

MELTING RELATIONSHIPS OF JADEITE AND ALBITE TO 45 KILOBARS WITH COMMENTS ON MELTING DIAGRAMS OF BINARY SYSTEMS AT HIGH PRESSURES

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ABSTRACT

Melting relations for jadeite and albite compositions were studied experimentally. From these data, the melting relations in the system $\text{NaAlSi}_3\text{O}_8\text{-SiO}_2$ involving jadeite, albite, quartz and nepheline were deduced. In order to obtain the correct phase diagram, we have derived all of the theoretically possible types of P - T - X diagrams for melting at high pressures in binary systems with four solid phases of different compositions and identified the type that fits our system. Details that are too fine to observe experimentally must include a eutectic between jadeite and albite and the incongruent melting of albite to jadeite plus quartz.

INTRODUCTION

Phases in the binary system $\text{NaAlSi}_3\text{O}_8\text{-SiO}_2$ include the minerals jadeite ($\text{NaAlSi}_2\text{O}_6$), albite ($\text{NaAlSi}_3\text{O}_8$), nepheline and carnegieite (NaAlSiO_4), the various polymorphs of silica, and complete binary liquids. There is possibly another nepheline phase called "N(1)" by Boyd and England (1956) and "nepheline II" by Robertson, Birch and MacDonald (1957) which is either stable or metastable at high pressures. This chemical system is interesting geologically because the P - T limits of stability of albite and jadeite and their breakdown products set P - T limits on the conditions that existed where these phases occur naturally in the blueschist facies. In addition, jadeite composition is an important component of pyroxenes under conditions corresponding to the upper mantle where eclogites are stable and basaltic magmas are generated.

EXPERIMENTAL

Starting materials. Glasses of jadeite and albite compositions were made by Dr. J. F. Schairer and were used directly for establishing the subliquidus boundaries. The glasses also were crystallized in bulk under conditions needed to produce various subsolidus starting assemblages.

The starting material was ground under alcohol in an agate mortar for several hours to an average grain size of 10-20 μm . It was essential to dry the ground material in nitrogen at temperatures of 900° to 1100°C for 30 to 45 minutes immediately before each experiment. The sample was still hot (at least 100°C) as it was introduced into the apparatus. This strict drying procedure was necessary because even the slightest amount of moisture causes a drastic lowering of the melting temperatures in this system making it impossible to untangle the dry relationships.

Apparatus. All experiments were of the quenching type. The single-stage, piston-cylinder apparatus of Boyd and England (1960) was used with modifications (Bell and England, 1967). The frictional corrections were not well understood when the present experiments were performed, and the "in-stroke/out-stroke" procedures established by Boyd, Bell, England and Gilbert (1966), Bell and England (1967), and Richardson, Bell and Gilbert (1968) were not employed. Instead the intended pressure was first applied. The temperature then was raised to the desired value (which lowered the pressure slightly), and the pressure readjusted. The results probably are not greatly in error—new, supported carbide pressure vessels were used in all experi-

ments with the consequence that friction corrections can be neglected (Bell and England, 1967).

Temperatures were measured with a platinum vs platinum 10 percent rhodium thermocouple. Although the temperatures were not corrected, it may be necessary to apply a correction for the effect of pressure on the thermoelectric effect, using a procedure outlined elsewhere (Beckett, Lloyd, Boyd and Bell, 1967). The correction would be of the order of +0.5°/kbar at 1000°C and +1.0°/kbar at 1400°C but has not been applied because investigations of the pressure correction are still in progress.

The temperature gradients in the high-pressure cell were calibrated by Boyd and England (1960). Frequent checks and comparisons were made in the present study by using a multiple thermocouple array. The maximum gradient observed was 10°C. The reported pressures do not contain any corrections for friction or strength of the material. Pressure precision is $\pm 1/2$ kbar. Temperature uncertainty is $\pm 10^\circ\text{C}$.

Detection of reaction. The various boundaries were determined by annealing samples consisting of glass or previously crystallized material and observing the first appearance of new phases and disappearance of others. Albite and jadeite melt in an extremely sluggish way and complete reaction was not observed within 15°C of the boundary. For subsolidus reactions reversible equilibria were located by using seeded assemblages (consisting of 10 percent seeds by weight) because these reactions were very sluggish also.

Experimental products. In samples containing a sufficient quantity of crystalline phases to diffract X-rays, this method was used to identify the crystalline phases. Table 1 gives d and cell dimensions of synthetic albite and jadeite. In samples consisting largely of glass the solid phases were identified by microscopic observations: quartz and coesite were always sufficiently coarse-grained that their indices of refraction could be measured; jadeite and albite were always less than 5 μm mean diameter but could be distinguished from their mean index; nepheline could be identified only by X-ray diffraction. The presence or absence of a trace of liquid was also identified by microscope. Glasses of albite and jadeite composition produced in runs above the liquidus were checked by the electron microprobe against the original glasses made by Schairer and the compositions were found to agree within the limits of the method (2.0 percent of the amount present). There was no evidence of any solid phases forming during quenching in any runs.

RESULTS

Jadeite composition. Figure 1 shows the results obtained for jadeite composition. Above a point marked S_{Jd} at

TABLE 1. UNIT-CELL PARAMETERS AND d REFINED BY LEAST SQUARES^a

	Parameter	Value	h	k	l	d (obs.), Å	d (calc.), Å
Jadeite synthesized from glass at 37.5 kbar, 1300°C. ^b	a	9.424(4) Å	0	6	1	1.3704	1.3715
	b	8.561(2)	4	4	0	1.5497	1.5495
	c	5.218(3)	1	5	0	1.6822	1.6819
	β	107.56°(4)	5	1	0	1.7583	1.7586
	Volume	401.3(4) Å ³	0	4	1	1.9669	1.9660
			-3	3	1	2.0664	2.0664
			3	3	0		2.0660
			1	1	2	2.1587	2.1583
			-3	1	2	2.2025	2.2044
			3	1	1		2.2030
			2	2	1	2.4143	2.4144
			-1	3	1	2.487	2.484
			-3	1	1	2.828	2.828
			3	1	0		2.827
			-2	2	1	2.921	2.917
			2	2	0	3.099	3.099
			0	2	1	3.245	3.245
			0	2	0	4.285	4.280
		-1	1	1	4.351	4.346	
Nepheline (coexisting with albite) synthesized from glass of jadeite composition at 20 kbar, 1100°C.	a	9.992(6) Å	2	0	3	2.3429	2.3429
	c	8.36(1)	3	1	0	2.403	2.400
	Volume	723(1) Å ³	2	2	0	2.499	2.498
			2	1	2	2.575	2.576
			3	0	0	2.893	2.885
			2	0	2	3.006	3.006
			2	1	1	3.040	3.046
			2	1	0	3.264	3.271
			2	0	1	3.837	3.843
			0	0	2	4.187	4.180
			2	0	0	4.316	4.327
Albite ^c (coexisting with nepheline) synthesized from jadeite at 20 kbar, 1100°C.	a	8.12(7) Å	1	3	1	2.88	2.86
	b	12.89(7)	1	-3	1	3.01	3.00
	c	7.10(6)	2	2	0	3.12	3.14
	α	92.5(9)°	0	0	2	3.19	3.19
	β	116.1(5)	0	4	0	3.20	3.22
	γ	90.3(8)	-1	1	2	3.36	3.38
	Volume	667(12) Å ³	1	1	-2	3.48	3.46
			1	3	0	3.65	3.66
			1	-3	0	3.75	3.74
			1	-1	1	3.84	3.87
			2	0	-1	4.03	4.02

