PHASE RELATIONS IN PORTIONS OF THE SYSTEM DIOPSIDE-NEPHELINE-KALSILITE-SILICA AND THEIR IMPORTANCE IN THE GENESIS OF ALKALINE ROCKS

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ABSTRACT

From phase relations in three planes, diopside—albite—sanidine (Morse 1968); diopside—nepheline—sanidine and diopside—albite—leucite, in the system diopside—nepheline—kalsilite—silica, a "quaternary" invariant point and "quaternary" minimum have been approximately located. These are very close both in composition and temperature to the reaction point and minimum in the undersaturated portion of the system nepheline—kalsilite—silica. From these relations, the crystallization paths of a large number of basic and felsic alkaline undersaturated lavas can be deduced, and the genetic connections between them discussed.

INTRODUCTION

As part of a long-term study on the effects of adding basic mineral molecules to Petrogeny's Residua System[1] (nepheline—kalsilite—silica) currently being investigated in this laboratory, phase relations have been determined for parts of the system diopside—nepheline—kalsilite—silica (Fig. 1). This system may be considered as the potash-rich extension of the simplified basalt tetrahedron (diopside—nepheline—forsterite—silica) of Yoder & Tilley (1962). As such it provides a physico-chemical basis for our understanding of the genesis of those rocks intermediate in composition between the alkaline basaltic types, containing large proportions of basic molecules and represented by the portion (diopside—nepheline—albite—forsterite) of the basalt tetrahedron; and the phonolitic rocks, containing much smaller amounts of basic molecules represented by the undersaturated portion (albite—nepheline—kalsilite—sanidine) of the residua system.

The phase relations described here are mainly pertinent to undersaturated alkaline rocks. Specifically we have determined relations in the planes diopside—nepheline—sanidine (RGP) and diopside—albite—leucite (MKS) lying close to the minimum of the nepheline—feldspar cotectic

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[1] For the remainder of this paper, this term is abbreviated to "the residua system".

boundary in the residua system (Schairer 1957), and close to the possible "quaternary" invariant point in the tetrahedron. These relationships are shown in Fig. 1.

From the present study and from relations in the system diopside—nepheline—silica (Schairer & Yoder 1960), diopside—leucite—silica (Schairer & Bowen 1938), diopside—albite—sanidine (Morse 1968) and the residua system (Schairer & Bowen 1935; Schairer 1957), it is possible to infer the phase relations within the petrologically important part of the tetra-

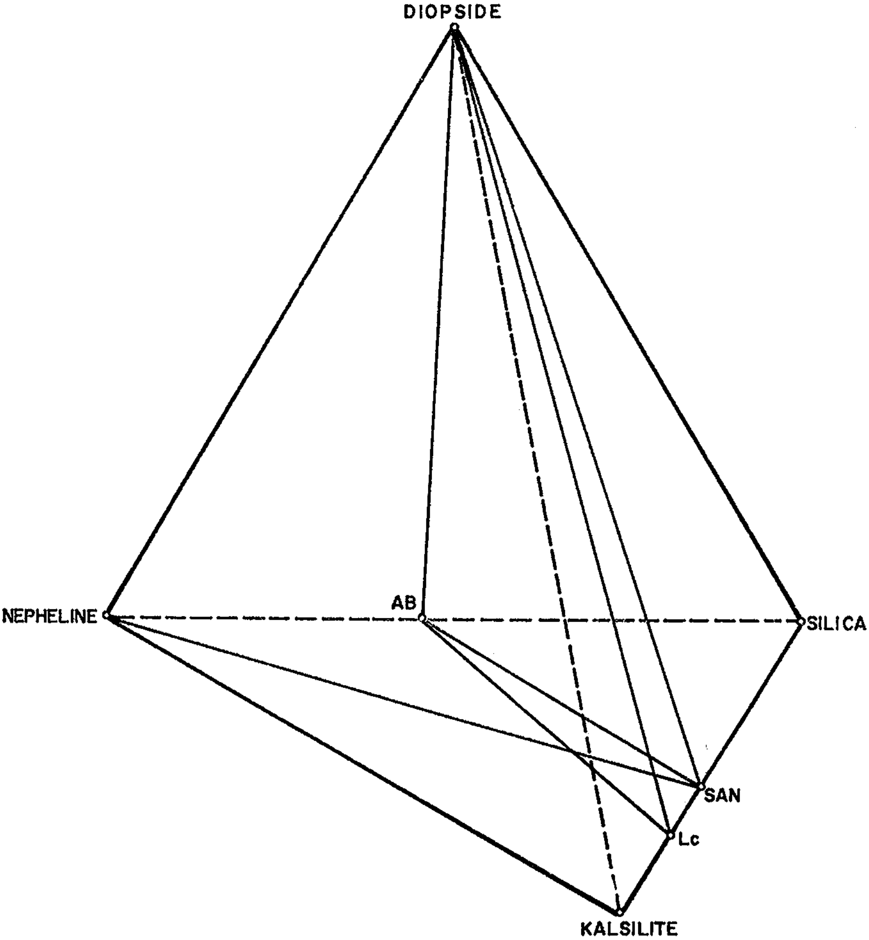

FIG. 1. Location of the three joins in the tetrahedron diopside—nepheline—kalsilite—silica.

