

The crystal structure of a K-poor Ca-rich silicate with the nepheline framework, and crystal-chemical relationships in the compositional space $(K, Na, Ca, \square)_8(Al, Si)_{16}O_{32}$

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Abstract : The crystal structure of a K-poor Ca-rich tectosilicate ($a = b = 9.982$, $c = 8.364$ Å, space group $P6_3$) with composition close to $Ca_7\square_1Na_6Al_8Si_8O_{32}$ has been refined using 364 independent reflections collected by a single-crystal X-ray diffractometer. The anisotropic refinement yielded a final R factor equal to 0.037 for the observed reflections. The tetrahedral framework is the same as that of nepheline, but the distribution of the Ca, Na, and K cations is quite unusual : the large A cavity is here statistically occupied by $(Ca + Na + K + \square)$, with one position at the K position of ordinary nephelines but occupied by $(Ca + Na + \text{minor } K + \square)$, and a second position labelled Ca' and occupied by $(Ca + Na + \square)$ displaced along the z axis at approximately 1.25 Å from the K position.

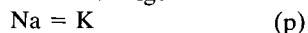
A review of the crystal structures in the compositional space $(K, Na, Ca, \square)_8(Al, Si)_{16}O_{32}$, which includes kalsilite, nepheline, lisetite, anorthite, tridymite and many polymorphs thereof, is also presented. This reveals that compositions close to the K_2Na_6 -, Na_2Na_6 - and $Ca_1\square_1Na_6$ - end-members distinguish themselves by having respectively "centred", "off-centred" and "displaced" cations in the large cation site.

Key-words : crystal structure, nepheline, feldspathoid, tectosilicate.

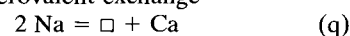
1. Introduction

The compositional space $(K, Na, Ca, \square)_8(Al, Si)_{16}O_{32}$ may be conveniently projected by a tetrahedron formed by a $K_8Na_8Ca_4\square_4$ basal triangle, where $Al = Si = 8$, lying below the apex $\square_8Si_{16}O_{32}$ which represents tridymite and all the other polymorphs of SiO_2 (Fig. 1a). The Na_8 apex may be regarded as the origin for considering the various cation exchanges involved.

Within the Al_8Si_8 basal triangle, the possible chemical substitution are best represented by the common homovalent exchange

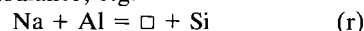


and by the heterovalent exchange



which relates lisetite to anorthite (Fig. 1a).

Within the tetrahedron, Si exceeds Al with vacancies replacing K, Na or Ca to compensate the charge imbalance, e.g.



as occurs in many mineral systems, for example from tremolite to edenite. Al cannot exceed Si without having extra alkali cations to bring the total $(K + Na + Ca)$ charge in excess of 8 ; such compositions, known in syntheses (Goldsmith, 1949 ; Cook *et al.*, 1977 ; Gregorkiewitz, 1980), lie below the Al_8Si_8 basal triangle but are not known in nature.

* The editorial committee of the journal was very sad to learn that Prof. G. Rossi died at the beginning of this year.

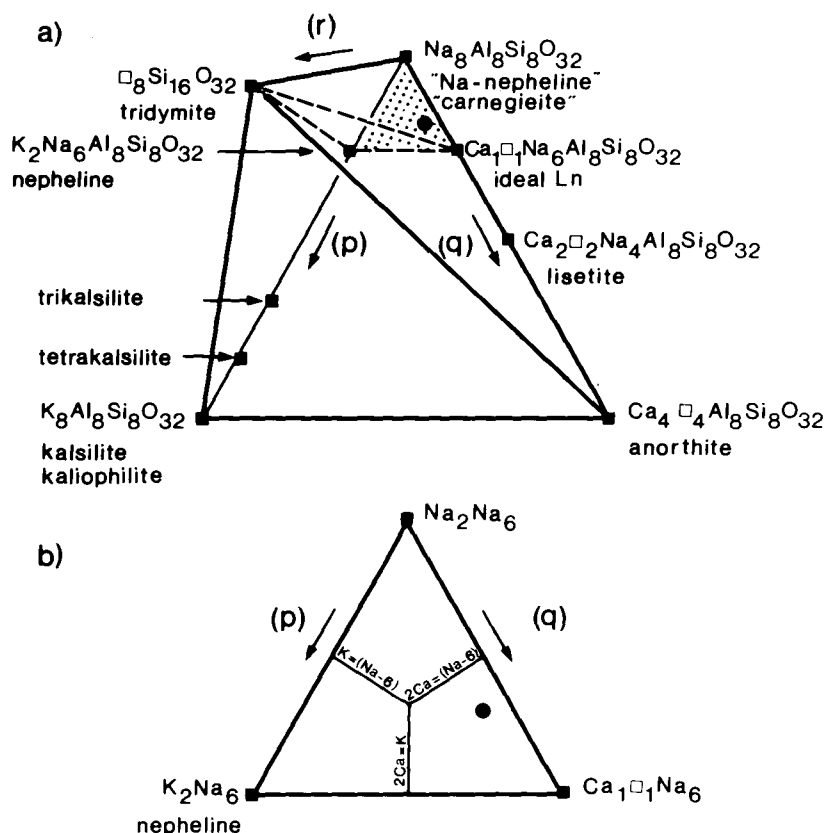


Fig. 1. a) The K_8 - Na_8 -($Ca_4\Box_4$)- $\Box_8$ tetrahedron in the K-Na-Ca-Al-Si-O system, where Al + Si = 16 per O = 32 and $\Box$ denotes a vacancy. The apices, of which the tridymite apex should be visualised above the basal K-Na-Ca triangle, represent the four possible ideal end-members of solid-solution in the nepheline group. The names of some minerals and synthetic products in this system are indicated, but in order to better appreciate their relationships, compositions are all written in the form of a nepheline formula, *i.e.* $X_8Y_8Z_8O_{32}$. The composition of Ln is represented by the solid dot which lies only slightly above the basal K-Na-Ca triangle. b) Enlargement of the Na-rich corner of the basal triangle showing compositional limits which could be used to subdivide this triangle into 3 equal areas. Note that if some Ca enters the smaller "oval" site (*i.e.* $(Na,K,Ca,\Box)_1(Ca,Na,\Box)_6$ instead of $Ca_1\Box_1Na_6$) this has no effect on the plotted position.

