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# MELTING RELATIONSHIPS IN THE SYSTEM $\text{NaAlSi}_3\text{O}_8\text{-NaCl-H}_2\text{O}$ AT 1 KILOBAR PRESSURE

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MELTING RELATIONSHIPS IN THE SYSTEM  
NaAlSi<sub>3</sub>O<sub>8</sub>-NaCl-H<sub>2</sub>O AT 1 KILOBAR PRESSURE

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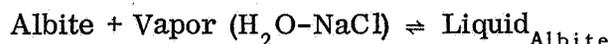
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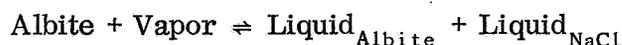
ABSTRACT

Phase relationships in the system NaAlSi<sub>3</sub>O<sub>8</sub>-NaCl-H<sub>2</sub>O are determined between 850°C and 950°C at 1 kilobar pressure; they appear to be ternary. In the bounding system NaCl-H<sub>2</sub>O a two-phase field containing NaCl-rich liquid and H<sub>2</sub>O-rich vapor is intersected at the temperature range of this investigation. This two-phase field must extend into the ternary system; however, the phase relationships in the ternary system are very simple and appear not affected by the presence of this field. In the bounding system NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O a wide miscibility gap occurs between liquid and vapor; in the system NaAlSi<sub>3</sub>O<sub>8</sub>-NaCl a wide miscibility gap extends between silicate-rich liquid and NaCl-rich liquid at temperatures in excess of 1100°C and at 1 bar pressure. Both miscibility gaps are connected through the ternary system separating a silicate liquid from a

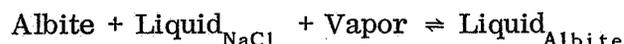
fluid phase with a composition close to the system NaCl-H<sub>2</sub>O and containing a small, unknown proportion of dissolved silicates. A temperature minimum is present on the ternary liquidus at 873 ± 5°C on a colinear three-phase equilibrium, representing a reaction which is isobaric invariant by restriction:



The liquid participating in this reaction has a composition which is in terms of the anhydrous components approximately 99.7 wt. % NaAlSi<sub>3</sub>O<sub>8</sub>, 0.3 wt. % NaCl; its H<sub>2</sub>O content is about 10 wt. %. It is expected that at lower pressures a peritectic type reaction



will occur together with the colinear three-phase reaction. These reactions will terminate in a singular point at lower pressures and a eutectic type reaction



will take place instead.

The results contrast with the system NaAlSi<sub>3</sub>O<sub>8</sub>-NaF-H<sub>2</sub>O (Koster van Groos and Wyllie, 1968a) and confirm previous conclusions from the system NaAlSi<sub>3</sub>O<sub>8</sub>-HCl-H<sub>2</sub>O and NaAlSi<sub>3</sub>O<sub>8</sub>-HF-H<sub>2</sub>O (Wyllie and Tuttle, 1961, 1964) that, whereas fluorine (or NaF) tends to remain in the liquid (magma), chlorine (or NaCl) passes preferentially into the vapor or fluid phase. The increase of the solubility of H<sub>2</sub>O in a silicate melt when a small quantity of chlorine is present cautions the use of widely accepted values for the solubility of H<sub>2</sub>O in

magmas. Coexistence of H<sub>2</sub>O-rich liquid inclusions and NaCl-rich liquid inclusions in various crystalline phases in igneous rocks may be indicative of low-pressure conditions (<1 kilobar) during capture of the inclusions.

MELTING RELATIONSHIPS IN THE SYSTEM  
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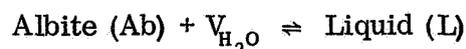
INTRODUCTION

The results presented in this paper form part of an investigation of the phase relationships in silicate-salt-water systems under pressure, following from studies of silicate systems in the presence of two volatile components. Results obtained in the systems NaAlSi<sub>3</sub>O<sub>8</sub>-HF-H<sub>2</sub>O and NaAlSi<sub>3</sub>O<sub>8</sub>-HCl-H<sub>2</sub>O (Wyllie and Tuttle, 1961, 1964) led to the selection of NaF and NaCl as salt components worthy of study. The historical background of the research was outlined in a paper dealing with the system NaAlSi<sub>3</sub>O<sub>8</sub>-NaF-H<sub>2</sub>O (Koster van Groos and Wyllie, 1968a). On the results of this investigation was reported previously (Koster van Groos and Wyllie, 1964; Koster van Groos, 1966).

All compositions in this paper will be expressed in weight percent unless mentioned otherwise.

PREVIOUS WORK

Albite melts at 1132°C at 1 kilobar pressure (Boyd and England, 1963); in the presence of H<sub>2</sub>O it melts at 910°C at this pressure, yielding a liquid containing 4.2 percent H<sub>2</sub>O (Burnham and Jahns, 1962). The coexisting vapor phase contains less than 1 percent NaAlSi<sub>3</sub>O<sub>8</sub> (Dr. C. W. Burnham, personal communication). The P-T projection of the reaction



is shown in figure 1A (Tuttle and Bowen, 1958).

The system NaCl-H<sub>2</sub>O has been the subject of many investigations, the most detailed and comprehensive study being the one by Sourirajan and Kennedy (1962). They investigated this system between 250°C and 700°C at pressures up to 1240 bars. A part of the P-T projection of this system, based on Sourirajan and Kennedy's data, is presented in figure 1A. It is evident that at any pressure lower than the maximum pressure  $P_{\text{max}}$  on the critical curve  $K_{\text{H}_2\text{O}}-K_{\text{NaCl}}$  the phase field L + V is intersected separating an H<sub>2</sub>O-rich vapor phase from an NaCl-rich liquid. At 1 kilobar pressure and at the temperature range of interest, between 860°C and 950°C, the phase field L + V is intersected over a wide range of compositions (figure 1B). NaCl melts at this pressure at 824°C (Clark, 1959); at low temperatures the phase NaCl·2H<sub>2</sub>O becomes stable, but this is not of interest for the results presented in this paper. This system contrasts with the systems NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O and NaF-H<sub>2</sub>O, which exhibit discontinuous critical curves and have wide miscibility gaps between the liquid and vapor phases (Koster van Groos and Wyllie, 1968a; figure 2).

The notation of Greig (1955) is used to designate the phase-elements. This notation is briefly discussed by Koster van Groos and Wyllie (1968b).

## EXPERIMENTAL METHOD

### Starting Materials

Reagent grade NaCl (from Fisher Inc.) was dried to constant weight at 700°C. A gel of albite composition was prepared using standard techniques (Luth and Ingamells, 1965), and then dehydrated at 1200°C. Distilled H<sub>2</sub>O was used as the third component. The solid components were ground to pass 200 mesh, and mixtures were prepared along the join NaAlSi<sub>3</sub>O<sub>8</sub>-NaCl as shown in figure 2 and homogenized in a mechanical shaker. Compositions along the dashed lines in figure 1 were obtained by adding the desired weight of H<sub>2</sub>O to the anhydrous mixtures.

### Apparatus and Technique

Anhydrous runs at 1 atmosphere pressure were made in a vertical quench furnace, with the samples sealed within gold or platinum capsules to prevent loss of material by volatilization. The runs under pressure were made in cold-seal pressure vessels using the quench technique described and discussed by Wyllie and Tuttle (1963) and Wyllie and Raynor (1965). Bulk compositions lying on the dashed joins of figure 2 were obtained by pipetting a known weight of H<sub>2</sub>O into a gold tube welded closed at one end, and then adding the required weight of an anhydrous mixture into the tube so as to make the desired weight percentage of H<sub>2</sub>O. The upper end of the gold tube was then welded shut, providing a small closed capsule containing the three components NaAlSi<sub>3</sub>O<sub>8</sub>, NaCl, and H<sub>2</sub>O in the required proportions. Thermocouples were calibrated against the melting

temperature of NaCl (800.5°C) at 1 atm., and temperature measurements are accurate to  $\pm 5^\circ\text{C}$  for runs of several hours duration, and to  $\pm 8^\circ\text{C}$  for runs of several days duration. Pressure measurements, using bourdon-tube gages, are believed accurate to  $\pm 50$  bars.\*

Equilibrium was not attained in the anhydrous join  $\text{NaAlSi}_3\text{O}_8$ -NaCl, and in parts of the join  $\text{NaAlSi}_3\text{O}_8$ -NaCl with 10 wt %  $\text{H}_2\text{O}$  percent, but there is good evidence that equilibrium was attained in the remaining joins (the dashed lines in figure 2). The results obtained for mixtures in the latter joins are consistent with each other as well as from join to join. Runs of long duration gave the same results as runs held at the same conditions for a shorter time. Reversibility was established by holding a run for a standard time in one phase field, and then holding the same sample for the same length of time at a lower temperature where a different phase assemblage is stable; no relics of the higher-temperature phase assemblage remained in these runs.

#### Identification of Phases

The phases present at the pressure and temperature of each run were determined from the appearance of the gold capsule itself after a quench, from the physical characteristics of the sample when removed from the capsule, from microscopic study of phases and textures in fragments of the crushed sample, and from X-ray powder diffraction patterns of the sample. The phases encountered are albite, silicate-rich liquid, NaCl-rich liquid, and a fluid phase whose composition varied continuously between  $\text{H}_2\text{O}$  and NaCl. The phase relationships

encountered can be treated as if they are ternary, although it is possible that coexisting liquid and fluid phases have compositions lying off the join  $\text{NaAlSi}_3\text{O}_8 - \text{NaCl} - \text{H}_2\text{O}$ . There is no evidence in our results for significant departure from ternary relationships. In some runs, trace amounts of minute crystals were observed but not identified. They have a refractive index in the same range as minerals of the sodalite group. This phase is present in such small amounts that it cannot cause any significant deviation from the essentially ternary phase relationships.

Albite crystallized in the disordered high albite modification (Mackenzie, 1957) as very small crystals. The largest crystals formed, in the presence of liquid, reached 0.2 mm in length. Phase fields containing primary halite (NaCl) were not intersected.

The silicate-rich liquids quenched to clear glasses without devitrification, in contrast with similar liquids in the system  $\text{NaAlSi}_3\text{O}_8 - \text{NaF} - \text{H}_2\text{O}$  (Koster van Groos and Wyllie, 1968a). The refractive index of these glasses is uniform; samples with different starting composition yielded glasses with a refractive index of  $1.502 \pm 0.002$ , measured under sodium light. The NaCl-rich liquid does not quench to a glass, but forms aggregates of halite crystals. This liquid is immiscible with the silicate-rich liquid; small spheres of the quenched NaCl-rich liquid are preserved within the glass.

In this system all the runs contained a fluid phase ranging in composition from  $H_2O$  to NaCl and coexisting with silica-rich phases. This phase is represented by the symbols V for the  $H_2O$ -rich gaseous phase, by  $L_{NaCl}$  for the NaCl-rich liquid, and by F for the fluid phase of intermediate composition. The composition of the fluid phase coexisting with the silicate liquid  $L_{Ab}$  is indicated by the nature of the inclusions trapped in the glass representing the quenched silicate liquid. The  $H_2O$ -rich inclusions contain two-phase assemblages consisting of an aqueous solution and a gas bubble. In runs with a high NaCl content three-phase assemblages are present in the inclusions: halite crystals, an aqueous solution and a gaseous phase. These three-phase inclusions are illustrated on a macroscopic scale in PLATE 1A, and on a microscopic scale in PLATE 1B. The inclusions in glasses from high-temperature runs with low  $H_2O$  contents consist almost entirely of halite crystals with only a small amount of solution and gas present.

An attempt to determine the composition of the three-phase inclusions by measuring the dimensions and calculating the volume of the different phases was abandoned because of the uncertainties in the determination of the volumes. However, the composition of these inclusions in each run appears to be uniform. In a series of runs with varying composition, containing 10 percent  $H_2O$ , inclusions containing a gaseous phase as well as three-phase assemblages were found to coexist. Thus, in these runs the composition of these inclusions was not uniform.

Because of considerations to be discussed later it is assumed that these runs do not represent equilibrium conditions.

## EXPERIMENTAL RESULTS

It has been stated that no evidence was obtained to indicate that the phase relationships on this join are not ternary, although a detailed study of liquid and fluid compositions would be necessary to confirm that liquid-fluid tie-lines remain in the composition plane. The discussion is not greatly changed if it happens that the phase relationships are not quite ternary.

### NaAlSi<sub>3</sub>O<sub>8</sub> - NaCl

The reconnaissance runs made at atmospheric pressure in a quench furnace are listed in Table 1. Equilibrium was not attained. At 1020°C, where albite should have formed, the gel did not begin to crystallize in runs of 240 hours duration. A glass, representing the quenched NaAlSi<sub>3</sub>O<sub>8</sub> gel, coexisted with halite crystals which represent quenched NaCl-rich liquid. There was no evidence that this liquid, quenched from a temperature well above the melting temperature of NaCl (800.5°C), contained more than a very small amount of dissolved silicates. This suggested immiscibility between an NaAlSi<sub>3</sub>O<sub>8</sub>-rich liquid ( $L_{Ab}$ ) and an NaCl-rich ( $L_{NaCl}$ ) liquid above the melting temperature of albite (1118°C). This possibility was investigated at 1150°C. Samples containing 1% and 2.5% NaCl produced clear glasses. Samples containing 5% NaCl quenched to glasses with spherical inclusions, containing halite aggregates, which are interpreted to represent former globules of immiscible NaCl-rich liquid.

