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EXPERIMENTAL STUDY OF THE SYSTEM DIOPSIDE – ALBITE – NEPHELINE AT P(H_2O) = P(TOTAL) = 2 AND 10 KBAR AND AT P(TOTAL) = 28 KBAR

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ABSTRACT

Bulk compositions of many nephelinites, melanephelinites, urtites, phonolites and tephrites plot in the system diopside – albite – nepheline. A study of the system under various pressures and temperatures both in the presence and absence of H_2O thus has relevance in the genesis of these rock types. Sixty-five experiments were conducted on 20 starting compositions at 28 kbar under dry conditions. The primary phase volumes of nepheline$_{ss}$, clinopyroxene and albite$_{ss}$ were encountered. The four-phase assemblage Cpx + Pl + Qtz + L occurs at 1200 ± 5°C toward the albite-rich side of the subsystem, whereas in the nepheline-rich portion, the three-phase assemblage of Cpx + Ne$_{ss}$ + L is obtained at 1249 ± 5°C. The clinopyroxene is a solid solution in the series $CaMgSi_2O_6$ (diopside) – $NaAlSi_2O_6$ (jadeite) at 28 kbar. This confirms the observation of Bell & Davis (1969), who suggested complete solid-solution between the two phases at this pressure and above. A nephelinitic or a melanephelinitic magma on further crystallization yields a phonolitic liquid. The same system was also studied at P(H_2O) = P(total) = 10 and 2 kbar. Eighteen experiments were done at 10 kbar, and the "isobaric invariant" point was observed at $Di_4Ab_{46.6}Ne_{49.4}$ and 835 ± 5°C, whereas this point lies at $Di_5Ab_{66}Ne_{29}$ (885 ± 5°C) at P(H_2O) = P(Total) = 2 kbar. The invariant point at 10 kbar is a reaction point, where the equilibrium assemblage comprises Cpx + Ne$_{ss}$ + Ab$_{ss}$ + L + V. The reaction point at 2 kbar corresponds to the composition of many nepheline-bearing mafic to felsic rocks. The present data at 10 and 2 kbar [P(H_2O) = P(Total)] indicate that a phonolitic liquid can be obtained by the following schemes of fractionation: i) melanephelinite ⟶ nephelinite ⟶ phonolite, and ii) "trachyte" ⟶ phonolite.

Keywords: diopside, nepheline, albite, phase relations, upper mantle condition, experimental petrology.

SOMMAIRE

La composition chimique de plusieurs néphélinites, mélanéphélinites, urtites, phonolites et tephrites est assez proche du système diopside – albite – néphéline. Une étude de ce système sous conditions variées de pression et de température, avec ou sans H_2O, a donc une certaine importance pour comprendre la genèse de cette suite de roches. Nous avons effectué soixante-cinq expériences sur 20 mélanges à sec à 28 kbar. Les volumes primaires de néphéline$_{ss}$, clinopyroxène et albite$_{ss}$ ont été croisés. L'assemblage à quatre phases Cpx + Pl + Qtz + L apparait à 1200 ± 5°C vers le côté du pôle albite du sous-système, tandis que dans la portion du système se rapprochant du pôle néphéline, nous obtenons l'assemblage à trois phases Cpx + Ne$_{ss}$ + L à 1249 ± 5°C. Le clinopyroxène est une solution solide de la série $CaMgSi_2O_6$ (diopside) – $NaAlSi_2O_6$ (jadéite) à 28 kbar. Ce résultat confirme l'observation de Bell et Davis (1969), qui proposaient une solution solide complète entre les deux phases à cette pression et au-delà. Un magma néphélinitique ou bien mélanéphélinitique sujet à une cristallisation progressive mènerait à un liquide phonolitique. Nous avons étudié le même système aux conditions P(H_2O) = P(total) = 10 et 2 kbar. Dix-huit expériences ont été effectuées à 10 kbar, et le point "invariant isobare" a été défini à $Di_4Ab_{46.6}Ne_{49.4}$ et 835 ± 5°C, tandis que le point correspondant à P(H_2O) = P(Total) = 2 kbar se trouve à $Di_5Ab_{66}Ne_{29}$ et 885 ± 5°C. Le point invariant à 10 kbar représente une réaction impliquant l'assemblage Cpx + Ne$_{ss}$ + Ab$_{ss}$ + L + V à l'équilibre. Ce point à 2 kbar correspond à la composition de plusieurs roches néphéliniques mafiques et felsiques. D'après les données acquises à 10 et à 2 kbar [P(H_2O) = P(Total)], un liquide phonolitique peut résulter des schémas suivants de fractionnement: i) mélanéphélinite ⟶ néphélinite ⟶ phonolite, et ii) "trachyte" ⟶ phonolite.

Mots-clés: diopside, néphéline, albite, relations de phases, conditions du manteau supérieur, pétrologie expérimentale.

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INTRODUCTION

The system diopside – albite – nepheline is one of the most important subsystems of the simplified basalt tetrahedron, diopside – nepheline – forsterite – silica, of Yoder & Tilley (1962). Bulk compositions of many nephelinites, melanephelinites, urtites, phonolites and "tephrites" also plot near this plane. Study of this subsystem at variable pressures and temperatures with or without H_2O thus has relevance in the genesis of these rock types. Furthermore, the join diopside–jadeite constitutes a thermal barrier at high pressure, and controls the course of crystallization of liquid forming melanephelinite – nephelinite – phonolite or tholeiitic rock series (Yoder & Tilley 1962).

Omphacite is one of the two important essential minerals of eclogite (Kushiro 1969, Holland 1983). The bulk composition of omphacite lies on the join diopside–jadeite, which is a part of the plane diopside – albite – nepheline at a pressure typical of the upper mantle. We thus studied the system at 28 kbar.

Many rocks belonging to the nephelinite series contain amphibole (White *et al.*1972, Woolley & Jones 1987, Downes 1987). White *et al.* (1972), therefore, concluded that under suitable $P(H_2O)$ conditions, rocks of these series should be converted to amphibolites. We planned another series of experiments to evaluate the effects of H_2O in the system at $P(H_2O) = P(\text{Total}) = 2$ and 10 kbar.

REVIEW OF WORK ON THE SYSTEM DIOPSIDE – ALBITE – NEPHELINE

The system diopside – albite – nepheline consists of the following bounding joins: 1) nepheline–albite, 2) diopside–nepheline, and 3) diopside–albite. A phase-equilibrium study of the join nepheline–albite was made by Bowen & Schairer (1935) and Schairer (1950). Bell & Roseboom (1969) studied the system nepheline–SiO_2 up to 40 kbar and variable temperatures. They presented phase relations on the join diopside–jadeite at variable temperatures at 30 and 40 kbars. At 30 kbar, they showed that it is divided into two portions with two eutectic points. The eutectic point on the nepheline-rich side is present at $Ab_{60}Ne_{40}$, and the one in the albite-rich portion occurs at $Ab_{70}Ne_{30}$. The subsolidus assemblage (nepheline$_{ss}$ + jadeite$_{ss}$) appears slightly below 1285°C in the nepheline-rich side, whereas in the albite-rich portion, the subsolidus assemblage of jadeite$_{ss}$ and albite$_{ss}$ occurs at 1200°C. Robertson *et al.* (1957) suggested that all the phases in this nepheline–albite subsystem are solid solutions.

The phase-equilibrium study at atmospheric pressure on the join diopside–albite was made first by Bowen (1915), and later by Schairer & Yoder (1960). The same join was studied at high pressure by Kushiro (1965, 1969). His investigation on five compositions ($Di_{80}Ab_{20}$), ($Di_{70}Ab_{30}$), (Di_{55} Ab_{45}), ($Di_{40}Ab_{60}$), and ($Di_{25}Ab_{75}$) (wt%) at 1350, 1250, 1150 and 1050°C at pressures between 10 and 35 kbar yielded two different assemblages: 1) omphacite + plagioclase + quartz, and 2) omphacite + quartz. He established the P–T coordinates of the breakdown of albite to form jadeite + quartz, and studied the incorporation of the jadeite component in the clinopyroxene structure.

Bowen (1928), and later Schairer *et al.* (1962) studied the join diopside–nepheline at one atmosphere pressure. They showed that the join cuts the primary phase volumes of carnegieite$_{ss}$, nepheline$_{ss}$, forsterite$_{ss}$ and diopside$_{ss}$. The assemblage nepheline$_{ss}$ + forsterite$_{ss}$ + liquid appears at 1193 ± 3°C, and melilite coprecipitates with it at 1170 ± 20°C. The five-phase assemblage of nepheline$_{ss}$ + forsterite$_{ss}$ + melilite + diopside$_{ss}$ + liquid appears at 1135 ± 10°C, and forsterite$_{ss}$ reacts out at 1100 ± 15°C. The composition of residual liquids formed under atmospheric pressure in the system nepheline–diopside was studied by Yoder & Kushiro (1972).

The experimental study of the join nepheline–diopside under variable pressures (up to 28 kbar) by Singh *et al.* (2000) established the presence of a pseudoeutectic point at $Ne_{70}Di_{30}$ and 1420°C. Melilite and forsterite$_{ss}$ are completely absent in all their runs at 28 kbar. On the basis of eleven runs performed by them at 25, 20 and 15 kbar and 1000°C, they concluded that the complete disappearance of melilite and forsterite$_{ss}$ takes place at 17.5 ± 2.5 kbar.

EXPERIMENTAL TECHNIQUES

A hydrothermal unit (Model HR–IB–2) manufactured by M/S Leco Corporation, Tem–Pres Division, State College, Pennsylvania 16823, U.S.A., was used to conduct experiments at 2 kbar [$(P(H_2O) = P(\text{Total})$] at the National Centre of Experimental Mineralogy and Petrology, Allahabad.

Most experiments at 10 and 28 kbar were performed using a piston–cylinder apparatus (Boyd & England 1960) at the same centre. Several experiments on the join diopside–jadeite were conducted at the National Physical Laboratory, New Delhi, using a 200 tonne cubic-press apparatus designed by Hall (1966).

Pure NaCl and NaCl–Pyrex assemblies were used in the case of runs with piston–cylinder apparatus to the highest temperatures. Measurement of temperatures was made with $Pt–Pt_{90}Rh_{10}$ thermocouples and are considered to be accurate to ±5°C, without taking into account the effect of pressure on e.m.f. Pressure was calibrated at 1000°C against the reactions fayalite + quartz = orthosilicate (1.41 GPa; Bohlen *et al.* 1980) and quartz ⇔ coesite (3.07 GPa; Bose & Ganguly 1995). Pressure measurements are considered to be accurate to ±0.05 GPa.

