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GAULTITE, A NEW ZEOLITE-LIKE MINERAL SPECIES FROM MONT SAINT-HILAIRE, QUEBEC, AND ITS CRYSTAL STRUCTURE

T. SCOTT ERCIT AND JERRY VAN VELTHUIZEN

Research Division, Canadian Museum of Nature, Ottawa, Ontario K1P 6P4

ABSTRACT

The new mineral species *gaultite* occurs as euhedral, multifaceted crystals to 0.5 mm in a sodalite inclusion at the contact of hornfels and nepheline–sodalite syenite, Poudrette Quarry, Mont Saint-Hilaire, Rouville County, Québec. It is colorless to pale mauve, has a white streak, vitreous luster and a bright apple-green fluorescence under short-wave ultraviolet radiation. The measured density is 2.52(4) g cm^{-3}; the hardness is 6. It is biaxial (+), α 1.520(1), β 1.521(1), γ 1.524(1), $2V$ 61.3(4)° (590 nm), is nonpleochroic, with $X \parallel a$, $Y \parallel c$ and $Z \parallel b$. The average chemical composition (wt.%) is: Na_2O 16.6, ZnO 19.2, SiO_2 52.6, H_2O(calc.) 11.3, total 99.7. The empirical formula is $Na_{4.28}Zn_{1.88}Si_{6.99}O_{18}\cdot 5H_2O$ which, considered with structural data, gives the ideal formula $Na_4Zn_2Si_7O_{18}\cdot 5H_2O$ (Z = 8). The strongest six lines of the X-ray powder pattern [*d* in Å, *I* in %] are 6.35(100), 4.96(30), 3.24(60), 3.17(40), 3.14(40), 2.82(30). The unit-cell parameters are *a* 10.211(3), *b* 39.88(2), *c* 10.304(4) Å, *V* 4196(2) Å^3, space group *F2dd*. The crystal structure of gaultite was solved by Patterson methods; refinement of the structure using 1210 observed reflections (Mo$K\alpha$) converged to R = 2.5, wR = 2.8%. Gaultite shows no chemical disorder. There are five tetrahedral sites; four of these are occupied by Si, and one by Zn. Polymerization of the tetrahedra results in a framework based on a complex three-dimensional stacking of 4.8^2 Schläfli nets. Na occurs in two sites that represent voids in the framework of tetrahedra. Na1 is [6]-coordinated and positionally ordered; Na2 is positionally disordered, split into [5]- and [6]-coordinated sites. Bond-valence analysis unambiguously shows three H_2O groups, two of which are ordered, with ordered protons, one of which is disordered, in agreement with the results of IR spectroscopy. The structure of gaultite is similar to those of lovdarite and the synthetic zeolite VPI–7, the latter of which may be the synthetic analogue of gaultite.

Keywords: gaultite, new mineral species, crystal structure, zeolite-like tectosilicate, Mont Saint-Hilaire, Québec.

SOMMAIRE

La gaultite, nouvelle espèce minérale, se présente en cristaux allant jusqu'à 0.5 mm; ils sont idiomorphes, à faces multiples, et se trouvent dans une inclusion de sodalite au contact entre une cornéenne et la syénite à néphéline–sodalite dans la carrière Poudrette, au mont Saint-Hilaire, comté de Rouville, Québec. Il s'agit d'un minéral incolore ou mauve pâle à rayure blanche, à éclat vitreux, et montrant une fluorescence vert-pomme brillant à la lumière ultraviolette (onde courte). La densité mesurée est de 2.52(4), et la dureté, 6. La gaultite est biaxe positive, α 1.520(1), β 1.521(1), γ 1.524(1), $2V$ 61.3(4)° (590 nm), et non pléochroïque, avec $X \parallel a$, $Y \parallel c$, et $Z \parallel b$. La composition chimique moyenne (en %, poids) est: Na_2O 16.6, ZnO 19.2, SiO_2 52.6, H_2O (calculé) 11.3, pour un total de 99.7. La formule empirique est $Na_{4.28}Zn_{1.88}Si_{6.99}O_{18}\cdot 5H_2O$; à la lumière de données structurales, la formule idéale serait $Na_4Zn_2Si_7O_{18}\cdot 5H_2O$ (Z = 8). Les six raies les plus intenses du spectre de diffraction X [méthode des poudres; *d* en Å(*I*)] sont: 6.35(100), 4.96(30), 3.24(60), 3.17(40), 3.14(40), 2.82(30). Les paramètres réticulaires sont: *a* 10.211(3), *b* 39.88(2), *c* 10.304(4) Å, *V* 4196 Å^3, groupe spatial *F2dd*. Nous avons affiné la structure cristalline de la gaultite par méthodes de Patterson, en utilisant 1210 réflexions observées (rayonnement Mo$K\alpha$), jusqu'à un résidu R de 2.5% (wR = 2.8%). Cette espèce ne montre aucun désordre atomique. La structure possède cinq sites tétraédriques, dont quatre sont occupés par le Si, et un par le Zn. La polymérisation des tétraèdres mène à un agencement tridimensionnel complexe de réseaux 4.8^2 de Schäfli. Le Na occupe deux sites qui représentent des lacunes dans la trame de tétraèdres; le Na1 a une coordinence [6] et se trouve ordonné dans sa position, tandis que le Na2 est sujet à un désordre de position, selon qu'il occupe un site à coordinence [5] ou un autre à coordinence [6]. Une analyse des valences de liaisons démontre de façon non ambiguë la présence de trois groupes H_2O, dont deux sont ordonnés, avec des protons dont la position est ordonnée, et l'autre est désordonné, ce qui concorde avec les résultats de la spectroscopie dans l'infrarouge. La structure de la gaultite ressemble à celle de la lovdarite et du zéolite synthétique VPI–7; ce dernier pourrait bien être l'analogue synthétique de la gaultite.

(Traduit par la Rédaction)

Mots-clés: gaultite, nouvelle espèce minérale, structure cristalline, tectosilicate à aspects zéolitiques, mont Saint-Hilaire, Québec.

