THE STRUCTURE OF NOSEAN, IDEALLY Na$_8$[Al$_6$Si$_6$O$_{24}$]SO$_4$·H$_2$O

ISHMAEL HASSAN* AND H. DOUGLAS GRUNDY

Department of Geology, McMaster University, Hamilton, Ontario L8S 4M1

ABSTRACT

The average structure of nosean has been refined in space group $P\bar{4}3n$ to an R of 0.057. The cations in AlO$_4$ and SiO$_4$ tetrahedra (present in a ratio 1:1) are fully ordered, but the framework oxygen atoms are positionally disordered over two independent 24(i) sites. The interframework Na$^+$ cations are located on three independent sets of 8(e) positions that are close to each other on the body diagonals of the cubic structure (sites C1, C2, and C3). The sulfur atom of the SO$_4^{2-}$ group is located on the 2(a) site at the center and corners of the cube, and its oxygen atoms are on an 8(e) site, indicating that the SO$_4^{2-}$ group is in one orientation instead of two. The cages contain [Na$_4$·SO$_4$]$^{2+}$ and [Na$_4$·H$_2$O]$^{4+}$ clusters in a 1:1 ratio, and these clusters are ordered because of net differences in charge and size between them. This cluster ordering also gives rise to antiphase domain boundaries (*APBs*). The space group for each domain is P23, a subgroup of $P\bar{4}3n$. An 'ideal' nosean structure, modeled in space group P23, has several important properties, among which are its uses in the rationalization of the crystal chemistry of nosean and predictions of domains and *APBs*.

Keywords: sodalite group, nosean, crystal structure, antiphase domain boundaries, cluster ordering, hauyne, lazurite.

SOMMAIRE

La structure moyenne de la noséane a été affinée dans le groupe spatial $P\bar{4}3n$ jusqu'à un résidu R de 0.057. Le rapport 1:1 des cations dans les agencements tétraédriques AlO$_4$ et SiO$_4$ implique un degré d'ordre parfait, mais les atomes d'oxygène de la trame possèdent un désordre de position impliquant deux sites indépendants de multiplicité 24(i). Les atomes de Na des interstices de la trame occupent trois positions indépendantes (C1, C2 et C3) de multiplicité 8(e), qui sont proche) les unes des autres le long des diagonales de la structure cubique. L'atome de soufre du groupe SO$_4^{2-}$ occupe la position 2(a) au centre et aux coins du cube, et les atomes d'oxygène qui lui sont associés occupent une position 8(e), ce qui montre que le groupe SO$_4^{2-}$ possède une seule orientation et non deux. Les cages contiennent des groupements de [Na$_4$·SO$_4$]$^{2+}$ et de [Na$_4$·H$_2$O]$^{4+}$ dans un rapport de 1:1. L'agencement de ces groupements est ordonné à cause des différences électrostatiques et dimensionnelles. La mise en ordre de ces groupements a comme conséquence la formation de domaines déphasés. Le groupe spatial de chaque domaine est P23,

qui est un sous-groupe de $P\bar{4}3n$. Une structure "idéale" de la noséane, suivant le modèle du groupe spatial P23, possède plusieurs propriétés importantes, dont une rationalisation de la cristallochimie de la noséane, et une prédiction de la formation de domaines et de parois entre domaines déphasés.

(Traduit par la Rédaction)

Mots-clés: groupe de la sodalite, noséane, structure cristalline, parois entre domaines déphasés, mise en ordre des groupements atomiques, hauÿne, lazurite.

INTRODUCTION

Sodalite-group minerals include sodalite, nosean, hauyne, "hackmanite" (a fluorescent variety of sodalite), and lazurite (a sulfur-rich analog of hauyne). These minerals occur almost exclusively in alkali-rich, silica-deficient igneous rocks. Lazurite, however, and occasionally sodalite, occur in metasomatized limestone. Nosean and hauyne occur typically in volcanic rocks, and sodalite and "hackmanite", in plutonic rocks. These occurrences suggest that a relatively high temperature is required for the incorporation of the relatively large SO$_4^{2-}$ group into the structure of sulfatic sodalites (nosean, hauyne, and lazurite).

Taylor (1967) proposed the formula Na$_8$[Al$_6$Si$_6$O$_{24}$]SO$_4$·nH$_2$O for pure nosean and (Na$_{5-8}$K$_{0-1}$Ca$_{0-2}$□$_{0-1}$)$_8$[Al$_6$Si$_6$O$_{24}$](SO$_4$)$_{1-2}$·nH$_2$O for the nosean–hauyne series, where □ denotes vacancies in the cation sites. Complete solid-solution exists between nosean and hauyne at 600°C and 1000 bars P(H$_2$O) (Van Peteghem & Burley 1963); however, a transmission electron microscopy (TEM) study indicates that such a solid solution may be limited (Hassan & Buseck 1989b).

The sulfatic sodalites contain SO$_4^{2-}$ groups as the dominant interframework anion, and they exhibit complex satellite reflections as well as diffuse streaking (Taylor 1967, Schulz 1970, Hassan *et al.* 1985). The origins of these reflections are not known in detail, but they do indicate that the structures of sulfatic sodalites are incommensurately modulated. For this reason, these minerals were studied by TEM (Morimoto 1978, Tsuchiya & Takéuchi 1985, Hassan & Buseck 1987, 1989a,b). For hauyne, Saalfeld (1961) suggested a supercell six times that of the subcell, but Taylor (1967) showed that the superstruc-

ture reflections in sulfatic sodalites generally do not give rise to an integral multiple cell; their superstructures are thus incommensurate. Schulz & Saalfeld (1965) demonstrated that the intensity of the streaked reflections in nosean can be markedly weakened by heat treatment. All the atomic positions in nosean contribute to the superstructure reflections, which are caused by the interframework cations (Schulz 1970). Positional disorder and satellite reflections occur in lazurite (Hassan *et al.* 1985), and they are similar to those in nosean. All the sulfatic sodalites exhibit disorder of interframework ions. The framework oxygen atoms are positionally disordered over two sets of 24(*i*) sites in lazurite, but they occupy one set of such sites in hauyne. Satellite reflections were not detected in X-ray precession photographs of hauyne (Hassan 1983), but electron diffraction does show diffuse, streaked satellite reflections (Hassan & Buseck 1989b).

