

Preliminary phase equilibria of the nepheline–diopside system under variable pressures (up to 28 kb) and temperatures

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Abstract. The nepheline–diopside join defines the ultra-alkaline portion of the basalt tetrahedron and the bulk composition of nephelinitic rocks lie in this join. Schairer and others established that under atmospheric pressure, the join cuts through the primary phase volumes of olivine_{ss}, carnegieite_{ss} and nepheline_{ss}. Melilite coexists with nepheline_{ss}, olivine_{ss} and diopside_{ss} below $1160 \pm 10^\circ\text{C}$ and olivine reacts out at low temperature.

Experimental studies on seven compositions show the presence of a pseudoeutectic at $\text{Ne}_{70}\text{Di}_{30}$ and 1420°C , where diopside_{ss}, nepheline_{ss} and liquid are in equilibrium. Olivine and melilite do not appear in the system and the assemblage below $1225 \pm 20^\circ\text{C}$ is diopside_{ss} + nepheline_{ss}.

Four compositions studied at 1000°C show the appearance of the assemblage diopside_{ss} + nepheline_{ss} + melilite at 15 kb, whereas diopside_{ss} and nepheline_{ss} are the stable phases at 20 and 25 kb. The appearance of melilite is therefore restricted to a pressure of 18 ± 3 kb. Diopside_{ss} and nepheline_{ss} coexist without olivine and melilite in albite–nepheline–diopside and sanidine–nepheline–diopside system. However, this study shows that feldspar-free nephelinitic rocks, which are devoid of melilite, may have crystallized under mantle conditions, whereas their melilite-bearing counterparts equilibrated at a shallower depth within the crust.

Keywords. Nepheline; diopside; phase equilibria; melilite.

1. Introduction

The join nepheline–diopside defines the ultra-alkaline portion of the basalt tetrahedron of Yoder and Tilley (1962). This join is particularly important as it cuts through the primary phase volumes of nepheline_{ss}, carnegieite_{ss}, forsterite_{ss} and diopside_{ss}. Melilite appears as a subliquidus phase at a temperature of $1200 \pm 15^\circ\text{C}$ (Bowen 1928, Schairer *et al* 1962). Olivine subsequently reacts out and the subsolidus assemblage comprises nepheline_{ss} + melilite + diopside_{ss}. An experimental study of this join at variable temperatures in atmospheric pressure by these workers explain the ubiquitous appearance of melilite in many nepheline- and pyroxene-bearing volcanic rocks all over the world (Le Bas 1977, Spencer 1969, Duda and Schminke 1978).

It has been noted, however, that there are olivine- and melilite-free alkalic rocks containing both nepheline and augite (Le Bas 1977). The diopside–nepheline system was studied at 28 kb to see if the appearance of melilite and olivine is eliminated at high pressure. This assumption is prompted by the fact that akermanite is stable only at low pressure (Yoder 1973). Most experiments have been carried out at 28 kb as this particular pressure is close to the top of the asthenosphere (Green and Liebermann 1976).

2. Experimental technique

A 200-ton cubic press was used for the investigation. Experimental studies of the system with a piston-cylinder apparatus (Boyd and England type) is now in progress.

The cubic press has six tungsten carbide anvils with equal square faces and 12.5 mm long edges. Anvils move synchronously towards the centre by hydraulic rams and press the sample in the form of a cube.

The pressure was calibrated at room temperature with respect to the phase transitions of Bi (I–II) at 25.4 kb and Yb (fcc–bcc) at 39 kb (figures 1a and b).

The reaction cells were made of pyrophyllite and the temperature was measured with a Pt-Pt₉₀Rh₁₀ thermocouple placed at the centre of the reaction zone of a pyrophyllite cell through a hole. A digital multimeter was used to measure the e.m.f. generated across the thermocouple junction. The temperature gradient within the cube was measured with three thermocouples, one at the centre, one at the top and