INTRODUCTION

In recent years, a number of new mineral species have been found at Mont Saint-Hilaire, Québec, as products of reaction between alkaline syenitic magma, now represented by the intrusive complex, and various xenolithic materials. The subject of the present study, gaultite (formally UK 84, Chao *et al.* 1990), is one such species; herewith we describe its properties and structure. It is named for Robert Allan Gault (1943 –), our colleague at the Canadian Museum of Nature, for his many contributions toward the understanding of the mineralogy of Mont Saint-Hilaire, culminating in a special issue of *The Mineralogical Record* (Horvath & Gault 1990). Both the mineral and its name have been approved by the Commission on New Minerals and Mineral Names, IMA. The holotype sample is deposited at the Canadian Museum of Nature (CMN 81513).

LOCATION AND OCCURRENCE

The mineral occurs in a cavity in a single specimen taken from the center of a 12-m^3 inclusion of sodalite syenite, approximately 5 m from a contact of hornfels and nepheline–sodalite syenite at the Poudrette Quarry, Mont Saint-Hilaire, Rouville County, Québec. Associated minerals are: aegirine, analcime, cancrinite, catapleiite, chabazite, eudialyte, galena, graphite, lovozerite-group minerals, makatite, microcline, nepheline, natrolite, phillipsite, polylithionite, pyrite, serandite, sodalite, steenstrupine, ussingite, villiaumite, vitusite, vuonnemite, and two unidentified species (UK 38 and UK 53). Gaultite was the last of its paragenesis to form.

PHYSICAL AND OPTICAL PROPERTIES

Gaultite occurs as euhedral, equant, multifaceted crystals up to 0.5 mm in diameter, with an average size of 0.25 mm. Predominant forms include $\{010\}$, $\{110\}$, $\{\bar{1}10\}$, $\{021\}$, $\{151\}$ and $\{1\bar{5}1\}$; subordinate to these are $\{111\}$, $\{\bar{1}11\}$, $\{131\}$, $\{\bar{1}31\}$, $\{171\}$, $\{\bar{1}71\}$ and $\{011\}$ (Fig. 1). The point group of the mineral is strongly pseudo-*mmm* (actual point group is 2*mm*). As viewed down [001], crystals have a pseudohexagonal outline (Fig. 1b), and [010] projections may show pseudofourfold symmetry (Fig. 1c); however, considered as a whole, the mineral is distinctly orthorhombic (Fig. 1a). Both single crystals and aggregates of randomly oriented crystals can be found.

The mineral ranges from colorless to pale mauve, and is invariably transparent. It fluoresces bright apple-green in short-wave ultraviolet radiation, and has a strong pale green cathodoluminescence under an electron beam. The luster is vitreous, and the streak, white. The hardness is approximately 6. The mineral is brittle, has perfect $\{101\}$ and $\{010\}$ cleavages and a poor $\{021\}$ cleavage; some surfaces show a conchoidal fracture. The density, 2.52(4) g cm^{-3}, measured by a sink–float method using mixtures of bromoform and butanol, matches the calculated density of 2.52 g cm^{-3}. Gaultite does not readily dissolve in 1:1 HCl, but does show very slight etching after prolonged exposure.

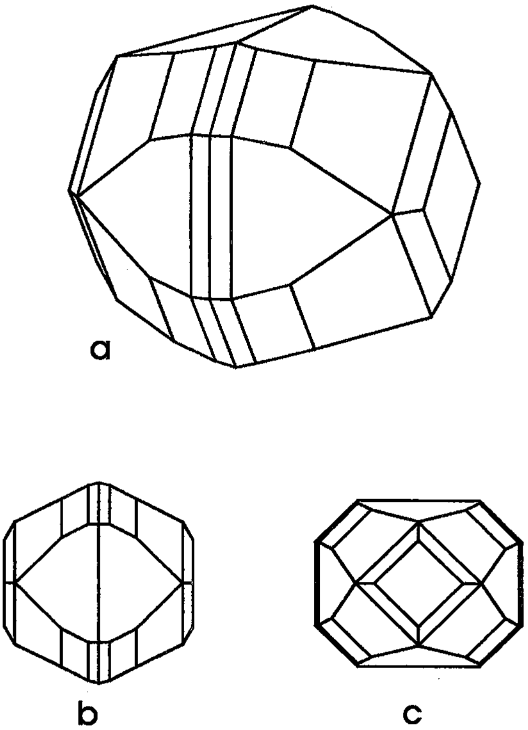

FIG. 1. Crystal drawings of gaultite: (a) inclined projection, (b) [001] projection, (c) [010] projection.

Gaultite is biaxial positive and nonpleochroic. Indices of refraction were measured with a spindle stage, using the Becke line method and a 590 nm gel filter: α 1.520(1), β 1.521(1), γ 1.524(1). The 2*V* angle, determined from extinction curves refined from spindle-stage data using the program EXCALIBR (Bloss 1981), is 61.3(4)°, which compares well with the calculated value of 2*V*, 60°. Comparison of these data with a duplicate set of extinction data (546 nm gel filter) shows dispersion of all optical directions except the acute bisectrix, with $r > v$, weak to moderate. The orientation of the optic axes is $X \parallel a$, $Y \parallel c$ and $Z \parallel b$.

CHEMISTRY

A chemical analysis was done with a JEOL 733 electron microprobe using Tracor–Northern 5500 and 5600 automation (wavelength-dispersion mode). Operating conditions were: 15 kV, 20 nA beam current, 40 μm beam diameter (to minimize a degradation of the sample). All samples were examined for chemical heterogeneities by back-scattered electron imaging; all such images show no signs of heterogeneity. In an energy-dispersion spectrum collected for 50 s, only Na, Si and Zn were detected. The following standards were used: tugtupite (Na*K*α), willemite (Zn*K*α), and diopside (Si*K*α); in addition, Ca, Mn, Al, K and F were sought, but not detected. Data for standards were collected for 50 s or 0.25% precision (1σ level), whichever was attained first; data for samples were collected for 50 s or 0.5% precision. Sodium–zinc overlap was corrected for prior to data reduction. Data reduction was done with a conventional ZAF routine in the Tracor–Northern TASK series of programs. The electron-microprobe data gave Na_2O 16.6, ZnO 19.2, SiO_2 52.6, total 88.4 wt.% (average of two analyses).

