

Table 4. Summary of five-membered-ring parameters for five crystal structures

For a definition of q and φ see text. $\langle\theta\rangle$ is the average of the five endocyclic bond angles, $r(\theta, |\tau|)$ the correlation coefficient between endocyclic bond angles and the absolute value of the opposite torsion angles.

	RT-Si ₃ I ₁₀	LT-Si ₃ I ₁₀	LT-Si ₃ Br ₁₀	RT-Si ₃ Ph ₁₀	RT-As ₃ Me ₁₀
q	0.545 (6)	0.544 (6)	0.543 (5)	0.634 (4)	0.865 (5)
φ	-69.4 (9)	-66.3 (9)	-66.1 (8)	-97.2 (6)	-152.7 (4)
$\varphi \pmod{36}$	2.6 (9)	5.7 (9)	5.9 (8)	10.8 (6)	28.0 (4)
$\langle\theta\rangle$	105.3 (4)	105.4 (4)	105.4 (5)	104.5 (6)	101.8 (16)
$r(\theta, \tau)$	0.80	0.83	0.94	0.88	0.75

The same quantity can also be obtained from the 1-4 distance, using the dihedral angle $\tau(=\tau_{3456})$ and assuming that $\theta_4 = \theta_5 = \bar{\theta}$, the average over all five bond angles,

$$d^2 = R^2(1 - 2\cos\bar{\theta})^2 + 4R^2\sin^2\bar{\theta}\sin^2(\tau/2).$$

Equating the two right sides, squaring and rearranging yields:

$$\cos\theta = \frac{1}{2} - (1 - \cos\bar{\theta})^2 + \sin^2\bar{\theta}\cos\tau.$$

With $\bar{\theta} = 105.35^\circ$, the value observed in the three halogenide structures, we obtain

$$\cos\theta = 0.93 \cos\tau - 1.1.$$

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The Structure of Lazurite, Ideally $\text{Na}_6\text{Ca}_2(\text{Al}_6\text{Si}_6\text{O}_{24})\text{S}_2$, a Member of the Sodalite Group

BY I. HASSAN

Earth and Planetary Sciences, Erindale Campus, University of Toronto, Mississauga, Ontario, Canada L5L 1C6

R. C. PETERSON

Department of Geological Sciences, Queen's University, Kingston, Ontario, Canada K7L 3N6

AND H. D. GRUNDY

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

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Abstract. Cubic, $P\bar{4}3n$, $Z = 1$, two different specimens: (1) Afghanistan, $\text{Na}_{8.56}(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4)_{1.56}\text{S}_{0.44}$, $M_r = 1075.14$, $a = 9.105$ (2) Å, $V = 754.8$ Å³, $D_x = 2.39$ Mg m⁻³, graphite-monochromatized Mo $K\alpha$ radiation, $\lambda K\alpha = 0.71069$ Å,

$\mu = 1.18$ mm⁻¹, $F(000) = 530$; (2) Baffin Island, $\text{Na}_{8.16}(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4)_{1.14}\text{S}_{0.86}$, $M_r = 1039.06$, $a = 9.054$ (1) Å, $V = 742.2$ Å³, $D_x = 2.42$ Mg m⁻³ graphite-monochromatized Cu $K\alpha$ radiation, $\lambda K\alpha = 1.54178$ Å, $\mu = 9.31$ mm⁻¹, $F(000) = 512$. R factors

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for unique observed substructure reflections measured on automated four-circle single-crystal X-ray diffractometer are 0.070 for 156 reflections of an Afghanistan sample and 0.063 for 115 reflections of a Baffin Island sample. The 1:1 ratio of Al to Si is completely ordered. There is positional disorder of (1) framework O atoms over two sets of 24(*i*) positions, (2) interframework cations over three sets of 8(*e*) positions, and (3) SO₄ groups in two orientations for the Baffin Island sample but one in the Afghanistan specimen. The S²⁻ ions are in separate and different-size cages from those of the SO₄²⁻ ions and this gives rise to the positional disorder of the framework O atoms. The observed superstructure reflections appear to be caused by the positional and/or substitutional ordering of all the atoms in the structure.