The aluminosilicate framework of the sodalite-group minerals has a 1:1 ratio of AlO_4 and SiO_4 tetrahedra that are fully ordered. This framework structure is characterized by rings consisting of AlO_4 and SiO_4 tetrahedra; four-membered rings are parallel to {100} planes, and six-membered rings are parallel to {111} planes about the corners of the cubic cell. The linkage of these rings gives rise to cubo-octahedral cages that center on the corners and the center of the cubic cell (see Fig. 1 of Hassan & Grundy 1984). The cages can accommodate a variety of interframework cations and anions by cooper-

ative rotation of the AlO_4 and SiO_4 tetrahedra through the so-called tilt angles ϕ_{Al} and ϕ_{Si}, respectively, from their position in a fully expanded structure (see Fig. 2 of Hassan & Grundy 1984). The diversity of interframework ions is limited by spatial and charge requirements of the framework.

The space group $P\bar{4}3n$ was used to refine the structures of "hackmanite", basic (hydroxy) sodalite, sodalite, hauyne, and lazurite (Peterson 1983, Hassan 1983, Hassan & Grundy 1983a, 1984, Hassan *et al.* 1985). However, the structure of nosean was previously determined in space group $P\bar{4}3m$ (Schulz & Saalfeld 1965, Schulz 1970). Space group $P\bar{4}3n$ allows the AlO_4 and SiO_4 tetrahedra to be ordered, and the interframework ions to be disordered; the reverse is the case in space group $P\bar{4}3m$. The former situation does not violate the aluminum avoidance principle (Loewenstein 1954); the space group $P\bar{4}3n$ is assumed and used in the present structural refinement (a preliminary report has been presented by Hassan & Grundy 1983b). The purpose of this study, besides the determination of the structure in space group $P\bar{4}3n$, is to provide a structure that forms a basis for understanding the complex satellite reflections.

EXPERIMENTAL

The nosean used in this study is from Laacher See, Germany (Royal Ontario Museum no. M5279). A different specimen from this locality was chemically analyzed (Table 1), and we assumed that this composition is representative of our material.

Precession photographs show sharp substructure reflections and satellite reflections that occur along the $<110>^*$ and $<112>^*$ directions (Figs. 1a, b). The type-*s* satellite reflections indicate a supercell of $6.5 \times d_{110} (= 6.5 \times 6.423 = 41.75 Å)$, so that the nosean superstructure is incommensurate. Space group $P\bar{4}3n$, which allows reflections of the form *hhl*, $l = 2n$, was assumed and used in the structural refinement. However, weak reflections of the form *hhl*, $l = 2n + 1$, which violate the space group $P\bar{4}3n$, are present, especially in electron-diffraction patterns (*e.g.*, {100} reflections; see Hassan *et al.* 1985, Hassan & Buseck 1987, 1989a,b). Type-*u* satellite reflections occur along $<100>^*$ directions (Fig. 1c). Moreover, the nosean structure has a strong body-centered pseudosymmetry; the main reflections thus can be classified into two groups: one group of strong reflections satisfies the body-centered missing rule (*hkl*, $h + k + l = 2n$, denoted type *p*) and the other group of weaker reflections does not satisfy the rule (*hkl*, $h + k + l = 2n + 1$, called type *p'*).

The cell parameter was determined by the least-squares method using monochromatic $MoK\alpha$ radiation, and 15 reflections having $10° < 2\theta < 35°$, automatically centered on a four-circle single-crystal

TABLE 1. CHEMICAL ANALYSIS†, CRYSTAL DATA†† AND DATA COLLECTION INFORMATION FOR NOSEAN

Oxide	Wt. %	Cell	contents†††	Miscellaneous	
Al_2O_3	29.63	Al	5.91	a_0 (Å)	9.084(2)
SiO_2	35.96	Si	6.09	V (Å3)	749.60
Fe_2O_3	0.42	Fe	0.05	Density$_{calc.}$ (gcm-3)	2.21
MgO	0.16	Mg	0.04	Crystal size (mm)	0.20 x 0.20
Na_2O	21.94	Na	7.20		x 0.33
K_2O	1.06	K	0.23	μ (cm-1)	8.02
CaO	1.30	Ca	0.24	μR	0.20
H_2O+	0.90	H_2O	0.51	Maximum 2θ	65°
SO_3	6.82	SO_4	0.87	$0 \le h, k, l \le$	13
S	0.26	S	0.08	Total no. of intensities	1675
Cl	0.59	Cl	0.17	No. of unique reflections	328
	99.04			No. of non-equiv. $|F_0| > 3\sigma |F|$	146
O=Cl,S	0.19			Final *R$_{(o)}$	0.054
Total	98.85			Final **R$_{w(o)}$	0.049

Chemical Formula

$Na_{7.20}Ca_{0.24}K_{0.23}[Al_6Si_6O_{24}](SO_4)_{0.87}\cdot0.51H_2O$

†Wet chemical analysis no. 21 from Taylor (1967).
††Space group P43n; Z = 1; Radiation/monochromator = Mo/C; $\lambda(MoK\alpha)$ = 0.71069 Å; *R = $\Sigma(|F_0| - |F_c|)/\Sigma|F_0|$; **R$_w$ = [$\Sigma w(|F_0| - |F_c|)2/\Sigma w|F_0|2]1/2$, w = 1.
†††Based on Al + Si = 12.0.

