8 to 20 kb. Pressure-temperature and pressure-composition projections presenting these data are given as figure 1. Liquidus curves were determined at 8, 12.3, and 20 kb and are given in figure 2, with the liquidus diagram obtained by Schairer and Bowen (1956) at atmospheric pressure. The terminations of the liquidus curves at the albite composition are from Boyd and England (1963). The composition of the eutectic liquid at 8 kb is slightly silica-rich relative to the 1 atm data of Schairer and Bowen. At 1 atm, the stable silica phase at the eutectic is presumably tridymite, though Schairer and Bowen observed only cristobalite (p. 162). At higher pressures the eutectic liquid becomes richer in albite. With increasing pressure, the solidus temperature increases, and

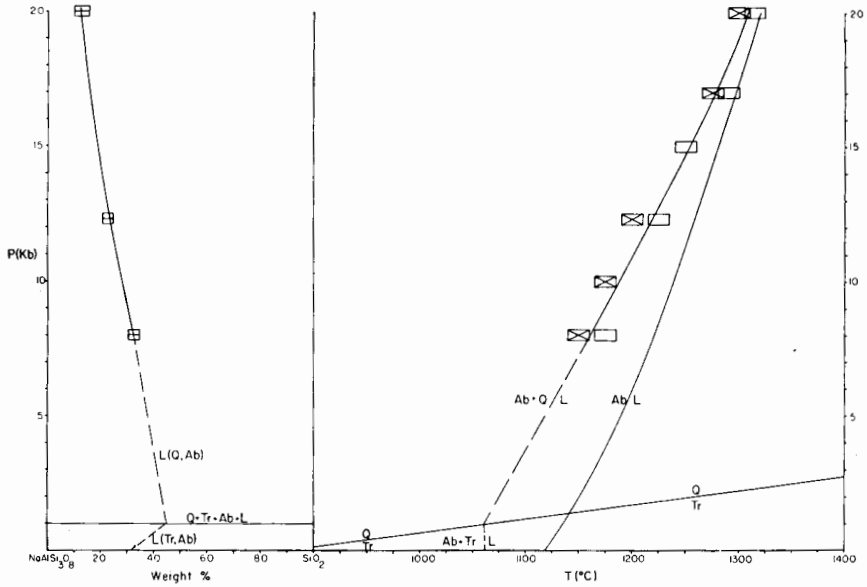

Fig. 1. Pressure–temperature–composition diagram: $NaAlSi_3O_8$–SiO_2. The P-T projection is shown at the right. Experimental data points (table 1) shown as boxes on the figure: boxes with crosses—Ab + Q, open boxes—liquid present in addition to albite, quartz, or both. The univariant curve Ab + Q = L is extrapolated below 8 kb and terminates (stably) at a postulated invariant point: Q + Tr + Ab + L at approximately 1060°C, at 1 kb. The Q = Tr reaction is from Tuttle and England (1955) and Kennedy and others (1962). The Ab = L reaction is from Boyd and England (1963). The P-X projection shown at the left illustrates the variation in composition of the univariant liquid coexisting with Ab and Tr at pressures below 1 kb or with Ab and Q at pressures greater than 1 kb. The size of the symbols corresponds to the uncertainty in the data. The atmospheric pressure data is from Schairer and Bowen 1956. Abbreviations used are: Ab, albite; Q, quartz; Tr, tridymite, and L, liquid. Other complexities introduced by the polymorphism of the silica phases are ignored.

the isobaric difference in temperature between the eutectic reaction and the albite melting temperature decreases. The quartz liquidus extending to higher temperatures from the eutectic is quite steep at all pressures.

EXPERIMENTAL RESULTS: $KAlSi_3O_8$–SiO_2

The experimental data are presented in table 2. The temperature of the eutectic reaction (Sa + Q = L) was determined at 10, 15, and 20 kb. The pressure-temperature and pressure-composition projections are given as figure 3. The temperature of the incongruent melting of sanidine at 10 kb was found to be 1285° ± 10°C, in agreement with Lindsley's (1966) value of slightly greater than 1290°C. Isobaric liquidus diagrams at 10 and 20 kb are given in figure 4 as is the diagram of Schairer and Bowen (1955) at 1 atm. The composition of the eutectic liquid at 10 and 20 kb is silica-poor relative to the 1 atm eutectic liquid, which involves tridymite (stably) rather than quartz.

TABLE 1

Critical experimental data:

$NaAlSi_3O_8$-SiO_2

Run no.	P*, bars	P, kb	T, °C	t, hours	Weight % Ab	Weight % Q	Initial condition	Results
1565	223	8	1150	1	70	30	Xl	Ab + Q + Gl
1581	223	8	1150	1	70	30	Xl	Ab + Q
1564	223	8	1175	1	70	30	Xl	Ab + Q + Gl
1555	278	10	1175	1	70	30	Xl	Ab + Q
1552	343	12.3	1200	2	70	30	Xl	Ab + Q
1549	343	12.3	1225	2	70	30	Xl	Ab + Q + Gl
1553	343	12.3	1225	1	70	30	Xl	Ab + Q + Gl
1548	343	12.3	1250	2	70	30	Xl	Q + Gl
1582	418	15	1250	1	70	30	Xl	Ab + Q + Gl
1562	474	17	1275	1	70	30	Xl	Ab + Q
1563	474	17	1290	1	70	30	Xl	Ab + Q + Gl
1554	557	20	1250	1	70	30	Xl	Ab + Q
1556	557	20	1275	1	70	30	Xl	Ab + Q
1559	557	20	1300	1	70	30	Xl	Ab + Q
1544	557	20	1315	1	70	30	Xl	Q + Gl
1589	223	8	1200	0.5	90	10	gel	Ab + Gl
1586	223	8	1175	1.5	75	25	gl	tr Ab + Gl
1588	223	8	1175	0.5	70	30	gl	Gl
1592	223	8	1175	1	65	35	gl	Q + Gl
1590	223	8	1200	1	65	35	gl	Gl
1594	223	8	1300	2	60	40	gl	Gl + Q
1597	223	8	1350	1.5	60	40	gl	Gl
1567	343	12.3	1225	1	90	10	gel	Ab + Gl
1566	343	12.3	1250	1	90	10	gel	Gl
1576	343	12.3	1225	1	75	25	gl	Gl + Q
1574	343	12.3	1250	1	75	25	gl	Gl
1551	343	12.3	1200	2	70	30	gl	Gl + Ab + Q
1550	343	12.3	1225	1	70	30	gl	Gl + Q
1575	343	12.3	1325	1	70	30	gl	Gl + Q
1558	343	12.3	1350	2	70	30	gl	Gl
1579	343	12.3	1400	1	65	35	gl	Gl + Q
1577	343	12.3	1425	1	65	35	gl	Gl
1572	343	12.3	1450	0.5	60	40	gl	Gl + Q
1578	343	12.3	1475	1.5	60	40	gl	Gl + Q
1580	343	12.3	1525	0.5	60	40	gl	Gl + Q(1)
1583	343	12.3	1450	1	50	50	gl	Gl + Q
1584	343	12.3	1450	1	40	60	gl	Gl + Q
1568	557	20	1315	3	90	10	gel	Ab + Gl
1593	557	20	1450	0.5	75	25	gl	Gl + tr
1587	557	20	1525	0.5	75	25	gl	Gl
1596	557	20	1500	1	70	30	gl	Gl + Q
1595	557	20	1525	1	70	30	gl	Gl

P*, piston hydraulic pressure.

(1) Glass showed many similarities to a two-liquid assemblage, which was not similar to that in run 1578, 1583, or 1584.

Abbreviations: Xl, crystalline starting material; gel, gel starting material; gl, glass starting material; Ab, albite; Q, quartz; Gl, glass; tr, trace amounts.

TABLE 2

Critical experimental data:

$KAlSi_3O_8$-SiO_2

Run no.	P*, bars	P, kb	T, °C	t, hours	Weight % Or	Weight % Q	Initial condition	Results
1608	278	10	1125	1	80	20	Xl	Sa + Q
1606	278	10	1150	1	80	20	Xl	Sa + Q + Gl
1601	418	15	1225	1	80	20	Xl	Sa + Q
1603	418	15	1250	1	80	20	Xl	Sa + Q + tr Gl
1609	557	20	1300	1	80	20	Xl	Sa + Q
1607	557	20	1325	1	80	20	Xl	Sa + Q + Gl
1647	278	10	1275	1	90	10	gel	Sa + Gl
1643	278	10	1290	1	90	10	gel	Lc + Gl
1627	278	10	1300	1	90	10	gel	Lc + Gl
1640	278	10	1250	1	80	20	gel	Sa + Gl
1622	278	10	1250	1	80	20	gel	Sa + Gl
1632	278	10	1275	1	80	20	gel	Gl
1617	278	10	1275	1	80	20	gel	Gl
1616	278	10	1125	1	70	30	gl	Sa + Q + Gl
1614	278	10	1150	1	70	30	gl	Sa + Gl
1638	278	10	1175	1	70	30	gl	Gl
1612	278	10	1200	1	70	30	gl	Gl
1620	278	10	1125	1	60	40	gl	Gl + Sa + Q
1645	278	10	1275	1	60	40	gl	Gl + Q
1648	278	10	1325	1	60	40	gl	Gl
1625	278	10	1350	1	40	60	gel	Gl + Q
1642	557	20	1400	1	90	10	gel	Sa + Gl
1644	557	20	1425	1	90	10	gel	Gl
1637	557	20	1375	1	80	20	gel	Sa + Gl
1633	557	20	1400	1	80	20	gel	Gl
1629	557	20	1300	1	70	30	gl	Sa + Q + tr Gl
1639	557	20	1350	1	70	30	gl	Gl + Q
1641	557	20	1375	1	70	30	gl	Gl + Q
1635	557	20	1400	1	70	30	gl	Gl
1646	557	20	1475	1	60	40	gl	Gl + Q
1649	557	20	1525	1	60	40	gl	Gl

P*, piston hydraulic pressure.

Abbreviations: Xl, crystalline starting material; gel, gel starting material; gl, glass starting material; Sa, sanidine; Q, quartz; Gl, glass; tr, present in trace amounts.