hedron (Fig. 1). Because of the complex solid solutions occurring in this system, the relations can only be described in terms of the six-component system (K_2O–Na_2O–CaO–MgO–Al_2O_3–SiO_2). However, for simplicity, these relations are described in this paper in terms of the tetrahedron of Fig. I. The reader should, therefore, be aware that terms such as invariant point, univariant line, *etc.* are not being used *sensu stricto*. In this paper, therefore, we are concerned only with a portion of the six-component system, if it can be represented as oxides. In Fig. 1 the relations in the portion of the system exclusive of the forsterite volume can be represented in terms of the diopside—nepheline—kalsilite—silica system. Phase relations within the primary forsterite field cannot be represented by these four components. However the petrological conclusions given here are believed to be valid despite the simplifications in representing the system as four components.

Details of the complex phase chemistry and particularly of the trends of residual liquids in the system will be given elsewhere. The present paper stresses only the petrological implications of the study.

EXPERIMENTAL METHODS

Forty-four homogeneous glasses were prepared in the diopside—nepheline—sanidine and diopside—albite—leucite joins using the method of Schairer (1959). An additional glass of the composition of the reaction point in the residua system with 5 weight percent diopside was also made. Glasses, crystallized at atmospheric pressure or hydrothermally at 1 kb P_{H_2O} in sealed capsules (Goranson 1931) using cold seal pressure vessels (Tuttle 1949), were used as starting material for all experiments.

Experiments were carried out in standard furnaces (Schairer 1959) using the quenching technique (Shepherd *et al.* 1909). Temperatures were measured with thermocouples calibrated at the melting points of diopside and NaCl and are accurate to ± 10°C with the exception of certain runs in the system diopside—nepheline—sanidine, done through the courtesy of Dr. J. F. Schairer at the Geophysical Laboratory, in which temperatures are within ± 3°C.

Phases were identified by the petrographic microscope, by *x*-ray diffraction and, in a few cases, using an MAC-400 electron microprobe.

RESULTS

a) *The join diopside—nepheline—sanidine (RGP)*

Results of quenching experiments in the join diopside—nepheline—sanidine are shown in Fig. 2. This system has olivine[1], nepheline, diopside and leucite as liquidus phases and melilite and feldspar as subliquidus phases. It contains two piercing points, one (A) at $Ne_{51}Di_{21}San_{28}$ at 1158 ± 10°C, where nepheline, diopside and olivine coexist with liquid; the other (B) at $Ne_{44.5}Di_{12}San_{43.5}$ at 1120 ± 5°C where nepheline, leucite and diopside coexist with liquid. Due to the non-ternary nature of this system liquids upon crystallization move off the join into the under-saturated portion of the diopside—nepheline—kalsilite—silica system. The presence of olivine as a liquidus phase and melilite as a subliquidus phase

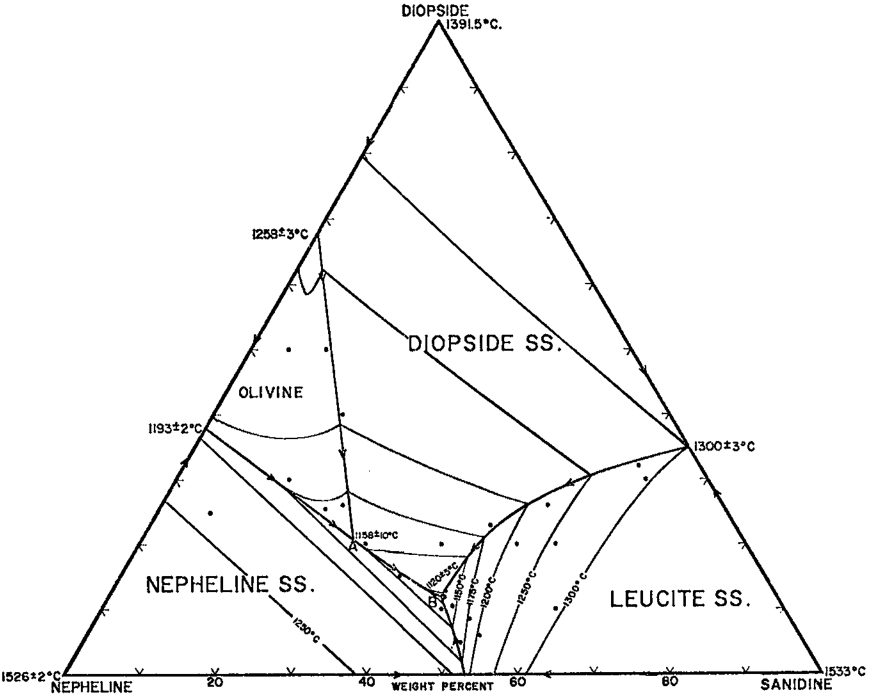

FIG. 2. Phase relations in the system diopside—nepheline—sanidine. Solid dots represent compositions in weight percent.

