

Si-Al Ordering in Nephelines

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Abstract. Different degrees of Si-Al ordering are demonstrated to exist in nepheline on the basis of five crystal structure refinements on specimens with different geologic origins and laboratory treatments. Disorder increases in the sequence; gneissic-igneous plutonic-volcanic nepheline and appears to increase as a result of laboratory heat treatment. The four independent tetrahedral sites can be divided into two pairs with one pair of sites always less ordered than a second pair in a simple regular relationship.

Very little has been written on the Si-Al order-disorder relationship in the rock-forming mineral nepheline, $(\text{Na}, \text{K}) \text{Al}_{1-x} \text{Si}_{1+x} \text{O}_4$, due to the paucity of detailed structural data available. By analogy with the feldspars and other framework tectosilicates it could well be reasoned that nepheline would also show a variable degree of Si-Al ordering depending largely on geologic origin. Conversely, due to the presence of an approximate 1:1 Si-Al ratio (which allows a particularly simple alternating ordering scheme as in anorthite), all nephelines could conceivably be essentially fully ordered regardless of thermal history.

Recent crystal structure refinements of several nephelines now allow a preliminary estimate to be made of the silicon-aluminium distribution in this mineral. Nephelines studied include a specimen from a nepheline-scapolite-biotite gneiss at Bancroft, Ontario—both before and after heating to 900°C in air (Foreman and Peacor, 1970)—a specimen from a plutonic nepheline syenite from Larvig, Norway (Dollase, 1970), and a specimen from the ejected volcanic blocks of Monte Somma, Vesuvius, Italy (Simmons and Peacor, in prep.). In addition a specimen of the Larvig nepheline was treated in molten NaCl at ~805° for 48 hrs. (Two 24 hour periods separated by washing and replacement of NaCl in order to remove the exchanged K⁺ ions) (Dollase and Freeborn, in prep.).

The five structure refinements are approximately of equivalent accuracy which, however, is only moderate by present day standards due to (1) the pseudosymmetry of this structure-type—near $P6_3/m$ symmetry—and (2) the thermal and positional disorder resulting in high apparent temperature factors which occurs in all samples studied. The Table lists the averages of bond lengths from oxygens to the atoms on each of the four independent tetrahedral sites, T_1 through T_4 . T_1 and T_2 occupy positions on three-fold axes and there are two each of such sites per 32 oxygen-unit cell. There are six each of the general position (symmetry 1) sites T_3 and T_4 per unit cell. Because there is positional disorder of one of the oxygen atoms, and since some bonds are symmetry-related, the estimated

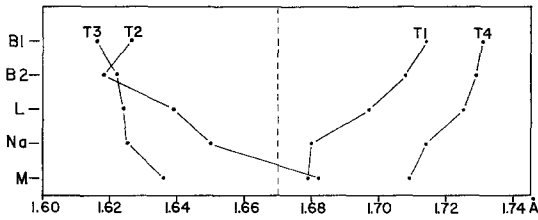


Fig. 1. Mean T -O bond lengths (in Å) for the four independent tetrahedral sites in nepheline. The letters refer to the different nephelines listed in the Table

Table. *Nepheline bond-length averages (uncorrected for thermal motion)*

Crystal	Chemical analysis	T_1 -O	T_2 -O	T_3 -O	T_4 -O
Bancroft (before heating)	$K_{1.32}Na_{5.64}Ca_{0.36}Al_{7.93}Si_{8.07}O_{32}$	1.714	1.626	1.616	1.731
Bancroft (after heating)	$K_{1.32}Na_{5.64}Ca_{0.36}Al_{7.93}Si_{8.07}O_{32}$	1.708	1.618	1.622	1.729
Larvig, Norway	$K_{1.4}Na_{5.5}Ca_{0.3}Al_{7.5}Si_{8.5}O_{32}$	1.697	1.639	1.624	1.725
Na-exch. Larvig	$Na_{7.3}Ca_{0.2}Al_{7.5}Si_{8.5}O_{32}$	1.680	1.650	1.625	1.714
Monte Somma	$K_{1.18}Na_{4.46}Ca_{0.91}Al_{7.78}Si_{8.30}O_{32}$	1.679	1.682	1.636	1.709

error of the T_1 and T_2 bond-length averages is ~ 0.015 Å. For T_3 and T_4 they are estimated to be ~ 0.01 Å. It is because the differences shown in the Table are only a few estimated standard errors at most, that the conclusions reached below must be regarded as tentative until confirmed (or modified) by further and, if possible more precise, data.