The powder infrared-absorption spectrum (IR) of gaultite was obtained at the Canadian Conservation Institute using a Boem MB 120 FTIR instrument equipped with a diamond-anvil microsample cell. A single crystal was crushed in the cell, which minimized the amount of adsorbed water. The spectrum of gaultite (Fig. 2) is very similar to that of stilbite, attesting to the zeolite-like structure of the mineral. Absorption envelopes at 1600 and 2800–3600 cm^{-1} indicate the presence of H_2O as molecular water. The presence of broad and narrow bands in the 2800–3600 cm^{-1} region is interpreted to be due to both well-ordered and disordered H_2O in the structure (see below), resulting in the sharp and broad absorption maxima, respectively.

The results of the electron-microprobe study, in conjunction with those of the IR study and of the structure analysis, indicate an empirical formula $Na_{4.28}Zn_{1.88}Si_{6.99}O_{18}\cdot 5H_2O$, Z = 8 for gaultite, which implies minor Na–Zn disorder or a minor analytical error. The amount of water calculated according to stoichiometry is 11.3 wt.%, which matches the deficit of 11.6% in the analytical total.

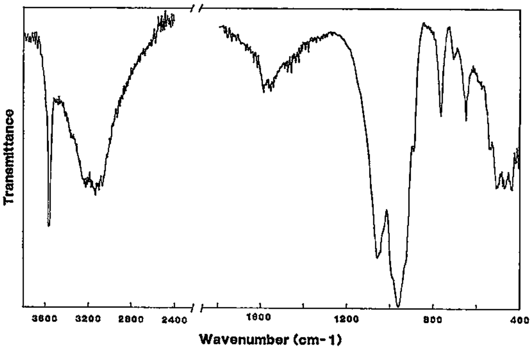

FIG. 2. Infrared spectrum of gaultite.

CRYSTAL STRUCTURE

X-ray crystallography

Precession photographs of gaultite were taken using Zr-filtered Mo*K*α radiation. The mineral has *Fmmm* diffraction symmetry. The h^*0l^* photograph shows weak pseudotetragonal symmetry; however, intensity relationships and the measurable metric inequivalence of *a** and *c** indicate the true symmetry. The extinction conditions and diffraction symmetry unambiguously give the space group *F*2*dd*. The X-ray powder-diffraction pattern for gaultite is given in Table 1; indices were assigned in conjunction with the results of the precession study. Refinement of the powder-diffraction data with the CELREF program of Appleman & Evans (1973) gives *a* 10.211(3), *b* 39.88(2), *c* 10.304(4) Å, *V* 4196(2) Å³.

Collection of X-ray intensity data

Intensity data were collected on a hand-ground ellipsoid (0.17 × 0.15 × 0.11 mm) made from the

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR GAULTITE

hkl	*d* (calc)	*d* (obs)	*I*
040	9.97	10.00	1
131	6.37	6.35	10
151	5.37	5.36	2
080	4.99	4.96	3
220	4.95		
042	4.58	4.57	1
222	3.568	3.562	<1
242	3.408	3.409	<1
0120	3.323	3.324	<1
113	3.245	3.240	6
1111	3.243		
262	3.184	3.167	4
133	3.162		
2100	3.143	3.140	4
331	3.140		
351	2.995	2.996	2
282	2.933	2.928	1
173	2.826	2.821	3
1131	2.825		
193	2.623	2.621	<1
024	2.555	2.553	1
400	2.553		
0160	2.493	2.491	2
2140	2.488		
2122	2.450	2.441	<1
313	2.413	2.414	1
3111	2.412		
333	2.379	2.378	1
480	2.272	2.278	1
1133	2.233	2.233	2
1171	2.232		
264	2.173	2.168	<1
0104	2.164		
393	2.122	2.125	<1
284	2.088	2.086	<1
4120	2.024	2.027	1
4102	1.984	1.988	<1
155	1.958	1.958	<1
175	1.904	1.905	<1
1173	1.903		
3133	1.899	1.896	<1
3171	1.898		
195	1.838	1.836	<1
1211	1.837		
424	1.806	1.807	2
3153	1.789	1.787	<1
513	1.754	1.755	<1
5111	1.753		
553	1.714	1.713	<1
2164	1.690	1.689	2
1135	1.687		
4104	1.651	1.650	<1
660	1.649		
593	1.632	1.634	<1
5151	1.600	1.599	1
3193	1.584	1.583	1
286	1.547	1.550	<1
0126	1.526	1.526	<1
2242	1.511	1.510	<1
3213	1.493	1.494	<1
4164	1.466	1.467	1
2126	1.462	1.463	<1
731	1.436	1.435	<1
2224	1.424	1.423	<1
426	1.421		
751	1.421		
644	1.406	1.406	2
575	1.406		
6142	1.406		
5173	1.405		
5211	1.378	1.375	<1
791	1.373		
0282	1.372		
684	1.366	1.366	<1
5193	1.347	1.345	2
1273	1.345		
4242	1.344		
337	1.344		
753	1.324	1.324	<1
5135	1.311	1.310	<1
5231	1.311		

114.6 mm Gandolfi camera; Ni-filtered Cu*K*α radiation; film corrected for shrinkage; *I* visually estimated.

TABLE 2. MISCELLANEOUS STRUCTURAL INFORMATION FOR GAULTITE

a (Å):	10.231(4)	μ (cm^{-1}, Mo$K\alpha$):	29
b:	39.91(2)	Total no. of $\|F_o\|$:	1283
c:	10.339(4)	No. $\|F_o\| > 3\sigma(\|F_o\|)$:	1210
Space group:	$F2dd$	Final R (obs)%:	2.51
Composition:	$Na_4Zn_2Si_7O_{18} \cdot 5H_2O$	Final wR (obs)%:	2.80
Z	8		

$R = \sum(|F_o| - |F_c|)/\sum|F_o|$

$wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/[\sigma^2(|F_o|) + 0.000245(|F_o|)^2]$

gaultite crystal used in the precession study. The intensity data were collected with a Nicolet $R3m$ four-circle diffractometer at the University of Manitoba, using the experimental method of Ercit *et al.* (1986). Twenty-five intense reflections (to $2\theta = 27°$) were used to center the crystal; least-squares refinement of the setting angles gave the orientation matrix used for data collection and the unit-cell parameters given in Table 2. One octant of reciprocal space was collected to a $2\theta_{max}$ of 60°. The data were empirically corrected for absorption using a ψ-scan calibration data-set corrected for an ellipsoidal shape (R[azim.] = 1.1% after correction). Data reduction (correction for Lorentz, polarization and background effects) was done with the SHELXTL PC system of programs.

