

## ZONING IN SOME VOLCANIC NEPHELINES

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### ABSTRACT

Microprobe analyses of optically zoned nephelines show that the zoning can be due either to replacement of aluminum by iron, or to variation in the relative amounts of silica and alkalis. Iron-rich nepheline from Ol Doinyo Lengai, Tanzania contains as much as 4.6 percent iron. In nepheline with patchy extinction, there is a large variation in the amount of excess silica. It is thought that both the optical and analytical inhomogeneity are the result of incipient unmixing of alkali feldspar from these nephelines.

### INTRODUCTION

Zonal structure in nepheline was reported as early as 1871 by Allport (1871), and subsequently other workers have described the same phenomenon. Boricky (1874) figures zoned nephelines from Bohemia; Künzli (1901) discovered zoned nephelines in a nepheline tephrite from Ol Dionyo Lengai in Tanzania; Shand (1922) mentioned zoned nepheline from a foyaite near Leeuwfontein, South Africa; Becke and Hibsich (1926) described zoned nephelines in phonolites from Billin and Brux in Bohemia; Ödman (1930) found that nephelines from Mt. Elgon in East Africa were zoned; and Sahama (1959) pictures zoned nephelines from the Toror Hills in Uganda. In 1939 Shand summarized the earlier work, showing that the controlling factor was silica content, and that in his specimens calcium content had little to do with the zoning.

Bowen in 1912 found that as the amount of  $\text{CaAl}_2\text{Si}_2\text{O}_8$  in solid solution in nepheline increased,  $\omega$  remained constant, but  $\epsilon$  increased continuously until it first became equal to  $\omega$  (and the mineral became isotropic) and then greater than  $\omega$  (at which point the mineral became positive in optic sign). This is important, for only Becke and Hibsich (1926) have described precisely this optical change in natural nephelines, and it may be that the nephelines described by them are indeed quite rich in the anorthite molecule.

All other zoned nephelines described are optically negative and do not pass through isotropy to a positive optic sign. In some the zoning is cryptic and only revealed by staining (Shand, 1939) or by detecting extremely small changes in birefringence with the aid of special optical compensators (Sahama, 1959). In others the change in refractive index is marked, but there is either no change in birefringence (Künzli, 1901), or the change in refractive index is accompanied by a substantial change in birefringence (Ödman, 1930).

In order to determine the chemical basis for the optical zoning in

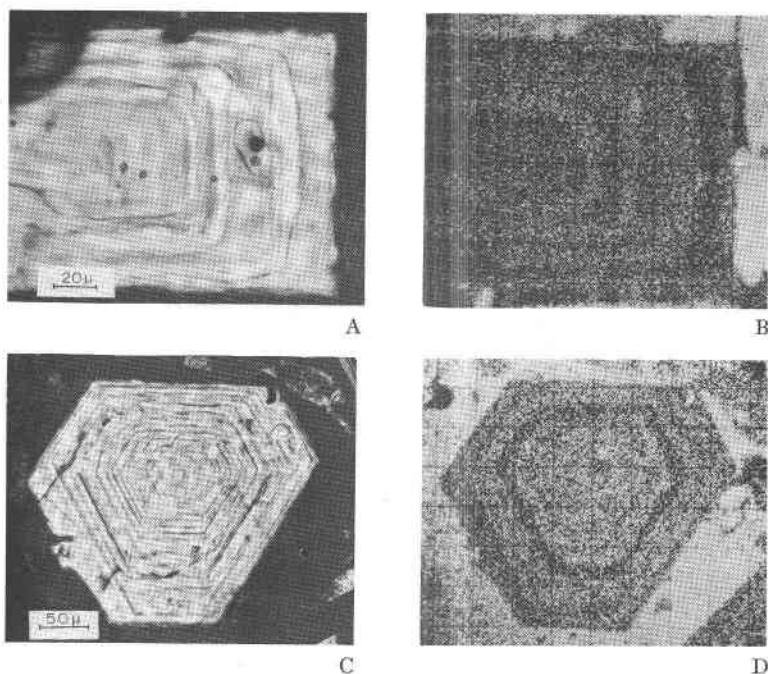


Fig. 1. A, C) Nepheline crystals 1 and 2 respectively from 64-8-1K showing prominent zoning. The photographs were taken in plane polarized light. B, D) Beam scanning photographs of the two crystals taken using  $\text{FeK}_\alpha$  radiation from the mineral. The density of the dots is proportional to the iron content of the nepheline.