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[1] All phases encountered in this study are complex solid solutions, herein simplified to their standard mineral names.

has been reported by other workers investigating systems containing diopside and nepheline (Bowen 1922; Yoder & Tilley 1962; Onuma & Yagi 1967). For bulk compositions with more than 10 weight percent sanidine, crystallization of melilite is, however, inhibited.

b) *The join diopside—albite—leucite (MKS)*

Results of experiments in this join are shown in Fig. 3. Diopside, leucite and feldspar (containing Ab, Or and An molecules) are liquidus phases. The system contains one piercing point (P) at $Di_4Ab_{62}Lc_{34}$ at 1040 ± 10°C where diopside, feldspar and leucite coexist with liquid. Due to the pseudoternary nature of this join, liquids, upon crystallization, leave the join and proceed toward a quaternary invariant point, in the undersaturated portion of the system diopside—nepheline—kalsilite—silica.

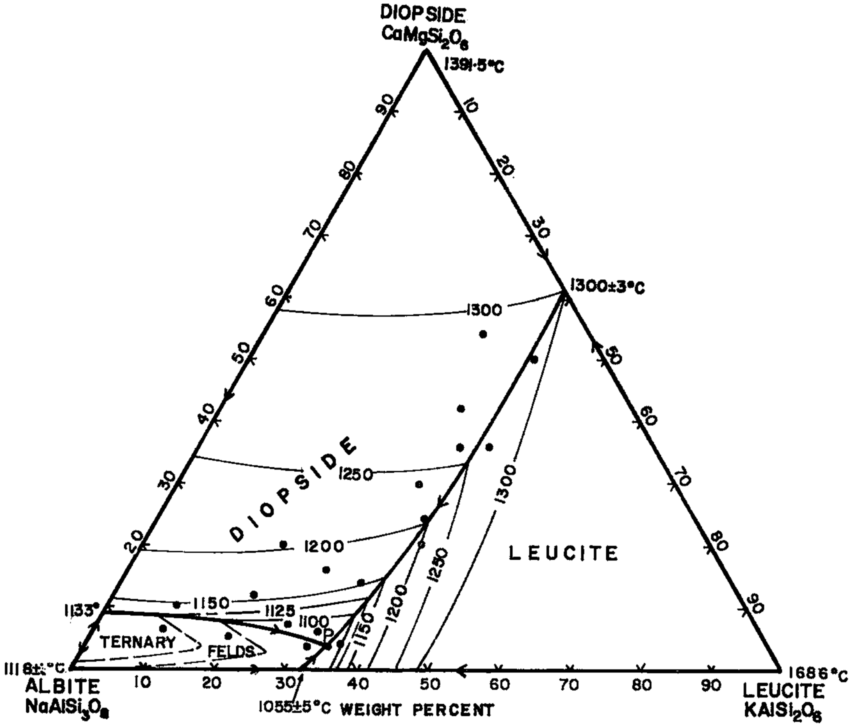

FIG. 3. Phase relations in the join diopside—albite—leucite. Solid dots represent the compositions in weight percent.

c) *The join diopside—albite—orthoclase*

A portion of this join, determined by Morse (1968), is given as Fig. 4. Although not exactly located, this join contains a piercing point (Q) with 2-3 weight percent diopside at approximately 1060°C where diopside, feldspar and leucite coexist with liquid.

d) *Relations in the system diopside—nepheline—kalsilite—silica*

From the data on the bounding systems and these three joins, certain univariant lines, along which three solid phases coexist with liquid, can be located in the diopside—nepheline—kalsilite—silica system. These lines are shown in Fig. 5 and listed in Table 1. Line EQPR′ along which diopside, leucite, feldspar and liquid coexist, originates on the diopside—leucite—silica face of the tetrahedron (Fig. 5), cuts the diopside—albite—sanidine system at approximately 1060°C at Q and the diopside—albite—leucite system at 1040°C at P and proceeds to the point R′. Line BR′, along which diopside, nepheline, leucite and liquid coexist, originates somewhere on the diopside—nepheline—leucite system (a yet undetermined), cuts the diopside—nepheline—sanidine system at B (Fig. 2) at 1120 ± 5°C and moves to R′. The line HM′R′, along which diopside, nepheline, feldspar and liquid coexist, originates on the diopside—nepheline—silica bounding system at H and proceeds towards R′. As discussed later, liquids may not reach this point. The line R-R′, along which feld-

