Phase-equilibrium studies in the system $NaAlSiO_4$ (*nepheline*)–$KAlSiO_4$ (*kalsilite*)–SiO_2–H_2O

With Plate IX

By D. L. Hamilton and W. S. MacKenzie

Department of Geology, Manchester University

Summary. Phase-equilibrium relations have been determined at 1000 kg/cm^2 water pressure for compositions within the system $NaAlSi_3O_8$–$KAlSi_3O_8$–$NaAlSiO_4$–$KAlSiO_4$ in the area adjacent to the temperature minimum. The composition and temperature of the minimum are $Ne_{50}Ks_{19}Qz_{31}$ and $750° \pm 7°$ C respectively. The compositions of 102 plutonic rocks and 122 extrusive rocks, from Washington's tables, that carry 80 % or more of normative Ab+Or+Ne have been plotted; the areas of high density show a marked similarity to the positions of the low-temperature regions of the synthetic system and suggest that many undersaturated rocks are derived by fractional crystallization from a trachytic magma.

Introduction

THIS paper is mainly concerned with the presentation and discussion of phase-equilibrium relationships in the system $KAlSiO_4$ (kalsilite), $NaAlSiO_4$ (nepheline), $NaAlSi_3O_8$ (albite), $KAlSi_3O_8$ (orthoclase), H_2O. This system is part of the system SiO_2–$KAlSiO_4$–$NaAlSiO_4$ which Bowen (1937) named 'Petrogeny's Residua System' because experimental studies of silicate systems have shown that residual liquids resulting from fractional crystallization become enriched in alkalis and/or silica. It is deduced that in natural magmas containing a large number of components, fractionation will produce residual liquids enriched in alkalis, alumina, and silica. The salic constituents, which form the major proportion of these liquids, can be represented in composition in the system SiO_2–$KAlSiO_4$–$NaAlSiO_4$. Granite composition can be represented on the silica-rich side of the alkali feldspar join, syenites on the join, and nepheline syenites on the silica-poor side of the join. These observations have been used in support of the theory that fractional crystallization is the main factor in differentiation of magmas to produce certain rock types whose compositions can be represented within the system SiO_2–$KAlSiO_4$–$NaAlSiO_4$.

Schairer and Bowen (1935) determined the mutual melting relations of minerals in the system SiO_2–$KAlSiO_4$–$NaAlSiO_4$ and Bowen (1937) further discussed the applications of this system to the origin of certain rock types. There is, however, ample evidence from natural rocks that water may be an important constituent of magmas and it is logical to study the effect of water on the equilibrium relations. This has been done for the silica-rich part of the system by Tuttle and Bowen (1958) and the present work is concerned with the silica-poor part of the system or what may be called the 'phonolite' or 'nepheline syenite' system.

At an early stage in this study it was agreed that work should be restricted to the sodium-rich part of the system since R. F. Fudali of Pennsylvania State University had begun an investigation of the potassium-rich part of the system. The equilibrium diagram shown in fig. 1 is very similar to the preliminary diagram published by one of us (Hamilton, 1961) but the present diagram incorporates the data obtained by Dr. Fudali for the potassium-rich part of the system. The diagram was drawn in consultation with Dr. Fudali and the present authors are grateful to him for his collaboration in providing the data for the potassium-rich part of the diagram.

Experimental methods

The method of making homogeneous gels used as starting materials for the experimental studies has been described in previous publications (Hamilton and MacKenzie, 1960; Hamilton, 1961) and is an adaptation of the method of Roy (1956).

A total of thirty-five compositions were prepared initially each weighing 5 grams. In a few cases intermediate compositions were prepared by making mechanical mixtures of weighed amounts of two adjacent compositions. Cold seal pressure vessels (Tuttle, 1949) were used for all the experiments and the sealed-tube technique (Goransen, 1931) was adopted to ensure that no leaching of the charges took place. The thermocouples were calibrated at the melting point of zinc (419·5° C) and sodium chloride (801° C) and the temperatures are estimated to be within ±5° of the values quoted. All the experiments were made at a pressure of water of 1000 kg/cm^2 and the water pressure is estimated to have been kept within ±20 kg/cm^2 of this value throughout each experiment.

Identification of the phases present in the products of each experiment was made by means of a petrographic microscope and in some cases X-ray diffraction patterns were recorded using a Philips highangle diffractometer. The compositions of the feldspars were determined from the position of the $\bar{2}01$ reflection in X-ray diffraction patterns (Bowen and Tuttle, 1950) using $KBrO_3$ as an internal standard (Orville, 1958). Nepheline compositions were also determined from