^a X-ray diffraction data were obtained during Cu radiation with Ni filter and a NaF internal standard. $\text{CuK}\alpha = 1.54178$ Å except for 2θ values of jadeite larger than 37.0° , where $\text{CuK}\alpha_1 = 1.54051$ Å. Some graphite was present in all samples. Standard deviations given in parentheses.

^b The jadeite pattern was indexed and the cell refined by L. W. Finger.

^c Albite synthesized in this study produced poor X-ray diffraction patterns, resulting in a poor refinement of the unit cell. The calculated cell parameters are much nearer those of high albite than those of low albite, as one would expect. However, the large standard deviations preclude stating that it is definitely high albite.

about 30 kbar, jadeite melts congruently but between 25 and 29 kbar, it melts incongruently to albite + liquid. Below 25 kbar jadeite is no longer stable on the liquidus, being replaced by albite + nepheline. This pair of phases melts to albite + liquid down to at least 10 kbar. At one atm, Greig and Barth (1938) found a eutectic in the system $\text{NaAlSi}_3\text{O}_8$ - $\text{NaAlSi}_3\text{O}_8$ between albite and nepheline with jadeite composition falling on the nepheline side of the eutectic, and later work by Schairer and Bowen (1947) and Schairer and Yoder (1960) agrees with this.

Since at low pressures the jadeite composition melts to nepheline + liquid but at high pressures to albite + liquid, the eutectic composition must cross the jadeite composition moving toward nepheline with higher pressures as predicted by Robertson, Birch, and MacDonald. The pressure of this crossing is not known but is shown as 2.5 kbar in Figure 1.

The intersection of the eutectic albite + nepheline \leftrightarrow liquid with the reaction of jadeite \leftrightarrow albite + nepheline must produce an invariant point (I_{jd}) involving all four

phases. This point was located approximately by Robertson, Birch, and MacDonald (1957) in apparatus using nitrogen as the pressure medium. They reversed the reaction jadeite \leftrightarrow nepheline + albite in the range 600° to 1100°C using minerals as starting materials but because they could not obtain very close limits (about 3.5 kbar at 700°C) by this method they also used synthetic jadeite glass as well as synthetic analcite for starting materials.

In addition to runs resulting in either jadeite or albite + nepheline a number of their runs produced all three phases. Because most of these runs fell in the jadeite field as established by using natural mineral as starting materials, they finally drew their curve for jadeite \leftrightarrow albite + nepheline ($P = 1000 + 18.5 T$) on the assumption that jadeite always formed within its field of stability while nepheline and albite could form metastably on the jadeite side of the reaction.

Newton and Kennedy (1968) using natural minerals as starting materials located two brackets on the jadeite \leftrightarrow albite + nepheline curve. Although their curve diverges from the curve of Robertson, Birch and MacDonald (1957), their data are in reasonable agreement with it. Newton and Kennedy's 700° bracket straddles the curve of Robertson, Birch and MacDonald and their 800° bracket misses it by only 0.3 kbar.

Boettcher and Wyllie (1968b) encountered problems of metastable crystallization of albite, nepheline and analcite from glass starting materials but like Robertson, Birch and MacDonald, they assumed jadeite formed only in its stability field and located two brackets, one at 620° and one at

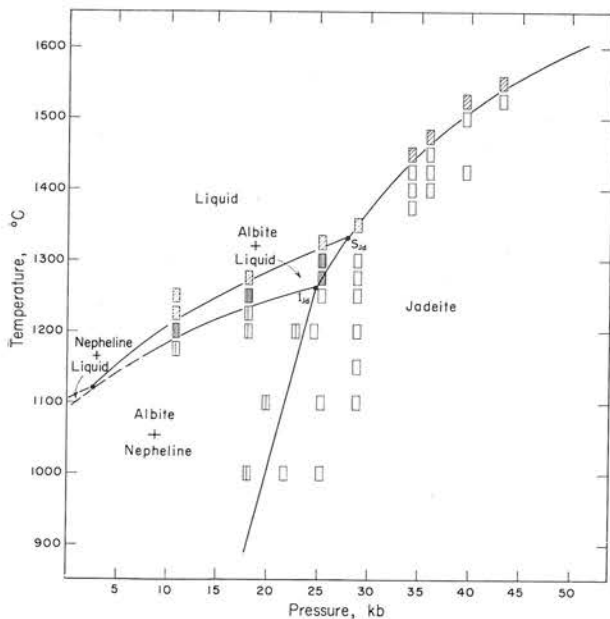


FIG. 1. Results of experiments for jadeite composition. The boundary between albite + nepheline and albite + liquid is from Luth's (1968) work on the albite + nepheline eutectic. S_{Jd} and I_{Jd} are explained in text.

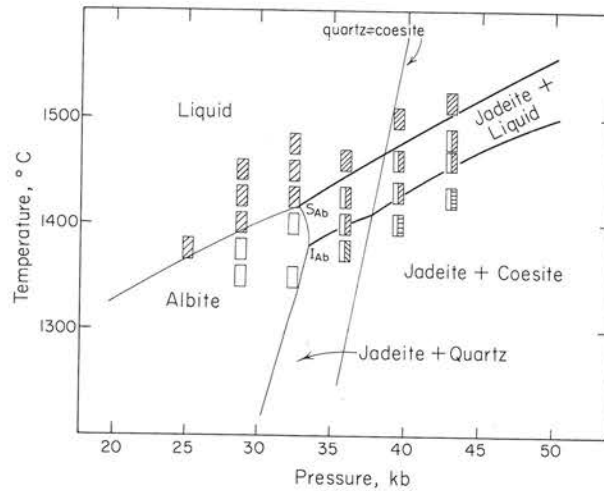


FIG. 2. Results of experiments for albite composition. The congruent part of the albite melting curve is after Boyd and England (1963). The curve between S_{Ab} and I_{Ab} is based on unpublished data (not shown) of Boyd, S_{Ab} and I_{Ab} are explained in text.

