REFINEMENT OF THE CRYSTAL STRUCTURE
OF A VOLCANIC NEPHELINE[1]

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ABSTRACT

The structure of nepheline from a volcanic environment has been refined by least–squares to an R–value of 6.2%. An oxygen atom, $O(1)$, is confirmed to occupy an off–axis position. Temperature factors are high for all atoms, as they are for recent refinements of nephelines from other environments. This is indicative of a domain structure. The T–O distances indicate that there is a considerable degree of Al–Si disorder between the $T(1)$ and $T(2)$ sites, as consistent with rapid cooling from a high–temperature environment. However, the $T(3)$ and $T(4)$ sites, as in other nephelines, show a high degree of order for Si and Al, respectively. The domain structure is explained in terms of (1) vacancies at the K sites, (2) the off–axis displacement of $O(1)$.

INTRODUCTION

The crystal structure of nepheline, $KNa_3[AlSiO_4]_4$ (space group $P6_3$, $a = 10.01$, $c = 8.40$Å, $Z = 2$) was determined originally by Buerger *et al.* (1954) and Hahn and Buerger (1955), using a specimen of volcanic nepheline from Monte Somma, Italy. They concluded that there are four non–equivalent tetrahedral sites and that Al and Si were ordered on $T(1)$ and $T(2)$, which are on 3–fold axes, and disordered on $T(3)$ and $T(4)$ which are in general position. More recently, Foreman and Peacor (1971) refined the structure of a nepheline from a low temperature pegmatitic environment and found that Al and Si are highly ordered on all four T sites. In addition, Dollase (1970) has refined the structure of a plutonic nepheline from Larvig, Norway, and Dollase and Freeborn (in prep.) have determined the structure of a Na–exchanged Larvig specimen. Their results imply that there is an intermediate degree of Al–Si order.

These refinement results are consistent with the suggestion of Sahama (1962) that nephelines of quenched high temperature origin retain a higher degree of Al–Si disorder. His work was based on thermal expansion and birefringence data as a function of tempera-

ture for a variety of nephelines. However, infrared absorption spectra obtained by Sahama (1965), using, in part, the same specimens as in the 1962 study, indicated that there were no differences attributable to Al–Si order–disorder transformations.

Sahama (1962) found that Monte Somma nepheline appeared to be one of the most highly disordered nephelines. Recent refinements of other nephelines of relatively high accuracy indicate that there is a regular change in degree of Al–Si order consistent with their conditions of formation, but in a way inconsistent with the degree of order on $T(1)$ and $T(2)$ as reported by Buerger, *et al.* (1954) for Monte Somma nepheline. Their refinement was based on a limited amount of intensity data. In order to define the structural relations for a high–temperature nepheline to a higher degree of accuracy, we therefore undertook a new refinement of this material.

Dr. Wayne Dollase kindly provided us with a sample of Monte Somma nepheline, from the same hand specimen which provided the material used by Buerger *et al.* in their original structure determination. Precession and Weissenberg photographs of cleavage fragments were consistent with symmetry $P6_3$, the space group obtained by previous investigators. There was no indication of any twinning from these photographs, although Buerger *et al.* (1954) encountered twinning problems with this material. Unit–cell dimensions were determined from a least–squares refinement of a powder diffractometer pattern, using quartz as an internal standard and $CuK\alpha$ radiation. The refined parameters are $a = 10.003 \pm .002$ and $c = 8.381 \pm .003$Å. The composition used was that determined by Bannister and Hey (1931) and corresponds to: $K_{1.18}Na_{4.46}Ca_{0.91}Al_{7.78}Si_{8.30}O_{32}$. Subsequent to the refinement, electron microprobe analyses was carried out on two separate cleavage fragments. There were no significant detectable differences in composition within each grain, and the compositions of each were the same within standard error. The average composition, normalized to 16 Al + Si, was determined to be: $K_{1.28}Na_{5.36}Ca_{0.28}Al_{7.92}Si_{8.08}O_{32}$. The Al:Si ratio is nearly the same as in the analyses by Bannister and Hey, as is the amount of K. Although the relative amounts of Na and Ca differ, the total of large cations for the two analyses is not significantly different.

REFINEMENT

The crystal used for the determination of intensity data was a cleavage fragment mounted along the c–axis measuring approximately $0.3 \times 0.1 \times 0.5$ mm. Intensity data were measured using the Supper–Pace automated system, which employs measurement of background on both sides of a peak scan. The direct $MoK\alpha$ X–ray beam was monochromated with a flat crystal of pyrolytic graphite, and intensities were detected with a scintillation counter. The crystal was

carefully examined for twinning by determining the relative intensities of reflections which are brought into coincidence by the twin operation. Reflections of the type hkl and khl were observed such that one was very intense and the other near zero in intensity. These comparisons confirmed that if a twin component existed it had a volume less than 1 percent of the entire crystal.