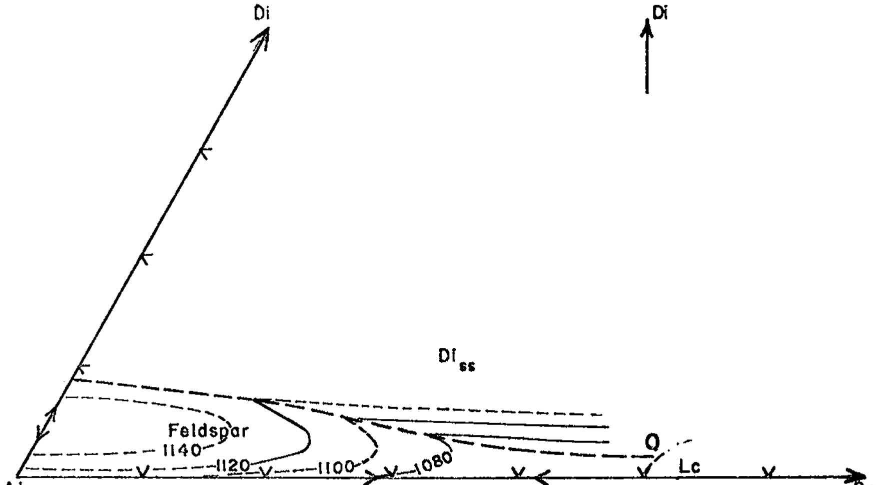

FIG. 4. Phase relations in the join diopside—albite—orthoclase. (after Morse 1968).

spar, nepheline, leucite and liquid coexist, originates at R on the residua system and proceeds to R′.

The intersection of these four univariant lines at R′ produces one of the quaternary invariant points in the diopside—nepheline—kalsilite—silica system at which diopside, nepheline, leucite, feldspar and liquid are in equilibrium. From extrapolation of the univariant lines, this point contains between 4 and 7 weight percent diopside and must be at a temperature less than, or close to, 1020°C. Due to the viscous nature of liquids near this point, experimental attempts to obtain its composition and temperature have not been very successful. Runs on the composition of the point R with 5 weight percent diopside produced diopside and liquid at 1045 ± 10°C and diopside, nepheline and feldspar at 970 ± 20°C, indicating that point M′ may contain less than 5 percent diopside.

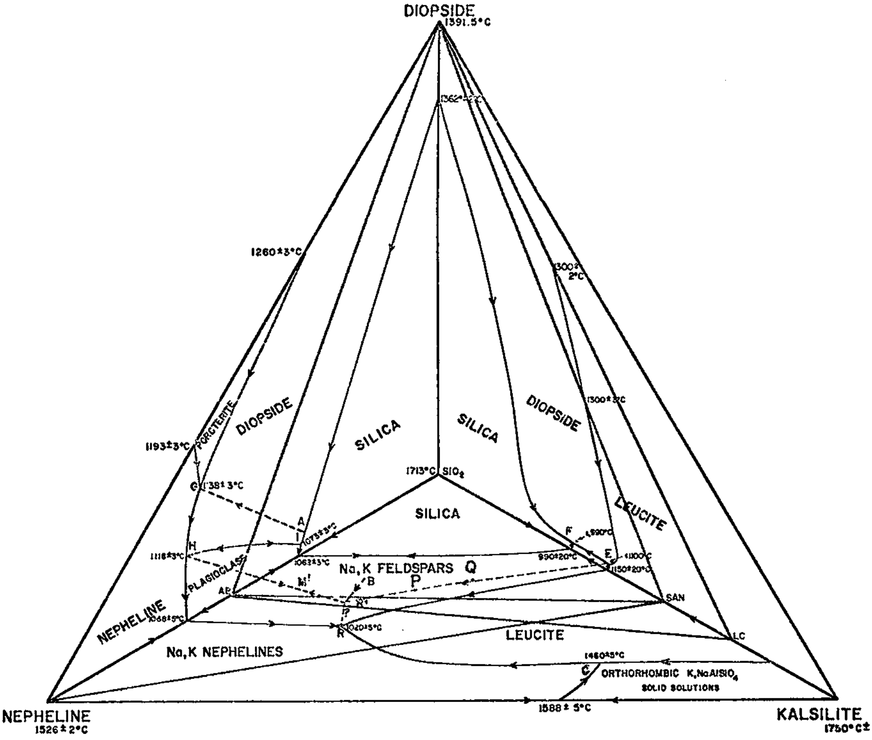

Fig. 5. Liquidus phase relations for the tetrahedron diopside—nepheline—kalsilite—silica. The dashed lines represent univariant lines.

