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# THE CRYSTAL STRUCTURE OF HAUYNE AT 293 AND 153 K

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## ABSTRACT

The structure of hauyne, ideally $Na_6Ca_2[Al_6Si_6O_{24}](SO_4)_2$, has been refined using separate intensity data-sets collected from the same single crystal at temperatures of 293 and 153 K, respectively. The refinements were done in space group $P\bar{4}3n$, and the final *R* indices are 0.036 and 0.039 for the 293 and 153 K data sets, respectively. The Al:Si ratio is 1:1; these atoms are completely ordered. There is positional disorder of the interstitial cations (Na, K, and Ca) over three independent 8(e) positions (sites *C*1, *C*2, and *C*3) that are close to each other on the body diagonals of the cubic cell. The *C*1, *C*2, and *C*3 sites are occupied by K, Ca, and Na, respectively. The sulfur atom of the $SO_4^{2-}$ group is displaced off the 2(a) position to an 8(e) position, but the oxygen atoms have remained at an 8(e) position, indicating that the $SO_4$ group is in one orientation instead of two. The present study also suggests that OH is a significant component of hauyne. There is no positional disorder of the framework oxygen atoms in this sample of hauyne, and satellite reflections were not observed in X-ray precession photographs. These results contrast with those for nosean and lazurite, wherein the framework oxygen atoms occupy two sets of 24(i) positions and the observed satellite reflections arise from the positional modulation of the framework oxygen atoms.

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

## SOMMAIRE

Nous avons affiné la structure cristalline de la hauyne, de formule idéale $Na_6Ca_2[Al_6Si_6O_{24}](SO_4)_2$, en utilisant des données d'intensité obtenues pour le même cristal à 293 et 153 K, respectivement. Les affinements, dans le groupe spatial $P\bar{4}3n$, ont donné un indice *R* final de 0.036 et 0.039, respectivement. Le rapport Al:Si est de 1 à 1, et ces atomes sont complètement ordonnés. Par contre, il y a désordre parmi les cations interstitiels (Na, K et Ca) sur les huit positions 8(e) indépendantes (sites *C*1, *C*2 et *C*3), qui sont rapprochées l'une de l'autre le long des diagonales de la maille cubique. Les sites *C*1, *C*2 et *C*3 contiennent K, Ca et Na, respectivement. Les atomes de soufre du groupe $SO_4^{2-}$ sont déplacés de la position 2(a) à la position 8(e), mais les atomes d'oxygène s'en tiennent à la position 8(e), indication que le groupe $SO_4$ possède une seule orientation et non deux. Nos résultats font penser que le OH serait un composant important de la hauyne. Il n'y a aucun désordre de position dans le cas des atomes d'oxygène du réseau, du moins dans notre échantillon, et nous ne voyons aucune réflexion satellite dans les clichés de précession. Ces résultats diffèrent donc du cas de la noséane et de la lazurite, dans lesquels les atomes d'oxygène du réseau occupent deux ensembles de positions 24(i), et la présence de réflexions satellites découle d'une modulation dans la position des atomes d'oxygène.

(Traduit par la Rédaction)

*Mots-clés*: groupe de la sodalite, hauyne, structure cristalline, mise en ordre de groupements, bordures des domaines antiphasés.

## INTRODUCTION

Hauyne, ideally $Na_6Ca_2[Al_6Si_6O_{24}](SO_4)_2$, is a sodalite-group mineral closely related to the other sulfatic members, nosean and lazurite. These minerals contain $SO_4^{2-}$ groups as the dominant interstitial anion, and they generally show complex satellite reflections (Saalfeld 1961, Taylor 1967, Schulz 1970, Hassan *et al.* 1985). The origin of the satellite reflections is not known in detail, but their presence does indicate that the structures of the sulfatic sodalites are incommensurately modulated; as a consequence, these minerals have been studied by transmission electron microscopy (TEM; Morimoto 1978, Tsuchiya & Takéuchi 1985, Hassan & Buseck 1989a, b). The hauyne specimen used in this study does not show satellite reflections on precession photographs; this specimen thus may provide a clue as to the origin of the incommensurate-modulated structure of sulfatic sodalites.