nepheline, line traverses were made and beam-scanning photos were taken with the EMX microprobe at Berkeley. Analyzed nepheline and feldspars were used as standards for the determination of Na, K, Ca, Si and Al, and analyzed olivine was used for the determination of Fe. All iron was assumed to be in the ferric state as it was found that there was an antipathetic relation between iron and aluminum in the mineral.

#### IRON-ALUMINUM ZONING

Nepheline crystals with striking concentric zoning were collected by Dr. R. L. Hay on the northern slope of Ol Doinyo Lengai about two miles south of Lake Natron, Tanzania. The nepheline crystals are found in a zeolitized lapilli tuff or mudflow deposit (64-8-1K) of late Pleistocene age in association with sodic hedenbergite as the only other primary volcanic mineral. The size of the crystals varies from about 0.1 mm to several millimeters, and the zoning is seen in both rectangular and hexagonal sections (see Figs. 1A, 1C). It is possible that the material described

here is related to that described by Künzli (1901), as his material was also collected from Ol Doinyo Lengai.

The optical property which enables one to observe the zoning in these crystals is variation in refractive index. There is a marked change in refractive index from zone to zone, but the birefringence changes only slightly from one zone to another. The birefringence was determined by measuring both  $N_o$  and  $N_e$  in several zones on single grains mounted on a spindle stage and was found to range from 0.004 to 0.005. Knowing that the birefringence was constant or nearly so, only variation in one index needed to be determined to fix approximately the range in both refractive indices. The minimum and maximum values of  $\omega$  found were 1.541 and 1.551, respectively, which gives a variation in  $\epsilon$  of 1.536 to 1.547. By analogy with other silicate minerals, it is assumed that lower refractive indices correspond to lower iron contents, and higher refractive indices to higher iron contents of the nepheline. For example, iron sanidine prepared by Wones and Appleman (1961) has a  $\beta$  refractive index of 1.595 which is much higher than the normal  $\beta$  refractive index of sanidine (1.522).

Two crystals of the nepheline from Ol Doinyo Lengai were selected for analysis and in each a line free of inclusions and at right angles to the zoning was chosen (Figs. 1A, 1C). Points were analyzed at five micron intervals along this line from the center to the edge of the crystal. First the points were analyzed for Na, Ca and K, and subsequently the same points were analyzed for Fe, Si and Al. The combined data yielded a

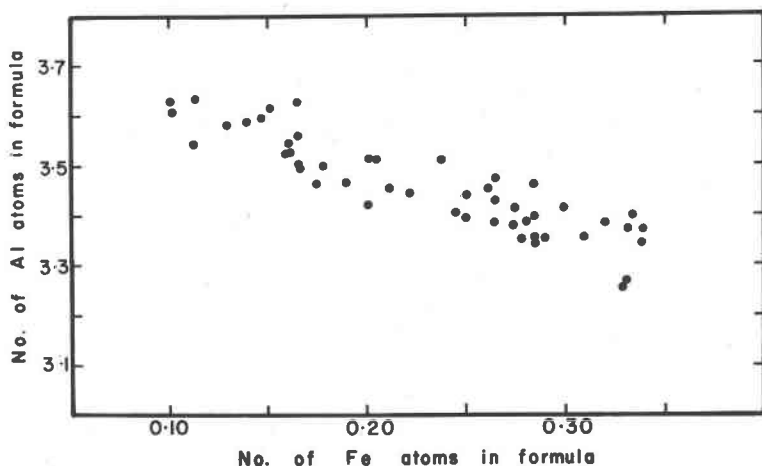


FIG. 2. Plot of Fe against Al in formulas of nephelines from 64-8-1K. See text for discussion.

