

PHASE EQUILIBRIUM RELATIONS IN THE SYSTEM  
 $\text{CaMgSi}_2\text{O}_6$ (diopside)- $\text{NaAlSiO}_4$ (nepheline)- $\text{NaAlSi}_3\text{O}_8$ (albite)-  
 $\text{H}_2\text{O}$  at 1,000 kg/cm<sup>2</sup> WATER VAPOR PRESSURE

A. D. EDGAR,<sup>1</sup> *Dept. of Geology, University of Manchester,  
 Manchester, England.*

ABSTRACT

Phase equilibrium relations for part of the system  $\text{CaMgSi}_2\text{O}_6$ - $\text{NaAlSiO}_4$ - $\text{NaAlSi}_3\text{O}_8$ - $\text{H}_2\text{O}$  have been determined at 1,000 Kg/cm<sup>2</sup> water vapor pressure. The minimum melting temperature in this system lies on the  $\text{NaAlSiO}_4$ - $\text{NaAlSi}_3\text{O}_8$ - $\text{H}_2\text{O}$  join at  $835 \pm 5^\circ$  C. at the composition  $\text{Ne}_{27}\text{Ab}_{73}$ . The size of the primary phase field of plagioclase, appearing at the liquidus surface, is considerably smaller at this water vapor pressure than it is under conditions of atmospheric pressure. A comparison between liquidus relations in this system and normative compositions of rocks of the nepheline syenite clan suggests that crystal-liquid equilibria have been involved in the genesis of many of these rocks.

INTRODUCTION

As part of a more comprehensive investigation into the effects of adding pyroxenes and other basic mineral molecules to the silica-poor part of petrogeny's residua system ( $\text{NaAlSiO}_4$ - $\text{KAlSiO}_4$ - $\text{SiO}_2$ ) currently being investigated in this laboratory, a study of the system  $\text{CaMgSi}_2\text{O}_6$ - $\text{NaAlSiO}_4$ - $\text{NaAlSi}_3\text{O}_8$ - $\text{H}_2\text{O}$  has been undertaken at 1,000 kg/cm<sup>2</sup> water vapor pressure. The compositions represented by this system are approximately those of many rocks of the nepheline syenite clan. A comparison between liquidus relations in the experimental system and normative compositions of 289 intrusive and extrusive rocks of this type indicates that the majority of these rock compositions plot in the low temperature area of the synthetic system, thus suggesting that crystal-liquid equilibria have played an important role in the genesis of many of these rocks.

The high melting temperatures encountered in this system have severely restricted the number of liquidus determinations that can be made using conventional externally heated pressure vessels. However, liquidus determinations have been possible at albite-rich compositions containing up to 10 weight per cent.  $\text{CaMgSi}_2\text{O}_6$ ; this being the important compositional area for the interpretation of the genesis of common undersaturated alkaline rocks. In this paper, the results obtained along the join  $\text{CaMgSi}_2\text{O}_6$ - $\text{NaAlSi}_3\text{O}_8$ - $\text{H}_2\text{O}$  and in the pseudo-ternary system will be presented and discussed. The results of a study along the  $\text{NaAlSiO}_4$ - $\text{NaAlSi}_3\text{O}_8$ - $\text{H}_2\text{O}$  join have already been given (Edgar, *in press*). The high liquidus temperatures found along the third join of this system,  $\text{CaMgSi}_2\text{O}_6$ - $\text{NaAlSiO}_4$ - $\text{H}_2\text{O}$ , have prohibited any experimental work being

<sup>1</sup> Present address: Dept. of Geology, University of Western Ontario, London, Ontario, Canada.

carried out in the present study. This system has, however, recently been reinvestigated at atmospheric pressure by Schairer *et al.* (1962).

#### EXPERIMENTAL METHODS

*Starting materials.* The majority of compositions used in this study consisted of gels, prepared using a modification of the method described by Roy (1956). A few compositions used in the  $\text{NaAlSiO}_4\text{-NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$  join consisted of glasses, kindly loaned by Dr. J. W. Greig, formerly of the Geophysical Laboratory, Washington, the preparation of which has been described elsewhere (Greig and Barth, 1938).

