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EXPERIMENTAL INVESTIGATION OF SILICATE SYSTEMS CONTAINING TWO VOLATILE COMPONENTS

PART II. The Effects of NH_3 and HF, in Addition to H_2O on the Melting Temperatures of Albite and Granite*

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ABSTRACT. Addition of NH_3 to water-albite and water-granite mixtures at constant pressure raises the melting temperatures of albite and granite, whereas addition of HF to these mixtures causes marked lowering of melting temperatures. Results obtaind at 2750 bars pressure for charges containing 1:1 weight ratio of silicate to total volatiles are presented as perspective TX projections from within isobaric prisms onto the volatile faces of the prisms. In the presence of H_2O alone at 2750 bars pressure, albite melts between 795°C and 810°C, and granite begins to melt at 670°C; in the presence of 8.2 weight percent NH_3 solution, the melting interval of albite is 805°C to 825°C, and granite begins to melt at 690°C; in the presence of 8 weight percent HF solution, the melting interval of albite is 610°C to 685°C, and granite begins to melt at 595°C. No chemical reaction was detected in systems containing NH_3, but considerable reaction occurs with HF. With increasing HF concentration in the system $NaAlSi_3O_8$–H_2O–HF, quartz becomes a stable phase and the system is no longer ternary. In the presence of HF solutions, albite crystals grow much larger than in the presence of H_2O alone.

INTRODUCTION

This is the second in a series of papers describing the effects of volatile materials, in addition to water, on the melting temperatures of rock-forming silicates. In this study we are primarily interested in the melting relations of granite, and we have therefore investigated a series of "systems" granite–H_2O–second volatile. As a basis for interpreting the results obtained in these complex systems, we have also investigated a series of systems $NaAlSi_3O_8$–H_2O–second volatile. These can be treated as ternary systems, at least for low concentrations of the second volatile and the results can be presented in simple phase diagrams.

In Part I (Wyllie and Tuttle, 1960) we described the phase relations in ternary "systems" $NaAlSi_3O_8$–H_2O–second volatile. The treatment was geometrical, and its purpose was to give a three-dimensional picture of the phase spaces, surfaces, and lines within ternary isobaric (TX) prisms for such systems. Three possible arrangements of the liquidus and vaporus field boundaries between the bounding binary systems $NaAlSi_3O_8$–H_2O and $NaAlSi_3O_8$–C, where C is a second volatile component, were described: (1) They pass continuously in temperature and composition from one binary system to the other, (2) they have a temperature maximum, and (3) they have a temperature minimum. Previously published data on the effects of CO_2 and H_2O on the melting temperatures of feldspars and granite (Wyllie and Tuttle, 1959) were compared with the theoretical models. This paper describes the effects of NH_3 and HF, in addition to H_2O, on the melting temperatures of albite and

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granite. Results are presented in perspective TX projections from within isobaric TX prisms, and familiarity with Part I is required for complete comprehension of the diagrams.

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EXPERIMENTAL METHOD

Starting materials.—The silicates used were: (1) Synthetic albite glass, (2) albite crystallized hydrothermally from the glass, (3) natural granite (Westerly, Rhode Island), and (4) homogeneous glass prepared by repeated fusion of the granite. The albite glass was prepared using the method described in detail by Schairer and Bowen (1956), and crystalline albite was prepared in large sealed gold capsules using the method described by Mackenzie (1957). The Westerly is a plagioclase-microcline-quartz granite, with biotite and muscovite; its chemical, normative, and modal compositions are tabulated by Tuttle and Bowen (1958, table 11).

Solutions of NH_3 with required concentrations were prepared from distilled H_2O and "Baker Analyzed" ammonia. Their compositions were checked by titration against standardized HCl solutions, and they were stored in a cool place in tightly stoppered bottles to minimize NH_3 loss by evaporation. After completion of the runs, the solutions were checked again by titration, and the averages of concentrations before and after the experiments were taken as the true values. The solutions of HF were prepared from distilled H_2O and "Baker Analyzed" concentration hydrogen fluoride. The ingredients were mixed in the appropriate volumetric proportions to give solutions of the required concentrations, and these were stored in a cool place in tightly stoppered polyethylene bottles to minimize evaporation losses. These solutions were not standardized, but they are believed to be accurate to within 0.5 weight percent HF.

Equipment and method.—Charges were sealed inside gold capsules 15 mm long, with 2.5 mm internal diameter and 0.1 mm wall thickness. Gold tubes were cleaned with pipe cleaners, then soaked thoroughly in dilute HCl and washed in several changes of distilled water. One end of the tube was welded shut in a carbon arc and an aqueous solution of NH_3 or HF of known concentration was pipetted into the tube. The required weight of the silicate starting material was added, and the open end of the tube was sealed temporarily in the jaws of a vise to insure that no volatiles escaped during final welding in the carbon arc. The welding method has been described in detail by Tuttle and England (1955). The weights of solution and silicate within the sealed capsule were obtained by subtraction. This method provides a small closed system containing three components in the required proportions (up to the limit of solubility of the second volatile in H_2O) which can be maintained at constant pressure and temperature until equilibrium is attained.