Introduction. Lazurite, (Na,Ca)₈Al₆Si₆O₂₄(SO₄,S,Cl)₂ (Strunz, 1970), a naturally occurring member of the aluminosilicate–sodalite group, is similar to the sulfatic members, nosean and hauyne. The isotypic, cubic minerals in the sodalite group (Hassan, 1982; Hassan & Grundy, 1983*a,b*, 1984*a*; Peterson, 1983) are polymorphic with the isotypic, hexagonal minerals of the cancrinite group (Grundy & Hassan, 1982; Hassan & Grundy, 1984*b*; Pahor, Calligaris, Nardin & Randaccio, 1982). The aluminosilicate framework (Al₆Si₆O₂₄)⁶⁻ of these mineral groups is well defined with a 1:1 ratio of AlO₄ and SiO₄ tetrahedra. These tetrahedra are fully ordered in the space groups *P43n* and *P6₃* for the sodalite group and the cancrinite group respectively.

The framework of aluminosilicate–sodalite consists of alternating AlO₄ and SiO₄ tetrahedra which are cornered-linked to give cubo-octahedral cavities or sodalite cages (see Fig. 1 of Hassan & Grundy, 1984*a*). The cages can accommodate a variety of cations and anions by adapting to different sizes due to the cooperative rotations of the framework tetrahedra (see Fig. 2 of Hassan & Grundy, 1984*a*). The diversity of interframework ions is limited by spatial requirements and by the requirements of electrical neutrality of the negatively charged framework oxygens.

The mineralogy of lazurite has been given considerable attention in the past due to its similarity to ultramarines (Brogger & Backstrom, 1891; Jaeger, 1929). However, due to the difficulty in separating pure samples, chemical analyses are often quite poor. Taylor (1967) chemically analysed two lazurite specimens from the lapis lazuli deposits of Sary-Sang, Afghanistan by 'semi-microanalytical methods'. These analyses, however, are unsatisfactory since the sum of the interframework ions appears quite high. Hogarth & Griffin (1976) gave chemical analyses for several lazurite specimens but, in order to reduce the excess interframework anions, they assumed that sulfur replace some framework oxygens. They also observed

cubic (isotropic) and non-cubic (anisotropic and pleochroic) varieties of lazurite.

Superstructure reflections have been observed from single crystals of nosean and hauyne (Saalfeld, 1959, 1961; Ito & Sadanaga, 1966; Taylor, 1967; Schulz, 1970) but evidence of superstructure reflections from single crystals of lazurite is less established. Taylor (1967) could not obtain a single crystal from his lazurite specimen #20 from Afghanistan; however, his examination of a composite grain suggested the presence of superstructure reflections. The complex superstructure reflections observed from the sulfatic sodalite minerals have been classified as incommensurate (Taylor, 1967; Sadanaga, Takéuchi & Morimoto, 1978). The origin of these reflections is not known in detail, though from a single-crystal structure determination of nosean, Schulz (1970) suggested that all the atoms in the structure contribute to the formation of the superstructure reflections. The purpose of the present study is to examine the detailed substructure of lazurite. This is a necessary starting point for understanding the complex superstructures of the sulfatic sodalite-group minerals.

Two different specimens of lazurite have been studied simultaneously (Peterson, 1984). The Afghanistan specimen was examined at McMaster University and that of the Baffin Island at Queen's University. Due to the similarities of the two studies, the results are combined and compared in the present paper.

Experimental. Deep-blue lazurites, optically isotropic, automatic four-circle single-crystal diffractometer, cell parameters determined by least-squares refinement of automatically centered reflections; Lorentz, polarization, background effects and spherical-absorption corrections.