In the case of experiments with the cubic press, the pressure calibration was carried out with respect to high-pressure phase transformation of Bi (I–II) at 25.4 kbar, Yb (f_{cc}–b_{cc}) at 39 kbar, and Ba (I–II) at 55 kbar (all at room temperature). The reaction cell used for experimental study is made of pyrophyllite in the form of a cube (16 mm). Pressure was applied with tungsten carbide anvils (12.5 mm). In this case, high-temperature calibration experiments also were performed on the following phase transitions: quartz–coesite (3.2 GPa at 1250°C; Bose & Ganguly 1995), and fayalite–γ-Fe_2SiO_4 (0.5 GPa at 1000°C; Yagi *et al.* 1987).

Synthetic natrosilite ($Na_2O.2SiO_2$) and reagent-grade $CaCO_3$, MgO, Al_2O_3 and pure quartz (99.9% SiO_2) were used as sources of Na_2O, CaO, MgO, Al_2O_3 and silica, respectively. For the preparation of $Na_2O.2SiO_2$, the method of Schairer & Bowen (1956) was used. Schairer's (1950) method of preparation of glasses and crystallization of starting materials was used. All glasses were crystallized at 1 atm at 800°C for 7 days. All high-pressure runs were conducted on these crystallized starting materials.

TABLE 1. COMPOSITION OF CLINOPYROXENE CRYSTALLIZED IN THE SYSTEM DIOPSIDE – ALBITE – NEPHELINE AT 28 KBAR AND VARIOUS TEMPERATURES

Starting Composition Temperature	$Di_{35}Ab_7Ne_{58}$ 1249°C	$Di_{30}Ab_{19}Ne_{51}$ 1249°C	$Di_{20}Ab_{52}Ne_{28}$ 1203°C	$Di_{49}Ab_{33}Ne_{18}$ 1200°C	$Di_{80}Ab_{13}Ne_7$ 1203°C	$Di_{10}Ab_{30}Ne_{60}$ 1200°C
SiO_2 wt%	55.71	54.16	58.01	57.78	56.29	51.95
Al_2O_3	17.25	20.44	22.56	9.54	5.27	27.02
Na_2O	8.32	5.24	8.54	6.25	3.52	14.59
CaO	9.66	11.08	5.07	15.51	20.03	3.35
MgO	9.02	7.94	3.32	11.43	14.54	2.42
Total	99.96	98.86	97.50	100.51	99.65	99.33
Si *apfu*	1.914	1.953	1.994	2.010	1.975	1.801
Al	0.700	0.869	0.914	0.392	0.218	1.104
Mg	0.464	0.427	0.170	0.594	0.761	0.125
Ca	0.356	0.428	0.186	0.579	0.753	0.124
Na	0.552	0.365	0.569	0.422	0.240	0.881

Cation proportions calculated on the basis of six atoms of oxygen per formula unit (*apfu*).

TABLE 2. COMPOSITION OF CLINOPYROXENE IN EQUILIBRIUM WITH LIQUID AT VARIABLE TEMPERATURES FROM VARIOUS STARTING MATERIALS

	a ($Di_{50}Jd_{50}$) 1564°C		b ($Di_{20}Jd_{80}$) 1440°C		c ($Di_{10}Jd_{90}$) 1400°C		d (Di_3Jd_{97}) 1365°C	
	L	Cpx	L	Cpx	L	Cpx	L	Cpx
CaO wt%	9.32	16.31	3.88	7.51	1.81	4.40	0.78	1.55
MgO	6.70	11.72	2.59	5.40	1.30	3.16	0.56	1.12
Na_2O	9.71	5.65	13.02	10.85	14.25	12.62	14.76	14.40
Al_2O_3	16.14	9.33	21.43	17.91	23.46	20.93	24.46	14.66
SiO_2	58.03	56.94	58.75	57.29	59.27	58.57	59.31	59.11
Total	99.90	99.95	99.67	98.96	100.09	99.68	99.87	99.84
Comp.	$Di_{50}Jd_{50}$	$Di_{63}Jd_{37}$	$Di_{20}Jd_{80}$	$Di_{29}Jd_{71}$	$Di_{10}Jd_{90}$	$Di_{17}Jd_{83}$	Di_3Jd_{97}	Di_6Jd_{94}

Compositions a, b, c and d are plotted in Figure 1. The letters a, b, c and d refer to initial compositions; a: $Di_{50}Jd_{50}$, b: $Di_{20}Jd_{80}$, c: $Di_{10}Jd_{90}$, d: Di_3Jd_{97}. The temperature of crystallization of the pyroxenes is recorded below the bulk composition. L: liquid, (glass), Cpx: clinopyroxene.

TABLE 3. COMPOSITION OF NEPHELINE AND PLAGIOCLASE IN THE RUN PRODUCTS

	1	2	3	4	5	6	7	8	9
Na_2O wt%	20.38	20.40	21.79	21.77	21.31	11.71	11.64	10.75	11.78
Al_2O_3	33.53	33.56	35.84	35.82	35.06	19.59	19.71	20.98	19.49
SiO_2	46.06	46.02	42.37	42.41	40.54	68.51	68.34	66.44	68.56
CaO	-	-	-	-	-	0.18	0.31	1.81	0.05
Total	99.97	99.98	100.00	100.00	96.91	100.00	100.00	99.98	99.88

1. Nepheline crystallized from the mixture $Di_{10}Ab_{45}Ne_{45}$ at $P(H_2O) = P(Total) = 2$ kbar and 902°C. Nepheline contains 14.3 wt.% albite component in solid solution.
2. Nepheline crystallized from the mixture $Di_5Ab_{47.5}Ne_{47.5}$ at $P(H_2O) = P(Total) = 2$ kbar and 820°C. Nepheline contains 14.1 wt.% albite component in solid solution.
3. Nepheline crystallized from the mixture $Di_{29}Ab_{59}Ne_{12}$ at 28 kbar and 1015°C. Nepheline contains 0.25 wt.% albite component in solid solution. Duration: 10 hours.
4. Nepheline crystallized from the mixture $Di_{29}Ab_{59}Ne_{12}$ at 28 kbar and 1015°C. Nepheline contains 0.36 wt.% albite component in solid solution. Duration: 30 hours.
5. Nepheline crystallized from the mixture $Di_{16}Ab_{70}Ne_{14}$ at 28 kbar and 1200°C. Nepheline contains 5 wt.% albite component in solid solution.
6. Plagioclase crystallized from the mixture $Di_{11}Ab_{57}Ne_{32}$ at 10 kbar and 675°C. Plagioclase contains about 1 wt.% anorthite component.
7. Plagioclase crystallized from the mixture $Di_3Ab_{62}Ne_{35}$ at 2 kbar and 836°C. Plagioclase contains 1.41 wt.% anorthite component.
8. Plagioclase crystallized from the mixture $Di_{16}Ab_{70}Ne_{14}$ at 28 kbar and 1200°C. Plagioclase contains 9 wt.% anorthite component.
9. Plagioclase crystallized from the mixture $Di_{29}Ab_{59}Ne_{12}$ at 28 kbar and 1248°C. Plagioclase contains 0.27 wt.% anorthite component.

Electron-microprobe analyses (accelerating voltage 15 kV, and sample current 20 nA) were made of clinopyroxene (Tables 1, 2), nepheline and plagioclase (Table 3) and glass. A beam of approximately 3 μm in diameter was used. All analyses were done with a JEOL JSM–5300 electron microprobe analyzer at the University of Texas at Dallas. The run products obtained from high-pressure experiments were crushed for optical and X-ray-diffraction studies with Cu*K*α radiation. The phases identified in this study are clinopyroxene, nepheline and plagioclase. The solubility of the various components in these phases at different pressures is discussed below.

The criteria chosen to ascertain equilibrium are based on the following principles: i) homogeneous distribution of phases in the glasses and uniform occurrence of phases in case of a subsolidus run, ii) absence of corroded or zoned crystals, iii) agreement of data at same temperatures for runs of nearby compositions, iv) consistency of experimental results for similar compositions under isobaric-isothermal conditions for varying lengths of time, and v) application of phase-equilibria rules to check for equilibrium assemblage (Boettcher & Wyllie 1969). Quench phases could be easily identified by the development of a feathery texture.

RESULTS AND DISCUSSION

The system diopside – albite – nepheline at 28 kbar

Twenty compositions were prepared to study the system diopside – albite – nepheline. Altogether, sixty-five experiments were done under variable temperatures at 28 kbar to determine the phase-equilibrium relations. Results of experiments are summarized in Figure 1 and Table 4. The melting point of diopside (1720°C) and that of albite (1320°C) at 28 kbar were taken from Boettcher *et al.* (1982). The liquidus data for jadeite and compositions along the join diopside–jadeite at this pressure are obtained from Bell & Davis (1969).

The present study (Fig. 1) shows that the join has primary phase-fields for nepheline$_{ss}$, albite$_{ss}$ and clinopyroxene (omphacite). Reference to the study of Singh *et al.* (1999) on the join diopside–nepheline indicates that at 28 kbar, the pseudoeutectic occurs at $Ne_{70}Di_{30}$ and 1420°C. The experimental studies of Windom & Boettcher (1981) and Gupta *et al.* (1987) show that the nepheline–albite join cuts the primary phase-volumes of nepheline$_{ss}$, clinopyroxene and albite$_{ss}$. Thus the field of clinopyroxene, present over a large portion of the diagram, also extends to the nepheline–albite join. Be-