In an attempt to clarify the nature of point R′, relations around the point have been expanded as shown in Fig. 6. It is unlikely that R′ is a quaternary eutectic as two of the univariant lines *i.e.* ER′ and RR′ leading to it are "reaction" lines involving leucite and liquid. The possibility of liquids proceeding from R′ to R is also unlikely as diopside crystallizes after the beginning of leucite reaction with liquid for all compositions in the diopside—nepheline—sanidine and diopside—albite—leucite systems, and hence this is probably also the case for compositions lying within the tetrahedron. The point R′ is a quaternary invariant point of the peritectic type where the last of the leucite disappears by reaction with the liquid. The ultimate goal of the liquid after leaving R′ is not known but from the appearance of diopside, nepheline and feldspar at 970 ± 20°C for compositions in the planes diopside—nepheline—sanidine and diopside—albite—leucite as well as in the quaternary composition within the tetrahedron, it appears likely that liquids are consumed some-

TABLE 1.

a. Univariant lines controlling crystallization in the tetrahedron diopside—nepheline—kalsilite—silica :

Solid Phases[1]	*Piercing Points in Systems of the tetrahedron*
ne + ol + di	A & G (Fig. 5)
di + ne + lc	B (Fig. 5 and 8)
di + lc + fels	E, Q and P (Fig. 5 and 8)
ne + lc + fels	R (Fig. 5 and 8)
di + ne + fels	H (Fig. 5 and 8)
di + fels + sil	F & I (Fig. 5 and 8)
ks + lc + ne	C (Fig. 5 and 8)
di + ne + ks[2]	K (Fig. 8)
di + lc + ks[2]	J (Fig. 8)

b. Univariant lines controlling crystallization outside the volume of the tetrahedron diopside—nepheline—kalsilite—silica :

ne + ol + mel
di + ol + mel
ne + mel + di
ne + di + fels[2]
ne + di + wo[2]

[1] The following abbreviations are used :

ne = nepheline
ol = olivine
di = diopside
lc = leucite
fels = feldspar
sil = silica
ks = kalsilite
mel = melilite
wo = wollastonite

[2] Univariant lines from theoretical considerations.

where on the line HR′. Such a composition on the line HR′ (Fig. 5) represents a minimum melting composition referred to as a "quaternary" minimum M′ in Figs. 5 and 6. The compositional and temperature limits of this minimum cannot be determined but from theoretical considerations and limited experimental data its existence is a strong possibility. Such a minimum is analogous to the minimum M (Figs. 5 and 6) in the residua system.

PETROLOGICAL IMPLICATIONS

Phase relations in the system diopside—nepheline—kalsilite—silica show that residual liquids in the early stages of crystallization may follow two distinct trends, one soda–rich, the other potash–rich. In the later stages of crystallization, these two trends converge and, under certain conditions, the final liquids from both trends may crystallize at a "quaternary" minimum M′ (Fig. 6) producing an assemblage of diopside, nepheline and feldspar corresponding to a simplified phonolite. Each trend is discussed from the date in Table 2 and the flow diagram (Fig. 8) indicating the possible phase assemblages and corresponding simplified rock types.

Within the olivine phase volume the existence of a compositional plane which divides liquids crystallizing melilites from those which crystallize olivine alone, has been inferred from the studies in the system diopside—nepheline—sanidine. In this volume liquid compositions containing 10 weight percent or less of sanidine crystallize melilite as a *subliquidus* phase over a temperature interval of 30° to 60°. In this restricted tempera-

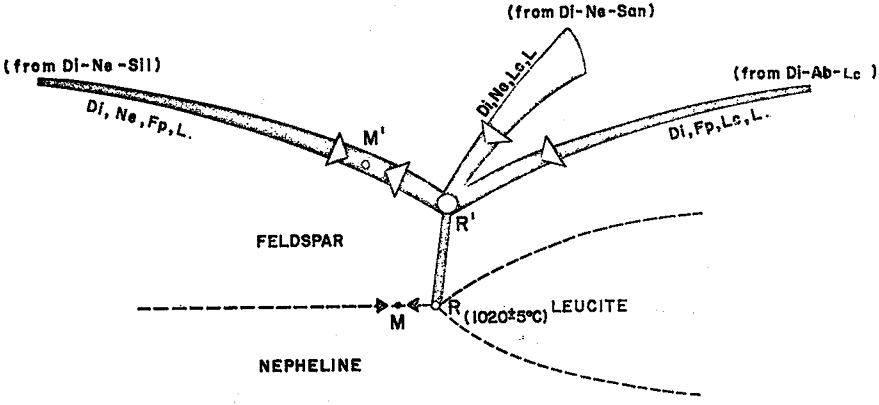

FIG. 6. Expanded view of the region around the point R′ in the system diopside—nepheline—kalsilite—silica.

ture and compositional range, melilite, olivine, pyroxene, nepheline and liquid coexist at some probable invariant point lying outside the tetrahedron diopside—nepheline—kalsilite—silica. This assemblage corresponds to a simplified olivine melilite nephelinite. On further cooling melilite and olivine disappear by reaction with liquid. After their final disappearance, under equilibrium conditions, liquids trend toward M′ (Fig. 5) but never attain it and the final assemblage, nepheline and diopside, equivalent to a simplified nephelinite, is obtained. This suggests that nepheline-pyroxene rocks may be the low temperature equivalents of olivine-melilite rocks. Details on the phase relations involved in the production of these assemblages will be given in a subsequent paper.