(a) Afghanistan specimen

Sary-Sang, Afghanistan (donated by the Royal Ontario Museum, M16745); 0.20 × 0.20 × 0.28 mm; chemical analyses [Taylor (1967), analysis #20] of a sample from same locality (wt%): SiO₂ 31.34, Al₂O₃ 26.27, Fe₂O₃ 0.27, MgO 2.47, CaO 7.97, Na₂O 15.75, K₂O 1.02, SO₃ 8.71, S 1.84, Cl 0.78, H₃O⁺ 3.87, total 100.29, less O = Cl, S 0.67, net 99.62; calculated cell contents (based on Al + Si = 12): Si 6.04, Al 5.96, Fe 0.04, Mg 0.71, Ca 1.65, Na 5.88, K 0.25, $\sum_c = 8.53$, SO₄ 1.26, S 0.66, Cl 0.26, $\sum_a = 2.18$. Nicolet P3 diffractometer, graphite-monochromatized Mo K α radiation; θ -2 θ scan mode; 2 θ scan range ($K\alpha_1 - 0.85^\circ$) to ($K\alpha_2 + 0.85^\circ$); variable scan rates 3 to 29.3° min⁻¹ depending on intensity of a prescan; cell parameters, 15 reflections (10° < 2 θ < 32°); all reflections (2006) with +*h* +*k* +*l* (0 ≤ *h, k, l* ≤ 14) below 2 θ = 70°; two standard reflections, 112, 222, monitored after every 50 reflections did not change; $\mu R = 0.27$; 391 unique reflections, 156 considered

observed on the criterion $F_o > 2.8\sigma(F)$; all crystallographic calculations made using *XRAY76* (Stewart, 1976).^{*} Precession photographs (Fig. 1)^{*} show sharp substructure reflections and complex superstructure reflections similar to those observed for nosean (see Fig. 2, Schulz, 1970); symmetry of substructure reflections is consistent with space group $P\bar{4}3n$.

(b) Baffin Island specimen

Crystal $0.23 \times 0.23 \times 0.20$ mm; chemical analysis [Hogarth & Griffin (1976), #6-1] (wt%): SiO₂ 33.3, Al₂O₃ 26.4, CaO 5.3, Na₂O 18.8, K₂O 0.02, SO₃ 10.91, S 1.72, Cl 0.20, total 96.65, less O = Cl, S 0.91, net 95.74; calculated cell contents (based on Si + Al = 12): Si 6.20, Al 5.80, Ca 1.06, Na 6.79, K 0.01, $\sum_c = 7.86$, SO₄ 1.53, S 0.60, Cl 0.06, $\sum_a = 2.19$. Enraf-Nonius CAD-4 diffractometer, graphite-monochromatized Cu K α radiation; cell parameters, 21 reflections ($25^\circ < \theta < 32^\circ$); θ - 2θ scan mode; variable scan rate 1.34 to $10^\circ \text{ min}^{-1}$ depending on intensity of prescan; all reflections (2216) with $\pm h \pm k \pm l$ below $\sin\theta/\lambda = 0.46 \text{ \AA}^{-1}$ [$2\theta(\text{Cu K}\alpha) = 90^\circ$]; three standard reflections measured every half hour showed no significant change in intensity; $\mu R = 1.0$; reflections averaged in $\bar{4}3m$ give 336 unique reflections with 115 considered observed based on $I > 3\sigma(I)$; agreement between symmetry-equivalent structure factors 2.8%; all crystallographic calculations made using *SDP* package (Frenz, 1982). Precession photographs (Fig. 2)^{*} show a well defined subcell with no systematic extinctions together with a weaker supercell. The refined supercell parameter of $a = 54.2(2) \text{ \AA}$ is equal to six times that of the subcell. The superstructure reflections in this plane (Fig. 2) show no streaking. Although this supercell appears commensurate, in general they are incommensurate (Taylor, 1967). The list of structure factors shows several weak reflections of the class hhl , $l = 2n + 1$ which violate $P\bar{4}3n$ symmetry. This may be due to the nature of the superstructure reflections of this sample. Nevertheless, the refinement was undertaken in $P\bar{4}3n$ as attempts at refinement in $P\bar{4}3m$ added many more parameters without significant improvement in the model.