The starting materials used in the preparation of gels were:

- $\text{SiO}_2$ : tetra-ethyl orthosilicate ( $\text{C}_2\text{H}_5$ )<sub>4</sub>SiO<sub>4</sub> was kindly provided by Monsanto Chemicals Limited. The yield of SiO<sub>2</sub> obtained by gelling a weighed amount of this material was determined to be 99.7 per cent of the calculated amount, the deficiency probably being due to a small amount of ethyl alcohol impurity. This deficiency was allowed for in weighing the tetra-ethyl orthosilicate.
- $\text{Al}_2\text{O}_3$ : a finely divided aluminum powder was provided through the courtesy of the British Aluminum Company, and the purity of this material was stated to be 99.99 per cent.
- $\text{Na}_2\text{O}$  and  $\text{CaO}$ : carbonates of "Analar" grade were used as sources of  $\text{Na}_2\text{O}$  and  $\text{CaO}$ .
- $\text{MgO}$ : "pure magnesium metal" was kindly provided by Magnesium Elektron Limited, and used as a source of MgO.

The compositions of the gels were considered to be correct if, on synthesizing, no unusual mineral phases or excessive amounts of glass were produced at subliquidus temperatures; and, if synthesized at higher temperatures, systematic changes in the liquidus curves were produced.

*Apparatus.* All quenching experiments were carried out in Tuttle "cold-seal" pressure vessels (Tuttle, 1949) and using the sealed tube technique (Goranson, 1931). The temperature measurements were made with chromel-alumel thermocouples and continuously recorded on a Honeywell-Brown recording potentiometer. The thermocouples were calibrated at the melting points of zinc (419.5° C.) and sodium chloride (801° C.). The temperatures are believed to be within  $\pm 5^\circ$  C. of the stated values. All experiments were done at a water vapor pressure of 1,000 kg/cm<sup>2</sup>, measured on a Bourdon tube-type pressure gauge capable of recording the pressure to within  $\pm 4$  per cent of 1,000 kg/cm<sup>2</sup>.

*Identification of products.* In each experiment the products consisted of one of the following, in addition to a hydrous fluid: nepheline and glass, plagioclase and glass, diopside and glass, or glass alone. All runs were examined under the petrographic microscope and by x-ray powder methods using a Phillips high-angle x-ray diffractometer with filtered Cu radiation.

## EXPERIMENTAL RESULTS

*The system CaMgSi<sub>2</sub>O<sub>6</sub>(diopside)-NaAlSi<sub>3</sub>O<sub>8</sub>(albite)-H<sub>2</sub>O.* The high melting temperatures encountered in this system permitted the determination of only a very small portion of the liquidus surface. The results obtained, however, for both the liquidus surface and for the field boundary between the diopside plus liquid, and diopside plus plagioclase plus liquid fields indicate that the phase relations for this system at 1,000 kg/cm<sup>2</sup> water vapor pressure are similar to those determined by Schairer and Yoder (1960) for the system at atmospheric pressure with the exception that liquidus temperatures are lowered by about 200° C. at this pressure of water vapor. The temperature of the intersection of the plagioclase and diopside liquidus surfaces was found to be 930 ± 5° C. at the composition Di<sub>9</sub>Ab<sub>91</sub>,<sup>1</sup> and the maximum on the plagioclase liquidus surface to be 945 ± 5° C. at the composition Di<sub>5</sub>Ab<sub>95</sub>.

The crystallization of plagioclase, rather than pure albite, from liquids containing some calcium in this system and in the CaMgSi<sub>2</sub>O<sub>6</sub>-NaAlSiO<sub>4</sub>-NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O system has been described as the "plagioclase effect" (Bowen, 1945). The exact compositions of plagioclase crystallized in the present study cannot be determined, but mean refractive index measurements indicate that the plagioclase is not rich in the anorthite molecule. Further evidence of the plagioclase composition has been obtained by Professor J. V. Smith of the University of Chicago. Professor Smith has kindly determined the composition of the plagioclase crystallizing from the bulk compositions Di<sub>5</sub>Ab<sub>95</sub> and Di<sub>10</sub>Ab<sub>90</sub> by means of the electron probe microanalyser and reports plagioclase compositions of An<sub>10</sub> to An<sub>20</sub>. However, the presence of very small inclusions of a calcium-bearing phase in the plagioclase crystals may be affecting these results.

*The system CaMgSi<sub>2</sub>O<sub>6</sub>(diopside)-NaAlSiO<sub>4</sub>(nepheline)-NaAlSi<sub>3</sub>O<sub>8</sub>(albite)-H<sub>2</sub>O.* The results of quenching experiments in this system are given in Table 1 and shown graphically in Fig. 1. This diagram is a projection from the water component on to an anhydrous plane<sup>2</sup> and shows the field boundaries which delimit the primary phases appearing on the liquidus surface. Figure 2 is a portion of the same diagram, but liquidus isotherms have been included and the names of the primary phases removed for clarity. The lowest melting temperature at 1,000 kg/cm<sup>2</sup> water vapor pressure, occurs on the NaAlSiO<sub>4</sub>-NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O join, at 835 ± 5° C. and

<sup>1</sup> All compositions are expressed in terms of standard mineral molecules, as weight percentages.

