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NEPHELINE: STRUCTURE OF THREE SAMPLES FROM THE BANCROFT AREA, ONTARIO, OBTAINED USING SYNCHROTRON HIGH-RESOLUTION POWDER X-RAY DIFFRACTION

Sytle M. ANTAO[§]

Department of Geoscience, University of Calgary, Calgary, Alberta T2N 1N4, Canada

Ishmael HASSAN

Department of Chemistry, University of the West Indies, Mona, Kingston 7, Jamaica

Abstract

The crystal structure of three samples of nepheline (ideally, $K_2Na_6[Al_8Si_8O_{32}]$) from the Bancroft area of Ontario (1a, b: Egan Chute, 2: Nephton, and 3: Davis Hill), each with different types of superstructure reflections, has been studied using synchrotron high-resolution powder X-ray diffraction (HRPXRD) data and Rietveld structure refinement. The samples have different origins. The structure was refined in space group $P6_3$. The R_F^2 index, number of unique observed reflections, pseudohexagonal subcell parameters, and site-occupancy factor (sof) for the K site are as follows: Sample 1b: $R_F^2 = 0.0433$, $N_{obs} = 1399$, $a = 9.99567(1)$, $c = 8.37777(1)$ Å, $V = 724.907(2)$ Å^3, and K (sof) = 0.716(1). Sample 2: $R_F^2 = 0.0669$, $N_{obs} = 1589$, $a = 10.00215(1)$, $c = 8.38742(1)$ Å, $V = 726.684(1)$ Å^3, and K (sof) = 0.920(1). Sample 3: $R_F^2 = 0.0804$, $N_{obs} = 1615$, $a = 9.99567(1)$, $c = 8.37873(1)$ Å, $V = 724.991(1)$ Å^3, and K (sof) = 0.778(2). Sample 2 has the largest sof for K and the largest volume. The satellite reflections in the three nepheline samples were observed in the HRPXRD traces and give rise to different incommensurate superstructures. The Al and Si atoms in the T_3 and T_4 sites are ordered differently in the three samples, which may indicate the presence of a domain structure based on Al–Si order. The positions for the Al and Si atoms were interchanged in two samples because of the resulting <*T*–O> distances. The slight excess of Si over Al atoms, characteristically encountered in well-analyzed samples of nepheline, is reflected in the <*T*–O> distances.

Keywords: nepheline, crystal structure, incommensurate superstructure, Al–Si order, HRPXRD approach, Bancroft area, Ontario.

Sommaire

Nous avons étudié la structure cristalline de trois échantillons de néphéline (de composition idéale $K_2Na_6[Al_8Si_8O_{32}]$) de la région de Bancroft, en Ontario (1a, b: Egan Chute, 2: Nephton, et 3: Davis Hill), chacun avec des différences dans les réflexions dues à la surstructure, en utilisant la diffraction X à haute résolution sur poudre avec rayonnement synchrotron (HRPXRD) et un affinement de ces données par la méthode de Rietveld. Ces échantillons ont une origine distincte. La structure a été affinée dans le groupe spatial $P6_3$. L'indice R_F^2, le nombre de réflexions uniques observées, les paramètres de la sous-maille pseudo-hexagonale, et les facteurs d'occupation du site K (sof) suivent. Echantillon 1b: $R_F^2 = 0.0433$, $N_{obs} = 1399$, $a = 9.99567(1)$, $c = 8.37777(1)$ Å, $V = 724.907(2)$ Å^3, et K (sof) = 0.716(1). Echantillon 2: $R_F^2 = 0.0669$, $N_{obs} = 1589$, $a = 10.00215(1)$, $c = 8.38742(1)$ Å, $V = 726.684(1)$ Å^3, et K (sof) = 0.920(1). Echantillon 3: $R_F^2 = 0.0804$, $N_{obs} = 1615$, $a = 9.99567(1)$, $c = 8.37873(1)$ Å, $V = 724.991(1)$ Å^3, et K (sof) = 0.778(2). C'est l'échantillon 2 qui possède le facteur d'occupation du site K le plus élevé, et la maille la plus volumineuse. Les réflexions satellites des trois échantillons de néphéline, telles qu'observées dans les tracés HRPXRD, mènent à des surstructures incommensurables différentes. Les atomes de Al et de Si des sites T_3 et T_4 sites sont ordonnés différemment dans les trois échantillons, ce qui pourrait indiquer la présence de domaines différant dans leurs degrés d'ordre Al–Si. Les positions des atomes de Al et de Si sont interchangées dans deux des échantillons à cause des distances <*T*–O> qui en résultent. Le léger excédent de Si par rapport à Al qui caractérise les échantillons bien analysés de néphéline se voit dans le bilan des distances <*T*–O>.

(Traduit par la Rédaction)

Mots-clés: néphéline, structure cristalline, superstructure incommensurable, ordre Al–Si, technique HRPXRD, région de Bancroft, Ontario.

[§] *E-mail address*: antao@ucalgary.ca

INTRODUCTION

Nepheline, ideally $Na_3K[Al_4Si_4O_{16}]$, is an important rock-forming mineral that has wide occurrences in silica-poor alkaline igneous rocks, related pegmatites, and in alkali-metasomatized gneisses. Nepheline is an intermediate member of a solid solution that extends from $Na[AlSiO_4]$ to $K[AlSiO_4]$ (kalsilite). Both nepheline and kalsilite have a tridymite-type framework structure (*e.g.*, Sahama 1958, Capobianco & Carpenter 1989, McConnell *et al.* 1991, Carpenter & Cellai 1996, Xu & Veblen 1996).

Diffraction data from nepheline show satellite reflections with a wide range of intensity and sharpness (Sahama 1958, 1962, McConnell 1962, 1981, McConnell *et al.* 1991). The satellite reflections indicate that nepheline has a modulated structure with an incommensurate supercell. Various models have been proposed for the nepheline supercell (McConnell 1962, 1981, Parker & McConnell 1971, Parker 1972, Merlino 1984, McConnell *et al.* 1991, Hayward *et al.* 2000, Angel *et al.* 2008). These satellite reflections in nepheline were studied using single-crystal X-ray diffraction, high-resolution transmission electron microscopy (HRTEM), selected-area electron diffraction (SAED) patterns, and thermal analyses by Hassan *et al.* (2003). Currently, the origin of the satellite reflections in nepheline is not fully understood.