Structure refinements

(a) *Afghanistan specimen*. Initial positional parameters were calculated using the geometric sodalite model of Hassan & Grundy (1984a). Atomic scattering factors for neutral atoms were taken from Cromer & Mann (1968). A full-matrix least-squares technique was used to refine the atomic coordinates and isotropic temperature factors of the framework atoms (Al, Si and O)

Table 1. Atomic positional parameters, occupancy factors and thermal parameters ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

	Occupancy	Site	x	y	z	$U_{\text{iso}}(\text{\AA}^2)$
(a) Afghanistan sample						
Al	1.00	6 (d)	$\frac{1}{2}$	0	$\frac{1}{2}$	34*
Si	1.00	6 (c)	$\frac{1}{2}$	$\frac{1}{2}$	0	39*
O(1)	0.50	24 (i)	0.133 (2)	0.147 (2)	0.545 (2)	39 (4)
O(2)	0.50	24 (i)	0.157 (2)	0.158 (2)	0.474 (2)	39 (3)
Na(1)	0.35 (2)	8 (e)	0.178 (2)	0.178	0.178	52 (9)
Na(2)	0.50 (2)	8 (e)	0.231 (1)	0.231	0.231	41 (4)
Na(3)	0.22 (2)	8 (e)	0.305 (3)	0.305	0.305	35 (8)
S	1.00	2 (a)	0	0	0	168 (9)
O(3)	0.78 (5)	8 (e)	0.598 (2)	0.598	0.598	212 (22)
(b) Baffin Island sample						
Al	1.00	6 (d)	$\frac{1}{2}$	0	$\frac{1}{2}$	37 (1)
Si	1.00	6 (c)	$\frac{1}{2}$	$\frac{1}{2}$	0	38 (1)
O(1)	0.37 (1)	24 (i)	0.133 (2)	0.144 (2)	0.551 (1)	46 (4)
O(2)	0.40 (1)	24 (i)	0.153 (2)	0.161 (2)	0.474 (2)	54 (4)
Na(1)	0.43 (3)	8 (e)	0.196 (1)	0.196	0.196	60 (5)
Na(2)	0.30 (3)	8 (e)	0.245 (2)	0.245	0.245	35 (5)
Na(3)	0.29 (2)	8 (e)	0.317 (2)	0.317	0.317	61 (8)
S	1.00	2 (a)	0	0	0	137 (8)
O(3)	0.36 (3)	8 (e)	0.598 (3)	0.598	0.598	205 (3)
O(4)	0.21 (3)	8 (e)	0.402	0.402	0.402	140 (4)

* $U_{22} = U_{33}$; $U_{12} = U_{13} = U_{23} = 0$; Al: $U_{11} = 62(5)$, $U_{22} = 19(1)$; Si: $U_{11} = 13(2)$, $U_{22} = 52(2)$.

using unit weights and a variable overall scale factor. The Al and Si atoms had unusually large temperature factors, compared to that of sodalite (Hassan & Grundy, 1984a), but they were of similar magnitude. The parameters of the O atom in a 24(i) position, similar to that in sodalite, did not refine successfully and a difference Fourier map showed that its electron density was quite elongated. This site was therefore divided between two 24(i) positions with equal occupancy factors. Both of these sites, O(1) and O(2), then refined easily and their temperature factors were of similar magnitude. A similar framework was also found in nosean (Hassan & Grundy, 1983b). The parameters of the cage cations on an 8(e) site, similar to that in sodalite, could not be refined successfully and due to their large temperature factors and through difference Fourier sections three 8(e) sites were used to model the electron density. These sites together with their refined occupancy factors are shown in Table 1(a). Three similar sets of cation sites were also found in nosean (Hassan & Grundy, 1983b).

The S atom fully occupies the 2(a) site as indicated by its refined occupancy factor of 0.97 (4). O atoms of the SO₄ group could occupy 8(e) positions with $x = 0.60$ and/or $x = 0.40$. If both sets of sites are occupied, the positions would be at the corners of a cube with an edge of 1.82 \AA . Although a difference Fourier map showed electron density at both positions, that with $x = 0.60$ was higher. The coordinate and occupancy factor of the O atom, O(3), at this position refined easily, and a subsequent map did not show any significant electron density at $x = 0.40$. Moreover, refinements with O atoms at both positions were unsuccessful, confirming that the O atoms of the SO₄ group occupy only one set of 8(e) positions in this

* List of structure factors and Figs. 1 and 2 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42067 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

sample. Furthermore, both the S and O(3) atoms of the SO_4 group have temperature factors that are of similar but large magnitude. In nosean, Hassan & Grundy (1983*b*) found that the SO_4 group also occupies one position in contrast with the results of Schulz (1970).