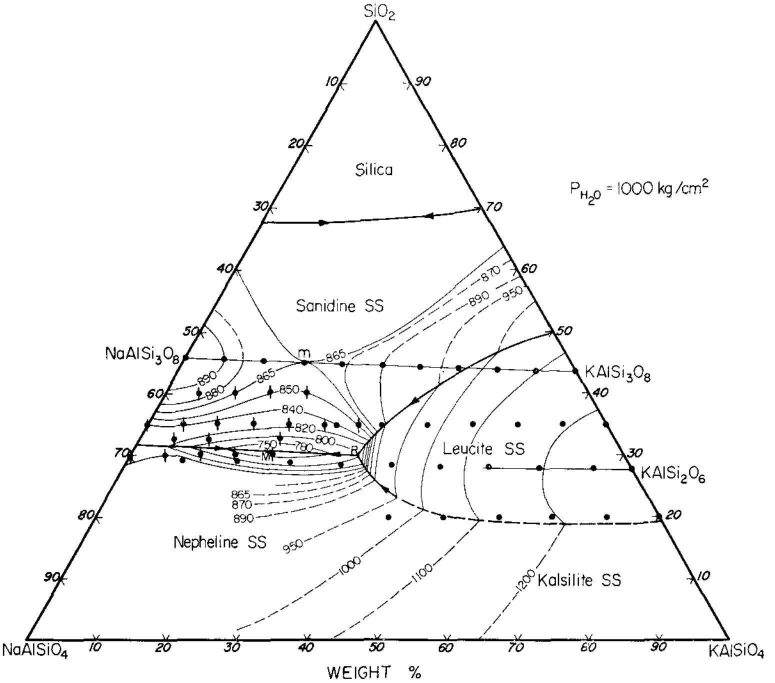

Fig. 1. The equilibrium diagram for part of the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2–H_2O at P_{H_2O} = 1000 kg/cm² projected on to the anhydrous base. ɸ = liquidus temperatures determined in the present work. ● = liquidus temperatures determined by Fudali or by Tuttle and Bowen (1958). *m* = alkali feldspar minimum. *M* = $NaAlSi_3O_8$–$KAlSi_3O_8$–$NaAlSiO_4$–$KAlSiO_4$ temperature minimum. Composition of *M* = $Ne_{50}Ks_{19}Qz_{31}$. Temperature of *M* = 750°±7°. The position of the boundary separating the fields of nepheline solid solutions from kalsilite solid solutions has not been determined.

X-ray powder diffraction patterns using the data of Hamilton and MacKenzie (1960) for the positions of the $20\bar{2}2$ and $21\bar{3}0$ reflections for nephelines with the maximum amount of solid solution of SiO_2 at 700° C. Most of the experiments in which the nepheline compositions were required were carried out at temperatures above 800° C and an error is thereby introduced: this error is small and has been neglected.

Experimental results

(i) *The liquidus surface.* Quenching experiments were made on seventeen compositions in the sodium-rich part of the system to determine the liquidus surface. The results of these experiments are listed in table I and in fig. 1 is shown a projection of the liquidus surface on the anhydrous base of the system.[1] Each composition investigated in the present study is denoted by a solid circle with a short vertical line through it. The data on compositions on the join $NaAlSi_3O_8$–$KAlSi_3O_8$ are taken from Bowen and Tuttle (1950) and those on the remaining compositions are from Fudali (unpublished data). To ensure that equilibrium was attained in all experiments two types of starting material were used in the experiments, viz. chemical powder (or gel) and finely crushed glass. The latter was prepared by holding a chemical powder above its liquidus temperature, quenching the run, and grinding the glass to a finely divided state. In most cases the liquidus temperature determined using the chemical powder as starting material, i.e. approaching the liquidus from a low-temperature assemblage, was 5°–10° C above that obtained using the ground glass, i.e. approaching the liquidus from a high-temperature material. This difference persisted even though runs of up to seven days duration were made.

The most likely explanation of this discrepancy is that the melts are extremely viscous and this inhibits both the precipitation of crystals a few degrees below the true liquidus and the solution of crystals a few degrees above the true liquidus temperature.

(ii) *The nepheline–feldspar field boundary.* The position of the field boundary, separating the nepheline field from the feldspar field,[2] which is drawn in fig. 1 was determined from the data given in table I. Compositions were held a few degrees below their liquidus temperature and the products of the runs examined optically. The morphology of the crystals was the most useful property for distinguishing feldspar from the nepheline since the feldspar usually has a lath or needle shape when enclosed in glass whereas the nepheline usually has a hexagonal or

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[1] Although the system under investigation is quaternary the effect of small amounts to H_2O dissolved in the silicate liquid will be nelected here to simplify the presentation of the data. The water contents of the liquids have not been determined and the diagrams used are projections from the four component system on to the anhydrous base: this procedure can be adopted here because no hydrous minerals are considered although analcite did form in a few experiments on nepheline-rich compositions.

[2] The nephelines and feldspars encountered in this study are ternary solid solutions and binary solid solutions respectively but for brevity the words solid solution will be omitted.

TABLE I. Critical experiments which determined the liquidus surface for compositions marked ⧳ on fig. 1

Abbreviations: Feld = feldspar, Neph = nepheline, P = chemical powder

Code no.	Run no.	Initial composition			Temp. °C	Duration days	Initial condition	After run
		Ne	Ks	Qz				
1	427	55	5	40	900	5	P	All Glass
	438	55	5	40	890	4	P	All Glass
	434	55	5	40	880	2	P	Glass and Feld
2	435	50	10	40	875	2	P	All Glass
	418	50	10	40	865	2	P	Glass and Feld
3	352	45	15	40	860	4	P	All Glass
	346	45	15	40	850	2	P	Glass and Feld
4	343	40	20	40	855	1	P	All Glass
	307	40	20	40	848	1	Glass	Glass and rare Feld
	496	65	0	35	850	2	P	All Glass
	501	65	0	35	840	3	P	Glass and Feld
11	651	60	5	35	850	3	Glass	All Glass
	657	60	5	35	840	2	Glass	Glass and Feld
12	183	55	10	35	845	1	Glass	All Glass
	184	55	10	35	840	1	P	Glass and rare Feld
	685	55	10	35	835	4	Glass	Glass and Feld
	81	50	15	35	840	2	P	All Glass
13	689	50	15	35	830	3	Glass	All Glass
	694	50	15	35	825	4	Glass	Glass and Feld
14	195	45	20	35	825	1	P	Glass & rare Feld
	194	45	20	35	825	1	Glass	All Glass
	698	45	20	35	820	3	Glass	Glass and Feld
15	223	40	25	35	845	2	Glass	All Glass
	712	40	25	35	835	2	P	Glass and rare Feld
	723	40	25	35	830	2	Glass	Glass and Feld
16	221	35	30	35	865	2	P	All Glass
	224	35	30	35	855	1	Glass	Glass and rare Feld
	566	62·5	5	32·5	835	7	Glass	All Glass
	565	62·5	5	32·5	835	7	P	Glass and rare Feld and Neph
	547	62·5	5	32·5	825	4	P	Glass and Feld and Neph
	650	57·5	10	32·5	825	3	Glass	All Glass
	563	57·5	10	32·5	815	4	Glass	Glass and rare crystals
	661	57·5	10	32·5	800	2	Glass	Glass and Feld and Neph
	545	47·5	20	32·5	810	1	P	All Glass
	655	47·5	20	32·5	795	2	Glass	Glass and Feld and Neph