A great variety of natural and/or synthetic mineral structures are known along the K_8 - Na_8 join: kalsilite, trikalsilite, tetrakalsilite, several types of kaliophilite (*e.g.* see the review by Merlino, 1984), nepheline, and several types of orthorhombic, hexagonal or cubic polymorphs of the Na_8 -end-member (*e.g.* see the review by Henderson & Roux, 1977, and below in section 5.3). All of these phases are generally described as feldspathoids and most may be regarded as stuffed derivatives of tridymite or of cristobalite.

On the $2Ca > K$ side of the Al_8Si_8 basal

triangle, feldspar (*i.e.* anorthite) or feldspar-like (*i.e.* lissetite) structures occur. In this paper we describe a new crystal structure: that of a natural feldspathoid with $2Ca > 1$ (Fig. 1a). It has a nepheline topology, rather than the "carnegieite"-, beryllonite-, or kaliophilite-topologies (see the review by Merlino, 1984, p. 457), and is the first natural X-ray refined nepheline-like structure with extensive solid-solution along exchange (q), *i.e.* with vacancies in the large cation site due to the presence of Ca rather than, due to the common replacement of Al by Si (exchange (r)). This mineral, which

will be referred to here by the symbol Ln (as in the abstract by Rossi *et al.*, 1985), occurs closely associated with the other new tectosilicate lisetite ($\text{CaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}$; Rossi *et al.*, 1985, 1986; Smith, 1984; Smith *et al.*, 1986) in retrogressed jadeite-clinopyroxenite layers in the Liset eclogite pod, Norway. Smith (1988) reviews the peculiar mineralogy of the Norwegian coesite-eclogite province, which includes Liset, and provides a comprehensive bibliography. Kechid & Smith (1985) summarise the petrological evolution of the Liset eclogite pod.

The objectives of this paper are to describe the crystal structure refinement of Ln and to compare and contrast the feldspathoid structures in the $\text{Na} > 6$ part of the Al_8Si_8 basal triangle (Fig. 1b).

The recognition of this crystal structure as a new mineral with a new name is under consideration by the I.M.A., but the content of this paper is independent of the outcome of the I.M.A. application.

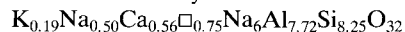
2. Chemical composition

An EMP (electron microprobe) study to establish the limits of compositional variation of Ln from Liset is in progress. Here we record only the mean of 10 analyses of the refined crystal Ln1 extracted from rock layer G201, fragment b, horizon 7 (Table 1).

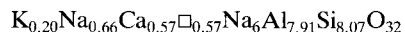
The EMP analytical technique and standards are described in Smith *et al.*, (1986). The analysed contents of Mg, Ni, Mn, Fe, Cr, and Ti

are all < 0.03 wt.% oxide; they are most probably due to minor contamination from micron-sized inclusions frequently observed in Ln at Liset such that these contents are henceforth ignored.

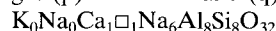
Taking into account the structure of Ln, the formula of Table 1 may be recast as:



The composition may be plotted on the basal triangle by recalculating ($2\text{Ca} + \text{Na} + \text{K}$) = 8 and extracting the (r) cation exchange by adjusting Si to fit 32 oxygens. This leads to the formula



The (Al + Si) values (15.97 and 15.98) are close enough to the ideal value of 16 to allow any other possible cation substitution to be ignored. The idealised end-member closest to this composition (Fig. 1b), obtained by operating exchanges (p) in reverse and (q), is



The many other available analyses of Ln at Liset (unpublished data) indicate K_2O either lower (as low as 0.04 %) or higher but always with $2\text{Ca} > \text{K}$. We are thus clearly dealing with the right-hand side of Fig. 1a and 1b. The analysis in Table 1 is quite typical such that there is no need to doubt its validity.

3. Crystal structure refinement

Two crystals of Ln, Ln1 and Ln2, picked from crushed rock from respectively horizons G201b7 and G201b9 of the same rock

Table 1. Wavelength dispersive electron microprobe analyses of crystal Ln1 from rock sample G201b7.

Chemical analysis		Structural formula		
n. spots	10		*	**
SiO_2	43.72	Si	8.25	8.07
TiO_2	0.00			
Al_2O_3	34.69	Al	7.72	7.91
Cr_2O_3	0.03			
Fe_2O_3	0.00	(Si+Al)	15.97	15.98
MnO	0.01			
MgO	0.01			
NiO	0.00			
CaO	2.78	Ca	0.56	0.57
Na_2O	17.76	Na	6.50	6.66
K_2O	0.80	K	0.19	0.20
total	99.80%	(Ca+Na+K)	7.25	7.43

* This structural formula was calculated on the basis of 32 oxygens, and ignoring the Ti, Cr, Fe, Mn, Mg and Ni contents

** The same formula recalculated to $(2\text{Ca}+\text{Na}+\text{K}) = 8$ charges and adjusting Si to fit 64 total charges in order to extract the cation exchange (r) (Fig. 1a)

fragment, were used for the X-ray data collection and lattice parameter determination. These were accomplished with a Philips PW 1100 four-circle automated single-crystal diffractometer. The diffraction behaviour of the crystals was not very good: the diffraction profiles were broad, thus explaining the rather high value obtained for R_{sym} (6.46 %) and the rather low number of reflections with $I \geq 3 \sigma(I)$. Ln is hexagonal, space group $P6_3$; no superstructure reflections were seen on long-exposure precession photographs. The results of the structure refinements were quite similar, and therefore crystal data and details of the data collection and refinement are given only for crystal Ln1 (Table 2), for which the EMP analysis is reported in Table 1.

Table 2. X-ray crystal and refinement data for crystal Ln1 from rock sample G201b7.

a = b (Å)	9.982(1)
c "	8.364(1)
Unit cell volume (Å ³)	721.7
Space group	$P6_3$
Crystal dimensions (mm)	0.3 x 0.2 x 0.1
Radiation	MoK α
Scan mode	$\omega/2\theta$
Scanwidth (°)	2.1
θ range (°)	2–30
Measured reflections	1732
Independent reflections	748
Observed reflections *	364
R_{sym} ** (x 100)	6.46
R_{obs} (x 100)	3.66
R_{all} (x 100)	10.41

* Only the reflections with $I \geq 3 \sigma(I)$ were considered as observed.