The isotropic thermal parameters of only the Al and Si atoms could be converted to the anisotropic form. This resulted in convergence of the model to $R = 0.070$ and $wR = 0.059$ (with $w = 1$) for the 156 observed reflections based on $F_o > 2.8\sigma(F)$. A final difference Fourier map was featureless with max. height 0.40 and min. $-0.60 \text{ e } \text{Å}^{-3}$ at 2(*a*). In the final cycles of refinement the maximum and average least-squares shifts over error were 0.12 and 0.02 respectively.

(*b*) *Baffin Island specimen*. The atomic and isotropic thermal parameters were refined using the least-squares technique and unit weighting for all reflections. Scattering curves of Cromer & Waber (1974) for neutral atoms and anomalous-dispersion corrections of Cromer (1974) were used. Starting parameters were taken from Peterson (1983). Through difference Fourier sections, a similar aluminosilicate framework and Na parameters (Table 1*b*) were found but, in contrast to the Afghanistan sample, both sets of sulfate O positions [O(3) and O(4)] were used to model the observed electron density. The sulfate O positions were constrained to be at equal distance from the 2(*a*) site as high correlation did not allow simultaneous refinement. The 2(*a*) site was assumed to be filled with S and the O atoms O(3) and O(4) have occupancies 0.36 (3) and 0.21 (3) indicating a preference for one orientation. The occupancies of S, O(3) and O(4) (Table 1*b*) indicate 1.14 SO_4^{2-} and 0.86 S^{2-} per cell. Hogarth & Griffin (1976) give 1.53 SO_4^{2-} and 0.60 S^{2-} for this lazurite. The Na occupancies sum to 1.02; however, Ca is present in the analysis of Hogarth & Griffin (1976) which has not been accounted for. The position of Ca in the structure cannot be directly determined using the present data set. The sum of the occupancies of the two framework O sites is 0.77 (2) instead of 1.0. This may be due to the inability of a model with two isotropic atoms to account for the total electron density in this region.

No significant residual electron density remained in the difference Fourier sections after the final cycle of least squares with $R = 0.063$ for 115 observed reflections with $I > 3\sigma(I)$. Removal of the reflections which violate the *n* glide results in $R = 0.056$ for 103 observed reflections. In the final cycle of refinement the maximum and average least-squares shifts over error were 0.51 and 0.10 respectively.

Table 2(*c*) shows the tetrahedral framework bond lengths and angles to be consistent with an ordered Al—Si distribution. The Na—O distances are all reasonable except for the short Na(1)—O(3) and Na(3)—O(4) distances which are not true interatomic separations but the result of partial occupation of two sites which would

not be filled in any one unit cell. The geometry of the SO_4 groups is consistent with SO_4 groups in other minerals (Ondik & Smith, 1968).

Table 2. *Interatomic distances (Å) and angles (°), with e.s.d.'s in parentheses, and valence sums*