<sup>2</sup> Water is present in all liquids of this system, although no attempt has been made to determine these water contents. This method of representing liquidus results may be adopted here, as no hydrous minerals have been formed in the temperature ranges investigated in this system.

TABLE 1. EXPERIMENTAL DATA FOR THE SYSTEM  $\text{CaMgSi}_2\text{O}_6$  (DIOPSIDE)- $\text{NaAlSiO}_4$  (NEPHELINE)- $\text{NaAlSi}_3\text{O}_8$  (ALBITE)- $\text{H}_2\text{O}$  AT 1,000 KG/CM<sup>2</sup> WATER VAPOR PRESSURE

<i>a) Runs with diopside as primary phase on the liquidus surface</i>				
Run No.	Composition	Temperature (° C.)	Time (hours)	Phases
Di = diopside; Ne = nepheline; Plag = plagioclase				
71T	Di <sub>7.5</sub> Ne <sub>32.5</sub> Ab <sub>60</sub>	910	22	Glass
79T	Di <sub>7.5</sub> Ne <sub>32.5</sub> Ab <sub>60</sub>	905	22	Glass + Di (v. minor)
76T	Di <sub>7.5</sub> Ne <sub>32.5</sub> Ab <sub>60</sub>	900	46	Glass + Di + Ne (v. minor)
69T	Di <sub>7.5</sub> Ne <sub>30</sub> Ab <sub>62.5</sub>	910	22	Glass
78T	Di <sub>7.5</sub> Ne <sub>30</sub> Ab <sub>62.5</sub>	900	46	Glass + Di + Ne (v. minor)
73T	Di <sub>7.5</sub> Ne <sub>20</sub> Ab <sub>72.5</sub>	915	22	Glass
70T	Di <sub>7.5</sub> Ne <sub>20</sub> Ab <sub>72.5</sub>	910	22	Glass + Di (v. minor)
85T	Di <sub>7.5</sub> Ne <sub>20</sub> Ab <sub>72.5</sub>	900	42	Glass + Di + Plag (v. minor)
74T	Di <sub>10</sub> Ne <sub>35</sub> Ab <sub>55</sub>	920	22	Glass
80T	Di <sub>10</sub> Ne <sub>35</sub> Ab <sub>55</sub>	915	22	Glass + Di (minor)
24T	Di <sub>10</sub> Ne <sub>30</sub> Ab <sub>60</sub>	920	10	Glass
93T	Di <sub>10</sub> Ne <sub>30</sub> Ab <sub>60</sub>	910	22	Glass + Di + Plag (v. minor)
65T	Di <sub>10</sub> Ne <sub>20</sub> Ab <sub>70</sub>	920	20	Glass
83T	Di <sub>10</sub> Ne <sub>20</sub> Ab <sub>70</sub>	910	22	Glass + Di
64T	Di <sub>10</sub> Ne <sub>20</sub> Ab <sub>70</sub>	900	54	Glass + Di + Plag (v. minor)
77T	Di <sub>10</sub> Ne <sub>15</sub> Ab <sub>75</sub>	920	22	Glass + Di (v. minor)
89T	Di <sub>10</sub> Ne <sub>15</sub> Ab <sub>75</sub>	910	22	Glass + Di + Plag (v. minor)
81T	Di <sub>15</sub> Ne <sub>35</sub> Ab <sub>50</sub>	915	20	Glass + Di (minor) + Ne (minor)
82T	Di <sub>15</sub> Ne <sub>35</sub> Ab <sub>50</sub>	920	20	Glass + Di (minor) + Ne (v. minor)
(ex 81T)				Ne less than 81T
91T	Di <sub>15</sub> Ne <sub>10</sub> Ab <sub>75</sub>	920	8	Di + Plag + glass (minor)
92T	Di <sub>15</sub> Ne <sub>10</sub> Ab <sub>75</sub>	935	8	Di + Plag + glass
(ex 91T)				Plag less than 91T
<i>b) Runs with nepheline as primary phase on liquidus surface</i>				
94T	Di <sub>5</sub> Ne <sub>35</sub> Ab <sub>60</sub>	910	22	Glass
90T	Di <sub>5</sub> Ne <sub>35</sub> Ab <sub>60</sub>	905	18	Glass + Ne (v. minor)
86T	Di <sub>5</sub> Ne <sub>35</sub> Ab <sub>60</sub>	900	46	Glass + Ne (minor) + Di (v. minor)
38T	Di <sub>5</sub> Ne <sub>30</sub> Ab <sub>65</sub>	890	70	Glass
29T	Di <sub>5</sub> Ne <sub>30</sub> Ab <sub>65</sub>	880	74	Glass + Ne + Di (v. minor)
14T	Di <sub>10</sub> Ne <sub>40</sub> Ab <sub>50</sub>	900	44	Ne + Plag + Di (v. minor) + glass (minor). Ne greater than Plag
16T	Di <sub>15</sub> Ne <sub>45</sub> Ab <sub>40</sub>	920	10	Ne + Di (minor) + Plag (v. minor) + glass (minor)
94T	Di <sub>20</sub> Ne <sub>40</sub> Ab <sub>40</sub>	905	22	Ne + Di (minor) + Plag (v. minor)