All runs were made in cold-seal pressure vessels (Tuttle, 1949) which were heated externally by nichrome furnaces (see also Harker and Tuttle, 1955). Temperatures were controlled by galvanometer-type controllers. Pressures were applied to the capsules by pumping water into the system with an air-operated pump. Pressures were measured by Bourdon gauges. The furnace

was lowered over the pressure vessel containing the sealed capsules, and, when the required pressure developed, it was maintained at this level by bleeding the system through a valve. The walls of the capsules collapsed in response to the external pressure, which was thus transmitted to the liquid and vapor phases within. At the end of a run the furnace was raised from the pressure vessel, which was quenched by a blast of compressed air; the quench was sufficiently rapid to freeze the equilibrium in the silicate melt. The pressure was not released until the charges were cool enough to insure that the capsules would not expand and burst. After comparing the weight of a sealed capsule with its weight before the run to make sure that there had been no leakage, the capsule was cut open. The charges were dried, crushed, and examined using an X-ray diffractometer, and in immersion media using a petrographic microscope.

Pressure measurements are believed to be accurate to 3 percent, and temperature measurements to $\pm$ 5°C. When runs at close temperature intervals were required to locate boundaries, as in the system $NaAlSi_3O_8$–H_2O–NH_3 (fig. 1), the critical points were determined by holding a series of four charges in the same pressure vessel at a fixed pressure and temperature. For example, charges containing albite plus (1) H_2O, (2) 1.75 percent NH_3, (3) 3.75 percent NH_3, and (4) 8.2 percent NH_3 solutions were held at 800°C in the same pressure vessel at the same time (fig. 1, table 1). Melting was observed in three charges, but not in the fourth. A similar run at 795°C revealed no melting in any of the charges. The temperature measurement is not sufficiently accurate to locate the boundary if all these points had been determined in separate runs in different pressure vessels, but the method used fixes the relative position of the boundary.

RESULTS

General remarks.—In order to represent a ternary system in three dimensions, one of the variables, pressure, temperature, and composition, must be fixed. Since it is convenient experimentally to work under isobaric conditions, we fixed the pressure, and most of the results were obtained at a constant pressure of 2750 bars. This corresponds to a depth of 11.2 km in the Earth's crust, assuming a cover of sediments with an average density of 2.5.

The complete representation of phase relations in molecular or weight percentages differs considerably for systems containing both silicates and volatiles, and molecular percentages were used exclusively in Part I. However, weight percentages are more familiar when we think of natural rocks, and these will be used to present the results. Most of the results are illustrated in perspective TX projections from within isobaric prisms onto the faces representing volatile components of the prisms. These diagrams show the proportions of the two volatile components in liquids and vapors without showing the proportion of silicate, and plotting them in molecular or weight percentages would make little difference. Later in this series, when the effects of the different volatiles are compared, the results will be converted into molecular percentages in order to facilitate structural interpretation of the data.

Results for the "systems" granite plus two volatiles have been plotted in the same way by treating the granite as though it were a single silicate com-

ponent. There is such a great difference between the physical and chemical properties of the volatile materials on the one hand, and of the albite or granite on the other, that it seems not unreasonable to regard the granite and the crystalline assemblages appearing under different conditions as one "silicate component" in a "ternary" system containing two volatile components. The TX projections permit us to see the effect of the second volatile component, in addition to H_2O at fixed pressure, compared to the effect of H_2O alone.

In all the systems studied, attention was first concentrated on charges containing 50 percent (by weight) of the silicate. From figure 5C in Part I, it is clear that for a given concentration of an aqueous solution the temperature of beginning of melting is not affected by the ratio of silicate to solution (total volatiles), but the liquidus temperature can vary considerably with this ratio. Charges for liquidus measurements were therefore weighed out carefully, whereas for solidus measurements the weights were estimated. With practice it is not difficult to keep the ratio of silicate to solution within the limits of 40 to 60 weight percent without weighing. Measurements near the liquidus field boundary and within the vapor-deficient region will be described in later papers, after the effects of the various volatile materials on the solidus have been detailed.

The systems containing albite, H_2O, and a second volatile have been treated as ternary, although the state of the volatile components within the sealed capsules is not known. For instance, in the system $NaAlSi_3O_8$–H_2O–NH_3 some or all of the following constituents could be present: H_2O, H_2, O_2, H^+, OH^-, NH_3, N_2, NH_4OH, and NH_4^+. However, if we attempted to consider the products of reaction between the volatile materials as separate components, the treatment would become hopelessly involved. H_2O is regarded as a single component in hydrothermal systems, although some dissociation undoubtedly occurs at elevated temperatures. The results obtained in this system are readily understood if the composition NH_3 is taken as the third component, and similiar arguments apply to other systems.

The silicate phases do not react with H_2O in the experimental PT range, but in most systems studied some chemical reaction does occur with the second volatile material. With increasing concentration of the second volatile, the reaction may increase to such an extent that it cannot be neglected. For instance, in the system $NaAlSi_3O_8$–H_2O–HF, quartz crystallizes when the amount of HF in the aqueous solution added to albite exceeds 4 weight percent (with 50 percent total volatile). Although the system can no longer be regarded as ternary, it is convenient to plot the results as though it remained ternary, and this procedure is followed below.