THE SYSTEMS $NaAlSi_3O_8$–H_2O AND $KAlSi_3O_8$–SiO_2–H_2O

The experimental data presented in the previous section were obtained at high (8-20 kb) pressures in the dry system. However, they provide important limiting conditions on equilibria involving H_2O-undersaturated liquids in the hydrous systems.

In figure 5A the composition of the eutectic liquid in the system $NaAlSi_3O_8$–SiO_2–H_2O is shown as a function of pressure. The 1 atm data is from Schairer and Bowen, the points at 1, 2, 3, 4 kb from Tuttle and Bowen (1958), and at 5 and 10 kb from Luth, Jahns, and Tuttle

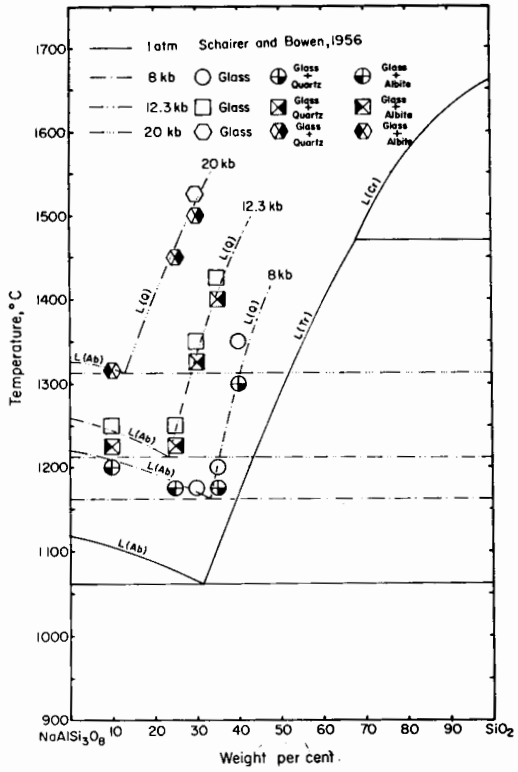

Fig. 2. Isobaric (± 0.2 kb) temperature-composition diagrams for the system $NaAlSi_3O_8$–SiO_2. L(Cr), L(Tr), L(Q), and L(Ab) denote the liquidus curves of each pressure and the primary phases present as, respectively, cristobalite, tridymite, quartz, and albite.

(1964). The H_2O content of the eutectic liquids is approximate. In figure 5B a schematic diagram at 10 kb is given, from the data of Luth, Jahns, and Tuttle (1964) for $NaAlSi_3O_8$–Hi_2O and Kennedy and others (1962) for SiO_2–H_2O.[1] If it is assumed that P_{H_2O} in the H_2O-undersaturated melt at a P_{total} of 10 kb is given by the experimental determination of the liquid compositions for the H_2O-saturated liquid at lower P_{total}, then the boundary curve L (Ab, Q) must pass through the points given in figure 5A. This is equivalent to assuming that pressure affects the equilibria *only* through the variable P_{H_2O} and implies that a change in pressure has no effect on equilibria in the system $NaAlSi_3O_8$–SiO_2. Clearly this would be a special case; however, in the absence of data in the dry system or the H_2O undersaturated region, it is the simplest of the possible cases. That it is not the case is shown in figure 5C, which incorporates the new experimental data presented in this paper. Consequently

[1] Burnham (personal commun., 1965) and Stewart (1967) did not observe a second critical end point in the system SiO_2–H_2O at pressures below 10 kb.