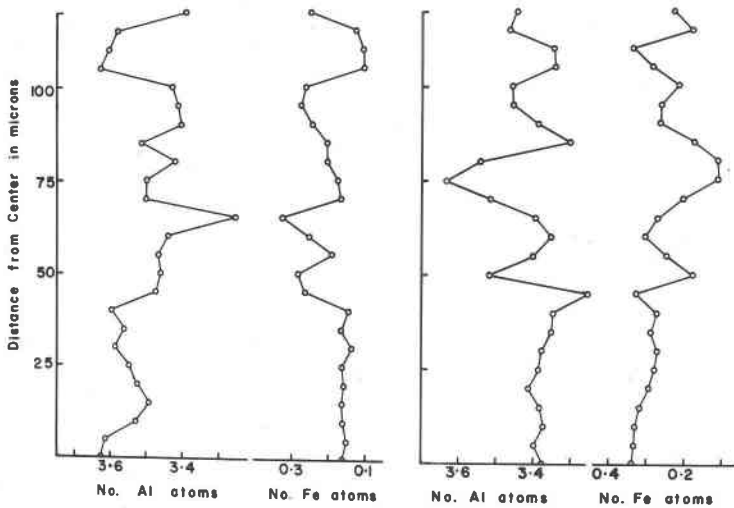


FIG. 3. Variation in Al and Fe in crystals 1 and 2 from center to edge, plotted at a five micron interval. Data for crystal 1 are on left; for crystal 2 on right.

complete analysis for each point, the totals of which vary from 99.0 to 101.6 percent. These and other crystals were also analyzed for Ba, Ti, Mn and Mg, all of which are below the limit of detection with the microprobe. Mineral formulas were calculated for each analysis on the basis of eight oxygens, and the number of iron atoms in the formula was plotted against the number of aluminum atoms (Fig. 2) and also plotted along a line representing the line of traverse from the center to the edge of the crystal (Fig. 3).

From the figures it is readily seen that there is a regular variation of iron with aluminum, aluminum increasing when iron decreases and vice versa. The lack of complete correspondence is due in part to analytical error, but may also be in part due to variations in the silica content at the points examined. The sum of Si and Fe was plotted against Al, but the correspondence was only slightly improved if at all, from which it is concluded that the main substitution is iron for aluminum. In addition the slope of the best line drawn through the points in Figure 3 is near unity, which supports the hypothesis that iron atoms substitute for aluminum atoms in tetrahedral sites. Plots of sodium, potassium and calcium content show little variation from center to edge of the crystal.

Beam-scanning X-ray photos of the same crystals photographed in Figures 1A and 1C are reproduced as Figures 1B and 1D. These photos were taken using Fe  $K_{\alpha}$  radiation emitted by the mineral, and show that the iron distribution is truly zonal.

Average analyses of the two nepheline crystals are given in Table 1 where it is seen that the average iron content is much higher than the amount generally encountered in nephelines. Individual zones may contain as much as 4.6 percent  $\text{Fe}_2\text{O}_3$ , whereas the amount ranges from 0.1 to 1.8 percent in other analyzed nephelines (Deer *et al.*, 1963).

Lattice parameters were determined from an X-ray powder pattern using silicon as an internal standard. The resultant values are  $a = 10.001 \pm .001 \text{ \AA}$  and  $c = 8.393 \pm .001 \text{ \AA}$  yielding a cell volume of  $728.4 \text{ \AA}^3$  which is in good agreement with the data given by Smith and Tuttle (1957) and Donnay *et al.* (1959) for nepheline of like potassium content (*i.e.*, with  $\text{K} = 1.6$  on the basis of 16 oxygens). Thus the substitution of iron for aluminum does not affect the lattice parameters of nepheline nearly so much as the substitution of potassium for sodium,

TABLE 1. AVERAGE ANALYSES OF NEPHELINES FROM SAMPLE 64-8-1K

	Crystal 1	Crystal 2	Range Crystal 1	Range Crystal 2
$\text{SiO}_2$	44.1	44.4	42.8-45.0	43.1-45.0
$\text{Al}_2\text{O}_3$	30.7	30.0	28.5-32.0	28.4-31.6
$\text{Fe}_2\text{O}_3$	2.67	3.46	1.42-3.83	1.56-4.61
$\text{CaO}$	0.06	0.09	0.03-0.09	0.04-0.13
$\text{Na}_2\text{O}$	16.5	16.1	15.8-16.6	15.5-16.6
$\text{K}_2\text{O}$	6.4	6.5	6.1-6.8	6.0-6.7
Totals	100.43	100.55		

which is to be expected, as the difference in ionic radius is much less between  $\text{Fe}^{+3}$  and Al than between K and Na.