A total of 700 independent reflections were measured. These were corrected for absorption ($\mu = 10.5$ cm^{-1}) and Lorentz–polarization factors, the polarization correction being modified for the polarization of the direct beam. Minimum observable intensity values were assigned to weak reflections on the basis of standard counting statistics.

Full–matrix least–squares refinement was employed under the following conditions: 1. The initial structure parameters were those obtained by Foreman and Peacor (1971) for nepheline from Bancroft, Ontario. 2. All atoms were assumed to be half–ionized and form factors were obtained from the International Tables (1962). 3. The weighing scheme devised by Cruickshank (1965) was used, except that all reflections with intensity values less than minimum observable values were rejected. 4. Refinement of variables was carried out in the general sequence of the scale factor and atomic coordinates, isotropic temperature factors and anisotropic temperature factors. Refinement was completed with cycles during which all coordinates and anisotropic temperature factors were allowed to vary. The final R–value is 6.2 percent. The refined atomic coordinates and temperature factors are listed in Tables 1 and 2, and structure factors are listed in Table 5[1].

DISCUSSION

The refined structural parameters are very close to those obtained by Dollase (1970) and Foreman and Peacor (1970). The general nature of the structure has been described in detail by these authors and will not be repeated here. Values of selected interatomic distances and angles are listed in Tables 3 and 4. These were computed utilizing both the least–squares variance–covariance matrix and lattice parameter standard errors.

Silicon–aluminum distribution

As noted above, Hahn and Buerger (1955) determined that the $T(1)$ and $T(2)$ sites were occupied by Al and Si, respectively. Average T–O bond distances were 1.78 ± .02 and 1.64 ± .03Å. $T(3)$ and $T(4)$ had average T–O distances of 1.675 ± .01 and 1.685 ± .015Å, indicating that Al and Si were disordered on these sites.

The T–O average bond distances for these two pairs of sites ob-

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TABLE 1

COORDINATES AND EQUIVALENT
ISOTROPIC TEMPERATURE FACTORS*

	x	y	z	$B_{equiv.}$ $(Å^2)$
Na	.9972 (2)	.4432 (2)	.9913 (11)	1.8
K**	0	0	.9893	3.0
T(1)	1/3	2/3	.1877 (11)	1.1
T(2)	1/3	2/3	.7990 (11)	1.6
T(3)	.0933 (2)	.3344 (2)	.3090 (10)	.9
T(4)	.0934 (2)	.3318 (2)	.6824 (10)	.9
O(1)	.3327 (53)	.7024 (36)	.9846 (41)	2.5
O(2)	.0269 (4)	.3168 (5)	.4921 (13)	2.0
O(3)	.1713 (7)	.5235 (8)	.7210 (14)	2.9
O(4)	.1647 (5)	.5108 (6)	.2393 (12)	1.5
O(5)	.2258 (5)	.2873 (6)	.3099 (12)	1.2
O(6)	.2229 (6)	.2657 (6)	.6892 (15)	1.7

*Standard errors in parentheses
**Defines the origin of z

TABLE 2

ANISOTROPIC TEMPERATURE FACTORS*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	.0082(3)	.0050(2)	.0054(3)	.0032(2)	.0004(4)	.0003(4)
K**	.0102(3)	.0102	.0097(5)	.0051	0	0
T(1)**	.0036(3)	.0036	.0035(5)	.0018	0	0
T(2)**	.0060(4)	.0060	.0040(5)	.0030	0	0
T(3)	.0021(2)	.0023(2)	.0044(3)	.0009(1)	-.0009(2)	-.0003(2)
T(4)	.0027(2)	.0033(2)	.0027(3)	.0016(2)	-.0012(2)	-.0005(2)
O(1)	.0113(18)	.0079(38)	.0105(29)	.0081(31)	-.0083(27)	-.0068(27)
O(2)	.0062(5)	.0120(6)	.0044(6)	.0061(5)	-.0021(7)	-.0018(8)
O(3)	.0066(8)	.0057(7)	.0183(15)	.0035(6)	.0001(8)	.0022(8)
O(4)	.0022(5)	.0022(4)	.0103(7)	.0005(4)	-.0004(5)	.0016(5)
O(5)	.0037(5)	.0069(6)	.0029(7)	.0038(4)	-.0005(5)	.0000(6)
O(6)	.0063(6)	.0044(5)	.0082(9)	.0038(5)	-.0011(6)	.0003(6)

*Standard errors in parentheses
** $\beta_{22} = {}^2\beta_{12} = \beta_{11}; \beta_{13} = \beta_{23} = 0$