TABLE 4. EXPERIMENTAL RESULTS IN THE SYSTEM DIOPSIDE – NEPHELINE – ALBITE AT 28 KBAR AND VARIOUS TEMPERATURES

Composition	Duration	T (°C)	Assemblage
$Di_{35}Ab_{07}Ne_{58}$	12	1443	all Gl
(1.537)	20	1349	trace Cpx + Gl
	23	1249	Cpx + Ne + Gl
	30	1002	major Ne + minor Cpx + moderate Ab
$Di_{30}Ab_{19}Ne_{51}$	12	1480	all Gl
(1.533)	12	1470	trace Cpx + L
	20	1349	minor Cpx + Gl
	23	1249	minor to moderate Cpx + moderate Ne + minor Ab + Gl
	30	1003	major Cpx + major Ne + moderate Ab
$Di_{21}Ab_{44}Ne_{35}$	20	1442	trace Cpx + Gl
(1.519)	24	1349	trace Cpx + Gl
	26	1247	rare Cpx + moderate Ne + minor Ab + Gl
	30	1003	major Cpx + moderate Ne + minor Ab
$Di_{29}Ab_{59}Ne_{12}$	15	1441	rare Cpx + Gl
(1.521)	20	1349	rare Cpx + Gl
	25	1248	major Pl + major Cpx + rare Gl
	20	1015	major Pl + major Cpx + minor Qtz?
$Di_{10}Ab_{45}Ne_{45}$	10	1452	all Gl
(1.507)	15	1351	all Gl
	20	1202	moderate Cpx + minor Ne + minor Ab + Gl
	25	1058	major Cpx + major Ne + moderate Ab
$Di_{30}Ab_{40}Ab_{30}$	10	1452	trace Cpx + Gl
(1.528)	15	1352	trace Cpx + Gl
	20	1200	trace Cpx + rare Ne + Gl
	30	1101	major Cpx + minor Ne + Gl
$Di_{11}Ab_{57}Ne_{32}$	10	1452	all Gl
(1.505)	20	1351	Cpx + Gl
	25	1101	Cpx
$Di_{16}Ab_{70}Ne_{14}$	10	1452	trace Cpx + Gl
(1.509)	15	1351	trace Cpx + Gl
	21	1200	major Pl + minor Cpx + minor Qtz + Gl
	25	1050	major Pl + minor Cpx + moderate Qtz
$Di_{40}Ab_{50}Ne_{10}$	11	1452	trace Cpx + Gl
(1.535)	18	1350	major Cpx + minor Pl + Gl
	21	1200	minor Cpx + minor Pl + Qtz + Gl
	25	1100	major Pl + major Cpx + minor Qtz
$Di_{10}Ab_{30}Ne_{60}$	16	1504	all Gl
(1.513)	21	1454	all Gl
	27	1353	major Cpx + minor Ne + Gl
	20	1200	major Ne + minor Cpx + minor Qtz
$Di_{0}Ab_{50}Ne_{50}$	7	1505	all Gl
(1.499)	21	1454	all Gl
	30	1354	trace Cpx + Gl
$Di_{5}Ab_{55}Ne_{40}$	16	1505	all Gl
(1.503)	15	1455	all Gl
	20	1325	minor Cpx + trace Ne + Gl
$Di_{5}Ab_{75}Ne_{20}$	16	1505	all Gl
(1.495)	21	1455	all Gl
	15	1455	all Gl
	25	1353	minor to moderate Pl + rare Cpx + Gl
$Di_{20}Ab_{52}Ne_{28}$	25	1203	Cpx + rare Gl
(1.515)			
$Di_{49}Ab_{33}Ne_{18}$	15	1452	Cpx + moderate Gl
(1.543)	20	1200	Cpx + minor Ab
	30	1101	Cpx + minor Ab (?)
$Di_{80}Ab_{13}Ne_{07}$	22	1303	Cpx
(1.579)	25	1203	Cpx
$Di_{50}Jd_{50}$	28	1550	Cpx + Gl
(1.543)	28	1530	Cpx + Gl
	28	1505	Cpx + Gl
$Di_{20}Jd_{80}$	28	1440	Cpx + Gl
(1.518)	28	1420	Cpx + Gl
$Di_{10}Jd_{90}$	28	1400	Cpx + Gl
(1.508)	28	1390	rare Cpx + trace Ab (?) + Gl
$Di_{3}Jd_{97}$	20	1365	minor Ab + Gl
	20	1355	minor Cpx + minor Ab (?) + rare Gl

Terms such as "trace", "minor", "major" and "rare" refer to amounts of crystals in the run products. The index of refraction of the glass is reported in parentheses in the first column. All glasses were crystallized at 1 atm. and 800°C for seven days. All runs were conducted on these crystallized starting materials. The bulk composition of the starting mixtures (column 1) is reported in weight %. The duration of the experiments is reported in hours.

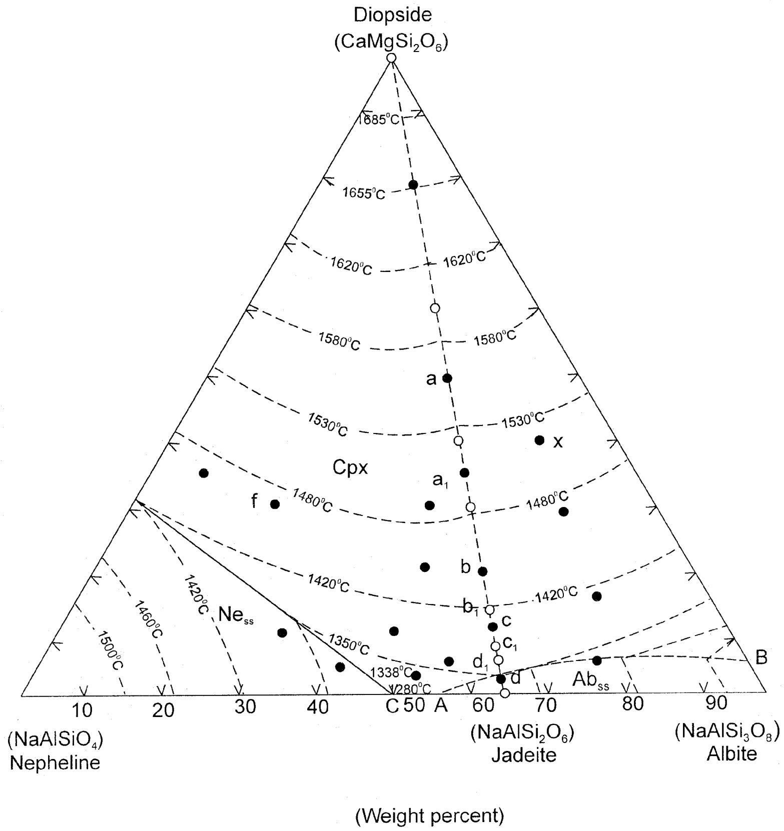

FIG. 1. Liquidus phase relations in the system diopside – albite – nepheline at 28 kbar and variable temperatures (present study). Solid circles indicate starting materials crystallized from homogeneous glasses. Open circles (a$_1$, b$_1$, c$_1$, and d$_1$, *etc.*) represent compositional plot of glasses (determined by EPMA from run product) in equilibrium with different clinopyroxenes, compositions of which are shown in Table 2).

cause jadeitic clinopyroxene has an incongruent melting relation with liquid, and the field of albite$_{ss}$ is extended along the join, the diopside – albite – nepheline plane does not have a four-phase point, and the composition of the liquid coexisting with Cpx + Ne$_{ss}$ + Ab$_{ss}$ does not lie in this plane. This observation is consistent with the conclusion of Windom & Boettcher (1981) and Gupta *et al.* (1987). Bell & Davis (1969) also demonstrated the incongruent melting behavior of albite to a pressure slightly above 28 kbar. On the basis of liquidus data related to compositions Di$_5$Ab$_{55}$Ne$_{40}$, Di$_{11}$Ab$_{57}$Ne$_{32}$, Di$_{16}$Ab$_{70}$Ne$_{14}$ and Di$_5$Ab$_{75}$Ne$_{20}$, the albite$_{ss}$ – clinopyroxene phase boundary can be extended to the composition Di$_8$Ab$_{92}$, which correspond to the pseudo-eutectic point along the join diopside–albite. The liquidus temperatures for the diopside–nepheline join were obtained from Singh *et al.* (2000). If the isotherms are plotted with reference to the liquidus data obtained in the present study, they match well with those of the early investigators, as mentioned above. The liquidus isotherms show a gradual slope along the diopside–jadeite join (except for a gentle hump showing a thermal maximum near the jadeite end).

The data in Table 4 indicate that subsolidus assemblages for bulk compositions Di$_{30}$Ab$_{19}$Ne$_{51}$, Di$_{21}$Ab$_{44}$Ne$_{35}$, Di$_{10}$Ab$_{45}$Ne$_{45}$, Di$_{30}$Ab$_{40}$Ne$_{30}$ and Di$_{10}$Ab$_{30}$Ne$_{60}$, lying in the nepheline-rich portion of the diopside – albite– nepheline system, consist of Cpx + Ne$_{ss}$ + Ab$_{ss}$. The mixtures Di$_{29}$Ab$_{59}$Ne$_{12}$, Di$_{16}$Ab$_{70}$Ne$_{14}$, Di$_{40}$Ab$_{50}$Ne$_{10}$ and Di$_5$Ab$_{75}$Ne$_{20}$, with compositions in the albite-rich portion of the system, consist of the subsolidus assemblage of Cpx + Ab$_{ss}$ + Qtz. The compositions Di$_{11}$Ab$_{57}$Ne$_{32}$, Di$_{20}$Ab$_{52}$Ne$_{28}$, Di$_{49}$Ab$_{33}$Ne$_{18}$ and Di$_{80}$Ab$_{13}$Ne$_7$, lying on the diopside–jadeite join, yielded only clinopyroxene. In the case of composition $Di_{20}Ab_{52}Ne_{28}$, however, in addition to clinopyroxene, a small amount of plagioclase also was noted.

Clinopyroxene crystallizing from compositions $Di_{35}Ab_7Ne_{58}$, at 1249°C, $Di_{30}Ab_{19}Ne_{51}$ at 1249°C and $Di_{10}Ab_{30}Ne_{60}$ at 1200°C contain 32, 28 and 11 mole % diopside and 55, 37 and 88 mole % of jadeite, respectively (Table1), which shows that other pyroxene components include $CaAlSiAlO_6$ (Ca-Tschermaks component), $MgAlSiAlO_6$ (Mg-Tschermaks component), $Ca_{0.5}AlSi_2O_6$ and $Mg_{0.5}AlSi_2O_6$. Table 1 also includes compositions of pyroxenes crystallized from three other mixtures at different temperatures.

In contrast, clinopyroxenes crystallizing from compositions lying on the diopside–jadeite join at 1203 ± 5°C can be expressed in terms of $CaMgSi_2O_6$ and $NaAlSi_2O_6$ only (Table 2). The proportion of the jadeite component in these compositions, however, conforms to the reaction relation nepheline + albite ↔ 2 jadeite. As the nepheline + albite content in the starting composition increases, the jadeite content also increases. The jadeite (Jd) and diopside (Di) contents of clinopyroxenes crystallized from three different compositions ($Di_{20}Ab_{52}Ne_{28}$, $Di_{49}Ab_{33}Ne_{18}$ and $Di_{80}Ab_{13}Ne_7$) at 28 kbar are, respectively, $Di_{14}Jd_{86}$, $Di_{60}Jd_{40}$ and $Di_{78}Jd_{22}$. X-ray-diffraction studies of clinopyroxene crystallizing from three mixtures $Di_{20}Ab_{52}Ne_{28}$ (equivalent to $Di_{20}Jd_{80}$), $Di_{49}Ab_{33}Ne_{18}$ (equivalent to $Di_{49}Jd_{51}$) and $Di_{80}Ab_{13}Ne_7$ (equivalent to $Di_{80}Jd_{20}$) have been made. In this study, three very sensitive X-ray reflections of clinopyroxene, 002, 310 and 221, were chosen; their positions were determined with pure NaCl as an internal standard. We note that from pure diopside to jadeite there is a systematic linear variation in the positions of these three reflections (Fig. 2). These data and the absence of any other phase in the temperature range of this study indicate a complete solid-solution between these two end members at 28 kbar.