X-ray diffractometer. The cell parameter and other information pertinent to X-ray data collection and refinement are presented in Table 1. All reflection intensities were measured in an octant on a Syntex $P2_1$ diffractometer operating in the θ–2θ scan mode, with a 2θ scan range of $(K\alpha_1 - 0.85°)$ to $(K\alpha_2 + 0.85°)$ and variable scan rates of $3°$ to $29.3°$ min^{-1}, depending on the intensity of a preliminary scan. The intensities of the two standard reflections, 330 and 404, which were monitored after every 50 reflections, did not change. The data were corrected for Lorentz, polarization, background effects, and spherical absorption (Table 1). Equivalent reflections were then averaged to produce a unique data-set. All crystallographic calculations were made using the XRAY76 Crystallographic Programs (Stewart 1976).

STRUCTURE REFINEMENT

Atomic scattering factors for neutral atoms were taken from Cromer & Mann (1968). For the framework atoms (Al, Si, and O), initial isotropic temperature-factors were those of sodalite, and initial positional parameters were calculated using a geometrical model for sodalite (Hassan & Grundy 1984).

A full-matrix least-squares method was used to refine the atomic coodinates and isotropic temperature-factors of the framework atoms using unit weights and a variable overall scale-factor. The Al and Si atoms had unusually large temperature-factors, but they were of similar magnitude. The oxygen atom on a 24(i) position did not refine, and a difference Fourier map showed that its electron density was elongate; this site, therefore, was divided between two 24(i) positions, with equal occupancy factors. Both of these sites, O1 and O2, were refined, and their temperature factors were found to be identical (Table 2).

The interframework atom positions were examined through electron-density sections and least-squares refinements. The positional coordinate of a single interframework cation 8(e) position, similar to that in sodalite, did not refine, and its isotropic temperature-factor was found to be unusually large. The interframework cations were finally allocated to three 8(e) positions that are close to each other. The coordinates of these cation sites within a cage (C1, C2, and C3) and their occupancy factors are given in Table 2.
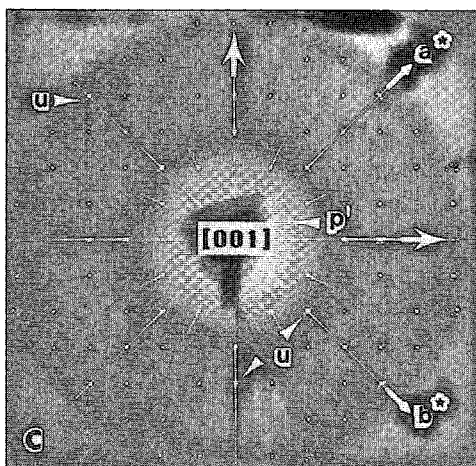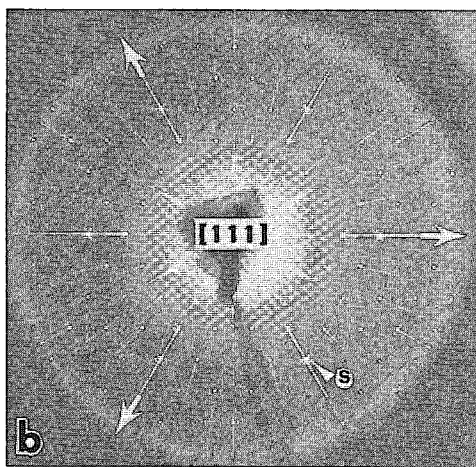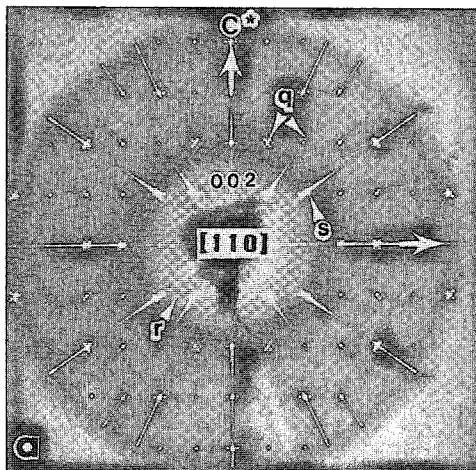
FIG 1. Precession photographs for nosean. The unlabeled arrows point to <110>* directions. (a) [110] zone showing satellite reflections along <110>* (type s) and <112>* (type q) directions; type-r reflections occur midway between main spots, along <110>* directions; (b) [111] zone showing type-s satellite reflections along <110>* directions; and (c) [001] zone showing strong type-p reflections, weaker reflections of the class 0kl, $k + l = 2n + 1$ ($=$ type p', e.g., {210}), and type-u satellite reflections along <100>* directions. $\mu = 20°$; MoKα radiation, and Zr filter.