** $R(\text{sym}) = \sum_i (|I_{hi}| - \bar{I}) / \sum_i \bar{I}$, where $\bar{I} = (\sum_i^{\text{eq}} I_{hi}) / N_{\text{eq}}$, and N_{eq} is the number of measured equivalent reflections.

In nephelines, the ratios of the intensities of the reflections (320) and (230), as well as (730) and (370), are related to the twinning of the crystal (Dollase, 1970). In the present case, the first ratio (119:2,496) indicates around 5 % twinning. The other two reflections were too weak to give an accurate estimate of the twinning. A better estimate was therefore obtained by means of a least-square procedure on all the reflections, devised by F. Mazzi (personal communication), which yielded 4.6 % twinning. An appropriate correction was thus applied to the structure factors before each least-squares cycle.

The initial atomic parameters were from Foreman & Peacor (1970), after exchanging the x and y coordinates to conform to the data collection. During the refinement, carried out in the space group $P6_3$, the atomic coordinates, the anisotropic thermal parameters and the occupancy factors were allowed to vary in separate cycles for each of the two pseudo-centrosymmetric atomic positions. Only in the last two cycles the parameters of all the atoms were allowed to vary simultaneously.

The difference Fourier map showed residual electron density around the K position and principally down the z axis, with a discrete maximum at 1.25 Å from K. This maximum, which is alternative with respect to K, was labelled Ca' since its distances with the oxygen atoms were compatible with calcium (and also sodium). Its occupancy was allowed to vary in the subsequent least-squares cycles. The last difference Fourier map still revealed residual electron density in the vicinity of the K and Ca' positions, well above the noise level but without any discrete peak.

The conclusion is that the large A cavity is affected by a strong positional disorder, witnessed also by the large and highly anisotropic thermal parameters of K and Ca' (see the thermal ellipsoid of Ca' with its long major axis parallel to z). In this situation only two discrete peaks (K and Ca') were considered in the refinement. The site occupancy refinement of K and Ca', since also large amounts of vacancy are present, can give only a fairly rough estimate of their mean atomic numbers, but no quantitative indication on the site population.

No chemical constraint was used during the refinement; scattering factors for (Na⁺ + vacancy), (Ca²⁺ + Na⁺), (K⁺ and Na⁺) were used respectively in the Na, Ca' and K positions, where Na refers here to the smaller "oval" cavity and K refers to the centre of the larger "hexagonal" A cavity (Fig. 2). The O, Al and Si atoms were assumed to be half-ionized; atomic scattering factors were taken from the International Tables for X-Ray Crystallography (1974). The final conventional R factor was 0.037 for the observed reflections with $I \geq 3 \sigma(I)$ ($R = 0.104$ for all the reflections). The list of structure factors is available on request from the authors (G.R., R.O.).

The final atomic parameters for crystal Ln1 are given in Tables 3 and 4. Bond distances — uncorrected and corrected for the riding

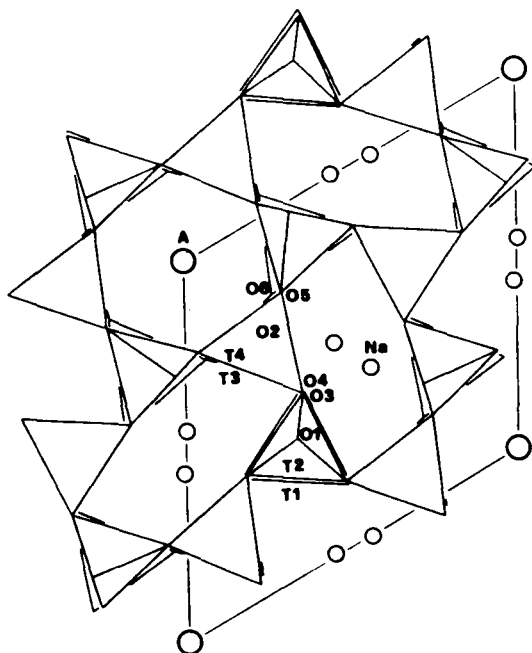


Fig. 2. The structure of $K_2Na_6Al_8Si_8O_{32}$ hexagonal nepheline projected on to the (0001) plane (from Merlino, 1984), showing the collapse of the tridymite-type hexamer ring around the Na atom in the smaller "oval" cationic site. For the sake of clarity, only one O1 position is shown, but in nephelines each O1 atom is displaced from the three-fold axis in the direction of one of the surrounding alkali atoms (Hahn & Buerger, 1955).

motion of the oxygens over the linked tetrahedral cations (Busing & Levy, 1964) — are listed

Table 3. Atomic fractional co-ordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2$) for crystal Ln1.

Site	x	y	z	B_{eq}
Na (0.98(1) Na + 0.02 □) §	9945(3)	4423(3)	9902(10)	1.7(8)
K (Na+Ca+K+□) §	0	0	9854(7)	4.7(2)
Ca' (Ca+Na+□) §	0	0	8358	10.2(2.6)
T1 (Al)	3333	6666	1805(6)	2.0(6)
T2 (Si)	3333	6666	7951(5)	0.9(1)
T3 (Si)	926(2)	3325(2)	3028(3)	1.3(5)
T4 (Al)	955(2)	3340(3)	6768(3)	1.5(1)
O1	3324(28)	7128(14)	9727 *	3.9(8)
O2	298(5)	3200(7)	4886(22)	3.8(2)
O3	1755(5)	5256(5)	7196(10)	2.9(2)
O4	1620(6)	5067(5)	2297(10)	3.2(2)
O5	2280(5)	2868(5)	2990(7)	2.2(1)
O6	2233(6)	2686(7)	6825(7)	2.5(2)

§ see text

* held constant to fix the origin

The traditional (Hahn and Buerger, 1955) nomenclature of the sites in K_2Na_6 -nepheline has been maintained, with Ca' introduced to represent the displaced site. Site assignments based on the X-ray refinement results and on the electron microprobe analyses have been also indicated. Numbers in parentheses are e.s.d.'s referred to the last digit.

in Table 5. The correction has proved to be necessary for crystals in the nepheline mineral group which have large temperature factors due to positional disorder averaged over domain structures. The presence of different local cation occupancies (particularly the vacancy in the large A cavity) causes positional disorder in the coordinating oxygens. Moreover, in nephelines, each O(1) atom is displaced from the three-fold axis in the direction of one of the surrounding Na atoms, which corresponds to a tilting of the T1 and T2 tetrahedra in order to relieve strain. In this situation (remembering also that the Ln crystals are twinned), it is difficult to precisely evaluate the T-O bond lengths. On the other hand, the work by Stebbins *et al.* (1986) with ^{29}Si NMR techniques has definitely solved the question of Al/Si ordering in the nepheline group; their data allowed them to state that the Al/Si disorder, as inferred by X-ray diffraction, "is long-range only, and is the result of averaging over domains with short-range order".