Water vapor present in all products.

TABLE 1—(continued)

c) Runs with plagioclase as primary phase on liquidus surface

Run No.	Composition	Temperature (° C.)	Time (hours)	Phases
51T	Di <sub>5</sub> Ne <sub>25</sub> Ab <sub>70</sub>	920	18	Glass
55T	Di <sub>5</sub> Ne <sub>25</sub> Ab <sub>70</sub>	910	18	Glass+Plag (v. minor)
48T	Di <sub>5</sub> Ne <sub>25</sub> Ab <sub>70</sub>	900	22	Glass+Plag+Di (v. minor)
63T	Di <sub>5</sub> Ne <sub>20</sub> Ab <sub>75</sub>	910	24	Glass
44T	Di <sub>5</sub> Ne <sub>20</sub> Ab <sub>75</sub>	900	30	Glass+Plag (v. minor)+Di (v. minor)
54T	Di <sub>5</sub> Ne <sub>15</sub> Ab <sub>80</sub>	920	17	Glass+Plag (minor)
40T	Di <sub>5</sub> Ne <sub>15</sub> Ab <sub>80</sub>	900	32	Glass+Plag+Di (minor)
97T	Di <sub>5</sub> Ne <sub>10</sub> Ab <sub>85</sub>	935	8	Glass+Plag (v. minor)
98T	Di <sub>5</sub> Ne <sub>10</sub> Ab <sub>85</sub>	915	18	Glass+Plag+Di (v. minor)
58T	Di <sub>10</sub> Ne <sub>10</sub> Ab <sub>80</sub>	920	18	Glass+Plag (minor)+Di (v. minor)

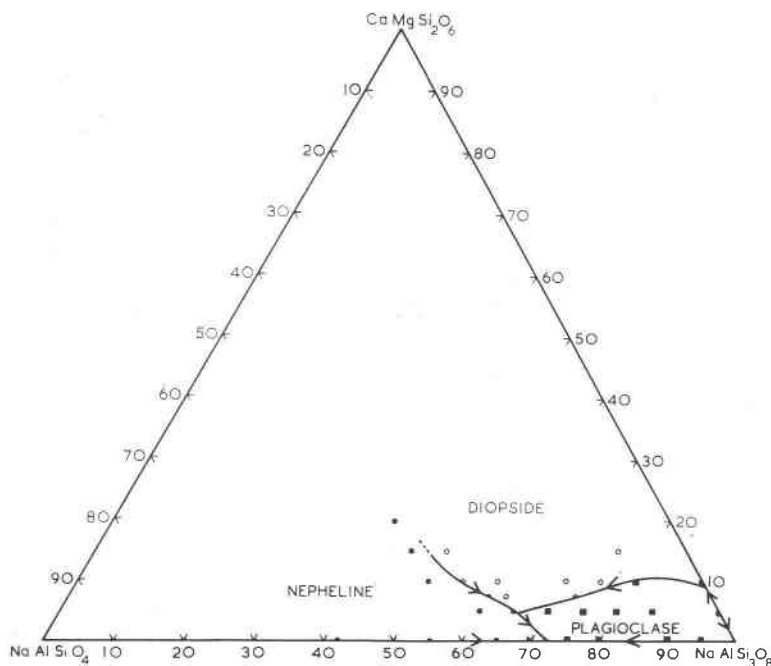


FIG. 1. Phase relations in the system CaMgSi<sub>2</sub>O<sub>6</sub> (diopside)-NaAlSi<sub>3</sub>O<sub>4</sub> (nepheline)-NaAlSi<sub>3</sub>O<sub>8</sub> (albite)-H<sub>2</sub>O at 1,000 kg/cm<sup>2</sup> water vapor pressure.