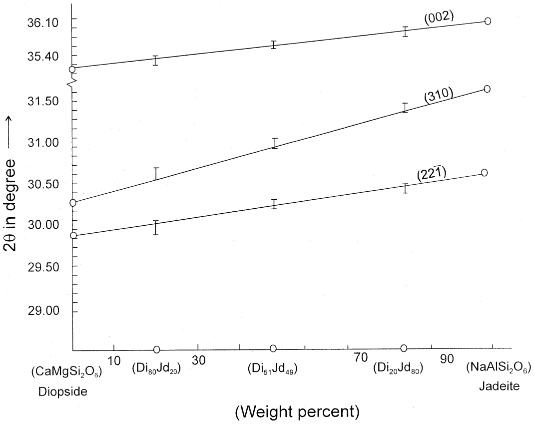

FIG. 2. A plot of 2θ *versus* interplanar spacings for clinopyroxenes crystallizing from compositions lying on the join diopside–jadeite at 28 kbar and 1203°C.

The presence of quartz in the albite-rich portion of the join is related to the breakdown of albite to jadeite + quartz (Mirwald & Massone 1980, Ishbulatov & Kosyakov 1990). At 28 kbar, the breakdown temperature for the above reaction is 1130°C (Newton & Kennedy 1968). The diopside content of pyroxene is found to increase with the rise in temperature.

Course of crystallization of liquid in the plane diopside – albite – nepheline at 28 kbar

It can be noted from Table 3 (anal. 8) that albite crystallizing from the composition $Di_{16}Ab_{70}Ne_{14}$ at 1200°C contains 9 wt.% of $CaAl_2Si_2O_8$, and nepheline incorporates 5 wt.% albite in solid solution (anal. 5). Hence, the composition of liquids does not strictly lie on the plane diopside – albite – nepheline. If the minor amount of anorthite in plagioclase (9 wt.%) is ignored, however, then the course of crystallization of liquid in this plane can be described as follows. From a liquid of composition "a" ($Di_{50}Jd_{50}$), an omphacitic pyroxene ($Di_{63}Jd_{37}$, Table 2, Fig. 1) crystallizes first, then the liquid composition should move along the join diopside–jadeite toward the univariant curve A–B, but at "a_1" ($Di_{36}Jd_{64}$, Fig. 1), crystallization ceases as the solidus is reached at 1564°C. The composition of "a_1" has been determined on the basis of analyses of liquid formed at the above-mentioned temperature. From a melt of composition "b" ($Di_{20}Jd_{80}$, Fig. 1), an omphacite ($Di_{29}Jd_{71}$, Table 2) crystallizes at 1440°C. The final composition of the liquid ($Di_{13}Jd_{87}$) is depicted by "b_1". Likewise, from a liquid of composition "c" ($Di_{13}Jd_{87}$, Fig. 1), an omphacite ($Di_{16}Jd_{84}$, Table 2) precipitates at 1400°C, but the liquid (Di_8Jd_{92}) freezes out at 1390°C, when the composition of the melt reaches point "c_1" (Fig. 1).

From a liquid of composition "d" ($Jd_{97}Di_3$, Table 2), a plagioclase ($Ab_{91}An_9$) crystallizes first at 1365°C, but is joined by a pyroxene ($Jd_{94}Di_6$, Table 2). The solidus is reached at 1360°C, when the melt's composition reaches point "d_1". The composition of liquids in equilibrium with the pyroxenes at different temperatures at 28 kbar is plotted in Figure 3, along with the diagram of Bell & Davis (1969). The study confirms the observation that the diopside–jadeite phase diagram has a loop-like structure similar to that of the forsterite–fayalite and anorthite–albite systems (Fig. 3).

A liquid of composition "x" ($Di_{30}Ne_{10}Ab_{60}$), lying toward the SiO_2-rich side of the plane diopside – albite – nepheline (Fig. 1), should yield a pyroxene ($Di_{21}Jd_{79}$) at 1450°C. Plagioclase and quartz coprecipitate, however, along with pyroxene at 1330°C. A liquid of composition "f" ($Di_{30}Ne_{51}Ab_{19}$, Fig. 1) yields a pyroxene of composition $Di_{40}Jd_{60}$ at 1470°C. If the temperature is lowered to 1400°C, nepheline appears as an additional phase.

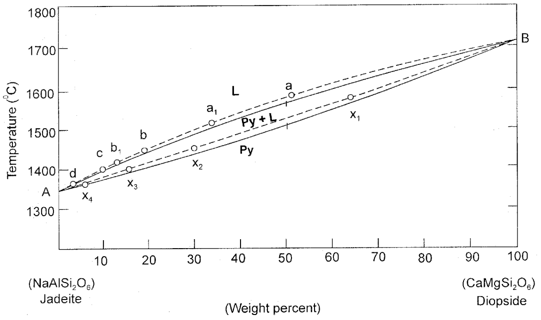

FIG. 3. Phase relations in the join jadeite–diopside at 30 kbar and variable temperatures (bold lines, Bell & Roseboom 1969). The diagram shown by dotted lines is established in the present study at 28 kbar and different temperatures. The points a, b, c and d represent composition of initial liquids (also see Fig. 1) in equilibrium with omphacite of compositions X_1, X_2, X_3 and X_4, respectively. The points a_1, b_1, c_1 and d_1 (also see Fig. 1) represent compositions of the final liquids.

In eclogite, exsolution of jadeite in clinopyroxene is noted (Smyth 1980). Robinson (1982) suggested that the presence of Na–Al pyroxene in tholeiitic gabbro and in many common rocks is a result of the breakdown of plagioclase. Curtis & Gittins (1979) have observed that in strongly silica-undersaturated metamorphic rocks of the Red Wine Complex, Labrador, the breakdown of nepheline plus sodic plagioclase stabilizes jadeite and omphacite, coexisting in equilibrium.

The albite content of $nepheline_{ss}$ crystallized from the composition $Di_{29}Ab_{59}Ne_{12}$ and 1015°C at 28 kbar is only 0.25–0.36 wt.% (Table 3, anal. 3, 4), compared to 20 wt.% albite in the same phase at 1 kbar (Edgar 1964). The anorthite content of albite in the same system at 28 kbar is only 0.27 ± 0.01 wt.% at 1248°C (Table 3, anal. 9).

Study of the system diopside – albite – nepheline at $P(H_2O) = P(Total) = 2$ kbar

Ten experiments were made on eight compositions at $P(H_2O) = P(Total) = 2$ kbar to locate the reaction point in the system diopside – albite – nepheline. The experimental findings are summarized in Table 5 and Figure 4. Our study clearly demonstrates that this plane cuts the

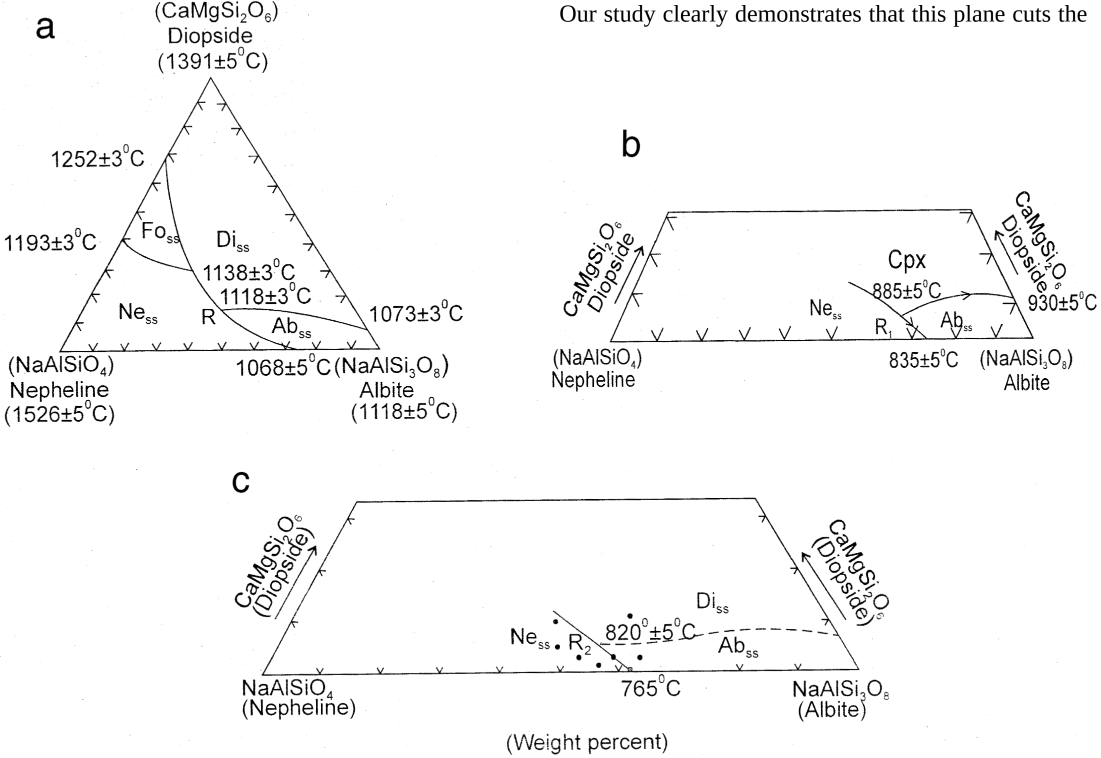

FIG. 4. Phase relations in the system diopside – albite – nepheline at different temperatures and pressures $[P(H_2O) = P(Total)]$. a) Phase relations in the system diopside – albite – nepheline at 1 atmosphere pressure and different temperatures (after Schairer & Yoder 1960). b) Phase relations in the join diopside – albite – nepheline at 1 kbar $[P(H_2O) = P(Total)]$ and at variable temperatures (after Edgar 1964). c) Phase relations in the join diopside – albite – nepheline at 2 kbar $[P(H_2O) = P(Total)]$ and various temperatures (this study).