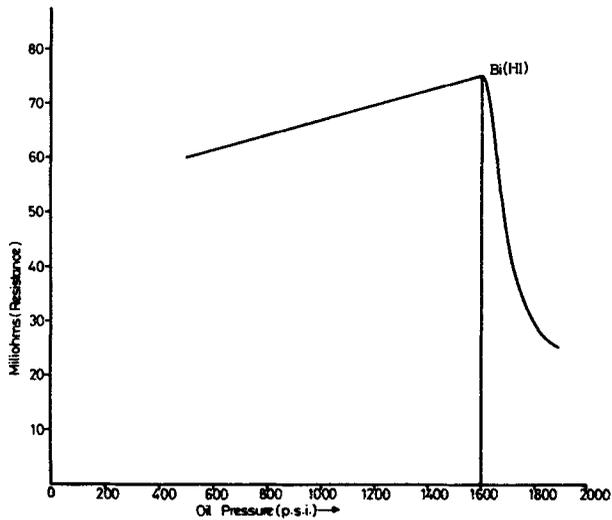


Figure 1a. Pressure calibration with respect to phase transformation of Bi(I–II).

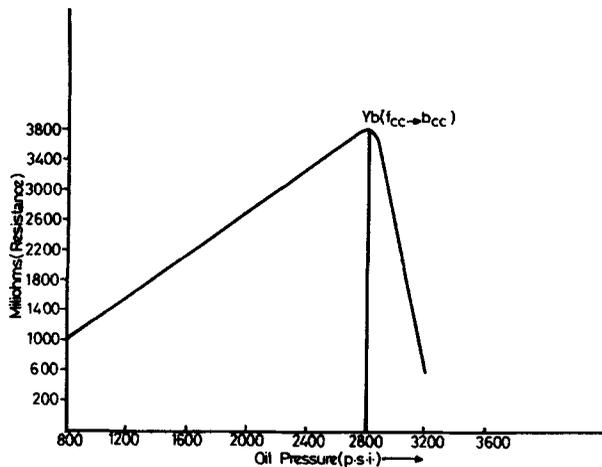


Figure 1b. Pressure calibration with respect to phase transformation of Yb(fcc – bcc).

the other at the side of the cube. It was noted that with respect to the centre, the temperature was lower by 30°C at the top, and it was lower by 20°C at the sides. Care was taken to place the sample exactly at the centre so that experiments could be performed at the hot spot.

The following seven compositions were prepared to study the join (i) $\text{Ne}_{80}\text{Di}_{20}$ ($N_{\text{gl}}:1.533$), (ii) $\text{Ne}_{70}\text{Di}_{30}$ ($N_{\text{gl}}:1.535$), (iii) $\text{Ne}_{60}\text{Di}_{40}$ ($N_{\text{gl}}:1.541$), (iv) $\text{Ne}_{50}\text{Di}_{50}$ ($N_{\text{gl}}:1.555$), (v) $\text{Ne}_{40}\text{Di}_{60}$ ($N_{\text{gl}}:1.565$), (vi) $\text{Ne}_{30}\text{Di}_{70}$ ($N_{\text{gl}}:1.575$) and (vii) $\text{Ne}_{20}\text{Di}_{80}$ ($N_{\text{gl}}:1.581$). The refractive indices of the glasses are given in brackets.

As a source of silica, pure quartz crystals collected from Matheran, Maharashtra, were used. These were crushed uniformly to about 200 mesh. Fine silica powder was treated with the dilute HCl for a few days. The material were thoroughly washed with distilled water and dried in an oven. Gravimetric analysis shows that dried silica contains 99.8% SiO_2 and the remainder is constituted of various oxides.

High purity reagent grade Al_2O_3 , CaCO_3 (Sarabhai M Chemicals Baroda), Na_2CO_3 (Glaxo Laboratories) and MgO (LOBA Chemico Indoaustranal) were used as a source of alumina, calcium oxide, sodium disilicate and magnesia. Sodium disilicate was prepared by the same method as suggested by Bowen and Schairer (1938). Before preparing the starting material the chemicals were preserved in an oven at 100°C for 2–3 hours. MgO and Al_2O_3 were kept in alumina boats which were heated at 1000°C for 24 hours.

The required quantity of chemicals was mixed in stoichiometric proportion and ground in an agate mortar with acetone for an hour. The powdered material were then fused to glasses at 1440°C, the refractive indices of which were determined under microscope to check the homogeneity of the glasses. The glasses were crushed to fine powder and thereafter crystallized at 700–800°C. The samples were kept in the furnace till complete crystallization was achieved. The phases were identified using a petrological microscope or by the X-ray diffraction technique using CuK_α radiations.