4. Description and discussion of the structure

4.1. The tetrahedral framework

The tetrahedral framework of Ln is the same as that of K_2Na_6 -nepheline (Hahn & Buerger, 1955; see Fig. 2 and the discussion in section 5.2). The only significant difference from the crystals in the nepheline mineral group so far

Table 4. Anisotropic thermal parameters ($\times 10^4$) for crystal Ln1. They are defined by :

$$\exp - (h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk \beta_{12} + 2hl \beta_{13} + 2kl \beta_{23}).$$

Site	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	63(3)	50(3)	49(3)	20(2)	3(9)	-38(7)
K	159(10)	159(10)	162(18)	79(18)	0	0
Ca'	52(44)	52(44)	981(270)	26(2)	0	0
T1	76(3)	76(3)	57(5)	38(5)	0	0
T2	28(2)	28(2)	38(4)	15(2)	0	0
T3	40(2)	4(1)	79(3)	2(2)	22(3)	16(2)
T4	27(2)	107(3)	39(2)	44(2)	15(3)	21(3)
O1	235(30)	154(36)	38(21)	120(29)	-3(53)	-51(36)
O2	87(6)	295(14)	57(6)	138(8)	-6(21)	-17(33)
O3	31(6)	42(6)	233(13)	17(5)	-7(8)	32(8)
O4	69(7)	19(5)	231(14)	11(5)	-39(9)	2(7)
O5	32(5)	69(6)	109(8)	10(5)	-25(8)	-30(8)
O6	129(8)	151(9)	53(6)	125(8)	-32(8)	-42(8)

4.2. The extra-framework cations

The mean atomic number — expressed in terms of neutral atoms — which was obtained from X-ray refinement of Ln for the Na site is 10.76, corresponding to 0.98 Na + 0.02 □. This value of the m.a.n. might also result from the simultaneous presence of 0.815 Na + 0.090 Ca + 0.095 □ (in this hypothesis all the calcium detected during the probe analysis would be located at the Na site). However, taking into account : i) the low and almost isotropic thermal factor of Na (compared to those of K and Ca') ; ii) the fact that a m.a.n. so close to 11 is

Table 5. Bond distance (Å) for crystal Ln1 before and after the correction for riding motion (Busing & Levy, 1964). The mean e.s.d. is 0.002 Å.

	uncorr.	corr.		uncorr.	corr.
T1 - O1 (x 1)	1.799	1.818	T2 - O1 (x 1)	1.556	1.596
- O4 (x 3)	1.706	1.721	- O3 (x 3)	1.626	1.645
T1 - O	1.729	1.745	T2 - O	1.608	1.633
T3 - O2	1.656	1.686	T4 - O2	1.684	1.708
- O4	1.635	1.653	- O3	1.702	1.723
- O5	1.629	1.638	- O5	1.705	1.706
- O6	1.611	1.629	- O6	1.699	1.710
T3 - O	1.633	1.651	T4 - O	1.698	1.712
Na - O1	2.553	2.564	K - O2 (x 3)	3.056	3.044
- O2	2.504	2.508	- O5 (x 3)	3.048	3.036
- O3	2.685	2.689	- O6 (x 3)	2.983	2.973
- O3	2.753	2.753	K - O	3.029	3.018
- O4	2.871	2.874	Ca' - O5 (x 3)	2.637	2.580
- O4	2.479	2.485	- O6 (x 3)	2.797	2.749
- O5	2.506	2.508	Ca' - O	2.715	2.664
- O6	2.579	2.581			
Na - O	2.616	2.620			

refined is that the tetrahedral mean bond lengths of Ln are in the sequence T2-O < T3-O < T4-O < T1-O (instead of T3-O < T2-O < T1-O < T4-O for K_2Na_6 -nephelines), the variational range being larger than in the other published structures (Merlino, 1984). The inversion in the sequence is probably related to the different composition in the surrounding alkali sites. In fact, in Ln no Ca should be present at the "oval" Na cavity (see the next section), whereas in all the (K,Na)-nephelines so far refined, at least 0.3 Ca atoms per 32 oxygens substitute for Na at this site. It should be remembered that in the nepheline mineral group, the T1 and T2 tetrahedra are surrounded only by Na sites, whereas the T3 and T4 tetrahedra are surrounded by a combination of Na and K (partly vacant) sites. The synthetic $(K_{0.96}Na_{0.96})Na_6$ -nepheline refined by Gregorkiewicz (1984) also shows slight T1, T4 inversion ($\langle T1-O \rangle = 1.730$, $\langle T4-O \rangle = 1.726$ Å).

unlikely to derive — in the case of this overall chemical composition — from a combination of Na + all the detected Ca + □ rather than from Na plus a small amount of vacancy ; iii) the presence of an alternative position in the A cavity, which had never been noticed in Na-nephelines, it appears more realistic to assume that the Na site is occupied almost only by sodium, even if small amounts of calcium and vacancy cannot be excluded. Furthermore, if all the calcium is located at the Na position, much more sodium would be available to fill the A site ; the A site would then result to have less vacancies (1.76 Na + 0.20 K + 0.04 □) than the Na site, which seems rather strange. In Ln, therefore, the small "oval" alkali site seems to be occupied only by Na, and has the same eight-coordinated geometry as the corresponding site in K_2Na_6 -nepheline : the $\langle Na-O \rangle$ bond distance is 2.62 Å in specimen Ln1 compared with the average of 2.62 Å for

the six different nephelines reported by Gregorkiewicz (1984).