at the composition  $\text{Ne}_{27}\text{Ab}_{73}$ . The reaction point at which diopside, nepheline and plagioclase coexist with liquid occurs at  $885 \pm 5^\circ \text{C}$ . and at a composition of  $\text{Di}_{15}\text{Ne}_{29}\text{Ab}_{66}$ . This composition is considerably richer in the albite molecule and poorer in the diopside molecule than the corresponding point in the "dry" system (Schairer and Yoder, 1960); and produces at  $1,000 \text{ kg/cm}^2$  water vapor pressure a much smaller area on the liquidus surface in which plagioclase is the primary phase. Because

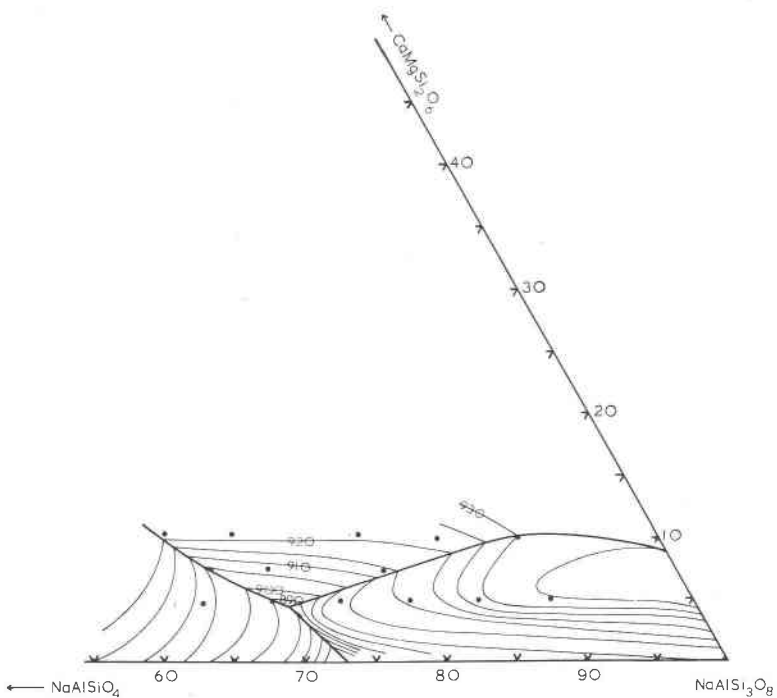


FIG. 2. Liquidus isotherms for the experimentally determined part of the system  $\text{CaMgSi}_2\text{O}_6$  (diopside)- $\text{NaAlSiO}_4$  (nepheline)- $\text{NaAlSi}_3\text{O}_8$  (albite)- $\text{H}_2\text{O}$  at  $1,000 \text{ kg/cm}^2$  water vapor pressure.

of the close similarities in the minimum melting compositions of the system  $\text{NaAlSiO}_4$ - $\text{NaAlSi}_3\text{O}_8$ , both under conditions of  $1,000 \text{ kg/cm}^2$  water vapor pressure and at atmospheric pressure (Greig and Barth, 1938); and in the composition of the intersection of the plagioclase and diopside liquidus surfaces under conditions of  $1,000 \text{ kg/cm}^2$  water vapor pressure and at atmospheric pressure (Schairer and Yoder, 1960), the smaller plagioclase field in the pseudo-ternary system cannot be explained in terms of the relative lowering of the melting points of the

end-members by the presence of this water vapor pressure, as has been done for the system diopside-anorthite (Yoder, 1954).

The liquidus isotherms for the experimentally determined part of this system (Fig. 2) show that the plagioclase field forms a hump extending from the CaMgSi<sub>2</sub>O<sub>6</sub>-NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O join, parallel to the NaAlSiO<sub>4</sub>-NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O join but with diminishing height as compositions become richer in NaAlSiO<sub>4</sub>. This hump is a result of the "plagioclase effect," the liquidus temperatures increasing as compositions move away from the albite-rich end of the NaAlSiO<sub>4</sub>-NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O join, due to solid solution of the anorthite molecule.