The aluminosilicate framework of the sodalite-group minerals has a 1:1 Al:Si ratio; these atoms are fully ordered. The structure has four-membered rings of $AlO_4$ and $SiO_4$ tetrahedra that are parallel to {100}. These rings are further linked to form six-membered rings that are parallel to {111}. The overall linkage of these rings gives rise to cubo-octahedral cages (*e.g.*, Fig. 1 of Hassan & Grundy 1984). The cages can accommodate a variety of interstitial cations and anions by cooperative rotation of the $AlO_4$ and $SiO_4$ tetrahedra (by angles $\phi_{Al}$ and $\phi_{Si}$, respectively) from their positions in a fully expanded structure (see Fig. 2 of Hassan & Grundy 1984). The range of interstitial ions is limited by spatial and charge requirements of the framework.

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TABLE 1. CHEMICAL COMPOSITION OF HAUYNE FROM VALLE BIACHELLA, SACROFANO, ITALY*

| Oxide | Wt. % | Cell contents** | |
|---|---|---|---|
| $Al_2O_3$ | 27.0 | Al | 6.05 |
| $SiO_2$ | 31.3 | Si | 5.95 |
| $Na_2O$ | 11.8 | Na | 4.35 |
| $K_2O$ | 3.9 | K | 0.95 |
| CaO | 11.2 | Ca | 2.28 |
| $SO_3$ | 14.2 | S | 2.03 |
| | 99.4 | | |

*Microprobe Analysis by Lindsay Keller, Arizona State University

**Based on Al + Si = 12.0; $a$=9.120(6) Å

## EXPERIMENTAL

The hauyne sample used in this study is from Sacrafano, Italy (Royal Ontario Museum no. M35731). A different specimen from this locality was chemically analyzed (Table 1), and we assume this composition to be representative of our material. Precession photographs show sharp substructure reflections and no satellite reflections. Space group $P\bar{4}3n$ was assumed and used in the structure refinement.

An initial refinement with the data set collected at 293 K (room temperature) indicates significant positional and substitutional disorder of the interstitial atoms in hauyne; another data set from the same single crystal was thus collected at 153 K to better define the parameters of the interstitial atoms. The cell parameter was determined by the least-squares method using monochromatic Mo$K\alpha$ radiation and 15 reflections having $10° < 2\theta < 35°$, automatically centered on a four-circle single-crystal X-ray diffractometer. The cell parameter and other information pertinent to X-ray data collection and refinements are presented in Table 2. All reflection intensities were measured in an octant on a Syntex $P2_1$ diffractometer operating in the $\theta$–$2\theta$ scan mode, with a $2\theta$ 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, 622 and 404, monitored after every 50 reflections, did not change during the experiment. The data were corrected for Lorentz, polarization, background effects, and spherical absorption (Table 2). Equivalent reflections were then averaged to produce unique data-sets. All crystallographic calculations were done 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 O1), the initial isotropic temperature-factors used were those of sodalite, and initial positional parameters were calculated using the geometrical model for sodalite (Hassan & Grundy 1984).

TABLE 2. CRYSTAL DATA* AND INFORMATION ON DATA COLLECTION FOR HAUYNE AT 293 AND 153 K

| Miscellaneous | 293 K | 153 K |
|---|---|---|
| a (Å) | 9.1164(5) | 9.1097(8) |
| V ($Å^3$) | 757.65 | 755.98(8) |
| $Density_{calc.}$ ($g/cm^{-3}$) | 2.41 | 2.42 |
| Crystal size (mm) | 0.23 x 0.23 x 0.17 | |
| $\mu$ ($cm^{-1}$) | 13.02 | 13.06 |
| Maximum 2Θ | 65° | 55° |
| 0 < h, k, l < | 13 | 11 |
| Total no. of intensities | 1649 | 1087 |
| No. of unique reflections | 329 | 219 |
| No. of non-equiv. $\lvert F_o \rvert > 3\sigma \lvert F \rvert$ | 164 | 133 |
| Final **R | 0.036 | 0.039 |
| Final ***$R_w$ | 0.033 | 0.036 |

*Space group $P\bar{4}3n$; Z = 1; Radiation/monochromator = Mo/C; MoKα =0.71069Å

**$R=\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$; ***$R_w=[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert Fo\rvert^2]^{1/2}$, w = 1.