#### SILICA AND ALKALI ZONING

Nephelines in two specimens of phonolite from the Schlossberg, Brux, Czechoslovakia were analyzed and the analytical results are plotted as Figure 5, along with analyses of nepheline from the Wolf Rock phonolite of Cornwall. A photograph of a nepheline crystal from one of the Schlossberg phonolites is reproduced as Figure 4, where it will be seen that the center is nearly unzoned, but a distinct rim is present. This narrow peripheral zone is of both lower refractive index and lower birefringence than the center of the crystal because the centers have *on the average* more potassium and less silica than the edges, both of which act to lower the refractive index of the edge (see Winchell, 1941). The nepheline phenocrysts from these phonolites have a queer patchy extinction, not unlike that of anorthoclase, although less pronounced. Many nephelines

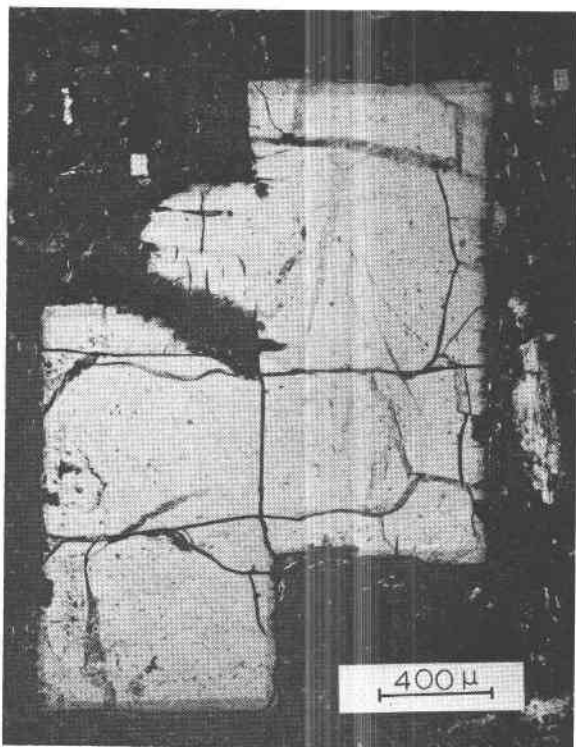


FIG. 4. Zoned nepheline from the Schlossberg phonolite 88-16. The zoning is confined to a rim richer in silica and soda and is lower in both birefringence and refractive index. Photograph taken under crossed polaroids.

from igneous rocks have extinction of this type, although it has not often been recorded.

Iron is present in only small amounts and the  $\text{Fe}_2\text{O}_3$  content rises gradually from 0.25–0.30 percent in the centers to 0.40–0.60 percent near the edge, reaching values as high as 1.2–1.4 percent at the very rim. These latter high values are confined to the last 10 or 15  $\mu\text{m}$  at the crystal edge, and are accompanied by a drop in alumina content of the same order of magnitude. Calcium is virtually absent in these nephelines; values range from 0.01 to 0.04 percent  $\text{CaO}$ .

None of the nepheline specimens in the collections at Berkeley exhibits isotropy or positive optical sign, and all analyzed specimens are very poor in calcium (0.10%). The most calcic nepheline known was described by Bannister and Hey (1931) and has a calcium content of 4.44 percent, which corresponds to 22 percent anorthite. According to Bowen's data such a mineral should have very low birefringence with both re-

fractive indices near 1.537, and it should be of positive optical sign. Bannister and Hey (1931), however report values of 1.5299 for  $N_o$  and 1.5266 for  $N_e$ , which yield a birefringence of 0.0033. These data are reconcilable if we assume that the effect of calcium as reported by Bowen (1912) holds only for nepheline which is virtually potassium free. Most natural nephelines contain considerable potassium and for potassic nephelines it may be that the effect of calcium is different.