800°C. The curve of Robertson, Birch and MacDonald is about 0.5 kbar above their 620° bracket and about 1.0 kbar above their 800° bracket. The low-pressure sides of both brackets are based on the breakdown of crystalline jadeite but the high-pressure sides seem less certain. The high-pressure side of their 620° bracket is based on (1) runs using glass as starting material, and (2) one run that started with crystalline nepheline plus albite and finished with the same plus analcite, liquid, and questionable jadeite ($Jd?$). The high-pressure limit of their 800° bracket was based on a run starting with albite glass which produced all three phases, albite, nepheline, and jadeite.

In view of the foregoing, we will use the curve of Robertson, Birch and MacDonald because at 800°C and below, it lies between the data of Newton and Kennedy (1968) and those of Boettcher and Wyllie (1968b), is based on the only data between 800° and melting, and when extrapolated fits with our data locating the invariant point. The curve of Boettcher and Wyllie also passes through our invariant point (I_{Jd}) because they used it as the high temperature end of their curve, but the curve of Newton and Kennedy passes above the point by 2.5 kbar.

J. F. Schairer (oral commun.) believes that nepheline may have a composition that is a little off our binary at one atmosphere because he has found it impossible to crystallize nepheline from glass without forming β -alumina. However, we did not observe any β -alumina in our runs.

Albite composition. Figure 2 shows the results for albite composition to be a somewhat distorted mirror image of those for jadeite. An invariant point (I_{Ab}) must exist where the two curves meet that mark the high temperature and low pressure limits of the jadeite plus quartz field. One

TABLE 2. EXPERIMENTS ON ALBITE AND JADEITE COMPOSITIONS

Temp. (°C)	Pressure (kbar)	Time (hr)	Reactants	Products
Jadeite Composition				
1000	18.0	3.0	Jd(+Ab+Ne)	Ab+Ne(+Jd)
1000	21.5	3.0	Ab+Ne	Ab+Ne+Jd
1000	25.1	3.0	Ab+Ne	Ab+Ne+Jd
1100	19.5	2.5	Jd(+Ab+Ne)	Ab+Ne
1100	25.1	2.5	Ab+Ne	Ab+Ne+Jd
1100	28.7	2.5	Ab+Ne	Ab+Ne+Jd
1150	28.7	3.0	Ab+Ne	Ab+Ne+Jd
1175	10.7	2.0	G	Ab+Ne
1200	10.7	1.0	Ab+Ne	Ab+G
1200	18.0	2.0	G	Ab+Ne
1200	22.5	5.0	Jd(+G)	Ab+Ne(+G)
1200	24.5	5.0	Ab+Ne	Ab+Ne+Jd
1200	28.7	2.3	Ab+Ne	Ab+Ne+Jd
1225	10.7	2.0	Ab+Ne	G+(Ab)
1225	18.0	2.0	Ab+Ne	Ab+Ne
1250	10.7	1.0	Ab+Ne	G+(Ab)
1250	18.0	1.4	Ab+Ne	Ab+G
1250	25.1	1.0	Ab+Ne	Ab+Ne+Jd
1250	28.7	1.3	Ab+Ne	Ab+Ne+Jd
1275	18.0	1.0	Ab+Ne	G+(Ab)
1275	25.1	1.0	Jd	Ab+G
1275	28.7	3.0	Ab+Ne	Ab+Ne+Jd
1300	25.1	3.5	Ab+Ne	Ab+G
1300	28.7	1.0	Ab+(Ne)+G	Jd+(Ab+G)
1325	25.1	1.0	Ab+Ne	G
1350	28.7	1.0	Jd	G
1375	34.0	2.0	Jd	Jd
1400	34.0	2.0	G	Jd+(G)
1400	36.0	1.3	Jd	Jd
1425	34.0	1.0	G	Jd+(G)
1425	36.0	0.5	G	Jd
1425	39.5	1.0	G	Jd
1450	34.0	1.0	Jd	G
1450	36.0	1.0	G	Jd+(G)
1475	36.0	1.0	G	Jd
1500	39.5	1.0	G	Jd
1525	39.5	1.0	Jd	G+(Jd)
1525	43.0	1.0	G	Jd
1550	43.0	1.0	Jd	G
Albite composition				
1350	28.7	0.5	G	Ab
1350	32.3	0.5	G	Ab
1375	25.1	1.0	Ab	G+(Ab)
1375	28.7	0.5	G	Ab
1375	35.8	1.0	Jd+Q+C	Jd+Q
1400	28.7	0.5	Ab	G+(Ab)
1400	32.3	1.0	G	Ab
1400	35.8	1.0	Jd+Q+C	Jd+G
1400	39.5	1.0	Jd+Q+C	Jd+C
1425	28.7	1.0	Ab	G
1425	32.3	0.7	Ab	G
1425	35.8	1.0	Jd+C+Q	Jd+G
1425	39.5	1.0	Jd+C+Q	Jd+G
1425	43.0	1.0	Jd+C+Q	Jd+C
1450	28.7	1.0	Ab+(G)	G
1450	32.3	1.0	Ab	G
1460	35.8	1.0	Jd+Q+C	G+(Jd)
1460	39.5	1.0	Jd+Q+C	Jd+G
1460	43.0	1.0	Jd+Q+C	Jd+G

TABLE 2—(Continued)

Temp. (°C)	Pressure (kbar)	Time (hr)	Reactants	Products
1475	32.3	1.0	Ab	G
1480	43.0	1.0	Jd+Q+C	Jd+G
1500	39.5	1.0	Jd+Q+C	G
1515	43.0	1.0	Jd+Q+C	G

Abbreviations used: Ab=albite, C=coesite, G=glass, Jd=jadeite, Ne=nepheline, Q=quartz, ()=phase present in trace amounts.

of these curves is the jadeite plus quartz eutectic and the other is the curve where albite \leftrightarrow jadeite + quartz. Boettcher and Wyllie (1968b) have compared their data on the latter curve with those of Birch and LeComte (1960) and of Newton and Smith (1967), and with the calculated curves of Hlabse and Kleppa (1968). Newton and Kennedy (1968) have also studied this reaction. All of the above investigators worked between 500° and 1000°C and brackets set by different authors disagree by no more than 0.5 kbar, although curves of individual authors extrapolated beyond their range of data show a greater divergence.

Our invariant point I_{Ab} lying at least 350 degrees above the next highest data point helps to establish the slope of the curve. Figure 2 indicates that I_{Ab} must lie at about 32.5 ± 1 kbar and $1350 \pm 20^\circ\text{C}$. This is in agreement with the straight line drawn by Boettcher and Wyllie (1968b) through all of the data available at that time including our preliminary data (Bell and Roseboom, 1965). Although Newton and Smith (1967) recognized that some curvature would be expected because of the disordering of albite, the experimental data are beginning to place rather severe limitations on the amount of curvature possible.