TABLE 3. REFINED AND CALCULATED OCCUPANCY-FACTORS* AND CHEMICAL FORMULAE FOR HAUYNE

| Site | 1<br>Na | 2<br>K | 3<br>Ca | 4<br>Anal. | 5<br>Cation |
|---|---|---|---|---|---|
| C1 | 0.33 | 0.19 | 0.18 | 0.12K | 0.20K |
| C2 | 0.52 | 0.30 | 0.29 | 0.30Ca | 0.30Ca |
| C3 | 0.54 | 0.31 | 0.30 | 0.54Na | 0.54Na |

Chemical Formulae

(a) Charge balance model: $(Na_{4.5}Ca_{2.0}K_{1.0})_{\Sigma 7.5}[Al_6Si_6O_{24}](SO_4)_{1.50}(?OH)_{0.50}$
(b) Refinement: $(Na_{4.3}Ca_{2.4}K_{1.6})_{\Sigma 8.3}[Al_6Si_6O_{24}](SO_4)_{1.52}(?OH)_{1.68}$
(c) Chemical analysis: $(Na_{4.35}Ca_{2.28}K_{0.95})_{\Sigma 7.58}[Al_6Si_6O_{24}](SO_4)_{2.03}$

Löhn & Schulz (1968) data:
(d) Chemical analysis $(Na_{4.82}Ca_{2.22}K_{0.91})_{\Sigma 7.95}[Al_6Si_6O_{24}](SO_4)_{1.56}(?OH)_{1.05}$
(e) Refinement: $(Na_{5.09}Ca_{2.28}K_{0.81})_{\Sigma 8.18}[Al_6Si_6O_{24}](SO_4)_{1.5}(?OH)_{1.46}$

*Column 1: Obtained by refinement using Na scattering curve.
Column 2: Obtained by converting column 1 into K atoms.
Column 3: Obtained by converting column 1 into Ca atoms.
Column 4: Obtained by chemical analysis.
Column 5: Obtained by refinement using each atom scattering curve.

TABLE 4. ATOMIC POSITIONAL PARAMETERS, OCCUPANCY FACTORS, AND THERMAL PARAMETERS ($Å^2 \times 10^3$) FOR HAUYNE AT 293 AND 153 K

| Atoms | Sites | Occupancies | Coordinates | 293 K | 153 K |
|---|---|---|---|---|---|
| Al | 6(d) | 1.0 | x | 1/4 | 1/4 |
| | | | y | 0 | 0 |
| | | | z | 1/2 | 1/2 |
| | | | $U_{equiv.}$* | 9 | 7 |
| Si | 6(e) | 1.0 | x | 1/4 | 1/4 |
| | | | y | 1/2 | 1/2 |
| | | | z | 0 | 0 |
| | | | $U_{equiv.}$ | 9 | 6 |
| O1 | 24(i) | 1.0 | x | 0.1443(5) | 0.1443(5) |
| | | | y | 0.1559(5) | 0.1558(6) |
| | | | z | 0.4681(4) | 0.4669(5) |
| | | | $U_{equiv.}$ | 23 | 20 |
| C1 | 8(e) | 0.20(2) K | x | 0.6636(9) | 0.6640(12) |
| | | | $U_{iso.}$ | 19(2) | 13(3) |
| C2 | 8(e) | 0.30(2) Ca | x | 0.7008(8) | 0.7009(9) |
| | | | $U_{iso.}$ | 32(2) | 25(3) |
| C3 | 8(e) | 0.54(1) Na | x | 0.7374(5) | 0.7392(8) |
| | | | $U_{iso.}$ | 17(2) | 18(2) |
| S | 8(e) | 0.19(1) | x | 0.4657(9) | 0.4669(11) |
| | | | $U_{equiv.}$ | 50 | 45 |
| O2 | 8(e) | 0.75 | x | 0.5972(24) | 0.5995(27) |
| | | | $U_{iso.}$ | 163(11) | 145(12) |

*$U_{equiv.} = 1/3(U_{11}+U_{22}+U_{33})$

Refinement of the structure (Table 3) was done on the set of intensities measured at room temperature by a full-matrix least-squares method using unit weights and a variable overall scale-factor. The positional coordinates of the framework atoms were refined, as well as their isotropic and subsequently their anisotropic temperature-factors. The refined temperature-factors (Tables 4, 5) for the framework atoms showed no unexpected values, and the resulting geometry of the framework (Table 6) was found to be comparable to that sodalite (Hassan & Grundy 1984); this indicates complete order among Al and Si atoms. In particular, the temperature factors for Al and Si atoms are of similar magnitude, and the framework oxygen atom, O1, occupies only one set of 24 (i) positions; these results differ from those of Löhn & Schulz (1968), wherein a refinement of a hauyne from Monte Somma, Italy gave an *R* index of 0.082. In addition, the present results are in contrast to those found for nosean and lazurite; their structures contain two sets of 24 (i) positions for the framework oxygen atoms, and the temperature factors for the Al and Si atoms are of similar but larger magnitude than those in hauyne (Hassan *et al.* 1985, Hassan & Grundy 1989).