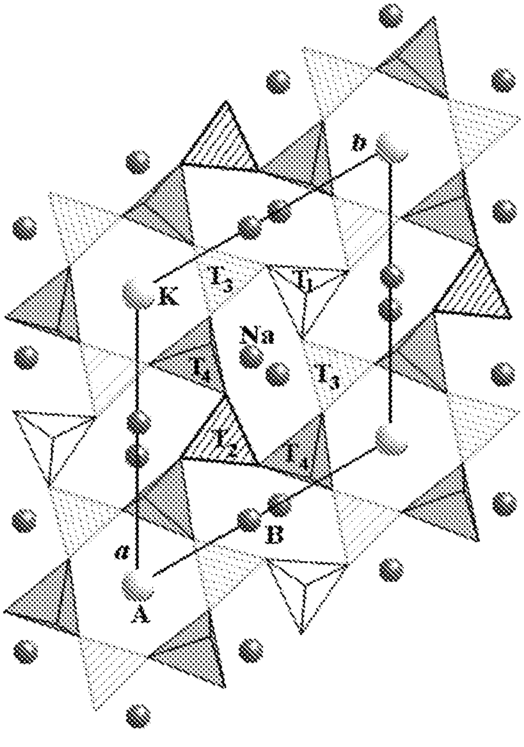

FIG. 1. Crystal structure of nepheline projected down the **c** axis. Site *A* is hexagonal and contains K atoms and vacancies, and site *B* is oval and contains the Na atoms. The T_2 and T_3 tetrahedra have apices pointing downward, and T_1 and T_4 point upward.

The aim of the present study is to compare the nepheline structure from three samples from the Bancroft area showing different developments of satellite reflections using high-resolution powder X-ray diffraction (HRPXRD) data and Rietveld refinement of the structure. The results indicate differences in Al–Si order and site-occupancy factors (sof) for the K site.

BACKGROUND INFORMATION

The crystal structure of nepheline was reviewed by Merlino (1984). The structure is a stuffed derivative of tridymite with approximately half the Si atoms replaced by Al, and with Na and K as interstitial charge-balancing cations (Buerger *et al.* 1954, Hahn & Buerger 1955, Schiebold 1930). The structure of nepheline consists of four independent tetrahedra (T = Al or Si) per unit cell (Fig. 1). The T_1 and T_2 sites occupy special positions on the three-fold axes, and T_3 and T_4 occupy general positions. The apices of the tetrahedra occupied by T_1 and T_4 cations are arranged in one direction along the **c** axis, and those occupied by T_2 and T_3 point in the opposite direction. The cavities in the framework are too large for the small Na atom to occupy their centers and still maintain proper bonding to the framework oxygen atoms located in the channel walls. Therefore, the framework is distorted by rotation of the framework tetrahedra about the six-fold axis, so the apical oxygen atoms, O1, are distributed slightly off the threefold axis toward one of the three neighboring Na atoms. In nepheline, two of the six-membered rings are hexagonal, and six are oval in shape. The Na atoms fully occupy six small oval *B* cavities, and the K atoms occupy two large hexagonal *A* cavities, thus giving $Na_6K_2[Al_8Si_8O_{32}]$ as an ideal composition for nepheline.

In nepheline, the Al and Si atoms are partially ordered over the tetrahedral sites. The T_1 and T_4 sites are Al-rich, and the T_2 and T_3 sites are Si-rich. The T_1–T_2 (not T_3–T_4) pair is bonded to the positionally disordered O1 atoms. In addition, the T_1 and T_2 tetrahedra are surrounded by only Na atoms, whereas the T_3 and T_4 tetrahedra are surrounded by both K and Na atoms (Fig. 1).

The structure of nepheline was refined for specimens from various geological origins (Dollase 1970, Foreman & Peacor 1970, Dollase & Peacor 1971, Simmons & Peacor 1972, Dollase & Thomas 1978, Gregorkiewitz 1984, Tait *et al.* 2003, Hassan *et al.* 2003, Angel *et al.* 2008). The structure of a Ge-substituted analog of nepheline is also available (Hammond & Barbier 1998). A comparison of the crystal structure of the nepheline crystals used indicates minor structural differences, such as in Al–Si distribution on the one hand, and K and vacancy distribution on the other, which suggest that the differences may be a function of bulk composition, growth conditions, or thermal history. These relationships are of interest because of their geological implications, but their exact effects and interplay are still unknown.

DESCRIPTION OF THE SAMPLES

In this study, we have examined three distinct samples of nepheline from the Bancroft area, in southeastern Ontario. The samples seem to have distinct origins. The first sample from Egan Chute on the York River, near Bancroft, is a constituent of a nepheline – scapolite – albite gneiss, and is of metasomatic origin. The white nepheline crystals are about 2 to 5 mm in size. The second sample is from Nephton, near Blue Mountain. The large crystals (2 to 3 cm; no rock sample was available) are greyish white and quite pure. The sample probably originated from a nepheline syenite quarry in Nephton that was used to supply nepheline for ceramic production (*e.g.*, American Nepheline Co., later called Indusmin Ltd). Presently, Unimin Canada Ltd. at Blue Mountain, Nephton, is mining nepheline syenite filler for the plastics industry. This sample thus appears to have formed from a nepheline syenitic magma. Keith (1939) reported on the petrology of the alkaline intrusive at Blue Mountain. Additional information on the nephelinized paragneisses of the Bancroft area is available (Gummer & Burr 1943, 1946). The third nepheline sample is from Davis Hill, near Bancroft. The crystals are quite large (3 × 3 × 3 cm; no rock sample was available) and hexagonal in shape, similar to that shown in Figure 14 of Moyd (1990). The color varies from pinkish white to grey; the nepheline seems to be of magmatic origin. Calcite-cored vein dikes containing large crystals of nepheline, biotite, and albite antiperthite crystals were reported from Davis Hill by Moyd (1949, 1990) and Gummer & Burr (1943, 1946). This Davis Hill nepheline sample appears to originate from a carbonate magma. The three samples used in this study thus are of distinct origins: (1) metasomatic (Egan Chute), (2) silica-undersaturated syenitic magma (Nephton), and (3) carbonate magma (Davis Hill).

EXPERIMENTAL

The structure of nepheline from the same bulk hand-specimen sample from Egan Chute (sample 1) was refined by Foreman & Peacor (1970) and Hassan *et al.* (2003). Sample 2 is from Nephton, and sample 3 is from Davis Hill. Results of analyses obtained on the same electron microprobe and using the same procedure are given in Table 1 (for details, see Hassan *et al.* 2003). Analyses made at about six different spots on each sample indicate that they are homogeneous. The chemical analysis of the Egan Chute nepheline reveals the presence of some Ca, unlike the other two samples. It is possible that the Egan Chute nepheline evolved from plagioclase during the metasomatic process.