TABLE 3

CATION-OXYGEN INTERATOMIC DISTANCES*

Na	O(1)	2.629 (27)		$T(2)$	O(1)	1.60 (3)
	O(2)	2.530 (5)		3	O(3)	1.669 (8)
	O(3)	2.686 (9)			ave.	1.651
	O(3)	2.722 (10)				
	O(4)	2.836 (8)		$T(3)$	O(2)	1.646 (9)
	O(4)	2.540 (9)			O(4)	1.644 (6)
	O(5)	2.472 (7)			O(5)	1.614 (5)
	O(6)	2.624 (8)			O(6)	1.608 (7)
K	3 O(2)	3.043 (4)			ave.	1.628
	3 O(5)	3.021 (7)				
	3 O(6)	2.986 (8)		$T(4)$	O(2)	1.706 (8)
					O(3)	1.702 (8)
$T(1)$	O(1)	1.74 (3)			O(5)	1.740 (7)
3	O(4)	1.683 (5)			O(6)	1.725 (5)
	ave.	1.697			ave.	1.718

*Standard errors in parentheses

tained in this study (Table 3) are indicative of a different Al–Si order–disorder relation. The average $T(3)$–O and $T(4)$–O distances (1.628 and 1.718 Å, respectively) are consistent with a high degree of order of Si and Al. Occupancies, calculated using the relation between average T–O distance and occupancy established by Jones (1968), are $Si_{0.84} Al_{0.16}$ and $Si_{0.27} Al_{0.73}$ for $T(3)$ and $T(4)$, respectively. Since $T(3)$ and $T(4)$ are on general positions, the average of the 4 independent T–O distances for each is relatively precise.

$T(1)$ and $T(2)$ are on 3–fold axes. Of the four T–O distances for each, three are symmetrically equivalent and the fourth is to O(1).

TABLE 4

O-T-O ANGLES AND O-O DISTANCES FOR TETRAHEDRA

$T(1)$			
	O(4)-O(1)	2.82(1) Å	111.4°(12)
	O(4)-O(1)	2.48(3)	93.0 (5)
	O(4)-O(1)	2.80(5)	109.7 (15)
	3 O(4)-O(4)	2.83(3)	113.7 (3)
$T(2)$			
	O(3)-O(1)	2.50(4)	100.1 (8)
	O(3)-O(1)	2.79(3)	117.6 (18)
	O(3)-O(1)	2.84(4)	120.4 (13)
	3 O(3)-O(3)	2.66(1)	105.7 (4)
$T(3)$			
	O(2)-O(4)	2.73(1)	112.5 (3)
	O(2)-O(5)	2.64(1)	108.1 (3)
	O(2)-O(6)	2.68(1)	110.6 (3)
	O(4)-O(5)	2.66(1)	109.6 (3)
	O(4)-O(6)	2.61(1)	106.6 (4)
	O(5)-O(6)	2.63(1)	109.5 (3)
$T(4)$			
	O(2)-O(3)	2.66(1)	102.5 (4)
	O(2)-O(5)	2.81(1)	109.4 (3)
	O(2)-O(6)	2.80(1)	109.4 (4)
	O(3)-O(5)	2.81(1)	109.7 (4)
	O(3)-O(6)	2.88(1)	114.7 (3)
	O(5)-O(6)	2.86(1)	110.9 (3)

The position of the latter atom is inaccurately determined, since it occupies a position slightly offset from the three–fold axis with a site occupancy factor of 1/3. As the refinement progressed, the position of $O(1)$ was subject to relatively large fluctuations about its final position. This positional disorder is reflected in the high standard errors for $O(1)$ distances. There is, therefore, only one relatively precise T–O distance for $T(1)$ and $T(2)$, and the relative Al–Si occupancies for these sites, determined from this distance are then relatively imprecise. Nevertheless, the $T(1)$–$O(4)$ and $T(2)$–$O(3)$ distances (1.683 and 1.669 Å, respectively) are indicative of a high degree of Al–Si disorder on both of those sites. The specific occupancies determined from the relation given by Jones are $Si_{0.49}Al_{0.51}$ and $Si_{0.58}Al_{0.42}$ for $T(1)$ and $T(2)$ respectively. We emphasize that these values are relatively imprecise since they are determined using only one T–O distance for each tetrahedron. A further complication is the pseudosymmetry, $P6_3/m$, discussed in detail by Dollase (1970). This requires that the $T(1)$–$O(4)$ and $T(2)$–$O(3)$ distances be pseudosymmetrically related, and thus they have a high correlation. Additional concern regarding the accuracy of these distances is implied by the fact that the Al–Si ratio determined from T–O distances is 7.1:8.9, whereas chemical analysis yields a ratio of 7.7:8.3.