A few runs (not reported in Table 2) near the invariant point on the quartz-coesite transition indicated that the transition should lie at higher pressures than that indicated by most of the other runs as well as by data for pure silica. Quartz from these anomalous runs showed the $26.67^\circ 2\theta$ (Cu rad.) peak shifted to lower values by as much as 0.25° . Apparently the quartz has formed a solid solution, but whether it is stable or metastable is not yet clear and the subject is still under investigation. Some quartz solid solutions have been reported. For example, Schreyer and Schairer (1961) found extensive metastable solid solution toward MgAl_2O_4 .

Melting at high pressures in binary systems. Because some of the details of phase equilibria presented for this system occur over too small a P - T range to be resolved when allowing for the uncertainties in the experimental work, we will first outline the various theoretical possibilities and then see which may be compatible with the data.

We will consider melting relations in a binary multisystem which contains four crystalline phases of different

compositions. These phases will be numbered 1-4 according to their sequence along the composition line. As long as the phase compositions are always in the same sequence, the crystalline phases can be of fixed compositions or solid solutions and the phase relations will be essentially unchanged.

It is important that the reader note the following conventions. In any univariant or invariant assemblage, the sequence of citation of phase labels will always correspond to the sequence of phases along the composition lines. Thus (12L4) stands for an invariant assemblage in which the coexisting liquid lies between phases 2 and 4. The invariant point at which this assemblage is stable will be designated I_2 , the numeral 2 corresponding to the middle crystalline phase of the assemblage. We have already used I_{Jd} in Figure 1 and I_{Ab} in Figure 2 to designate invariant points where jadeite (Jd) and albite (Ab) were the middle crystalline phases. The point at which a particular phase changes from congruent to incongruent melting will be indicated by an S with the phase indicated by subscript.

Figure 3 shows what happens as an intermediate phase (phase 2 in this case) becomes unstable with increasing (or decreasing) pressure. Seen in P - T projection, congruent melting ($2 \leftrightarrow L$) on the left meets tangentially with the eutectic 1L2 and changes into the incongruent melting curve 12L. The point of transition (S_2) between congruent and incongruent melting of phase 2 is called a singular point type m. Curve 12L continues as an incongruent melting curve and ends at an invariant point where it meets the subsolidus breakdown curve (124) of phase 2. These two curves plus that of $2 \leftrightarrow L$ outline the extreme P - T limits of phase 2. The other two univariant curves are the eutectic between phases 2 and 4 (curve 2L4) which must approach the invariant point from the same pressure region as 12L, and the eutectic between 1 and 4 which must pass off to the right since it can only occur at pressures where 2

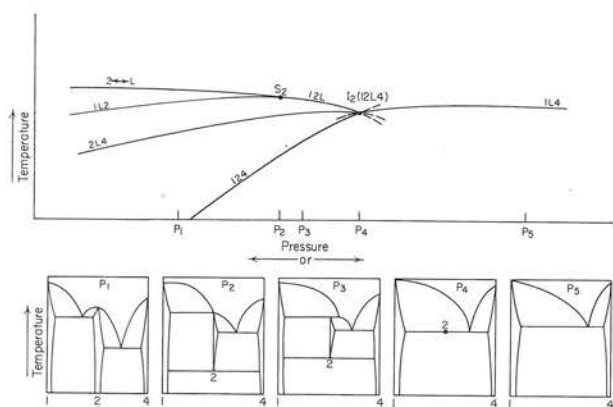


FIG. 3. P - T projection and constant P sections of a binary system whose intermediate phase (2) becomes unstable toward the right. Congruent melting ($2 \leftrightarrow L$) changes to incongruent (12L) at S_2 and the phase disappears from the liquidus at I_2 . Curves limiting P - T stability of phase 2 are shaded. P could increase either toward right or left.

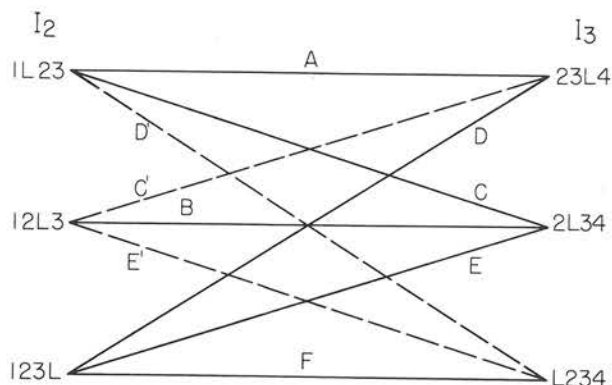


FIG. 4. Possible compositional sequences of phases at invariant point I_2 are listed at left; of I_3 , at right; lettered straight lines connect all possible pairs of such points. Dashed lines marked C' , D' , and E' connect pairs that are mirror images of C , D , and E .

is no longer stable on the liquidus. (Note that a eutectic can be recognized from the notation when L occurs between the two numbers whereas L on either end indicates incongruent melting of the middle phase.) In the foregoing we have made the physically reasonable assumption that L is always on the higher temperature side of any reaction. The three curves involving L will usually have positive slopes but that of curve 124 will vary widely, the only limits being that the metastable extension of 124 must lie between 1L4 and 12L.

Suppose that another solid (phase 3) with a composition between 2 and 4 were stable on the liquidus over some pressure range. There are three possible P - T arrangements of the intermediate phases 2 and 3 as follows: (1) one is stable at higher pressures and one at lower, there being no overlap of their stable regions on a P - T diagram; (2) the same, except that the stable regions overlap; (3) both are stable over some pressure range and with continuous increase or decrease in pressure, first one and then the other becomes unstable.

Case (1) is quite simple: the P - T diagram consists of a diagram like Figure 3 plus its mirror image. The plane of symmetry would lie to the right of P_4 and the two invariant points would be connected by the curve 1L4. Depending on the slopes, the two subsolidus curves, 123 and 234, may or may not intersect to form another invariant point, 1234.

Case (2) corresponds to the $\text{NaAlSi}_3\text{O}_8$ - SiO_2 system, where albite is the phase stable at low pressures and jadeite at high pressures with their stability conditions overlapping. The breakdown curves of phases 2 and 3 must now be 123 and 234 respectively. On reaching the melting range, each breakdown curve will be joined by a liquid to generate invariant points I_2 and I_3 . Since it is highly improbable that the composition of this liquid would be the same as that of any of the solid phases, the compositional sequence of phases at invariant point I_2 could be 1L23, 12L3 or 123L and that of I_3 could be L234, 2L34 or 23L4.