Structure refinement

The structure refinement was done with SHELXTL PC. Scattering curves for neutral atoms were taken from Cromer & Mann (1968), and anomalous scattering factors, from Cromer & Liberman (1970).

A sharpened Patterson map was calculated, from which the positions of a Zn site, four Si sites, three Na sites and eleven O sites were derived. Several cycles of full-matrix least-squares refinement of this model, refining all U(Zn,Si) values, but with U(O,Na) values constrained at 0.015 Å^2, gave $R = 10.4$, $wR = 12.4\%$. A difference map and bond lengths calculated at this stage showed evidence of split Na and O sites, and of incorrect assignments of sites. To investigate this further, all U(Na) values were constrained at 0.015 Å^2, and all U(O) values were refined. The refinement converged to $R = 7.0$, $wR = 8.2\%$, showed one Na assignment to be invalid, and gave evidence of an additional O site. The model was appropriately modified; with all displacement parameters refined, this fully isotropic model converged to $R = 6.1$, $wR = 6.9\%$. The model showed two obvious problems: the displacement parameter for one of the oxygen atoms was found to be large ($U = 0.072$ Å^2), and large maxima (to 4 eÅ^{-3}) were located about one of the Na atoms, indicative of positional disorder of the Na atom. At this stage, the anomalous Na site was split, and the displacement parameters of all other atoms were modeled as being anisotropic. Refinement of the model converged to $R = 3.0$, $wR = 2.8\%$. This stage of the refinement showed that the anomalous oxygen atom is positionally disordered about the twofold axis. That atom shows extreme anisotropy; one of its displacement parameters is very large (0.1586 Å^2). Furthermore, inspection of the model showed that three of the oxygen atoms represent H_2O groups; difference maps at this stage showed evidence of hydrogen atoms about two of the oxygen atoms. As the electron-microprobe-derived composition is deficient in Zn and shows excess Na, the occupancy of the Zn site was refined; the result, 0.998(4) atoms, shows that the Zn site is fully occupied by Zn, and that the electron-microprobe results are in error. The final model has one Zn site, four Si sites, nine O sites, three OW sites, three Na sites and four H sites; Na2 is split into two half-occupied sites (Na2′ and Na2″), and OW3 is positionally disordered. Hydrogen atoms H2 to H4 were not well behaved (overly short H–O separations); consequently, "soft" constraints on bond length were applied to H–O bonds involving these atoms, by adding the constraints as additional weighted observations in the least-squares matrix. Although H atoms were not located about the OW3 site, bond-valence analysis showed unequivocally that it represents an H_2O group (see below). The final stage of refinement employed a σ^{-1} weighting scheme, with a term to downweigh the contribution of intense reflections. Refinement of the final model gave $R = 2.51$, $wR = 2.80\%$ ($R = wR = 2.85\%$ for all 1283 data). All maxima in the final difference-Fourier map were within ± 0.5 eÅ^{-3}.

The observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 3. ATOMIC PARAMETERS FOR GAULTITE

	Occupancy	x	y	z	U_{eq}
Zn		1/4	0.05464(1)	0.33774(5)	109(1)
Si1		0.2810(1)	0.16421(3)	0.0909(1)	94(3)
Si2		0.2461(1)	0.09015(3)	0.0554(1)	97(3)
Si3		0.5355(1)	0.07200(3)	0.0439(1)	87(3)
Si4		0.6058(2)	0	0	90(5)
Na1		0.0445(2)	0.12519(6)	0.3003(2)	259(7)
Na2′	0.5	0.3275(5)	0.2396(1)	0.0561(4)	225(9)
Na2″	0.5	0.3622(5)	0.2534(1)	0.0871(5)	327(11)
O1		0.5082(4)	0.03154(7)	0.0355(3)	145(9)
O2		0.3993(3)	0.09110(9)	0.0116(3)	136(9)
O3		0.2105(4)	0.12776(8)	0.1113(3)	152(9)
O4		0.5772(4)	0.08149(9)	0.1914(3)	176(10)
O5		0.4174(3)	0.16520(8)	0.1708(3)	139(10)
O6		0.1466(3)	0.08424(8)	0.4480(3)	122(9)
O7		0.2141(4)	0.06228(9)	0.1568(3)	192(10)
O8		0.1914(3)	0.00868(8)	0.3740(3)	139(10)
O9		0.1861(3)	0.19363(8)	0.1328(3)	179(10)
OW1		0.1347(4)	0.1602(1)	0.4621(4)	241(12)
OW2		0.1693(4)	0.2768(1)	0.1296(4)	214(11)
OW3		0.4831(7)	0.2517(3)	0.2210(8)	332(21)
H1		0.146(6)	0.180(1)	0.445(5)	100
H2		0.070(5)	0.160(1)	0.511(5)	100
H3		0.085(6)	0.269(1)	0.144(5)	100
H4		0.180(6)	0.287(1)	0.204(4)	100

All U values are Å^2 x 10^4; all U(H) values are fixed.