An isobaric section at 2750 bars through the PTX model for the system $NaAlSi_3O_8$–H_2O lies between the first and second critical end-points (see Part I), and this is also probably true for many of the systems $NaAlSi_3O_8$–second volatile. However, addition of the second volatile may lead to the intersection of critical curves and surfaces in the isobaric prism, but since we are dealing experimentally with quite low concentrations of the second volatile, this is unlikely to occur within the PTX range of the present studies. The aqueous phase

coexisting with silicate liquids and crystalline material is thus a fluid phase which can be transformed continuously into vapor of liquid by suitable variation of P, T, and X. The nature of this phase was discussed in Part I and hereafter it will be called a vapor to distinguish it clearly from the silicate liquid phase.

Although nitrogen is apparently unimportant in magmatic systems, the system $NaAlSi_3O_8$–H_2O–NH_3 is described first. It was selected as the most suitable to illustrate the principles outlined in Part I because chemical reaction between albite and NH_3 solutions could not be detected. The second system, $NaAlSi_3O_8$–H_2O–HF, has direct bearing on crustal melting and magmatic processes, but it is complicated by chemical reaction between HF and albite.

$NaAlSi_3O_8$–H_2O–NH_3.—The critical runs at 2750 bars pressure, listed in table 1 and illustrated in figure 1, show that the addition of NH_3 to H_2O at constant pressure raises the melting temperature of albite. This system is therefore either of the type illustrated in figures 5, 6A, 7A, and 8 in Part I, or possibly one with a maximum on the field boundaries, figures 6C, 7C, and 9 in Part I.

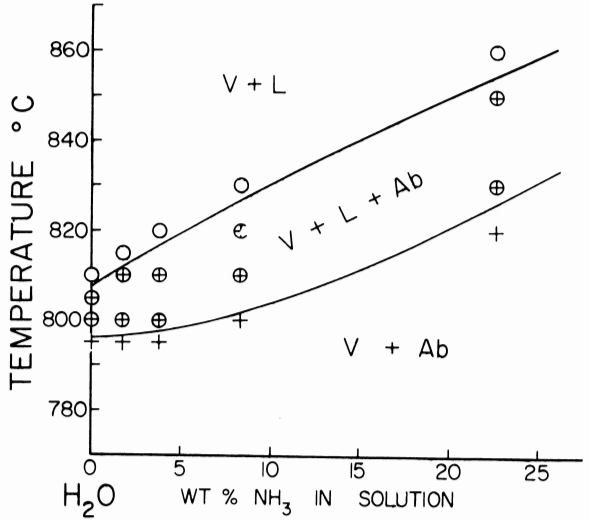

Fig. 1. Perspective TX projection for the system $NaAlSi_3O_8$–H_2O–NH_3 at 2750 bars pressure, determined for a 1:1 weight ratio of $NaAlSi_3O_8$ to total volatiles. The lower curve is a projection of the vaporous field boundary, V(L + Ab), and the upper curve is the liquidus for these compositions. The liquidus field boundary would project at a higher temperature than the upper curve (see fig. 2B).

The axis above the H_2O composition is a projection of the isobaric section in the system $NaAlSi_3O_8$–H_2O. Theoretically, albite should melt directly to a liquid in the presence of excess water vapor at constant pressure but, in fact, there is a melting interval of about 10°C. However carefully a silicate mineral may be prepared, it would be fortuitous if it were exactly on composition, and even the purest of synthetic minerals will exhibit a melting interval. Greig (1927) and Yoder (1952) have discussed this matter in some detail. A trace

TABLE 1

Results of quenching experiments in the system $NaAlSi_3O_8$–H_2O–NH_3 and the "system" granite–H_2O–NH_3. Pressure: 2750 bars

Initial Silicate Material	Weight Percent Silicate	Temp. °C	Time Hours	Result
		$NaAlSi_3O_8$–H_2O		
crystalline	ca.50*	795	3.00	V + Ab
crystalline	ca.50	800	2.25	V + L + Ab
glass	ca.50	805	2.50	V + L + Ab
crystalline	ca.50	810	2.00	V + L
		$NaAlSi_3O_8$—1.75 weight percent NH_3 solution		
crystalline	51	795	3.00	V + Ab
crystalline	52	800	2.25	V + L + Ab
glass	48	810	2.00	V + L + Ab
glass	50	815	2.00	V + L
		$NaAlSi_3O_8$—3.75 weight percent NH_3 solution		
crystalline	49.5	795	3.00	V + Ab
crystalline	ca.50	800	2.25	V + L + Ab
crystalline	53.0	810	2.00	V + L + Ab
glass	50.0	820	1.50	V + L
		$NaAlSi_3O_8$—8.2 weight percent NH_3 solution		
crystalline	49.5	800	2.25	V + Ab
crystalline	48.0	810	2.00	V + L + Ab
crystalline	50.5	820	1.75	V + L + Ab
glass	52.0	830	2.25	V + L
		$NaAlSi_3O_8$—22.5 weight percent NH_3 solution		
crystalline	49.0	820	2.25	V + Ab
crystalline	ca.50	830	2.50	V + L + Ab
crystalline	52.0	850	1.00	V + L + Ab
glass	50.0	860	1.00	V + L
		Granite–H_2O		
crystalline	ca.50	665	24.0	V + crystals
crystalline	ca.50	675	24.0	V + L + crystals
		Granite—8.2 weight percent NH_3 solution		
crystalline	ca.50	680	48.5	V + crystals
crystalline	ca.50	700	22.5	V + L + crystals

* Ca.50: Between 40 and 60 weight percent. The proportions were estimated for solidus measurements.

of impurity affects the liquidus temperature only slightly, and the melting temperature is normally taken as that at which the last crystal disappears. A more reasonable representation of the phase relationships would therefore be given if the lower curve in figure 1 were moved upwards through 10°C until it meets the upper curve on the H_2O axis.