Refractive indices of the glasses were measured in sodium light. A run containing 1% NaCl produced a glass with a refractive index of 1.488; with 2.5% NaCl present the refractive index increased to 1.490. In all runs containing the spherical NaCl inclusions, the refractive index of the glass was 1.490. These measurements suggest that the solubility of NaCl in the silicate liquid is about 2.5%. This value is in good agreement with the determination of Bateson and Turner (1939) who found that glass with the composition  $\text{SiO}_2 = 75$  percent,  $\text{CaO} = 9.2$  percent and  $\text{Na}_2\text{O} = 15.8$  percent dissolves up to 2.34 percent NaCl and  $1400^\circ\text{C}$  and 1 bar pressure. An earlier study, however, reported a much lower solubility of NaCl, 0.86% at  $1200^\circ\text{C}$  and 1 bar pressure, in an obsidian melt (Zünckel and Hempel, 1917).

Mixtures with the composition  $\text{Ab}_{10}\text{NaCl}_{90}$  at  $1150^\circ\text{C}$  contained a large amount of silicate glass. This indicates that the solubility of  $\text{NaAlSi}_3\text{O}_8$  in the NaCl-rich liquid is also very low.

These results provide the schematic phase diagram shown in figure 3, with a wide miscibility gap between the two liquids. The lowering of the melting points of albite and of halite is assumed to be small. The results obtained in the ternary system provide additional evidence for the existence of this miscibility gap.

Marialite,  $(3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaCl})$  an end-member of the scapolite solid-solution series, is stable in parts of this system. However, the temperatures at which this system was studied are too high to encounter this phase (Eugster and Protska, 1960).

NaAlSi<sub>3</sub>O<sub>8</sub>-NaCl-H<sub>2</sub>O

This system is investigated between 850°C and 950°C at 1 kilobar pressure along the sections indicated with the dashed lines in figure 2. The phase fields intersected by these sections with the exception of the section containing 10% H<sub>2</sub>O are shown in figures 4 and 5. Definitive runs are listed in Table 2.

The results for the section NaAlSi<sub>3</sub>O<sub>8</sub>-NaCl with 10% H<sub>2</sub>O present are not illustrated because equilibrium was probably not attained in parts of the section. As is mentioned earlier, in many runs in this section the NaAlSi<sub>3</sub>O<sub>8</sub>-rich glass contained three-phase inclusions with halite crystals, an aqueous solution and a vapor phase, as well as much smaller inclusions, containing a gaseous phase. The coexistence of these two types of inclusions can be interpreted as evidence that the two-phase field L + V in the system NaCl-H<sub>2</sub>O (see figure 1B) extends into the ternary system to form the phase field L<sub>Ab</sub> + L<sub>NaCl</sub> + V. However, many of these runs made over a range of compositions and temperatures also contained albite. Because the phase rule requires that at equilibrium conditions four phases cannot coexist over a range of compositions and temperatures in an isobaric section of a ternary system, and because no other evidence indicates that this system is not ternary, it is concluded that in these runs equilibrium was not attained. In runs at 940°C very few of the one-phase inclusions were found and it is assumed that these runs were near equilibrium. Unfortunately, the equipment did not allow these runs to be maintained at the high temperatures for a sufficient length of time to reach equilibrium. Another possibility is that the

gaseous inclusions represent trapped air bubbles, but also then equilibrium was not attained. The results in this section do indicate that, again, a large liquid immiscibility gap is present between  $\text{NaAlSi}_3\text{O}_8$ -rich liquids and NaCl-rich liquids. Furthermore, at constant temperature, runs with increasing amounts of NaCl contain less and less of the  $\text{NaAlSi}_3\text{O}_8$ -rich liquid while the amount of albite increases. These observations are consistent with the interpretation of the other sections. The results of several runs in this section were used in the figures 4 and 5 because they agreed with regard to the silicate phases with the results of the runs containing higher  $\text{H}_2\text{O}$  contents, which are assumed to represent equilibrium.

Figure 4 shows the phase fields intersected by the composition joins with 50% and 80%  $\text{H}_2\text{O}$  present; only the part of the section in which  $\text{NaAlSi}_3\text{O}_8$  constitutes more than 50% of the anhydrous mixture is shown. The precision of the temperature measurements ( $\pm 5^\circ\text{C}$ ) is indicated by the run symbols. The figure shows that, although the runs indicate the position of a narrow three-phase field, its boundaries could not be located in a definitive fashion by these runs. Therefore, location of the phase boundaries for each individual join depended upon interpretation of the results obtained throughout the ternary system, and upon the ternary phase relationships so determined. Figures 4 and 5 confirm that the phase boundaries located in this way are consistent with the results of individual runs in the various joins.

In the binary system  $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$  at 1 kilobar pressure, the three phases albite, silicate liquid and vapor coexist in isothermal equilibrium along a three-phase line at  $910^\circ\text{C}$  (Koster van Groos and Wyllie, 1968a; figure 2A). When NaCl is added to the binary system, it dissolves in the liquid and vapor phases, and the ternary three-phase assemblage  $\text{Ab} + \text{L}_{\text{Ab}} + \text{V}$ , represented by an isothermal three-phase triangle, extends to lower temperatures. The three-phase triangle generates a three-phase space, and intersection of this space by the composition joins produces the narrow fields plotted in figures 4A and 4B. The results indicate that addition of a small amount of NaCl causes the three-phase fields to descend steeply to  $873^\circ\text{C}$ . Addition of more NaCl causes the temperature of the three-phase fields to rise, but only slightly.

The results plotted in figure 5 show the phase fields intersected by the three dashed joins passing through  $\text{H}_2\text{O}$  in figure 2;  $\text{Ab}80\text{NaCl}20\text{-H}_2\text{O}$ ,  $\text{Ab}50\text{NaCl}50\text{-H}_2\text{O}$  and  $\text{Ab}20\text{NaCl}80\text{-H}_2\text{O}$ ; they illustrate the effect of  $\text{H}_2\text{O}$  on the phase relationships in the dry system  $\text{NaAlSi}_3\text{O}_8\text{-NaCl}$ . Figure 3 shows the isobaric invariant three-phase assemblage  $\text{Ab} + \text{L}_{\text{Ab}} + \text{L}_{\text{NaCl}}$  at an estimated temperature of  $1095^\circ\text{C}$  at 1 bar. At 1 kilobar pressure, this temperature would probably be somewhat higher ( $1100^\circ\text{C}$  is assumed in this study). When  $\text{H}_2\text{O}$  is added to the system, it dissolves in each liquid and the ternary three-phase assemblage then descends to lower temperatures, with isothermal three-phase triangles generating a three-phase space. The runs plotted in figure 5 demonstrate the existence of this

three-phase space, and of the two-phase fields  $L_{Ab} + L_{NaCl}$  and  $Ab + L_{NaCl}$  occurring above and below it. The two-phase fields extend back to the dry binary system, as shown in figure 3. Again, although the runs show the position of the three-phase fields, the precision of temperature measurement does not permit accurate location of its boundaries; these are based on consideration of the results obtained for the system as a whole.

The boundary limiting the vapor field (the dashed line in figure 5) was not located experimentally, and the termination of the three-phase field  $Ab + L_{Ab} + V$  at the vapor field is based on extrapolation of results obtained in these joins, and consideration of the ternary system. Similarly, the interpretation of the complete results for the ternary system indicates that the join in figure 5A intersects the ternary minimum for the three-phase field, whereas the joins in figures 5B and 5C do not.

The results plotted in figures 4 and 5 and listed in table 2 show that marialite does not coexist with the silicate liquid at 1 kilobar pressure. According to figure 3, marialite melts incongruently at 860°C at 1 bar, yielding an NaCl-rich liquid, the effect of pressure on the melting behavior has not been determined although it is unlikely that application of 1 kilobar pressure would cause a significant change in temperature. Marialite, thus, appears to become unstable just a few degrees below the minimum temperature of 873°C on the silicate liquidus at 1 kilobar pressure. Continued depression of the silicate liquidus temperature

at higher pressures could lead to the appearance of marialite as a primary phase on the silicate liquidus.

The maximum H<sub>2</sub>O content of the silicate rich liquid is an important parameter in this system. Over a major part of the system the silicate-rich liquid coexists with a fluid phase. Therefore, this liquid will be saturated with an NaCl-H<sub>2</sub>O mixture, having a composition which is dependent on the composition of the fluid with but which is not necessarily the same. Unfortunately, the derivation of the maximum value for the H<sub>2</sub>O content of the silicate-rich liquid through geometric considerations, which was successful in the system NaAlSi<sub>3</sub>O<sub>8</sub>-NaF-H<sub>2</sub>O (Koster van Groos and Wyllie, 1968a), was not feasible, due to the difficulties in the determination of the precise location of the phase boundaries at the various temperatures. Therefore, the maximum H<sub>2</sub>O content in the silicate-rich liquid was determined by the method of weight-loss through ignition only.

The number and size of the two-phase and three-phase inclusions in the glass beads was found to vary from run to run. Glass beads which were poor in inclusions were selected optically. These beads were ground and dried in acetone, in order to remove most of the inclusions. Then these samples were heated to 1000°C for 4 seconds in order to determine the weight-loss. Table 3 shows the results of these determinations. The weight-loss varies between 8 and 9.5%. Because it was attempted to determine the maximum H<sub>2</sub>O content it is assumed that the highest value represents this maximum content. Some H<sub>2</sub>O may have

diffused from the glass during the quench; therefore, a value for the maximum solubility of  $H_2O$  in the silicate liquid of 10 percent is adopted. This compares with a value of 4.2% for the solubility of  $H_2O$  in the silicate liquid of the system  $NaAlSi_3O_8 - H_2O$  at  $920^\circ C$  (Burnham and Jahns, 1962).

The NaCl content of the silicate liquid  $L_{Ab}$  containing the maximum  $H_2O$  content was not determined directly but the ternary phase relations indicate this NaCl content to be very low; this will be discussed later.

#### DISCUSSION OF THE RESULTS

The experimental results show that the miscibility gaps present in the bounding systems  $NaAlSi_3O_8 - H_2O$  and  $NaAlSi_3O_8 - NaCl$  are continuous with each other and separate a silicate-rich liquid from a fluid phase with a composition which varies continuously from an aqueous vapor to an NaCl liquid. No evidence was found to indicate that an isothermal reaction with the phase assemblage  $Ab + L_{Ab} + L_{NaCl} + V$  is intersected by any of the sections studied. The presence of such a reaction would necessitate the coexistence of an NaCl-rich liquid with an aqueous vapor and, with the exception of some runs with low  $H_2O$  contents which showed evidence of non-equilibrium, no indication of this was found.

Wyllie and Tuttle (1960) described and illustrated the phase relationships for a number of systems  $Ab - H_2O - C$ , where C is a second volatile component.

The phases involved in these hypothetical systems were albite, silicate-rich liquid, and a vapor phase with composition ranging continuously between  $H_2O$  and the second volatile C. The phase relationships in the ternary system at  $NaAlSi_3O_8$ - $NaCl$ - $H_2O$  at 1 kb and at temperatures above  $873^\circ C$  are directly analogous to those in one of the hypothetical systems  $Ab$ - $H_2O$ - $C$ , with  $NaCl$  behaving as a second volatile component. The system conforms to the type illustrated by Wyllie and Tuttle (1960) in figure 7D, with perspective TX projection in figure 6D, and isobaric isothermal sections in figure 10. Detailed description of the phase relationships in the system  $Ab$ - $NaCl$ - $H_2O$  is therefore unnecessary.

The ternary phase relationships, based on the results shown in figures 4 and 5, are illustrated in the figures 6, 7, 8 and 9. Isobaric isothermal sections, in part schematic, are shown for  $900^\circ C$  and  $873^\circ C$  in figure 6; an enlarged version showing detail in the  $900^\circ C$  isotherm is shown in figure 7. The fluid phase (from  $L_{NaCl}$  to aqueous V) is represented by a narrow field remaining close to the binary system  $NaCl$ - $H_2O$ , indicating that the silicate is only slightly soluble in the fluid. Apparently, solution of this small proportion of the silicate in the binary system  $NaCl$ - $H_2O$  is sufficient to close off the binary miscibility gap  $L + V$  illustrated in figure 1B; the limits of the ternary miscibility gap extending from this  $L + V$  loop in the system  $NaCl$ - $H_2O$  (see figure 1B) are, therefore, not plotted.

The descent of two three-phase triangles,  $Ab + L_{Ab} + V$  and  $Ab + L_{Ab} + L_{NaCl}$ , from the binary systems  $Ab-H_2O$  and  $Ab-NaCl$ , respectively, was mentioned in the results section, and these are shown at  $900^\circ C$  in figures 6A and 7. These triangles move toward each other with decreasing temperature, pivoting around  $Ab$ , until they become coincident with the isobaric, isothermal, colinear phase assemblage  $Ab + L_{Ab} + V$  at  $873^\circ C$ , as is illustrated in figure 6B. Figure 4 provided two accurately located points on this temperature minimum, and the line through these points has also to pass through the corner Albite.

Figures 3 and 5 indicate that the three-phase triangle  $Ab + L_{Ab} + L_{NaCl}$  descends steeply from the binary system  $Ab-NaCl$  in the temperature interval  $1100^\circ C$  to about  $900^\circ C$ , but that from  $900^\circ C$  to the minimum at  $873^\circ C$ , this triangle has to pivot all the way from its position in figure 6A to the ternary minimum line in figure 6B. The position of the trailing edge of the triangle at  $900^\circ C$ , which is the boundary between the triangle and the two-phase field  $Ab + L_{NaCl}$  (figure 7), was located from the runs listed in Table 2. The intersection of this boundary with the estimated position of the fluid field boundary locates a corner of this triangle. The combined results from all joins were used to estimate the position of the same corner of the three-phase triangles at  $910^\circ C$  and  $920^\circ C$ . The results were not sufficiently accurate to determine the location of the corners of the three-phase triangles at the liquid field  $L_{Ab}$ . Therefore, they were placed on a smooth, continuous curve descending from the bounding systems to  $L_{Ab} (Ab, V)$  which was selected to fit the results. Albite forms the

third corner of the triangles. The second three-phase triangle, descending from Ab-H<sub>2</sub>O, remains very close to this binary system as is indicated by the experimental results in figure 4.