Crystals of nepheline were hand-picked under a binocular microscope and finely ground in an agate mortar and pestle for synchrotron high-resolution powder X-ray diffraction (HRPXRD) experiments performed at beamline 11–BM, Advanced Photon Source, Argonne National Laboratory. The sample was loaded into a kapton capillary and rotated during the experiment at a rate of 90 rotations per second. The data were collected to a maximum 2θ of about 50° with a step size of 0.0005° and a step time of 0.07 s/step. Beamline optics consist of a platinum-coated collimating mirror, a dual Si (111) monochromator, and a platinum-coated vertically focusing mirror. The HRPXRD trace was collected with twelve silicon crystal analyzers that increase detector efficiency as well as reduce the angular range to be scanned and, therefore, allow rapid acquisition of data. A silicon and alumina NIST standard (ratio of $^1/_3$ Si to $^2/_3$ Al_2O_3) was used to calibrate the detector response, zero offset, and to determine the wavelength used in the experiment [λ = 0.40241(2) Å]. Data were merged by interpolating measured counts onto a regularly spaced grid and by applying corrections for small differences in wavelength (~1 eV). Additional details of the experimental set-up are given elsewhere (Antao *et al.* 2008, Lee *et al.* 2008, Wang *et al.* 2008).

RIETVELD STRUCTURE-REFINEMENT

The crystal structure was modeled using the Rietveld method (Rietveld 1969) that is incorporated in the GSAS program (Larson & Von Dreele 2000) and using the EXPGUI interface (Toby 2001). Initial structural parameters were taken from Hassan *et al.* (2003). The background was modeled with a Chebyschev polynomial. The reflection-peak profiles were fitted using a profile of type 3 in the GSAS program. The structure refinements were carried out by varying parameters in the following sequence: scale factor, background, cell, zero shift, profile, atomic positions, isotropic displacement parameters, and site-occupancy factor (sof) for the K site. Finally, all variables were refined simultaneously. Anisotropic displacement parameters are commonly not used in Rietveld refinements (Redfern *et al.* 1999, Fechtelkord *et al.* 2001, Antao *et al.* 2005). The isotropic displacement parameters were constrained so that U (Al1) = U (Si1), and U (Al2) = U (Si2). This constraint gives rise to reasonable and expected isotropic-displacement parameters for all the atoms in nepheline. The compositions obtained from the refinements agree well with the results of the chemical analyses. The cell parameters and other information regarding data collection and refinement are given in Table 2. The positional coordinates and isotropic displacement parameters are given in Table 3.

The bond distances are given in Table 4. The nepheline single-crystal (SXTL) structure obtained by Hassan *et al.* (2003) was re-refined using the new unit-cell parameters obtained from this study, and the results are included in the Tables.

Discussion

Bond-distances and site occupancies obtained by HRPXRD and single-crystal diffraction are of comparable accuracy (Antao *et al.* 2008). However, unit-cell parameters from HRPXRD are of higher accuracy than with the single-crystal method.

The cell parameters of the pseudohexagonal subcell of the three nepheline samples, although of similar magnitude, are different and related to the K content (Tables 1, 2). The K site contains various amounts of vacancies, □, and the Na site is fully occupied by Na atoms (Table 3). The sample with the largest sof for the K site has the largest volume, as expected (Tables 2, 3). The presence of small amounts of Ca atoms, which typically substitute for Na atoms, was not considered in the structure refinement because the Na site is filled with Na atoms, as indicated by the chemical analyses and also from refinement of the sof using the Na atom scattering curve. Bond-strength calculations by Hassan *et al.* (2003) indicate some interesting features in sample 1. The bond-strength sum for the Na site is 0.934 valence units (*vu*), which indicates that the Na^+ cation

TABLE 1. COMPOSITION OF THREE SAMPLES OF NEPHELINE FROM THE BANCROFT AREA, ONTARIO

Sample	1 Egan Chute	2 Nephton	3 Davis Hill		1 Egan Chute	2 Nephton	3 Davis Hill
SiO_2 wt.%	42.68	41.62	43.14	Si *apfu*	8.21	8.04	8.32
Al_2O_3	34.25	35.08	33.96	Al	7.77	7.98	7.72
Na_2O	16.23	16.24	16.10	Na	6.05	6.08	6.02
K_2O	5.38	7.44	6.20	K	1.32	1.83	1.53
CaO	1.09			Ca	0.22		
MnO	0.01			Mn	0.00		
P_2O_5	0.02			P	0.00		
Others	0.04						
Total	99.67	100.37	99.40				

On the basis of 32 atoms of oxygen, the formulae are as follows:
1. sample from Egan Chute: $(K_{1.32}\square_{0.68})(Na_{6.05}Ca_{0.22})[Al_{7.77}Si_{8.21}O_{32}]$,
2. sample from Nephton: $(K_{1.83}\square_{0.17})(Na_{6.08})[Al_{7.98}Si_{8.04}O_{32}]$,
3. sample from Davis Hill: $(K_{1.53}\square_{0.47})(Na_{6.02})[Al_{7.72}Si_{8.32}O_{32}]$.

TABLE 2. UNIT-CELL AND RIETVELD PARAMETERS FOR THE THREE SPECIMENS OF NEPHELINE FROM THE BANCROFT AREA

	SXTL Egan Chute 1a	HRPXRD Nephton 2	HRPXRD Egan Chute 1b	HRPXRD Davis Hill 3
N_{obs}	736	1589	1399	1615
R_F^2	R1 = 0.0415	0.0669	0.0433	0.0804
a (Å)	9.99567(1)	10.00215(1)	9.99567(1)	9.99567(1)
c (Å)	8.37777(1)	8.38742(1)	8.37777(1)	8.37873(1)
c/a	0.83814	0.83856	0.83814	0.83824
V (Å)^3	724.907(2)	726.684(1)	724.907(2)	724.991(1)

The structure was refined in space group *P*6$_3$. Mo*K*α radiation was used for the single-crystal (SXTL) data; for the HRPXRD data, λ = 0.40241(2) Å.