TABLE 5. RESULTS OBTAINED FROM EXPERIMENTAL STUDIES OF THE SYSTEM DIOPSIDE – ALBITE – NEPHELINE AT $P(H_2O) = P(Total) = 2$ KBAR AND VARIOUS TEMPERATURES

Composition	Duration	T (°C)	Assemblage
$Di_{11}Ab_{57}Ne_{32}$	18	836	major Cpx + moderate Pl + Gl + V
$Di_3Ab_{62}Ne_{35}$	18	836	major Pl + minor Cpx + Gl + V
$Di_5Ab_{55}Ne_{40}$	18	858	trace Ne + rare Cpx + Gl + V
$Di_8Ab_{56}Ne_{36}$	18	858	minor to rare Cpx + rare Pl + Gl + V
$Di_8Ab_{56}Ne_{36}$	29	903	all Gl + V
$Di_{10}Ab_{45}Ne_{45}$	24	902	moderate Ne + rare Cpx + Gl + V
$Di_5Ab_{47.5}Ne_{47.5}$	23.5	820	major Ne + minor Cpx + rare Pl + Gl + V
$Di_3Ab_{52}Ne_{45}$	23.5	820	major Ne + rare Pl + trace Cpx + Gl + V
$Di_{1.5}Ab_{56}Ne_{42.5}$	23	820	major Ne + rare Pl + Gl + V

Terms such as "trace", "minor", "major" and "rare" refer to amounts of crystals in the run products. The bulk composition of the starting mixtures (column 1) is reported in weight %. The duration of the experiments is reported in hours.

TABLE 6. RESULTS OBTAINED FROM EXPERIMENTAL STUDIES OF THE SYSTEM DIOPSIDE – ALBITE – NEPHELINE AT $P(H_2O) = P(Total) = 10$ KBAR AND VARIOUS TEMPERATURES

Composition	Duration	T (°C)	Assemblage*
$Di_{10}Ab_{30}Ne_{60}$	18.25	675	minor to moderate Cpx + moderate to rare Ne + Gl + V
$Di_{10.5}Ab_{47}Ne_{42.5}$	20	675	minor Pl + rare Cpx + Gl + V
$Di_{16}Ab_{70}Ne_{14}$	15.5	675	moderate Cpx + Gl + V
$Di_5Ab_{55}Ne_{40}$	16.5	675	minor Cpx + rare Pl + trace Ne + Gl + V
$Di_3Ab_{62}\ Ne_{35}$	17.5	675	moderate Pl + rare Cpx + Gl + V
$Di_{11}Ab_{57}Ne_{32}$	17	675	major Cpx + minor to moderate Pl + Gl + V
$Di_5\ Ab_{75}Ne_{20}$	15.5	675	minor Pl + trace Cpx + Gl + V
$Di_{10}Ab_{45}Ne_{45}$	16	700	moderate Ne + moderate Cpx + trace Pl + Gl + V
$Di_5Ab_{40}Ne_{55}$	18.25	700	moderate Pl + moderate Ne + trace Cpx + Gl + V
$Di_{7.5}Ab_{35}Ne_{57.5}$	9.50	700	trace Cpx + trace Ne
$Di_3Ab_{52}Ne_{45}$	21.5	665	major Ne + minor Cpx + minor Pl + Gl + V
$Di_3Ab_{52}Ne_{45}$	23.5	650	moderate Pl + trace Cpx+ Gl + V
$Di_8Ab_{85}Ne_7$	21	665	major Pl + minor Cpx + Gl + V
$Di_9Ab_{73.4}\ Ne_{17.6}$	20.5	665	major Pl + trace Cpx + V
$Di_3Ab_{44}Ne_{53}$	18.5	630	major Ne + major Cpx + rare Pl + Gl + V
$Di_0Ab_{50}Ne_{50}$	22	610	major Ne + moderate Pl + trace Gl + V
$Di_0Ab_{100}Ne_0$	2.25	675	minor Ab + Gl + V
$Di_0Ab_{100}Ne_0$	4	685	L + V

Terms such as "trace", "minor", "major" and "rare" refer to amounts of crystals in the run products. The bulk composition of the starting mixtures (column 1) is reported in weight %. The duration of the experiments is reported in hours.

primary phase-volumes of clinopyroxene, plagioclase and nepheline$_{ss}$ [*cf.* Fig. 4 with Fig. 4a of Schairer & Yoder (1960) and Fig. 4b of Edgar (1964)]. The phase assemblage at variable temperatures exhibits a very flat liquidus surface. Table 3 (anal. 1, 2) shows that about 14.1 to 14.3 wt.% of albite goes into the nepheline structure in solid solution at 1200°C. Edgar (1964) showed that 10 to 20% anorthite is incorporated in the albite structure. The X-ray-diffraction peaks 002, 310 and 211 of clinopyroxene crystallizing from the mixture $Di_3Ab_{62}Ne_{35}$ at 836°C occur, respectively, at 35.41°, 30.45° and 29.80° 2θ Cu$K\alpha$. The same reflections for pure diopside are observed at 35.38°, 30.42° and 29.78°, suggesting that the diopside appearing at 836°C and 2 kbar [$P(H_2O) = P(Total)$] is a solid solution. We assume that it contains Ca- and Mg-Tschermaks components. At 2 kbar, the amount of anorthite going into the structure of albite is 1.41 wt.% (anal. 7, Table 3). The reaction point ($Di_5Ab_{54.5}Ne_{40.5}$) at which clinopyroxene, plagioclase, nepheline and liquid are in equilibrium is shifted toward the nepheline-rich side as compared to Edgar's study (1964) of the diopside – nepheline – albite system at $P(H_2O) = P(Total) = 1$ kbar. The nepheline–albite "isobaric eutectic" composition changes from $Ne_{27}Ab_{73}$ at 1 kbar $P(H_2O)$ to $Ne_{49.5}Ab_{50.5}$ under $P(H_2O) = 2$ kbar. Jones & MacKenzie (1989) have shown that in the system nepheline – kalsilite – SiO_2, where anorthite (4 to 12 wt.%) is added, the nepheline–plagioclase boundary shifts toward more silica-undersaturated compositions. We observed that the increase in $P(H_2O)$ also drives the nepheline–plagioclase "isobaric eutectic" to the nepheline-rich side.

The system diopside – albite – nepheline at $P(H_2O) = P(Total) = 10$ kbar

The liquidus temperatures for nepheline and diopside at 10 kbar [$P(H_2O) = P(Total)$] are taken from Boettcher & Wyllie (1969) and Yoder (1965), respectively. Diopside melts congruently at 1265°C, and nepheline melts to a liquid of its own composition at 692°C. The present experimental results are summarized in Table 6 and Figure 5. This diagram is a projection from the H_2O apex onto the anhydrous diopside – albite – nepheline plane and shows the field boundaries, which limit the primary phases. The liquidus surface at 10 kbar [$P(H_2O) = P(Total)$] cuts the primary volumes of nepheline, clinopyroxene and plagioclase. The plagioclase crystallizing from bulk composition $Di_{10}Ab_{29}Ne_{61}$ at 1250°C contains about 1 wt.% An (anal. 6, Table 3) in its structure. This system can be treated as being ternary if one ignores the small amount of calcium entering the albite structure. The X-ray-diffraction studies of pyroxenes crystalling from the bulk composition $Di_{11}Ab_{57}Ne_{32}$ at 675°C and 10 kbar [$P(H_2O) = P(Total)$]

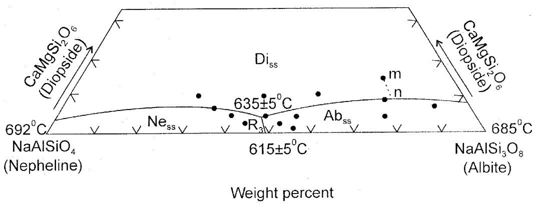

FIG. 5. Liquidus phase relations in the system diopside – albite – nepheline at 10 kbar [$P(H_2O = P(Total)$] and various temperatures.

TABLE 7. SHIFT IN THE COMPOSITION OF THE REACTION POINT IN THE SYSTEM DIOPSIDE – NEPHELINE – ALBITE

Pressure	Temperature	Composition	Source
1 atm	1118 ± 3°C	$Di_{15}Ab_{44}Ne_{41}$	Schairer & Yoder (1960)
1 kbar $P(H_2O)$	885 ± 5°C	$Di_5Ab_{66}Ne_{29}$	Edgar (1964)
2 kbar	820 ± 5°C	$Di_5Ab_{50.5}Ne_{49.5}$	Present study
10 kbar $P(H_2O) = P(total)$	635 ± 5°C	$Di_4Ab_{46.6}Ne_{49.4}$	Present study

show 002, 310 and 221 reflections at 35.395°, 30.518° and 29.985° 2θ Cu*K*α. The same reflections for pure diopside are observed at 35.38°, 30.42° and 29.78° 2θ Cu*K*α. This observation suggests that the diopside departs from the end-member composition.

The phase diagram demonstrates the expansion of the pyroxene phase-volume at the albite-rich end as well as at the nepheline-rich side. Figure 3 shows that in contrast to the field of pyroxene obtained at atmospheric pressure (Schairer & Yoder 1960; Fig. 4a), it is further enlarged at 1 (Edgar 1964; Fig. 4b) and 10 kbar (Fig. 5). At 10 kbar, the clinopyroxene field increases at the expense of albite and nepheline. This finding illustrates the fact that a silica-undersaturated liquid of composition at the reaction point (clinopyroxene + nepheline$_{ss}$ + albite$_{ss}$ + liquid) will be enriched in the clinopyroxene component at the expense of nepheline and plagioclase with increasing depth in a H_2O-rich environment. This conclusion is also supported by the experimental studies on the join nepheline–albite between 1 and 5 kbar [$P(H_2O) = P(Total)$] and will be discussed later. This relationship indicates the possibility of generating ultra-alkaline liquids under a gentle geothermal gradient and mostly beneath and within the continental lithosphere.

In contrast to the field of plagioclase at $P(H_2O) = P(Total) = 1$ kbar, its field $P(H_2O) = 10$ kbar is expanded (*cf.* Fig. 5 with Figs. 4a, b). The composition of the reaction point at various pressures and their corresponding temperatures are summarized below.

The data on diopside–nepheline join at 10 kbar [$P(H_2O) = P(Total)$] are discussed by Singh *et al.* (2000), who reported the assemblage Na-rich amphibole + clinopyroxene + nepheline + liquid; the pseudo-eutectic occurs at Di_5Ne_{95} (680°C). Along the nepheline–albite join, the isobaric eutectic shifts toward the nepheline-rich side with increasing pressure in the presence of H_2O. The results of previous investigators at various pressures and temperatures are given in Table 7. Boettcher & Wyllie (1969) presented a schematic diagram for the univariant curve Ne + Ab + V = L based on topological considerations. Their study shows that the gradient of temperature is very steep: from 1 to 2 kbar: 65°C per kbar, between 2 to 5 kbar: 35°C per kbar, in the range of 5 to 6 kbar: 27°C per kbar and it becomes nearly vertical between 6 and 10 kbar with a constant slope of 3.6°C per kbar (Fig. 6). Hence, for a phonolitic composition, the liquidus temperature in a hydrous regime will decrease with an increase in pressure. The "isobaric eutectic" compositions also should change considerably.