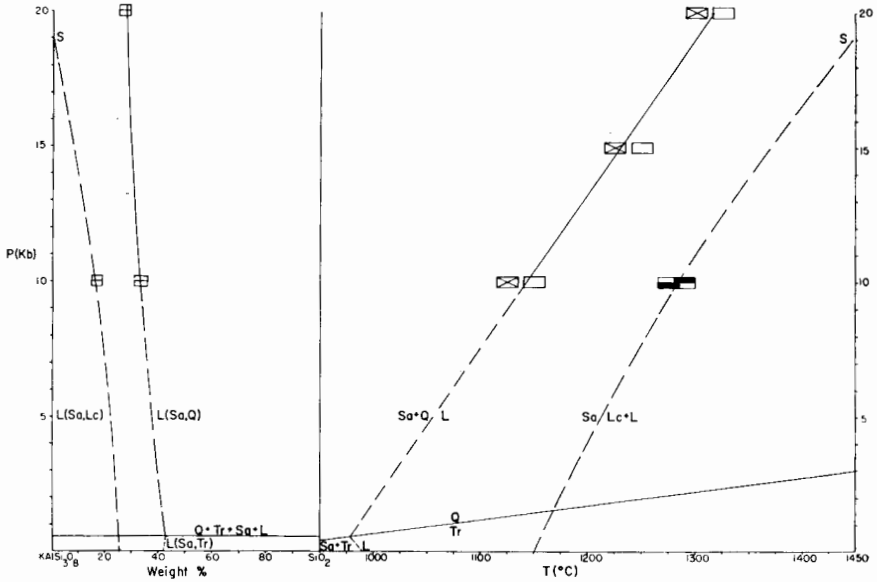

Fig. 3. Pressure–temperature–composition diagram: $KAlSi_3O_8$–SiO_2. The P-T projection is shown at the right. Experimental data points (table 2) pertaining to the Sa + Q = L and Sa = Lc + L univariant equilibria are shown as boxes on the figure: boxes with crosses—Sa + Q, open boxes—liquid present in addition to Sa, Q, or both, box shaded below—Sa + L, box shaded above—Lc + L. Point S is the singular point on the Sa + Lc + L univariant curve discussed by Lindsley (1967). The Q = Tr reaction is from Tuttle and England (1955) and Kennedy and others (1962). The P-X projection shown at the left illustrates the postulated variation in composition of the univariant liquids that coexist with Sa + Lc, Sa + Q, or Sa + Tr. All relationships below 10 kb are extrapolated to correlate with the 1 atm data of Schairer and Bowen (1955). The size of the symbols in both P-T and P-X corresponds to the relative uncertainty in the data. Abbreviations used are: Q, quartz; Tr, tridymite; Lc, leucite; Sa, sanidine; and L, liquid.

P_{H_2O} in the H_2O-undersaturated liquids and P_{total} must be considered as independent variables. These two variables are independent in the sense that one, P_{H_2O} (or partial pressure of H_2O in the melt) is pertinent to homogeneous equilibria, and the other, P_{total}, is of concern in the analysis of heterogeneous equilibria. At this point it should be emphasized that figure 5B is incorrect, and that 5C is valid in terms of the available data. In the system $KAlSi_3O_8$–SiO_2–H_2O the same relationship holds at P_t = 10 kb. This is shown in figure 6A where the dashed curve has the same significance as the curve in figure 5A. The 10 kb diagram for the system $NaAlSi_3O_8$–SiO_2–H_2O (fig. 5C) is reproduced in figure 6B for direct comparison.

Although data in the dry system was not obtained at pressures below 8 kb, extrapolations to lower pressures regarding the eutectic liquid composition, as shown in figures 1 and 3, are possible.

Figures 6C and 6D show possible diagrams at P_t = 5 kb for the systems $KAlSi_3O_8$–SiO_2–H_2O and $NaAlSi_3O_8$–SiO_2–H_2O respectively as

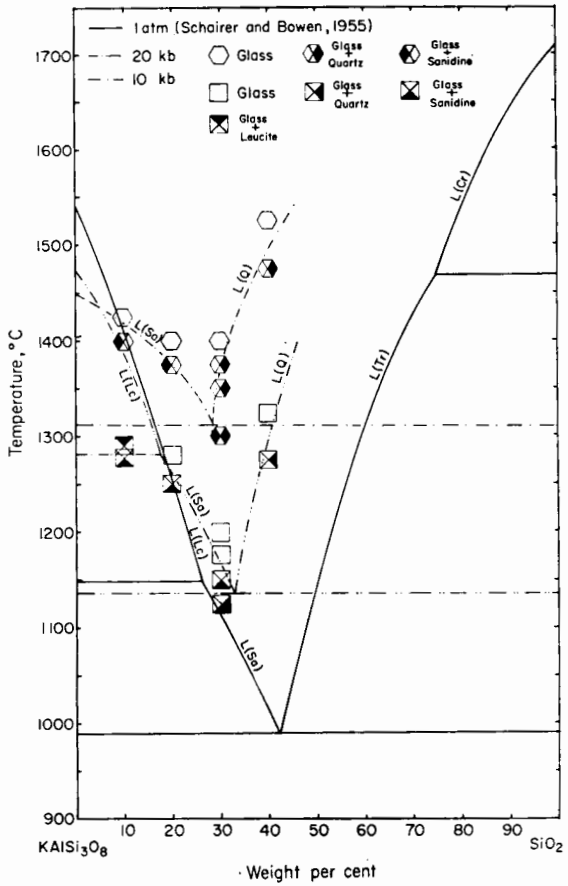

Fig. 4. Isobaric (± 0.2 kb) temperature–composition diagrams for the system $KAlSi_3O_8$–SiO_2. L(Cr), L(Tr), L(Q), L(Sa), and L(Lc) denote the liquidus curves at each pressure and the primary phase present as, respectively, cristobalite, tridymite, quartz, sanidine, and leucite.

do figures 6E and 6F at $P_t = 1$ kb. Figures 6C to 6F represent long-range extrapolations of the available data and should be treated in a qualitative fashion. They do serve to illustrate the general relationship and again indicate that P_{H_2O} and P_{total} must be treated as independent variables.

In the diagrams given in figures 6C to 6F, certain complexities concerning the coexistence of various polymorphs of silica with ternary liquids have not been shown in view of the lack of data. The boundary curve denoting the composition of liquids coexisting with leucite and sanidine is shown in figures 6A, C, E. This boundary curve crosses the $KAlSi_3O_8$–H_2O join at $P \cong 2.7$ kb (Goranson, 1938), generating a singular point on the univariant P-T curve involving sanidine, leucite, liquid, and