TABLE 3. ATOM COORDINATES AND U PARAMETERS (Å^2) FOR THE THREE SPECIMENS OF NEPHELINE

		1a	2	1b	3
Al1	*x*	2/3	2/3	2/3	2/3
	y	1/3	1/3	1/3	1/3
	z	**0.1903(7)**	**0.1875(3)**	**0.8057(3)**	**0.8035(4)**
	U	0.011(1)	0.0100(1)	0.0114(2)	0.0096(2)
Si1	*x*	2/3	2/3	2/3	2/3
	y	1/3	1/3	1/3	1/3
	z	**0.8020(6)**	**0.7984(2)**	**0.1901(3)**	**0.1934(3)**
	U	0.013(1)	0.0100(1)	0.0114(2)	0.0096(2)
Si2	*x*	0.3339(3)	0.3337(2)	0.3374(2)	0.3305(2)
	y	0.0938(2)	0.0927(2)	0.0970(2)	0.0929(2)
	z	**0.3103(2)**	**0.3104(1)**	**0.6852(2)**	**0.6842(2)**
	U	0.012(1)	0.00938(6)	0.01031(8)	0.00880(8)
Al2	*x*	0.3321(3)	0.3332(2)	0.3307(1)	0.3369(2)
	y	0.0931(3)	0.0938(2)	0.0916(2)	0.0948(2)
	z	**0.6839(2)**	**0.6842(2)**	**0.3111(2)**	**0.3105(2)**
	U	0.011(1)	0.00938(6)	0.01031(8)	0.00880(8)
K1	*x*	0	0	0	0
	y	0	0	0	0
	z	0.9918(14)	0.9950(3)	1.0006(4)	0.9992(4)
	U	0.027(1)	0.0202(2)	0.0263(3)	0.0209(4)
	sof	0.685(2)	0.920(1)	0.716(1)	0.778(2)
Na1	*x*	0.4430(2)	0.44424(7)	0.44318(6)	0.44381(8)
	y	0.9970(2)	0.99778(8)	0.99665(8)	0.9973(1)
	z	0.9957(11)	1.0019(4)	0.9893(4)	0.9987(4)
	U	0.023(1)	0.02620(2)	0.0227(2)	0.0259(2)
O1	*x*	0.7102(10)	0.7073(5)	0.7154(4)	0.7125(6)
	y	0.3399(16)	0.3371(9)	0.3371(7)	0.3452(11)
	z	0.9920(40)	0.9874(6)	1.0054(6)	1.0063(14)
	U	0.030(3)	0.028(1)	0.027(1)	0.022(1)
O2	*x*	0.3174(5)	0.3159(1)	0.3199(1)	0.3166(1)
	y	0.0271(4)	0.0261(1)	0.0310(1)	0.0280(1)
	z	0.4912(15)	0.4995(4)	0.5008(5)	0.4996(6)
	U	0.029(1)	0.0245(3)	0.0318(3)	0.0234(2)
O3	*x*	0.5237(6)	0.5236(3)	0.5154(3)	0.5138(3)
	y	0.1730(7)	0.1759(3)	0.1655(3)	0.1672(3)
	z	0.7358(17)	0.7223(3)	0.7182(3)	0.7198(3)
	U	0.033(2)	0.0313(7)	0.0346(7)	0.0234(2)
O4	*x*	0.5095(7)	0.5112(2)	0.5188(3)	0.5195(3)
	y	0.1621(7)	0.1627(3)	0.1751(3)	0.1734(3)
	z	0.2493(17)	0.2390(3)	0.2362(2)	0.2347(3)
	U	0.032(2)	0.0225(6)	0.0274(8)	0.0234(2)
O5	*x*	0.2859(7)	0.2861(2)	0.2852(3)	0.2663(4)
	y	0.2273(8)	0.2235(3)	0.2308(4)	0.2236(4)
	z	0.3117(14)	0.3140(2)	0.3046(3)	0.3008(3)
	U	0.020(1)	0.0136(6)	0.0310(9)	0.0234(2)
O6	*x*	0.2680(7)	0.2651(2)	0.2680(3)	0.2834(4)
	y	0.2238(8)	0.2235(2)	0.2182(4)	0.2252(4)
	z	0.6884(14)	0.6938(2)	0.6862(3)	0.6828(4)
	U	0.022(1)	0.0159(6)	0.0153(7)	0.0234(2)

The occupancy for each of Al1, Si1 and O1 is 1/3. Other sites are fully occupied, except for the K1 site. The positions of the *T* sites (shown in bold) in the 1b and 3 structure are interchanged when compared to the 1a and 2 structure because of the resulting <*T*–O> distances. Al1 and Al2 are in some cases referred to as T_1 and T_4, respectively, and Si1 and Si2, as T_2 and T_3, respectively.

TABLE 4. BOND DISTANCES [Å] AND ANGLES [°] IN NEPHELINE

	SXTL 1a	HRPXRD 2	HRPXRD 1b	HRPXRD 3	
Al1–O1 ×3	1.71(3)	1.723(6)	1.737(6)	1.748(13)	Al1–O1 ×1
† Al1–O4 ×3	**1.718(7)**	**1.692(2)**	**1.761(2)**	**1.746(3)**	*** Al1–O3 × 3**
<Al1–O>	1.716	1.700	1.755	1.746	<Al1–O>
Si1–O1 ×3	1.64(3)	1.633(5)	1.617(6)	1.621(13)	Si1–O1 ×1
*** Si1–O3 ×3**	**1.621(7)**	**1.637(2)**	**1.580(2)**	**1.577(2)**	**† Si1–O4 ×3**
<Si1–O>	1.626	1.636	1.589	1.588	<Si1–O>
Si2–O2	1.631(12)	1.695(3)	1.655(4)	1.656(5)	Si2–O2
† Si2–O4	**1.615(8)**	**1.660(3)**	**1.579(2)**	**1.624(3)**	*** Si2–O3**
Si2–O5	1.628(6)	1.601(3)	1.678(3)	1.576(3)	Si2–O5
Si2–O6	1.624(9)	1.579(2)	1.670(3)	1.611(3)	Si2–O6
<Si2–O>	1.625	1.634	1.645	1.617	<Si2–O>
Al2–O2	1.722(12)	1.665(3)	1.684(4)	1.692(5)	Al2–O2
*** Al2–O3**	**1.722(7)**	**1.684(3)**	**1.749(3)**	**1.708(3)**	**† Al2–O4**
Al2–O5	1.719(9)	1.767(2)	1.667(3)	1.752(3)	Al2–O5
Al2–O6	1.720(6)	1.743(3)	1.664(3)	1.738(4)	Al2–O6
<Al2–O>	1.721	1.715	1.691	1.723	<Al2–O>
Na1–O1	2.567(9)	2.585(4)	2.520(3)	2.551(4)	Na1–O1
Na1–O2	2.525(4)	2.527(1)	2.520(1)	2.531(1)	Na1–O2
Na1–O3	2.659(16)	2.809(4)	2.703(3)	2.765(4)	Na1–O3
Na1–O3	2.758(14)	2.665(4)	2.673(3)	2.648(4)	Na1–O3
Na1–O4	2.565(16)	2.454(4)	2.585(4)	2.500(4)	Na1–O4
Na1–O4	2.788(14)	2.890(4)	2.870(3)	2.926(3)	Na1–O4
Na1–O5	2.477(10)	2.528(3)	2.465(4)	2.622(4)	Na1–O5
Na1–O6	2.583(11)	2.598(3)	2.637(4)	2.500(4)	Na1–O6
<Na–O>	2.615	2.632	2.622	2.630	<Na–O>
K1–O2 ×3	3.046(4)	3.0376(9)	3.0543(9)	3.035(1)	K1–O2 ×3
K1–O5 ×3	3.019(10)	3.015(3)	3.093(3)	2.982(4)	K1–O5 ×3
K1–O6 ×3	2.984(11)	2.980(3)	2.917(3)	3.014(4)	K1–O6 ×3
<K–O>	3.016	3.011	3.021	3.010	<K–O>
O1–O1	0.704(14)	0.674(5)	0.814(4)	0.713(7)	O1–O1
Al1–O1–Si1	151.9(5)	153.2(2)	147.4(2)	151.7(3)	Al1–O1–Si1
Si2–O2–Al2	138.0(2)	137.91(6)	139.64(6)	138.63(8)	Si2–O2–Al2
Si1–O3–Al2	140.4(5)	140.7(2)	136.9(2)	139.5(2)	Si1–O3–Al2
Al1–O4–Si2	140.4(5)	140.1(2)	144.1(2)	142.0(2)	Al1–O4–Si2
Si2–O5–Al2	141.0(8)	140.8(2)	145.2(2)	143.4(2)	Si2–O5–Al2
Si2–O6–Al2	141.7(8)	143.2(2)	140.3(2)	141.6(2)	Si2–O6–Al2
<*T*–O–*T*>	142.23	142.65	142.24	142.80	<*T*–O–*T*>