TABLE I (*cont.*)

Code no.	Run no.	Initial composition Ne	Ks	Qz	Temp. °C	Duration days	Initial condition	After run
21	372	65	5	30	840	4	P	Glass and rare Neph
	371	65	5	30	840	4	Glass	All Glass
	397	65	5	30	832	2	Glass	Glass and Neph and Feld
23	379	55	15	30	795	3	P	Glass and rare Neph and Feld
	610	55	15	30	795	3	Glass	All Glass
	612	55	15	30	780	3	Glass	Glass and Neph and Feld
24	364	50	20	30	800	3	P	Glass and rare Crystals
	380	50	20	30	790	2	Glass	All Glass
	683	50	20	30	780	2	Glass	Glass and rare Neph

rectangular outline (Plate IX). A few compositions close to the field boundary precipitated both nepheline and feldspar and it was not possible in such cases to tell which was the primary phase or to be certain if the composition lay exactly on the field boundary. The field boundary as shown in fig. 1 is almost a straight line, but if it were possible to locate its position more accurately it would probably have some slight curvature.

The position and melting temperature of the ternary minimum (*M*) was determined approximately from the isotherms close to the field boundary. By mixing two or more compositions several attempts were made to prepare a composition which had no interval of melting; such a composition would indicate exactly the composition of the minimum and its melting point. The smallest interval of melting determined from these mixtures was 15° C which could have been due to either (*a*) the the mixtures not having the exact composition of the minimum, or (*b*) non-equilibrium difficulties which have already been mentioned. The composition of the minimum was more accurately located by using three-phase boundaries and this is described below.

(iii) *Conjugation lines, three-phase boundaries, and crystallization curves.* Crystallization in the sodium-rich part of this system cannot be discussed until conjugation lines and three-phase boundaries have been determined. Bowen (1915) and Osborn and Schairer (1941) have discussed the methods of locating three-phase boundaries. The methods used in the present study are described below.

(*a*) *Conjugation lines.* To determine the position of a conjugation line, the composition of the solid phase in equilibrium with liquid must be found. X-ray methods are available for finding the composition of alkali feldspars and the nepheline solid solutions in this system. In many systems it is possible to determine directly the composition of a glass from its refractive index but in the present case this would be very inaccurate because of the small variations in refractive index with composition. An accurate method of determining the liquid compositions is to hold a charge a few degrees below its liquidus temperature so that the percentage of crystals in equilibrium with liquid is small, say 1 % of crystals. The liquid composition is then virtually identical with that of the starting material, and a line from the solid phase composition to the bulk composition is a very close approximation to the required conjugation line. In the present study it is necessary to have between 5 % and 10 % crystals present to determine their composition from an X-ray powder diffraction pattern so that a different method of locating the liquid composition must be used.

The temperature drop below the liquidus temperature necessary to produce the required proportion of crystals in the present work varies depending on the original bulk composition: in some cases as much as 25° C drop in temperature is required. The conjugation line is drawn from the crystal composition through the bulk composition and produced until it intersects the liquidus isotherm for the temperature of the experiment. The data for the determination of conjugation lines obtained in this way are given in table II and their slopes are represented in fig. 2 by short heavy lines drawn through the bulk compositions to the liquid compositions; the complete conjugation lines are not shown to avoid confusion with the three-phase boundaries represented in the same diagram.

(*b*) *Three-phase boundaries.* Compositions for which feldspar is the primary phase were held at successively lower temperatures until the liquid and feldspar were joined by nepheline. The composition of the liquid in equilibrium with both feldspar and nepheline is on the field boundary at the point where the relevant liquidus isotherm cuts it. If the composition of the feldspar is determined a three-phase boundary may be drawn joining the feldspar and liquid compositions. If enough nepheline is in the product of the run to enable its composition to be determined, a second three-phase boundary may be drawn joining the liquid and nepheline compositions. The two main sources of error in this method are: (*a*) method of determining compositions of the solid phase, (*b*) method of fixing the composition of the liquid. The compositions of the feldspar and nepheline were determined by the X-ray methods and in the case of feldspar this method is probably accurate to ±1·5 % Or and for the nephelines about ±2 % Ne. There is, however an alternative way of finding the composition of the liquid, which does not depend on an accurate knowledge of the isotherms and is therefore considered more accurate than that described above.

