Canadian Mineralogist
Vol. 21, pp. 549-552 (1983)

THE STRUCTURE OF HACKMANITE, A VARIETY OF SODALITE, FROM MONT ST-HILAIRE, QUEBEC

R.C. PETERSON

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

ABSTRACT

The crystal structure of a photochromic variety of sodalite, known as hackmanite, was refined from Mo*K*α(Zr) data in space group $P\bar{4}3n$ [*a* 8.877(2) Å]. The chemical formula is $Na_{7.50}Fe^{2+}_{0.05}[Si_{6.07}Al_{5.93}]O_{24}Cl_{1.99}(SO_4)_{0.01}$. In contrast to the results of an earlier refinement (Löns & Schulz 1967), the thermal parameters for the two tetrahedral sites are found to be similar. There is no evidence of tetrahedral cation disorder.

Keywords: sodalite, hackmanite, crystal structure, aluminosilicate framework, Mont St-Hilaire, Quebec.

SOMMAIRE

La structure cristalline d'une variété photochromique de sodalite, connue sous le nom d'hackmanite, a été affinée dans le groupe spatial $P\bar{4}3n$ [*a* 8.877(2) Å] à partir de données obtenues avec Mo*K*α(Zr). La formule chimique est $Na_{7.50}Fe^{2+}_{0.05}[Si_{6.07}Al_{5.93}]O_{24}Cl_{1.99}(SO_4)_{0.01}$. Contrairement aux résultats de l'affinement précédent (Löns & Schulz 1967), les paramètres thermiques des deux sites tétraédriques sont semblables. On n'observe aucune indication de désordre cationique dans les tétraèdres.

(Traduit par la Rédaction)

Mots-clés: sodalite, hackmanite, structure cristalline, charpente aluminosilicate, mont St-Hilaire, Québec.

INTRODUCTION

The sodalite structure was originally determined by Pauling (1930) and subsequently refined by Löns & Schulz (1967) using intensities collected with multiple-film Weissenberg exposures. The structure consists of a framework of alternating aluminum- and silicon-containing tetrahedra. The tetrahedra are linked to form six-membered rings in the plane normal to the three-fold axes of symmetry and four-membered rings in the plane normal to the four-fold axes. These rings are then connected to form a framework structure with a large cavity, centred at the origin, which contains the chlorine and sodium atoms.

The refinement of Löns & Schulz (1967) with isotropic thermal parameters indicates a much greater thermal motion for the aluminum site relative to the silicon site, which could be related to disorder among tetrahedral cations. The ordering of tetrahedral cations in zeolitic frameworks is of interest to those studying the properties of this group of minerals and, for this reason, an accurate X-ray structure refinement was completed to determine whether the higher temperature-factor for the larger tetrahedral site is present in other specimens of sodalite.

The variety of sodalite chosen is referred to as hackmanite. It exhibits the phenomenon of photochromism, being pink on a freshly fractured surface and fading to colorless on exposure to light within a few minutes. The coloration can be reactivated by exposure to X radiation or a high-energy electron beam and, for this reason, has been investigated as material useful in electronic information-display systems. The cause of the photochromism has been investigated by several workers and attributed to the presence of sulfur (Kirk 1955), the presence of H^- (Medved 1954), an F centre in conjunction with an O^{2-} ion on a chloride vacancy (Ballentyne & Bye 1970) and F centres at a Cl vacancy involving a trapped electron tetrahedrally co-ordinated by Na atoms (Hodgson *et al.* 1967, McLaughlan & Marshall 1970, Hassib *et al.* 1977).

EXPERIMENTAL

The hackmanite was collected from the De Mix quarry on the northern slope of Mont St-Hilaire, Quebec. The crystals exhibit dodecahedral morphology and are up to 1 cm in diameter in a matrix of nepheline and perthitic feldspar. The chemical composition obtained using an ARL SEMQ microprobe analyzer operating at 15 kV is listed in Table 1. Analyses of several grains show that sulfur content ranges from 0.05 to 0.30 wt.% SO_3. The higher sulfur contents are correlated with more intense photochromic and fluorescent behavior. The formula calculated from the microprobe data (Table 1) is very close to the ideal formula for sodalite: $Na_8Al_6Si_6O_{24}Cl_2$. The deficiency in Na is attributed to loss during analysis even though the electron beam was defocused to minimize the loss of sodium.

A sphere of hackmanite was ground to a diameter of 0.16 mm (μ = 0.9078 cm^{-1}), and X-ray intensities were collected with Mo*K*α(Zr) radiation to a sin θ/λ limit of 1.00Å^{-1}. Atomic scattering factors for Na, Si, Al, O, and Cl were taken from Table 2.2, International Tables of X-ray Crystallography (vol.