The positions of the interstitial atoms were examined on electron-density sections and by least-

TABLE 5. ANISOTROPIC TEMPERATURE-FACTORS* ($Å^2 \times 10^3$) FOR HAUYNE AT 293 AND 153 K

| Atom | | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|
| Al | 293 K | 8(3) | 9(2) | 9 | 0 | 0 | 0 |
| | 153 K | 4(2) | 9(1) | 9 | 0 | 0 | 0 |
| Si | 293 K | 9(3) | 10(2) | 10 | 0 | 0 | 0 |
| | 153 K | 7(2) | 5(1) | 5 | 0 | 0 | 0 |
| O1 | 293 K | 15(3) | 23(3) | 30(2) | 12(2) | 1(2) | 2(3) |
| | 153 K | 14(3) | 19(3) | 25(4) | 12(2) | 1(3) | -1(3) |
| S | 293 K | 50(5) | 50 | 50 | -10(4) | -10 | -10 |
| | 150 K | 45(7) | 45 | 45 | -12(4) | -12 | -12 |

$^*U_{ij} = \exp - [U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl]$

squares refinement. The positional coordinate of one interstitial cation at the 8(e) position, similar to that in sodalite, did not refine properly, and its isotropic temperature-factor is unusually large. This site was finally modeled by three 8(e) positions that are close to each other (Tables 3, 4).

A difference-Fourier map, calculated with the S atom removed from the 2(a) position, shows that the S atom is not at the 2(a) site, but displaced to the 8(e) site with coordinates (*x, x, x*), $x = 0.47$ (Figs. 1a, b). An analogous Fourier map calculated with the O2 oxygen atom removed from the structure model shows a large electron-density peak at one 8(e) site and a much smaller electron-density peak at another 8(e) site; these small maxima are merely tails of equivalent O2 atoms that occur below (Fig. 1c). All the peaks for the O2 site occur at the corners of a cube with edges of 1.8Å. The O2 site ($x = 0.60$) corresponds to the oxygen atoms of the $SO_4$ group. When the O2 site is included in the structural model, the resulting difference-Fourier map was found to be featureless, which indicates that the small electron-density peaks ($x = 0.40$) represent residual density from equivalent O2 sites below.

The calculated and observed structure-factors for the reflections 110 and 200 show large disagreements. The measured intensity for these reflections seems reasonable, but they could be affected by extinction; these reflections thus were temporarily removed from the structural model, and the refinement continued. The occupancy of the O2 site was set at 0.75 to be consistent with the occupancy of the S site. The temperature factor for the O2 site then refined on its own. Subsequently, the allowable positional and temperature parameters of all the sites were refined simultaneously, which resulted in convergence to an *R* index of 0.037. With this refined set of structural parameters and the reflections 110 and 200, an *R* factor of 0.043 was calculated.

The occupancy of the three *C* sites by Na, K, or Ca atoms, as indicated by the chemical formulae (Table 3), can be considered by examining refined population-parameters, distances to the framework oxygen atoms, and valence-sum calculations (Brown & Altermatt 1985). When the occupancy factors are compared with those expected from the chemical composition (Table 3), the results indicate that the K atom occupies the *C*1 site, the Na atom occupies

TABLE 6. INTERATOMIC DISTANCES (Å), ANGLES (°), AND VALENCE SUMS (v.u.) FOR HAUYNE

| Atoms | | 153 K | 293 K | Atoms | | 153 K | 293 K |
|---|---|---|---|---|---|---|---|
| $AlO_4$ tetrahedron | | | | | | | |
| Al-O1 | 4 x | 1.741(5) | 1.742(5)* | Si-O1-Al | | 149.3(3) | 149.7(3) |
| O1-O1 | 4 x | 2.814(7) | 2.815(6) | $\phi_{Si}$ | | 12.0 | 12.4 |
| | 2 x | 2.902(7) | 2.902(7) | $\phi_{Al}$ | | 12.9 | 11.6 |
| Mean O1-O1 | | 2.843 | 2.844 | Al/Si-O | | 1.670 | 1.670 |
| | | | | $SO_4$ group | | | |
| O1-Al-O1 | 4 x | 107.8(2) | 107.8(2) | S-O2 | 3 x | 1.480(11) | 1.447(9) |
| | 2 x | 112.9(2) | 112.8(2) | | 1 x | 2.092(15) | 2.076(13) |
| Mean O1-Al-O1 | | 109.5 | 109.5 | Mean S-O2 | | 1.633 | 1.604 |
| $SiO_4$ tetrahedron | | | | | | | |
| Si - O1 | 4 x | 1.599(5) | 1.597(4)** | O2-S-O2 | 3 x | 90.0(6) | 88.8(6) |
| O1 - O1 | 4 x | 2.566(7) | 2.564(6) | | 3 x | 120.0(7) | 120.0(7) |
| | 2 x | 2.698(7) | 2.695(6) | Mean O2-S-O2 | | 105.0 | 104.4 |
| Mean O1-O1 | | 2.610 | 2.608 | | | | |
| | | | | Bond-valence sums | | | |
| O1-Si-O1 | 4 x | 106.8(2) | 106.8(2) | *Al = 4 x 0.72 = 2.88 v.u. | | | |
| | 2 x | 115.1(2) | 115.0(2) | **Si = 4 x 1.12 = 4.49 v.u. | | | |
| Mean O1-Si-O1 | | 109.6 | 109.5 | | | | |