TABLE 2. ATOMIC POSITIONAL PARAMETERS, OCCUPANCY FACTORS, AND ISOTROPIC THERMAL PARAMETERS ($\mathring{A}^2$ x 10^3), WITH e.s.d.'s IN PARENTHESES

Atom	Site	Occupancy	x	y	z	U_{iso}
Al	6(d)	1.0	1/4	0	1/2	31*
Si	6(e)	1.0	1/4	1/2	0	28*
O1	24(i)	0.5	0.137(3)	0.146(3)	0.544(2)	39(3)
O2	24(i)	0.5	0.153(3)	0.160(3)	0.457(2)	35(3)
C1	8(e)	0.21(2)	0.303(2)	0.303	0.303	21(5)
C2	8(e)	0.34(3)	0.674(1)	0.674	0.674	46(7)
C3	8(e)	0.46(1)	0.733(1)	0.733	0.733	29(3)
O3	8(e)	0.12	0.470(3)	0.470	0.470	24(16)
S	2(a)	0.49(2)	0	0	0	161(15)
O4	8(e)	0.49	0.405(3)	0.405	0.405	131(17)

*$U_{22} = U_{33}$; $U_{12} = U_{13} = U_{23} = 0$; Al: $U_{11} = 39(5)$, $U_{22} = 26(3)$; Si: $U_{11} = 20(3)$, $U_{23} = 32(3)$

A difference Fourier map, calculated with the S atom removed from the structure, shows that this atom is indeed on the 2(a) site (Fig. 2a), in contrast to what is found in hauyne, where it is displaced to an 8(e) site. The O_4 oxygen atoms of the SO_4^{2-} group refined to an 8(e) position (x, x, x), where x = 0.4352, and its isotropic temperature-factor was found to be larger than that of the S atom. An O4 position at x = 0.40 would give a reasonable S–O bond distance of about 1.5 Å; the site therefore was divided between two 8(e) positions, O3 and O4. The occupancy factor of the O4 site was constrained to equal that of the S site, and that for O3 was set at 0.12, on the assumption that O3 represents one oxygen atom of the H_2O molecule per cell; the chemical analysis of Taylor (1967) showed about 0.5 H_2O per cell. A Fourier map calculated with the O4 oxygen atom removed from the structural model showed the corresponding electron-density peak at x = 0.40, and a smaller electron-density peak on a related 8(e) site (x = 0.60, Fig. 2b). These peaks occur at the corners of a cube with edges of 1.82 Å. A similar Fourier map, calculated with O3 (x = 0.46) removed from the model, also indicates small electron-density peaks on a related 8(e) position (x = 0.54; Fig. 2c). In Figures 2b and 2c, the smaller peaks are residual electron density from the O3 and O4 positions below the plane of the map, because a final difference Fourier map was found to be featureless. One O3 position can be occupied per cage, so in a unit cell, one cage contains an H_2O molecule and the other cage contains an SO_4^{2-} group. Thus the ideal formula for nosean is $Na_8[Al_6Si_6O_{24}]SO_4 \cdot H_2O$.

The calculated and observed structure-factors for the reflections 110 and 220 show large disagreement. (A copy of the table of structure factors is available at nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2). The measured intensity for these reflections seemed reasonable, but they could be affected by extinction. These reflections were temporarily removed, and the refinement continued.

The isotropic temperature-factors for Al and Si atoms were converted to the anisotropic form, and subsequently the allowable positional and temperature coordinates of all the sites were refined simultaneously. The refinement converged to an R factor of 0.057 and an R_w of 0.049. Using this refined set of structural parameters and including the reflections 110 and 220, an R factor of 0.068 and an R_w of 0.062 were obtained. The final structural parameters are listed in Tables 2 and 3.

DISCUSSION

Average structure of nosean
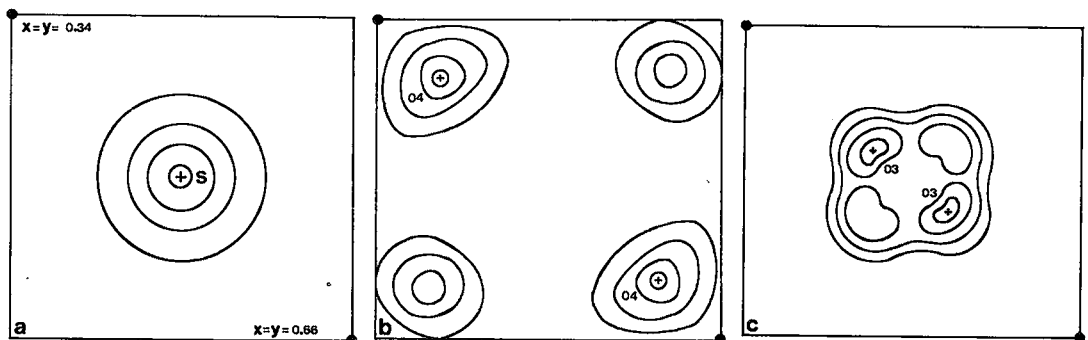
The present work shows that the sulfur atom is

FIG 2. Difference Fourier maps: (a) (001) section, calculated with the S atom removed from the model, indicating that the S atom is on the 2(a) position (z = 0.50; R = 0.086); (b) (001) section through an 8(e) site (z = 0.40; R = 0.070) showing the location of the O4 atom of the SO_4^{2-} group; (c) (001) section calculated with the O3 site removed from the structural model (z = 0.46; R = 0.063). In (b) and (c), the two larger peaks, with coordinates (x, x, x), where x = 0.40 and 0.46, correspond to oxygen atoms of the SO_4^{2-} group and the H_2O molecule, respectively, whereas the two smaller peaks at x = 0.60 and x = 0.54 indicate small amounts of electron density that are residuals of the O4 and O3 sites below the plane of the map. Contour interval is 1 $e/\mathring{A}^3$ in (a) and 0.2 $e/\mathring{A}^3$ in (b) and (c). The (x, y) coordinates are the same in all the plots.

on a 2(*a*) position, as was found in a lazurite, but not in hauyne, where it is on a 8(*e*) site. The oxygen atoms of the SO_4^{2-} group occupy only one set of 8(*e*) positions, as lazurite and hauyne. Schulz (1970) reported for nosean an SO_4^{2-} group, which occupies two orientations that are rotated 90° with respect to one another, as was found in a lazurite specimen (see Hassan *et al.* 1985).