3. Crystalline phases

Nepheline_{ss} forms prismatic, low-birefringent crystals near the liquidus. It was identified by its reflections (002), (201) and (210); others are masked by reflection of diopside_{ss}.

Diopside has a prismatic form near the liquidus. The $Z\Lambda C$ varies from 38 to 40° and is easily recognized by its reflections at (021), (220) and (22 $\bar{1}$). Other reflections are overlapped by those of nepheline.

Melilite appears as an important phase in the runs at 15 kb and was identified by its reflections (110), (210) and (211). Microprobe studies are in progress to determine the extent of solid solution of jadeite in clinopyroxene and $\text{NaCaAlSi}_2\text{O}_7$ in melilite.

In the case of the composition $\text{Ne}_{80}\text{Di}_{20}$ metastable octahedral spinel and rounded crystals of corundum appeared due to loss of alkali.

4. Results and discussion

Altogether 37 runs were made at different pressures and temperatures of which 26 runs were performed at 28 kb and 11 at 25, 20 and 15 kb and 1000°C.

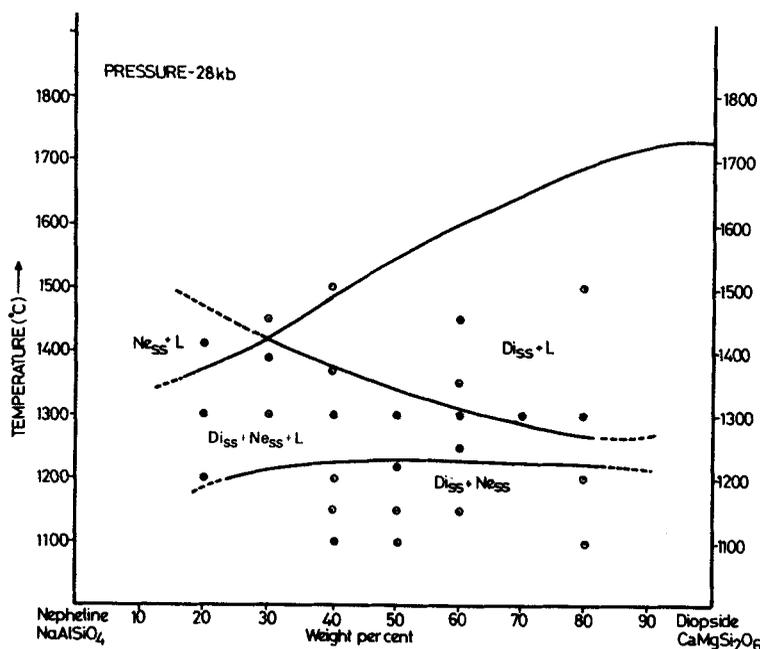


Figure 2. Phase relation in the system diopside-nepheline at variable temperatures under 28 kb.

The results of the experimental runs at 28 kb are summarized in figure 2 and table 1. The most interesting aspect of the study is the complete disappearance of melilite and olivine in this join under high pressure (figure 2). Because of the possible inclusion of alumina in diopside_{ss} and nepheline_{ss}, and the presence of a liquid phase below the appearance of diopside_{ss} the join should be termed as pseudobinary. X-ray studies of pyroxenes show that the reflection at 29.85° ($22\bar{1}$) shifts towards 30.59° ($\bar{2}21$) and it may include minor amounts of jadeite in diopside_{ss}. The pseudoeutectic of the system occurs at $Ne_{70}Di_{30}$ and $1420^\circ C$.

The melting temperature of diopside at 28 kb was taken from Williams and Kennedy (1969).

Spinel appears as a phase in 3 runs (table 1). As the glass was made at $1440^\circ C$, appearance of spinel may be related to the loss of Na_2O in the original starting material, hence spinel is considered to be a metastable phase, which does not appear in any other runs. Experiments in sealed capsules with gel and sintered material for this particular mixture are in progress.