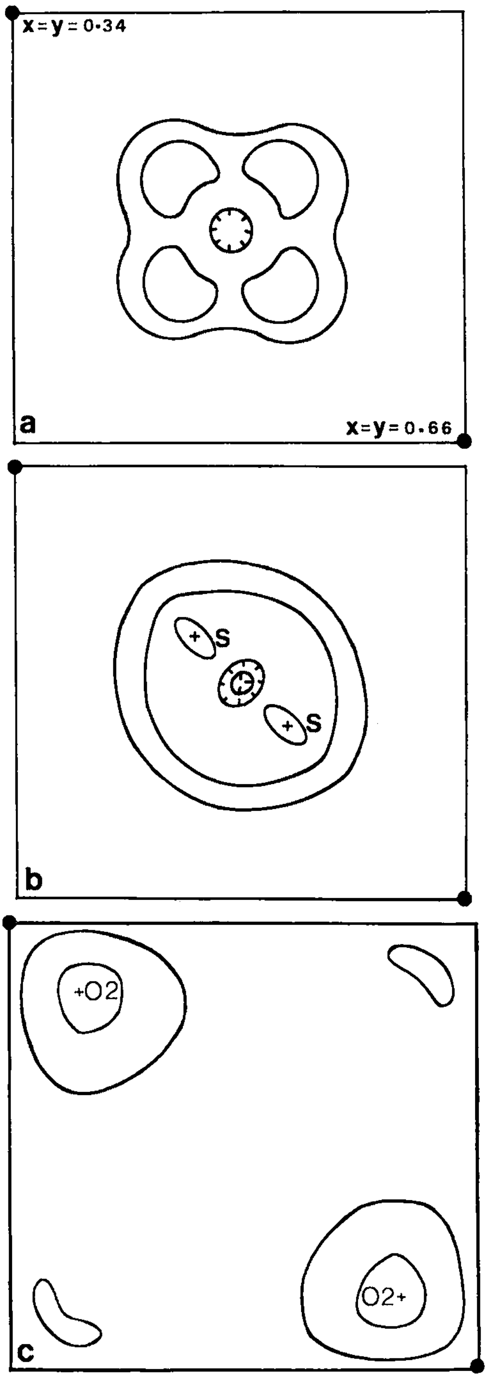

FIG. 1. Difference-Fourier maps: (a) (001) section through the 2(a) site ($z$ = 0.5), calculated with the S atom removed from the structural model ($R$ = 0.067), showing that the S atom is not at the 2(a) position; (b) (001) section through an 8(e) site ($z$ = 0.47) showing the location of the S atom. Contour interval = 1 e/Å$^3$. (c) (001) section calculated with the O2 site ($z$ = 0.60) removed from the structural model ($R$ = 0.051). The two large peaks with coordinate ($x$, $x$, $x$), $x$ = 0.60, correspond to oxygen atoms of the SO$_4$ group; the two smaller peaks ($x$ = 0.40) indicate small amounts of electron density that are residuals from equivalent O2 sites below. Contour interval: 0.5 e/Å$^3$. The ($x$, $y$) coordinates are the same on all maps.

the *C*3 site, but the Ca atom could be at either of the *C*2 and *C*3 sites.