The occupancy factor for the S site indicates that $[Na_4 \cdot SO_4]^{2+}$ clusters make up 50% of the structure, and the remaining 50% of the cages presumably contain $[Na_4 \cdot H_2O]^{4+}$ clusters. These results give an ideal formula of $Na_8[Al_6Si_6O_{24}]SO_4 \cdot H_2O$ for nosean, which does not disagree significantly from the chemical formula (Table 1) or with the present structural refinement. The $[Na_4 \cdot SO_4]^{2+}$ and $[Na_4 \cdot H_2O]^{4+}$ clusters are present in a 1:1 ratio, and their net charge and size differences could lead to cluster ordering, as confirmed by HRTEM imaging (Hassan & Buseck 1987, 1989a).

The Na atoms can be assigned to the nearby $C1$, $C2$, $C3$ positions by considering their coordinations. The $C1$ and $C2$ sites are close to either the S or O4 oxygen atom of the SO_4^{2-} group (Table 3b), so that occupancy of either $C1$ or $C2$ site excludes the SO_4^{2-} group from that cage. The $C3$ site forms a reasonable bond-distance to the O4 oxygen atom, and it is quite remote from the S atom (Table 3b). Therefore, the O4 oxygen atoms of an SO_4^{2-} group are coordinated to Na atoms on the $C3$ sites that are in adjacent cages. The SO_4^{2-} group occupies 50% of the cages, so that the occupancy factor of the $C3$ site should be 0.50, as confirmed by the refinement. The 50% occupancy of the $C3$ sites forces the SO_4^{2-} group to be in one orientation.

The occupancy factors indicate that the $C2$ site is occupied more frequently than the $C1$ site (Table 2), because the $C2$ site is within bonding distance of three O3 positions, whereas the $C1$ site is within bonding distance of only one such position (Table 3b). Therefore, the occupancy factors of the $C1$ and $C2$ sites should be 0.125 and 0.375, respectively. Although the refinement confirms the value for the $C1$ site-occupancy factor, the value for the $C2$ site is slightly higher (Table 2). The $C1$, $C2$ and O3 sites are within a cage. If this cage is at the center of the unit cell, then the Na atoms on the $C3$ sites are also within this cage, but they are bonded to the SO_4^{2-} groups in cages centered on the corners of the unit cell.

The temperature factors for Al and Si (*i.e.,* T) atoms are identical and similar to those in lazurite, but they are approximately three times larger than those found in sodalite and hauyne, thus suggesting possible positional disorder for these atoms. The framework oxygen atoms occupy two sets of 24(*i*) positions with equal frequency, and their thermal parameters are of similar magnitude (Table 2). The

TABLE 3a. INTERATOMIC DISTANCES (Å), ANGLES (°), AND VALENCE SUMS, WITH e.s.d.'s IN PARENTHESES

		AlO4	SiO4
T-O1	4 x	1.72(3)	1.61(3)
O1-O1	4 x	2.77(4)	2.62(4)
	2 x	2.84(4)	2.64(4)
Mean		2.79	2.63
O1-T-O1	4 x	111(1)	110(1)
	2 x	107(1)	109(1)
Mean		109.7	109.7
T-O2	4 x	1.71(3)	1.63(3)
O2-O2	4 x	2.82(4)	2.58(4)
	2 x	2.94(4)	2.74(4)
Mean		2.86	2.63
O2-T-O2	4 x	105(1)	105(1)
	2 x	118(1)	120(2)
Mean		109.3	110
[ϕO1]		-16.8	-17.8
[ϕO2]		9.2	9.6
Si-O1-Al		148(1)	
Si-O2-Al		147(2)	
Al/Si-O1		1.695	
Al/Si-O2		1.670	
Si-Al		3.212(1)	
		SO_4^{2-}	
S-O4	4 x	1.54(1)	
O4-S-O4	6 x	109.5(9)	

Bond-valence sums for Al and Si:

$Al = 4 \times 0.5 \times (0.770 + 0.791) = 3.12$ v.u.
$Si = 4 \times 0.5 \times (1.024 + 0.971) = 3.99$ v.u.

TABLE 3b. IMPORTANT CATION-OXYGEN DISTANCES (Å) AND VALENCE SUMS (v.u.), WITH e.s.d.'s IN PARENTHESES

Atoms			Na	
C1-O1	3 x	2.46(2)	3 x 0.5 x	0.162
-O1	3 x	3.01(2)	3 x 0.5 x	0.052
-O2	3 x	2.44(3)	3 x 0.5 x	0.169
-O2	3 x	3.04(2)	3 x 0.5 x	0.069
-O3	1 x	2.62(2)	1 x	0.114
				0.762 v.u.
-O4	1 x	1.59		
-S	1 x	3.09(1)		
C2-O1	3 x	2.35(2)	3 x 0.5 x	0.109
-O1	3 x	3.38(2)	3 x 0.5 x	0.027
-O2	3 x	2.73(3)	3 x 0.5 x	0.091
-O2	3 x	2.84(3)	3 x 0.5 x	0.073
-O3	1 x	2.62(2)	1 x	0.113
				0.563 v.u.
-O4	3 x	2.65(2)		
-S	1 x	2.74(1)		
C3-O1	3 x	2.35(2)	3 x 0.5 x	0.207
-O1	3 x	3.06(2)	3 x 0.5 x	0.048
-O2	3 x	2.39(2)	3 x 0.5 x	0.190
-O2	3 x	2.75(2)	3 x 0.5 x	0.087
-O3	3 x	3.54(2)		
-O4	1 x	2.70(1)	1 x	0.096
				0.894 v.u.
-S	1 x	4.20(1)		

Bond-valence sums for O1:

	O1
From Al and Si	0.770 + 1.024
From C1	+ 0.162 + 0.052 = 2.01 v.u.
From C2	+ 0.109 + 0.027 = 1.93 v.u.
From C3	+ 0.207 + 0.048 = 2.05 v.u.