#### DISCUSSION

The most interesting features of the iron-aluminum zoning in the Ol Doinyo Lengai specimens are the abrupt change in iron content across the zone boundaries, and the lack of a progressive change in iron content from center to edge superposed on the zoning. Ödman (1930) has stated for his specimens from Mt. Elgon that ". . . the zoning in the nepheline is not to be looked upon as a continuous series of different molecules, but as a rhythmic crystallization of two chemically different nephelines." This is not strictly true in the zones described here, for although the transition is abrupt, the amount of iron in the iron-rich zones is not constant, as can be seen from Figure 3. The Schlossberg specimens show a gradual increase in the amount of iron in the nepheline from center to edge, but this increase is not seen in the Ol Doinyo Lengai samples.

As the nephelines examined were contained in a tuff, it is impossible to say with what minerals the nepheline was in equilibrium as it crystallized, or even to guess the composition of the liquid from which it crystallized. However it may be assumed that either the conditions under which it crystallized were unusual, or the composition of the liquid from which it crystallized was unusual, for with the possible exception of Ödman's samples, there are no other recorded instances of zoning of this type.

In a glassy nephelinite lava with nepheline phenocrysts from Nyiragongo containing 10.58 percent iron with a ferric-ferrous ratio of 0.14 (I. S. E. Carmichael, pers. comm.) the nepheline has incorporated only 0.9 percent  $Fe_2O_3$ , an observation which suggests that in a liquid with a low ferric-ferrous ratio the ability of nepheline to accept iron is limited. Assuming that this is generally true and a high ferric-ferrous ratio is mandatory before nepheline can accept iron, there are a number of variables which might influence the iron content of this mineral. Carmichael and Nicholls (1967) have shown that the ferric-ferrous ratio in silicate liquids is dependent on temperature, oxygen fugacity and bulk composition, particularly alkali content. Thus the zoning may be a response to rapid changes in volatile pressure (possible due to repeated eruptions during the crystallization history of the nepheline). It is also possible that the zoning is in some way controlled by diffusion in the

liquid immediately surrounding the nepheline crystals as has been suggested to be the case for oscillatorily zoned plagioclase crystals by Bottinga *et al.* (1966). For example, as the growing nepheline crystal depletes its surrounding shell of liquid in  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ , a zone enriched in iron and other rejected components will develop. It is probable that in this enclosing liquid shell, the Fe/Al ratio increases as the nepheline crystal grows; however, the reason for the successive jumps in the iron content (Fig. 1) is perplexing, for a *progressive* increasing substitution of iron for aluminum seems more likely.

In the phonolite specimens there are two separate features of the compositional variation which require comment: 1) the clear difference in the *average* silica and potassium contents between the crystal centers and the peripheral rims, and 2) the variation in silica content within each portion of the crystals.

Nepheline becomes enriched in silica as it crystallizes in the system  $\text{NaAlSiO}_4\text{--NaAlSi}_3\text{O}_8$  (Grieg and Barth, 1938), reversing this trend at subsolidus temperatures (Hamilton, 1961). Hamilton and Mackenzie (1960) have shown that liquidus temperatures in the system  $\text{NaAlSiO}_4\text{--KAlSiO}_4\text{--SiO}_2$  are depressed by increase in water pressure, and suggest that subsolidus phase relations are virtually unchanged. Consequently the temperature at which the nepheline solidus intersects the nepheline-alkali feldspar solvus is also influenced by water pressure and the position of this line of intersection moves progressively towards  $\text{NaAlSiO}_4$  as the temperature of the liquidus is decreased. If a nepheline is crystallizing without feldspar at some elevated water pressure (say 1 or 2 kbar) and the water pressure is suddenly reduced, the nepheline will be out of equilibrium, and in order to reach equilibrium again, must become richer in silica. A crystallization history of this nature could perhaps explain the silica enrichment which has been found in the rims of the nepheline crystals from the Schlossberg. The same effect could be produced by quenching isobarically and could also explain the excess silica described here, though a combination of the two factors seems more likely.