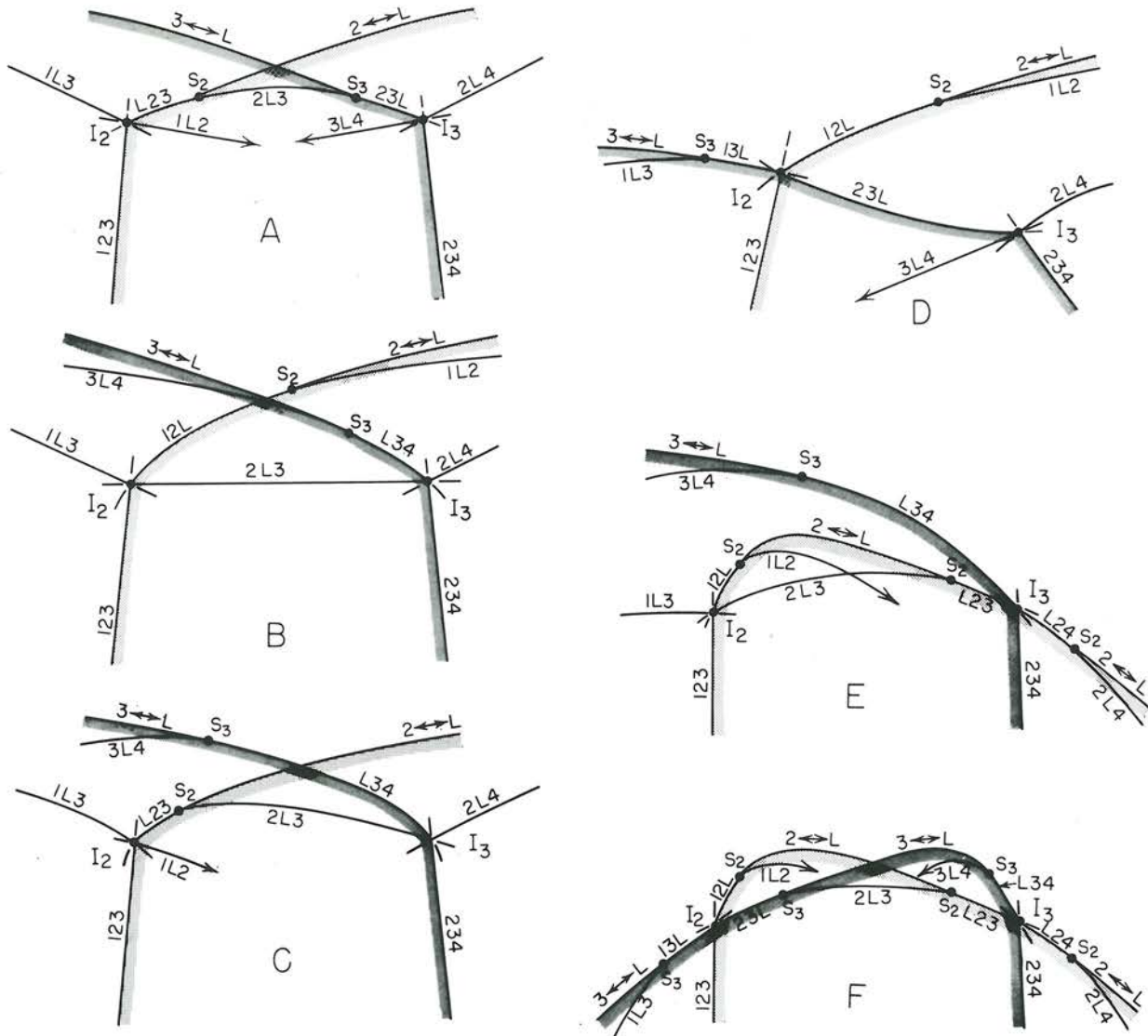


FIG. 5. The six possible types of P - T projections of binary systems having two intermediate phases whose stability ranges overlap on the liquidus, phase 2 being stable to the right and 3 to the left. An arrowhead indicates that the curve when extended may cross any of several different curves or sets of curves. Different shadings mark curves that bound P - T regions in which phases 2 and 3 respectively are stable. Letters A thru E correspond to those of FIG. 4.

If each possible I_2 can occur with each possible I_3 there would be nine combinations of two invariant points in all as indicated in Figure 4. If we discount three which are mirror images of others, there are only six general forms that the P - T diagrams may take. We have worked these out and they are labeled A through F in Figure 4. Their P - T projections are shown in Figure 5. C' , D' , and E' which are mirror images of C, D, and E can be obtained from the latter by simply numbering the solid phases in sequence, 4-3-2-1 instead of 1-2-3-4. For example, 23L4 becomes 32L1 or rather 1L23.

In constructing these diagrams, we have made the assumption that phase 3 will ultimately melt congruently at

the left side of the diagram while phase 2 must do the same at the right side. This is based on the idea that the farther away a phase exists from its breakdown curve, the greater is its stability relative to the same other solid phases.

All of the P - T diagrams of Figure 5 have one feature in common: the two invariant points are connected by a univariant curve along which the three phases, 2, 3, and L common to both invariant points coexist. However, the compositional sequences on this univariant curve near either invariant point can be L23, 2L3, or 23L. Different compositional sequences at the two invariant points require one or two singular points on the connecting curve at the

points where the sequence changes. Thus set A of Figure 5 requires the sequence to change from L23 at I_2 to 23L at I_3 , which necessitates the intermediate sequence 2L3 and two singular points S_2 and S_3 . The curve of congruent melting of a phase must, of course, lie on the opposite side of the singular point from the curve of incongruent melting of that phase.

In set B the sequence 2L3 is the same at both invariant points so the connecting curve does not require singular points. Since 12L and L34 are the incongruent melting curves of phase 2 and 3, it is on these that S_2 and S_3 must occur. Because S_2 and S_3 can occur anywhere along these curves a number of minor variations of this diagram are possible. Thus curves 3L4, L34, and $3 \leftrightarrow L$ can cross indifferently any of curves 1L2, 12L, and $2 \leftrightarrow L$.

In Figure 5C the sequence of L23 near I_2 must change to 2L3 before the curve reaches I_3 . This places singular point S_2 on this curve while S_3 must occur on the incongruent melting curve of phase 3, L34. Curve 1L2 can cross either 2L3 (and L34) or 234. S_3 can fall on either side of $2 \leftrightarrow L$.

In Set D the sequence 23L is the same at both invariant points; therefore they are connected by the single curve 23L. Because the singular point for phase 3 cannot occur on 23L, it must occur on 13L. Phase 2 has only a single incongruent melting curve (12L) and S_2 must occur on it.

Sets E and especially F present situations of increasing complexity and are probably very unlikely in any systems but are included for completeness. Set E requires not two but four singular points, three of them involving phase 2 plus phases 1, 3 and 4 respectively. Set F on the other hand requires a total of six singular points divided equally between phases 2 and 3.

