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SHELDRICKITE, A NEW SODIUM–CALCIUM–FLUOROCARBONATE MINERAL SPECIES FROM MONT SAINT-HILAIRE, QUEBEC

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ABSTRACT

Sheldrickite, ideally $NaCa_3(CO_3)_2F_3{\cdot}H_2O$, is a newly identified mineral species from Mont Saint-Hilaire, Quebec. It occurs as an aggregate of blocky, colorless to white crystals up to 2 mm wide, with individual crystals up to 0.1 mm, and as aggregates of silky white flakes to 2 mm across. Associated minerals include pectolite, shortite, microcline, polylithionite, arfvedsonite and minor molybdenite. The mineral has a vitreous to silky luster and a white streak. It is soft (Mohs hardness 3) and brittle, with an uneven fracture and good {001} parting. Sheldrickite is uniaxial positive, $\omega = 1.538(2)$ and $\varepsilon = 1.563(4)$. It is trigonal, space group $P3_2$, a 6.718(3), c 15.050(4) Å, V 588.3(3) Å^3, and $Z = 3$. The strongest seven X-ray powder-diffraction lines [d in Å (I)(hkl)] are: 5.809(30)(100), 5.010(30)(003), 3.358(30)(110), 2.791(50)(113), 2.508(40)(006), 2.010(100)(116) and 1.939(40)(300). The infrared spectrum is given. Three electron-microprobe analyses and a thermogravimetric analysis gave Na_2O 9.16 (9.11–9.24), CaO 48.84 (48.62–49.15), SrO 0.36 (0.33–0.40), F 16.17 (15.91–16.52), CO_2 25.81 and H_2O 5.61, O = F –6.81, total 99.14 wt.%. CO_2 was calculated by stoichiometry from the results of the crystal-structure analysis. The empirical formula based on 10 anions is $Na_{1.01}(Ca_{2.97}Sr_{0.01})_{\Sigma 2.98}(CO_3)_2[F_{2.90}(OH)_{0.07}]_{\Sigma 2.97}{\cdot}H_2O$ or, ideally, $NaCa_3(CO_3)_2F_3{\cdot}H_2O$. Dcalc. = 2.86 g/cm^3 and Dmeas. = 2.86(4) g/cm^3. The structure has been refined to $R = 4.6\%$ using a twinned crystal. The structure is layered on (001). One layer consists of $(CO_3)^{2-}$ groups oriented perpendicular to (001), the $Na\varphi_8$ polyhedra and the H_2O groups. A second layer consists of $Ca\varphi_9$ polyhedra and F^- anions. The structure of sheldrickite bears little resemblance to the chemically similar rouvilleite, but it seems to be a modification of the structures of bastnäsite and cebaite. The name honors George M. Sheldrick, creator of the SHELX software, widely used for the refinement of crystal structures.

Keywords: sheldrickite, new mineral species, carbonate, crystal structure, twinning, Mont Saint-Hilaire, Quebec.