TABLE II. Runs which determine conjugation lines
G = glass, Feld = feldspar, Ne = nepheline

Code no.	Run no.	Initial composition Ne	Ks	Qz	Temp. °C	Duration, days	Results with composition of crystalline phase
1	431	55	5	40	875	2	G+Feld ($Or_{3\cdot5}$ $Ab_{96\cdot5}$)
2	680	50	10	40	860	2	G+Feld ($Or_{10\cdot5}$ $Ab_{89\cdot5}$)
3	360	45	15	40	850	2	G+Feld ($Or_{20\cdot0}$ $Ab_{80\cdot0}$)
	818	42·5	17·5	40	835	2	G+Feld ($Or_{28\cdot0}$ $Ab_{72\cdot0}$)
4	686	40	20	40	840	4	G+Feld ($Or_{38\cdot5}$ $Ab_{61\cdot5}$)
11	700	60	5	35	835	3	G+Feld ($Or_{2\cdot5}$ $Ab_{97\cdot5}$)
12	709	55	10	35	815	2	G+Feld ($Or_{7\cdot5}$ $Ab_{92\cdot5}$)
13	713	50	15	35	805	4	G+Feld ($Or_{18\cdot5}$ $Ab_{81\cdot5}$)
14	509	45	20	35	810	2	G+Feld ($Or_{41\cdot5}$ $Ab_{58\cdot5}$)
15	729	40	25	35	820	2	G+Feld ($Or_{64\cdot5}$ $Ab_{35\cdot5}$)
21	377	65	5	30	830	3	G+Ne ($Ne_{87\cdot0}$ $Ks_{4\cdot0}$ Qz_9)
31	640	70	5	25	870	2	G+Ne ($Ne_{85\cdot4}$ $Ks_{6\cdot5}$ $Qz_{8\cdot1}$)
32	641	65	10	25	870	2	G+Ne ($Ne_{83\cdot0}$ $Ks_{9\cdot8}$ $Qz_{7\cdot2}$)
33	409	60	15	25	865	5	G+Ne ($Ne_{81\cdot6}$ $Ks_{11\cdot5}$ $Qz_{6\cdot9}$)
34	518	55	20	25	840	2	G+Ne ($Ne_{79\cdot2}$ $Ks_{14\cdot8}$ $Qz_{6\cdot0}$)
35	412	50	25	25	865	5	G+Ne ($Ne_{75\cdot8}$ $Ks_{19\cdot5}$ $Qz_{4\cdot7}$)

Compositions for which feldspar is the primary phase and which lie fairly close to the nepheline–feldspar field boundary were held at successively lower temperatures until the feldspar is joined by nepheline. The composition is then held a few degrees above the temperature at which the nepheline appeared so that the product consists of liquid and feldspar only. The composition of the feldspar is then determined and the composition of the liquid is very close to the field boundary, and assumed to lie on the field boundary at a point where a line from the feldspar composition through the bulk composition intersects the field boundary. The composition of the liquid is not exactly on the field boundary but, since the fractionation curves show only a slight curvature (see below) in the region close to the field boundary, no appreciable error in the slope of the three-phase boundary will be introduced. This point will be more fully explained in the section on fractionation curves.

Three-phase boundaries determined by this latter method are shown as dashed lines in fig. 2; the data from which they were drawn are set out in table III. For the sake of clarity no three-phase boundaries determined using the first described method are shown; those that were determined are in good agreement with the ones shown. Each three-phase boundary in the feldspar field has a corresponding one in the nepheline field and they meet at a point on the field boundary.

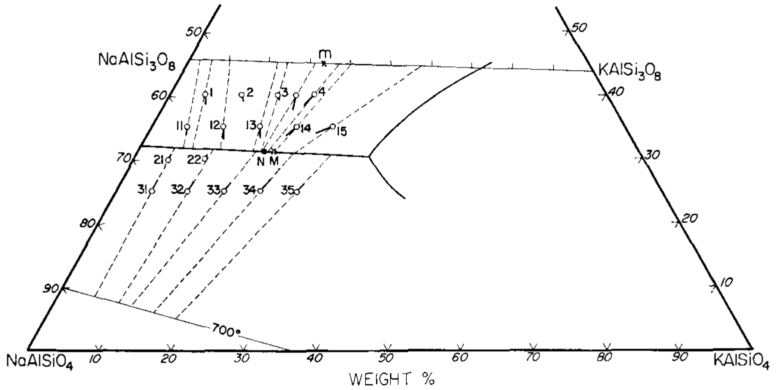

FIG. 2. Three-phase boundaries and conjugation lines in part of the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2–H_2O at P_{H_2O} = 1000 kg/cm^2 projected on to the anhydrous base. The dashed lines represent three-phase boundaries and the short thick lines represent the direction of conjugation lines. The data used for drawing these are given in tables II and III respectively. The numbered points correspond to the code numbers for compositions as given in table I. The line marked 700° is an approximation to the limit of nepheline solid solution at this temperature. m = alkali feldspar minimum. M = $NaAlSi_3O_8$–$KAlSi_3O_8$–$NaAlSiO_4$–$KAlSiO_4$ temperature minimum. N = intersection of the nepheline–feldspar field boundary and the three-phase boundary from m.

These two lines together with a straight line joining the relevant nepheline and feldspar compositions define a three-phase triangle. By a careful examination of the three-phase boundaries it is possible to fix the position of the 'ternary' minimum (M in figs. 1, 2, 3) more accurately than by using the isotherms on the liquidus surface. The liquid apex of the three-phase triangle points in the direction of falling temperature on the field boundary. The composition of the minimum determined in this way was found to be $Ne_{50}Ks_{19}Qz_{31}$ at P_{H_2O} = 1000 kg/cm^2 and 750°±7° C.