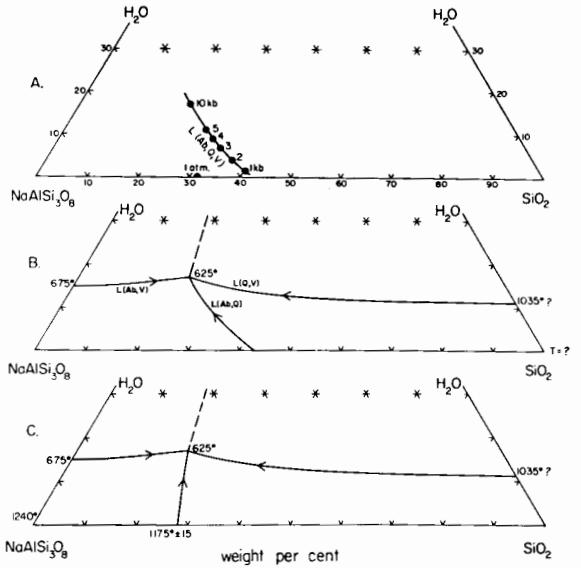

Fig. 5. Phase relations in the system $NaAlSi_3O_8$–SiO_2–H_2O.

A. Polythermal, polybaric composition diagram showing the variation in composition of univariant liquids coexisting with albite, quartz, and an aqueous vapor phase. One to four kb points from Tuttle and Bowen (1958), 5 to 10 kb points from Luth, Jahns, and Tuttle (1964). The 1 atm point is from Schairer and Bowen (1956) and refers to equilibria involving tridymite, not quartz.

B. Polythermal, composition diagram at 10 kb, showing the variation in composition of bivariant liquids that coexist with: Ab, V; Q, V; and Ab, Q, assuming that pressure affects the equilibria only through the variable P_{H_2O}. As discussed in the text, this diagram is not consistent with the available data.

C. Polythermal, composition diagram at 10 kb, which is similar to 5B, but is consistent with the data.

vapor. At pressures below the singular point the reaction is Sa + V = Lc + L and at pressures above the singular point the univariant reaction is Sa + Lc + V = L (see Scarfe, Luth, and Tuttle, 1966). Lindsley (1967) has shown that sanidine melts incongruently at pressures less than 19 kb in the binary system. Then a silica-undersaturated bulk composition in the system $KAlSiO_4$–SiO_2–H_2O could still produce, on fractional crystallization, a silica-oversaturated residual liquid at pressures greater than 2.7 kb if the H_2O content is sufficiently low.

H_2O-UNDERSATURATED LIQUIDS IN THE SYSTEM $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O

Of principal concern are the phase relations involving an H_2O-undersaturated liquid that coexists with either quartz and an alkali feldspar, or two alkali feldspars. The major features may be illustrated, in schematic fashion, at 10 kb. At this pressure there is some data overlap between the "dry" and "wet" studies.

Figure 7 is a schematic diagram illustrating possible phase relations in a part of the quaternary system at 10 kb. The saturation surface at

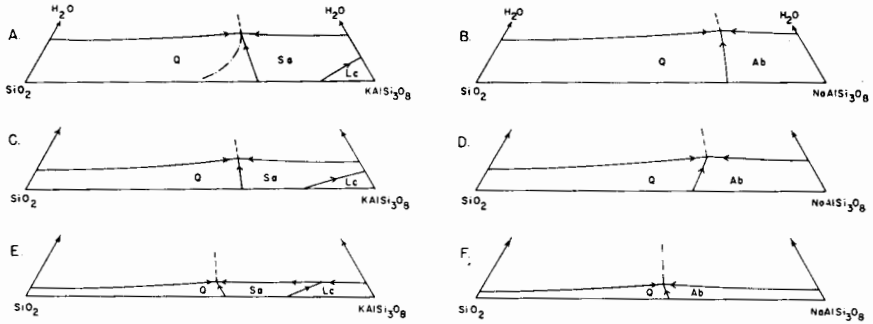

Fig. 6. Isobaric polythermal phase relations in the systems $KAlSi_3O_8$–SiO_2–H_2O and $NaAlSi_3O_8$–SiO_2–H_2O. These diagrams are schematic in large part and show the possible relations involving H_2O-saturated liquids coexisting with quartz and an aqueous vapor phase (dashed line) or either alkali feldspar and a vapor phase. Also shown are possible phase relations involving H_2O-undersaturated liquids. The direction of decreasing temperature on the boundary curves is shown by arrows.

A. $KAlSi_3O_8$–SiO_2–H_2O, P_t = 10 kb. The dash-dot curve has the same significance as the curve shown in figure 5A, Tuttle and Bowen (1958), Shaw (1963, and Luth, Jahns, and Tuttle (1964).

B. $NaAlSi_3O_8$–SiO_2–H_2O, P_t = 10 kb.

C. $KAlSi_3O_8$–SiO_2–H_2O, P_t = 5 kb.

D. $NaAlSi_3O_8$–SiO_2–H_2O, P_t = 5 kb.

E. $KAlSi_3O_8$–SiO_2–H_2O, P_t = 1 kb.

F. $NaAlSi_3O_8$–SiO_2–H_2O, P_t = 1 kb.

this pressure is divided into three portions:[2] L(Q, V), L(Ab*, V), and L(Or*, V). H_2O-undersaturated liquids exist below this surface. There are two surfaces in the H_2O-undersaturated region that concern us.