SOMMAIRE

Nous décrivons la sheldrickite, nouvelle espèce minérale de composition idéale $NaCa_3(CO_3)_2F_3{\cdot}H_2O$, provenant du mont Saint-Hilaire, Québec. On la trouve en agrégats de cristaux trappus incolores ou blancs atteignant 2 mm, avec les cristaux individuels jusqu'à 0.1 mm en longueur, et en agrégats de flocons soyeux jusqu'à 2 mm de diamètre. Lui sont associés pectolite, shortite, microcline, polylithionite, arfvedsonite, ainsi que molybdénite accessoire. La sheldrickite possède un éclat vitreux à soyeux et une rayure blanche. Elle est molle (dureté de Mohs 3) et cassante, avec une fracture inégale et un bon plan de séparation {001}. Elle est uniaxe positive, $\omega = 1.538(2)$ et $\varepsilon = 1.563(4)$. Il s'agit d'un minéral trigonal, groupe spatial $P3_2$, a 6.718(3), c 15.050(4) Å, V 588.3(3) Å^3 et $Z = 3$. Les sept raies les plus intenses du cliché de diffraction (méthode des poudres) [d en Å (I)(hkl)] sont 5.809(30)(100), 5.010(30)(003), 3.358(30)(110), 2.791(50)(113), 2.508(40)(006), 2.010(100)(116) et 1.939(40)(300). Nous l'avons caractérisé par spectroscopie dans l'infra-rouge. Trois analyses à la microsonde électronique et une analyse thermogravimétrique ont donné Na_2O 9.16 (9.11–9.24), CaO 48.84 (48.62–49.15), SrO 0.36 (0.33–0.40), F 16.17 (15.91–16.52), CO_2 25.81 et H_2O 5.61, O = F –6.81, total 99.14% (en poids). Nous avons calculé la proportion de CO_2 par stoéchiometrie selon les résultats de la détermination de la structure cristalline. La formule empirique, fondée sur une base de 10 anions, est $Na_{1.01}(Ca_{2.97}Sr_{0.01})_{\Sigma 2.98}(CO_3)_2[F_{2.90}(OH)_{0.07}]_{\Sigma 2.97}{\cdot}H_2O$ ou, de façon idéale, $NaCa_3(CO_3)_2F_3{\cdot}H_2O$. La densité calculée est égale à 2.86, et la densité mesurée, 2.86(4). Nous en avons affiné la structure jusqu'à un résidu R de 4.6% avec un cristal maclé; elle montre des couches dans le plan (001). Une couche contient des groupes $(CO_3)^{2-}$ perpendiculaires à (001), les polyèdres $Na\varphi_8$, et les groupes H_2O. Une seconde couche est faite de polyèdres $Ca\varphi_9$ et d'anions F^-. La structure ressemble peu à celle de la rouvilléite, qui lui ressemble chimiquement, mais semble être une modification de celles de la bastnäsite et de la cebaïte. Le nom honore George M. Sheldrick, créateur des logiciels SHELX, dont l'utilisation est répandue pour l'affinement des structures cristallines.

(Traduit par la Rédaction)

Keywords: sheldrickite, nouvelle espèce minérale, carbonate, structure cristalline, macle, mont Saint-Hilaire, Québec.

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INTRODUCTION

Mont Saint-Hilaire is known throughout the world for its diversity in mineral species. At this locality, 41 carbonate minerals have been identified (Horváth & Gault 1990), as well as ten undescribed species (Chao *et al.* 1990). Of the carbonate minerals, 16 contain the rare-earth elements (*REE*) as essential constituents (Grice 1996), 30 contain essential Ca or Na (or both), and nine contain essential F; most of the fluorocarbonates contain the *REE*. To date, there are only two known Na–Ca–F carbonate minerals, rouvilleite (McDonald *et al.* 1991) and sheldrickite, both of which occur at Mont Saint-Hilaire.

The new mineral described here, sheldrickite, found originally in the Poudrette quarry, Mont Saint-Hilaire, Rouville County, Quebec, is named in honor of Professor George M. Sheldrick (1942–), Institute for Organic Chemistry, University of Göttingen, creator of the SHELX series of programs now used by many crystallographers. The newest version SHELXL–93 contains a routine for refining structures of twinned crystals. Resolution of this structure and subsequent description of this new mineral were dependent on this program. The new mineral and the name were unanimously approved by the Commission on New Minerals and Mineral Names, IMA. Cotype material is housed in the collection of the Canadian Museum of Nature, catalogue nos. CMNMI 81530, CMNMI 81537, CMNMI 81538 and CMNMI 81539.