One further check on the composition of the minimum was carried out. Any composition for which the nepheline–feldspar tie-line passes through the minimum will begin to melt at the temperature of the minimum and thus compositions for which the nepheline–feldspar tie-line passes close to the minimum will begin to melt a few degrees above the temperature of the minimum. The temperatures of beginning of melting were determined for the following compositions: $Ne_{45}Ks_{15}Qz_{40}$, $Ne_{40}Ks_{20}Qz_{40}$, $Ne_{50}Ks_{15}Qz_{35}$, $Ne_{45}Ks_{20}Qz_{35}$, and $Ne_{60}Ks_{15}Qz_{25}$, and these were all within 20° of 750° C. From the data in table III it can be seen that the temperatures at which nepheline just disappears for the first four of these compositions are 775° C, 770° C, 775° C, and 780° C: the feldspar just disappears for the composition $Ne_{60}Ks_{15}Qz_{25}$ at 775° C. Thus it is clear that the feldspar–nepheline tie lines for these compositions must pass close to the composition of the minimum.

TABLE III. Runs which determine three-phase boundaries by liquid just reaching field boundary

(Water-vapour pressure = 1000 kg/cm²)

G = glass, Feld = feldspar, Ne = nepheline

Run no.	Initial composition Ne	Ks	Qz	Temp. ° C	Duration, days	Results with composition of crystalline phase
748	55	5	40	810	2	G+Feld ($Or_{6\cdot0}$ $Ab_{94\cdot0}$)
853	45	15	40	775	4	G+Feld ($Or_{24\cdot3}$ $Ab_{75\cdot7}$)
867	42·5	17·5	40	770	2	G+Feld ($Or_{31\cdot0}$ $Ab_{69\cdot0}$)
857	40	20	40	770	5	G+Feld ($Or_{36\cdot5}$ $Ab_{63\cdot5}$)
507	55	10	35	795	2	G+Feld ($Or_{10\cdot0}$ $Ab_{90\cdot0}$)
809	50	15	35	775	2	G+Feld ($Or_{21\cdot5}$ $Ab_{78\cdot5}$)
843	45	20	35	780	2	G+Feld ($Or_{40\cdot0}$ $Ab_{60\cdot0}$)
736	40	25	35	790	2	G+Feld ($Or_{58\cdot0}$ $Ab_{42\cdot0}$)
385	65	5	30	825	3	G+Ne ($Ne_{86\cdot2}$ $Ks_{5\cdot3}$ $Qz_{8\cdot5}$)
820	70	5	25	820	2	G+Ne ($Ne_{86\cdot6}$ $Ks_{4\cdot5}$ $Qz_{8\cdot9}$)
815	65	10	25	810	2	G+Ne ($Ne_{83\cdot5}$ $Ks_{9\cdot0}$ $Qz_{7\cdot5}$)
811	60	15	25	775	2	G+Ne ($Ne_{82\cdot0}$ $Ks_{11\cdot0}$ $Qz_{7\cdot0}$)
847	55	20	25	790	4	G+Ne ($Ne_{79\cdot4}$ $Ks_{14\cdot8}$ $Qz_{5\cdot8}$)
538	50	25	25	790	2	G+Ne ($Ne_{77\cdot4}$ $Ks_{17\cdot5}$ $Qz_{5\cdot1}$)

(c) *Fractionation curves.* Fig. 3 shows curves of perfect fractionation constructed from the available data on the conjugation lines, the conjugation lines being tangents to the fractionation curves. The fractionation curves in the nepheline field are nearly straight lines: it is improbable that any course of perfect fractionation where solid solution is involved will be a straight line, so it is likely that the courses of fractional crystallization in the nepheline field are slightly curved but that the method used to determine them was not accurate enough to show this. The fractionation curves in the feldspar field are curved for much of their length but near to the field boundary they are approximately straight lines. Thus for a particular composition, the feldspar in equilibrium with liquid a few degrees above the field boundary has virtually the same composition as the feldspar in equilibrium with liquid plus nepheline when the liquid just reaches the field boundary. The accuracy of the previously described method of determining three-phase boundaries depends on this property. One fractionation curve in fig. 3 is shown as a straight line extending from the point *m* to the point *N* on the nepheline–feldspar field boundary.

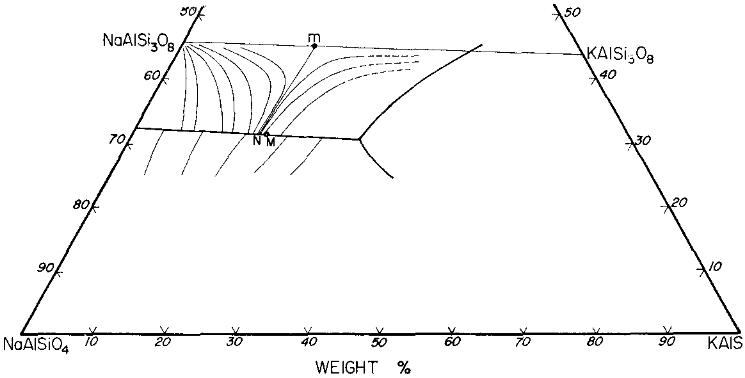

Fig. 3. Fractionation curves in part of the $NaAlSiO_4$–$KAlSiO_4$–SiO_2–H_2O system at $P_{H_2O} = 1000$ kg cm^2 projected on to the anhydrous base. See text for details of the construction of the curves.

This fractionation curve is unique in that its high-temperature extremity does not begin from either of the components $NaAlSi_3O_8$ or $KAlSi_3O_8$ but rather it extends from the point *m*, the minimum of the system $NaAlSi_3O_8$–$KAlSi_3O_8$–H_2O at $P_{H_2O} = 1000$ kg/cm^2: it is exactly analogous to a similar fractionation curve in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O (Tuttle and Bowen, 1958). Any liquid composition adjacent to this unique fractionation curve will under conditions of perfect fractionation change composition along a line almost parallel to the unique fractionation curve until it reaches the nepheline–feldspar field boundary and any liquid composition which falls exactly on the curve must remain on it until it reaches the nepheline–feldspar field boundary.