Because of the relatively high temperatures involved, all runs were of short duration (from one to three hours), and equilibrium was not attained.

However, there appears to be little doubt concerning the equilibrium assemblage. Many more runs were completed than those listed in table 1, and duplicate runs were frequently made using glass and crystalline material. Crystalline material was used for determination of the beginning of melting because a trace of glass is readily detected optically, whereas glass was used as a starting material for determination of the liquidus because the growth of a few crystals in glass is sufficient to indicate the "direction" of equilibrium.

When held one hour in the field V + L (fig. 1), crystalline material (with either pure H_2O or NH_3 solutions) was not completely melted. The charge consisted of a white raft of crystals surrounded by a border of glass, the thickness of which increased with the duration of the run. Under the same conditions no albite grew in a charge containing glass as a starting material. Crystalline material, if held in the field V + L + Ab in figure 1, was converted to a white raft of crystals surrounded by a translucent glass border containing dispersed albite crystals. With glass as a starting material, the product consisted of a translucent glass bead with albite crystals spread evenly throughout.

When crystals were used as a starting material, the phases present in the border, which developed around the raft of remnant albite, correspond to the phases produced when glass was used as a starting material. This is therefore believed to be the equilibrium assemblage although the albite and glass may not be in equilibrium proportions. If the runs could have been continued for a longer time, the remnant albite would probably have been converted to the material preserved in the border zone.

Melting undoubtedly began where vapor was in contact with the charge, and development of a zone of liquid around the crystals appeared to protect them from further melting until the vapor had time to diffuse through the outer zone. On the other hand, with glass as a starting material, nucleation of crystals in the presence of excess vapor appeared to proceed quite readily, although we do not know the length of time required for the attainment of equilibrium.

The results listed in table 1 show the equilibrium assemblages interpreted from the listed runs and from duplicate runs. Excess vapor was present in all charges, and microscopic examination revealed a few of the low index isotropic spheres characteristically precipitated during the quench from the vapor phase in silicate-water systems. The amount of albite dissolved in the vapor phase is not known.

The lower curve in figure 1, the temperature of beginning of melting, coincides with the projection of the vaporus field boundary V(L + Ab),[1] but the upper curve, giving the temperature of complete melting, is the liquidus curve for charges containing a 1:1 weight ratio of albite to total volatiles. It is *not* a projection of the liquidus field boundary (V)L(Ab), as are the similar curves in figure 6, Part I. The significance of the upper curve can most readily be explained by examining the melting behavior of a charge containing this ratio of albite to total volatiles.

Let us assume first that there is no maximum on the field boundaries, then

[1] See Part I for key to abbreviations.

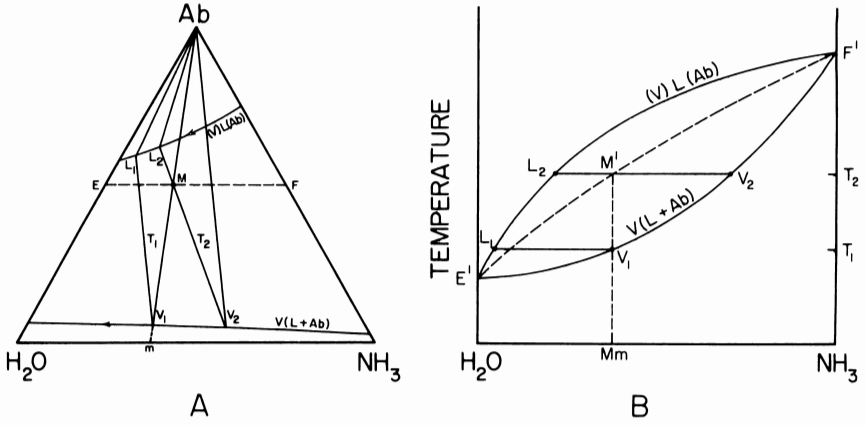

Fig. 2. Schematic isobaric polythermal projection (A) and perspective TX projection (B) of the system $NaAlSi_3O_8$–H_2O–NH_3, illustrating the melting behavior of the charge M, which contains 50 weight percent $NaAlSi_3O_8$ and 50 percent solution *m*. The solidus and liquidus temperatures for this charge are T_1 and T_2. Three-phase triangles, AbL_1V_1 and AbL_2V_2, are shown for these temperatures. The dashed line E'M'F' in figure 2B corresponds to the upper curve in figure 1.

figure 2 illustrates schematically their arrangement in the isobaric polythermal equilibrium diagram (fig. 2A) and in the perspective TX projection (fig. 2B). Two isothermal three-phase triangles are shown in each projection. The triangles V_1L_1Ab and V_2L_2Ab in figure 2A, at temperatures T_1 and T_2, appear in figure 2B as horizontal straight lines, V_1L_1 and V_2L_2, connecting pairs of points on the projected field boundaries. The line EF in figure 2A represents the 1:1 weight ratio line, giving the bulk compositions of the charges used to determine the upper curve in figure 1. Consider the charge with bulk composition M, consisting of 50 weight percent albite and 50 weight percent NH_3 solution with concentration *m*. The two three-phase triangles were chosen so that the sides V_1Ab and V_2L_2 intersect (in projection only) at M.