Nevertheless, it is clear that the $T(1)$ and $T(2)$ sites have a higher degree of Al–Si disorder than the $T(3)$ and $T(4)$ sites. Relative Al–Si order–disorder for all refined nephelines has been discussed in detail by Dollase and Peacor (1971). Their results[1] show that the Monte Somma nepheline described in this study has the highest degree of disorder of all nephelines whose structures have been refined. This result is consistent with the high temperature, volcanic origin of this material. The degree of disorder is not great, however, as shown by the nearly complete ordering of the general $T(3)$ and $T(4)$ sites. Thus the range of possible Al–Si disorder in nephelines is severely restricted.

Domain structure

McConnell (1962) and Sahama (1958) observed weak and diffuse reflections with apparently irrational indices, flanking $00l$ reflections with $l = 2n$. These reflections suggest the presence of a domain structure in nepheline. Foreman and Peacor (1970) discussed the probable nature of these domains, and suggested that they result from ordering of vacancies on the K site. McConnell suggested that ordering of Al

[1] Refinement of the Monte Somma nepheline has changed the T–O distances reported in Dollase and Peacor (1971) by about one sigma but has not changed the conclusion.

and Si might be the cause of the domain structure. The refinements of four different nephelines using X–ray diffraction data, including this work, have all failed to provide direct conclusive evidence as to the nature of the domain structure. However, all nephelines not only show the presence of the extra reflections, but they also have several unusual features in common. These are:

1. Chemical analyses of naturally occurring nephelines invariably exhibit an excess of Si relative to Al compared to the commonly accepted idealized composition $KNa_3Al_4Si_4O_{16}$. Vacancies at the K sites maintain charge balance. Additional vacancies at the K sites may result from substitution of Ca^{2+} for Na^{1+}. The total number of vacancies is generally about one third of the available K sites.

2. The T–O distances for all structure refinements, when used to compute the tetrahedral site occupancies, yield values of total Al and Si which are inconsistent with totals derived from chemical analysis. The number of Si atoms per unit cell derived from T–O distances is as high as 8.9 compared to a maximum of 8.5 from chemical analyses (Dollase and Peacor, 1971).

3. The isotropic and equivalent isotropic temperature factors for all refined structures are exceptionally large. The values shown in Table 1 of this study are typical, and are generally about three times those which are usually determined for well–ordered silicate structures. These values are probably a result of positional disorder, averaged over domains. Corresponding temperature factors for the volcanic nepheline of this study, and those for the ordered nepheline of low–temperature origin studied by Foreman and Peacor, are nearly equal. The positional disorder must therefore be independent of relative Al–Si order–disorder, and characteristic of all nephelines.

4. O(1) is displaced from the three–fold axes in all structures refined, occupying one of three different off–axis positions in different unit cells. This displacement occurs even in the nepheline refined with data obtained at a temperature of about 900°C (Foreman and Peacor, 1970). Dollase (1970) has suggested that this displacement results from an adjustment of O(1) to form a Na–O(1) bond in response to a local charge imbalance.

The high temperature factors exhibited by all atoms of all the refined nephelines and the presence of diffuse superstructure reflections indicate the existence of a domain structure which is independent of Si–Al order–disorder. The differences between subcells are caused principally by positional displacements of all atoms. Two explanations, perhaps interrelated, are consistent with such positional differences.

First, Foreman and Peacor (1970) suggested that ordered vacancies at the K sites would result in a superstructure cell, whose volume relation to the substructure unit cell is consistent with the observed ratio of vacant to occupied K sites. Such vacancies at the K sites must directly give rise to shifts in the positions of $O(2)$, $O(5)$, and $O(6)$, which are normally coordinated to the K atom, and indirectly to those atoms bonded to these oxygens.

Secondly, the shift of $O(1)$ from an axial position results in an unusually distorted geometry for the $T(1)$ and $T(2)$ tetrahedra. Values of $O-T-O$ angles in Table 4 are exceptional when compared to angles characteristic of $(Al,Si)O_4$ tetrahedra in well refined silicate structures. For example an $O(4)-T(1)-O(1)$ angle is 93° and an $O(3)-T(2)-O(1)$ angle is 120°. Similar distortion is characteristic of other refined nepheline structures. The atoms $O(4)$ and $O(3)$ must shift in response to the displacement of $O(1)$. For each of the three off–axis positions of $O(1)$, there must be three slightly different locations for $O(3)$ and $O(4)$. The refined positions for these atoms, then, are an average over the three different locations. The unusual value of the $O(4)-T(1)-O(1)$ angle is thus only apparent since the position of $O(4)$ is an average one. The displacement of $O(1)$ from the three–fold axis therefore results directly in displacements of $O(3)$ and $O(4)$, and indirectly in shifts in the positions of other atoms bonded to these oxygens.

We emphasize that the evidence for these kinds of domain structure is only indirect. However, it is interesting that the two different kinds of positional disorder together directly affect all six independent oxygens. This effect is consistent with the occurrence of temperature factors which are uniformly high for all atoms. There does not appear to be a more direct causal relationship between the two types of displacement, however.

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