The corners of the three-phase triangles generate field boundaries; the ternary phase diagram illustrated in figure 8 is based on the position of these field boundaries, the position of the three-phase minimum at 873°C, the composition of the silicate liquid L(Ab, V) at the minimum, and the limitations imposed by the bounding binary systems. The phase diagram is in part schematic; the isotherms plotted on the liquidus surface were not determined experimentally, although the runs themselves indicate that departure from these cannot be significant. This system corresponds to the type illustrated by Wyllie and Tuttle (1960) in figure 7D. The silicate liquidus surface for the primary crystallization of albite is limited to a small area enclosed by field boundaries passing through a temperature minimum at 873°C. The shape of the surface giving the composition of fluids coexisting with albite is shown schematically by the isotherms in the enlarged portion of figure 8. This surface extends steeply downwards to the field boundary separating it from the surface for the primary crystallization of halite; the latter boundary passes downwards towards H<sub>2</sub>O as illustrated schematically in figure 8, probably only slightly below the liquidus boundary in the system NaCl-H<sub>2</sub>O shown in figure 1B (compare figure 3 for its starting point at the NaCl-rich eutectic liquid between albite and halite).

The ternary critical curve extending from the critical point in the system NaCl-H<sub>2</sub>O (figure 1B) is not shown in figure 8. Our results require that this curve rises steeply in temperature from the binary system, and passes above the field boundary for the fluids ( $L_{\text{NaCl}}$  to aqueous V) coexisting with silicate liquid and albite, F (Ab,  $L_{\text{Ab}}$ ).

Because the molecular weights of the three components of this system are very different, the standard weight percent phase diagram provides a rather misleading representation. Therefore, the phase boundaries from figure 8 have been replotted in figure 9 in terms of mol percent, treating NaAlSi<sub>3</sub>O<sub>8</sub> as a single molecule.

The composition of the fluid phase F coexisting with the silicate liquid at any temperature between 1100°C and 873°C and at 1 kilobar pressure can be estimated from the results. Figure 10 shows the position of the tie-lines connecting these fluid phases, each one representing the leading edge of a three-phase triangle Ab +  $L_{\text{Ab}}$  +  $L_{\text{NaCl}}$ , with  $L_{\text{NaCl}}$  being transformed through a fluid F to the aqueous vapor V with decreasing temperature. The tie-lines provide the locus of the ruled surface beneath the miscibility gap  $L_{\text{Ab}}$  + F. This surface was constructed using the isotherms at 1100°C, 900°C and 873°C and the estimated position of the isotherms at 920°C and 910°C, to provide a smooth temperature change as was indicated by the results. The tie-lines are consistent with the isotherms shown on the liquid and fluid fields shown in figure 8. Because of the very

gentle slopes of the surfaces within this system at temperatures below 900°C as indicated by figure 10, and because of the narrow temperature interval of the three-phase fields resulting from this, the precision of the temperature control of the runs was insufficient to delineate the phase boundaries. Therefore, the phase boundaries in the figures 4 and 5 are based on the completed diagrams of figures 8 and 10 which in turn are based on the results presented in Table 2 and in the figures 4 and 5.

The NaCl content of the silicate liquid at the ternary minimum at 873°C and 1 kilobar pressure can be estimated from the position of this minimum (figure 8); the location of  $L_{Ab}$  ( $Ab, L_{NaCl}$ ) indicates that the composition of the liquid here is approximately 99.7 percent  $NaAlSi_3O_8$  and 0.3 percent NaCl, expressed in the anhydrous components, and contains about 10 percent  $H_2O$  in solution. This compares with a solubility of about 2.5 percent NaCl in the anhydrous silicate liquid at 1 bar pressure (this paper) and with a solubility of 4.2 percent  $H_2O$  in the silicate melt of the system  $NaAlSi_3O_8-H_2O$  at 920°C and 1 kilobar pressure (Burnham and Jahns, 1962). Thus, an increase of the  $H_2O$  content of the silicate liquid decreases the solubility of NaCl markedly, while the presence of NaCl increases the solubility of  $H_2O$ . This clearly demonstrates that a small change in the chemical composition can have a much larger effect on the solubility of  $H_2O$  than a moderate change in physical conditions: The presence of 0.3 percent NaCl causes an increase of the  $H_2O$  solubility comparable with an increase in pressure from 1 to 3 kilobars (Burnham and Jahns, 1962).

As compared to this system the maximum  $H_2O$  content of the silicate liquid in the system  $NaAlSi_3O_8-NaF-H_2O$  at  $688^\circ C$  and 1 kilobar pressure is 30 percent; the NaF content of this liquid is 14 percent, expressed in the anhydrous components (Koster van Groos and Wyllie, 1968a).

#### Courses of Crystallization

The silicate liquids in this system lie in the primary field of crystallization of albite, see figure 8. Upon cooling, these liquids will precipitate albite, which causes the composition of the liquids to move away from the albite corner till it reaches the liquid field boundary  $L_{Ab}$  (Ab, F). Here a second fluid phase F evolves which has a composition ranging from a very  $H_2O$ -rich vapor to a very NaCl-rich liquid. Further cooling causes the liquid to move along the liquid field boundary toward the minimum at  $873^\circ C$ , with a simultaneous precipitation of albite and evolution of the second fluid phase. The composition of this second fluid changes continuously and moves toward the minimum on the fluid field boundary  $F(Ab, L_{Ab})$  at  $873^\circ C$  (see figure 8) while remaining in equilibrium with the silicate liquid. The silicate liquid is used up when the tie-line connecting albite with the coexisting fluid phase F reaches the point representing the initial composition of the silicate liquid. Thus, only those liquids with an initial composition lying on the line connecting albite with the minimum will reach this minimum. The composition of the other silicate liquids lie either to the left or to the right of this line.

The fluid phase coexisting with the silicate liquids lying to the left of this line is an H<sub>2</sub>O-rich vapor which becomes slightly enriched with respect to NaCl while crystallization of the silicate liquid proceeds. The silicate liquids lying to the right of the line connecting albite with the minimum have a much larger range of compositions (figure 8). The fluids coexisting with this group of liquids can vary from NaCl-rich liquids to H<sub>2</sub>O-rich vapors (figure 10). The position of the tie-lines in figure 10 indicates that, during crystallization, the second fluid phase will be strongly enriched in H<sub>2</sub>O, especially when the temperature drops below 920°C.

The course of crystallization of various silicate liquids is illustrated with the following examples:

1. Consider a silicate liquid lying to the left of the line connecting albite with the minimum at 873°C. If this liquid contains 2 percent H<sub>2</sub>O and 0.05 percent NaCl, it will begin to precipitate albite at about 1030°C. The silicate liquid moves toward the field boundary L<sub>Ab</sub> (Ab, V) and reaches it at about 885°C. Approximately 30 percent of the silicate liquid is left, containing about 6.6 percent H<sub>2</sub>O and 0.16 percent NaCl. Upon further cooling an H<sub>2</sub>O-rich vapor forms (composition 99 percent H<sub>2</sub>O, 1 percent NaCl plus dissolved silicates) while albite continues to precipitate. At about 875°C the last of the silicate liquid, which contained about 9.5 percent H<sub>2</sub>O and 0.25 percent NaCl, is used up. The vapor here forms 2.05 percent of the sample, its composition is 97.6 percent H<sub>2</sub>O and

2.4 percent NaCl, plus some dissolved silicates. With further cooling the solubility of silicates in the vapor will decrease and a small amount of albite will continue to crystallize.

2. Next, consider silicate liquids lying to the right of the line connecting albite with the minimum. Figure 8 and 10 can be used to follow these examples. If a liquid contains 2 percent  $H_2O$  and 2 percent NaCl in solution, it will begin to precipitate albite at about  $1050^\circ C$ , and reach the field boundary  $L_{Ab} (Ab, L_{NaCl})$  at about  $1000^\circ C$ . About 80 percent of the initial amount of the silicate liquid is left. This liquid contains about 2.5 percent  $H_2O$  and 2.5 percent NaCl. Here a second fluid phase will form containing 95 percent NaCl (!), 5 percent  $H_2O$  and with some dissolved silicates. With further cooling, more albite precipitates and more of the NaCl-rich fluid phase is formed; its composition being continuously enriched with  $H_2O$  until it reaches at  $885^\circ C$  the composition NaCl50- $H_2O$ 50. Here, the tie-line connecting albite with this NaCl-rich phase reaches the bulk composition of the sample, and the last of the silicate-rich liquid, which contains here about 0.7 percent NaCl and about 91%  $H_2O$ , is used up. The NaCl and  $H_2O$  initially in the silicate liquid now form the fluid phase. Consequently this fluid phase constitutes 4 percent of the sample with a trace of silicates dissolved in it.

3. Now consider another liquid, lying to the right of the line connecting albite with the minimum, containing 2 percent  $H_2O$  and only 0.5 percent NaCl in

solution. Again, albite begins to crystallize at about 1050°C. The liquid moves toward the field boundary and reaches it at about 900°C; approximately 25 percent of the initial liquid remains, containing about 8 percent H<sub>2</sub>O and 2 percent NaCl. The second fluid phase appears here with a composition of NaCl170-H<sub>2</sub>O30. During further cooling the silicate liquid becomes more enriched with H<sub>2</sub>O, but its NaCl content decreases, this is to deduce from the shape of the liquid field boundary L<sub>Ab</sub> (Ab, F) which curves away from the NaCl corner of the diagram (figure 10). The composition of the second fluid changes from NaCl170-H<sub>2</sub>O30 at 900°C to NaCl120-H<sub>2</sub>O80 at 875°C. At this temperature, the tie-line connecting albite with the NaCl-H<sub>2</sub>O rich fluid reaches the bulk composition of the sample. The last trace of the silicate-rich liquid contained about 9.5 percent H<sub>2</sub>O and 0.4 percent NaCl.

These examples illustrate that silicate liquids which are very poor in NaCl with respect to H<sub>2</sub>O (example 1) cannot generate an NaCl rich fluid phase by crystallization. If the silicate liquid contains a moderate amount of NaCl (example 2) a second fluid phase can separate from this liquid which is extremely rich in NaCl while the silicate liquid contains only a fraction of its maximum possible H<sub>2</sub>O content. The third example shows that a small decrease in temperature (from 900°C to 875°C) causes a NaCl-rich fluid phase, coexisting with a silicate liquid, to change in composition to an H<sub>2</sub>O-rich fluid phase.

Fractional distillation can occur in this system when the  $H_2O$  rich fluid phase (example 1) or the  $NaCl-H_2O$  rich fluid phase (example 2, 3) is partially or completely removed. One way to achieve such a removal is by trapping this fluid phase in the growing albite crystals. Partial removal of the fluid phase by this process will cause the silicate liquids to reach lower temperatures, while with complete removal the composition of the silicate liquids will reach the minimum at  $873^\circ C$ . The composition of the fluid inclusions will show a continuous series of compositions from the initial composition of the fluid phase to the composition of the fluid at the minimum.

#### The Effect of Pressure

The system  $NaAlSi_3O_8-NaCl-H_2O$  was investigated at 1 kilobar pressure only. Available data from previous studies on the bounding systems, however, permit schematic delineation of the effect of pressure on the melting relationships of albite in this system. Such an extension of the results of this investigation is necessary in order to discuss some aspects of the phase relationships in the system granite- $NaCl-H_2O$  under natural conditions.

In the system  $NaCl-H_2O$  the phase field  $L + V$  is intersected at pressures below  $P_{max}$  (figure 1A). The range of compositions at which this field is intersected increases with decreasing pressure (see Sourirajan and Kennedy, 1962; Table 3). The effect of this  $L + V$  phase field on the melting relationships in the ternary system at various pressures is illustrated by a series of schematic

isobaric polythermal equilibrium diagrams (figure 11). The P - T projections of the corresponding univariant melting reactions are shown in figure 1A.

At a pressure higher than  $P_{\max}$  (figure 1A) the isobaric diagram exhibits a ternary minimum (figure 11A); a colinear three-phase equilibrium represents the intersection with the reaction



which is univariant by restriction. At lower pressures the phase relationships become more complex. The phase field  $\text{L} + \text{V}$  will be intersected along the bonding system  $\text{NaCl}-\text{H}_2\text{O}$ , forming a loop with a maximum  $K_{\max}$  and a minimum  $K_{\min}$ . This field extends into the ternary system. With decreasing pressure it is expected to intersect the surface  $\text{F}(\text{L}_{\text{Ab}})$ , generating two field boundaries  $\text{L}_{\text{NaCl}}(\text{L}_{\text{Ab}}, \text{V})$  and  $\text{V}(\text{L}_{\text{Ab}}, \text{L}_{\text{NaCl}})$  which are continuous through a maximum  $K_y$  and a minimum  $K_x$  (figure 11B); a third field boundary  $\text{L}_{\text{Ab}}(\text{L}_{\text{NaCl}}, \text{V})$ , which is indicated with the line  $K'_x - K'_y$ , is generated on the surface  $\text{L}_{\text{Ab}}(\text{F})$ . The volume between the three field boundaries represents the miscibility gap  $\text{L}_{\text{Ab}} + \text{L}_{\text{NaCl}} + \text{V}$ . The critical curve  $K_{\max} - K_{\min}$  of the phase field  $\text{L}_{\text{NaCl}} + \text{V}$ , see the dashed line in figure 11B, is interrupted between  $K_y$  and  $K_x$ .