TABLE 1. CHEMICAL COMPOSITION OF HACKMANITE

oxide	wt.%
SiO_2	37.95
Al_2O_3	31.42
FeO	0.39
MnO	0.08
Na_2O	24.16
K_2O	0.05
SO_3	0.09
Cl	7.33
	101.47
-O=Cl	1.65
Total	99.82

Formula based on $\Sigma(Si+Al) = 12$

$Na_{7.50}Fe^{+2}_{0.05}[Si_{6.07}Al_{5.93}]O_{23.83}Cl_{1.99}(SO_4)_{0.01}$

TABLE 3. ATOMIC POSITIONS AND TEMPERATURE FACTORS

ATOM		PARAMETER	ATOM	PARAMETER
Na	x	0.1778(1)	AL	1/4
	y	0.1778		1/2
	z	0.1778		0
	β11	0.0045(1)		0.0016(1)
	β22	0.0045		0.0016(1)
	β33	0.0045		0.0016
	β12	0.0002(1)		0
	β13	0.0002		0
	β23	0.0002		0
Si	x	1/4	0	0.1390(1)
	y	0		0.4382(2)
	x	1/2		0.1498(1)
	β11	0.0013(1)		0.0025(1)
	β22	0.0016(1)		0.0029(1)
	β33	0.0016		0.0031(1)
	β12	0		0.0003(1)
	β13	0		0.0013(1)
	β23	0		-.0002(1)
Cl	x	0		
	y	0		
	z	0		
	B	1.89(3)		

βij is of the form

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

IV), and are based on calculations made with relativistic Hartree–Fock wave functions (Doyle & Turner 1968). All atomic positions were assumed to be fully occupied. The 3652 measured reflections were corrected for Lorentz, polarization and absorption effects and sorted to 386 unique reflections in space group $P\bar{4}3n$, with an internal agreement of 3.4%. Least-squares refinement of 24 centred high-angle reflections led to an a cell edge of 8.877(2) Å. Using the atomic parameters of Löns & Schulz (1967) as initial parameters, several cycles of least-squares refinement using the program RFINE IV (Finger & Prince 1975) resulted in convergence with $R = \Sigma\|Fo|-|Fc\|/\Sigma|Fo| = 0.035$ and $WR = \Sigma w(|Fo|-|Fc|)/\Sigma w|Fo| = 0.047$ with $w = 1/(\sigma^2 + (0.02Fo)^2)^{1/2}$. Electron-density-difference Fourier maps calculated through the asymmetric unit showed no significant features. Table 2, which lists the observed and calculated structure-factors, has been deposited with the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DISCUSSION

Table 3 lists the resulting positional and thermal parameters for the atoms in the sodalite structure. The positional parameters are similar to the results of Löns & Schulz (1967); however, the temperature factors for the two distinct tetrahedral sites do not show the large difference seen in their study.

The bond lengths and angles are listed in Table 4. Calculations of the tetrahedral site-occupancies using the expression $Y = 6.4116X - 10.282$, in which X is the mean tetrahedral bond-length and Y is the fraction of Al relative to silicon in the site (Jones 1968), give 89% Al in the larger tetrahedral site and 9% Al in the smaller site. This is consistent with the value $Al/(Al + Si) = 0.49$ determined by microprobe analysis. Therefore, in this sodalite specimen there is no evidence for aluminum–silicon disorder within the tetrahedral site, as the small amount of Al indicated in the silicon site is within the uncertainty of the empirical expression of Jones (1968).

Figure 1 shows the co-ordination polyhedron around the sodium cation. It consists of a ditrigonally distorted six-membered ring oriented normal to the vector [111] (also the vector [Cl–Na]), with 3 oxygen atoms at 2.349(2) Å and 3 oxygen atoms at 3.08(2) Å. All six oxygen atoms do not lie in the same plane, as can be seen by the two distinct Cl–Na–O angles (Table 3). The sodium cation is located in a position away from the six-membered ring in the direction of the chlorine position.

Chlorine vacancies have been proposed as a possible cause of the photochromic behavior (Ballentyne & Bye 1970). Hodgson *et al.* (1967) estimated that 6×10^{19} free spins per mole would be necessary to produce the observed intensity of the photochromic effect. This number of free spins per mole corresponds to less than one F centre per thousand unit cells and therefore could not be detected by the crystal-structure refinement.

TABLE 4. HACKMANITE BOND-LENGTHS AND ANGLES

ATOM	DISTANCE	MULT.	ATOM	DISTANCE	MULT.
Si-O	1.617(2) A	4	Na-O	2.349(2) A	3
Al-O	1.744(1) A	4	Na-O	3.084(2) A	3
			Na-Cl	2.736(1) A	1
ATOM		MULT.	ATOM	ANGLE	MULT.
O-Si-O	107.6(1)°	4	O-Al-O	108.6(1)°	4
O-Si-O	113.3(1)°	2	O-Al-O	111.2(1)°	2
Al-O-Si	138.1(1)°		Cl-Na-O	114.9(1)°	3
			Cl-Na-O	101.1(1)°	3