The numerical values of the Table are serially plotted in Fig. 1, showing several regular trends. The order, $T_3 < T_2 < T_1 < T_4$, is generally followed but the difference between these averages decreases from the top of the Table downwards, in a roughly regular manner. Since there are four independent tetrahedral sites the differences in bond lengths will be considered in several stages, at first grouping some of the sites together. Fig. 2 compares the average bond length of the larger tetrahedra, T_1 and T_4 (taking into account their relative numbers per cell), with the average of the smaller tetrahedra, T_2 and T_3 . The five data points fall approximately along a line of slope -1 .

The compilations of framework aluminosilicate bondlengths versus site-occupancy by Smith and Bailey (1963), Jones (1968) and Ribbe and Gibbs (1969) document that such differences as seen in the Table reflect differences in the Si-Al occupancy of these sites¹. For example, a recent determinative relationship is that of Jones (1968) where mole percent Al occupancy = $6.4116D - 10.282$, (D = mean T -O bond length.) There are, however, several reasons why caution must be exercised in applying such a relationship to nepheline: (1) the total Al/Al + Si ratio obtained by application of such a relationship, is consistently lower, by about 0.03–0.04, than the values given by bulk chemical analyses. (2) The determinative relationships are made largely from structures with “normal” thermal disorder. Nepheline, however, appears to have abnormally large

¹ In addition the individual structure studies show site-occupancy refinement or temperature factor effects which also indicate that the large sites are Al-rich and small sites Si-rich.

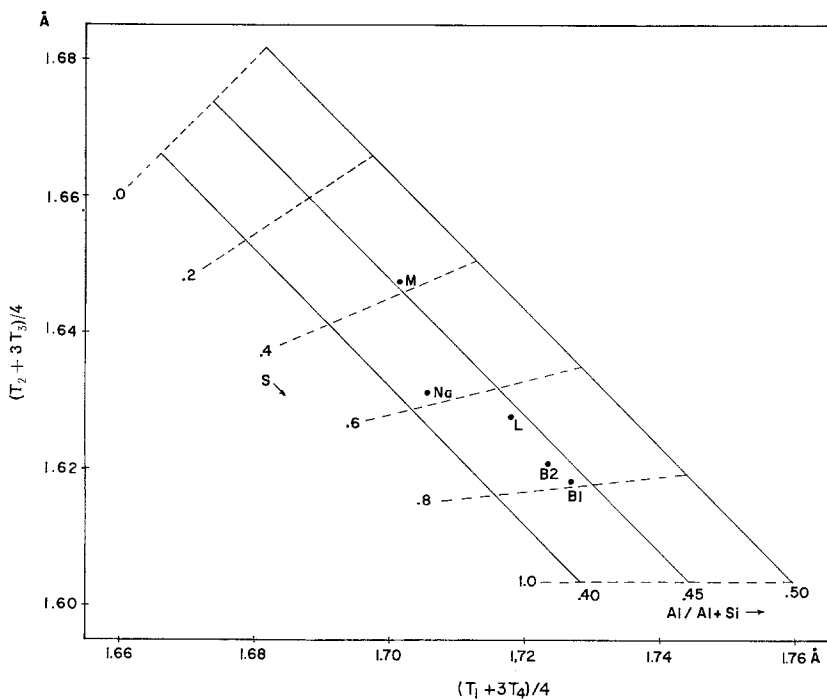


Fig. 2. Comparison of the average bond-length to the Al-rich sites (T_1 and T_4) with the average bond-length to the Si-rich sites (T_2 and T_3). The estimated standard error of these averages is $\approx 0.01 \text{ \AA}$

temperature factors (probably due to a domain structure of some sort, and thus in part representing positional disorder). There is, therefore, a larger additive "thermal" correction in the case of nepheline, or put another way, the uncorrected nepheline bond lengths are slightly too short to be applied to the same (uncorrected) scale as the "normal" tectosilicates. (3) Since the coordination numbers, bond strengths, bond angles, etc. in nepheline differ from those found in other tectosilicates (particularly the feldspars) the bond length-occupancy relationship may also differ between nepheline and (for example) feldspars.