With a further decrease in pressure the miscibility gap  $\text{L}_{\text{Ab}} + \text{L}_{\text{NaCl}} + \text{V}$  will be intersected over a larger range of compositions and temperatures, and at a pressure  $P_K$  (figure 11C) its minimum  $K_x$  will just touch the fluid field boundary  $\text{F}(\text{Ab}, \text{L}_{\text{Ab}})$  at  $K$ , and similarly, its minimum  $K'_x$  will touch the liquid

field boundary  $L_{Ab}$  (Ab, F) at  $K'$ . This generates the singular point K, see figure 1A. The three phases of the miscibility gap  $L_{Ab} + L_{NaCl} + V$  are here just in equilibrium with albite, while simultaneously  $L_{NaCl} = V$ . Only the lower part of the critical curve of the miscibility gap  $L_{NaCl} + V$  is shown in figure 11C, see the dashed line  $K - K_{min}$ .

At lower pressures the three phases of the miscibility gap will coexist with albite while  $L_{NaCl} \neq V$ . Four phases can coexist in a ternary system only at univariant conditions; thus an univariant curve will extend downward from K (figure 1A), representing the peritectic type reaction



An isobaric polythermal diagram at these conditions is shown in figure 11D. Reaction (1) and (2) are indicated with respectively the dot-dashed line and the triangle a-b-c. Note that the composition of  $L_{Ab}$  participating in reaction (2) lies outside the triangle  $Ab - L_{NaCl} - V$  (see Ab-b-c).

A further decrease in pressure will cause the composition of  $L_{NaCl}$  and V to diverge till the composition of V participation in reaction (2) and the composition of the fluid F participating in reaction (1) is the same ( $F = V$ ). Therefore, the compositions of the silicate-rich liquid  $L_{Ab}$  participating in both reactions will be the same also and lie on the line Ab-c. At this pressure reaction (1) and (2) terminate in the singular point S (figure 1A). The isobaric polythermal diagram at this pressure  $P_S$  is illustrated in figure 11E.

At lower pressures the composition of the liquid  $L_{Ab}$  will lie within the triangle  $Ab - L_{NaCl} - V$  (see Ab-b-c in figure 11F). The univariant reaction at pressures below  $P_S$  is, therefore, of the eutectic type:



This reaction extends downward from S. An isobaric equilibrium diagram at these pressures is illustrated in figure 11F. The curvature of these univariant reactions is not known; and the curvature of the melting reaction in the system  $NaHSi_3O_8 - H_2O$  was used as model.

The phase relationships determined at 1 kilobar pressure do not indicate that either reaction (2) or (3) is intersected. This means that the pressure at the singular point K is less than 1 kilobar. It is expected that the miscibility gap  $L_{NaCl} + V$  will intersect the fluid surface  $F(L_{Ab})$ , see figure 11B, but the conditions at this intersection are probably out of the experimental range of the equipment used. Because this lack of information, a diagram similar to the one illustrated in figure 11A is used to illustrate the phase relationships of this system at 1 kilobar pressure.

It is evident that the course of crystallization in this system is strongly dependent on pressure. At pressures in excess of  $P_K$  (figure 1A) the composition of both the silicate-rich liquid  $L_{Ab}$  and the coexisting fluid phase F change continuously with decreasing temperature, as is discussed earlier. At a pressure between  $P_K$  and  $P_S$ , a silicate liquid which is undersaturated with the fluid phase

will, upon crystallization become saturated and reach the liquid field boundary  $L_{Ab}$  (Ab, F). If the composition of the silicate liquid here contains less  $H_2O$  than the silicate liquid at a (see figure 11D), this liquid will reach a with further crystallization of albite and reaction (2) occurs. Depending on the original composition of the silicate liquid this reaction will proceed isothermally until either  $L_{Ab}$  or  $L_{NaCl}$  is used up. If  $L_{Ab}$  is used up first, albite is left in the present of  $L_{NaCl}$  and V. Continued cooling will cause some precipitation of albite which was dissolved in the fluid phases; the composition of the fluid phases will converge till they meet at  $K_x$  (figure 11D). If  $L_{NaCl}$  is used up first crystallization will proceed following the path discussed earlier. For both cases it is evident that, if the fluid phase is continuously removed the silicate liquid will reach the minimum. If fluid inclusion are formed, the composition of these inclusions will show a compositional gap instead of a continuous compositional change from NaCl-rich to  $H_2O$ -rich. At pressures lower than  $P_s$  (figure 1A) a eutectic type reaction occurs, and effective removal of the fluid phase will not significantly change the course of crystallization of the silicate liquid. Here possible liquid inclusions will show a wide compositional gap, except for liquids with an initial composition lying outside the triangle Ab-b-c.

#### PETROLOGICAL APPLICATIONS

The average chlorine content of igneous rocks is about 0.02 percent (Behne, 1953; Correns, 1956). It is mainly incorporated in minerals such as biotite and hornblende, where it replaces the hydroxyl ion. Furthermore it is presently

dissolved in volcanic glasses and in aqueous saline inclusions in minerals such as quartz and feldspar (A. O. Sorby, 1858; Faber, 1941; Correns, 1956; Carmichael, 1962; Smith, 1903; Roedder, 1963; Roedder and Coombs, 1967). The chlorine content of the various igneous rocks does not vary much, but acid rocks are slightly richer in chlorine than basic rocks. Alkalic rocks such as nepheline syenites and alkalic ultrabasic rocks are unusually high in chlorine. Extrusive rocks appear to contain a smaller amount of chlorine than the intrusive equivalents; however, volcanic glasses, especially pantelleritic glasses (Carmichael, 1962), are high in chlorine. This seems to indicate that much of the chlorine in a magma is expelled during crystallization (Kuroda and Sandell, 1953).

The solubility of  $H_2O$  in a magma under a certain set of physical conditions is fairly well established experimentally (Tuttle and Bowen, 1958; Burnham and Jahns, 1962; Yoder and Tilley, 1962). The presence of "mineralizers" will affect the solubility of  $H_2O$  as well as the beginning of melting of the silicate melt (Niggli, 1937; Tuttle and Bowen, 1958; Smith, 1963; Wyllie and Tuttle, 1964). The conclusions of Wyllie and Tuttle (1964) and of von Platen (1965) that chlorine does not significantly lower the temperature of the beginning of melting of a granite is supported by the results presented in this paper. This can be contributed to the low solubility of chlorine in silicate melts; the current study shows that, in the presence of  $H_2O$ , only 0.3 percent NaCl (or 0.18 percent chlorine) dissolves in an albitic melt at the minimum temperature of melting at 1 kilobar

pressure. The increase of the solubility of  $H_2O$  in this melt by a factor of two-and-a-half as compared to a melt without NaCl in solution supports the conclusions of a previous paper (Koster van Groos and Wyllie, 1968a) that mineralizers can cause a significant increase of the solubility of  $H_2O$  in silicate melts, and that the  $H_2O$  content of residual magmas may be consistently higher than indicated by laboratory experiments in silicate- $H_2O$  systems.

The results in the system  $NaAlSi_3O_8 - NaF - H_2O$  (Koster van Groos and Wyllie, 1968a) and the present one confirm the conclusions of Wyllie and Tuttle (1964) that, while fluorine remains in the liquid phase, chlorine passes into the vapor phase. The presence of primary aqueous saline fluid inclusions in igneous rocks indicates that at some stage of the crystallization of the magma such a "vapor" phase was present. From the discussion on the effect of pressure it is evident that, if a series of saline liquid inclusions shows a continuous variation in composition from saline liquids to aqueous liquids with a very low salt content, the pressure at which these fluids were captured was high enough to inhibit the development of two fluid phases coexisting with the silicate melt (compare figure 11A, B). Such a series of inclusions could be present in subsolvus granites (Tuttle and Bowen, 1958). If the composition of the inclusions is not continuous but shows a compositional break between saline liquids and aqueous liquids, the pressure at the time of formation of these inclusions must have been moderate or low. These inclusions would probably occur in low-pressure or hypersolvus granites (compare figure 11E, F).

In a study of liquid inclusions Roedder and Coombs (1967) could distinguish four types, based on compositional differences, and some types with intermediate compositions resulting from mixing of the principal types. Two types of inclusions were very abundant, one containing a large halite crystal, an aqueous solution and a gas bubble which may contain  $\text{CO}_2$ , and one containing a dilute water solution and a gas bubble with  $\text{CO}_2$ . These inclusions were presumably dense saline fluids and dense aqueous fluids at the time of capture. These two types of inclusions may represent the two coexisting fluid phases in equilibrium with a silicate melt which are present at moderate or low pressures (compare figure 11E, F), as was discussed earlier. The host rock is a hypersolvus granite, which is also indicative of low pressure. Roedder and Coombs suggest that the aqueous fluid phase was formed by boiling of the saline fluid during a pressure drop or other causes. In view of the preceding it seems likely that crystallization of the melt will also result in the formation of both saline and aqueous fluid phases without a drop in pressure. A few primary inclusions with intermediate compositions either result from capture of the fluid at a higher pressure or, more likely, by the occasional trapping of both fluid phases in one inclusion. In the samples investigated by Roedder and Coombs (1967) some of both types of inclusions were present in the cores of oligoclase crystals; this would mean that in these rocks both saline and aqueous fluids were present throughout the major part of crystallization, and consequently, that these granites crystallized almost completely at low pressure.

The aqueous saline fluid inclusions in the samples studied by Roedder and Coombs appear to be composed mainly of NaCl, H<sub>2</sub>O and CO<sub>2</sub>. The system NaCl-H<sub>2</sub>O-CO<sub>2</sub> was studied by Takenouchi and Kennedy (1965) up to 450°C and 1400 bars pressure. An extension of this study to higher temperatures and pressures, and an investigation of the effect of fluid compositions lying in this system on the melting of granites combined with a determination of the composition of the coexisting aqueous and saline fluids with the granitic melts would be useful. Determination of the composition of coexisting pairs of fluid inclusions in granitic rocks could then lead to quantitative data on both temperature and pressure at which these inclusions were trapped.

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Table 1

Results of Runs in the System  $\text{NaAlSi}_3\text{O}_8$ -NaCl at 1 Bar Pressure.

Abbreviations: glass = silica-rich liquid or unreacted material

$L_{\text{NaCl}}$  = sodium chloride liquid.

Composition in Wt. %	Temp. °C	Time in Hours	Results
Ab99NaCl1	1150	240	glass
	1130	48	glass
Ab97.5NaCl2.5	1150	240	glass
	1130	48	glass
	1020	240	glass
	940	48	glass
Ab95NaCl5	1150	240	glass + $L_{\text{NaCl}}$
	1130	48	glass + $L_{\text{NaCl}}$
	1020	240	glass + $L_{\text{NaCl}}$
	940	48	glass + $L_{\text{NaCl}}$
	850	24	glass + $L_{\text{NaCl}}$
Ab90NaCl10	1150	240	glass + $L_{\text{NaCl}}$
	1020	240	glass + $L_{\text{NaCl}}$
	940	48	glass + $L_{\text{NaCl}}$
Ab70NaCl30	1150	240	glass + $L_{\text{NaCl}}$
Ab50NaCl50	1150	240	glass + $L_{\text{NaCl}}$
Ab30NaCl70	1150	240	glass + $L_{\text{NaCl}}$
Ab10NaCl90	1150	240	glass + $L_{\text{NaCl}}$
	1020	240	glass + $L_{\text{NaCl}}$
	850	24	glass + $L_{\text{NaCl}}$

Table 2

Definitive Runs in the System  $\text{NaAlSi}_3\text{O}_8$ - $\text{NaCl}$ - $\text{H}_2\text{O}$  at 1 Kilobar Pressure.

Abbreviations: Ab = albite,  $L_{\text{Ab}}$  =  $\text{NaAlSi}_3\text{O}_8$ -rich liquid,

$L_{\text{NaCl}}$  =  $\text{NaCl}$ -rich liquid, F = fluid, V = vapor.