The present study at 15, 20 and 25 kb are summarized in table 2, which shows the appearance of melilite at 15 kb. Yoder and Kushiro (1972) made microprobe analyses of melilite from a composition $Ne_{50}Di_{50}$ that was crystallized at $1125^\circ C$ for 10 days at one atmospheric pressure. According to their calculation, the composition of the melilite corresponds to $Ak_{61}Sm_{38}Gh_1$. Reference to the experimental study of pure akermanite by Kushiro (1964), suggests that it is stable at $1480^\circ C$ and 14 kb. Kushiro states that in the presence of sodium melilite the stability of akermanite-rich melilite increases. Therefore, the established stability of melilite to 18 ± 3 kb seems reasonable. The presence of melilite and olivine in the diopside-nepheline system was

Table 1. Experimental results of system diopside-nepheline at 28 kb.

Composition	T(°C)	P(kb)	Results
Ne ₈₀ Di ₂₀ (1)	1410 ± 20°C	28	Sp* + Ne + Gl
Ne ₈₀ Di ₂₀ (2)	1300°C	28	Ne + Sp* + Di + Cor* + Gl
Ne ₈₀ Di ₂₀ (3)	1200°C	28	Ne + Sp* + Di + Cor* + Gl
Ne ₇₀ Di ₃₀ (1)	1450°C	28	Glass
Ne ₇₀ Di ₃₀ (2)	1390 ± 10°C	28	Di + Ne + Gl
Ne ₇₀ Di ₃₀ (3)	1300°C	28	Di + Ne + Gl
Ne ₆₀ Di ₄₀ (1)	1500 ± 10°C	28	Glass
Ne ₆₀ Di ₄₀ (2)	1370 ± 10°C	28	Di + Ne + Gl
Ne ₆₀ Di ₄₀ (3)	1300 ± 0°C	28	Ne + Di + Gl
Ne ₆₀ Di ₄₀ (4)	1200 ± 0°C	28	Ne + Di
Ne ₆₀ Di ₄₀ (5)	1150 ± 10°C	28	Ne + Di
Ne ₆₀ Di ₄₀ (6)	1100 ± 10°C	28	Ne + Di
Ne ₅₀ Di ₅₀ (1)	1300°C ± 16	28	Ne + Di + Gl
Ne ₅₀ Di ₅₀ (2)	1210°C ± 10°	28	Ne + Di
Ne ₅₀ Di ₅₀ (3)	1152 ± 8°C	28	Ne + Di
Ne ₅₀ Di ₅₀ (4)	1100 ± 8°C	28	Ne + Di
Ne ₄₀ Di ₆₀ (1)	1450 ± 30°C	28	Di + Gl
Ne ₄₀ Di ₆₀ (2)	1350 ± 0°C	28	Di + Gl
Ne ₄₀ Di ₆₀ (3)	1300 ± 10°C	28	Ne + Di + Gl
Ne ₄₀ Di ₆₀ (4)	1250 ± 10°C	28	Ne + Di + Gl
Ne ₄₀ Di ₆₀ (5)	1150 ± 0°C	28	Ne + Di
Ne ₃₀ Di ₇₀ (1)	1300 ± 0°C	28	Di + Gl
Ne ₂₀ Di ₈₀ (1)	1500 ± 0°C	28	Di + Gl
Ne ₂₀ Di ₈₀ (2)	1300 ± 20°C	28	Di + Gl
Ne ₂₀ Di ₈₀ (3)	1200 ± 0°C	28	Di + Ne
Ne ₂₀ Di ₈₀ (4)	1100 ± 10°C	28	Di + Ne

Sp: Spinel, Cor: Corundum, Ne: Nepheline, Di: Diopside, Gl: Glass.

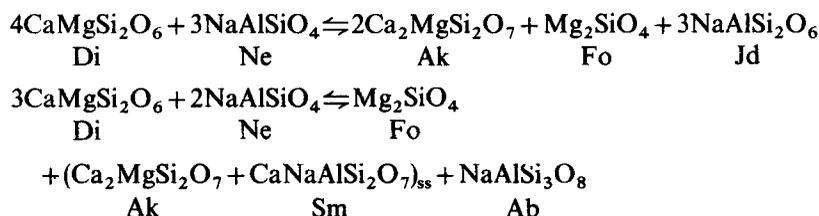
*Metastable phases.