TABLE 4. ANISOTROPIC DISPLACEMENT PARAMETERS FOR GAULTITE

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn	116(2)	105(2)	106(2)	13(2)	22(2)	-6(2)
Si1	91(6)	106(5)	84(5)	-3(4)	-19(5)	15(5)
Si2	99(6)	97(5)	96(6)	3(4)	-22(5)	10(5)
Si3	79(6)	98(5)	82(5)	-4(5)	-6(5)	16(4)
Si4	95(8)	82(8)	93(8)	13(7)	0	0
Na1	284(12)	220(11)	273(11)	47(9)	-118(10)	6(9)
O1	139(17)	89(14)	206(15)	3(12)	37(16)	14(14)
O2	69(15)	188(17)	150(16)	-9(14)	-19(14)	29(13)
O3	147(16)	129(16)	182(17)	-27(13)	39(14)	-29(13)
O4	156(17)	293(21)	80(16)	-17(14)	-5(14)	-13(15)
O5	115(16)	198(17)	106(17)	-4(13)	-40(13)	-1(14)
O6	147(16)	107(16)	111(16)	-1(12)	47(13)	27(13)
O7	290(22)	154(17)	134(16)	34(14)	-43(16)	-44(14)
O8	160(18)	117(17)	139(16)	24(12)	26(14)	1(14)
O9	152(18)	147(18)	238(19)	-41(14)	-10(15)	32(15)
OW1	287(23)	162(19)	273(22)	23(16)	14(18)	28(17)
OW2	190(20)	204(19)	248(20)	-14(15)	36(16)	-40(17)

All U values are Å^2 x 10^4

Description of the structure

The refined values of the positional parameters and the equivalent isotropic displacement parameters are given in Table 3, anisotropic displacement parameters are in Table 4, selected interatomic distances are in Table 5, and bond angles and polyhedral edge-lengths are in Table 6. A perspective view of the structure of gaultite is shown in Figure 3.

All Zn and Si atoms in the structure are tetrahedrally coordinated. The ZnO_4 and SiO_4 tetrahedra are in an all-corner-linked arrangement, and form a framework. This arrangement results in low degrees of distortion of all tetrahedra, including the (internally) more weakly bonded ZnO_4 tetrahedron. Although the [101] projection (Fig. 3) seems complex, a [010] projection shows the framework to consist of a stacking of 2-dimensional 4.8^2 Schläfli nets (Fig. 4; type 38 of Smith 1978) with periodic insertions of connective nodes of tetrahedra between sheets (alternations of two sheets and one layer of nodes). Linkage between these sheets occurs *via* both SiO_4 and ZnO_4 tetrahedra.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN GAULTITE

Si1-O3	1.637(4)	Zn-O6	1.953(4)	Na2"-O7	2.571(7)
-O4	1.626(4)	-O7	1.931(4)	-O8	2.338(6)
-O5	1.623(4)	-O8	1.966(3)	-O9	3.028(7)
-O9	1.584(4)	-O9	1.961(4)	-OW2	2.226(7)
<Si1-O>	1.618	<Zn-O>	1.953	-OW3′	2.347(10)
				<Na2"-O>	2.502
Si2-O2	1.632(4)	Na1-O2	2.972(4)		
-O3	1.650(4)	-O3	2.591(4)	H1-OW1	0.83(4)
-O5	1.621(4)	-O6a	2.469(4)	-OW2	1.90(4)
-O7	1.563(4)	-O6b	2.456(4)		
<Si2-O>	1.617	-OW1a	2.345(5)	H2-OW1	0.83(5)
		-OW1b	2.367(5)	-O5	2.28(5)
Si3-O1	1.641(3)	<Na1-O>	2.533		
-O2	1.623(4)			H3-OW2	0.94(6)
-O4	1.628(4)	Na2′-O1	3.008(6)	-O8	1.84(6)
-O6	1.585(4)	-O4	3.076(6)		
<Si3-O>	1.619	-O8	2.325(6)	H4-OW2	0.87(4)
		-O9	2.468(6)	-O9	1.86(4)
Si4-O1 x2	1.648(4)	-OW2	2.323(6)		
-O8 x2	1.608(4)	-OW3	2.382(9)	OW3-OW3′	0.62(2)
<Si4-O>	1.628	<Na2′-O>	2.597		
				Na2′-Na2"	0.73(1)

TABLE 6. EDGE LENGTHS (Å) AND BOND ANGLES (°) IN POLYHEDRA IN GAULTITE

Si1 Tetrahedron		
O3-O4	2.675(5)	110.2(2)
-O5	2.663(5)	109.5(2)
-O9	2.650(5)	110.7(2)
O4-O5	2.549(5)	103.4(2)
-O9	2.647(5)	111.1(2)
O5-O9	2.654(5)	111.7(2)
<O-O>	2.640	
<O-Si1-O>		109.4

Si2 Tetrahedron		
O2-O3	2.634(5)	106.7(2)
-O5	2.565(5)	104.0(2)
-O7	2.677(5)	113.8(2)
O3-O5	2.648(5)	108.1(2)
-O7	2.656(5)	111.5(2)
O5-O7	2.644(5)	112.2(2)
<O-O>	2.637	
<O-Si2-O>		109.4

Si3 Tetrahedron		
O1-O2	2.637(5)	107.8(2)
-O4	2.659(5)	108.8(2)
-O6	2.692(5)	113.1(2)
O2-O4	2.629(5)	107.9(2)
-O6	2.628(5)	110.0(2)
O4-O6	2.617(5)	109.0(2)
<O-O>	2.644	
<O-Si3-O>		109.4

Si4 Tetrahedron		
O1-O1	2.622(6)	105.5(3)
O1-O8 x2	2.670(5)	110.2(2)
-O8 x2	2.639(5)	108.3(2)
O8-O8	2.695(6)	113.9(3)
<O-O>	2.656	
<O-Si4-O>		109.4

Zn Tetrahedron		
O6-O7	3.211(5)	111.5(1)
-O8	3.145(5)	106.7(1)
-O9	3.235(5)	111.5(1)
O7-O8	3.112(5)	105.9(1)
-O9	3.267(5)	114.1(2)
O8-O9	3.147(5)	106.5(1)
<O-O>	3.186	
<O-Zn-O>		109.4

Na1 Polyhedron		
O2-O6a	2.628(5)	56.9(1)
-O6b	4.404(5)	108.1(1)
-OW1a	3.696(6)	86.9(1)
-OW1b	3.100(5)	70.2(1)
O3-O6a	3.945(5)	102.4(1)
-O6b	3.663(5)	93.0(1)
-OW1a	3.929(6)	104.7(2)
-OW1b	3.807(6)	100.8(2)
O6a-OW1a	3.037(5)	77.8(1)
-OW1b	3.630(6)	97.9(2)
O6b-OW1a	3.666(6)	98.9(2)
-OW1b	3.037(5)	78.5(1)
<O-O>	3.545	
<O-Na1-O>		89.7