When M is heated in a closed system, it consists of V + Ab until it reaches temperature T_1 when the vapor composition is V_1 on the vaporus field boundary. At T_1, M is about to enter the three-phase triangle V_1L_1Ab, and a trace of liquid L_1 develops. Note that this occurs wherever M may lie on the line V_1Ab, i.e. for a charge containing a solution of a given composition, *m*, the temperature of beginning of melting *is independent of the ratio of silicate to solution* (*total volatiles*). Between the temperatures T_1 and T_2, the charge M lies within the three-phase space V + L + Ab, and the compositions of the vapor and liquid change along the vaporus field boundary from V_1 to V_2 and along the liquidus field boundary from L_1 to L_2. At T_2 the last trace of albite melts, and the charge consists of V_2 + L_2. At temperatures greater than T_2 the charge lies within the two-phase space V + L.

The temperature of complete melting is the temperature at which the V + L(Ab) side of a three-phase triangle passes through the bulk composition of the charge. Note that for a charge containing a solution of a given composition, *m*, if the silicate:solution ratio is greater than 1:1, this will occur at a

higher temperature than T_2; if the ratio is less than 1:1, it will occur at a lower temperature.

The V + L(Ab) side of the three-phase triangles generates the ruled surface V + L(Ab), and the temperature of complete melting for any charge with bulk composition between the two field boundaries is thus the temperature at which a vertical line through the bulk composition intersects the V + L(Ab) surface. The point M′ in figure 2B is a projection of the point of intersection with this surface of a vertical line through M, and the dotted line E′M′F′ in figure 2B represents the intersection of a vertical plane through EF (fig. 2A) with the surface V + L(Ab). The experimentally determined upper curved line in figure 1 thus corresponds to the dotted line E′M′F′ in figure 2B.

Each point on this curve represents equilibrium between a vapor on the projected vaporus field boundary and a liquid on the liquidus field boundary, which is not shown. The vapor is richer and the liquid is poorer in NH_3 than the bulk composition of the charge. For a given volatile composition in figure 1, the liquidus field boundary projects at a higher temperature than the upper curved line (compare with fig. 2B).

Field boundaries in the system could exhibit a maximum for some concentration of NH_3 greater than 25 weight percent (see figs. 6C and 7C, Part I), but for that portion of the system with field boundaries ascendant from $NaAlSi_3O_8$–H_2O (as in fig. 1) charges would behave in the manner described above.

Because addition of NH_3 to H_2O raises the melting temperature compared to that in the presence of H_2O alone, we may conclude that the total molar percentage of volatiles dissolved in the silicate melt becomes smaller as the concentration of NH_3 in the volatile components is increased.

Albite crystallized from glass in the presence of NH_3 solutions appeared identical with that crystallized in the presence of H_2O. Products were examined both optically and with an X-ray diffractometer, but no detailed structural studies were made. The high-temperature form of albite was found in all runs (Mackenzie, 1957).

Only one point was determined on the solidus of the "system" granite–H_2O–NH_3. The critical runs are listed in table 1. Using a charge with approximately 50 weight percent granite and a solution containing 8.2 weight percent NH_3, the temperature of beginning of melting at 2750 bars pressure lies between 680°C and 700°C. In the presence of H_2O alone at the same pressure, the temperature of beginning of melting is 670°C ± 5°C. Granite therefore behaves in the same manner as albite; the melting temperature in the presence of excess vapor is raised when the proportion of NH_3 in the vapor is increased at constant pressure.

$NaAlSi_3O_8$–H_2O–HF.—The critical runs at 2750 bars pressure (listed in tables 1 and 2 and illustrated in fig. 3) show that the addition of HF to H_2O at constant pressure lowers considerably the melting temperature of albite when compared with its melting temperature in the presence of H_2O alone. The system is not ternary because extensive chemical reaction occurs between HF and albite. Quartz appears as a stable phase when the concentration of HF in the aqueous solution exceeds 4 weight percent. The curves in figure 1 are thus

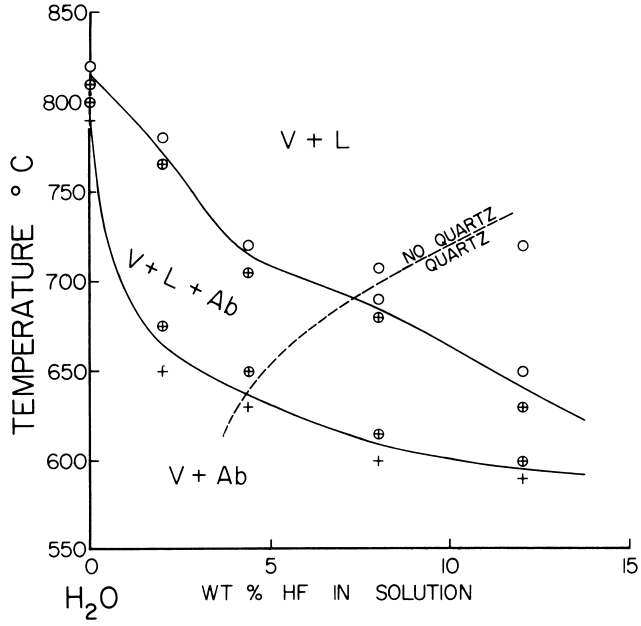

Fig. 3. Perspective TX projection for the system $NaAlSi_3O_8$–H_2O–HF at 2750 bars pressure, determined for a 1:1 weight ratio of $NaAlSi_3O_8$ to total volatiles. The lower curve is a projection of the solidus, and the upper curve is a projection of the upper stability limit of albite for these compositions. Quartz is stable to the right of the dashed line, and here the system is no longer ternary. Only a trace of quartz is present above the upper curve.