The first of these surfaces, the L(Ab*, Or*) surface, is limited by the boundary curves; L(Ab*, Or*) in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–H_2O, and L(Ab*, Or*, V), L(Ab*, Or*, Q) in the quaternary system and by a fourth curve which extends from the termination of the L(Ab*, Or*) curve in the ternary system into the tetrahedron. The latter curve denotes a series of quaternary liquids which can coexist with a critical phase, the alkali feldspar at the crest of the solvus. If the alkali feldspar crystalline solutions are limited to a binary series between $NaAlSi_3O_8$ and $KAlSi_3O_8$ this curve is isothermal. The termination of the isothermal curve within the tetrahedron is at a point that denotes the composition of a liquid that coexists with a critical phase (alkali feldspar) and quartz.

The second surface, the L(AbOr*, Q), of interest in the H_2O-undersaturated region is a slightly more complex surface in that it is divided into two portions at temperatures below that of the critical temperature of the alkali feldspar solvus and is continuous at temperatures above this value. This surface originates on the saturation surface with the two boundary curves L(Q, Ab*, V) and L(Q, Or*, V) which meet at the eutectic L(Q, Ab*, Or*, V). These two boundary curves meet the

[2] The notation employed is that of Dr. J. W. Greig (personal commun., 1964). Ab* and Or* refer to binary crystalline solutions enriched in albite or orthoclase respectively. When the end members are referred to, the asterisk is omitted.

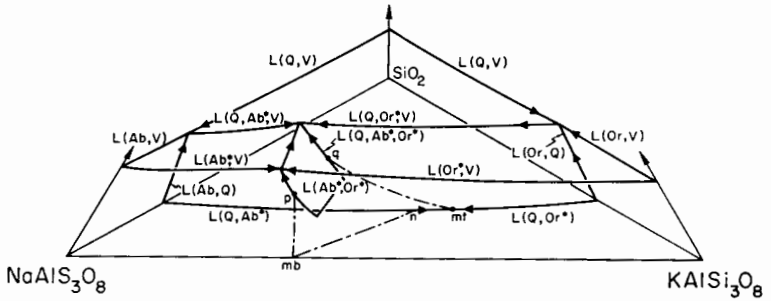

Fig. 7. Schematic isobaric-polythermal tetrahedron at 10 kb for the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O. The nomenclature and significance of the various elements are discussed in the text. Apex of tetrahedron is H_2O.

L(Q, Ab) and L(Q, Or) boundary curves in the systems $NaAlSi_3O_8$–SiO_2–H_2O and $KAlSi_3O_8$–SiO_2–H_2O respectively, which also serve to limit the extension of the L(AbOr*, Q) surface in the ternary hydrous systems. The boundary curve in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2 which defines liquids coexisting with quartz and an alkali feldspar provides a termination of the base of the tetrahedron for this surface. This surface is divided into two parts by its juncture with the previously described L(Ab*, Or*) surface. The intersection of these two surfaces corresponds to the L(Ab*, Or*, Q) boundary curve described previously.

It is not possible to discuss in detail crystallization paths of H_2O-undersaturated liquids in the absence of pertinent data. However, several controlling features may be pointed out. The importance of the two surfaces, L(Ab*, Or*) and L(AbOr*, Q), discussed previously is obvious concerning crystallization of quartz and an alkali feldspar, two alkali feldspars, or quartz and two alkali feldspars from an H_2O-undersaturated liquid. Of particular importance in the analysis of both equilibrium and fractional crystallization in ternary systems are fractionation curves, specifically the unique fractionation curve (Osborn and Schairer, 1941, p. 139). Schematic unique fractionation curves in the two ternary systems $NaAliSi_3O_8$–$KAlSi_3O_8$–SiO_2 and $NaAlSi_3O_8$–$KASi_3O_8$–H_2O are shown respectively as *mb-n* and *mb-p* in figure 7. Osborn and Schairer (1941) discuss the importance of the unique fractionation curve in governing the distribution of other fractionation curves. In the quaternary system there will be another unique fractionation curve on the L(AbOr*, Q) surface, extending from the ternary minimum, *mt*, to some point on either the L(Ab*, Or*, Q) or L(Q, Or*, V) boundary curve. In figure 7 the former case is presented where the quaternary unique fractionation curve terminates at *q*. It seems reasonable that a unique fractionation curve such as *mt-q* will be of major importance in consideration of both equilibrium and fractional crystallization of H_2O-undersaturated granitic liquids.

Although the isobaric diagrams at pressures less than 10 kb are based on even less data than figure 7, diagrams may be constructed showing *possible relations*. Rather than use full tetrahedra to illustrate the

features at other pressures, the surfaces L(Q, V), L(Ab*, V), L(Or*, V), L(Ab*, Or*), and L(AbOr*, V) are projected onto the base of the tetrahedron from the H_2O apex. The appropriate surfaces in the quaternary system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O shown in figure 7 are given in this type of projection in figure 8A, at 10 kb. Figure 8B represents possible relations at 5 kb. The L(Ab*, Or*) surface is somewhat reduced in size at 5 kb. On further decrease in pressure this surface will disappear when no quaternary liquids coexist with a critical feldspar. This has taken place between 5 kb and 1 kb as illustrated in figure 8C, at 1 kb. The unique fractionation curve is shown in each of the three projections as a dash-dot line. The origin of the unique fractionation curve on the base of the tetrahedron is controlled by the position of the minimum on the ternary boundary curve. In figures 8A, B, C this origin is located schematically. If the case is as shown in these three diagrams, then the projections of these unique fractionation curves (fig. 8D) pass through the maxima in abundance of analyzed granitic (greater than 80 percent normative ab + or + Q) rocks, Tuttle and Bowen, 1958, p. 79).