Composition in Wt. % + 10% $\text{H}_2\text{O}$	Temp. °C	Time in Hours	Interpreted Phase Assemblage
Ab90NaCl10	925	2	Ab + $L_{\text{Ab}}$ + $L_{\text{NaCl}}$
Ab50NaCl50	950	2	$L_{\text{Ab}}$ + $L_{\text{NaCl}}$
Ab40NaCl60	945	2	Ab + $L_{\text{Ab}}$ + $L_{\text{NaCl}}$
<u>Composition in Wt. % + 50% <math>\text{H}_2\text{O}</math></u>			
Ab99NaCl1	890	48	Ab + $L_{\text{Ab}}$ + V
Ab97.5NaCl2.5	885	120	Ab + $L_{\text{Ab}}$ + V
	875	48	Ab + V
	870	24	Ab + V
Ab95NaCl5	885	120	$L_{\text{Ab}}$ + V
	875	48	Ab + $L_{\text{Ab}}$ + V
	870	24	Ab + V
Ab90NaCl10	885	120	$L_{\text{Ab}}$ + V
	875	48	Ab + $L_{\text{Ab}}$ + V
	870	24	Ab + V
Ab85NaCl15	885	120	Ab + $L_{\text{Ab}}$ + V
	875	48	Ab + $L_{\text{Ab}}$ + V
Ab80NaCl20	895	24	Ab + $L_{\text{Ab}}$ + V
	875	48	Ab + $L_{\text{Ab}}$ + V
	873	24	Ab + V
Ab50NaCl50	885	120	Ab + $L_{\text{Ab}}$ + F
	875	48	Ab + F

Table 2 (Continued)

Composition in Wt. % + 80% H <sub>2</sub> O	Temp. °C	Time in Hours	Interpreted Phase Assemblage
Ab95NaCl5	885	24	Ab + L <sub>Ab</sub> + V
	875	48	Ab + L <sub>Ab</sub> + V
	870	48	Ab + V
Ab90NaCl10	885	24	L <sub>Ab</sub> + V
	875	48	Ab + L <sub>Ab</sub> + V
	870	48	Ab + V
Ab85NaCl15	885	24	L <sub>Ab</sub> + V
	875	48	Ab + L <sub>Ab</sub> + V
Ab80NaCl20	885	24	L <sub>Ab</sub> + V
	875	48	Ab + V
Ab50NaCl50	885	120	L <sub>Ab</sub> + V
	875	48	Ab + V
Composition: Ab80NaCl20 <u>H<sub>2</sub>O content:</u>			
5	935	2	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
8	900	24	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
9	935	3	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
10	950	2	L <sub>Ab</sub> + L <sub>NaCl</sub>
	905	24	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
	895	24	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
15	900	24	L <sub>Ab</sub> + L <sub>NaCl</sub>
	897	24	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
19	890	30	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
20	895	24	L <sub>Ab</sub> + L <sub>NaCl</sub>
21	873	24	Ab + L <sub>NaCl</sub>

Table 2 (Continued)

Composition: Ab80NaCl20 H <sub>2</sub> O Content:	Temp. °C	Time in Hours	Interpreted Phase Assemblage
40	895	24	L <sub>Ab</sub> + F
50	895	24	L <sub>Ab</sub> + F
	873	24	Ab + F
70	873	24	Ab + L <sub>Ab</sub> + V
72	870	48	Ab + V
80	885	24	L <sub>Ab</sub> + V
	875	48	Ab + V
	870	48	Ab + V
90	870	48	Ab + V
Composition: Ab50NaCl50 H <sub>2</sub> O Content:			
8	905	36	Ab + L <sub>NaCl</sub>
10	950	2	L <sub>Ab</sub> + L <sub>NaCl</sub>
	935	2	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
	900	13	Ab + L <sub>NaCl</sub>
15	898	24	Ab + L <sub>NaCl</sub>
20	905	36	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
	898	24	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
	890	36	Ab + L <sub>NaCl</sub>
25	898	24	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
29	885	36	Ab + L <sub>NaCl</sub>
30	892	14	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
31	905	36	L <sub>Ab</sub> + L <sub>NaCl</sub>
36	897	36	L <sub>Ab</sub> + F

Table 2 (Continued)

Composition: Ab50NaCl50 H <sub>2</sub> O Content:	Temp. °C	Time in Hours	Interpreted Phase Assemblage	
50	885	36	Ab + L <sub>Ab</sub> + F	
	875	48	Ab + F	
	60	895	25	L <sub>Ab</sub> + F
		895	25	L <sub>Ab</sub> + F
	80	895	25	L <sub>Ab</sub> + V
		875	48	Ab + L <sub>Ab</sub> + V
85	895	25	L <sub>Ab</sub> + V	
Composition: Ab20NaCl80 H <sub>2</sub> O Content:				
10	945	2	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>	
	925	2	Ab + L <sub>NaCl</sub>	
20	905	24	Ab + L <sub>NaCl</sub>	
28	900	48	L <sub>Ab</sub> + L <sub>NaCl</sub>	
30	897	14	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>	
37	887	24	Ab + L <sub>Ab</sub> + F	
51	887	24	Ab + L <sub>Ab</sub> + F	
58	887	24	L <sub>Ab</sub> + F	
60	880	30	Ab + L <sub>Ab</sub> + F	
70	880	30	Ab + L <sub>Ab</sub> + V	
80	880	30	L <sub>Ab</sub> + V	

Table 2 (Continued)

Composition: Ab50NaCl50 H <sub>2</sub> O Content:	Temp. °C	Time in Hours	Interpreted Phase Assemblage
50	885	36	Ab + L <sub>Ab</sub> + F
	875	48	Ab + F
	895	25	L <sub>Ab</sub> + F
	895	25	L <sub>Ab</sub> + F
	895	25	L <sub>Ab</sub> + V
	875	48	Ab + L <sub>Ab</sub> + V
85	895	25	L <sub>Ab</sub> + V
Composition: Ab20NaCl80 <u>H<sub>2</sub>O Content:</u>			
10	945	2	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
	925	2	Ab + L <sub>NaCl</sub>
20	905	24	Ab + L <sub>NaCl</sub>
28	900	48	L <sub>Ab</sub> + L <sub>NaCl</sub>
30	897	14	Ab + L <sub>Ab</sub> + L <sub>NaCl</sub>
37	887	24	Ab + L <sub>Ab</sub> + F
51	887	24	Ab + L <sub>Ab</sub> + F
58	887	24	L <sub>Ab</sub> + F
60	880	30	Ab + L <sub>Ab</sub> + F
70	880	30	Ab + L <sub>Ab</sub> + V
80	880	30	L <sub>Ab</sub> + V

Table 3

Determination of the H<sub>2</sub>O content of silicate glass by the method of weight-loss on ignition. The sample was held in carefully cleaned platina foil and heated to about 1000°C for 4 seconds. Weights are expressed in milligrams.

Composition of the run	Temp. °C	Time in Hours	Weight of Glass Before Ignition	Weight-loss	H <sub>2</sub> O Content in Percent
Ab95NaCl5 + 50% H <sub>2</sub> O	900	48	315.0	28.50	9.0
Ab95NaCl95 + 40% H <sub>2</sub> O	880	70	14.45	1.37	9.5
Ab85NaCl15 + 30% H <sub>2</sub> O	905	20	9.50	.72	7.6
Ab80NaCl20 + 40% H <sub>2</sub> O	900	24	58.60	5.35	9.1
Ab70NaCl30 + 40% H <sub>2</sub> O	895	48	23.80	1.95	8.2

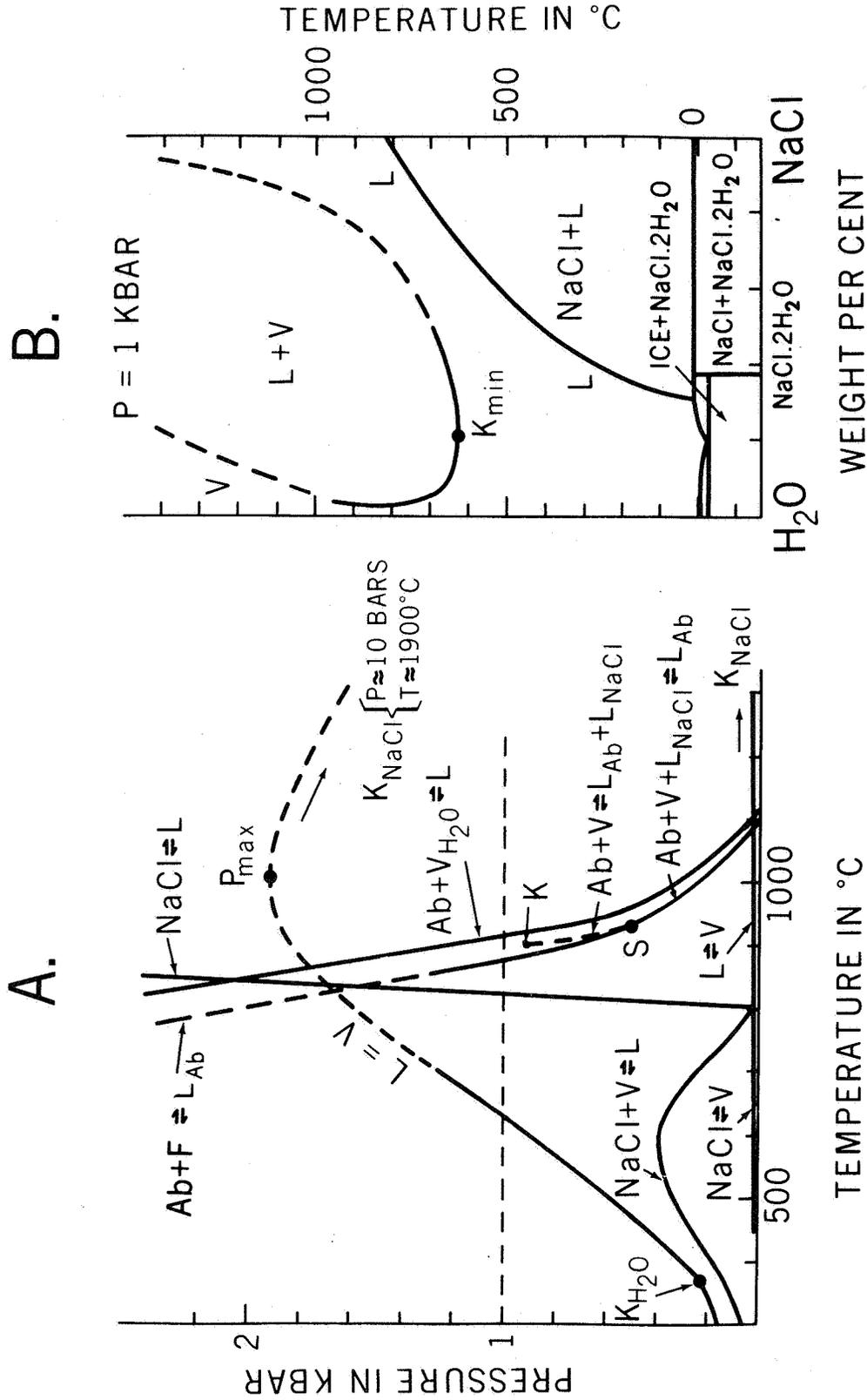


Figure 1-(A) P-T projection of parts of the phase relationships in the systems  $NaAlSi_3O_8 - H_2O$ ,  $NaCl-H_2O$  and  $NaAlSi_3O_8 - NaCl-H_2O$ . The location of the critical curve  $L = V$  from  $K_{H_2O}$  to  $K_{NaCl}$  is partly estimated (dashed line); the location of the maximum  $P_{max}$  is also estimated. For discussion see text. The abbreviations are listed in Table 2. (B) Isobaric section through the system  $NaCl-H_2O$  at 1 kilobar pressure. This section is indicated with the thin dashed line in figure 1A. The phase fields  $Ice + L$  and  $NaCl \cdot L$  are not labelled.

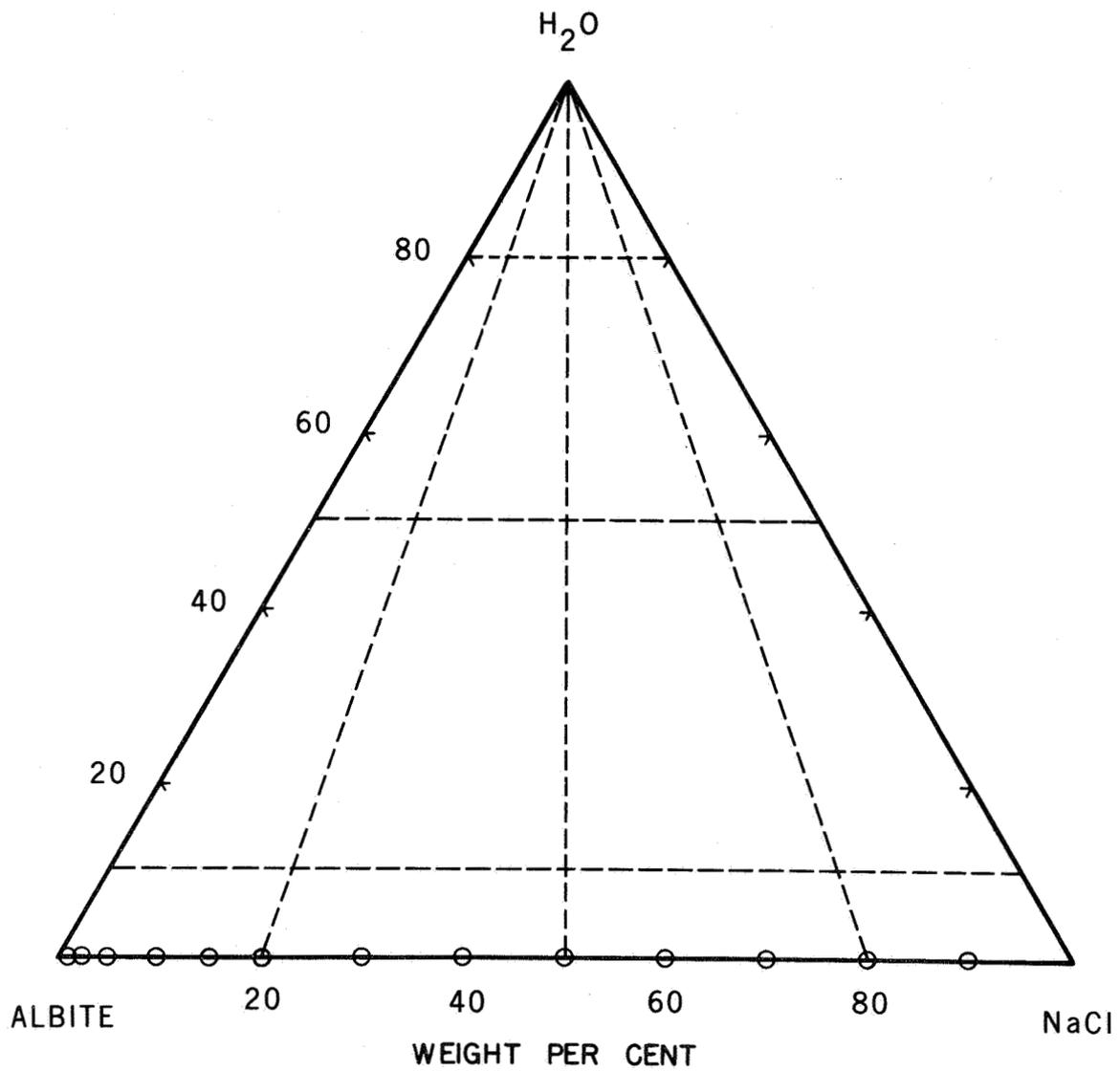


Figure 2—The composition triangle  $\text{NaAlSi}_3\text{O}_8\text{-NaCl-H}_2\text{O}$ . The circles indicate the dry starting mixtures; the dashed lines indicate the sections investigated.