With these reservations in mind, the points plotted in Fig. 2 can be compared with a grid of expected values (using Jones' linear bond length-occupancy relationship) for different Al/Al + Si ratios (solid lines) and different degrees of order (dashed lines). The order parameter, s , is 0 for a totally disordered case and is 1 for a totally ordered case. The interrelationship of the values is: average mole percent Al in $T_1, T_4 = (\text{Al}/\text{Al} + \text{Si}) (1 + s)$. All other Si, Al occupancies can be calculated from mass balance, and complete site-occupancy considerations.

Fig. 2 then suggests that the nephelines group about a compositional line², $\text{Al}/\text{Al} + \text{Si} = 0.45$ and that the degree of ordering decreases from $\sim 80\%$ for the

² The true compositions of the nephelines studied are probably slightly more aluminous than indicated in Fig. 2 (cf. Table) due to the generally higher nepheline temperature factors as mentioned above. Since this should affect all the tetrahedra more or less equally the grid should probably be displaced slightly toward the lower left corner of Fig. 2 in order to read off unbiased compositions. (The order estimates should be unaffected.)

gneissic Bancroft nepheline (preheat data) to 65% order for the plutonic Larvig nepheline and to $\sim 40\%$ for the volcanic Monte Somma nepheline. Heat treatment of the Bancroft nepheline has moved the data point in the direction of disorder, but the shift is smaller than the estimated standard error. For the molten NaCl treated Larvig nepheline, disorder also seems to have increased. There is, however, an indicated composition change. Since experiments were performed under conditions which are inconsistent with such chemical change, this effect must merely reflect the random error present in the data.

The apparent variations in degree of ordering seem at least consistent with the geologic origin or laboratory treatment of the samples. Sahama (1962) has interpreted differences in the optical properties of nephelines as due to differences in the Si-Al ordering. By his method he concludes that the Monte Somma nepheline is among the most disordered nephelines studied. Subrata Ghose (personal communication) has noted that most nephelines give ^{27}Al nmr signals indicative of partial order and that a specimen from the Bancroft area (Davis Hill, Dunganon Township), gave evidence of being the most ordered of the specimens he studied³.

Geometrically the ordering scheme is the expected one with the Al-rich tetrahedra sharing all four corners with Si-rich tetrahedra and vice versa. This type of aluminum-aluminum avoidance in the nepheline structure produces a polar crystal with all "Al" tetrahedra pointing along the positive c-axis and all "Si" tetrahedra pointing along the negative c-axis (see Dollase, 1970, for a drawing of the structure). In the preceding any differences between the two aluminous sites, T_1 and T_4 , or between the two siliceous sites, T_2 and T_3 , have been ignored. These differences are now considered.

In Fig. 1 the deviation of a point from a central (disordered) value of $\sim 1.67 \text{ \AA}$ indicated the degree of ordering of these sites. It can be seen that the T_1 and T_2 values are, to a first approximation, symmetrically displaced from a disordered value, and, similarly, the T_3 and T_4 values are roughly mirror images. That is, in all cases, the T_3, T_4 pair of sites shows an approximately equal degree of ordering, and also the T_1 and T_2 pair are (roughly) equally ordered. However, the degree of ordering of the T_1, T_2 pair is always less than that for the T_3, T_4 pair. A comparison of the degree of ordering of these pairs is shown in Fig. 3 by plotting the differences between the T_1 and T_2 bond-length averages versus the difference between the T_3 and T_4 bond-length averages. Also shown are the theoretical values for a totally disordered case (*DO*) and a completely ordered case (*OR*) with (apparent) $\text{Al}/\text{Al} + \text{Si} = 0.45$. The plot is remarkably (and, in view of the estimated standard errors, somewhat fortuitously) regular. The dashed line is a suggested path of ordering from a completely disordered nepheline, through the various examples studied, toward a completely-ordered phase. Although different thermal histories could lead to different order-disorder paths, only one need be invoked to account for the data collected so far. The interesting

³ According to Ghose, nepheline ^{27}Al nmr spectra are intermediate in character between those of adularia and sanidine. They show a sharp central line whose position is unaffected by crystal orientation but whose width is slightly orientation dependant. Satellite lines are not in general detectable except for broad inner satellites observed in the case of the Davis Hill specimen. These results, coupled with the ^{23}Na nmr spectra suggest a partially ordered, twinned, domain model for nepheline.