On the contrary, the arrangement of the atoms in the large "hexagonal" cavity centred by the z crystallographic axis (A cavity) is in this case very peculiar, being different from those in K_2Na_6 -nepheline and in hexagonal Na-exchanged nepheline (see section 5.2). This cavity is too large to contain Ca or Na atoms at its geometrical centre (the K position) which is occupied by all the K atoms in K_2Na_6 -nephelines. In the Na-exchanged nepheline (Dollase & Thomas, 1978), the Na atoms in this cavity are off-centred (site name: Na') along the x direction (Fig. 3), nearly at the same z coordinate as K in K_2Na_6 -nepheline; in this way, an irregular one-sided coordination is obtained, in which the bond lengths are more appropriate for the smaller Na cations ($\langle Na'-O \rangle = 2.87 \text{ \AA}$ for the six nearest oxygens).

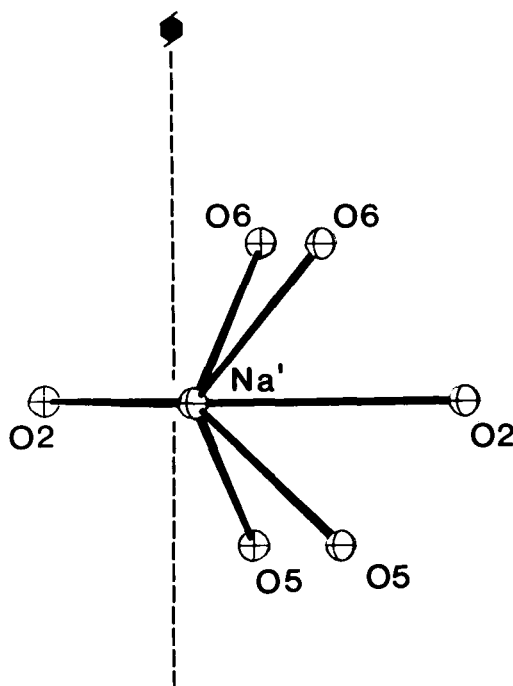


Fig. 3. The Na coordination in the large cavity in the Na-exchanged nepheline (Dollase & Thomas, 1978), showing the off-centred Na' position.

In Ln, the simultaneous presence of K, Na and Ca (and of vacancy) in the K cavity, as inferred from the EMP analysis after subtracting

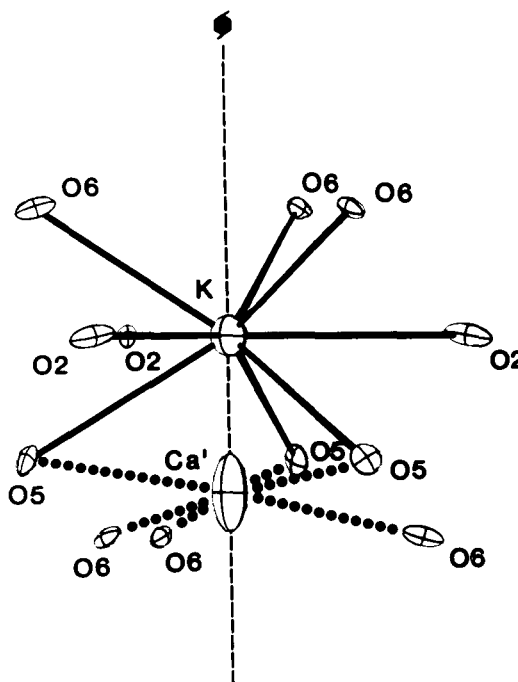


Fig. 4. The arrangement of the cations in the large cavity around the 6_3 axis (A cavity), showing the coordination of the larger K cation in K_2Na_6 -nepheline; in Ln, this site is occupied by some Na, all the available K and most of the Ca. Also shown is the alternative Ca' position, $1.25 \text{ \AA}$ along the z axis, occupied in Ln by the remaining Ca and Na.

the 6 Na atoms at the Na site, results in a complex and partly disordered situation. An alternative position along the z axis (indicated as Ca' in Fig. 4) is present; the shape of the electron density near K indicates a continuous positional disorder, with one maximum at $1.25 \text{ \AA}$ from the K site. This position (alternative with respect to that of K) allows a different and more suitable coordination for Ca and Na with six oxygen atoms at an average corrected $\langle Ca'-O \rangle$ distance of $2.66 \text{ \AA}$ (Table 5) instead of the nine-coordinated K at an average corrected $\langle K-O \rangle$ distance of $3.02 \text{ \AA}$. Ca' (at $0,0,0.8358$) is bonded to three O5 oxygens ($Ca'-O5 = 2.637 \text{ \AA}$) and to three O6 ($Ca'-O6 = 2.797 \text{ \AA}$) oxygens. The difference in this two bond distances is justified by the fact that O5 is linked only to Ca' because no K can be simultaneously present at $0,0,0.9854$, whereas O6 is linked both to Ca' and to K at $0,0,0.4854$ which can coexist with Ca' at $0,0,0.8358$ ($Ca'-K =$

2.93 Å). The position occupied by K in K_2Na_6 -nepheline (labelled K in Fig. 4) in Ln hosts all the available K and some (Ca+Na), and has the same geometry as that of K_2Na_6 -nepheline (Simmons & Peacor, 1972). Owing to the simultaneous presence of these cations, it is impossible in this case to detect the off-centering of Na already reported for the Na-exchanged nepheline. The inspection of the final difference Fourier map indicates no relevant discrete residual peak, but a diffuse residual electron density both parallel to z (towards the Ca' position) and moving away from it (towards the Na' position). The model with only two discrete positions in the large and spread electron density of the A cavity cannot account for the residual diffuse electron density, and for this reason the total number of electrons of the K and Ca' sites represents only 70 per cent of the total number of electron resulting from the microprobe analysis. On the other hand, no significant local enrichment in Na and Ca, which could denote the presence of spurious phases, was noticed during the EMP session: therefore, a fraction of Na and Ca cations must be disordered inside the cavity.

It should be noted that almost one half of the large sites are vacant in Ln, because part of the anionic charge is balanced by the excess of Si (cation exchange (r)), and the presence of the divalent Ca (cation exchange (q)) reduces the need for alkali cations at this position.