projections from isobaric multicomponent space, and comparison with the ternary models derived in Part I should be made with caution. However, the plotted curves appear to be indicative of a minimum on the field boundaries for some concentration of HF greater than 12 weight percent (figs. 6D, 7D, and 10 in Part I).

Because temperatures involved in this system are lower than in $NaAlSi_3O_8$–H_2O–NH_3, longer runs were possible, and it was not difficult to establish equilibrium. Many more runs were completed than those listed in table 2, and many duplicate runs were made using glass and crystalline starting materials. Several runs of much longer duration were completed to check equilibrium. The same results were obtained in 312 hrs as in 18 hrs.

In the systems $NaAlSi_3O_8$–H_2O and $NaAlSi_3O_8$–H_2O–NH_3 the temperature of beginning of melting was readily determined by the appearance of glass of low refractive index. In the system $NaAlSi_3O_8$–H_2O–HF the situation was complicated to some extent by the precipitation of low index phases from the vapor during the quench. In some runs below the solidus of figure 3 there appeared to be a trace of glass locally developed, but for a given bulk composition the solidus was taken as the temperature at which a small amount of glass developed uniformly throughout the charge; above this temperature the proportion of glass developed increased regularly.

TABLE 2

Results of quenching experiments in the system $NaAlSi_3O_8$–H_2O–HF and the "system" granite–H_2O–HF. Pressure: 2750 bars

Initial Silicate Material	Weight Percent Silicate	Temp. °C	Time Hours	Result
		$NaAlSi_3O_8$—2 weight percent HF solution		
crystalline	ca.50*	650	18	V + Ab
crystalline	ca.50	675	21	V + L + Ab
glass	57	780	29	V + L
		$NaAlSi_3O_8$—4.3 weight percent HF solution		
crystalline	ca.50	630	20	V + Ab + Qz**
crystalline	ca.50	650	18	V + L + Ab
glass	52	705	19	V + L + Ab
glass	50	720	19	V + L
		$NaAlSi_3O_8$—8 weight percent HF solution		
crystalline	ca.50	600	22	V + Ab + Qz
crystalline	ca.50	615	312	V + L + Ab + Qz
glass	50	680	20	V + L + Ab + Qz
glass	50	690	18	V + L + Qz
glass	50	705	19	V + L
		$NaAlSi_3O_8$—12 weight percent HF solution		
crystalline	ca.50	590	23	V + Ab + Qz
crystalline	ca.50	600	22	V + L + Ab + Qz
glass	51	630	26	V + L + Ab + Qz
glass	51	650	18	V + L + Qz
glass	55	720	19	V + L + Qz
		Granite—4.3 weight percent HF solution		
crystalline	ca.50	600	6	V + crystals
crystalline	ca.50	610	2	V + L + crystals
		Granite—8 weight percent HF solution		
crystalline	ca.50	595	392	V + crystals
crystalline	ca.50	600	25	V + L + crystals
		Granite—12 weight percent HF solution		
crystalline	ca.50	590	28	V + crystals
crystalline	ca.50	595	28	V + L + crystals

* Between 40 and 60 weight percent. The proportions were estimated for solidus measurements.

** Qz = quartz.

If the system were not complicated by reaction, the lower curve in figure 3 would represent a projection of the vaporus field boundary V(L + Ab), and the upper curve a projection of the liquidus for compositions with a 1:1 weight ratio of silicate to total volatiles. In fact, the lower curve is a projection of the solidus for the system while the upper curve represents the upper stability limit of albite for these compositions. The latter is not a projection of the liquidus because quartz is stable to higher temperatures for the higher HF concentrations.

The part of the system free of quartz (fig. 3) may be regarded as ternary, but even here it is unlikely that the compositions of liquids and vapors can be represented in terms of the three components. The significance of the upper curve can be understood by examining the melting behavior of a charge such as M in the system $NaAlSi_3O_8$–H_2O–NH_3 (fig. 2). In figure 2 and in the accompanying discussion, if HF were substituted for H_2O, and H_2O were substituted for NH_3, the treatment and conclusions would be identical. Therefore, each point on the upper curve in figure 3 (when quartz is absent) represents equilibrium between a vapor on the projected vaporus field boundary (solidus) and a liquid on the liquidus field boundary, which is not shown. The vapor is poorer and the liquid is richer in HF than the bulk composition of the charge.

Because the addition of HF to H_2O at constant pressure lowers the melting temperature of albite compared to that in the presence of H_2O alone, we may conclude that the total molar percentage of volatiles dissolved in the silicate melt becomes greater as the concentration of HF in the volatile components is increased. Preliminary solubility measurements indicate that this is so; these results will be presented in a later paper, together with other solubility data.