In this system any departure from a straight line of this unique fractionation curve must be slight but experimentally no departure from linearity can be detected. This is discussed more fully below.

A few curves of perfect equilibrium crystallization were constructed in the feldspar field. The method used to determine these curves was as follows. A given composition was crystallized at a series of temperatures and the composition of the feldspar in equilibrium with liquid was determined by the X-ray method. The composition of the liquid is taken at the point where the line joining the solid phase composition to the bulk composition intersects the isotherm for the experiment. The equilibrium curve is the line joining the series of liquid compositions determined in this way. A number of equilibrium curves were determined in the feldspar field and their shapes were nearly identical with the fractionation curves shown in fig. 3 and for this reason they are not plotted. The similarity between the fractionation curves and the equilibrium curves may be accounted for by the small range in temperature between the feldspar join and the feldspar–nepheline field boundary.

(iv) *The unique fractionation curve.* In their discussion of the system pseudowollastonite–åkermanite–gehlenite, Osborn and Schairer (1941) made it clear that the unique fractionation curve extending from the binary minimum in the system åkermanite–gehlenite did not intersect the boundary, between the field of melilite solid solution and pseudowollastonite, at the ternary minimum. These authors stressed that in a system of this type the intersection may occur at any place on the field boundary and if it occurred at the ternary minimum it would be a unique case. Tuttle and Bowen (1958), in their study of the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O, re-emphasized this statement by Osborn and Schairer and used the term 'thermal valley' to describe what we have called here the 'unique fractionation curve'. In a recent textbook, F. G. Smith (1962) has drawn a theoretical diagram of a system of the same type in which the binary minimum is joined to the ternary minimum by a straight line which cuts a number of fractionation curves; this line he described as a thermal valley. An additional *curved* line representing the unique fractionation curve is also drawn. Smith states that 'in discussing compositional changes in the residual liquid of systems fractionating by crystallization, the thermal valley has less significance than the singular fractionation curve'.

The present writers have been unable to find any justification for the straight line joining the binary minimum to the ternary minimum and we have therefore assumed that the thermal valley on the liquidus surface is coincident with the unique fractionation curve and that the two terms may be used as synonyms.

Osborn and Schairer (1941) could not detect experimentally any departure from a straight line in a unique fractionation curve of similar type to that considered here but these authors state that it seems improbable that any fractionation curve within a ternary solid solution field can be a straight line over its entire length. MacKenzie and Carmichael (unpublished work) unsuccessfully attempted to prove that a unique fractionation curve of this type, in a system with a ternary liquid and a binary solid solution, will be a straight line over its entire length. Carmichael (1963) has noted that if the thermal valley in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O is a straight line it will be an effective 'thermal barrier', since it will be a three-phase boundary as well as a fractionation curve and hence liquids crystallizing under equilibrium conditions cannot cross it: we have already noted that liquids crystallizing under conditions of perfect fractionation cannot cross this curve and hence, although it is a low-temperature valley, this curve may provide an effective barrier to the crossing of liquids if it is a straight line: if it has only a slight curvature, liquids will not be able to cross it very far. Thus liquids whose compositions fall on the potassium-rich side of the thermal valley are likely to have been derived from liquids initially even richer in potassium, rather than from sodium-rich liquids. The importance of this observation will become apparent in the following section.

Petrological considerations

The phase diagram in fig. 1 is very similar to the equivalent part of the dry system investigated many years ago by Schairer and Bowen (1935), the main difference being the considerable reduction in the size of the leucite field: this was of course anticipated from the work of Bowen and Tuttle (1950) on the system $NaAlSi_3O_8$–$KAlSi_3O_8$–H_2O. As a result of this reduction in the leucite field the nepheline–feldspar field boundary covers a greater part of the diagram than in the dry system and it is relatively easy to determine that there is a minimum on this field boundary and hence the invariant point is a reaction point and not a eutectic. Schairer and Bowen (1935) showed this as a reaction point in the dry system but Schairer published a new diagram of this system in 1950 indicating that it was a ternary eutectic because he was unable to be certain in these very viscous dry melts that a minimum existed on the field boundary (personal communication from Dr. Schairer). A number of workers have reproduced the later diagram although from the present work it appears that the original diagram was probably correct.

Bowen (1937) drew attention to the low-temperature trough extending from the quartz–feldspar field boundary to the nepheline–feldspar field boundary and showed that a large number of analyses of rocks, presumed to represent the last fractions of fractional crystallization of igneous magmas, plotted in this low-temperature trough. More recently Tilley (1958) has noted that the distribution of average analyses of certain undersaturated rocks correspond to a line approximating to the 35 % Qz composition in this system and these fall fairly close to the feldspar–nepheline field boundary or its extension in the present system. It is known that the leucite field is further reduced with increased pressure of water and so the average leucite phonolite composition Tilley, 1958) may also lie close to the extended nepheline–feldspar field boundary and only enter the leucite field on the release of pressure of water.