If one considers an arbitrary liquid composition at $Di_{16}Ab_{70}Ne_{14}$ (point "m", Fig. 5), the first phase to appear on cooling will be clinopyroxene, and with a fall in temperature, plagioclase appears, as the composition of the liquid reaches the diopside – albite$_{ss}$ – liquid univariant line at point "n". At the reaction point, nepheline will coprecipitate in addition to clinopyroxene and plagioclase in the liquid. Likewise, if a liquid of composition $Di_5Ab_{40}Ne_{55}$ lying on the nepheline$_{ss}$ + albite$_{ss}$ + L univariant curve crystallizes, nepheline and clinopyroxene will precipitate simultaneously; once the liquid reaches the reaction point, plagioclase also will appear as the third phase. With a decrease in temperature, clinopyroxene fractionates out, and the liquid moves toward a phonolite minimum. According to Morse (1980), the nepheline–albite eutectic corresponds to simplied phonolitic compositions and hence, the liquidus for a hydrous phonolitic magma at a depth of 33 km = 10 kbar can be taken to be 635 ± 5°C (Fig. 5). The assemblage corresponding to the reaction point can be ideally treated as a tephritic composition.

Petrological importance of the system diopside – albite – nepheline studied under 28 kbar and variable temperatures

Along the join diopside–nepheline studied under atmospheric pressure, forsterite$_{ss}$ and melilite appear in addition to diopside and nepheline, which gives rise to an assemblage similar to a olivine–melilite nephelinite. Olivine reacts out at 1138 ± 3°C, and the final assemblage comprises melilite, nepheline, diopside and liquid. If albite is added at atmospheric pressure, there is still a field of forsterite$_{ss}$, and an invariant point occurs. Forsterite$_{ss}$, nepheline$_{ss}$ and diopside$_{ss}$ are in equilibrium with liquid at this point, but forsterite$_{ss}$ subsequently reacts out and a nephelinitic liquid devoid of melilite is produced. Thus an olivine nephelinitic magma without melilite can be generated at shallow depth. As the join diopside–jadeite is stabilized at 28 kbar, it acts as a thermal barrier. Thus, from liquids of compositions lying in the undersaturated portion of the diopside–jadeite join within the diopside – nepheline – albite plane, the final assemblage corresponds to a "nephelinitic" liquid, which itself is a product of a melanephelinite. If the composition of the initial liquid lies on the silica-saturated side of the thermal barrier, the final product is represented by a "quartz tholeiite". The clinopyroxene crystallizing in the system diopside – albite – nepheline at 28 kbar is a solid solution of diopside and jadeite (Table 1). Such high-pressure nephelinites should be characterized by omphacitic pyroxene; but during the ascent of the magma, the jadeite content of the clinopyroxene should decrease.

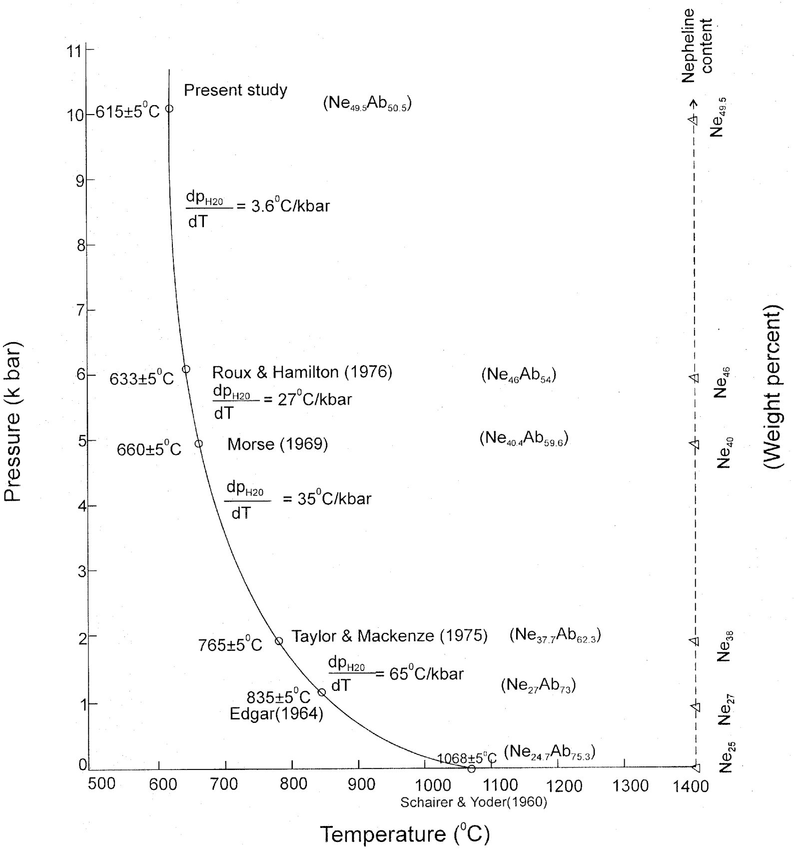

FIG. 6. Drop in liquidus temperatures for the nepheline–albite "isobaric eutectics" as a function of water vapor pressure and temperature (data from various sources as mentioned in the figure).

The normative compositions of liquids in the dry systems (Table 8) at 28 kbar correspond to simplified phonotephritic, tephriphonolitic and phonolitic compositions (Le Bas *et al.* 1986).

Petrogenetic implication of the diopside – albite – nepheline system at $P(H_2O) = P(Total) = 2$ and 10 kbar

Our experimental study of the system diopside – albite – nepheline – H_2O at 2 and 10 kbar was conducted to test whether the modal and normative compositions of nepheline-bearing trachytes, phonolites, tephrites, tephriphonolites and nephelinites have any relationship with the invariant point determined under variable P–T conditions. If the bulk compositions of these rocks are plotted in terms of clinopyroxene – feldspathoid – sodium-rich alkali feldspar, one finds that the maximum cluster occurs in and around the 10 kbar invariant point. Edgar (1964) plotted the normative compositions of 120 plutonic rocks containing 80% or more normative alkali pyroxene, nepheline and alkali feldspar (Fig. 7). Points R_1 and R_2 correspond to the reaction points, where nepheline$_{ss}$, albite$_{ss}$ and clinopyroxene are in equilibrium. The curves marked A–R_1 and A–R_2 correspond to the phase boundaries of clinopyroxene and albite$_{ss}$ at 1 and 2 kbar, respectively. Both the 1 and 2 kbar reaction points lie in the shaded area, where the bulk compositions of many syenites plot. The 1 and 2 kbar reaction points, however, do not lie in the maximum density area, presumably because in the experimental system K and Fe are missing.

Figure 8 shows a plot of bulk composition of many phonolites, nephelinites, urtites and trachytes from all over the world on the 10 kbar isobaric diagram. We note that the majority of bulk compositions of phonolites (shown as triangles within the field marked "C") occur around the 10 kbar reaction point, and some plot along the line Y–R_3 or Z–R_3 corresponding to the clinopyroxene–nepheline$_{ss}$ or clinopyroxene–albite$_{ss}$ phase

TABLE 8. COMPOSITIONS OF FOUR REPRESENTATIVE LIQUIDS (QUENCHED TO GLASS) IN THE SYSTEM DIOPSIDE – NEPHELINE – ALBITE

Composition		Na_2O	CaO	MgO	Al_2O_3	SiO_2	Total
$Di_{40}Ab_{50}Ne_{10}$	Gl	8.60	10.50	7.13	13.15	60.61	99.99
	SM	8.09	10.36	7.94	13.31	60.80	100.50
$Di_0Ab_{50}Ne_{50}$	Gl	12.21	0.00	0.00	30.26	57.53	100.00
	SM	16.82	0.00	0.00	27.67	55.52	100.01
$Di_5Ab_{75}Ne_{20}$	Gl	10.65	1.27	1.27	21.88	64.99	100.06
	SM	13.23	1.30	0.93	21.76	62.79	100.01
$Di_5Ab_{55}Ne_{40}$	Gl	13.70	1.14	1.17	27.10	56.59	100.00
	SM	15.23	1.30	0.93	25.05	57.50	100.01

Gl: glass compositions from runs at 28 kbar and 1450 ± 5°C; note that the glass is observed in the run products. Each composition of Gl is the average result of two analyses. The bulk composition of the starting material (SM) in terms of the three components is given in the first column in wt.%.

boundaries. In Figure 8, the squares denote trachyte (marked by area "B"). The bulk compositions of trachyte plot along diopside–albite join and in the vicinity of the pseudoeutectic obtained at 10 kbar. The bulk composition of nephelinites plot in the area marked "A", close to the diopside–nepheline join, near the diopside end and containing as much as 25% normative albite. Compositions of pyroxene-poor nepheline-rich urtites plot in the area marked "D". On the basis of phase-equilibrium relations, we expect that nephelinitic rocks should crystallize first. Then the liquid should move along a path joining the nephelinitic composition and clinopyroxene and then proceed to the line Y–R_3. Later, with further crystallization, the liquid composition moves toward the reaction point "R_3", and a phonolitic magma is derived. Thus, a phonolite is obtained either from a nephelinitic or a trachytic magma. Some of these phonolites contain xenoliths of lherzolites [Jos Plateau, Nigeria (Nixon 1987); Klinghardt, Namibia (Lock & Marsh 1981); Auckland Island, New Zealand (Nixon 1987)]. That their bulk compositions plot around 10 kbar reaction point is consistent with the genesis of many phonolitic rocks at depth.

Figure 8 indicates that a phonolitic magma can be derived from either a trachytic magma (note the plot of bulk compositions along the line Z–R_3) or a nephelinitic magma. Wright (1963) and Saggerson & Williams (1964) suggested that nephelinites or melanephelinites are parental to phonolites. Nash *et al.* (1969) pointed out the association of nephelinitic and phonolitic rocks, but in their case study of Mount Suswa, Kenya, they considered an alkaline trachytic liquid as the parental magma for the phonolites. In general, they believed that the magmas of Mount Suswa could have been generated by partial or total fusion of silica-undersaturated syenitic plutonic parent, because xenoliths of syenite are observed in the lavas of Mount Suswa. In the present study, we observed that the five-phase point (clino-

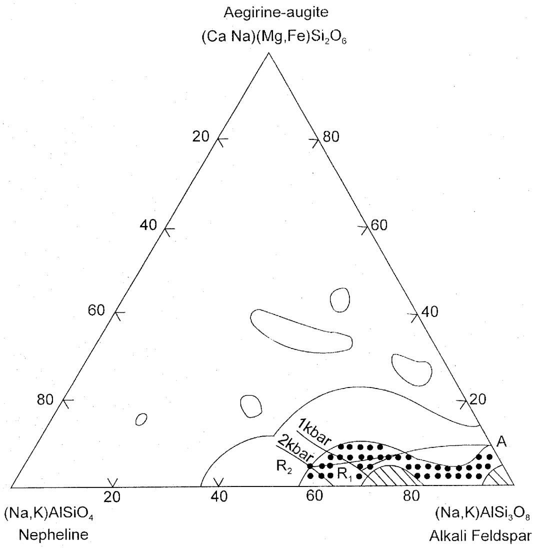

FIG. 7. Density distribution diagram for 129 plutonic rocks containing 80% or more normative (diopside + "acmite") – nepheline – (albite + orthoclase). The dotted area represents the locus of more than 75% of all compositions. The shaded area contains 15% of all the compositions, and remaining 10% is represented by unmarked areas. The phase relations obtained at 1 kbar [P(H_2O) = P(Total), after Edgar 1964] and 2 kbar [P(H_2O) = P(Total), present study] are superimposed onto this diagram.