All of these diagrams can be separated into two parts, one resembling Figure 3 and the other its mirror image, the two being superimposed and connected in various ways. In A, the two are attached by connecting 1L2 in Figure 3 to the same curve in its mirror image. In B, curve 2L4 of Figure 3 connects the two parts. In C, curve 1L2 of Figure 3 is connected to 2L4 of its mirror image. In D, the situation is obscured by the fact that curve 23L (corresponding to 12L in Figure 3) is interrupted by the breakdown of phase 2 which produces an invariant point I_2 . However, the incongruent melting of phase 3 continues to the left as curve 13L, finally reaching S_3 . E and F are obscured by the presence of additional singular points. In E, phase 3 goes thru the usual change of incongruent to congruent melting but phase 2 first melts incongruently (12L), then congruently ($2 \leftrightarrow L$), but then goes through a second stage of incongruent melting (L23 and L24) and finally melts congruently again. In F, both phases 2 and 3 behave as did phase 2 of E.

The diagrams of Figure 5 can be applied to systems in which the solid phases can vary in composition so long as their relative positions along the composition axis do not change. If a third intermediate phase becomes stable it

may complicate things considerably. However, with five solid phases stable, we can consider subsystems of phases 1-4 (or 2-5) over the P - T range of our newly chosen component, phase 4 (or phase 2). In all cases, the congruent melting curve of an intermediate phase must change to an incongruent melting curve before reaching the limit of stability of that phase on the liquidus.

Near the beginning of this section we mentioned a fundamentally different situation (case 3) where the two intermediate phases are both initially stable and with change in pressure become unstable. Although it does not correspond to the system NaAlSiO_4 - SiO_2 , we might mention that it can be treated in the same manner as the foregoing and there are six possible diagrams.

Phase relations in the system NaAlSiO_4 - SiO_2 . We will now see which of the possible diagrams of Figure 5 best fits our data as shown in Figures 1 and 2. All of these Figures have been drawn in the same orientation to facilitate direct comparisons. The numbers of Figure 5 will be assigned to phases in the system as follows: (1) nepheline, (2) jadeite, (3) albite, (4) quartz. In all of the diagrams the shaded curves marking the P - T limits of phase 2 (which begin on the right with $2 \leftrightarrow L$ and end on the left with 123) correspond in Figure 1 to the curves bounding the jadeite field. I_2 and S_2 of Figure 5 correspond to I_{Jd} and S_{Jd} of Figure 1 whereas the curve 1L3 corresponds to the upper limit of the albite + nepheline field. The remaining two curves in Figure 1 which separate the liquid field from albite + liquid and nepheline + liquid are divariant and vary with composition; thus they do not appear in Figure 5. Figure 5 may be similarly related to Figure 2—the shaded curves indicating the P - T limits of phase 2 correspond to the curves bounding the albite field of Figure 2, while I_2 , S_2 and 2L4 are equivalent to I_{Ab} , S_{Ab} and the curve separating the jadeite + coesite field from jadeite + liquid. The curve in Figure 2 separating liquid from jadeite + liquid is divariant.

The compositional sequences at invariant points I_{Jd} and I_{Ab} indicate that diagram A of Figure 5 should be the correct one. It can be seen from Figure 1 that I_{Jd} must have the sequence of phases nepheline-liquid-jadeite-albite or 1L23 because the existence of the albite + liquid field in runs of jadeite composition means that the liquid must lie on the opposite side of jadeite composition from albite. Similarly in Figure 2, jadeite + liquid must add up to the bulk composition albite which indicates that the sequence of phase compositions near I_{Ab} will be jadeite-albite-liquid-quartz or 23L4. Other facts confirm the choice of diagram. Figure 1 clearly implies a singular point (S_{Jd}) where jadeite (2) stops melting congruently ($2 \leftrightarrow L$) and instead jadeite melts to albite + liquid (L23). This means that S_2 must lie on curve L23 (or a mirror image with S_3 on 23L). Only with sets A and C (or E and F) is this possible. C would require the albite congruent melting