### DISCUSSION OF RESULTS

*Correlation between experimental results and rocks of the nepheline syenite clan.* This investigation was undertaken in order to show whether there was any relationship between the experimentally determined synthetic system CaMgSi<sub>2</sub>O<sub>6</sub>-NaAlSiO<sub>4</sub>-NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O at 1,000 kg/cm<sup>2</sup> water vapor pressure and the normative compositions of rocks of the nepheline syenite clan. In order to demonstrate such a relationship, a procedure similar to that used by Tuttle and Bowen (1958) to compare the liquidus relations of the system NaAlSi<sub>3</sub>O<sub>8</sub>-KAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O with normative compositions of granitic rocks has been adopted. All rocks from Washington's Tables (1917) and some from the literature published since then, containing 80 per cent or more normative diopside+acmite+nepheline+albite+orthoclase<sup>1</sup> have been recalculated to 100 per cent and plotted in terms of normative pyroxene, normative feldspathoid and normative feldspar. Figure 3 shows the plot of 129 plutonic rocks and Fig. 4 the plot of 160 volcanic and hypabyssal rocks. Each diagram has been contoured to show density distribution, using a modification of the method described by Fairbairn (1949). Superimposed on each of these diagrams are the boundary curves determined in the present experimental investigation, and also the boundary curve (labelled A in Figs. 3 and 4) between the primary phase fields of pyroxene and plagioclase for the plane containing at 50:50 ratio of diopside to acmite in the system CaMgSi<sub>2</sub>O<sub>6</sub>-NaFeSi<sub>2</sub>O<sub>6</sub>-NaAlSiO<sub>4</sub>-NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O at 1,000 kg/cm<sup>2</sup> water vapor pressure. (Data for this plane has been kindly provided by J. Nolan, Manchester University).

Rocks of the nepheline syenite clan invariably contain some potassium and iron and the inclusion of orthoclase and acmite in these plots has been necessary in order to fulfil the 80 per cent normative requirements. The similar melting behavior of orthoclase and albite at the water

<sup>1</sup> None of the analyses used contain normative kalsilite.

vapor pressure used in this study is believed to justify the inclusion of the orthoclase molecule in the distribution diagrams. The consequences of the inclusion of acmite in these diagrams will be considered in a later section of this paper.

Examination of these distribution plots shows that the high-density areas of the normative constituents correspond closely to the minimum melting composition of the experimentally determined system. This sug-

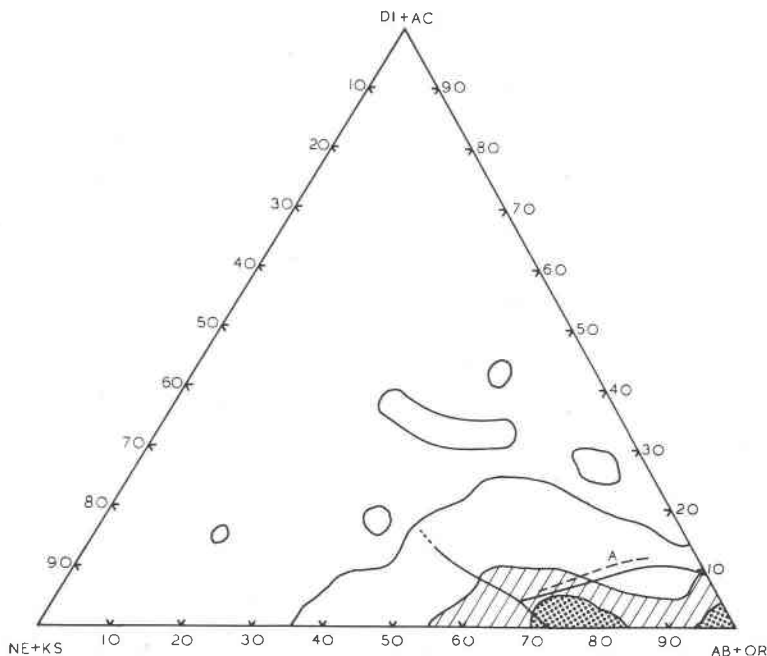


FIG. 3. Density distribution diagram for 129 plutonic rocks containing 80 per cent or more normative diopside+acmite+nepheline+albite+orthoclase. The curve, labelled A, delineates the boundary between the primary phase fields of pyroxene and plagioclase for the plane containing a 50:50 ratio of diopside to acmite in the system  $\text{CaMgSi}_2\text{O}_6$ - $\text{NaFeSi}_2\text{O}_6$ - $\text{NaAlSi}_3\text{O}_8$ - $\text{NaAlSi}_3\text{O}_8$ - $\text{H}_2\text{O}$  at 1,000 kg/cm<sup>2</sup> water vapor pressure. More than 75 per cent of all compositions plot in shaded area of this diagram.

gests that crystal=liquid equilibria have been involved in the genesis of many of these rocks.