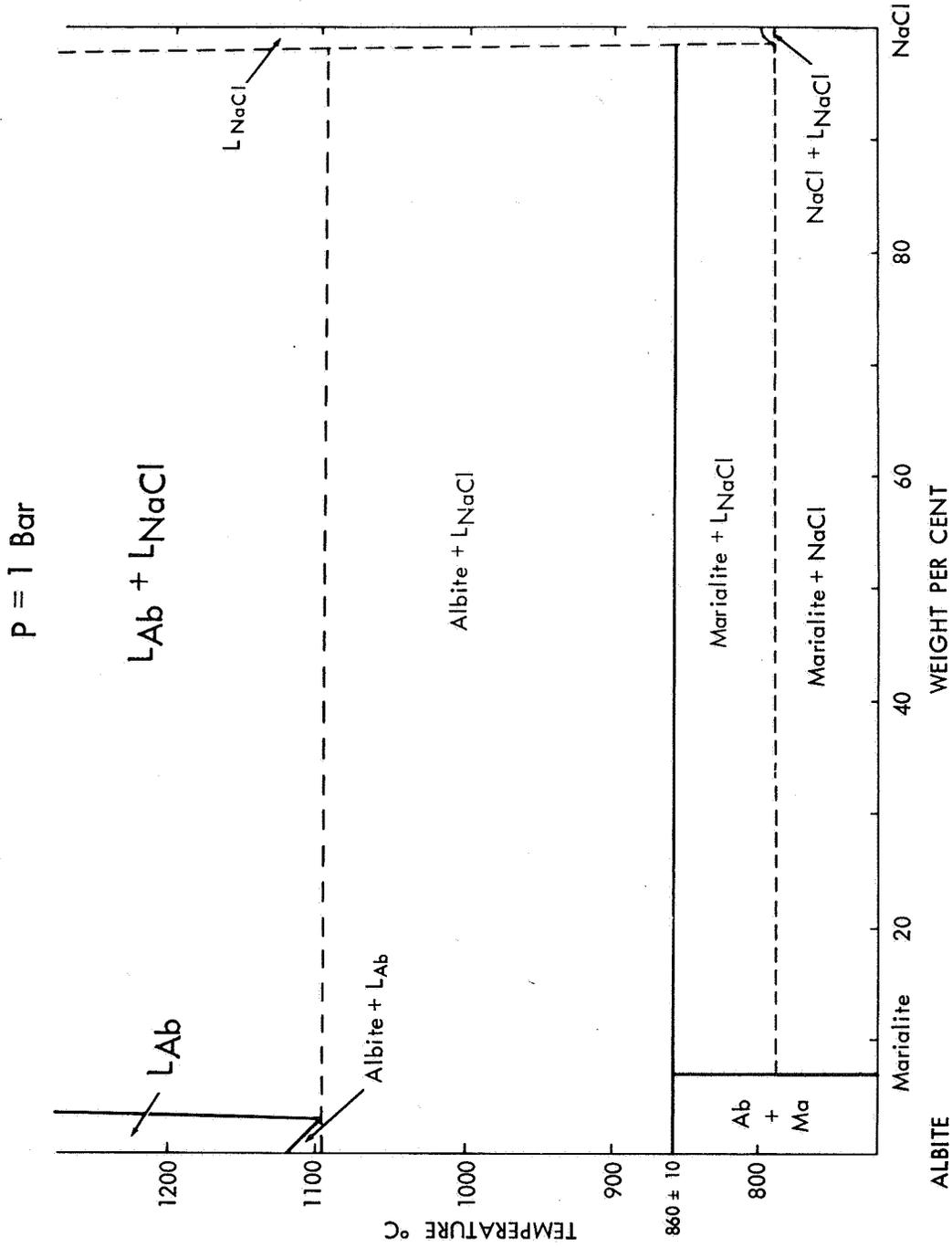


Figure 3—The system  $\text{NaAlSi}_3\text{O}_8$ - $\text{NaCl}$  at 1 bar pressure. For discussion see text. For abbreviations see Table 2.

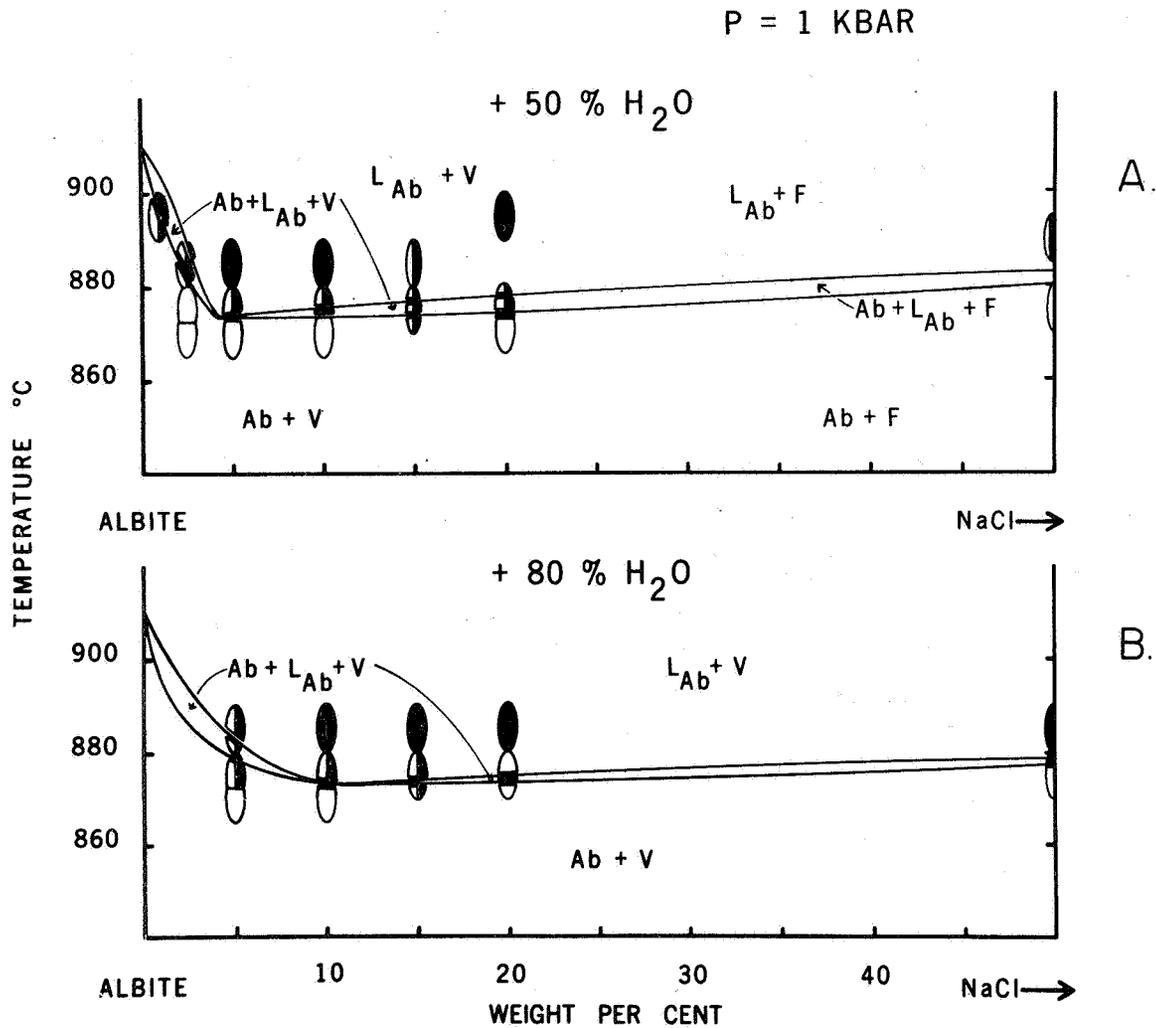


Figure 4—The sections  $\text{NaAlSi}_3\text{O}_8\text{--NaCl}$  with 50 and 80 percent  $\text{H}_2\text{O}$  present compositions with more than 50 percent  $\text{NaCl}$  are not shown. The ovals indicate the definitive runs; silicate-rich liquid is the only silicate phase in the closed ovals, albite is the only silicate phase in the open ovals, in the half-open ovals both albite and silicate-rich liquid are present. For abbreviations see Table 2.

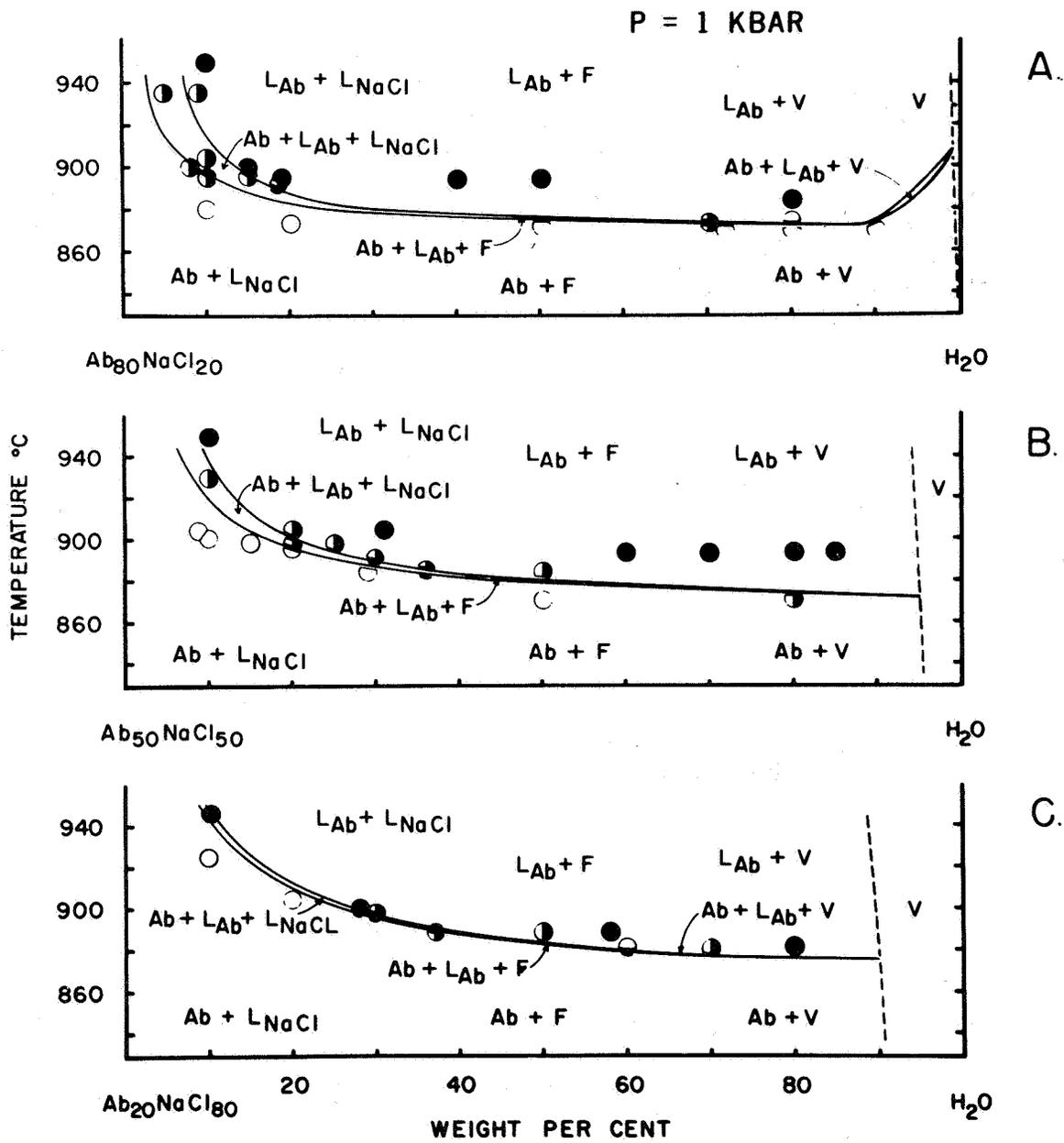


Figure 5—The composition joins Ab<sub>80</sub>NaCl<sub>20</sub>–H<sub>2</sub>O, Ab<sub>50</sub>NaCl<sub>50</sub>–H<sub>2</sub>O and Ab<sub>20</sub>NaCl<sub>80</sub>–H<sub>2</sub>O at 1 kilobar pressure. The circles indicate definitive runs. For abbreviations see Table 2.