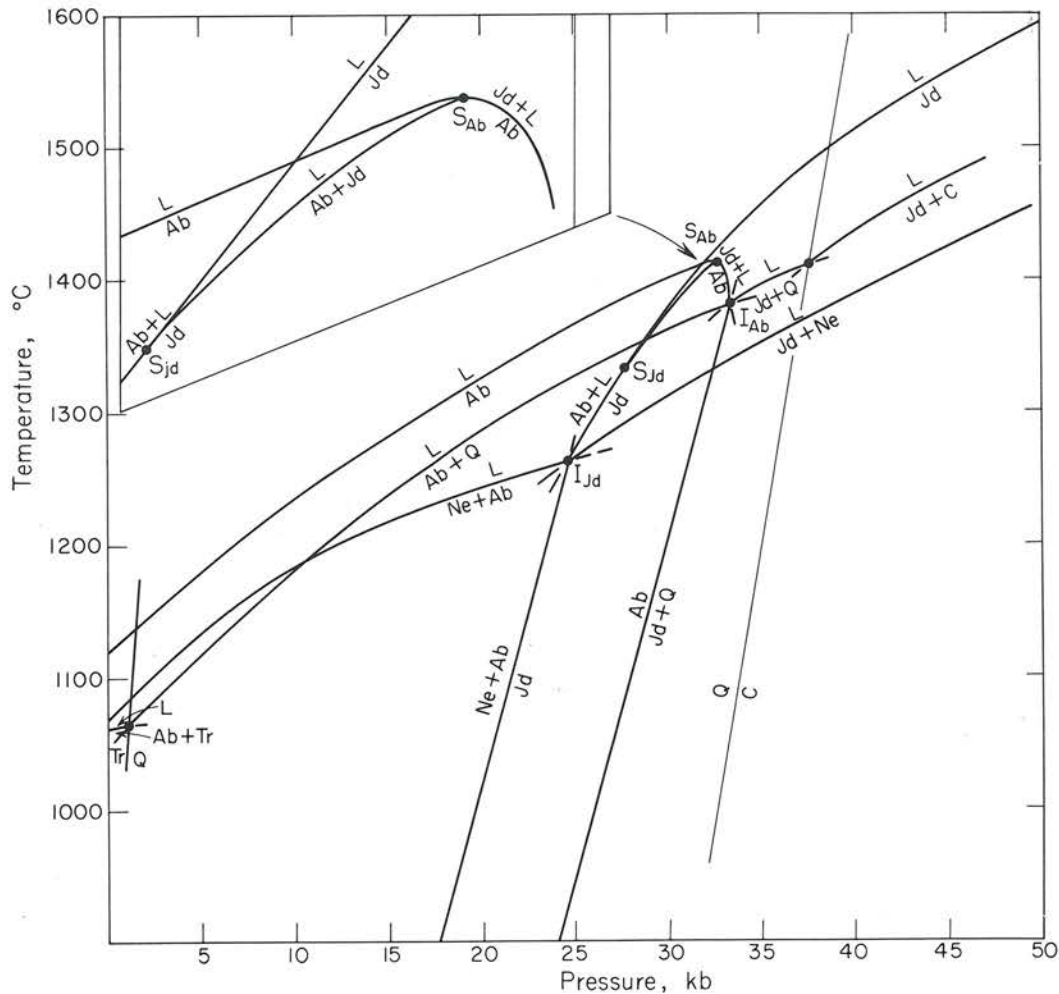


FIG. 6. P - T projection for the system nepheline-quartz. I_{Jd} , I_{Ab} , S_{Jd} and S_{Ab} correspond to I_2 , I_3 , S_2 and S_3 respectively of diagram A of Fig. 5. Ab, albite; C, coesite; Jd, jadeite; L, liquid; Ne, nepheline; Q, quartz; Tr, tridymite.

curve ($3 \leftrightarrow L$) to meet the albite + quartz eutectic ($3L4$) at a singular point (S_3 of Figure 6c) and it must be admitted that Luth's (1969) data which extend to 20 kbar show these two curves drawing closer to each other with increasing pressure.

However C also would require that part of the albite field be bounded by the reaction albite \leftrightarrow quartz + liquid ($L34$). This would appear in Figure 2 as a quartz + liquid field adjacent to the albite field instead of the jadeite + liquid field shown. Although such a quartz + liquid field might be so small that it was not observed, this solution would also require that the jadeite + liquid field, which was observed at 35.8 kbar and above, wedge out before 32.3 kbar where albite was observed. This wedging out would correspond to the composition of the quartz-jadeite eutectic passing thru albite composition and is analogous to the pinching out of the albite + liquid field in Figure 1.

The data of Figure 2 show no indication of such a shape for the jadeite + liquid field.

Still further evidence in favor of case A is the fact that any curve connecting the last known part of the albite melting curve (at 32.3 kbar and about 1410°C) to I_{Ab} in Figure 1 would have to have a steep negative slope and the available data on molar volumes of the phases indicate that the reaction albite \leftrightarrow jadeite + glass ($23L$ of case A) would have a negative slope while the reaction albite \leftrightarrow quartz + glass ($L34$ of case C) would probably not.

We will first look at data obtained on phases quenched at one atmosphere and then at data on glasses quenched from about 33 kb.

Using molar volumes given by Robie and Waldbaum (1968) we find that for one mole (262.224 g) of albite composition the following phases or assemblages have these molar volumes in cubic centimeters: albite glass 110.09,

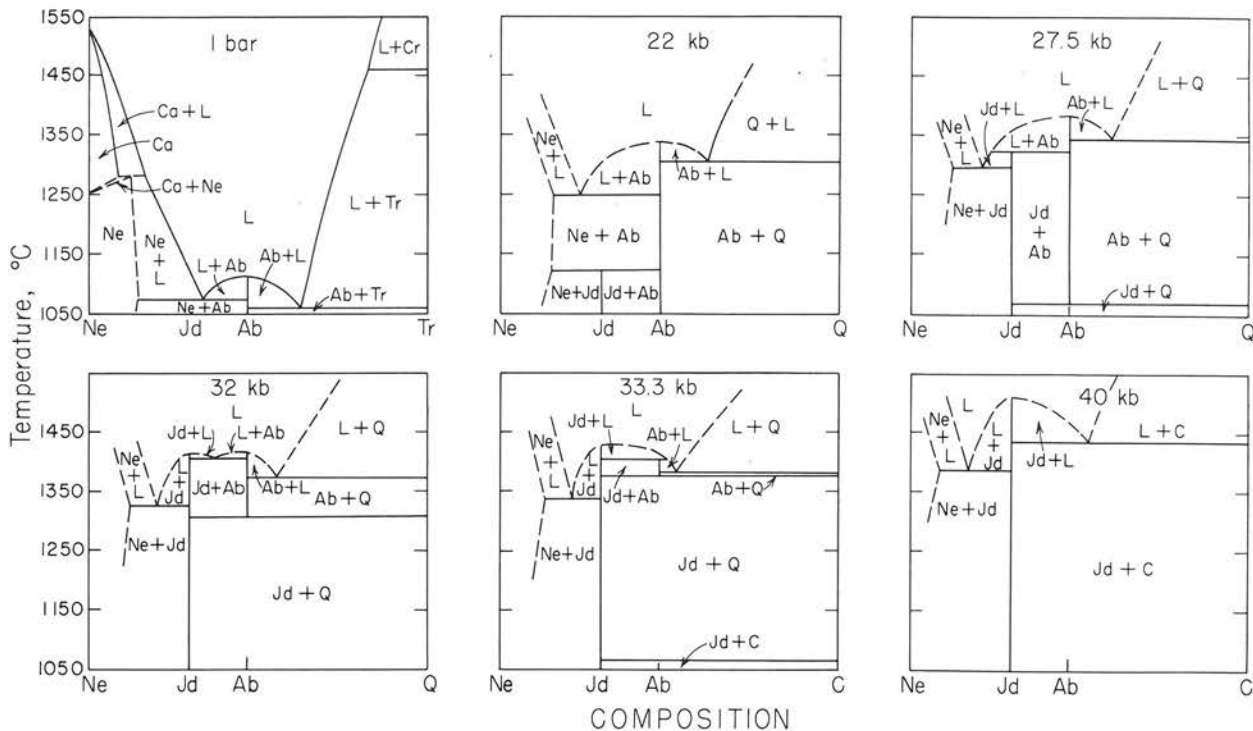


FIG. 7. Constant pressure sections for Fig. 6. Dashed lines indicate no data. Ca is carnegieite.

quartz + jadeite glass 105.51, albite 100.43, jadeite + glass (14.6 percent SiO_2 - 85.4 percent Ab) \sim 100.4, jadeite + quartz glass 87.67. The molar volumes of jadeite glass and the glass of intermediate composition were estimated from a linear extrapolation of specific volumes of quartz glass and albite glass. Assuming that the differences between molar volumes are the same at about 30 kbar, the reaction albite \leftrightarrow quartz + glass would have a positive slope for any possible glass composition from albite to beyond jadeite composition. On the other hand, the reaction albite \leftrightarrow jadeite + glass would have a positive slope as the glass changed composition from albite to about 15 percent SiO_2 - 85 percent Ab by weight and then have an increasingly negative slope as the glass became more siliceous.