Bond-valence sums for O2:

	O2
From Al and Si	0.791 + 0.971
From C1	+ 0.169 + 0.049 = 1.98 v.u.
From C2	+ 0.091 + 0.073 = 1.93 v.u.
From C3	+ 0.190 + 0.087 = 2.04 v.u.

T-cation bond lengths and valence sums to the framework oxygen atoms are indicative of complete ordering of the Al and Si atoms (Table 3a).

The atomic coordinates of the O1 and O2 oxygen atoms and equation (7) of the geometrical sodalite model of Hassan & Grundy (1984) can be used to estimate cell edges and the sizes of the two possible cages in nosean. The O1 coordinates give a cell edge of about 8.94 Å, and that for O2 is about 9.20 Å; the resulting mean cell edge, 9.07 Å, is close to that found experimentally, 9.084 Å. Therefore, the O2 oxygen atoms may be associated with the cage containing the larger $[Na_4 \cdot SO_4]^{2+}$ clusters, and the O1 oxygen atoms may be associated with the cage containing the smaller $[Na_4 \cdot H_2O]^{4+}$ clusters.

The sodalite framework is in a partly collapsed state as a result of cooperative rotation (angles ϕO_1 and ϕO_2 in Table 3a) of the TO_4 tetrahedra from a fully expanded state (see Fig. 2 of Hassan & Grundy 1984). From the fully expanded state, the TO_4 tetrahedra can be rotated in either a positive or negative sense. In nosean, the O1 oxygen atom of the TO_4 tetrahedra is associated with a negative rotation that has a magnitude about twice that of the corresponding O2 tetrahedra, which are rotated in a positive sense (Table 3a). Nosean structures consisting of O1 and O2 oxygen atoms are shown in Figures 3a and 3b, respectively. The four-membered rings in Figure 3a are contracted with respect to those based on the framework O2 positions (Fig. 3b). Similar contractions are present in [110] and [111] projections. In

particular, six-membered rings that are parallel to the {111} planes are pointing in opposite directions (*cf.* Figs. 3a with 3b).

Model structure for 'ideal' nosean

A model structure for 'ideal' nosean, based on the space group $P23$ and the formula $Na_8[Al_6Si_6O_{24}]SO_4 \cdot H_2O$, was extracted from the average structure that was determined in space group $P\bar{4}3n$. This model structure was further developed using the *DLS* modeling program of Villiger & Meier (1969), and representative bond-lengths taken from the sodalite structure (Hassan & Grundy 1984). The model structure was manipulated in order to minimize the deviation from electrostatic neutrality, as calculated from the bond-valence equations of Brown & Shannon (1973). During this process, the geometry of the SiO_4 and AlO_4 tetrahedra of the experimental sodalite structure was maintained as

TABLE 4. POSITIONAL PARAMETERS FOR 'IDEAL' NOSEAN BASED ON SPACE GROUP

P23 AND FORMULA $Na_8[Al_6Si_6O_{24}]SO_4 \cdot 0.0 - 1.0 H_2O*$

Atom	Site	Occupancy	x	y	z
Al	6(g)	1.0 Al	1/4	0	1/2
Si	6(h)	1.0 Si	1/4	1/2	0
O1	12(i)	1.0 O	0.1471	0.4467	0.1366
O2	12(j)	1.0 O	0.3373	0.3479	0.9638
C2	4(e)	1.0 Na	0.1683	0.1683	0.1683
C3	4(e)	1.0 Na	0.7354	0.7354	0.7354
O3	4(e)	0.25 O	0.4700	0.4700	0.4700
S	1(a)	1.0 S	0	0	0
O4	4(e)	1.0 O	0.9023	0.9023	0.9023
		Optional sites for substitution of Ca and/or K			
C1	4(e)	0 - 1.0 K†	0.3020	0.3020	0.3020
		0 - 0.25 Ca†			

*Atoms C1, C2, and C3 have the same nomenclature as the observed structure.
†C2 occupancy reduced by the same amount.

TABLE 5. CATION-SITE BOND DISTANCES AND

VALENCE BOND STRENGTHS (v.u.) FOR 'IDEAL'

NOSEAN WITH A CELL EDGE OF 8.89 Å

Na in C2			
C1-O1	3 x	2.526	0.425
-O2	3 x	2.880	0.163
-O4	3 x	2.554	0.394
			0.984 v.u
Na in C3			
C3-O1	3 x	3.029	0.109
-O2	3 x	2.281	0.824
-O4	1 x	2.599	0.116
			1.050 v.u.
Ca in C1			
C1-O1	3 x	2.417	0.889
-O2	3 x	3.085	0.146
-O3	1 x	2.620	1.000†
			0.894 v.u.

†OH- assumed, so bond length is probably different from that shown.

closely as possible, thereby forcing only the rotation of these tetrahedra. The derived positional parameters are given in Table 4, and representative bond-lengths, and their bond valence and cell edge are given in Table 5. This $P23$ model structure for nosean is shown in Figure 3c, for comparison with the average structure (Figs. 3a, b).