(a) The geometry of the AlO_4 , SiO_4 and SO_4 tetrahedra and valence sums for the Afghanistan sample			
Al—O(1)	4 × 1.76 (2)	Si—O(1)	4 × 1.58 (2)
O(1)—O(1)	4 × 2.92 (3)	O(1)—O(1)	4 × 2.60 (3)
	2 × 2.81 (3)		2 × 2.55 (3)
Mean	2.88	Mean	2.58
O(1)—Al—O(1)	4 × 111.5 (8)	O(1)—Si—O(1)	4 × 110.4 (9)
	2 × 105.5 (9)		2 × 107.7 (9)
Mean	109.5	Mean	109.5
Al—O(2)	4 × 1.69 (2)	Si—O(2)	4 × 1.67 (2)
O(2)—O(2)	4 × 2.67 (3)	O(2)—O(2)	4 × 2.64 (3)
	2 × 2.92 (3)		2 × 2.89 (3)
Mean	2.75	Mean	2.72
O(2)—Al—O(2)	4 × 104.7 (8)	O(2)—Si—O(2)	4 × 104.5 (8)
	2 × 119.6 (9)		2 × 119.9 (9)
Mean	109.7	Mean	109.6
Mean Al—O	1.726	Mean Si—O	1.627
Al—O(1)—Si	148.3 (9)	S—O(3)	4 × 1.54 (1)
Al—O(2)—Si	146.8 (9)	O(3)—O(3)	6 × 2.55 (2)
		O(3)—S—O(3)	6 × 109.5 (4)
Bond-valence sums			
Al = 4 × 0.5 × (0.698 + 0.845) = 3.086 v.u.			
Si = 4 × 0.5 × (1.113 + 0.878) = 3.982 v.u.			
(b) The most important cation—O distances and valence sums for the Afghanistan sample			
		Na	Ca
Na(1)—O(1)	3 × 2.63 (2)	3 × 0.5 × 0.110	× 0.168
—O(1)	3 × 3.38 (2)	3 × 0.5 × 0.027	× 0.038
—O(2)	3 × 2.71 (2)	3 × 0.5 × 0.095	× 0.144
—O(2)	3 × 2.82 (2)	3 × 0.5 × 0.076	× 0.114
Mean	$\frac{2.89}{2.89}$		
—S	1 × $\frac{2.82}{2.82}$ (1)	1 × 0.5	× 0.5
		$\frac{0.962 \text{ v.u.}}$	$\frac{1.196 \text{ v.u.}}$
Na(2)—O(1)	3 × 2.37 (2)	3 × 0.5 × 0.199	× 0.318
—O(1)	3 × 3.09 (2)	3 × 0.5 × 0.045	× 0.065
—O(2)	3 × 2.41 (2)	3 × 0.5 × 0.183	× 0.291
—O(2)	3 × 2.74 (2)	3 × 0.5 × 0.088	× 0.132
—O(3)	1 × 2.11 (1)	1 × 0.387	× 0.649
Mean	$\frac{2.69}{2.69}$	$\frac{1.150 \text{ v.u.}}$	$\frac{1.858 \text{ v.u.}}$
—S	1 × $\frac{3.65}{3.65}$ (1)		
Na(3)—O(1)	3 × 2.47 (2)	3 × 0.5 × 0.159	× 0.249
—O(1)	3 × 3.05 (2)	3 × 0.5 × 0.049	× 0.070
—O(2)	3 × 2.45 (2)	3 × 0.5 × 0.168	× 0.264
—O(2)	3 × 3.05 (2)	3 × 0.5 × 0.049	× 0.070
—O(3)	3 × 2.95 (1)	3 × 0.059	× 0.086
Mean	$\frac{2.79}{2.79}$	$\frac{0.815 \text{ v.u.}}$	$\frac{1.238 \text{ v.u.}}$
—S	1 × $\frac{3.081}{3.081}$ (1)		
Bond-valence sums for O(1) and O(2)			
	O(1)	O(2)	
From Al and Si	0.698 + 1.113	0.878 + 0.845	
From Na(1)	+ 0.110 + 0.027 = 1.948	+ 0.076 + 0.095 = 1.894	
From Na(2)	+ 0.199 + 0.045 = 2.055	+ 0.183 + 0.088 = 1.994	
From Na(3)	+ 0.159 + 0.049 = 2.019	+ 0.168 + 0.049 = 1.940	
(c) Selected bond lengths and angles for the Baffin Island sample			
Al—O(1)	4 × 1.74 (2)	Si—O(1)	4 × 1.61 (1)
O(2)	4 × 1.72 (1)	—O(2)	4 × 1.62 (1)
O(1)—Al—O(1)	4 × 111.7 (9)	O(1)—Si—O(1)	4 × 110.9 (9)
	2 × 105.1 (5)		2 × 106.7 (6)
O(2)—Al—O(2)	4 × 105.1 (8)	O(2)—Si—O(2)	4 × 104.3 (4)
	2 × 118.5 (8)		2 × 120.3 (8)
Na(1)—O(1)	3 × 2.48 (3)	Na(2)—O(1)	3 × 2.30 (2)
O(2)	3 × 2.56 (2)	—O(2)	3 × 2.36 (2)
—O(2)	3 × 2.76 (2)	—O(2)	3 × 2.76 (2)
—O(3)	1 × 1.54 (2)	—O(3)	1 × 2.30 (1)
—O(4)	3 × 2.94 (2)	—O(4)	1 × 2.47 (1)
—S	1 × 3.07 (2)	—S	1 × 3.84 (2)
S—O(3)	4 × 1.54 (1)	Na(3)—O(1)	3 × 2.47 (3)
—O(4)	4 × 1.54	—O(2)	3 × 2.49 (2)
		—O(3)	3 × 2.76 (1)
O(1)—O(2)	0.74 (2)	—O(4)	1 × 1.33 (1)
		—S	1 × 2.87 (1)