The thermal barrier provided by the feldspar join crossing the low-temperature trough can be seen to be still operative in this system at $P_{H_2O} = 1000$ kg/cm^2 since the minimum in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O is at 715° C and the minimum on the alkali feldspar join at the same pressure of water is at 865° C. In their now classic studies of the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O, Tuttle and Bowen (1958) found a striking correspondence between the position of the minimum in the synthetic system and the convergence field of rock compositions plotted on the same diagram using all the superior analyses in Washington's tables (1917) which contained more than 80 % of normative quartz + albite + orthoclase. It was impossible from these data alone to decide whether the controlling factor in determining the position of these points was that the liquids were from fractional crystallization of more basic liquids or from fractional melting of rocks of random composition (Tuttle and Bowen, 1958). A similar study has been made here by selecting from Washington's tables (1917) rocks which have 80 % or more of normative nepheline + albite + orthoclase; these were recalculated to 100 % of nepheline + kalsilite + quartz and plotted in the triangular diagram Qz–Ne–Ks.

Fig. 4 shows a contoured frequency diagram of a plot of 102 analyses of plutonic rocks and fig. 5 shows a similar plot of 122 analyses of extrusive rocks. Different methods of counting the points result in slightly different contours chiefly because of the limited number of analyses used; however, these differences are only in detail and the correspondence between the concentration of points representing rock analyses and the low-temperature region on the liquidus surface of this system is quite striking. In both diagrams the field boundaries between the fields of leucite, nepheline, and feldspar have been drawn in from fig. 1 and the alkali feldspar join is also drawn; the minimum on the feldspar join and that on the nepheline–feldspar field boundary at $P_{H_2O} = 1000$ kg/cm^2 are represented by crosses.

Preliminary experiments by Mr. Derek Taylor of Manchester University in this system at $P_{H_2O} = 2000$ kg/cm^2 indicate that the effect of further increasing the pressure of water is to cause the nepheline–feldspar field boundary to move away from the feldspar join and it is thus somewhat surprising that very few analyses in figs. 4 and 5 plot far below the field boundary, as determined at $P_{H_2O} = 1000$ kg/cm^2.

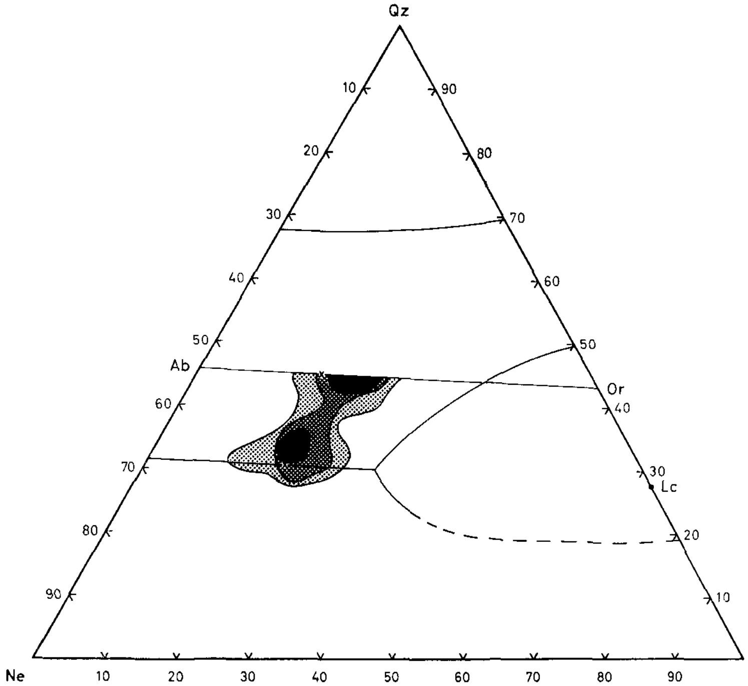

FIG. 4. Contour diagram illustrating the distribution of analyses of 102 plutonic rocks in Washington's tables (1917) that carry 80% or more of normative Ab+Or+Ne.

It is most unlikely that many of those rocks represented in these diagrams can be the result of fractional melting of sediments as this would require a most unusual composition for the sediments. There is thus very strong evidence that liquids resulting from fractional crystallization are involved in the genesis of many of the rocks of the nepheline-syenite clan.

There are a few rocks whose compositions plot well away from the thermal valley and some of these are undoubtedly of metasomatic origin, e.g. a corundum nepheline syenite from Renfrew, Ontario, is probably in this category.

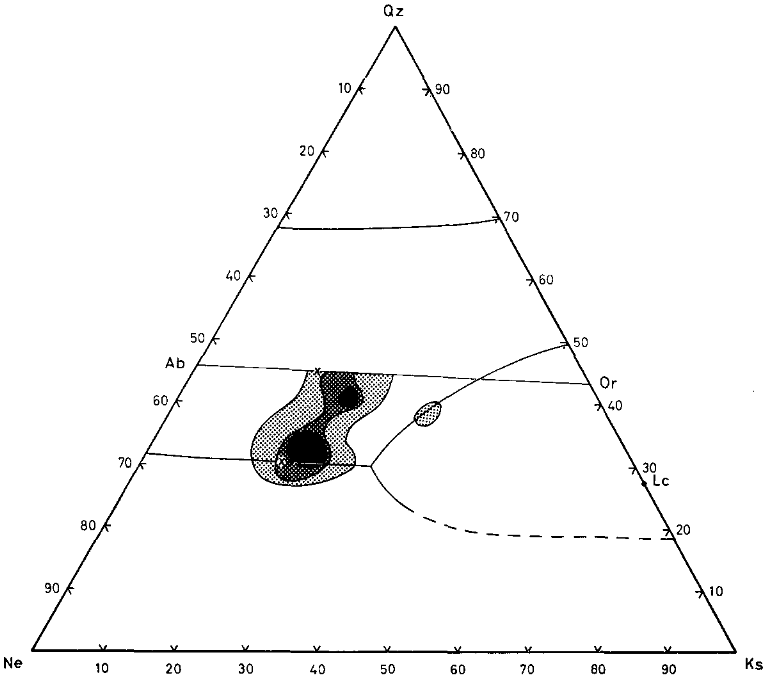

FIG. 5. Contour diagram illustrating the distribution of analyses of 122 extrusive rocks in Washington's tables (1917) that carry 80% or more of normative Ab + Or + Ne.