The ranges for the relevant cation–oxygen distances usually observed are: K–O: 2.6–2.9 Å, Ca–O: 2.2–2.4 Å, and Na–O: 2.2–2.5 Å (BIDICS, 1981). When these distances are compared to the distances between the *C* sites and framework oxygen atoms (Table 7), the results confirm that the K atom occupies the *C*1 site, but the Ca and Na atoms could occupy either the *C*2 or the *C*3 site. In sodalite and basic sodalite (Hassan & Grundy 1983, 1984), the Na atom occupies a position similar to the *C*3 site in hauyne; if the *C*3 site is occupied by Na atoms, then the Ca atoms presumably occupy the *C*2 site. The scattering curves for the respective cations were used in the structure refinement to determine the occupancy factors for each of these sites. The occupancy values (Table 3, column 5) are in satisfactory agreement with the chemical composition (Table 3, column 4), and resulted in a reduction of the *R* factor from 0.037 to 0.036. Although this decrease in the *R* factor is not significant at the 0.05 level according to the Hamilton test, the agreement with the chemical composition and the satisfactory bond-distances that result give confidence that the model is essentially correct. The occupancy of the *C*1, *C*2, and *C*3 sites by K, Ca, and Na, respectively, also is consistent with the bond-valence sums (Table 7).

The final *R* index for the structure at 153 K is 0.039; if we include reflections 110 and 200, the *R* value is 0.047. Except for smaller temperature-factors, the 153 K structure is not significantly different from that at 293 K (Tables 4, 5, 6). The structural parameters of the framework are similar (Table 6), but differences occur for structural parameters associated with the interstitial atoms (Table 7). A copy of the tables of structure factors is available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

## DISCUSSION

Löhn & Schulz (1968) reported on the presence of a SO$_4$ group in hauyne. It occupies two positions that are rotated 90° with respect to each other; with

TABLE 7. CATION-OXYGEN DISTANCES (Å) AND VALENCE SUMS** (v.u.) FOR HAUYNE

| Atoms | | 153 K | 293 K | | Na | K | Ca |
|---|---|---|---|---|---|---|---|
| C1-O1 | 3 x | 2.765(4) | 2.783(4) | 3 x | 0.07 | 0.17 | 0.11 |
| -O1 | 3 x | 2.995(5) | 2.992(6) | 3 x | 0.04 | 0.10 | 0.06 |
| -[O' on S]* | | 3 x | 2.457 | 1 x | 0.17 | 0.42 | 0.27 |
| | | | | Σ | 0.50 | **1.33** | 0.78 |
| -O2 | 1 x | 1.018(14) | 1.049(13) | | | | |
| -S | 3 x | 2.463(7) | 2.457(6) | | | | |
| C2-O1 | 3 x | 2.511(5) | 2.524(4) | 3 x | 0.14 | 0.35 | 0.22 |
| -O1 | 3 x | 2.871(6) | 2.864(5) | 3 x | 0.06 | 0.14 | 0.09 |
| -[O' on S]* | | 3 x | 3.033 | 1 x | 0.04 | 0.09 | 0.06 |
| | | | | Σ | 0.64 | 1.56 | 0.99 |
| -[O2'adjusted]* | | 1 x | 2.108 | 1 x | 0.44 | 1.07 | 0.68 |
| | | | | Σ | 1.04 | 2.04 | **1.61** |
| -O2 | 1 x | 1.600(15) | 1.636(13) | | | | |
| -S | 3 x | 3.036(6) | 3.033(5) | | | | |
| C3-O1 | 3 x | 2.372(5) | 2.386(4) | 3 x | 0.20 | 0.50 | 0.32 |
| -O1 | 3 x | 2.863(5) | 2.852(4) | 3 x | 0.06 | 0.14 | 0.09 |
| -O2 | 1 x | 2.204(15) | 2.214(13) | 1 x | 0.33 | 0.80 | 0.51 |
| | | | | Σ | **1.11** | 1.44 | 0.92 |
| -S | 3 x | 3.634(5) | 3.604(4) | | Valence Sums (v.u.) | | |

Bond-valence sums for O1:

From Al and Si 0.72 + 1.12 = 1.84 v.u.
From K on C1 + 0.17 + 0.10 = 2.11 v.u.
From Ca on C2 + 0.22 + 0.09 = 2.15 v.u.
From Na on C3 + 0.20 + 0.06 = 2.10 v.u.

**Based on the bond-distances from the 293 K structure

* [O'] represents the oxygen atom of the OH group on a vacant S site, and [O2'] represents an adjusted O2 position (see text)

the sulfur atom at a 2(a) position, this geometry leads to a regular tetrahedral group with a S–O bond length of 1.52 Å. They suggested that the interstitial cations force the $SO_4$ group out of the above position; their suggestion is confirmed in the present study. They too found two cation sites, which correspond to the *C*1 and *C*2 sites of this study. This present work shows that the sulfur atom is at the 8(e) position instead of the 2(a) position as in nosean and lazurite; however, the oxygen atoms of the $SO_4$ group occupy only one set of 8(e) positions. Because of the rigidity of the $SO_4$ group, the oxygen atoms are expected to be displaced from the body diagonals of the cell, as in basic sodalite (Hassan & Grundy 1983), but this effect could not be incorporated in the present structural model.