Albite crystallized from glass in the presence of HF solutions is several times larger than that crystallized in the presence of H_2O alone. The crystals are well formed, with prismatic habit. They are of such a size that detailed optical measurements may be possible. X-ray powder diffraction patterns showed that the high-temperature form of albite crystallized in all runs. In the presence of H_2O, runs of very long duration (months) are required for the lattice parameters of high-temperature albite to approach the values characteristic of the temperature of crystallization (Mackenzie, 1957). From a few trial runs it appears that addition of HF does not appreciably affect the rate of structural change despite the fact that HF is such an effective flux in the liquid phase.

The runs containing quartz lie to the right of the dashed line in figure 3. In general the amount of quartz increases with HF concentration and decreases with increasing liquid content. No quartz could be found in charges using 2 weight percent HF solution, and most quartz was developed in subsolidus runs using the 12 percent solution. Here, quartz constituted about 20 percent of a charge. In all runs above 640°C only a few percent quartz was present, barely sufficient to be detected by X-ray diffraction patterns. Thus, only a trace of quartz persisted above the stability field of albite. Several runs were completed between 580°C and 700°C, using a 20 weight percent HF solution. Albite had no stability field at this concentration, pressure and temperature range, quartz being the only stable crystalline phase.

The quartz crystallized as short hexagonal prisms doubly terminated by pyramids. The prism faces were always subordinate to the pyramids and were often absent altogether. This is the characteristic habit of β (high) quartz. No change could be detected in the habit of the quartz in the temperature interval 580°C to 710°C. According to Yoder (1950), the $\alpha \rightleftarrows \beta$ quartz inversion of this pressure occurs at 645°C.

In subsolidus runs the quartz crystals occurred singly or in clusters, and they were usually enclosed by low index isotropic material with the appearance

of glass. The refractive index of this material was somewhat lower than that of the glass developed by melting of albite. It appeared to be quite unrelated to melting, and it seems more likely that this is a gelatinous product resulting from the reaction between HF and albite. The material persisted above the soldius, but quartz was also enclosed in normal glass fragments, confirming that it was in equilibrium with the liquid. Occasionally, when glass was used as a starting material, large isolated albite crystals were partially surrounded by narrow envelopes of low index isotropic material. We have insufficient evidence to decide whether this is related to equilibrium conditions or whether it represents material deposited from the vapor phase during the quench.

Material precipitated from the vapor phase during the quench was far more abundant in this system than in $NaAlSi_3O_8$–H_2O or $NaAlSi_3O_8$–H_2O–NH_3, indicating that much more solid material was dissolved in the vapor. The deposit from the vapor phase formed a white crust on the walls of the gold capsule, increasing proportionately with the concentration of HF. This crust could sometimes be collected and examined separately from the main charge.

Three phases were recognized in the deposit: (1) The low index isotropic spheres found sparsely scattered through the charges in other systems were abundant. In runs using 2 and 4.3 weight percent HF solutions the spheres were clear, but with the 8 percent solution a few minute birefringent crystals were present in the centers of the spheres. With the 12 percent solution the central crystals were so closely packed that they were opaque. The spheres, with black centers, occurred in large clusters. (2) Fragments and shreds of low index isotropic material with the appearance of glass. The refractive index of this and of the spheres was just below 1.476. (3) The third phase consisted of colorless crystalline material, possibly comprising at least two minerals. The crystals were of various sizes and habit, sometimes prismatic but more often tabular, with many crystal faces. They had low birefringence and very low refractive index (much lower than 1.476).

In several runs the amount of vapor deposit was great enough to yield X-ray diffraction patterns. In all patterns recorded three peaks appeared quite strongly with d spacings 2·92, 5·70, and 5·25, in order of decreasing intensity. We were unable to identify the crystalline material from these data. The development of free quartz in many runs suggests that Na_2O and Al_2O_3 passed into the vapor phase preferentially, and it seems probable that the crystals precipitated by the vapor phase during the quench consist of one or more sodium aluminum fluorides, possibly hydrated. The low refractive indices of such minerals tend to support this possibility. In the presence of H_2O alone at 500°C and pressures less than 2000 bars, Na_2O and SiO_2 pass into the vapor phase in excess of the albite ratio, leaving an excess of Al_2O_3 in the solid (Morey, 1957).

In two runs the vapor phase was separated from the solid and liquid phases using a technique which will be described in a later paper. Measurements were made to determine the weight percentage of the vapor phase precipitated as solid material during the quench. At 760°C, using the 4.3 weight percent HF solution, the two runs gave values of 2.9 and 3.0 weight percent. Some H_2O and HF were chemically bound in the solid, hence the amount of