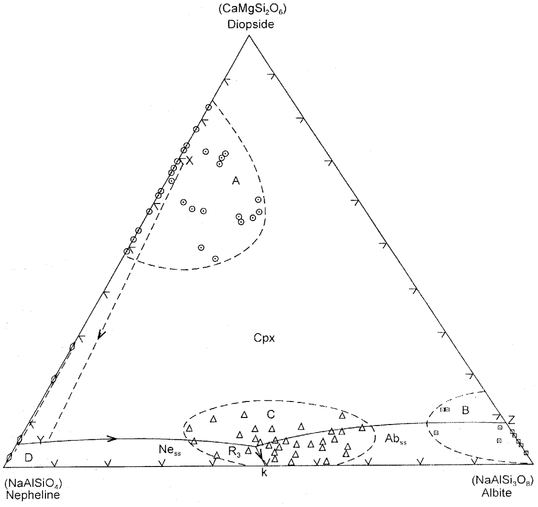

FIG. 8. Normative compositions of phonolites (triangles), nephelinites (circles), urtites (diamonds) and trachytes (squares) from various localities in the world plotted onto the 10 kbar H_2O-saturated section.

pyroxene + nepheline$_{ss}$ + albite$_{ss}$ + L + V) obtained at 2 kbar [$P(H_2O) = P(Total)$] plots in the "nepheline syenite" field. Alkali feldspar is a solid solution of $NaAlSi_3O_8$ and $KAlSi_3O_8$, and in absence of the latter component, compositions of many trachytes should not lie in the diopside – nepheline – albite plane. The "nepheline syenites" or "trachytes" discussed here refer to simplified varieties. In the 10 kbar [$P(H_2O) = P(Total)$] isobaric section, the phonolite compositions cluster around the reaction point.

Our experimental study of the system diopside – albite – nepheline indicates that from a liquid of composition "X" (Fig. 8), a melanephelinite can crystallize first, when the liquid composition reaches the univariant curve defined by nepheline + clinopyroxene + liquid (Y–R_3). Because the bulk composition ($Di_{70}Ab_2Ne_{28}$) is relatively closer to the diopside end-member, the proportion of diopside in the univariant assemblage should be greater than that of nepheline, and the univariant assemblage should be similar to a "simplified melanephelinite" rock. In the course of crystallization, if diopside is fractionated out, then the assemblage should be similar to a nephelinite. As the liquid composition reaches the invariant point "R_3", the assemblage should correspond to diopside + nepheline + sodic feldspar + liquid + vapor. In the absence of significant amounts of anorthite, the invariant assemblage cannot be strictly referred to as tephrite. The addition of 15–20% modal $KAlSi_3O_8$ should not significantly change the course of crystallization of the liquid. If a small amount of anorthite is added to the system, the univariant assemblage (Z–R_3) will correspond to a liquid typical of highly fractionated alkali basalt series, *i.e.*, a liquid similar to a mugearitic composition. Although the temperature and composition of the invariant point should change, the topology of the phase diagram is expected to be similar.

Role of H_2O in the system diopside – albite – nepheline under variable pressures

In comparison to the reaction point R, determined by Schairer & Yoder (1960) in the system diopside – albite – nepheline, the analogous point R_1 established at $P(H_2O) = P(Total) = 1$ kbar moves toward the albite-rich side (Edgar 1964). In our study, we note, however, that at 2 and 10 kbar, as the solubility of H_2O in the liquid increases, the "isobaric invariant points" (R_2 and R_3) shift systematically toward nepheline. This shift may be due to dissolution of larger amount of nepheline in the fluid phase, compared to albite at higher $P(H_2O) = P(Total)$. The shift in composition of the reaction point in the system diopside – albite – nepheline is given in Table 7. Yoder (1958) studied the systems albite–H_2O and nepheline–H_2O. He observed an important drop in the temperature of melting of nepheline relative to albite with increasing H_2O pressure. These observations confirm that dissolution of nepheline is indeed greater than that of albite in the fluid. A shift in the isobaric "invariant point" (R_1, Fig. 4b) of Edgar (1964) toward albite, therefore, does not seem to be in agreement with our observation and that of Yoder. The system diopside – albite – nepheline, therefore, needs to be restudied at $P(H_2O) = P(Total) = 1$ kbar.

Kushiro (1969) studied the system forsterite – diopside – SiO_2 at one atmosphere and under $P(H_2O) = P(Total) = 20$ kbar. Compared to its position determined at one atmospheric pressure, the eutectic point he established at $P(H_2O) = P(Total) = 20$ kbar is located closer to the SiO_2-rich end. The studies of Tuttle & Bowen (1958), Luth *et al.* (1964) and Luth (1976) on the albite – orthoclase – SiO_2 system at variable pressures up to 10 kbar, however, show that with increasing pressure (in presence of excess H_2O), the minimum or eutectic point moves away from the SiO_2-rich side. When anorthite is added as a component to the albite – orthoclase – SiO_2 system (von Platen 1965), the minimum points under $P(H_2O) = P(Total) = 2$ kbar shift away from the albite end toward the K-feldspar – quartz join. The above description suggests that the role of H_2O in shifting the minimum or eutectic points toward silica-saturated or undersaturated side is rather complex.

Taylor & MacKenzie (1975) studied the role of H_2O in the nepheline–albite system and observed that the "isobaric eutectic" gradually shifts toward the nepheline-rich side away from the SiO_2 end as pressure is increased from 1 atmosphere to 1 to 2 kbar. In our case, the system diopside – albite –nepheline at $P(H_2O) = P(total) = 1$, 2 and 10 kbar, the "isobaric eutectic" along the nepheline–albite join also shifts toward the nepheline end.

As the above discussion clearly demonstrates, the genesis of phonolites can be expressed in terms of a simple model system clinopyroxene – alkali feldspar – nepheline. The present experimental study at 10 and 28 kbar (with or without H_2O), therefore, helps one to understand the genesis of phonolites and related rocks, in cases where extensive crystal fractionation is believed to have taken place. According to Lippard (1973), trace-element data indicate that phonolites owe their origin to fractionation under subcrustal conditions. The phonolites also plot near the reaction point or in the vicinity of the diopside–albite or diopside–nepheline phase boundaries.

Figure 9 (LeBas 1987) shows a generalized trend from melanephelinite through nephelinite to phonolite, as observed in case of the rocks from eastern Uganda (Tyler & King 1967) and western Kenya (Le Bas 1977). The present study supports the trend established by Le Bas (1987). Barker *et al.* (1987) studied the nepheline-bearing rocks from the alkali igneous provinces of Kenya and northern Tanzania, both of which are associated with the African Rift Valley. The spatial distribution of melanephelinite, nephelinite, nepheline-bearing phonolite, trachyte and alkali basalt from the Kenyan alkali petrographic province can be predicted from the phase relations presented here. If 15–20%

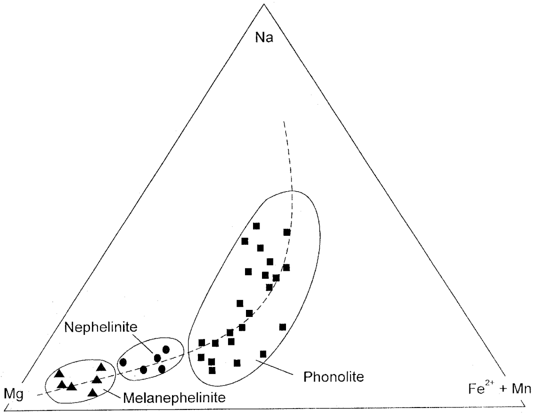

FIG. 9. Fractionation path from melanephelinite → nephelinite → phonolite plotted in terms of Na – (Fe^{2+} + Mn) – Mg (wt%) (after LeBas 1987). The arrow indicates fractionation trend of liquids as established by LeBas (1987).

alkali feldspar is added, then from a trachytic magma, a phonolitic liquid can be obtained. Downes (1987) also observed the presence of tephritic, phonolitic, and nephelinitic rocks in close proximity in the Massif Central region of France.

Strong (1972) carried out a detailed petrological study of the alkaline rocks of the Island of Moheli, western Indian Ocean, where alkali basalt and melanephelinite occur with small amounts of nephelinite, trachyte, and phonolite. From the isotopic signatures, Strong (1972) suggested an apparent differentiation from alkali basalt through melanephelinite and trachyte to phonolite. The present study does not suggest such a fractionation scheme. Rather, two trends are possible: 1) melanephelinite → nephelinite → phonolite, and 2) alkali basalt → trachyte → phonolite.

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REFERENCES

BARKER, D.S., MITCHELL, R.H. & MCKAY, D. (1987): Late Cretaceous nephelinite to phonolite magmatism in the Balcones province, Texas. *In* Mantle Metasomatism and Alkaline Magmatism (E.M. Morris & J.D. Pasteris, eds.). *Geol. Soc. Am., Spec. Pap.* **215**, 293-304.

BELL, P.M. & DAVIS, B.T.C. (1969): Investigation of a solvus in the system jadeite–diopside. *Carnegie Inst. Wash., Yearbook* **68**, 239-241.

________ & ROSEBOOM, E.H. (1969): Melting relationships of jadeite and albite to 45 kilobars with comments on melting diagrams of binary systems at high pressures. *Mineral Soc. Am., Spec. Pap.* **2**, 151-161.

BOETTCHER, A.L., BURNHAM, C.W., WINDOM, K.E. & BOHLEN, S.R. (1982): Liquids, glasses and the melting of silicates to high pressures. *J. Geol.* **90**, 127-138.