Discussion. Although this discussion applies specifically to the Afghanistan specimen, it is also applicable to the Baffin Island specimen. Important interatomic distances, angles and bond-valence sums (Brown & Shannon, 1973) about each atom are given in Table 2(a,b). The mean Al—O and Si—O distances of 1.73 and 1.63 Å, respectively, are similar to that in sodalite (Hassan & Grundy, 1984a; Peterson, 1983), basic sodalite, nosean (Hassan & Grundy, 1983a,b) and the Baffin Island sample. The Al³⁺ and Si⁴⁺ ions are also charge balanced (Table 2a). Thus the Al and Si sites are completely ordered. The large temperature factors for the Al and Si atoms suggest positional disorder but this could not be incorporated into the structural model. The O atoms of the framework are positionally disordered over two sets of 24(*i*) positions with equal frequency (as in nosean, Hassan & Grundy, 1983b) and their isotropic thermal parameters are of similar magnitude. These results contrast with that of sodalite and basic sodalite, in which the framework O atoms occupy only one set of 24(*i*) positions.

The three interframework cation sites are in close proximity so that occupancy of any one excludes the simultaneous occupancy of the other nearby positions. From bond distances (Table 2b), occupancy of the Na(1) position [compare Na(3) coordination in Baffin Island sample] excludes SO₄²⁻ from that cage but permits an S²⁻ ion to occupy a 2(*a*) position whereas occupancy of either the Na(2) position [compare Na(2) coordination in Baffin Island sample] or Na(3) position [compare Na(1) coordination in Baffin Island sample] excludes S²⁻ but includes SO₄²⁻ in that cage. It now remains to assign Na and Ca atoms to the three interframework cation positions and to determine the proportions of each different type of cage. This is done by a simple charge-balance concept which is quite useful in rationalizing the crystal chemistry of the sodalite-group minerals (Hassan, 1982).

In lazurite the different cages may contain [3Na.1Ca.1S]³⁺ or [3Na.1Ca.1SO₄]³⁺ ions. We may determine the proportion of these cages from the occupancy factors (Table 1a) of either the O(3) position [sum of O(3) and O(4) for Baffin Island sample] or the Na(1) position [Na(3) for Baffin Island sample], as in an S-bearing cage all four cations are disordered on the Na(1) site [whereas they are disordered on Na(3) for the Baffin sample]. The former gives 78% SO₄-bearing cages compared to 71% from the latter (whereas for the Baffin sample they correspond to 57% and 76% respectively). Based on 71% SO₄-bearing cages (76% for Baffin sample), Table 3 compares the refined occupancy factors of the interframework cation sites with values calculated for the two possible combinations of cations at the Na(2) and Na(3) sites [Na(1) and Na(2) for Baffin sample]. Combination (1) gives excellent agreement with the refined occupancy factor only for the Na(2) position, whereas combination (2)