OCCURRENCE

Mont Saint-Hilaire is an alkaline intrusive complex and one of the ten Monteregian Hills, a series of plutons aligned along the St. Lawrence Valley for almost 150 km eastward from Oka to Megantic. The cotype specimens were collected in 1991 by Canadian Museum of Nature staff and by a private collector, G. Haineault. At present, sheldrickite must be considered a very rare mineral, as there are only approximately 60 mg known to exist. The specimens were collected in the Poudrette quarry from a marble xenolith in nepheline syenite, close to a large unit of hornfels. Sheldrickite is intimately associated with shortite, $Na_2Ca_2(CO_3)_3$, the crystals being found in a cavity between shortite crystals and as flakes in thin seams between crystals of shortite. Other associated species include pectolite, microcline, polylithionite, arfvedsonite, aegirine, polylithionite, calcite, fluorite and minor molybdenite, leucosphenite, thenardite, thermonatrite, sphalerite, galena, schairerite and kogarkoite. This mineral assemblage is thought to be a late-stage hydrothermal infilling.

PHYSICAL AND OPTICAL PROPERTIES

Sheldrickite has two distinct habits: (1) it occurs as a $1 \times 1 \times 2$ mm aggregate of blocky twinned crystals, with individuals up to $0.1 \times 0.1 \times 0.1$ mm, and (2) more commonly as radiating thin white silky flakes to fibrous masses up to 2 mm wide. These two habits were established as the same species by X-ray diffraction, infrared spectroscopy, and electron-microprobe data. The mineral is colorless to white, with a white streak and vitreous luster. It is brittle with an uneven fracture, and has a good {001} parting. Sheldrickite is relatively soft (Mohs hardness 3) and does not fluoresce. The density, measured by displacement in toluene, is 2.86 ± 0.04 g/cm^3, which compares very well with the calculated density, 2.86 g/cm^3.

Sheldrickite is uniaxial positive, $\omega = 1.538(2)$ and $\varepsilon = 1.563(4)$ (for $\lambda = 589$ nm), and nonpleochroic. A Gladstone–Dale calculation gives a compatibility index of –0.044, which is regarded as superior (Mandarino 1981).

CHEMICAL COMPOSITION

Chemical analysis was done in wavelength-dispersion (WD) mode on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. Data reduction was done with a conventional ZAF routine in the Tracor Northern TASK series of programs. The operating voltage was 15 kV, and the beam current was 0.20 μA. Three points were analyzed on a single grain using a beam diameter of 50 μm. There was no apparent chemical zoning using the back-scatter electron detector. Data for all elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first. A 100-s energy-dispersion scan indicated no elements with Z greater than 8, other than those reported here. The presence of CO_2 and H_2O was confirmed by infrared spectroscopy, and the proportion of H_2O was established by thermogravimetric analysis. Standards used for the electron-microprobe analysis were: calcite ($CaK\alpha$), albite ($NaK\alpha$), celestine ($SrL\alpha$) and synthetic $Na_3La_2(CO_3)_4F$ ($FK\alpha$). Data for standards were collected for 50 s or 0.25% precision, whichever was attained first. The chemical composition (with ranges) is Na_2O 9.16 (9.11–9.24), CaO 48.84 (48.62–49.15), SrO 0.36 (0.33–0.40), F 16.17 (15.91–16.52), CO_2 25.81 and H_2O 5.61, O = F –6.81, total 99.14 wt.%; the proportion of CO_2 was calculated by stoichiometry from the results of a crystal-structure analysis (see below). The empirical formula based on 10 anions is $Na_{1.01}(Ca_{2.97}Sr_{0.01})_{\Sigma 2.98}(CO_3)_2[F_{2.90}(OH)_{0.07}]_{\Sigma 2.97}\cdot H_2O$ or, ideally, $NaCa_3(CO_3)_2F_3\cdot H_2O$.