Since the unique fractionation curves place severe restrictions on the distribution of other fractionation curves in the ternary systems and on the various surfaces in the quaternary system, their experimental location is of considerable importance. This information is not available at present, although the problem is under investigation.

H_2O IN GRANITIC MAGMAS

The general relationships postulated and discussed in the previous sections are based on an assumption that granitic magmas are rarely saturated with respect to H_2O throughout their crystallization interval. On the basis of a study involving H_2O-undersaturated as well as H_2O-saturated liquids in the system diopside–anothite–H_2O Yoder (1965) reached similar conclusions concerning basaltic magmas and suggested that they were applicable to granitic magmas. There are several other independent lines of reasoning that bear upon this assumption.

Ross (1964), Lipman (1966), McBirney (1963), Tuttle and Bowen (1958, p. 78), Wones and Eugster (1965), and White (personal commun., 1967) have suggested on the basis of a variety of lines of evidence that the H_2O content of the magmas that produced obsidians and rhyolites is less than 2 wt percent as an upper limit and probably on the order of 1 wt percent. Tuttle and Bowen's data (1958, p. 57-58) and those of Goranson (1938) and Burnham and Jahns (1962) suggest a pressure of less than 500 bars, if the melts which produced such rocks were saturated with respect to H_2O. The H_2O content of a plutonic granitic magma may be quite different. However, given the generalized dehydration series noted with increasing metamorphic grade, it seems unlikly that a sufficient amount of free H_2O is available in an anatectic environment to saturate a large body of granitic magma. If a free aqueous vapor phase is present in the antectic environment, the initial melt will be saturated with respect to H_2O. However, there is no necessity that it remain

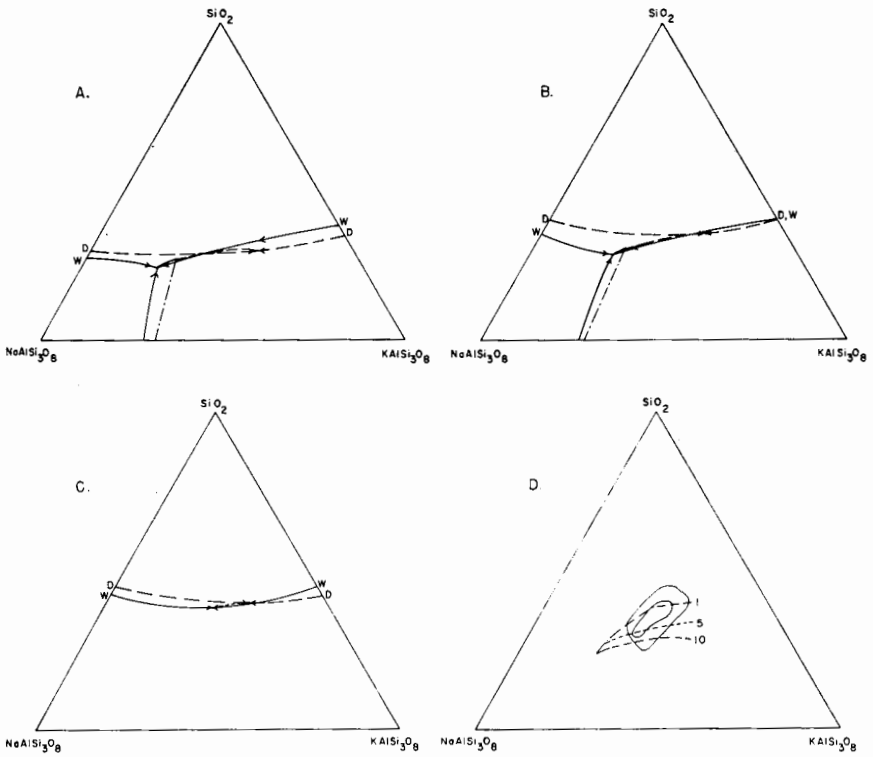

Fig. 8. Possible phase relations in the system $NaAlSi_3O_8$–$KAlSi_2O$–SiO_2 and the relationship to natural granites. Largely hypothetical.

A. Ten kb projection of the H_2O-saturated liquidus onto the anhydrous base of the tetrahedron and phase relations in the H_2O-undersaturated region. The dashed curve D-D represents equilibria in the anhydrous system and the minimum on the boundary curve. The solid curves with arrows show equilibria in the presence of a vapor phase. The dash-dot curve extends into the tetrahedron from the $NaAlSi_3O_8$–SiO_2–H_2O face and denotes the projection (anhydrous) composition of quaternary liquids which coexist with a critical alkali feldspar. The solid curve shown terminating at the quaternary eutectic, without an arrow, is the anhydrous projection of the L(Q, Ab*, Or*) curve (fig. 7). The dashed curve extending from the ternary minimum to the projection of the L(Q, Ab*, Or*) curve corresponds to the anhydrous projection of the unique fractionation curve *mt-q* shown in figure 7.