4.3. Relationships with lisetite

Ln is often associated with lisetite; the change in chemistry between the two phases is small (Lt is $Ca_2Na_4Al_8Si_8O_{32}$, Ln is ideally $Ca_1\Box_1Na_6Al_8Si_8O_{32}$; Fig. 1a) but is nevertheless significant. However, there is a complete change in the structure, from one more compact than that of the feldspars (lisetite) to the relatively loose structure of the feldspathoids (Ln). The most relevant aspect in this change is that an increment of about 2.5 % in the number of (Ca+Na+O) atoms — 16.7 % in the number of (Ca+Na) atoms — corresponds to an increment of about 6 % in the molar volume. These figures have to be compared with the increment of about 5.5 % in the number of (Ca+Na+O) atoms — 50 % in the number of (Ca+Na) atoms — with an increment of only 2 % in the molar volume from anorthite

($Ca_4Al_8Si_8O_{32}$) to lisetite. In the case of the change from lisetite to Ln, the greater molar volume increment corresponds to the larger quantity of voids, which should be favoured by lower pressure and/or higher temperature.

Despite the structures of lisetite and Ln being so different, a metric relationship between their unit cells (in lisetite $a = 8.260$, $b = 17.086$, $c = 9.654$ Å, and the space group is $Pbc2_1$; Rossi *et al.*, 1986) is evident:

$$\begin{aligned} a(Lt) &\approx c(Ln) & b(Lt) &\approx \sqrt{3} a(Ln) \\ c(Lt) &\approx a(Ln) \end{aligned}$$

Thus the cell of lisetite is close to the orthorhombic cell of Ln, the cell parameters of the latter being 1.2–3.4 % larger than those of the former. In other mineral pairs, such conditions can favour epitaxial intergrowth: lisetite and Ln are often in direct contact in thin section (Smith *et al.*, 1986), and epitaxial relationships between them are possible.

5. Crystal structures and chemical relationships in the compositional space $(K,Na,Ca,\Box)_8(Al,Si)_{16}O_{32}$

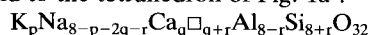
5.1. Cation substitutions

Nepheline is a common mineral in silica-undersaturated intrusive or extrusive rocks such as syenites and phonolites (*e.g.* see the review by Deer *et al.*, 1963). Its chemical formula is frequently written as $NaAlSiO_4$, but sometimes as $Na_4Al_4Si_4O_{16}$ or $Na_8Al_8Si_8O_{32}$, since the unit cell contains two formula units with $O = 16$. This simple formula does not take into account any of the three major substitutions (p), (q) and (r) discussed in section 1; although some extent of all these substitutions may be thought implicit by a writer, a reader may not think the same way. The common terminology Ne_xKs_y , where $Ne = Na_8Al_8Si_8O_{32}$ and $Ks = K_8Al_8Si_8O_{32}$, is thus misleading since igneous nephelines contain substantial K, due to exchange (p), with a K/Na ratio ranging mostly between 1/7 to 3/5 and an average K/Na ratio close to 2/6 (*i.e.* $Ne_{75}Ks_{25}$). This composition corresponds to the "ideal" nepheline formula: $K_2Na_6Al_8Si_8O_{32}$ (Hahn & Buerger, 1955) (Fig. 1a,b). The ideal ratio of 1/3 derives from the multiplicity of the large "hexagonal" cation site being one third of that of the small "oval" alkali cation site.

Most natural nephelines have an Al/Si ratio less than 1:1; this further substitution of Al by Si is compensated by vacancies substituting for Na and/or K by exchange (r) or its equivalent with K instead of Na, *i.e.* a combination of exchanges (p) and (r) (see Fig. 77 in Deer *et al.*, 1963, and Fig. 1 in Dollase & Thomas, 1978). Minor contents of Ca (*i.e.* Ca < or << 0.5 per O = 32) have been recorded in some natural nephelines (*e.g.* Deer *et al.*, 1963; Foreman & Peacor, 1970; Dollase & Thomas, 1978); this may be regarded as the result of substitution (q) or its equivalent with K instead of Na. Ca-bearing K-free nephelines have been synthesised by Bowen (1912), Goldsmith (1949), Donnay *et al.* (1959) and Roux (1979).

Small amounts of iron have also been recorded. This is generally considered to be Fe³⁺ (*e.g.* Deer *et al.*, 1963; Dollase & Thomas, 1978) occupying some tetrahedral sites, since both the small tetrahedral framework sites and the large extra-framework sites are not suited to occupancy by the medium-sized Fe²⁺ cation. As Al >> Fe³⁺ in natural nephelines, all Fe present may be combined with Al and thereafter ignored for most purposes. Significant proportions of other elements have not been reported such that the chemical system K-Na-Ca-Fe-Al-Si-O is adequate to deal with all natural nepheline-structure minerals.

An appropriate chemical formula for the family of nepheline-structure minerals may be written in terms of the Na₈Al₈Si₈O₃₂ end-member modified by application of the (p), (q) and (r) exchange vectors such that the formula corresponds to the tetrahedron of Fig. 1a:



where Al may include Fe³⁺. Donnay *et al.* (1959) proposed a similar formula but used the Si₁₆O₃₂ end-member as the origin. Note that these formulae do not constrain the site distribution of K, Na and Ca between the 2 large and 6 small sites.

In the following sub-sections we deal with three end-members of Fig. 1b, *i.e.* with p = 0 or 2, q = 0 or 1 and r = 0, and hence with Na ≥ 6.

5.2. The K₂Na₆- end-member

In terms of both chemistry (*i.e.* K/Na = 2/6) and structure (*i.e.* the space group *P6₃/m* or *P6₃*), this is "type" nepheline with the Hahn-

Buerger (1955) cell. Its structure (Fig. 2) can be described as a tridymite-type framework containing 32 oxygens per unit cell, in which half of the Si atoms are replaced by Al atoms. The tetrahedra pointing in one direction along the z axis are occupied by Si, whereas those pointing in the other direction are occupied by Al, *i.e.* perfect Al/Si ordering. Alkali atoms fill the eight resulting cavities and compensate for the charge imbalance in the tetrahedral framework. In nepheline, the distortion of the ideal high-tridymite framework, due to Si ↔ Al substitution and obtained by rotation of the tetrahedra around the hexagonal axis, produces two different kinds of cavities: one quarter of them are very slightly affected by this rotation pattern and maintain the original large size (the "hexagonal" A cavities), whereas for the other three quarters, the size is inversely dependent on the degree of rotation (the "oval" Na sites). In the ideal K₂Na₆- end-member, the six Na atoms occupy the six smaller cavities in an eight-fold coordination, whereas K in nine-fold coordination occupies a *central* position in the two large cavities. However, this ideal composition has never been found in nature; part of the ideal K atoms are always replaced by □ or Ca, and the Si:Al ratio is always higher than the ideal 1:1 value, *i.e.* exchanges (q) and (r) are always present.