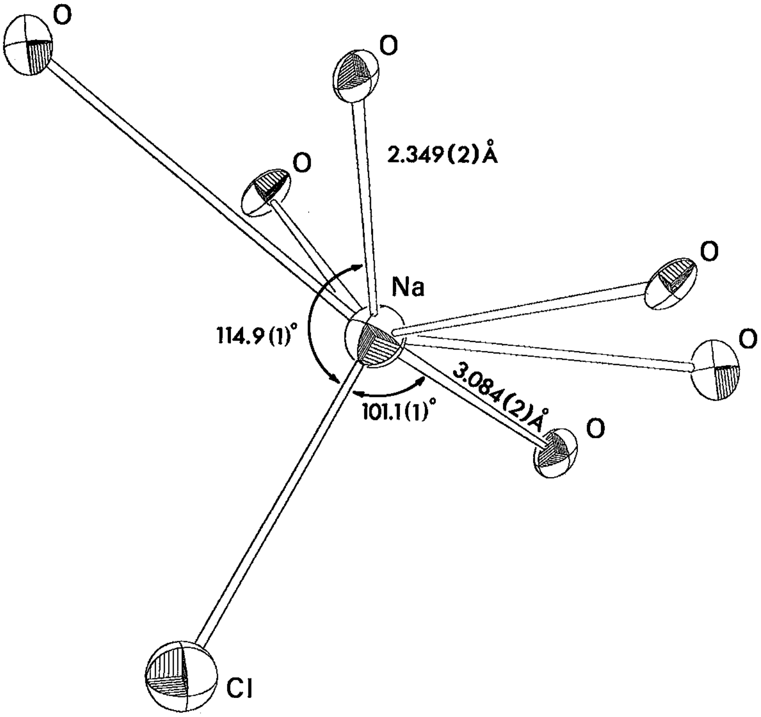

FIG. 1. ORTEP drawing (Johnson 1965) of the co-ordination sphere of sodium in sodalite. Ellipsoids represent 50% probability that a random point in the distribution will fall inside.

CONCLUSION

The present study confirms the sodalite structure described by Barth (1932) and refined by Löns & Schulz (1967). Thermal parameters for the two independent tetrahedral cation-sites are similar, in contrast to the earlier refinement. Calculations based on tetrahedral bond-lengths give no evidence of disorder between silicon and aluminum within these sites.

ACKNOWLEDGEMENTS

The author thanks G.V. Gibbs, who made available the four-circle-diffractometer system at the Virginia Polytechnic Institute and State University, Dr. M.E. Fleet, who carefully reviewed and improved the manuscript, and Ms. L. Harris, who typed the manuscript. This study was supported by the Natural Sciences and Engineering Research Council of Canada, grant A8009.

REFERENCES

BALLENTYNE, D.W.G. & BYE, K.L. (1970): The nature of photochromism in chlorosodalites from optical data. *J. Phys. D: Appl. Phys.* **3**, 1438-1443.

BARTH, T.F.W. (1932): The structures of the minerals of the sodalite family. *Z. Krist.* **83**, 405-414.

DOYLE, P.A. & TURNER, P.S. (1968): Relativistic Hartree-Fock X-ray and electron scattering factors. *Acta Cryst.* **A24**, 390-397.

FINGER, L.W. & PRINCE, E. (1975): A system of Fortran IV computer programs for crystal structure computations. *Nat. Bur. Standards Tech. Note* **854**.

HASSIB, A., BECKMAN, O. & ANNERSTEN, H. (1977): Photochromic properties of natural sodalite. *J. Phys. D: Appl. Phys.* **10**, 771-777.

HODGSON, W.G., BRINEN, J.S. & WILLIAMS, E.F. (1967): Electron spin resonance investigation of photochromic sodalites. *J. Chem. Phys.* **47**, 3719-3723.

IBERS, J.A. & HAMILTON, W.C., eds. (1974): *International Tables for X-ray Crystallography. IV. Revised and Supplementary Tables.* Int. Union Cryst., Kynoch Press, Birmingham, England.

JOHNSON, C.K. (1965): ORTEP: a Fortran thermal-ellipsoid plot program for crystal structure illustrations. *Oak Ridge Nat. Lab. Pap.* **3794.**

JONES, J.B. (1968): Al–O and Si–O tetrahedral distances in aluminosilicate framework structures. *Acta Cryst.* **B24,** 355-358.

KIRK, R. (1955): The luminescence and tenebrescence of natural and synthetic sodalite. *Amer. Mineral.* **40,** 22-31.

LÖNS, J. & SCHULZ, H. (1967): Strukturverfeinerung von Sodalith, $Na_8Si_6Al_6O_{24}Cl_2$. *Acta Cryst.* **23,** 434-436.

MCLAUGHLAN, S.D. & MARSHALL, D.J. (1970): Paramagnetic resonance of F-type centres in photochromic sodalites. *Phys. Lett.* **32A,** 343-344.

MEDVED, D. (1954): Hackmanite and its tenebrescent properties. *Amer. Mineral.* **39,** 615-629.

PAULING, L. (1930): The structure of sodalite and helvite. *Z. Krist.* **74,** 213-225.

Received July 6, 1982, revised manuscript accepted November 22, 1982.