Table 3. *Calculated and refined occupancy factors in terms of Na atoms*

	Site	Cage cations	Calculated occupancy factors	Refined occupancy factors
Afghanistan sample (based on 71% SO ₄)				
	Na(1)	3Na + 1Ca	0.35	0.35 (2)
(1)	Na(2)	3Na	0.53	0.50 (2)
	Na(3)	1Ca	0.32	0.22 (2)
(2)	Na(2)	2Na + 1Ca	0.68	0.50 (2)
	Na(3)	1Na	0.18	0.22 (2)
Chemical formulae				
(1)	Model:	Na ₆ Ca ₇ (Al ₄ Si ₆ O ₂₄)(SO ₄) _{1.42} S _{0.58}		
(2)	Refinement:	Na _{8.56} (Al ₄ Si ₆ O ₂₄)(SO ₄) _{1.56} S _{0.44}		
(3)	Chemical analysis:	Na _{5.88} Ca _{1.65} K _{0.22} (Al _{3.96} Si _{6.04} O ₂₄)(SO ₄) _{1.26} S _{0.66}		
Baffin Island sample (based on 76% SO ₄)				
	Na(3)	3Na + 1Ca	0.29	0.29 (2)
(a)	Na(2)	2Na	0.38	0.30 (3)
	Na(1)	1Na + 1Ca	0.53	0.43 (3)
(b)	Na(2)	1Ca	0.34	0.30 (3)
	Na(1)	3Na	0.57	0.43 (3)
Chemical formulae				
(1)	Model:	Na ₆ Ca ₇ (Al ₄ Si ₆ O ₂₄)(SO ₄) _{1.52} S _{0.48}		
(2)	Refinement:	Na _{8.16} (Al ₄ Si ₆ O ₂₄)(SO ₄) _{1.14} S _{0.86}		
(3)	Chemical analysis:	Na _{6.79} Ca _{1.00} (Al _{3.80} Si _{6.20} O ₂₄)(SO ₄) _{1.53} S _{0.60}		

agrees only for the Na(3) position. This disagreement suggests that both combinations are likely; and probably cages containing [4Na.SO₄]²⁺ and [2Na.2Ca.1SO₄]⁴⁺ in the ratio of 1:1 may also be present to some extent. A similar analysis of the Baffin Island sample (Table 3) shows that both combinations (*a*) and (*b*) are likely.

Bond-strength calculations (Brown & Shannon, 1973) for either Na or Ca atoms at the cation sites are given in Table 2(b). The values obtained for Na atoms on all the cation sites are close to the expected value of 1.0 valence units (v.u.) whereas the disagreement is quite large for Ca atoms except at the Na(2) site. Therefore, this analysis rules out Ca atoms occupying the Na(3) position, indicating a preference for combination (2) in the Afghanistan sample.

Table 3 compares chemical formulae obtained from (1) charge model; (2) refinement; and (3) chemical analysis. As Ca cannot be determined directly from the refinement, in terms of interframework cations, the chemical analyses agree better with the charge model. However, the total occupancy factor of the cations (Na⁺, K⁺, Ca²⁺) calculated from the chemical analyses in terms of Na gives 1.16 and 1.09 compared to 1.07 and 1.02 obtained from the refinements for the Afghanistan and Baffin samples respectively. In terms of the interframework anions, there is better agreement between the model and refinement for the Afghanistan sample but between the model and chemical analysis for the Baffin sample.

The framework O atoms are positionally disordered in lazurite because of the difference in size of the S- and SO₄-bearing cages which must be linked together to form a continuous three-dimensional framework. This is also found in nosean (Hassan & Grundy, 1983b), and

is due to the difference in size of the H₂O- and SO₄-bearing cages but not in hauyne (Hassan, 1982) where all the cages are filled only with SO₄ groups. The difference in cell edges for the two lazurite samples is due to the difference in K and SO₄ contents.

Comparing Tables 1(a) and 1(b), it is clear that both the Baffin Island and the Afghanistan specimens have identical framework parameters and similar interframework cation positional parameters. The main difference in the two specimens is in the SO₄ group. In the Afghanistan specimen the SO₄-group O atoms occupy one set of 8(e) positions whereas in the Baffin Island specimen they occupy two sets of 8(e) positions. However, in the latter one orientation is preferred (Table 1b).

The origin of the superstructure reflections in the sodalite-group minerals is not known in detail. Saalfeld (1961) suggested that the superstructure in hauyne is related to interframework atomic disorder while Schulz (1970) suggested that all the atoms in the structure of nosean probably contribute to the superstructure reflections. The present study agrees with Schulz (1970) since the structure refinements show (1) Al and Si atoms with large thermal parameters indicative of positional disorder; (2) positionally disordered framework O positions; and (3) interframework atoms which show positional/substitutional disorder. Therefore, it seems likely that all the atoms contribute to the superstructure reflections in the sulfatic members of the sodalite-group minerals. However, for the polymorphic cancrinite group minerals (Grundy & Hassan, 1982; Hassan & Grundy, 1984b), the positional/substitutional ordering of only the channel ions gives rise to the superstructure reflections.

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