Carmichael and MacKenzie (1963) in an experimental study of synthetic liquids of composition similar to pantellerites (peralkaline rhyolites) concluded that these would be the normal products of fractional crystallization of a trachytic liquid assuming the plagioclase effect (Bowen, 1945) to have operated. The alternative course of fractional crystallization of trachytic liquids is towards phonolites, and using the same reasoning as given by Carmichael and MacKenzie (1963), these phonolites should show a molecular excess of Na_2O and Al_2O_3. Of the total of 122 analyses of extrusive rocks plotted in fig. 4, forty have normative acmite testifying to this molecular excess of Na_2O over Al_2O_3: these forty analyses have the same general distribution with respect to the minimum at $P_{H_2O} = 1000\ \text{kg/cm}^2$ as the remainder of the analyses although they might be expected to show a tendency to plot towards the potassium-rich side of the minimum.

Most of the rocks whose compositions are well removed from the thermal valley lie on the potassium-rich side of the valley. Some of these may have been derived from an already undersaturated potassium-rich magma rather than by fractionation from a trachytic magma; the rocks whose compositions lie on the leucite–feldspar field boundary (fig. 5) are possibly of this type. Others may lie on the potassium-rich side of the thermal valley because the thermal valley in projection in the system $NaAlSiO_4$–$KAlSiO_4$–SiO_2 may be modified by other constituents of the natural melt and cannot be compared directly with the simplified melts in the synthetic system (cf. Carmichael and MacKenzie, 1963).

There is little evidence from the positions of the plotted analyses that many natural liquids have approached the minimum on the liquidus of the synthetic system from nepheline-rich compositions but this may be in part due to the nepheline-rich rocks not conforming to the limits imposed when selecting the analyses. King and Sutherland (1960) have noted that lavas of composition between trachyte–phonolite and nephelinite are very rare in eastern and southern Africa and they have therefore suggested that the trachytes and phonolites in these regions are products of mobilization of fenites and nepheline fenites.

The present study provides no evidence to indicate why trachytes should in some cases differentiate to alkali rhyolite and in other cases to phonolite. Bowen (1928) stressed the importance of incongruent melting compounds in providing alternative lines of descent in fractional crystallization and in the case of the alkaline rocks he proposed that the crystallization of leucite provided a possible mechanism for the production of both oversaturated and undersaturated liquids. Tilley (1958) further suggested that a certain flexibility might be introduced into the crystallization of alkaline rocks by the presence of the incongruent melting compound aegirine. It does seem very probable that the nature of the ferromagnesian mineral does control the future course of crystallization of trachytic liquids, but the answer to this problem must await further investigation and this is at present being carried out in Manchester University.

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References

BOWEN, N. L., 1915. Amer. Journ. Sci., ser. 4, vol. 39, p. 175.

—— 1928. The evolution of igneous rocks. Princeton Univ. Press.

—— 1937. Amer. Journ. Sci., ser. 5, vol. 33, p. 1.

—— 1945. *Ibid.*, Daly vol., p. 75.

—— and TUTTLE, O. F., 1950. Journ. Geol., vol. 58, p. 489.

CARMICHAEL, I. S. E., 1963. Quart. Journ. Geol. Soc. London, vol. 119, p. 95.

—— and MACKENZIE, W. S., 1963. Amer. Journ. Sci., vol. 261, p. 382.

GORANSEN, R. W., 1931. *Ibid.*, ser. 5, vol. 22, p. 481.

HAMILTON, D. L., 1961. Journ. Geol., vol. 69, p. 321.

—— and MACKENZIE, W. S., 1960. Journ. Petrology, vol. 1, p. 56.

KING, B. C. and SUTHERLAND, D. S., 1960. Science Progress, Pt. I, p. 298; Pt. II, p. 504; Pt. III, p. 709.

ORVILLE, P. M., 1958. Feldspar investigations. Ann. Rep. Dir. Geophy. Lab. Carnegie Inst. Washington, p. 206.

OSBORN, E. F. and SCHAIRER, J. F., 1941. Amer. Journ. Sci., vol. 239, p. 715.

ROY, R., 1956. Journ. Amer. Ceram. Soc., vol. 39, p. 145.

SCHAIRER, J. F., 1950. Journ. Geol., vol. 58, p. 512.

—— and BOWEN, N. L., 1935. Trans. Amer. Geophys. Union, 16th Ann. Meeting, p. 325.

SMITH, F. G., 1962. Physical Geochemistry. Addison-Wesley Publishing Co., Inc., Reading, Mass.

TILLEY, C. E., 1958. Quart. Journ. Geol. Soc. London, vol. 103, p. 323.

TUTTLE, O. F., 1949. Geol. Soc. Amer. Bull., vol. 60, p. 1727.

—— and BOWEN, N. L., 1958. Geol. Soc. America, Memoir 74.

WASHINGTON, H. S., 1917. U.S. Geol. Survey, Professional Paper, 99.

EXPLANATION TO PLATE

PLATE IX

Photomicrograph of a charge showing nepheline and feldspar crystals in glass, ×1200.

D. L. HAMILTON AND W. S. MACKENZIE: THE SYSTEM $NaAlSiO_4$–$KAlSiO_4$–SiO_2–H_2O