Na2′ Polyhedron		
O1-O4	2.659(5)	51.8(1)
-O8	2.639(5)	57.6(1)
-O9	3.797(5)	87.2(2)
-OW2	4.348(5)	108.6(2)
O4-O8	3.844(5)	89.6(2)
-O9	2.647(5)	55.7(1)
-OW3	4.684(10)	117.7(3)
O8-OW2	3.893(6)	113.7(2)
-OW3	3.603(9)	99.9(3)
O9-OW2	3.322(5)	87.8(2)
-OW3	3.930(10)	108.3(3)
OW2-OW3	3.493(9)	95.9(3)
<O-O>	3.572	
<O-Na2′-O>		89.5

Na2" Polyhedron		
O7-O8	3.110(5)	78.5(2)
-OW2	3.354(6)	88.4(2)
-OW3′	3.203(10)	81.1(3)
O8-O9	4.549(5)	115.0(2)
-OW2	3.893(6)	117.0(3)
-OW3′	4.210(9)	127.9(3)
O9-OW2	3.322(5)	76.8(2)
-OW3′	4.035(9)	96.5(3)
OW2-OW3′	3.740(9)	109.7(3)
<O-O>	3.713	
<O-Na2"-O>ax-eq		89.4
<O-Na2"-O>eq-eq		118.2

ax: axial, eq: equatorial

Sodium atoms in the gaultite structure occur in irregular channels in the framework of tetrahedra (Fig. 3). Na1 atoms occur in one type of channel bound by circuits of eight tetrahedra; these channels are typified by an elongate cross-section, with a short axis the edge-length of a NaO_6 octahedron. Na2 atoms occur in another type of channel, much larger in radius than the first, bound by only one more tetrahedron in a circuit (nine), but with a cross-section with a lower aspect-ratio than than the first type of channel.

The coordination polyhedron of Na1 is shown in Figure 5. The relatively low strengths of Na–O bonds, as compared to bonding within the framework of tetrahedra (Table 7), results in a significant degree of radial and angular distortion of the $Na1O_6$ octahedron (Tables 5, 6). The distortion of the $Na1O_6$ octahedron also is due in part to its coordination by four frame-

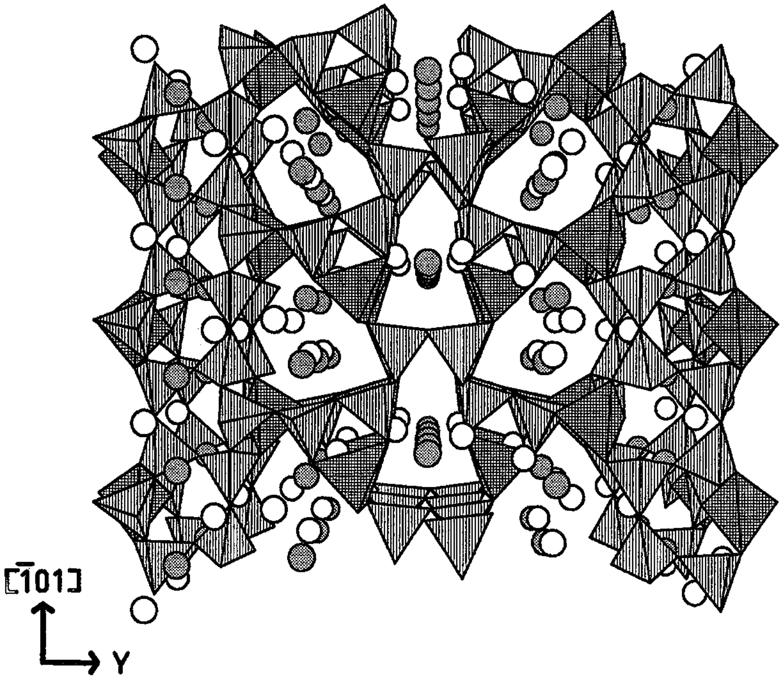

FIG. 3. Perspective view of the gaultite structure, projected along [101]. SiO$_4$ tetrahedra are ruled, ZnO$_4$ tetrahedra are cross-hatched, Na atoms are stippled, and the oxygen atoms of H_2O groups are shown as open circles.

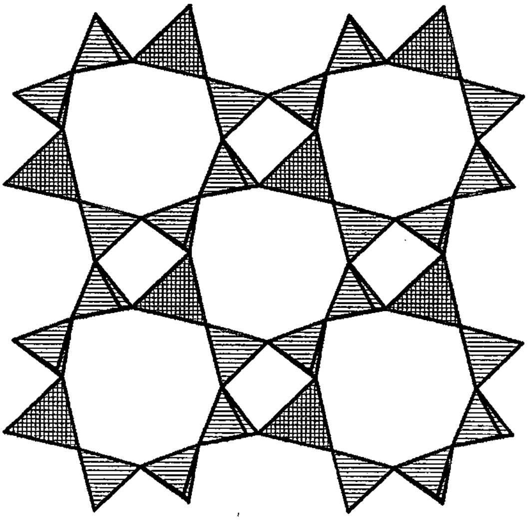

FIG. 4. View of a 4.8^2 Schläfli layer in gaultite. Polyhedron shading is as in Fig. 3.

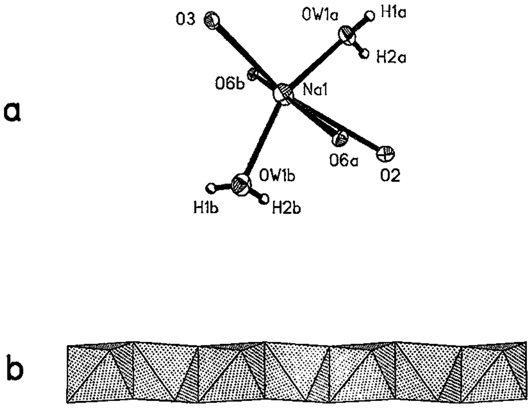

FIG. 5. The coordination polyhedron of Na1: (a) ball and stick model showing the arrangement of O atoms and H_2O groups; (b) polyhedral model showing polymerization of octahedra in straight chains. H_2O groups are apical in the edge-sharing chains.