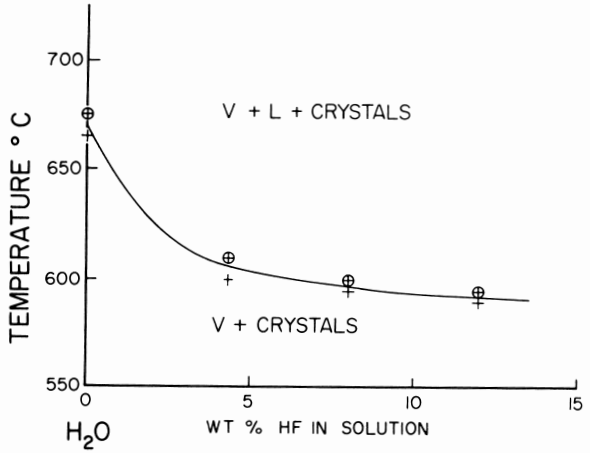

Fig. 4. Perspective TX projection for the "system" granite–H_2O–HF at 2750 bars pressure, determined for a 1:1 weight ratio (approximately) of granite to total volatiles. The curve is a projection of the solidus, and it shows the effect of HF in addition to H_2O, at constant pressure, on the temperature of beginning of melting of granite, compared to the effect of H_2O alone.

albite (in nonstoichiometric proportions) dissolved in the vapor phase was less than 2.9 weight percent.

Granite–H_2O–HF.—Six critical runs of 30 completed in this "system" are listed in table 2 and illustrated in figure 4. Granite behaves in the same manner as albite, i.e. the temperature of beginning of melting in the presence of excess vapor at constant pressure is lowered when the HF content of the charge is increased. Addition of a small percentage of HF produces a marked depression of the melting temperature, and further addition of HF produces a lesser effect; the curve for the beginning of melting begins to level off with increasing HF concentrations when the HF concentration reaches about 5 percent.

The lowering of the temperature of beginning of melting caused by addition of HF indicates that HF is more soluble in the liquid than is H_2O. In comparison with the model system $NaAlSi_3O_8$–H_2O–HF, the first liquid developed is richer in HF than is the bulk composition of the charge, i.e. the HF is more soluble in the liquid than H_2O. With increase in temperature for a given bulk composition, the feldspar passes into the liquid phase more readily than the quartz (established by optical and X-ray methods), and there is a wide temperature interval in which the charges consist of vapor + liquid + quartz + mica. Phase relations near the liquidus are not known for the "system" Westerly granite–H_2O, but from data on the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O (Tuttle and Bowen, 1958) and on the composition of this granite, the quartz should dissolve before the feldspar, leaving vapor + liquid + feldspar + mica (feldspar is the primary phase at this pressure).

Addition of HF to the "system" thus reduces the feldspar stability field relative to the quartz field. The feldspar is less stable in the presence of HF solutions than in the presence of H_2O, as would be expected, and the quartz appears to be more stable. This is suggested by the equilibrium assemblages

with HF solutions at 690°C, 730°C, and 760°C, where no feldspar remains. In each set of charges X-ray diffraction patterns demonstrate a proportional increase of quartz to HF content.

This effect may be caused or accentuated by preferential passage of alkali and alumina into the vapor phase, as in the system $NaAlSi_3O_8$–H_2O–HF, leaving the liquid relatively enriched in silica. However, in this "system", X-ray diffraction patterns of the white crust deposited on the walls of the gold capsules reveal quartz as well as other phases developed in the albite system. There are also peaks with *d* spacings 5·68, 2·97, and 2·92; the first is prominent and the other two are weak. Two correspond to the peaks found for the vapor deposit in the albite system, but the relative intensities are reversed. The crust contains low index tabular crystals and isotropic spheres very similar to those described for the albite system.

DISCUSSION

Some applications of these results to petrological processes have been discussed elsewhere (Tuttle and Wyllie, 1957), and further applications will be reserved until data on the effect of other volatile materials have been presented. However, it should be pointed out at this stage that, in the systems described so far, the effect of the second volatile material (CO_2, NH_3, and HF) on the melting relations of granite has been similar to the effect on albite, confirming that the ternary systems $NaAlSi_3O_8$–H_2O–second volatile are satisfactory models for the complex "systems" granite–H_2O–second volatile.

The results described were obtained at constant pressure. In order to represent the effect of pressure in three dimensions, one of the other variables must be fixed, for instance, the composition. Since the temperature of beginning of melting is independent of the ratio of silicate to solution, we need fix only the concentration of the solution to illustrate as a curve the PT variation for the beginning of melting of a silicate in the presence of two volatile materials. At 2750 bars pressure the temperature of beginning of melting of granite in the presence of 4.3 weight percent HF solution is 605°C, 65°C lower than in the presence of H_2O alone. The PT curve for the beginning of melting of granite in the presence of 4.3 percent HF solution probably remains about 65°C below that for melting in the presence of H_2O alone, at least for pressures greater than 1000 bars. Similar PT curves will pass through each point on the solidus in the TX projection in figure 4.

The chemical reaction between albite and HF is a function of the ratio of HF to albite. For the fixed weight ratio of 1:1 silicate to total volatiles, the percentage of quartz developed in the system $NaAlSi_3O_8$–H_2O–HF increases with increasing HF concentration. However, for a given HF solution increase of the silicate:volatile ratio will decrease the ratio of HF to albite and the extent of reaction will also decrease. Therefore, for bulk compositions near the liquidus field boundary there is a strong possibility that quartz will not develop and that the phase relations may remain effectively ternary for solutions of much higher HF concentration. These conditions correspond more closely to magmatic conditions that the experiments described above, using a considerable excess of vapor.

Part III of this series will describe the experimental studies on the melting relations of albite and granite in the presence of H_2O, together with HCl, P_2O_5, SO_3, and Li_2O.

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