5.3. The Na₂Na₆- end-member

This end-member at the pure Na apex has many polymorphs. At high temperature (> 1,254 °C), the cubic so-called "carnegieite" phase (Deer *et al.*, 1963) is stable, followed by "high"-nepheline of unknown structure at > 875 °C (Henderson & Roux, 1977). The typical hexagonal structure of nepheline is stable at medium temperature (> 190 °C). The alkali-deficient K_{0.03}Na_{7.30}Ca_{0.05}□_{0.62} Na-exchanged nepheline has some *off-centred* Na (Dollase & Thomas, 1978; see above for a discussion). The pseudo-hexagonal (supercell) apparently-orthorhombic structures (with or without a second phase) are stable at lower temperatures (Henderson & Roux, 1977; Henderson & Thompson, 1980). At very high pressure (> 180 kbar), the structure is that of calcium-ferri- (Liu, 1978). Natural compositions with K ≤ 0.2 per 32 oxygens are extremely rare and are always very fine-grained, which restricts the

possibility of determining their structural details. Cesàro (1920), Bannister (1931) and Donnay *et al.* (1959) all determined (for natural samples from Monte Somma, Italy) very low unit-cell *c* dimensions (8.32–8.33 Å) apparently compatible only with the type C nephelines described by Henderson & Roux (1977) in their X-ray powder diffraction work on synthetic $\text{Na}_8\text{Al}_8\text{Si}_8\text{O}_{32}$; it is however possible that some Ca replaces Na in these samples, as the cation exchange (q) hardly affects the cell parameters (Donnay *et al.*, 1959). No structural data is available for more recent reports of this composition in rocks from South Africa (Lapin, 1978), Kenya (Nash *et al.*, 1969) and Oman (Johan *et al.*, 1983). None of these samples are yet named officially as the all terms “nepheline”, “sodium-nepheline”, “Na-nepheline” and “carnegieite” do not have approval from the I.M.A. Commission on New Minerals and Mineral Names.

5.4. The $\text{Ca}_1\Box_1\text{Na}_6$ -end-member

This composition represents the K-free Ca-full equivalent of nepheline. The chemical formula of the crystal Ln1 whose structure is described here is $(\text{K}_{0.20}\text{Na}_{6.66}\text{Ca}_{0.57}\Box_{0.57})\text{Al}_{7.91}\text{Si}_{8.07}\text{O}_{32}$ (Table 1, section 2). It thus has substantial Ca ($q > 0.50$) but much less K ($p = 0.20$) and is therefore closest to the ideal $\text{Ca}_1\Box_1$ -end-member even if Ca is substantially less than 1.0 (Fig. 1a,b). The extent of the (r) cation exchange, as indicated by formula *, is about as small as that of the (p) cation exchange. In contrast to the central position of K in the K_2Na_6 -end-member and the off-centred position of Na in the Na_2Na_6 -end-member, some of Ca in the $\text{Ca}_1\Box_1$ -end-member is in a *displaced* position.

No other data is available to indicate the existence of additional polymorphs for mineral compositions close to that of Ln such that it is presently assumed that the Ca-displaced structure of Ln can occur in a wide range of compositions around that of Ln from Liset, *e.g.* in the quadrilateral field of Fig. 1b defined by $2\text{Ca} > \text{K}$ and $2\text{Ca} > (\text{Na}-6)$. The preliminary experimental works of Schairer (recorded by Donnay *et al.* (1959), p. 100) and of Roux (1979) suggested that a nepheline-like structure could extend only slightly beyond $\text{Ca} = 1$ ($\text{Ca} < 1.33$) and only with $\text{K} \approx 0$. Such composi-

tions require at least some Ca in the smaller “oval” sites in order to maintain full occupancy since $\text{Na} < 6$.

Goldsmith's (1949) syntheses examined by Donnay *et al.* (1959, p. 99–100) indicate nepheline-like structures with enormous Ca contents up to $\text{Ca} = 4.6$ but they concern the join $\text{Na}_8\text{Al}_8\text{Si}_8\text{O}_{32}$ – $\text{Ca}_8\text{Al}_{16}\text{O}_{32}$. Note that the latter theoretical end-member would plot on Fig. 1a at an extreme position along the tridymite-to-anorthite join extrapolated below the Al_8Si_8 basal triangle, *i.e.* it is related to $\text{Na}_8\text{Al}_8\text{Si}_8\text{O}_{32}$ by the exchange (r) in reverse to yield $\text{Na}_{16}\text{Al}_{16}\text{O}_{32}$ accompanied by exchange (q) to bring the 16 Na down to 8 Ca.

A literature search of natural “nepheline” compositions has not yet revealed any composition with a 2Ca/K ratio as high as that of Ln; four analyses compiled by Bannister (1931) do show $2\text{Ca} > \text{K}$ but Ln is presently the natural mineral with nepheline topology closest to the Na_8 – $\text{Ca}_4\Box_4$ join, and also the only crystal with $2\text{Ca} > \text{K}$ for which detailed structural information is available.

It thus appears that the new natural crystal-structure of Ln represents a compositional volume above, within, and below the Al_8Si_8 basal triangle in which a nepheline topology can exist.

6. Conclusions

1. The new structure of crystal Ln1 has the same aluminosilicate framework as nepheline, but has a chemical composition close to the ideal end-member formula $\text{Ca}_1\Box_1\text{Na}_6\text{Al}_8\text{Si}_8\text{O}_{32}$, and has two positions for the alkali atoms in the large A cavity: K and Ca'.

2. In crystal Ln1, about one quarter of the Ca atoms are displaced into the Ca' site along the *z* axis; the remainder either are disordered or stay in the K site along with, on average, almost half a vacancy.

3. Mineral compositions close to the three end-members in the system $\text{K}_2\text{Na}_6\text{Al}_8\text{Si}_8\text{O}_{32}$ – $\text{Na}_2\text{Na}_6\text{Al}_8\text{Si}_8\text{O}_{32}$ – $\text{Ca}_1\Box_1\text{Na}_6\text{Al}_8\text{Si}_8\text{O}_{32}$ have different cation coordinations in the large cationic sites, due to the different sizes and charges of these cations: these may be referred to as respectively “K-centred”, “Na-off-centred” and “Ca-displaced”.