B. Five kb projection of the H_2O-saturated liquidus onto the anhydrous base of the tetrahedron and phase relations in the H_2O-undersaturated region. The symbolism and general features are similar to those discussed in connection with 8A.

C. One kb projection of the H_2O-saturated liquidus onto the anhydrous base of the tetrahedron and phase relations in the H_2O-undersaturated region. Curve D-D is on the anhydrous base, and curve W-W gives the anhydrous projection of H_2O-saturated quaternary liquids which coexist with quartz, vapor, and an alkali feldspar. The unique fractionation curve is shown extending from the ternary minimum to the quaternary minimum, a special case.

D. The relationship of granitic compositions to the *postulated* unique fractionation curves on the L(Q, Ab*, Or*) surface at 10, 5, and 1 kb. The closed contours are from Tuttle and Bowen (1958, p. 79) and represent the >3, and >6 percent contours for the 571 analyzed plutonic rocks with >80 percent normative ab + Or + Q. The dash-dot curve is the polythermal-polybaric trace of the minimum-eutectic trend from 1 to 10 kb.

saturated as temperature continues to increase. It should be noted that a granitic magma forming in an anatectic environment will tend to act as a "sink" for free H_2O, thus tending to desiccate the surrounding rocks (also see Lundgren, 1966). The bulk compositions of the zoned pegmatites (Luth, Jahns, and Tuttle, 1964) tend to be more closely related to the H_2O-saturated minimum-eutectic trend than do the majority of granites. The same feature holds for the aplites in general. It has been suggested by many authors that a free vapor phase plays an important role in the genesis of both pegmatites and aplites.

If the anatectic granitic magma is H_2O-undersaturated as a general case, one of the more puzzling situations involving the application of experimental data to problems of the development of the granitic rocks may be considered. This concerns the upward migration of an anatectic magma in the Earth's crust after generation by partial or complete melting of preexisting rocks. The first melt to appear would be expected to be of granitic composition for a wide variety of rock types (Wyllie and Tuttle, 1961; Winkler, 1965). If the magma is saturated with respect to H_2O, it is possible for movement to take place upward in the crust (to a lower pressure regime) only over a very limited range, unless large amounts of superheat are postulated, or it is assumed that the upward rise of the magma is accompanied by an increase in temperature. This is a consequence of the negative P-T slope observed for the "granite" solidus reaction. However, if the anatectic environment is relatively dry, then the granitic melt might well be undersaturated with respect to H_2O. In order to obtain a significant amount of magma, then temperatures would be considerably greater than that of the solidus and possibly much higher than that of the H_2O-saturated liquidus. Seemingly this requires considerable superheat; however, most authors refer to superheat as an increase in temperature over the liquidus value, not the solidus. In general liquidus temperatures increase rapidly with increasing distance from the saturation surface. Consequently a given magma composition (in terms of ab, or, and Q) may seem to be superheated with reference to the saturation surface but may not be superheated when the H_2O content and true liquidus temperature are considered. Since this magma may exist at a temperature significantly greater than the solidus at the pressure (depth) of generation, it is possible for large scale upward migration of the melt to occur isothermally or even with a decrease in temperature.

In the previous discussion the role of amphibole and mica as reservoirs for H_2O has not been considered. We have been concerned only with free H_2O available for the melt. Studies by Wones and Eugster (1965), Luth (1967), Boyd (1959), Ernst (1961, 1962), and others suggest that biotites and amphiboles may coexist with quartz-alkali feldspar melt (hydrous, but not necessarily saturated) over a wide pressure-temperature range. Extrapolation of Evans' (1965) and Velde's (1966) data to pressures of the order of 5 to 10 kb suggests that muscovite may also coexist with a "granitic" melt in the anatectic environment. Given

appropriate conditions it is possible that crystallization of hydrous minerals such as biotite, amphibole, and muscovite may actually deplete the magma in H_2O. It should be explicitly noted that the presence of these hydrous minerals in a granite does not necessarily imply that a vapor phase was present at the time of crystallization. The only conclusion that can be drawn is that H_2O was available for structural incorporation in that particular phase. Little can be said as to whether the H_2O was available in a H_2O-undersaturated magma or in a free vapor phase.

Of fundamental importance in the analysis of a specific granitic body is the determination of what portion of the crystallization history took place in the presence of a free vapor phase. Fabric features such as miarolitic cavities, development of aplites and pegmatites in the granite and country rocks, and a wide contact metamorphic aureole all suggest the presence of a vapor phase. However, none of these features yield direct information on what portion of the crystallization history took place in the presence of a free vapor phase.

In the absence of data in the H_2O-undersaturated region, it has been assumed by most investigators in the application of experimental studies on this quaternary system to the origin and development of specific granites that either (1) a free vapor phase was present throughout the crystallization history or (2) pressure affects the equilibria only through the variable P_{H_2O}. Unfortunately in most cases the assumptions are implicit rather than explicitly stated. The analogue of this assumption in the ternary system is assuming that the case given by figure 5B is valid.

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