The 'ideal' nosean structure has a completely ordered aluminosilicate framework, two symmetry-independent cages, and two interframework cation positions, similar to the $C2$ and $C3$ positions of the average structure (note that these cation positions are four-fold equivalent in space group $P23$). The model structure can be modified further by including a third cation position, similar to the $C1$ position of the average structure, which facilitates the incorporation of the higher-charged Ca^{2+} ions and the larger K^+ ions into the structure. In the case of Ca^{2+} ions, an equivalent amount of H_2O must be replaced by OH^- for charge balance, whereas in the case of K^+ ions, the $C1$ position is displaced toward the center of the $[H_2O]$-bearing cage to give more realistic K–O distances.

Assuming an ideal ratio of $[SO_4]$- to $[H_2O]$-bearing cages of 1.0, then predictions can be made concerning the limits of solid solutions among Ca^{2+}, OH^- and K^+ ions in the structure. In a structure without vacant cation sites, the formula containing the maximum Ca is $Na_7Ca[Al_6Si_6O_{24}]SO_4 \cdot OH$, as there is room for one OH^- in a cage in the place of water. The corresponding formula for maximum K content is $Na_4K_4[Al_6Si_6O_{24}]SO_4 \cdot H_2O$, as only the $[H_2O]$-bearing cage has room for K^+ ions.

Using the nosean model structure, the chemical composition shown by the chemical analysis (Table 1) can be rationalized by first allocating the Ca^{2+} and K^+ ions to the $C1$ site. Enough Na^+ ions are then placed in the $C3$ site to satisfy the amount of SO_4^{2-} present, and the remaining Na^+ ions are assigned to the $C2$ site. As the two positions are close to each other, the sum of $C1$ and $C2$ must be less than or equal to 1.0. The derived nosean formula (Table 6) is consistent with the electron density observed from the structure refinement.

The nosean model structure has important properties. Firstly, it shows a possible structure for the nosean chemical composition in space group $P23$ and, secondly, it is a subset of the experimentally determined structure in space group $P\bar{4}3n$. Furthermore, if the model structure is translated by the n-glide of space group $P\bar{4}3n$ and the structural units are superimposed, the topology of the experimentally determined structure is produced (see Fig. 3). This result implies that the crystal used for the structure determination consists of domains of $P23$-type nosean separated by antiphase domain boundaries (*APBs*). Such a crystal could form at a high tem-
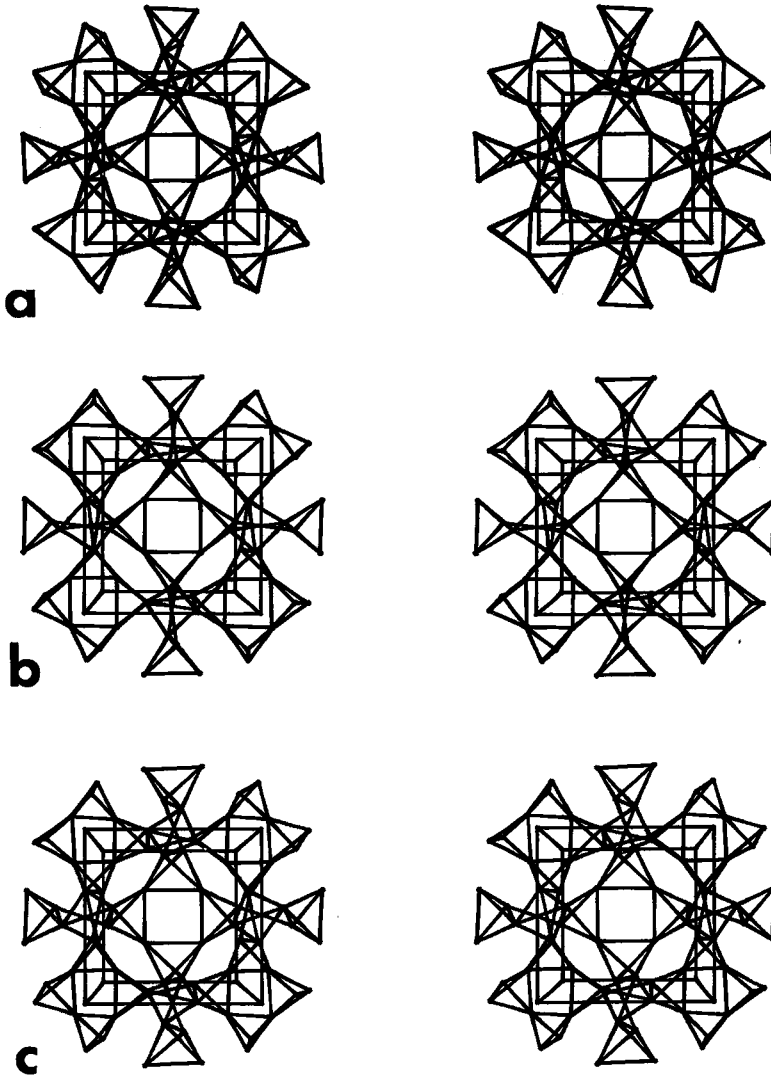
FIG 3. Stereoscopic *c*-axis projection of the upper half of the structure of nosean. (a) Framework tetrahedra based on the O1 experimental oxygen-atom positions, and (b) framework tetrahedra based on the O2 experimental oxygen-atom positions. In (a) and (b), the O1 and O2 tetrahedra can be described as rotations, in opposite directions, from a more symmetrical uncollapsed structure to these partly collapsed structures. (c) Framework tetrahedra based on the 'ideal' nosean model structure in space group *P*23.