________ & WYLLIE, P.J. (1969): Phase relationships in the system $NaAlSiO_4$–SiO_2–H_2O to 35 kbar pressure. *Am. J. Sci.* **267**, 875-969.

BOHLEN, S.R., ESSENE E.J. & BOETTCHER, A.L. (1980): Reinvestigation and application of olivine – quartz – orthopyroxene boundary. *Earth Planet. Sci. Lett.* **47**, 1-10.

BOSE, K. & GANGULY, J. (1995): Quartz–coesite transition revisited: reversed experimental determination at 500–1200°C and retrieved thermochemical properties. *Am. Mineral.* **80**, 231-238.

BOWEN, N.L. (1915): The crystallization of haplobasaltic, haplodioritic, and related magmas. *Am. J. Sci.* **190**, 161-185.

________ (1928): *The Evolution of the Igneous Rocks*. Princeton Univ. Press, Princeton, New Jersey.

________ & SCHAIRER, J.F. (1935): The system MgO–FeO–SiO_2. *Am. J. Sci.* **229**, 151-217.

BOYD, F.R. & ENGLAND, J.L. (1960): Apparatus for phase-equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750°C. *J. Geophys. Res.* **65**, 741-748.

CURTIS, W.L. & GITTINS, J. (1979): Aluminous and titaniferous clinopyroxenes from regionally metamorphosed agpaitic rocks in central Labrador. *J. Petrol.* **20**, 165-186.

DOWNES, H. (1987): Tertiary and Quaternary volcanism in the Massif Central, France. *In* Alkaline Igneous Rocks (J.G. Fitton & B.G.J. Upton, eds.). *Geol. Soc., Spec. Publ.* **30**, 517-530.

EDGAR, A.D. (1964): Phase equilibrium relations in the system nepheline – albite – water at 1,000 kg/cm^2. *J. Geol.* **72**, 448-460.

GUPTA, A.K., GREEN, D.H. & TAYLOR, W.R. (1987): The liquidus surface of the system forsterite – nepheline – silica at 28 kb. *Am. J. Sci.* **287**, 560-565.

HALL, H.T. (1966): Hydraulic ram design for modern high pressure devices. *Rev. Sci. Instrum.* **37**, 568-571.

HAMILTON, D.L. & MACKENZIE, W.S. (1965): Phase equilibrium studies in the system $NaAlSiO_4$ (nepheline) – $KAlSiO_4$ (kalsilite) – SiO_2 – H_2O. *Mineral. Mag.* **34**, 214-231.

HOLLAND, T.J.B. (1983): The experimental determination of activities in disordered and short-range order jadeite pyroxene. *Contrib. Mineral. Petrol.* **82**, 214-220.

ISHBULATOV, R.A. & KOSYAKOV, A.V. (1990): Problems of pressure estimation in high temperature experiments using solid media apparatus with particular reference to piston–cylinder and anvil-with-hole apparatus (Part I). *In* Special Issue on Experimental Petrology (A.K. Gupta, ed.). *Proc. Indian Acad. Sci.* (*Earth Planet. Sci.*) **99**, 119-132.

JONES, R.H. & MACKENZIE, W.S. (1989): Liquidus phase relationships in the system $CaAl_2Si_2O_8$ – $NaAlSi_3O_8$ – $KAlSi_3O_8$ – $NaAlSiO_4$ – $KAlSiO_4$ at $P(H_2O)$ = 5 kbar. *Contrib. Mineral. Petrol.* **101**, 78-92.

KUSHIRO, I. (1965): Clinopyroxene solid solutions at high pressures. *Carnegie Inst. Wash., Yearbook* **64**, 112-115.

________ (1969): Clinopyroxene solid solutions formed by reactions between diopside and plagioclase at high pressures. *Mineral. Soc. Am., Spec. Pap.* **2**, 179-191.

LE BAS, M.J. (1977): *Carbonatite–Nephelinite Volcanism*. John Wiley & Sons, New York, N.Y.

________ (1987): Nephelinites and carbonatites. *In* Alkaline Igneous Rocks (J.G. Fitton & B.G.J. Upton, eds). *Geol. Soc., Spec. Publ.* **30**, 53-83.

________, LE MAITRE, R.W., STRECKEISEN, A. & ZANETTIN, B. (1986): A chemical classification of volcanic rocks based on the total alkali–silica diagram. *J. Petrol.* **27**, 745-750.

LIPPARD, S.J. (1973): The petrology of phonolites from the Kenya Rift. *Lithos* **6**, 217-234.

LOCK, B.E. & MARSH, J.S. (1981): Tertiary phonolite volcanism in the Klinghardt Mountains of South West Africa/Namibia. *Trans. Geol. Soc. S. Afr.* **84**, 1-6.

LUTH, W.C. (1976): Resorption of silicate minerals. *In* The Alkaline Rocks (H. Sørensen, ed.). John Wiley & Sons, London, U.K. (500-515).

________, JAHNS, R.H. & TUTTLE, O.F. (1964): The granite at pressures of 4 to 10 kilobars. *J. Geophys. Res.* **69**, 759-773.

MIRWALD, P.W. & MASSONE, H.J. (1980): The low–high quartz and quartz–coesite transition to 40 kbar between 600° and 1600°C and some reconnaissance data of the effect of $NaAlO_2$ component on the low quartz–coesite transition. *J. Geophys. Res.* **85**, 6983-6990.

MORSE, S.A. (1969): Syenites. *Carnegie Inst. Wash., Yearbook* **69**, 112-120.

________ (1980): *Basalt and Phase Diagrams*. Springer-Verlag, New York, N.Y.

NASH, W.P. CARMICHAEL, I.S.E. & JOHNSON, R.W. (1969): The mineralogy and petrology of Mount Suswa, Kenya. *J. Petrol.* **10**, 409-439.

NEWTON, R.C. & KENNEDY, G.C. (1968): Jadeite, analcite, nepheline, and albite at high temperatures and pressures. *Am. J. Sci*. **266**, 728-735.

NIXON, P.H., ed. (1987): *Mantle Xenoliths*. John Wiley & Sons, Chichester, U.K.

ROBERTSON, E.C., BIRCH, F. & MACDONALD, G.J.F. (1957): Experimental determination of jadeite stability relations at 25000 bars. *Am. J. Sci.* **255**, 115-137.

ROBINSON, P. (1982): The composition space of terrestrial pyroxenes – internal and external limits. *In* Pyroxenes (C.T. Prewitt, ed.). *Rev. Mineral.* **7**, 419-494.

ROUX, J. & HAMILTON, D.L. (1976): Primary igneous analcite – an experimental study. *J. Petrol.* **17**, 244-257.

SAGGERSON, E.P. & WILLIAMS, L.A.J. (1964): Ngurumanite from Southern Kenya and its bearing on the origin of rocks in the northern Tanganyika alkaline district. *J. Petrol.* **5**, 40-81.

SCHAIRER, J.F. (1950): The alkali-feldspar join in the system $NaAlSiO_4$ – $KAlSiO_4$ – SiO_2. *J. Geol.* **58**, 512-517.

________ & BOWEN, N.L. (1956): The system Na_2O–Al_2O_3–SiO_2 . *Am. J. Sci.* **254**, 129-195.

________, YAGI, K. & YODER, H.S., JR. (1962): The system nepheline–diopside. *Carnegie Inst. Wash., Yearbook* **61**, 96-98.

________ & YODER, H.S., JR. (1960): The nature of residual liquids from crystallization with data on the system nepheline – diopside – silica. *Am. J. Sci.* **258A**, 273-283.

SINGH, P., ARIMA, M. & GUPTA, A.K. (2000): Phase equilibrium constraints on the petrogenesis of nephelinites with reference to the system diopside–nepheline under variable P–T conditions in the presence or absence of water. *J. Mineral. Petrol. Sci.* (in press).

SMYTH, J.R. (1980): Cation vacancies and the crystal chemistry of breakdown reactions in kimberlitic omphacites. *Am. Mineral.* **65**, 1185-1191.

STRONG, D.F. (1972): Petrology of the Island of Moheli, western Indian Ocean. *Geol. Soc. Am., Bull.* **83**, 389-406.

TAYLOR, D. & MACKENZIE, W.S. (1975): A contribution to the pseudoleucite problems. *Contrib. Mineral. Petrol.* **49**, 321-333.

TUTTLE, O.F. & BOWEN, N.L. (1958): Origin of granite in the system $NaAlSi_3O_8 – KAlSi_3O_8 – SiO_2 – H_2O$. *Geol. Soc. Am., Mem.* **74**.

TYLER, R.C. & KING, B.C. (1967): The pyroxenes of the alkaline igneous complexes of eastern Uganda. *Mineral. Mag.* **36**, 5-21.

VON PLATEN, H. (1965): Experimental anatexis and genesis of migmatites. *In* Controls of Metamorphism (W.S. Pitcher & G.W. Flinn, eds). John Wiley & Sons, New York, N.Y. (203-218).

WHITE, A.J.R., CHAPPELL, B.W. & JAKE_, P. (1972): Coexisting clinopyroxene, garnet, and amphibole from an "eclogite", Kakanui, New Zealand. *Contrib. Mineral. Petrol.* **34**, 185-191.

WINDOM, K.E. & BOETTCHER, A. (1981): Phase relations for the joins jadeite–enstatite and jadeite–forsterite at 28 kb and their bearing on basalt genesis. *Am. J. Sci.* **281**, 335-351.

WOOLLEY, A.R. & JONES, G.C. (1987): The petrochemistry of the northern part of the Chilwa alkaline province, Malawi. *In* Alkaline Igneous Rocks (J.G. Fitton & B.G.J. Upton, eds.). *Geol. Soc., Spec. Publ.* **30**, 335-355.

WRIGHT, J.B. (1963): A note on possible differentiation trends in Tertiary to Recent lavas of Kenya. *Geol. Mag.* **100**, 164-180.

YAGI, T., AKAOGI, M., SHIMOMURA, O., TOSHIHIRO, S. & AKIMOTO, S. (1987): In situ observation of the olivine spinel phase transformation in Fe_2SiO_4 using synchrotron radiation. *J. Geophys. Res.* **92**, 6207-6213.

YODER, H.S., JR. (1958): Effect of water on the melting of silicates. *Carnegie Inst. Wash., Yearbook* **57**, 189-191.

________ (1965): Diopside – anorthite – water at five and ten kbars and its bearing on explosive volcanism. *Carnegie Inst. Wash., Yearbook* **64**, 82-89.

________ & KUSHIRO, I. (1972): Composition of residual liquids in the nepheline–diopside system. *Carnegie Inst. Wash., Yearbook* **71**, 413-416.

________ & TILLEY, C.E. (1962): Origin of basalt magma: an experimental study of natural and synthetic rock systems. *J. Petrol.* **3**, 342-532.

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