* Bonded to O3 and † bonded to O4 (they are shown in bold) because the *T* positions are interchanged (see Table 3).

is slightly underbonded, and may be compensated by substituting a small amount of Ca^{2+} cations on the Na site. The chemical analyses do show some Ca atoms in sample 1 (Table 1). The significant feature is that the K site is severely underbonded (0.831 *vu* compared to the expected 1 *vu*). The K site, therefore, is not expected to be filled with K^+ cations or contain Na^+ and Ca^{2+} cations, because the charge will not be satisfied. To satisfy the charge on the K site, vacancies must be present. The 0.831 *vu* for sample 1 indicates a sof of 0.64 compared to 0.66 obtained from chemical analysis and 0.675 from refinement (see Hassan *et al.* 2003).

If the positional coordinates are compared for each dataset, they are seen to be similar (Table 3). After the <*T*–O> distances were computed, the Al1 and Si1 positions on one hand and Al2 and Si2 positions on the other had to be interchanged in two refinements because of the resulting <*T*–O> distances (see Table 3). The long and short distances correspond to Al and Si atoms, respectively. The average <K–O> and <Na–O> distances are similar for all four datasets obtained from the three samples (Table 4).

Because of the similar X-ray scattering factors of Al and Si atoms, their <*T*–O> distances are used to determine *T*-site occupancies. Usually a distance of about 1.74 Å corresponds to pure Al occupancy, and 1.61 Å corresponds to pure Si occupancy. Replacing the Al by Si atoms have little effect on the resulting <*T*–O> distances because of the similar scattering factors. However, one needs to keep track of the *T* sites.

Major differences occur in the <T–O> distances. These differences do not reflect the different experimental methods used to obtain the structural parameters, but reflect the presence of a domain structure based on Al–Si order. We have recently refined the structures of several minerals using HRPXRD data and compared the results with SXTL data and found that identical results were obtained for structures that are well known (Antao *et al.* 2008). This gives us confidence to state that the differences among samples that we observed for nepheline in this study are real and significant.

Tait *et al.* (2003) have shown that in nepheline of all origins, the degree of Al–Si order is high. Nuclear magnetic resonance (NMR) spectroscopic data also indicate high degrees of Al–Si order in natural and synthetic samples of nepheline (Hovis *et al.* 1992, Lippmaa *et al.* 1980, Stebbins *et al.* 1986). Previous studies have shown that the number of Si atoms derived from <T–O> distances is as high as 8.9 compared to a maximum of 8.5 from chemical analyses (*e.g.*, Dollase & Peacor 1971, Simmons & Peacor 1972).

The occupancies of the T sites can be inferred from the <T–O> distances, as is commonly done for feldspars. Nepheline is a framework aluminosilicate, as is sodalite, so the <T–O> distances 1.6100(2) Å for 100% Si and 1.7435(2) Å for 100% Al, as observed in sodalite (Antao *et al.* 2008), were used to obtain the T-site occupancies (Tables 5, 6). Comparing the single-crystal and powdered samples, the normalized sum of the site occupancies are nearly identical (Table 6; samples # 10 and 11), but they do not fully agree with the results of chemical analyses, which invariably indicate a slight excess of Si over Al atoms in nepheline, as was noted in several studies (see Fig. 2 in Hassan *et al.* 2003). The <T–O> distances for all previous refinements, when used to calculate occupancies of the tetrahedral sites, gave values of total Al and Si that are inconsistent with totals derived from chemical analyses. However, this effect can now be rectified in the following way.

We assume that the T_1 and T_2 sites are fully ordered, whereas the T_3 and T_4 sites are partially disordered in their Al,Si population. The observed <T_1–O> and <T_2–O> distances are considered misleading because the O1 site may be positionally modulated, such that the O1 position is not accurate. With those assumptions, there are six each of Al and Si atoms at the T_1 and T_2 sites. Using <T_3–O> and <T_4–O> distances to calculate occupancies at the T_3 and T_4 sites, the resulting occupancies based on <T–O> distances are similar to the results of the chemical analyses (Tables 5, 6; sample #10 has 1.03 versus 1.03, and sample #11 has 1.03 versus 1.06). The excess Si over Al, as commonly observed in chemical findings, is now confirmed for the first time. There are two exceptions (samples #6 and 11), where

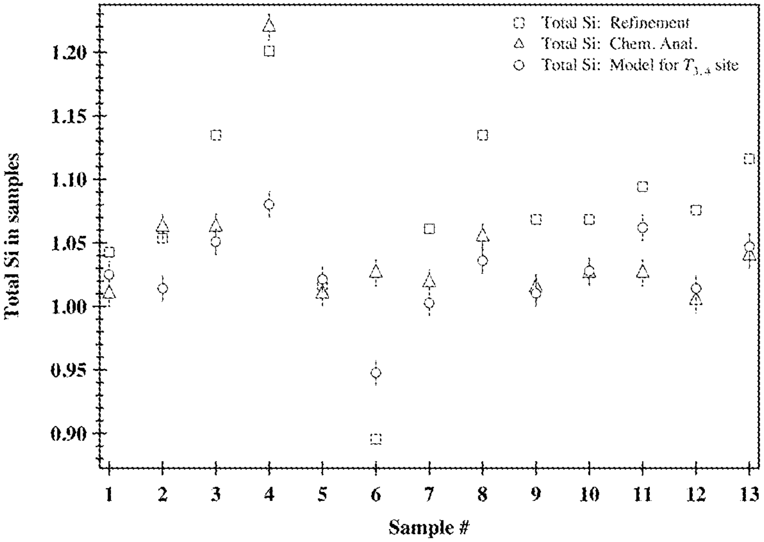

FIG. 2. The excess total Si over Al atoms in nepheline. The total amount of Si based on <T–O> distances obtained from refinement (squares) is invariably greater than that obtained from chemical analyses (triangles). If the T_1 and T_2 sites are assumed to be fully ordered with Al and Si atoms, then the total amount of Si based on <$T_{3/4}$–O> distances (circles) compare well with the chemical analyses within the ±0.015 error bars shown. Exceptions (#2, 4, and 6) are explained in the text. Sample numbers are explained in Table 5, and the values plotted are given in Table 6 for both Figures 2 and 3.