perature if the clusters of $[Na_4 \cdot SO_4]^{2+}$ and $[Na_4 \cdot H_2O]^{4+}$ were randomly distributed over the cages and conformed with space group $P\bar{4}3n$. On cooling, an ordering process could be initiated and driven by the differing spatial requirements of the clusters, and by the need to satisfy local charge-balance. Domains of ordered *P*23 nosean could easily nucleate in different parts of the crystal because the

TABLE 6. DISTRIBUTION OF NON-FRAMEWORK ATOMS OF NOSEAN SAMPLE M5279 BASED ON THE IDEALIZED NOSEAN P23 STRUCTURE AND CHEMICAL ANALYSIS

C1	0.6 Ca + 0.6 K	
C2	0.82 Na	Derived Formula
C3	0.98 Na	$Na_{7.2}Ca_{0.24}K_{0.24}[Al_6Si_6O_{24}](SO_4)_{0.98}(OH)_{0.24}$
O3	0.06 OH	
S	0.98 S	
O4	0.98 O	

aluminosilicate framework remains intact, and only a trivial rotation of the individual tetrahedra of the framework is needed for the ordering to proceed. Where the different parts of the crystal meet each other, and if the ordered regions are not in phase, then *APB*s would form and give rise to distinct domains. All such domains in the crystal are sampled by the X-ray-diffraction method; the structure determined from these data is an average structure. Moreover, chemical variations from the 'ideal' composition would result in a variety of clusters, so that the situation can be complicated further.

Positional ordering of the framework oxygen atoms on their two symmetry-independent positions can modulate the periodicities and give rise to incommensurate superstructures, and thus, the observed satellite-reflections on single-crystal X-ray-diffraction patterns (Fig. 1). A more detailed explanation of the origin of the satellite reflections and *APB*s is the subject of a HRTEM study by Hassan & Buseck (1987, 1989a,b).

REFERENCES

BROWN, I.D. & SHANNON, R.D. (1973): Empirical bond-strength – bond-length curves for oxides. *Acta Crystallogr.* **A29**, 266-282.

CROMER, D.T. & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree–Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.

HASSAN, I. (1983): *The Crystal Chemistry and Crystal Structure of the Sodalite and Cancrinite Groups of Minerals.* Ph.D. thesis, McMaster Univ., Hamilton, Ontario.

_____ & BUSECK, P.R. (1987): The incommensurate-modulated structures of sodalite-group minerals. *Geol. Soc. Am., Abstr. Programs* **19**, 695.

_____ & _____ (1989a): The incommensurate-modulated structure of noean, a sodalite-group mineral. *Am. Mineral.* **74**, 394-410.

_____ & _____ (1989b): Cluster ordering and antiphase domain boundaries in hauyne. *Can. Mineral.* **27**, 173-180.

_____ & GRUNDY, H.D. (1983a): Structure of basic sodalite, $Na_8Al_6Si_6O_{24}(OH)_2 \cdot 2H_2O$. *Acta Crystallogr.* **C39**, 3-5.

_____ & _____ (1983b): The crystal structure of nosean. *Geol. Assoc. Can. - Mineral. Assoc. Can., Program Abstr.* **8**, A30.

_____ & _____ (1984): The crystal structures of sodalite-group minerals. *Acta Crystallogr.* **B40**, 6-13.

_____, PETERSON, R.C. & GRUNDY, H.D. (1985): The structure of lazurite, ideally $Na_6Ca_2(Al_6Si_6O_{24})S_2$, a member of the sodalite group. *Acta Crystallogr.* **C41**, 827-832.

LOEWENSTEIN, W. (1954): The distribution of aluminum in the tetrahedra of silicates and aluminates. *Am. Mineral.* **39**, 92-96.

MORIMOTO, N. (1978): Incommensurate superstructures in transformation of minerals: *Recent Prog. Nat. Sci. Japan* **3**, 183-206.

PETERSON, R.C. (1983): The structure of hackmanite, a variety of sodalite, from Mont St-Hilaire, Quebec. *Can. Mineral.* **21**, 549-552.

SAALFELD, H. (1961): Strukturbesonderheiten des Hauyngitters. *Z. Kristallogr.* **115**, 132-140.

SCHULZ, H. (1970): Struktur- und Überstrukturuntersuchungen an Nosean-Einkristallen. *Z. Kristallogr.* **131**, 114-138

_____ & SAALFELD, H. (1965): Zur Kristallstruktur des Noseans, $Na_8[SO_4(Si_6Al_6O_{24})]$. *Tschermaks Mineral. Petrogr. Mitt.* **10**, 225-232.

STEWART, J.M. (1976): The XRAY 76 system. *Computer Science Center, Univ. Maryland, College Park, Maryland, Tech. Rep.* **TR-446.**

TAYLOR, D. (1967): The sodalite group of minerals. *Contrib. Mineral. Petrol.* **16**, 172-188.

TSUCHIYA, N. & TAKÉUCHI, Y. (1985): Fine texture of hauyne having a modulated structure. *Z. Kristallogr.* **173**, 273-281.

VAN PETEGHEM, J.K. & BURLEY, B.J. (1963): Studies on solid solution between sodalite, nosean and hauyne. *Can. Mineral.* **7**, 808-813.

VILLIGER, H. & MEIER, W.M. (1969): *DLS – A Fortran Program for the Least Squares Refinement of Interatomic Distances.* Inst. Kristallogr. Petrol., Eidnig. Tech. Hochschule, Zürich, Switzerland.