The thermogravimetric analysis of sheldrickite was done using a Mettler – Toledo TA8000 system (software version 3.0), which uses a Mettler TG50 module linked to a Mettler M3 microbalance. We used dry nitrogen as the purge gas, with a flow rate of 200 mL/min. The 2.528 mg sample of flaky material was ground to a fine powder and heated from room temperature to 350°C at a rate of 5°C min^{-1}. The

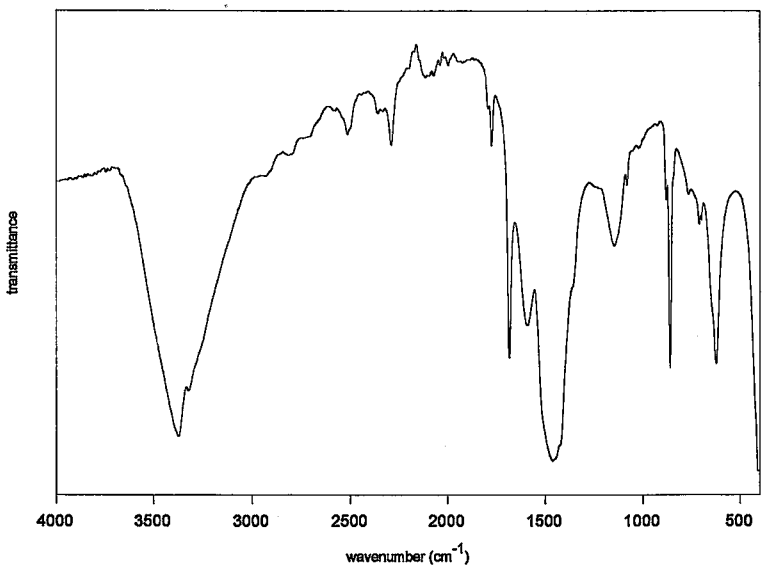

FIG. 1. Infrared spectrum of sheldrickite from a portion of a blocky crystal.

weight loss of 0.142 mg occurred in one continuous step between 160° and 265°C. This weight loss represents 5.61 wt.%, which agrees very well with that calculated from the results of the crystal-structure analysis (5.49 wt.%).

INFRARED SPECTRUM

The infrared spectrum of sheldrickite was obtained using a Bomen Michelson MB120 Fourier-transform infrared spectrometer with a diamond-anvil cell as a microsampling device. Two samples were analyzed; part of a blocky crystal (Fig. 1) and part of the flaky material. The two spectra varied only in the details of the fine structure in the bands for the asymmetric and symmetric stretching of the $[CO_3]$ group. The spectrum has sharp peaks, with a splitting of the $[CO_3]$ bands, indicative of a structure with more than one crystallographically distinct $[CO_3]$ group (this was shown to be the case in the crystal-structure determination). The infrared spectrum can be compared to that of rouvilleite, which has a very similar composition, $Na_3Ca_2(CO_3)_3F$ (McDonald *et al.* 1991). The notable difference in the two spectra is the absence of the O–H and H_2O bands. The absorption bands (cm^{-1}) in sheldrickite are assigned as follows: 3376: O–H stretching; 1687: H_2O bending; 1464: asymmetric stretching mode of $[CO_3]$; 1083: symmetric stretching of $[CO_3]$; 885 and 863: out-of-plane bending of $[CO_3]$; 715 and 704: in-plane bending of $[CO_3]$. The 628 cm^{-1} band could not be unequivocally assigned.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

Precession photographs show sheldrickite to be hexagonal, diffraction symmetry *6/mmm*, with possible space-group choices $P6_222$ and $P6_422$. With the solution of the crystal structure, it became apparent the true symmetry of sheldrickite is trigonal, space group $P3_2$, and the pseudohexagonal symmetry is due to merohedral twinning. X-ray powder-diffraction data, obtained with a Gandolfi camera having a diameter of 114.6 mm and using Cu$K\alpha$ radiation, are given in Table 1.