The density distribution plot of plutonic rocks (Fig. 3) shows two maxima of concentration, one around the minimum melting composition ( $\text{Ne}_{27}\text{Ab}_{73}$ ) of the experimental system, the other at the feldspar (silica)-rich side of this minimum. Over 75 per cent of the compositions plotted enclose these two areas. Seven per cent of the remaining compositions



are agpaitic rocks (Ussing, 1912), which contain an excess of  $Na_2O + K_2O$  with respect to the normal 1:1 molecular ratio of alkalis to alumina found in feldspars and nephelines. These rock compositions plot approximately in the center of the diagram (in the two areas nearest the pyroxene apex of the triangle). Some of the compositions plotted represent rocks that are possibly metasomatic in origin, and therefore, would not be expected to show any relationship to the low-temperature area of the

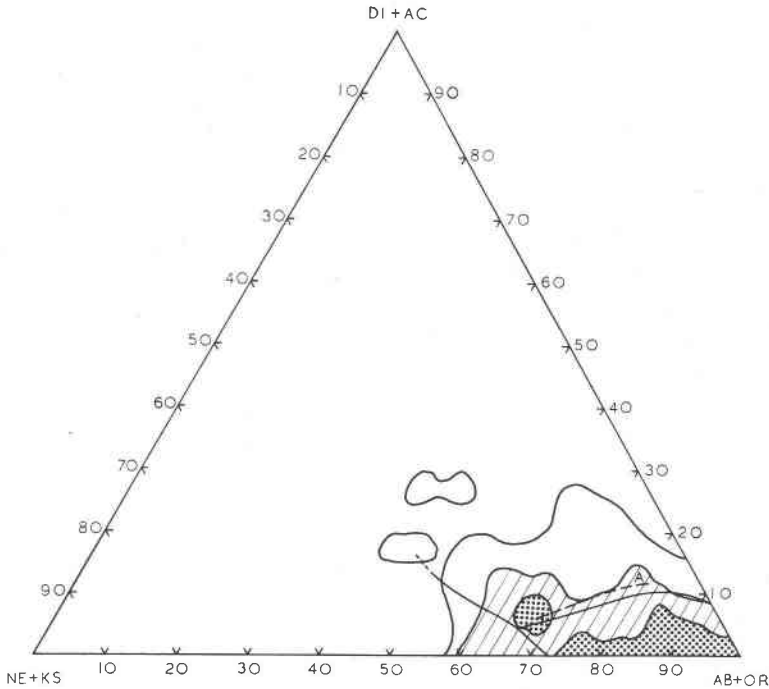


FIG. 4. Density distribution diagram for 160 volcanic and hypabyssal rocks containing 80 per cent or more normative diopside+acmite+nepheline+albite+orthoclase. The curve, labelled A, delineates the boundary between the primary phase fields of pyroxene and plagioclase for the plane containing a 50:50 ratio of diopside to acmite in the system  $CaMgSi_2O_6-NaFeSi_2O_6-NaAlSi_3O_8-NaAlSi_3O_8-H_2O$  at 1,000 kg/cm<sup>2</sup> water vapor pressure. More than 80 per cent of all compositions plot in shaded area of this diagram.

experimental system. The possibility that a number of the compositions plotted represent poor analyses cannot be overlooked.

Two maximum areas of concentration are also present in the plot of volcanic and hypabyssal rocks (Fig. 4). The compositions of volcanic rocks are concentrated in the area between the minimum melting composition of the experimental system and the feldspar apex; and the com-

positions of the hypabyssal rocks plot at compositions slightly richer in the pyroxene component than the minimum melting composition. (The small dotted area in Fig. 4 represents mainly hypabyssal rocks.) Less than 20 per cent of all the compositions used did not plot close to these two areas. These compositions may represent, particularly in the case of the hypabyssal rocks, rocks which have been altered subsequent to crystallization. Approximately 4 per cent of the hypabyssal and less than 1 per cent of the volcanic rock compositions used had agpaitic characteristics.