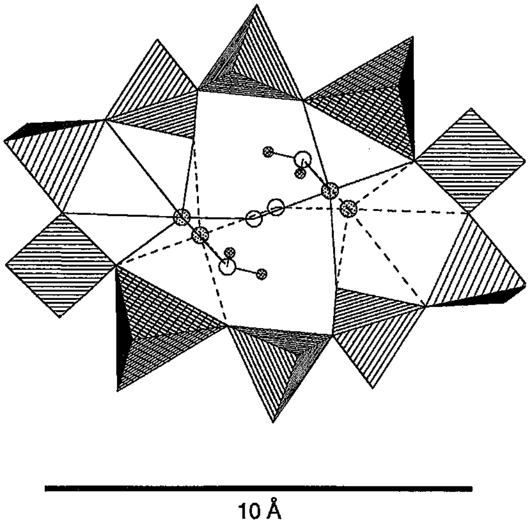

FIG. 6. Positional disorder and local ordering of Na2. Shading of polyhedra and atoms is as in Fig. 3, except H (darkly shaded spheres). Different local configurations of Na2 atoms are shown in different rule (solid *versus* broken rule).

work oxygen atoms and two H_2O groups, arranged equatorially and axially, respectively. Adjacent Na1 octahedra are cross-linked by *trans*-edge-sharing to form straight chains parallel to {101}; as expected, cross-linkage occurs *via* the equatorial oxygen atoms (Fig. 5). The coordination of Na1 can also be described as a distorted cube if two distant oxygen atoms at distances of 3.17 and 3.39 Å are taken into the coordination sphere; however, their bond-valence contribution is hardly significant, hence our description of Na1 as [6]-coordinated.

Na2 lies in a large channel, along with H_2O groups denoted by OW2 and OW3. The large radius of the channel restricts the number of oxygen atoms of the framework that can fall into the coordination sphere of Na2. In order to satisfy its bond-valence requirements, Na2 is split into half-occupancy of two sites, designated Na2′ and Na2″ here. The style of this positional disorder is shown in Figure 6. The Na2′ – Na2″ splitting occurs in a planar section of the channel, which is bound by a 10-membered ring of tetrahedra that statistically hosts two Na2 atoms. The Na2′ – Na2″ splitting brings O4 into the coordination sphere of Na2′ and O7 into the coordination sphere of Na2″, thus satisfying the bond-valence requirements of the cations. The H_2O group denoted by OW3 is affected by this local readjustment: OW3, which occupies the geometrical center of the ring, and is statistically coordinated by two Na2 atoms, is necessarily also positionally disordered, the consequence of a tug-of-war between Na2 atoms at opposite sides of the ring. Local ordering within the ring can be seen by inspection of Figure 6. If a Na2′ position is occupied on one side of the ring, the Na2″ position must be occupied on the other, and OW3 is displaced toward Na2′. This local pattern of order is not expressed over long ranges, and a refinement of the occupancy of Na2′ *versus* Na2″ shows no significant preference of one site over the other. Figure 7 shows the coordinations of Na2′ and Na2″. Na2′ is six-coordinated by two H_2O groups and four framework oxygen atoms, and the polyhedron is intermediate between an octahedron and a trigonal pyramid. Na2″ is five-coordinated by two H_2O groups and three framework oxygen atoms, and the polyhedron approximates a trigonal bipyramid with both H_2O groups in equatorial positions (Fig. 7, Table 6).

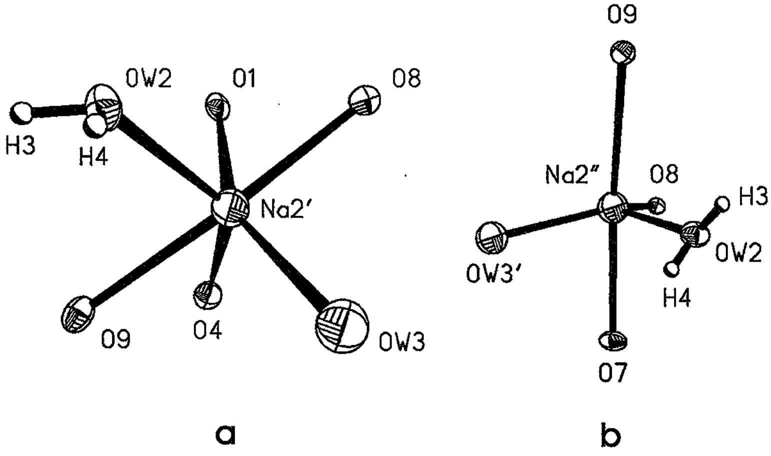

FIG. 7. Local coordination polyhedra for Na2.

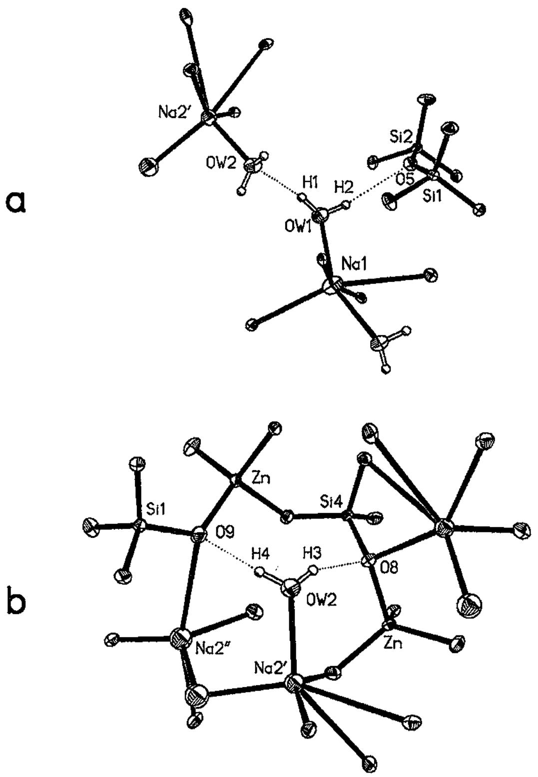

FIG. 8. Hydrogen bonding (dotted lines) for (a) OW1, (b) OW2.