TABLE 1. SHELDRICKITE: X-RAY POWDER DIFFRACTION DATA

I/I_o	d_{obs}	d_{calc}(Å)	*hkl*	I/I_o	d_{obs}(Å)	d_{calc}(Å)	*hkl*
30	5.809	5.818	100	<10	1.725	1.723	304
30	5.010	5.016	003	<10	1.674	1.672	009
30	3.358	3.359	110	10	1.652	1.653	216
<10	2.857	2.856	201	<10	1.613	1.613	310
50	2.791	2.791	113	<10	1.594	1.592	223
<10	2.713	2.713	202	10	1.535	1.534	306
40	2.508	2.508	006			1.536	313
<10	2.302	2.301	204	<10	1.496	1.496	119
		2.303	106	10	1.396	1.395	226
20	2.199	2.199	210	<10	1.356	1.357	316
100	2.010	2.009	116	<10	1.332	1.331	219
		2.014	213	<10	1.267	1.266	309
40	1.939	1.939	300	<10	1.252	1.252	228
		1.899	206	<10	1.231	1.230	413
<10	1.898	1.878	302	>10	1.184	1.185	229
10	1.809	1.809	303				

114.6 mm Gandolfi camera, Cu$K\alpha$ radiation, visually estimated intensities, indexing based on the cell $a = 6.718(3)$, $c = 15.050(4)$ Å.

TABLE 2. SHELDRICKITE: DATA-COLLECTION INFORMATION

Space Group	$P3_2$ (# 145)	Measured reflections	3895
a (Å)	6.726(2)	Merged reflections	1205
c (Å)	15.044(4)	Observed reflections [> 5σ(F)]	867
V (Å^3)	589.7(3)	Minimum transmission	0.344
Radiation	Mo$K\alpha$	Maximum transmission	0.606
Monochromator	Graphite	Refined parameters	140
μ (mm^{-1})	2.24	R (%)	4.6
	Unit-cell contents	$3[NaCa_3(CO_3)_2F_3 \bullet H_2O]$	

For the intensity-data measurements, a crystal fragment of cotype sheldrickite was used. Information relevant to the data collection and structure determination are given in Table 2. Reduction of the intensity data, structure determination and initial refinement of the structure were done with SHELXTL (Sheldrick 1990) package of computer programs.

Phasing of a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 1.124, indicative of a centrosymmetric space-group, which is in contrast to the space groups derived from precession photography. Attempts to solve the structure in the space groups $P6_222$ and $P6_422$ resulted in residual factors between $R = 41\%$ and $R = 29\%$. The combined figure of merit (CFOM) for several space groups in both the trigonal and hexagonal systems indicated a preference for space group $P3_221$. The phase-normalized structure-factors were used to give an E-map that located the two *Ca* sites, a *Na* site, and seven lighter-element sites. This model refined to $R = 16\%$, but could not be improved. In particular, the (CO_3) groups could not be located, and some O sites had unusual coordinations. The space-group symmetry was reduced to $P3_2$. This did not reduce the R factor, but it improved the model, such that one (CO_3) group was located. The next stage in the structure determination involved incorporating a twin law for the intensity data, using the program SHELXL–93 (G.M. Sheldrick, unpubl. data). Application of a twin by reflection on (001) immediately improved the model; it led to the location of the other (CO_3) group and reduction of the R index to 7.9%. In the final least-squares refinement, all atomic positions were refined with anisotropic-displacement factors to a final residual $R = 4.6\%$. Bond-valence calculations (Brese & O'Keeffe 1991) helped establish the F and H_2O sites. The addition of an isotropic-extinction factor did not improve the results. Inverting the polarity of the structure resulted in $R = 12\%$, indicating the correct orientation. The structure was checked for higher symmetry with the program MISSYM (Le Page 1987), which indicated a possible 2-fold axis of symmetry as in space group $P3_221$. This pseudosymmetry can be seen in Figure 2, but attempts to refine the structure in this space group gave an R index of 18%.