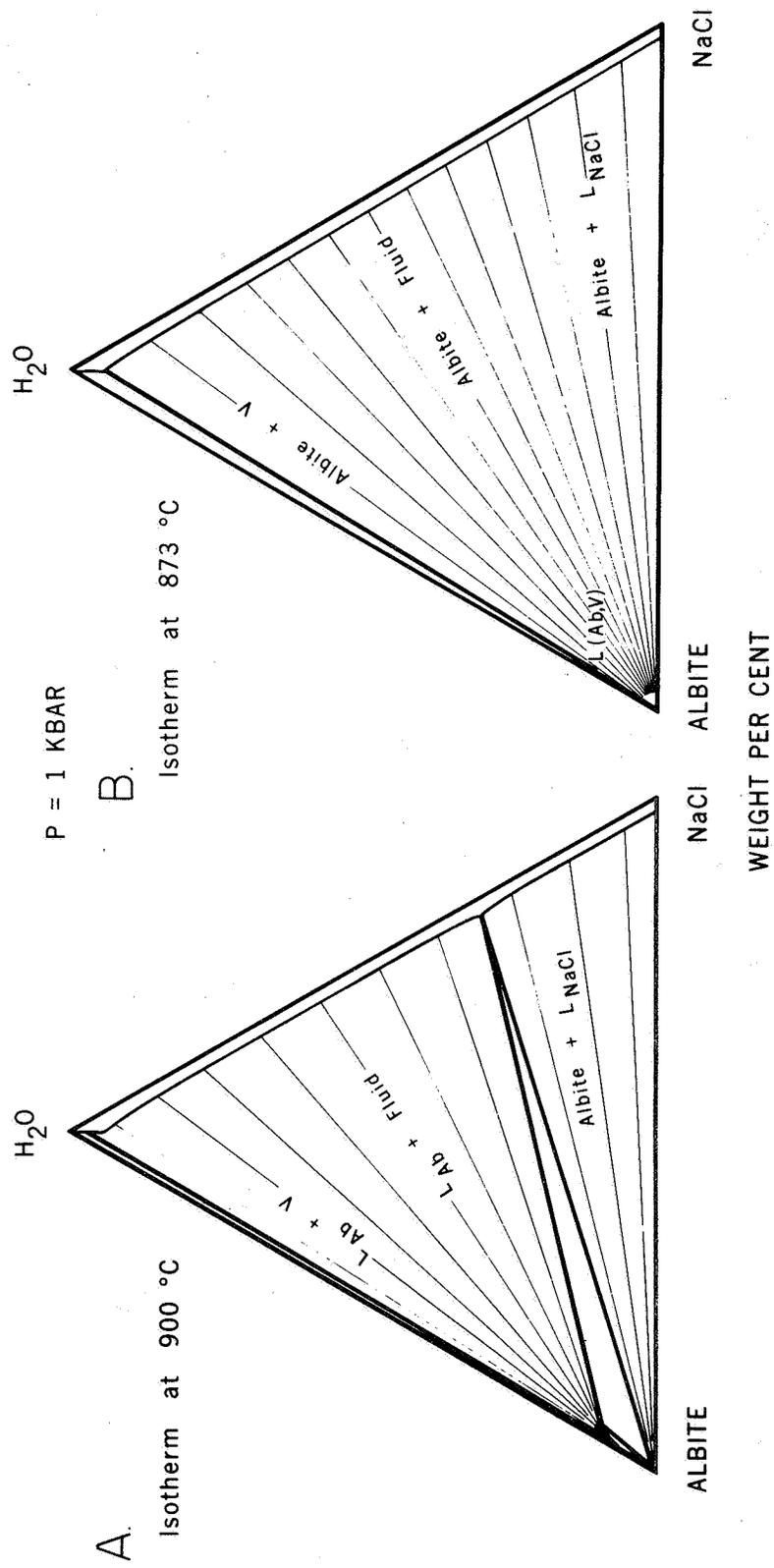


Figure 6—Isothermal sections through the systems  $\text{NaAlSi}_3\text{O}_8\text{-NaCl-H}_2\text{O}$  at 900 °C and 873 °C and 1 kilobar pressure. The composition of the liquid at the minimum at 873 °C is indicated with the symbol L (Ab, V). For abbreviations see Table 2.

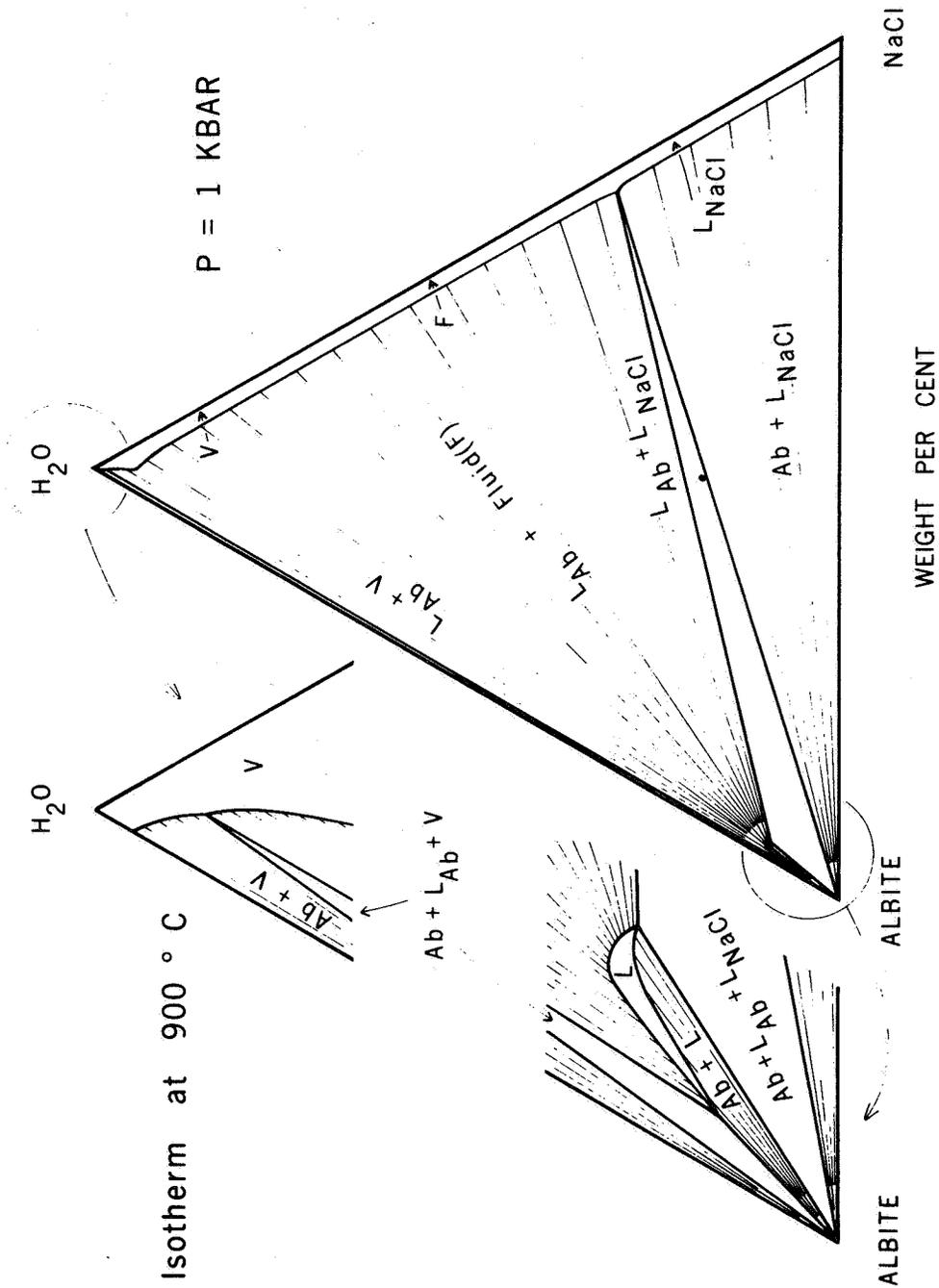


Figure 7—Isothermal section in the system  $\text{NaAlSi}_3\text{O}_8\text{-NaCl-H}_2\text{O}$  at  $900^\circ\text{C}$  and 1 kilobar pressure. The insets show the phase relationships near the albite corner and the  $\text{H}_2\text{O}$  corner schematically; the tie-lines are not experimentally determined. For abbreviations see Table 2.

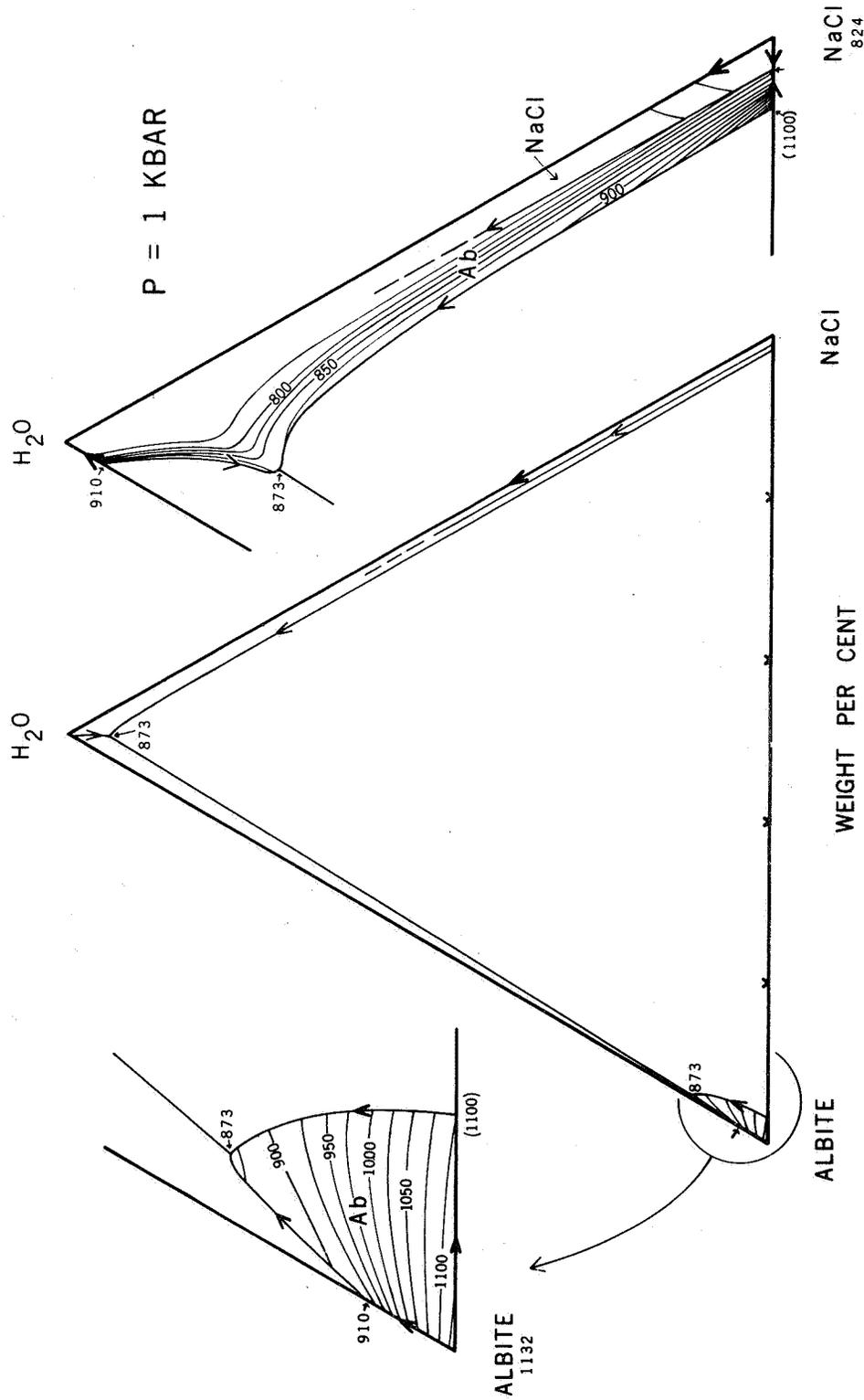


Figure 8—The system  $\text{NaAlSi}_3\text{O}_8$ - $\text{NaCl}$ - $\text{H}_2\text{O}$  at 1 kilobar pressure. The phase relationships near the albite corner and the  $\text{NaCl}$ - $\text{H}_2\text{O}$  side are, enlarged and distorted, shown in the insets.

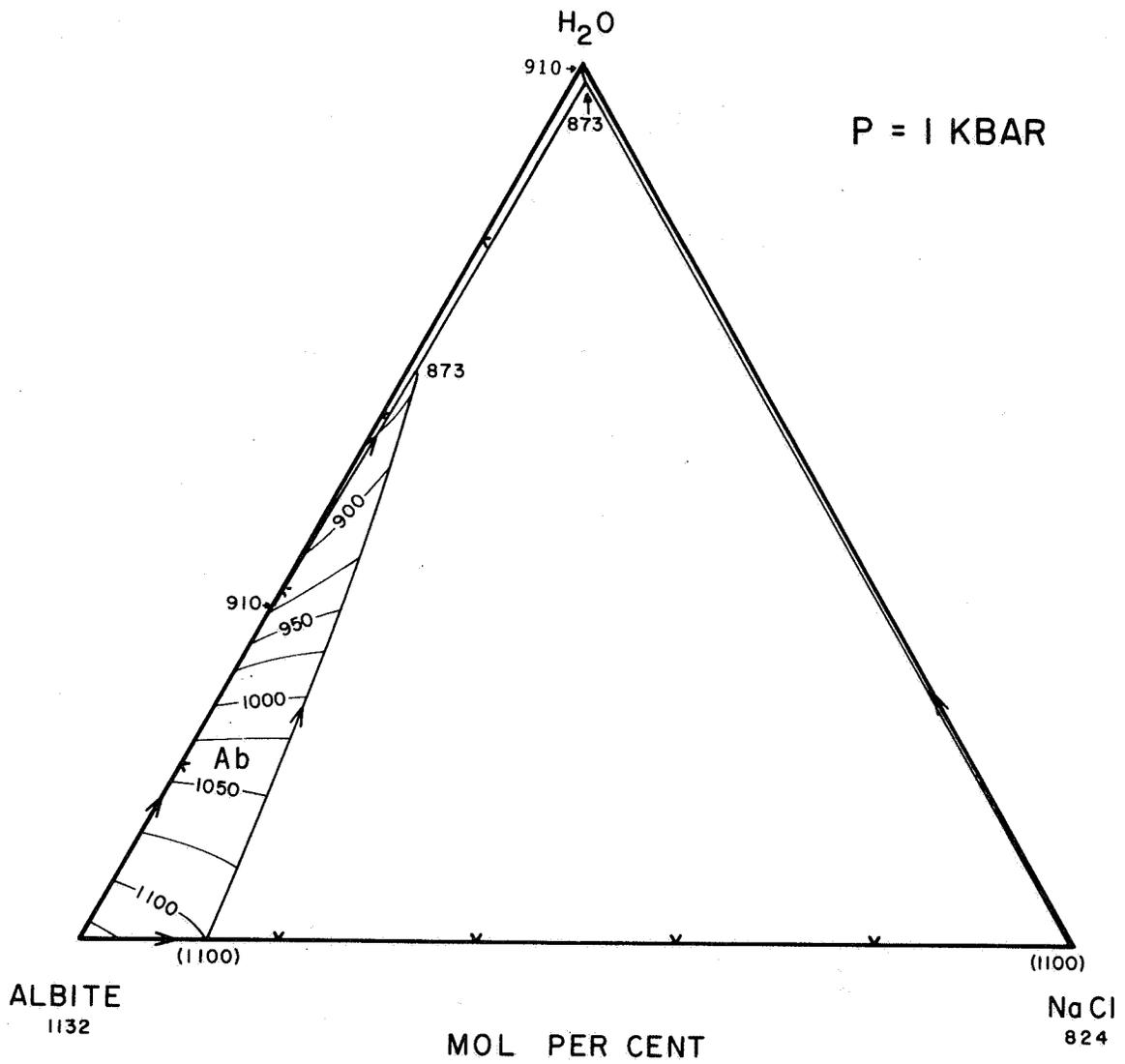


Figure 9—The system  $\text{NaAlSi}_3\text{O}_8\text{-NaCl-H}_2\text{O}$  at 1 kilobar pressure, expressed in mol percent. This diagram is derived from figure 8.