TABLE 7. BOND-VALENCE TABLE FOR GAULTITE

	Si1	Si2	Si3	Si4	Zn	Na1	Na2'	Na2"	SUMS	SUMS (with H)
O1			0.95	0.93 ×2↓			0.05 ÷2→		1.91	1.91
O2		0.97	1.00			0.05			2.02	2.02
O3	0.96	0.93				0.12			2.01	2.01
O4	0.99		0.98				0.04 ÷2→		1.99	1.99
O5	1.00	1.00							2.00	2.12
O6			1.10		0.49	0.16 0.16			1.92	1.92
O7		1.17			0.52			0.13 ÷2→	1.75	1.75
O8				1.04 ×2↓	0.47		0.22 ÷2→	0.22 ÷2→	1.73	1.92
O9	1.11				0.48		0.16 ÷2→	0.05 ÷2→	1.69	1.88
OW1						0.20 0.21			0.41	2.64
OW2							0.22 ÷2→	0.28 ÷2→	0.26	2.29
OW3							0.20	0.21	0.41	
SUMS	4.05	4.08	4.04	3.94	1.96	0.91	0.89	0.87		

- bond valences (*v.u.*) from constants of Brown (1981)

Figure 8 shows hydrogen bonding in gaultite. Bond-valence analysis (Table 7) and stereochemistry show that (1) for the H_2O group represented by OW1, H1 is hydrogen-bonded to OW2, and H2 to O5, and (2) for the H_2O group represented by OW2, H3 is hydrogen-bonded to O8, and H4 to O9. Although protons were not located about OW3, the low bond-valence sum to O7 and its proximity to OW3 (two O7 atoms, at 2.76 and 3.20 Å) imply that O7 is an acceptor of the protons of OW3. The high values of the hydrogen-inclusive bond-valence sums to OW1 and OW2 indicate that (1) the soft constraints applied to the length of O–H bonds are not completely effective, and (2) the electron density about H atoms is asymmetrical.

Comparison with other minerals and compounds

The framework of tetrahedra in gaultite shows many structural elements typical of zeolites; however, as gaultite has Zn as a framework cation, by current IMA standards, it is not formally a zeolite mineral, but instead, zeolite-like. In zeolite terminology, the secondary building units of the framework of the gaultite structure are a single 4-ring and a spiro-5 (Meier & Olson 1992). Although the single 4-ring, a quadrilateral of 4 nodes, is a common structural unit in many tectosilicates, the spiro-5 is rare, and warrants further discussion. The spiro-5 consists of two three-membered rings connected by a common node; the structural formula of the spiro-5 in gaultite is $[Zn_2Si_3O_{14}]^{12-}$, and the connective node is Si4. The spiro-5 is also found in other zeolite-like minerals and compounds such as lovdarite (a beryllosilicate; Merlino 1990) and the synthetic sodium–zinc silicate VPI–7 (Annen *et al.* 1991). The distance-least-squares refinement of the framework constituents of VPI–7 (Annen *et al.* 1991) shows the frameworks of VPI–7 and gaultite to be topologically identical (Figs. 9a, b). However, as shown by Annen *et al.* (1991), the frameworks of VPI–7 (thus also gaultite) and lovdarite are not identical; lovdarite (Fig. 9c) has a structure based upon a different stacking of 4.8^2 nets.

The $I\bar{4}m2$ symmetry of VPI–7 results in Si–Zn disorder; by comparison with gaultite, Zn would seem to be disordered over *T3* and *T5* of the structure of VPI–7. Given tetragonal pseudosymmetry in gaultite, and as VPI–7 was assigned the space group $I\bar{4}m2$ from powder data, not single-crystal experiments, it is possible that VPI–7 has lower symmetry and that its framework cations are ordered. Indeed, VPI–7 may be the synthetic analogue of gaultite (J.B. Higgins, pers. comm.); however, more work is needed on VPI–7 before the compositions and structures of it and gaultite can be compared in greater detail.

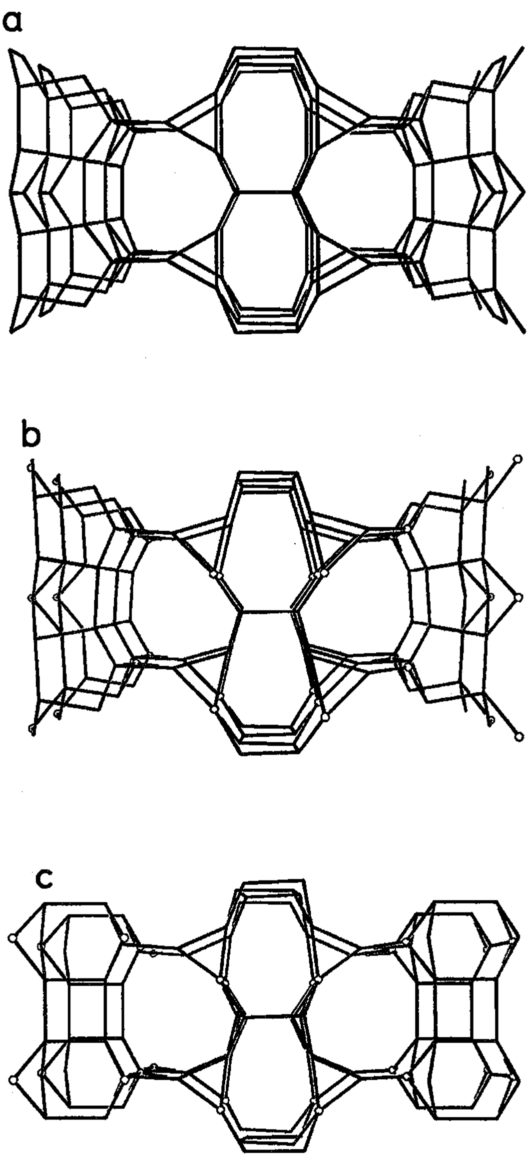

FIG. 9. Perspective views of the net representations of the tetrahedral frameworks in (a) synthetic zeolite VPI–7, (b) gaultite and (c) lovdarite. Open circles denote Zn atoms in the gaultite structure and Be atoms in the lovdarite structure; Si and Zn are disordered in VPI–7.

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