TABLE 5. CHEMICAL COMPOSITION AND MEAN BOND-DISTANCES (Å) IN NEPHELINE*

No.	*A* site	*B* site	Framework	T_1	T_2	T_3	T_4	*R*
1	$[K_{1.28}\square_{0.72}]$	$[Na_{5.36}Ca_{0.28}]_{\Sigma5.64}$	$[Al_{7.92}Si_{8.08}]O_{32}$	1.697	1.651	1.628	1.718	0.062
2	$[K_{1.40}\square_{0.60}]$	$[Na_{5.50}Ca_{0.30}]_{\Sigma5.80}$	$[Al_{7.50}Si_{8.50}]O_{32}$	1.693	1.649	1.624	1.725	0.080
3	$[Na_{1.50}\square_{0.50}]$	$[Na_{5.80}Ca_{0.20}]_{\Sigma6.00}$	$[Al_{7.50}Si_{8.50}]O_{32}$	1.680	1.650	1.625	1.714	0.074
4	$[K_{0.24}\square_{1.76}]$	Na_6	$[Al_{6.24}Si_{9.76}]O_{32}$	1.629	1.691	1.664	1.667	0.063
5	$[K_{0.96}Na_{0.96}\square_{0.08}]$	Na_6	$[Al_{7.92}Si_{8.08}]O_{32}$	1.730	1.624	1.621	1.726	0.064
6	$[K_{1.32}\square_{0.68}]$	$[Na_{6.05}Ca_{0.22}]_{\Sigma6.27}$	$[Al_{7.77}Si_{8.21}]O_{32}$	1.725	1.642	1.623	1.744	0.053
7	$[K_{1.91}\square_{0.09}]$	$Na_{6.04}$	$[Al_{7.72}Si_{8.15}]O_{32}$	1.731	1.606	1.616	1.736	0.018
8	$[K_{1.60}\square_{0.40}]$	$[Na_{6.21}Ca_{0.06}]_{\Sigma6.27}$	$[Al_{7.43}Si_{8.44}]O_{32}$	1.723	1.603	1.615	1.728	0.027
9	$[K_{1.76}\square_{0.24}]$	$[Na_{5.86}Ca_{0.13}]_{\Sigma5.99}$	$[Al_{7.84}Si_{8.12}]O_{32}$	1.732	1.605	1.616	1.734	0.017
10	$[K_{1.32}\square_{0.68}]$	$[Na_{6.05}Ca_{0.22}]_{\Sigma6.27}$	$[Al_{7.77}Si_{8.21}]O_{32}$	1.716	1.626	1.625	1.721	0.042
11	$[K_{1.32}\square_{0.68}]$	$[Na_{6.05}Ca_{0.22}]_{\Sigma6.27}$	$[Al_{7.77}Si_{8.21}]O_{32}$	1.755	1.589	1.645	1.691	0.043
12	$[K_{1.83}\square_{0.17}]$	$Na_{6.08}$	$[Al_{7.98}Si_{8.04}]O_{32}$	1.700	1.636	1.634	1.715	0.067
13	$[K_{1.53}\square_{0.47}]$	$Na_{6.02}$	$[Al_{7.72}Si_{8.32}]O_{32}$	1.746	1.588	1.617	1.723	0.080

1. Monte Somma, Italy (Simmons & Peacor 1972). 2. Larvik, Norway (Dollase 1970). 3. Na^+-exchanged Larvik nepheline (Dollase & Peacor 1971, Dollase & Thomas 1978). 4. Hydrothermally synthesized (Dollase & Thomas 1978). 5. Synthesized from NaF (Gregorkiewitz 1984). 6. Bancroft, Ontario, Canada (Foreman & Peacor 1970); chemical formula is as for our sample, as both are from the same sample. 7. Khibina–Lovozero complex, Kola Peninsula, Russia (Tait *et al.* 2003). 8. Bancroft, Ontario (Tait *et al.* 2003). 9. Monte Somma, Italy (Tait *et al.* 2003). 10 (= 1a). Egan Chute, Bancroft, Ontario (SXTL, this study, based on HRPXRD-derived unit-cell parameters). 11 (= 1b). Egan Chute, this study, based on HRPXRD Rietveld refinement. 12 (= 2). Nephton, Bancroft, Ontario (this study). 13 (= 3). Davis Hill, Bancroft, Ontario (this study). T_1 (= Al1) and T_4 (= Al2) are Al-rich; T_2 (= Si1) and T_3 (= Si2) are Si-rich (see text). * Our sample 1 (= 10, 11) is from a coarse-grained gneiss (size of nepheline of crystals 2–5 mm), whereas the other samples (12 and 13) are from a pegmatite (size of nepheline crystals 2–3 cm; no rock sample was available).

TABLE 6. *T*-SITE OCCUPANCIES BASED ON <*T*–O> DISTANCES*

Sample no.	1	2	3	4	5	6	7	8	9	10	11	12	13
Refinement													
Al1 = T_1	0.35	0.38	0.47	0.85	0.11	0.14	0.10	0.16	0.09	0.21	-0.08	0.33	-0.01
Si1 = T_2	0.69	0.70	0.69	0.39	0.89	0.75	1.02	1.04	1.03	0.87	1.14	0.80	1.15
Si2 = T_3	0.86	0.89	0.88	0.59	0.91	0.89	0.94	0.95	0.94	0.88	0.73	0.81	0.94
Al2 = T_4	0.19	0.14	0.22	0.57	0.13	0.00	0.06	0.12	0.08	0.17	0.39	0.22	0.16
Total Si	1.04	1.05	1.13	1.20	1.02	0.90	1.06	1.13	1.07	1.07	1.09	1.08	1.12
Si in Cell	8.34	8.43	9.08	9.61	8.14	7.16	8.49	9.08	8.55	8.55	8.75	8.61	8.93
Chemical analysis													
Total Si	1.01	1.06	1.06	1.22	1.01	1.03	1.02	1.06	1.02	1.03	1.03	1.01	1.04
Si in Cell	8.08	8.50	8.50	9.76	8.08	8.21	8.15	8.44	8.12	8.21	8.21	8.04	8.32
Model†													
Total Si	1.03	1.01	1.05	1.08	1.02	0.95	1.00	1.04	1.01	1.03	1.06	1.01	1.05
Si in Cell	8.20	8.11	8.41	8.64	8.17	7.58	8.02	8.29	8.08	8.22	8.49	8.11	8.38

* The *T*–O distance for 100% Si is taken to be 1.6100 Å, and that for 100% Al, 1.7435 Å. The entries are reported as (Si/100); the Al values are 1 – (Si/100) and are not given. † Calculated based on full occupancy of the Al1 and Si1 sites by 100% each for Al and Si, respectively, and partial disorder of Al and Si atoms at the Al2 and Si2 sites based on bond distances. Sample numbers correspond to those in Table 5.

the total amount of Si atoms from refinement (and bond distances) indicates a deficiency (Fig. 2).