Table 2. Experimental run in nepheline-diopside system at different pressure and 1000°C.

Composition	T°C	P(kb)	Results
Ne ₆₀ Di ₄₀ (1)	1000 ± 10°C	25	Ne + Di
Ne ₆₀ Di ₄₀ (2)	1000 ± 10°C	20	Ne + Di
Ne ₆₀ Di ₄₀ (3)	1000 ± 10°C	15	Ne + Di
Ne ₅₀ Di ₅₀ (1)	1000°C	25	Ne + Di
Ne ₅₀ Di ₅₀ (2)	1000 ± 8°C	20	Ne + Di
Ne ₅₀ Di ₅₀ (3)	1000 ± 0°C	15	Ne + Di + Mel
Ne ₄₀ Di ₆₀ (1)	1000 ± 8°C	25	Ne + Di
Ne ₄₀ Di ₆₀ (2)	1000 ± 8°C	20	Ne + Di
Ne ₄₀ Di ₆₀ (3)	1000 ± 0°C	15	Ne + Di + Mel
Ne ₃₀ Di ₇₀ (1)	1000 ± 15°C	20	Ne + Di
Ne ₃₀ Di ₇₀ (2)	1000 ± 13°C	15	Ne + Di

Mel: Melilite. For other symbols see table 1.

considered to be due to the following reactions (Schairer *et al* 1962, Yoder and Kushiro 1972):



The absence of melilite in some olivine-free nephelinitic rocks may be related, therefore, to their crystallization under high pressure (i.e. above 18 kb) or silica activity (Schairer and Yoder, 1960).

Kogarko *et al* (1984) who made an experimental study on the diopside-nepheline system with variable proportions of apatite at 1 atmosphere show that in the Ne-Di₉₅Ap₅ system below 1100°C, the assemblage comprises ne + di + ap + L, although, at high temperature melilite is a stable phase. The join Di₈₅Ap₁₅-Ne, melilite does not appear in the compositional range between (Di₈₅Ap₁₅)₈₀-Ne₂₀ and Di₈₀Ap₂₀. The absence of melilite and olivine in nepheline- and pyroxene-bearing rocks may also be related to the presence of apatite in the system. Their study of the nepheline-fluorapatite-diopside ternary system at 1 atmospheric pressure (Kogarko *et al* 1977), however, is not helpful in explaining the coexistence of nepheline and clinopyroxene without melilite.

Le Bas (1977) described olivine- and melilite-free but nepheline- and clinopyroxene-bearing plutonic rocks from Homa Bay, West Kenya, Africa. The exact rock types and their localities are as follows: ijolites from Homa Mt (HC309 and HC356), Ruri (N694 and N676), Rangwa (RR358, RR357 and RR356) and Usaki (U369, U1237, U1057, U271, U1119, U1097); urtites from Ruri (N672); micromelteigite from Rangwa (RR357A); (RRAV3) and Usaki (U1122); and alkali pyroxenite from Usaki (U87, U368, U1122A). These rocks may or may not contain minor amounts of apatite and melanite. The aforesaid rocks are devoid of amphibole and hence crystallization took place at high temperature and low P_{H₂O}.

Some of the apatite-rich rocks from these areas may be devoid of melilite and olivine because of the higher activity of F and P as suggested by Kogarko *et al* (1984). In this connection, mention may be made of apatite-bearing ijolite and urtite from Khibiny, USSR, which in some cases are devoid of olivine and melilites, but contain nepheline and clinopyroxene. Mansker *et al* (1979) also reported melilite- and olivine-free nephelinitic rocks from Oahu, Hawaii. In these rocks, the absence of olivine and melilite may be related to higher activities of F and P.

Acknowledgements

We thank the Department of Science and Technology, New Delhi (18(7)/81/STP-II) for awarding a grant to A K Gupta, and a research fellowship to P Singh. We thank Dr H S Yoder, Jr of the Geophysical Laboratory, Carnegie Institution of Washington for reviewing the first version of the script. This paper is dedicated to the late Sir C V Raman on the occasion of his birth centenary.

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