4. Despite great differences in the crystal structure and cell volumes between Ln and lise-

tite, the orthohexagonal cell of Ln is very similar to the cell of lisetite.

5. Ln considerably extends the known range of natural mineral chemical compositions towards K-free Ca-rich compositions.

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References

- Bannister, F. A. (1931) : A chemical, optical and X-ray study of nepheline and kaliophilite. *Mineral. Mag.*, **22**, 569-608.
- Bowen, N. L. (1912) : The binary system : $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8\text{-CaAl}_2\text{Si}_2\text{O}_8$. Abstract of Thesis, Massachusetts Institute of Technology, 1-14.
- Busing, W. R., Levy, H. A. (1964) : The effect of thermal motion on the estimation of bond lengths from diffraction measurements. *Acta Cryst.*, **17**, 142-146.
- Cesàro, G. (1920) : Mém. Acad. Roy. Belgique (Cl.Sc), Coll. in-8°, Sez. 2, 4, 1.
- Cook, L. P., Roth, R. S., Parker, H. S., Tegas, T. (1977) : The system $\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$. Part 1. Phases on the $\text{KAlSiO}_4\text{-KAlO}_2$ join. *Am. Mineral.*, **62**, 1180-1190.
- Deer, W. A., Howie, R. A., Zussman, J. (1963) : Rock-forming minerals, vol. 4, Framework silicates, Longmans, London.
- Dollase, W. A. (1970) : Least-squares refinements of the structure of a plutonic nepheline. *Z. Kristallogr.*, **132**, 27-44.
- , Thomas, W. H. (1978) : The crystal chemistry of silica-rich, alkali-deficient nepheline. *Contrib. Mineral. Petrol.*, **66**, 311-318.
- Donnay, G., Schairer, J. F., Donnay, J. D. H. (1959) : Nepheline solid solutions. *Mineral. Mag.*, **32**, 93-109.
- Foreman, N., Peacor, D. R. (1970) : Refinements of the nepheline structures at several temperatures. *Z. Kristallogr.*, **132**, 45-70.
- Goldsmith, J. R. (1949) : Some aspects of the system $\text{NaAlSiO}_4\text{-CaO-Al}_2\text{O}_3$. *Am. Mineral.*, **34**, 471-493.
- Gregorkiewitz, M. (1980) : Synthese und Charakterisierung poröser Silicate. Dissertation der Technischen Hochschule Darmstadt.
- , (1984) : Crystal structure and Al/Si ordering of a synthetic nepheline. *Bull. Minéral.*, **107**, 499-507.
- Hahn, T., Buerger, M. J. (1955) : The detailed structure of nepheline, $\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$. *Z. Kristallogr.*, **106**, 308-338.
- Henderson, C. M., Roux, J. (1977) : Inversion in sub-potassic nephelines. *Contrib. Mineral. Petrol.*, **61**, 279-298.
- , Thompson, A. B. (1980) : The low-temperature inversion in sub-potassic nephelines. *Am. Mineral.*, **65**, 970-980.
- International Tables for X-ray Crystallography (1974) : Kynoch Press, Birmingham, G.B., vol. IV, 99-101.
- Johan, Z., Dunlop, H., Le Bel, L., Robert, J.-L., Volfinger, M. (1983) : Origin of chromite deposits in ophiolitic complexes : evidence for a volatile and sodium-rich reducing fluid phase. *Forts. Mineral.*, **61**, 105-107.
- Kechid, S.-A., Smith, D. C. (1985) : The petrological evolution of the Liset eclogite pod, Norway. *Terra cognita*, **5**, 422.
- Lappin, M. A. (1978) : The evolution of a grospydite from the Roberts Victor Mine, South Africa. *Contrib. Mineral. Petrol.*, **66**, 229-241.
- Liu, L. (1978) : High-pressure phase transformations of albite, jadeite and nepheline. *Earth Planet. Sci. Lett.*, **37**, 438-444.
- Merlino, S. (1984) : Feldspathoids : their average and real structure, in Feldspars and Feldspathoids, structure, properties and occurrences, William L. Brown ed., NATO ASI Series vol. 137, Reidel Publishing Company, 435-470.
- Nash, W. P., Carmichael, I. S., Johnson, R. W. (1969) : The mineralogy and petrology of Mt. Suswa, Kenya. *J. Petrol.*, **10**, 409-439.
- Rossi, G., Oberti, R., Smith, D. C. (1986) : The crystal structure of lisetite, $\text{CaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}$. *Am. Mineral.*, **71**, 1378-1383.
- , Smith, D. C., Oberti, R., Kechid, S.-A. (1985) : Some crystal-chemical and petrological relationships between two new minerals in the system anorthite-nepheline. *Rend. Soc. It. Min. Petr.*, **40**, 424-425.
- Roux, J. (1979) : Etudes physicochimiques des feldspathoïdes et application aux problèmes pétrographiques. Thèse de Doctorat d'Etat, Paris Sud.
- Simmons, W. B. Jr., Peacor, D. R. (1972) : Refinement of the crystal structure of a volcanic nepheline. *Am. Mineral.*, **57**, 1711-1719.
- Smith, D. C. (1984) : Remarques cristallographiques et pétrogénétiques sur des minéraux inhabituels dans les élogites de Liset et Rekvika, Norvège. 10^e Réunion Annuelle Sciences Terre, Bordeaux, éd. Société Géologique de France, Abstracts, 511.
- (1988) : A review of the peculiar mineralogy of the "Norwegian coesite-eclogite province", with crystal-chemical, petrological, geochemical and geodynamical notes and an extensive bibliography. Chapter 1, pp. 1-206, in "Eclogites and eclogite-facies rocks", D. C. Smith editor, Elsevier, Amsterdam, in press.
- Kechid, S.-A., Rossi, G. (1986) : On the occur-

- rence of lisetite, $\text{CaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}$, a new tectosilicate in the system Ca-Na-Al-Si-O. *Amer. Mineral.*, **71**, 1372-1377.
- Stebbins, J. F., Murdoch, J. B., Carmichael, I. S. E., Pines, A. (1986) : Defects and short-range order in nepheline group minerals : a silicon - 29 nuclear magnetic resonance study. *Phys. Chem. Minerals*, **13**, 371-381.
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