Using the <$T_{3,4}$–O> distances reported for published structure of nepheline (Table 5), we used the above method to calculate the excess Si atoms. The results are presented in Table 6 and shown graphically in Figures 2 and 3. If we assume a reasonable error of ±0.015 *apfu* for the total amount of Si at the *T* sites and

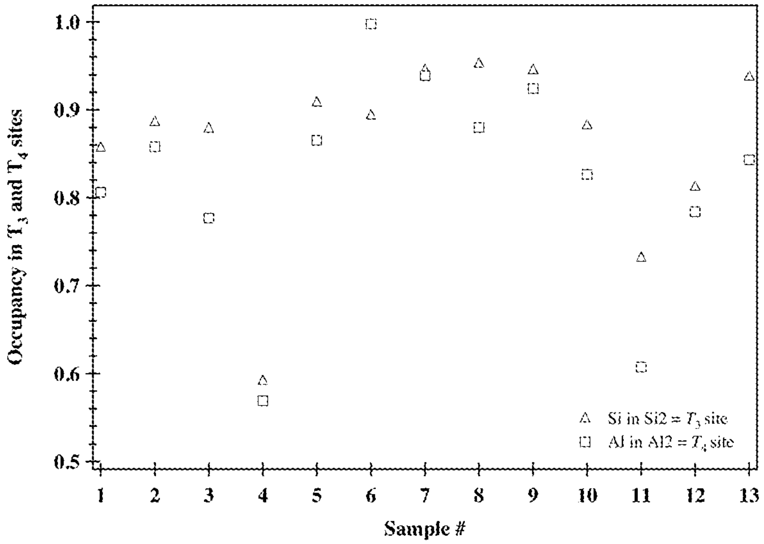

FIG. 3. The degree of order of Al and Si atoms at the T_3 and T_4 sites. The degree of order is high at both sites. Exceptions are explained in the text. The significant feature is that the single-crystal sample (#10) has a different order than the powdered sample (#11) because of the presence of possible APBs.

in that obtained from chemical analysis, the amount of Si reported in chemical analyses matches that obtained by the present calculation for nearly all the samples. The exceptions are samples #2, 4, and 6. Sample #4 has an unusual composition and is a synthetic sample (Table 5). For samples #2 and 6, the calculated amounts can match if the errors are increased (Fig. 2). We therefore conclude that the excess Si over Al, as observed in the chemical data on nepheline, can be accounted for by examining distances for the partially disordered T_3 and T_4 sites and assuming that the T_1 and T_2 sites are fully ordered.

The amount of disorder at the T_3 and T_4 sites is shown in Figure 3 in terms of Si and Al occupancies. The degree of order is quite high in most samples. Again, sample #4 is unusual, as mentioned above. The interesting observation is that the powdered sample (#11) is quite disordered compared to its single-crystal counterpart (#10). No difference in Al–Si order is expected between single crystal and powdered samples. The observed apparent differences in Al–Si order may arise from antiphase domain boundaries (APBs), which may be observed by TEM. If such APBs are destroyed on heating, then perfect Al–Si order is observed in nepheline (see Hassan & Antao 2010).

Based on full Al–Si order at the T_1 and T_2 sites and partial order at the T_3 and T_4 sites, the Al-avoidance rule may be broken at the APBs. However, when such APBs are destroyed, full Al–Si order is achieved at all T sites.

The excess Si over Al is balanced by vacancies at the A sites, as indicated by ☐ in the general formula, $\mathrm{Na_xK_yCa_z\square_{8-(x+y+z)}Al_{(x+y+2z)}Si_{16-(x+y+2z)}O_{32}}$ (see Deer *et al.* 1992). Further vacancies arise from substitution of Ca for Na atoms. For the single-crystal data on the Egan Chute nepheline, the proportion of vacancies found at the K site is 0.63 per formula unit, which requires the following theoretical charge-balanced formula: $\mathrm{(K_{1.37}\square_{0.63})Na_6[Al_{7.37}Si_{8.63}O_{32}]}$. The formula obtained by electron microprobe (EMP) analyses is $\mathrm{(K_{1.32}\square_{0.68})(Na_{6.05}Ca_{0.22})[Al_{7.77}Si_{8.21}O_{32}]}$, and in our calculation based on the present structure-refinement data, the formula $\mathrm{(K_{1.37}\square_{0.63})Na_6[Al_{7.78}Si_{8.22}O_{32}]}$ was obtained [see Tables 3 (#1a), and 6 (#10)], and it agrees with the EMP results. Small amounts of Ca atoms, detected by chemical analysis, will not have a significant effect on the above results or calculations.

Nepheline contains satellite reflections with irrational indices that give rise to a variety of modulated or incommensurate superstructures (Figs. 4a, b). The origins of the satellite reflections are not known in detail. As these reflections are observed with synchrotron HRPXRD, we have followed their disappearance with temperature and examined the resulting phase-transitions that occur with their disappearances. The results are given in a companion paper (Hassan & Antao 2010). In recent studies, the satellite reflections in nepheline were attributed to the O1 site (Gatta & Angel 2007), as was also suggested by Hassan *et al.* (2003), whereas

Angel *et al.* (2008) indicated that the satellites arise from a displacive modulation of the framework tetrahedra. We obtained interesting high-temperature structural results on all three nepheline samples mentioned in this paper. The results for the Egan Chute sample indicate the presence of three different sets of satellite reflections; two sets disappear at different temperatures, and one set remains up to 900°C. Different satellite reflections arise from (1) positional modulations of the O1 site, (2) K – □ order, and (3) Al–Si order (Hassan & Antao 2010).

The three samples used in this study are of distinct origins: (1) metasomatic (Egan Chute), (2) silica-undersaturated syenitic magma (Nephton), and (3) carbonate magma (Davis Hill). Their cell parameters are different, they contain different amounts of vacancies (and K content), and their satellite reflections are different. The cell volume for the Egan Chute, Nephton, and Davis Hill nepheline are 724.907(2), 726.684(1), and 724.991(1) Å^3, respectively, and their corresponding K (*sof* values) are 0.716(1), 0.920(1), and 0.778(2), respectively.The largest volume corresponds to the highest K (*sof*), which occurs in the Nephton sample. The higher temperature syenitic magma caused the structure to expand and incorporate the largest proportion of K atoms during the formation of nepheline sampled at Nephton. The composition of the Nephton sample and the temperature of formation are similar to those from Monte Somma, Italy (sample #9 in Table 5). Similarly, the lower-temperature metasomatic Egan Chute sample contains the least amount of K atoms, whereas the reworked carbonate magma at Davis Hill probably crystallized nepheline at a slightly higher temperature than that at Egan Chute.