The short S–S distance of 0.88 Å allows one sulfur atom per cage. The geometry of the resulting $SO_4$ group is not typical (Table 6). The S–O2 distance of 2.08 Å is longer than the S–O bond expected for the $SO_4$ group, but this distance can be shortened to the average value (1.60 Å) if one of the four O2 atoms, [O2′], is placed on an 8(e) position with $x = 0.5673$ instead of $x = 0.5972$; then the resulting *C*2–[O2′] distance would be a reasonable length of 2.11 Å instead of 1.64 Å (see Table 7). The small amount of electron density (0.19 electron/site) for the O2′ position is too small to be observed.

The chemical formula of Löhn & Schulz (1968) and that obtained from this refinement are not electrostatically neutral; they have excess positive charge, which may be balanced by $OH^-$ ions (Table 3). The present refinement indicates about 1.5 $SO_4$ per cell, so that 75% of the cages are occupied by $SO_4$ groups and the other 25% presumably contain OH groups. The OH group can reasonably be assumed to be at a S site where it is vacant; this position would allow one OH per cage.

With the K atom at the *C*1 site, the cage cannot accommodate a $SO_4$ group because of the short *C*1–O2 and *C*1–S distances that would result (Table 7). In this case, the cage may contain one OH at a vacant S site (*C*1–[O′] in Table 7). The satisfactory bond-valence sum that results for the K atom (Table 7) confirms that the *C*1 site is occupied by K atoms. The *C*2 site is much too close to O2 for a bond; if this site is occupied, then the cage may contain one OH group, which may be located at the S site (*C*2–[O′] in Table 7). A cage may have an $SO_4$ group and have one of the possible four *C*2 positions occupied, because one oxygen atom of the $SO_4$ group could move to the [O2′] position to give a (*C*2–[O2′] distance of 2.11 Å, comparable to the observed *C*3–O2 distance of 2.21 Å (Table 7). Four *C*3 positions in a cage can be occupied if the cage contains a $SO_4$ group in view of the *C*3–O2 distance (Table 7).

A simplified charge-balance model, similar to that for lazurite and nosean (Hassan & Grundy 1989, Hassan *et al.* 1985) can be used to rationalize the crystal chemistry of hauyne. A net residual charge of –3 v.u. can be assigned to the 12 framework oxygen atoms that form the cage. This net charge can be neutralized if the cage contains $[Na_3Ca{\bullet}SO_4]^{3+}$ clusters. The occupancy factor for the S site indicates that $[Na_3Ca{\bullet}SO_4]^{3+}$ clusters make up 75% of the structure, and this accounts for 4.5 Na, 1.5 Ca, and 1.5 $SO_4$ atoms per cell. As this is the number of Na atoms and $SO_4$ groups shown by the refinement, all of these ions have been accounted for. In an asymmetrical environment of the cations in a cage (*i.e.,* three Na and one Ca in a cage), the $Ca^{2+}$ cation would force the $S^{6+}$ cation off the 2(a) position, as indicated by the structure refinement.

The remaining 25% of the cages presumably contain $[K_2Ca{\bullet}OH]^{3+}$ clusters, with a vacant K atom, which accounts for one K, 0.5 Ca, and 0.5 OH ions per cell. These results give an overall composition of $Na_{4.5}Ca_{2.1}K_{1.0}[Al_6Si_6O_{24}](SO_4)_{1.5}(OH)_{0.5}$, which does not disagree significantly with the chemical formula (Table 3) or with the results of the present structure-refinement. If only $[Na_3Ca{\bullet}SO_4]^{3+}$ were present, the composition would be $Na_6Ca_2[Al_6Si_6O_{24}](SO_4)_2$, which is the ideal formula for hauyne. If $[K_2Ca{\bullet}OH]^{3+}$ were to occur exclusively, the composition would be $K_4Ca_2[Al_6Si_6O_{24}](OH)_2$, which is as yet unknown as an end member.