Silicate glasses undergo a nonreversible increase in density that is a function of pressure and we will assume for the sake of argument that in addition to this, the glasses have an elastic compressibility that is about the same as that of the crystalline phases. Boyd and England's (1963) data on albite suggest that this is not unreasonable since the irreversible change in density of albite glass at 33 kbar is enough to reduce the dp/dT of the albite melting curve to about two-thirds its initial slope—the actual decrease being from about $14^\circ/\text{kbar}$ to about $7^\circ/\text{kbar}$. The molar volume of albite glass at 33 kbar was estimated as follows: by means of the Gladstone and Dale relationship

(Larsen and Berman, 1934) a specific refractive energy of 0.2049 ± 0.0005 for albite glass was obtained using Boyd and England's index of 1.488 ± 0.001 and Robie and Waldbaum's (1968) molar volume of $110.09 \pm 0.19 \text{ cm}^3$. Combining this specific refractive energy with an index of 1.519 ± 0.002 for albite glass quenched from 33 kbar (estimated from Boyd and England's Figure 8) gave a molar volume of $103.5 \pm 0.4 \text{ cm}^3$ decreasing the change in volume of melting of albite from $9.66 \pm 0.21 \text{ cm}^3/\text{mole}$ to $3.1 \pm 0.4 \text{ cm}^3/\text{mole}$.

The density of silica glass quenched from 33 kbar is about 2.27 g/cm^3 according to data of Cohen and Roy (1961). Assuming as before that the specific volume of glass is a linear function of composition we find that the reaction albite \leftrightarrow quartz + glass could have a negative slope only after the glass reached a composition well over toward that of jadeite—about 72 percent Jd - 28 percent Ab by weight. On the other hand the reaction albite \leftrightarrow jadeite + glass would have a negative slope after only a small departure from albite composition—about 95 percent Ab - 5 percent SiO_2 .

Figure 6 combines the schematic arrangement shown in diagram A of Figure 5 with the data of Figures 1 and 2 to give a P - T projection of the system drawn to scale. From this, the temperature-composition sections shown in Figure 7 have been constructed. With respect to Figure 7, it should be remembered that except for Luth's (1968, 1969)

data on the albite-quartz eutectic, all of the data at pressures above 1 bar are on the jadeite, albite and quartz compositions and the shapes of the liquidus curves and limits of nepheline solid solution are hypothetical. Further details of the two singular points S_{Ab} and S_{Jd} probably cannot be resolved by present experimental techniques. For example, the small fields of $Jd + L$ and $L + Ab$ which lie between albite and jadeite compositions in the 32 kbar diagram of Figure 7 are too small to detect. In Figure 6 the incongruent melting curve of albite is so steep as to make detection difficult if it were looked for by varying temperature while holding pressure constant.

Comparison with other systems. Boettcher and Wyllie (1967, 1968a) have investigated the same system with water added ($NaAlSi_3O_8-SiO_2-H_2O$). It is clear from their work that the projected "binary" consisting of phases stable with H_2O -rich vapor has exactly the same form as that of the dry system except that the invariant point involving jadeite + albite + liquid + quartz (I_{ab} of Figure 6) is metastable, being concealed by reactions involving analcite. The presence of water lowers the other invariant point (I_{Jd}) and the two singular points (S_{Ab} and S_{Jd}) about 750° . An interesting feature is that the quartz-coesite transition causes almost no change in slope in the dry system but a great change in slope in the "wet" system.

Inspection of other systems involving four solid phases provides some other examples of our set A. In the system $KAlSi_3O_8-SiO_2$, Lindsley's (1966) investigation revealed a P - T projection which he recognized as closely analogous to our Figure 6. In Lindsley's system, the two singular points are nearly ten kbar apart and one invariant point (involving leucite + sanidine + liquid + quartz) would have to lie at negative pressures and does not appear on the diagram. Scarfe, Luth, and Tuttle (1966) studied the system $KAlSi_3O_8-SiO_2-H_2O$ up to 10 kbar. As before, we may project the phases stable with H_2O -rich gas or vapor to obtain a projected "binary" system. They present two possibilities which when projected turn out to be sets A and C. They state that their data support the one which corresponds to set A. Again one invariant point lies off of the diagram at negative pressures.

GEOLOGIC APPLICATIONS

The reaction albite \leftrightarrow jadeite + quartz must be near the maximum pressure at which any plagioclase can exist although some intermediate plagioclases may be stable to higher pressures. Hariya and Kennedy (1968) have recently mapped the P - T stability field of anorthite. It extends to higher melting temperatures than the stability field of albite but is always overlapped by the latter toward higher pressures. In the vicinity of I_{Ab} the albite field extends only about one or two kb above the anorthite field but this increases to about 5 kbar at $900^\circ C$. At present there are no data to indicate whether or not an intermediate feldspar might be stable to higher pressures than either

end member. Inasmuch as none of the breakdown products of anorthite (grossular, kyanite, quartz) form extensive solid solutions with those of albite (jadeite, quartz), one might expect by analogy with binary systems that intermediate plagioclases could be stable to higher pressures than the end members, at least in the simple system Ab-An or in anorthosites approaching it in composition. On the other hand, it is significant that in Green's (1967) studies of the subsolidus mineralogy at high pressures of high-alumina basalt, kyanite eclogite, and grosspydrite compositions and Green and Ringwood's (1967) similar studies of quartz tholeite and alkali basalt compositions, the plagioclase disappeared at pressures approximately equal to or a few kilobars below those of the anorthite breakdown. In these complex natural systems, the addition of Fe and Mg allows extensive pyroxene and garnet solid solutions to form at pressures below the albite and anorthite breakdown, the pyroxene accommodating jadeite, and $CaAl_2SiO_6$ components from the plagioclase and the garnet taking up grossular.

Because sanidine is stable to at least 40 kbar according to Lindsley (1966), its solid solution in plagioclase at high temperature would be expected to increase the stability to some extent.

Inasmuch as jadeite occurs exclusively in metamorphic rocks, the melting relations of jadeite described here cannot be applied directly to any volcanic rocks. However at pressures corresponding to those in the upper mantle, jadeite becomes an important constituent of pyroxene. Among the common components of pyroxene whose melting curves have been studied at high pressures, jadeite has the lowest temperatures of melting with the exception of ferrosilite which melts at lower temperatures at pressures above about 35 kbar (Lindsley, 1965).

The reaction jadeite \leftrightarrow albite + nepheline which sets minimum pressures below which jadeite is unstable appears to apply also to omphacitic pyroxenes with about 20 to 30 percent diopside. Bell and Kalb (1968) have shown that in the absence of silica, omphacite consisting of 70 percent jadeite—30 percent diopside breaks down at about the same pressure as pure jadeite, and Kushiro (1968, 1969) has shown that in the presence of silica the situation is similar.

The low-temperature portions of the albite and jadeite breakdown curves have been applied to metamorphic rocks for a number of years and need not be discussed here.

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