A comparison of Figs. 3 and 4 shows that the maximum concentrations of plutonic and volcanic rocks do not coincide. However, in both of these diagrams, the compositional trend is toward the feldspar-rich apex, and in the volcanic plot there is a complete sequence from the minimum melting composition of the experimental system to the feldspar apex. These trends suggest that many of the rocks of the nepheline syenite clan have a syenitic parentage. Some of the compositions, plotting on the nepheline-rich side of the minimum melting composition, probably do not belong to the same magmatic trend, but may be differentiates of a more basic parent, such as nephelinite. However, King and Sutherland (1960) have demonstrated, by means of variation diagrams, that in the alkaline rocks of eastern and southern Africa there are very few lavas of composition intermediate between a nephelinite and a trachyte-phonolite. This suggests that the more salic lavas are not derived from a basic nephelinitic parent.

*Significance of pyroxenes in rocks of the nepheline syenite clan.* One of the major difficulties in applying results obtained from a simplified experimental system to the genesis of rocks with diverse compositions such as the nepheline syenite clan is that of determining the effect of solid solution on the minimum melting composition of the experimental system. In this connection, the compositions of pyroxenes found in rocks of the nephelinite syenite clan vary considerably, but are rarely close to pure diopside in composition. Analyses of pyroxenes from nepheline syenites show that although many of them are fairly rich in the acmite molecule, some can carry about equal proportions of diopside, acmite and hedenbergite molecules (Miss R. Tyler, pers. comm.).

In order to make the experimental system correspond more closely to the compositions of the rocks, a series of compositions has been run, containing from 50 to 100 weight per cent of the acmite molecule, to the  $\text{CaMgSi}_2\text{O}_6\text{-NaAlSi}_3\text{O}_8\text{-NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$  system. These experiments, carried out by J. Nolan (pers. comm.), have shown that the addition of 50 weight per cent of the acmite molecule to this system does not appreciably alter the composition of the pyroxene, nepheline, plagioclase reac-

tion point, nor does this addition alter the position of the pyroxene-plagioclase field boundary (represented by the dashed line A in Figs. 3 and 4). With the addition of greater amounts of the acmite molecule, this boundary curve migrates away from the feldspar-feldspathoid join. The effect of the addition of the hedenbergite molecule has not been investigated. Therefore, provided some calcium and magnesium are available in the natural melt and can enter the pyroxene structure, it seems likely that the crystallization of this melt can be approximately represented by the system  $\text{CaMgSi}_2\text{O}_6\text{-NaAlSiO}_3\text{-NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$ , as the addition of large amounts of the acmite molecule has little effect on the size of the primary phase fields.

Tilley (1957) has suggested that the presence of mafic minerals in natural melts, particularly acmite which melts incongruently, may permit liquids to change compositions across the "thermal barrier" dividing saturated compositions from undersaturated ones. Until recently, no experimental support for such a mechanism was available. However, Yagi (1962), in a study of the system  $\text{NaFeSi}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$  at atmospheric pressure, has shown that all the compositions in this system, with 40 weight per cent or less of the acmite molecule, will melt congruently. As mentioned previously, some of the pyroxenes from rocks of the nepheline syenite clan contain roughly equal proportions of the acmite and diopside molecules. Hence, it seems likely that the mechanism proposed by Tilley may only be feasible in extreme cases, in which acmite is the predominant mineral molecule in the pyroxene.

*Ijolitic rocks.* Rocks of the ijolite series, consisting of varying proportions of nepheline and pyroxene but with very minor feldspar, are often closely associated with rocks of the nepheline syenite clan, and it was hoped that the normative distribution diagrams might show a compositional trend between the pyroxene-feldspathoid join and the low-temperature area in which the bulk of the rocks of the nepheline syenite clan plot. Although rocks of ijolitic composition have not been plotted in the distribution diagrams, no trend between these rocks and those of the nepheline syenite clan has been found. These results agree with the conclusions of King and Sutherland (1960), who showed by means of variation diagrams that no trend existed between nephelinites (which may be considered compositionally as the approximate volcanic equivalents of one of the end members of the ijolite series) and trachyte phonolites. This suggests that ijolites are not simply related to rocks of the nepheline syenite clan. Ijolitic rocks are commonly associated with carbonatites, but the influence of these carbonate-rich rocks on the genesis of ijolites is not clear.

Although the compositions of the pyroxenes in ijolites is very variable,

they are usually richer in the diopside molecule than pyroxene compositions of rocks of the nepheline syenite clan (Miss R. Tyler, pers. comm.), and therefore, it would appear that the pyroxene composition is not the controlling factor in the crystallization of these rocks. In contrast to the diopside-rich characteristics of ijolitic rocks, carbonatites commonly contain acmite-rich pyroxenes.

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