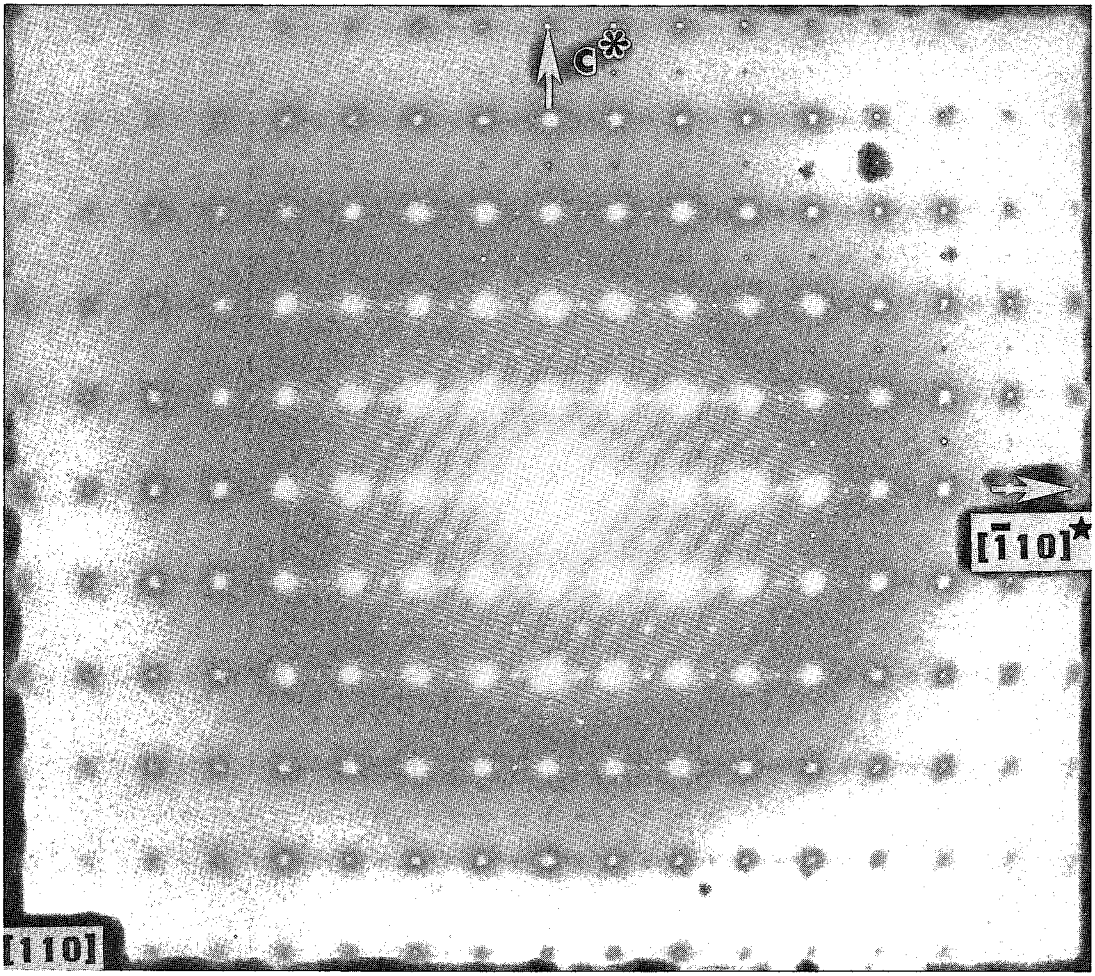

FIG. 2. A [110] zone electron-diffraction pattern of hauyne. Ordering reflections (*hkl*, $h+k+l = 2n+1$) occur as weak spots and diffuse, streaked satellite reflections toward the edges (Philips CM12, 120 kV). Neither type of reflections were observed in X-ray precession photographs.

The $[Na_3Ca{\bullet}SO_4]^{3+}$ and $[K_2Ca{\bullet}OH]^{3+}$ clusters may order and give rise to weak ordering reflections (general: *hkl*, $h+k+l = 2n+1$) and antiphase-domain boundaries (*APB*s). TEM studies reveal the presence of ordering reflections and diffuse streaked satellite reflections (Fig. 2) in addition to *APB*s in hauyne (Hassan & Buseck 1989a). The space group for each domain is *P*23, based on the ordering reflections, and this space group allows for sodalite-type structures (Hassan & Grundy 1989).

Although the hauyne specimen used in this study does not show any satellite reflections on precession photographs, such reflections have been reported for other samples (Taylor 1967), and their origin is discussed by Hassan & Buseck (1989a, b). The temperature factors for the framework atoms and the Al–O and Si–O distances in hauyne are comparable to those found in sodalite; in particular, the framework oxygen atoms occupy one set of 24(i) positions. The satellite reflections that are generally observed in sodalite-group minerals arise from positional ordering of the framework oxygen atoms over two independent sets of 24(i) positions, as in nosean and lazurite.

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