Under conditions of fractional crystallization the possible assemblages are much more diverse than under equilibrium conditions. Compositions within the olivine volume, upon fractionation may produce the assemblages in Table 2. A summary of the possible courses of fractionation is shown on Fig. 7.

TABLE 2. ASSEMBLAGES AND EQUIVALENT ROCK TYPES PRODUCED BY THE FRACTIONATION OF OLIVINE, OR MELILITE AND OLIVINE

Rock Type	*Assemblage*[1]
olivine nepheline	ne + ol + di
olivine melilite nephelinite	ne + ol + mel
olivine melilitite	di + ol + mel
melilite nephelinite	ne + mel + di
olivine melilite nephelinite	mel + ol + di + ne
phonolite	ne + di + fels
wollastonite nephelinite	ne + di + wo
wollastonite phonolite	ne + fels + di + wo

[1] See table 1 for abbreviations.

Under fractional crystallization, the three assemblages corresponding to the rock types, olivine nepheline, olivine melilitite and olivine melilite nephelinite cannot coexist. If olivine alone is fractionated, the trend is from an olivine nephelinite and hence, by several possible paths, to a wollastonite nephelinite, to a wollastonite phonolite or directly to a phonolite (Fig. 7). In nature, wollastonite molecules may form solid solutions with pyroxenes or combine with TiO_2 as sphene. Fractionation of both olivine and melilite produces an olivine melilitite—melilite—melilitite nephelinite—nephelinite trend. With further fractionation, the trend is the same as that given for olivine nephelinite as shown in Fig. 7. If fractionation occurs after the disappearance of olivine and melilite by reaction with liquid, residual liquids proceed towards the "quaternary" minimum M′ (Figs. 5 and 6) either directly, producing a phonolitic assemblage (nepheline, feldspar, diopside) ; or by way of the quarternary invariant point R′ (Figs. 5 and 6), producing assemblages corresponding to leucitophyres (leucite, nepheline, diopside), leucite phonolites (nepheline, leucite, feldspar, diopside) and finally phonolites.

The relationships described above are for compositions lying in, or close to, the olivine volume in the diopside—nepheline—kalsilite—silica system. Phase relations and their petrological implications for compositions lying in the nepheline—kalsilite—silica base of the tetrahedron diop-

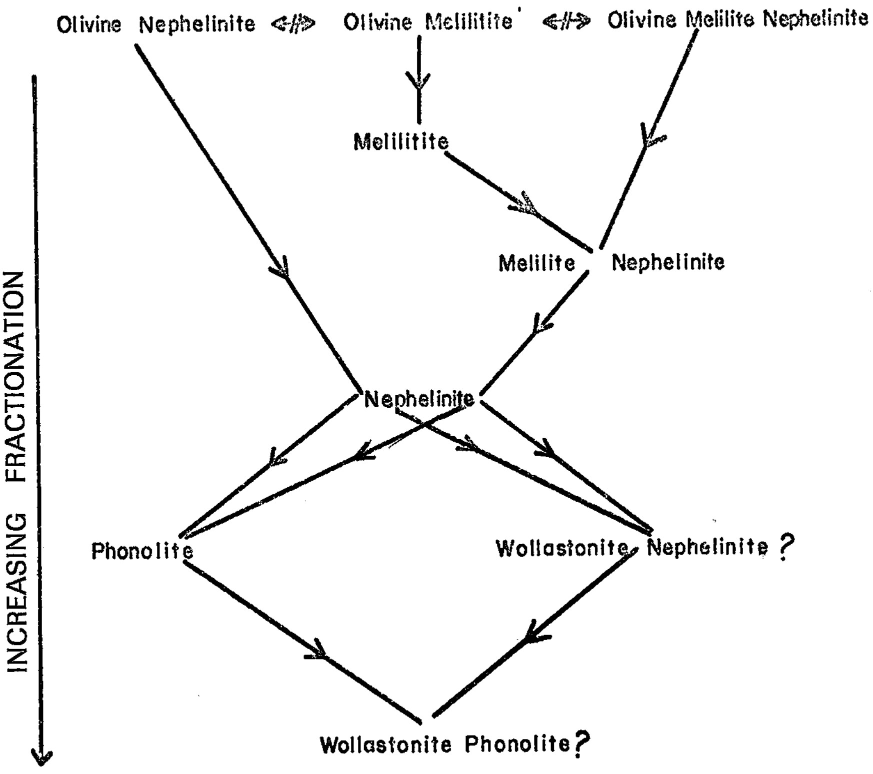

Fig. 7. Relationship between all possible rock types formed by fractional crystallization of olivine, or melilite and olivine.

side—nepheline—kalsilite—silica (Fig. 5) can be discussed with aid of the flow diagram given in Fig. 8 which schematically represents phase relations after the disappearance of olivine and melilite. The dotted lines at the bottom of the diagram give inferred relations in the front (kalsilite–rich) part of the tetrahedron in Fig. 5. Generally the top of this diagram represents silica–rich compositions. With equilibrium crystallization, liquids trend along the lines of Fig. 8 toward the quaternary invariant point R′, and hence to the "minimum" M′.