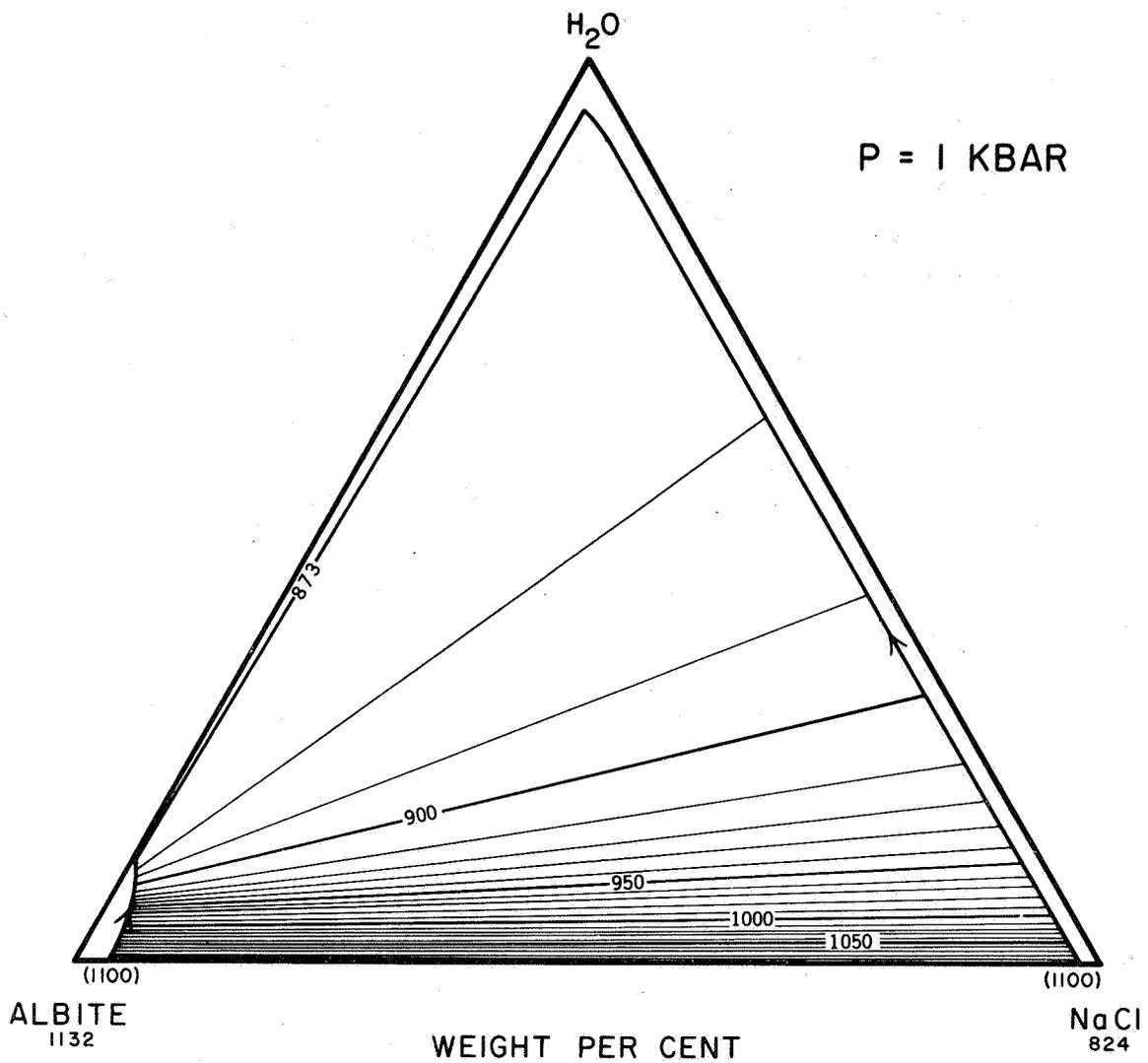


Figure 10—The tie-lines connecting silicate-rich liquids with the coexisting NaCl-H<sub>2</sub>O fluid phase in the system NaAlSi<sub>3</sub>O<sub>8</sub>-NaCl-H<sub>2</sub>O. These tie-lines form a ruled surface which is the low-temperature boundary of the miscibility gap between NaAlSi<sub>3</sub>O<sub>8</sub>-rich liquids and the second fluid phase.

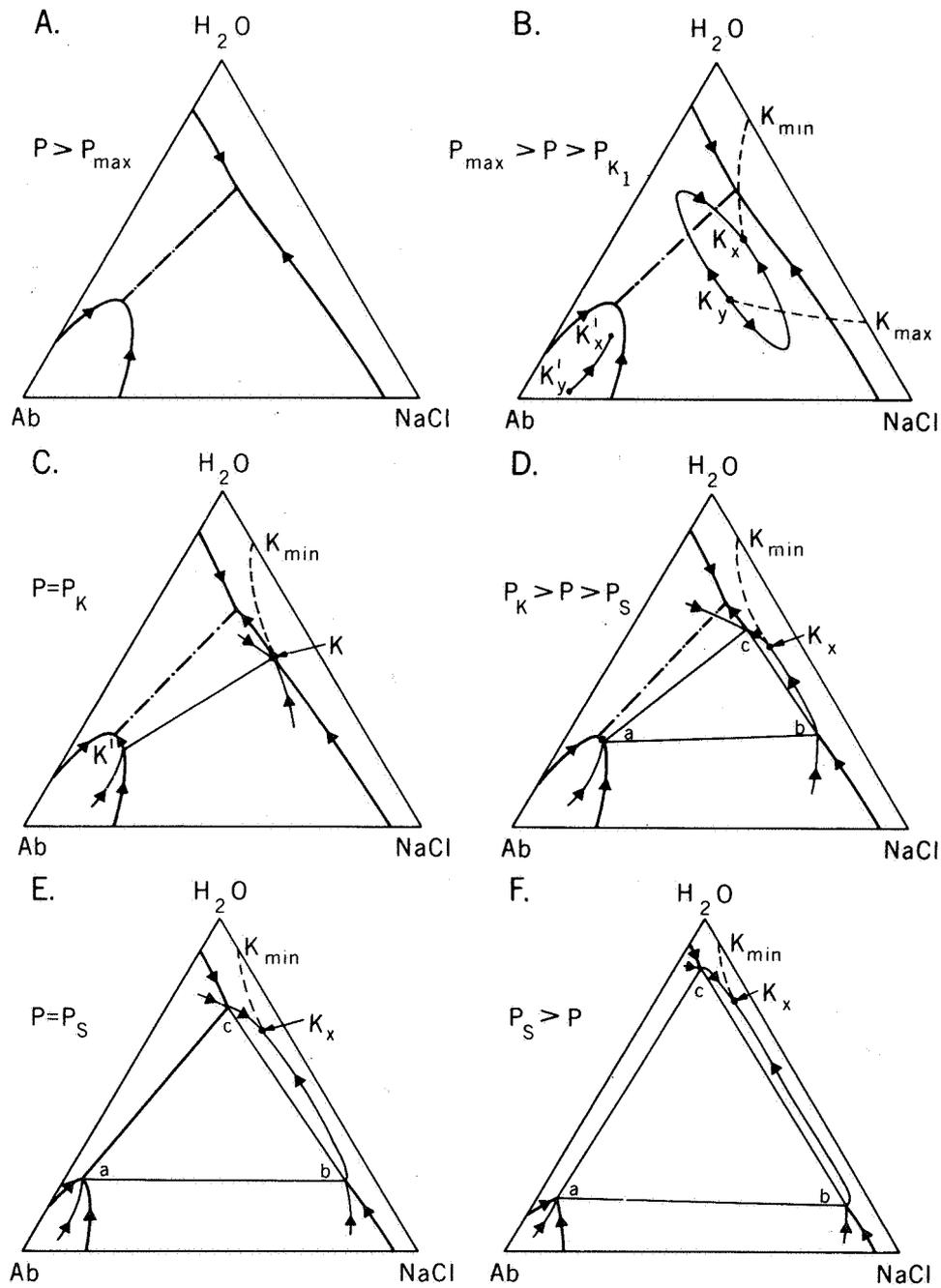


Figure 11—Polythermal isobaric sections through the system  $NaAlSi_3O_8-NaCl-H_2O$ , partly based on the  $P-T$  projection of the schematic phase relationships in this system as shown in figure 1A. For a discussion, see text.



Plate 1A—A bead of silicate glass containing three-phase inclusions of halite, saline aqueous liquid and vapor. The vapor forms the dark sphere within the inclusion. The bead is approximately 4 mm long. The run, with the composition  $\text{Ab}80\text{NaCl}20$  with 50 percent  $\text{H}_2\text{O}$  was held at  $895^\circ\text{C}$  for 72 hours.

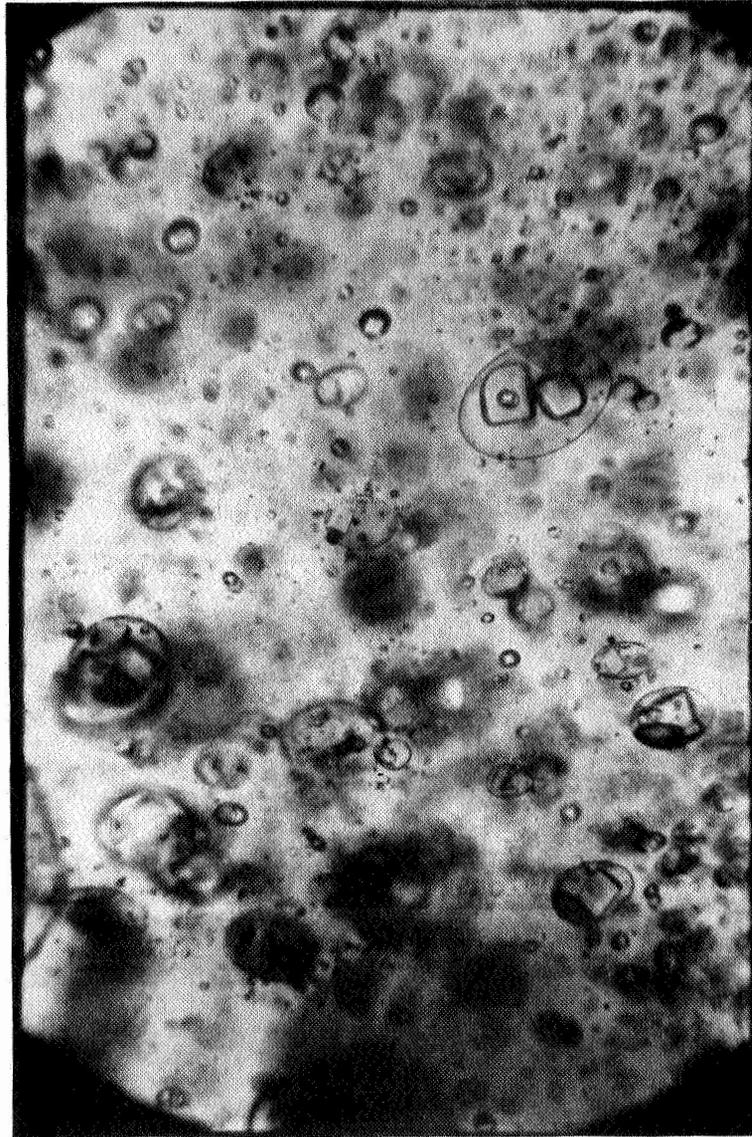


Plate 1B—Three-phase inclusions in silicate glass from a run with the composition  $\text{Ab}_{80}\text{NaCl}_{20}$  with 40 percent  $\text{H}_2\text{O}$  present, held at  $900^\circ\text{C}$  for 24 hours. The diameter of the larger inclusion in the center is about 0.1 mm. Note that the size of the inclusions varies considerably.