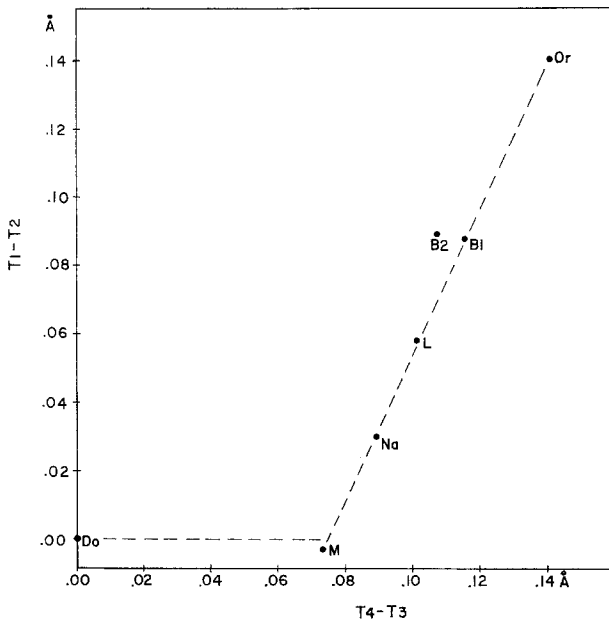


Fig. 3. Comparison of the (average) degree of ordering of the T_1 - T_2 sites with the (average) degree of ordering of the T_3 - T_4 sites. The estimated standard errors are ~ 0.015 for the abscissa and ~ 0.01 Å for the ordinate axis

point is that there is a higher tendency to order the T_3 - T_4 sites (perhaps an earlier onset of ordering with cooling) than in the case of the T_1 - T_2 sites. Provided the sites and their surroundings are sufficiently different, such nonuniform ordering seems plausible.

Besides the differences in site symmetries, there are major differences in the environment of the T_1 - T_2 pair as opposed to the T_3 - T_4 pair. The T_1 - T_2 pair is bonded to O(1), the oxygen atom which is positionally disordered (off the three-fold axis), whereas the T_3 - T_4 pair is not. The second nearest neighbors of the tetrahedral sites are the two independent alkali sites. For a nepheline with three Na's to one K, the T_1 - T_2 tetrahedra are surrounded by Na-atoms only, whereas the T_3 and T_4 tetrahedra are surrounded by a combination of Na and K atoms and vacant K sites. (The distribution of the small amount of Ca usually present is a further and unknown factor.) The exact mechanism whereby such structural differences would lead to non-uniform ordering probably involves correlations between the O(1) disorder, T occupancy, and K-site occupancy, i.e., a domain model.

A case was previously made (Dollase, 1970), with some supporting evidence, that the positional disorder of the O(1) atom provided a simple mechanism allowing a greater-than-unity Si/Al ratio in the T_1 , T_2 sites. If these sites are indeed more Si-rich than the T_3 , T_4 sites (as seems to be the case here except for the Monte Somma nepheline), such compositional differences could also influence the *degree* of ordering of these pairs of sites. In this case the ordering state of the nepheline will depend both on thermal history and composition.

Finally, it should be pointed out that the data plotted in the figures cover what could be called an intermediate range of ordering with no examples of nearly fully ordered or completely disordered nepheline. Sahama (1965) noted that for a great variety of nephelines the IR absorption bands, due to Si, Al-O vibrations, changed little from specimen to specimen in comparison to the well-defined changes observable in the case of the feldspars. This perhaps can be partly accounted for by considering that in an alkali feldspar an Al-rich site can contain between 25 to 100 percent Al, depending on the degree of order, whereas in nepheline, for the degrees of order encountered in this study, an Al-rich site could range from ~ 50 to 80 percent Al content, a much smaller range. However, this lack of major spectral change probably also indicates that more extreme degrees of ordering than found here are relatively uncommon in nature.

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