Liquids lying within the leucite volume, enclosed by the joins diopside—albite—sanidine and diopside—albite—leucite proceed toward R′ (Figs. 5 and 8), passing through the diopside—albite—leucite system (Fig. 3), and crystallizing leucite, K-rich feldspar and diopside corresponding to a simplified leucite trachyte. Compositions initially lying below the diopside—albite—leucite join (*i.e.* towards the more silica-undersaturated part) reach R′; (Fig. 8), where nepheline crystallizes and the resulting assemblage (nepheline, diopside, feldspar and leucite) corresponds to a simple leucite phonolite. At this point, the last leucite disappears by reaction with the liquid. However, the last liquid crystallizes on the line HR′ at some minimum to a diopside, nepheline, feldspar assemblage, corresponding to a simplified phonolite. Successive fractionation of leucite and diopside from this liquid produces a potash-rich trend from leucitite to leucite trachyte to phonolite. Successive fractionation of leucite and diopside from this liquid produces a potash-rich trend from leucitite to leucite trachyte to phonolite (or leucite phonolite). Extreme fractionation of leucite from liquids below the join diopside—albite—leucite can result in silica-oversaturated liquids, producing an end product corresponding to a rhyolitic composition.

Liquids from composition lying close to the diopside—nepheline—kalsilite face of the tetrahedron (Fig. 5) may proceed toward a postulated quaternary invariant point I (Fig. 8) where kalsilite inverts to nepheline. Natural counterparts of such liquids are rare but presumably would be simplified nepheline–leucite kalsilitites. On leaving I, liquids proceed toward R′, passing through point B (Fig. 2) on the diopside—nepheline—sanidine system and crystallizing leucite, nepheline and diopside corresponding to a simplified leucitophyre. Those reaching R′ crystallize feldspar and the liquid has the composition of a simple leucite phonolite. At R′, leucite disappears by reaction with liquid and the liquid proceeds to the "minimum" M′. Fractionation may produce a sequence of assemblages corresponding to rocks ranging in composition from nepheline–leucite kalsilitites to leucitophyres to leucite phonolites or phonolites.