CONCLUSIONS

The average structure of nepheline shows that, except for the O1 oxygen atom and some vacancies at the K site, all the other atoms in nepheline are well defined and contain no unusual features. If we assume that T_1 and T_2 are fully ordered with Al and Si atoms, then an excess Si over Al is observed using the $<T_{3,4}$–O> distances. The variable $<T_{3,4}$–O> distances indicate a domain structure for nepheline based on Al–Si order. In some samples, the *T* positions have to be interchanged to produce reasonable <*T*–O> distances that indicate the location of the Al and Si atoms. The satellite reflections in nepheline are easily observed in HRPXRD traces. Both the domain structure based on Al–Si order and the origin of the satellite reflections in nepheline are best analyzed using high-temperature structural data (see Hassan & Antao 2010).

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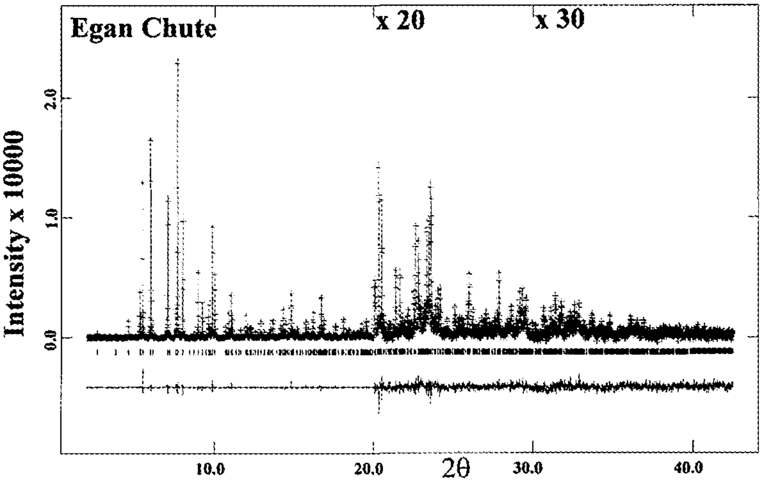

FIG. 4a. HRPXRD trace over a large range of 2θ for nepheline sample from Egan Chute at room temperature.

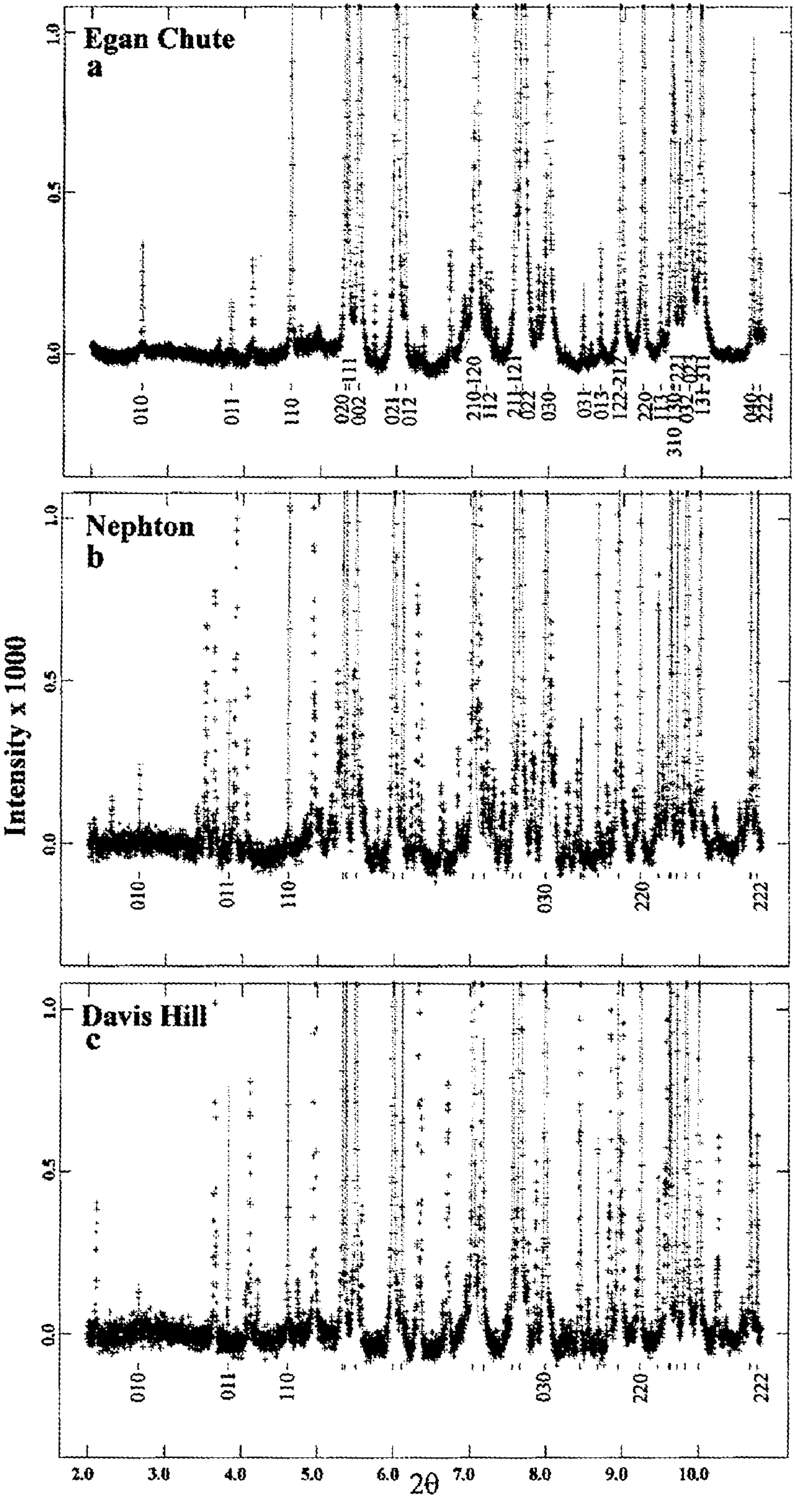
Egan Chute
a
Nephton
b
Davis Hill
c
Intensity x 1000
2θ
0.0
0.5
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
010
011
110
020=111
002
021
012
210-120
112
211-121
022
030
031
013
122-212
220
113
310
130=221
032-023
131-311
040
222

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Fig. 4b. HRPXRD traces for nepheline samples at room temperature over a small range of 2θ showing the superstructure reflections in (a) Egan Chute, (b) Nephton, and (c) Davis Hill samples. Calculated (continuous) and observed (crosses) profiles are shown. The difference curve ($I_{obs} - I_{calc}$) is shown at the bottom. The short vertical lines indicate the positions of the allowed reflections and Miller indices (no bars on any index) for the subcell. The satellite reflections are unmarked and not fitted; about 12 satellite reflections are contained in each trace.

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