From Figure 5 it is seen that the range in silica content in these nephelines is considerable, both in the cores and in the margins of the crystals. The range in silica content measured in the microprobe standard nepheline is shown by the thick barred line in Figure 5. This line is included only to demonstrate that the range in composition cannot be ascribed to analytical error alone.

It must be emphasized that the points in Figure 5 do not represent a progressive trend; there is neither a progressive increase or decrease in silica as one moves from point to point toward the edge of a crystal. Instead the amount of silica appears to vary randomly within the crystal



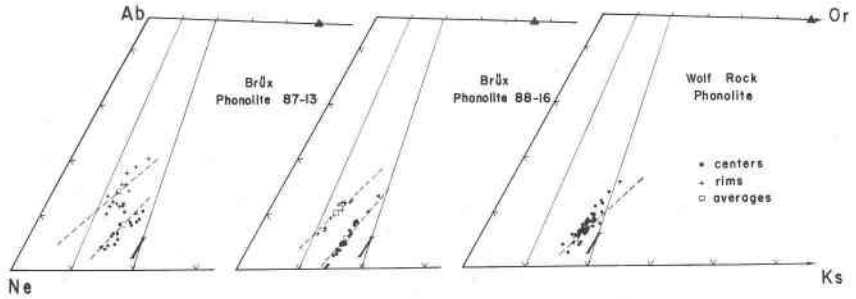


FIG. 5. Weight percent plot of data for nephelines from three phonolites in the diagram nepheline-kalsilite-silica. The triangle represents the average composition of the groundmass feldspar in each specimen. The dashed lines are joins of the average groundmass feldspar with averages of the nepheline points. The short barred line represents the total variation in composition measured in the standard nepheline. The thin lines between the alkali feldspar join and the nepheline-kalsilite join are lines of constant Na/K ratio (9:1 and 5:1). Tick marks along the upper edge are in 10 percent increments along the join Ab/Or.

cores and within the marginal zone. The analyzed points do not fall along lines of constant Na/K ratio (see Fig. 5) but rather along lines which are more closely (though not exactly) approximated by the joins of the average nepheline with the coexisting groundmass feldspar. It is possible that the inhomogeneity seen optically and reflected in the analysis is the result of incipient unmixing of a once-homogeneous nepheline to a nepheline with less excess silica and an alkali feldspar. If this is the case, then the bulk composition of the alkali feldspar will be given by extending a line drawn through the analyzed points of the nepheline to the alkali feldspar join. In this way each point may be represented by a nepheline on the nepheline-kalsilite join, and a feldspar on the albite-orthoclase join. Extrapolating the lines for the data given in Figure 5 yields values of  $Or_{48}$  for 87-13 (centers);  $Or_{37}$  for 88-16 (centers); and  $Or_{37}$  for the Wolf Rock phonolite. These values represent estimated bulk compositions *only* of the alkali feldspar, for at temperatures below the alkali feldspar solvus, two feldspars rather than one would be exsolved.

The amount of feldspar necessary to account for the greater part of the variation in silica content of the nephelines shown in Figure 5 is about 5 percent, which will make its detection by X-ray methods difficult. This problem may be further aggravated if two feldspars rather than one have exsolved from the nepheline. Tuttle and Smith (1958) have given schematic diagrams for subsolidus phase relations in the system  $NaAlSi_3O_8$ — $KAlSi_3O_8$ — $SiO_2$  and consider that alkali feldspar exsolution from neph-

line may take place to give a "perthitic" type of structure. Hamilton (1961), however, has proposed that the Al/Si framework in nephelines at subsolidus temperatures is permanent since perthitic textures have not been observed, even in nephelines coexisting with perthitic feldspar; there is also no experimental evidence which supports unmixing.

Two attempts were made to find alkali feldspar lines in powder patterns of nephelines showing patchy extinction, but both were unsuccessful. This is somewhat disconcerting, but not wholly unexpected, for the amount of feldspar expected is small. If further X-ray work proves that there is no alkali feldspar present this hypothesis must be abandoned, but until such time it seems the most likely explanation for the scatter in the analytical data. Further support is given to this hypothesis by the more restricted scatter in silica content of a nepheline which does not show patchy extinction. This nepheline is found in an etindite from Mt. Etinde, Cameroon (Carmichael, unpublished work).

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