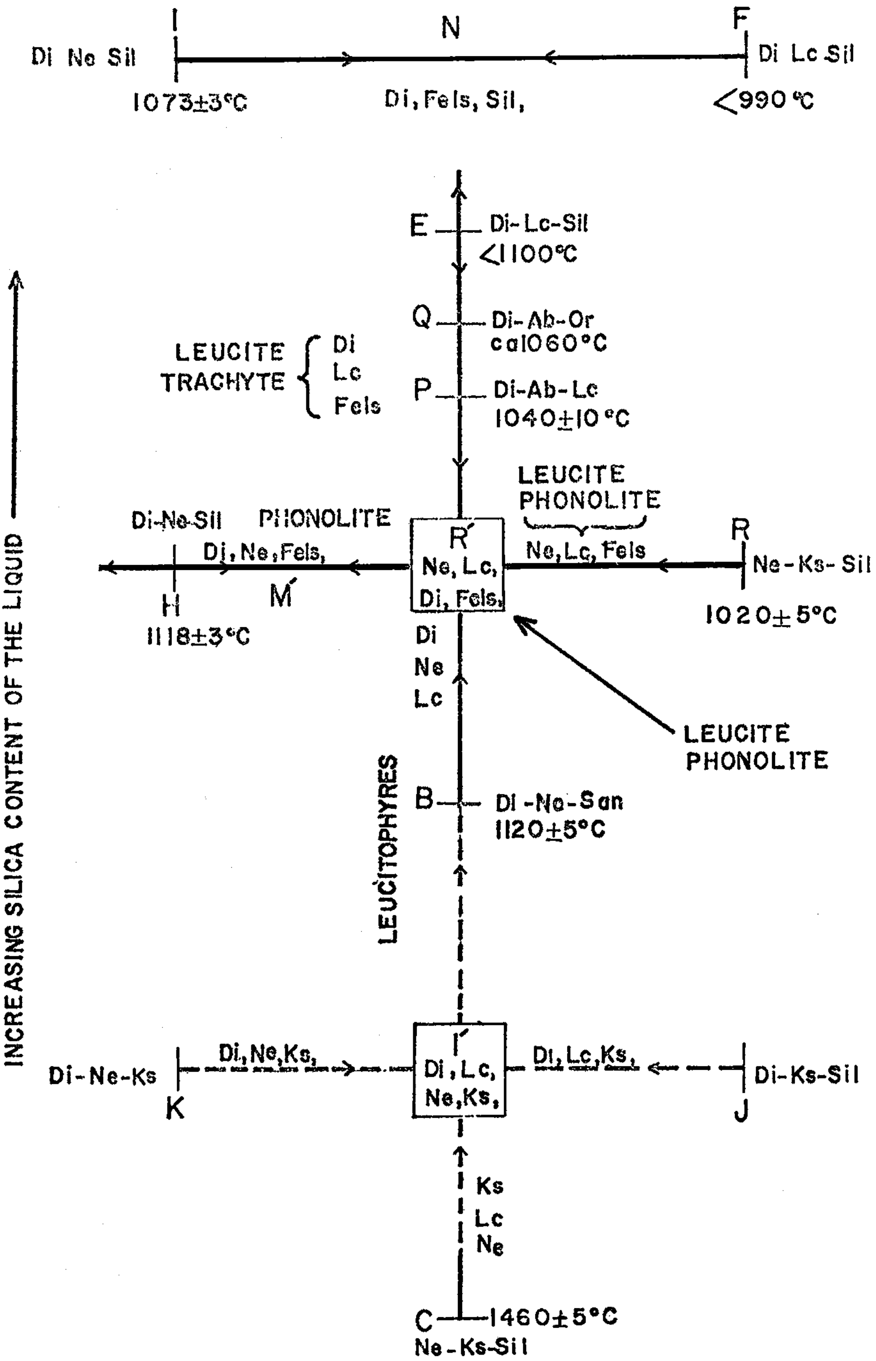

FIG. 8. Flow diagram showing the univariant and invariant equilibria involving liquid lying within the tetrahedron diopside—nepheline—kalsilite—silica. Abbreviations are given

CONCLUSIONS

Phase relations within portions of the diopside—nepheline—kalsilite—silica system indicate the presence of a "quarternary" minimum, analogous to, and closely corresponding in temperature and composition to the reaction point and minimum in the residua system nepheline—kalsilite—silica (Schairer 1957). The system diopside—nepheline—kalsilite—silica provides a much better physico-chemical basis for our understanding of the genesis of a larger number of alkaline undersaturated rocks than does the residua system alone. Of particular importance in this respect is that the system represents basic alkaline lavas with both sodic and potassic affinities, which can be shown to be connected genetically with their more felsic counterparts.

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REFERENCES

BOWEN, N.L. (1922) : Genetic features of alnöitic rocks from Isle Cadieux, Quebec. *Am. Jour. Sci.*, **3**, 1-34.

GORANSON, R.W. (1931) : The solubility of water in granite. *Am. Jour. Sci.*, **22**, 481-502.

MORSE, S.A. (1968) : Syenites. *Ann. Rept., Geophys. Lab., Carnegie Inst. Wash., Yearbook* **67**, 113-120.

ONUMA, K. & YAGI, K. (1967) : The system diopside-åkermanite-nepheline. *Am. Mineral.*, **52**, 227-243.

SCHAIRER, J.F. (1957) : Melting relations of the common rock-forming silicates. *Jour. Am. Ceramic Soc.*, **40**, 215-235.

——— (1959) : Phase equilibria with particular reference to silicate systems. In *Physiochemical measurements at high temperatures.* Editors Bockvis, White and Mackenzie, Butterworths Scientific Publications. London, 394 pp.

SCHAIRER, J.F. & BOWEN, N.L. (1935) : Preliminary report on equilibrium — relations between feldspathoids, alkali-feldspars, and silica. *Am. Geophys. Un. Trans., 16th Ann. Mtg.*, Pt. 1, 325-328.

——— (1938) : The system leucite-diopside-silica. *Am. Jour. Sci.*, **35-A**, 289-309.

SCHAIRER, J.F. & YODER, H.S., Jr. (1960) : The nature of residual liquids from crystallization, with data on the system nepheline-diopside-silica. *Am. Jour. Sci., Bradley Volume,* **258-A**, 273-283.

Shepherd, E.S., Rankin, G.A. & Wright, E.F. (1909) : The binary systems of alumina with silica, lime and magnesia. *Am. Jour. Sci.*, **28**, 293-333.

Tuttle, O.F. (1949) : Two pressure vessels for silicate water studies. *Geol. Soc. Am. Bull.* **60**, 1727-1729.

Yoder, H.S., Jr. & Tilley, C.E. (1962) : Origin of basaltic magmas : An experimental study of natural and synthetic rock systems. *Jour. Petrology* **3**, 342-532.