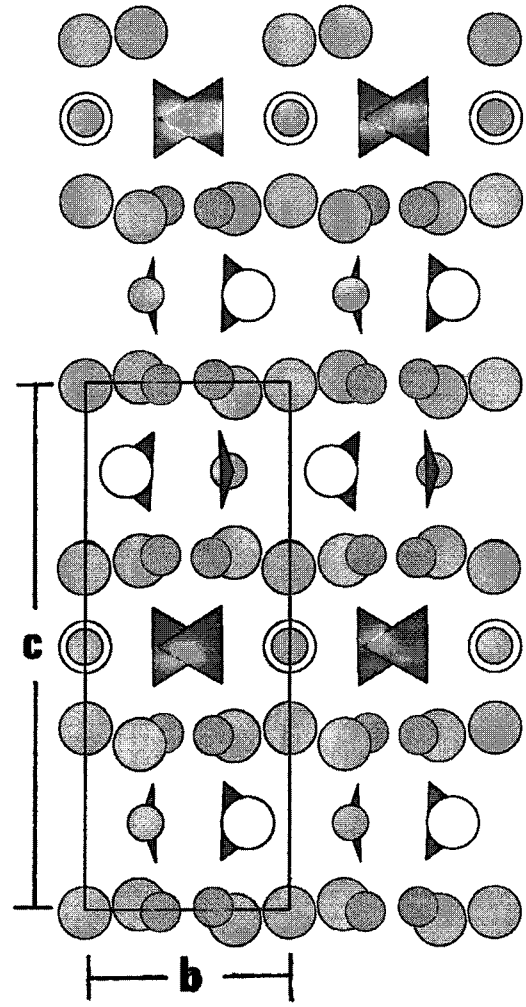

FIG. 2. The structure of sheldrickite projected along [100]. Dark triangles represent (CO_3) polyhedra, large unshaded circles, H_2O groups, large light-shaded circles, F atoms, small light-shaded circles, Na atoms, and small dark-shaded circles, Ca atoms.

Table 3 contains the final positional and equivalent isotropic-displacement parameters and bond-valence sums, and Table 4 contains selected interatomic distances and angles. Anisotropic displacement factors and observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0S2.

TABLE 3. SHELDRICKITE: ATOMIC COORDINATES, ISOTROPIC DISPLACEMENT FACTORS ($Å^2$ X 10^3) AND BOND VALENCE SUMS (vu)

Atom	*x*	*y*	*z*	U_{eq}	BVS*
Na	0.001(1)	0.297(1)	0.165(1)	23(1)	1.10
Ca1	0.6161(4)	-0.0009(7)	0	11(1)	2.06
Ca2	-0.0011(5)	0.6284(4)	0.0045(4)	8(1)	2.02
Ca3	0.3706(5)	0.3710(5)	-0.0043(4)	161)	2.07
C1	-0.433(2)	0.317(2)	0.168(1)	12(2)	4.00
C2	-0.568(2)	0.752(2)	0.169(1)	13(2)	4.00
O1	0.664(2)	0.348(2)	0.090(1)	16(4)	2.03
O2	0.668(2)	0.333(1)	0.238(2)	13(3)	2.26
O3	0.353(2)	0.273(2)	0.167(1)	17(2)	1.69
O4	0.321(2)	0.654(2)	-0.092(2)	15(2)	2.22
O5	0.336(2)	0.666(1)	-0.239(2)	15(3)	2.06
O6	-0.354(2)	0.921(2)	0.165(1)	25(2)	1.74
OW	0.203(2)	0.202(2)	-0.169(1)	22(2)	0.28
F1	0.997(1)	0.266(2)	0.010(1)	23(2)	1.00
F2	0.271(1)	0.002(2)	-0.005(1)	18(2)	0.95
F3	0.730(2)	0.734(2)	-0.020(1)	15(2)	1.02

* constants from Brese and O'Keeffe (1991)

TABLE 4. SHELDRICKITE: INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Na polyhedron		Ca1 polyhedron		Ca2 polyhedron		Ca3 polyhedron	
Na-F3	2.23(1)	Ca1-F1	2.28(1)	Ca2-F2	2.25(1)	Ca3-F2	2.23(1)
Na-F1	2.35(1)	Ca1-F3	2.28(1)	Ca2-F3	2.28(1)	Ca3-F1	2.26(1)
Na-O6	2.46(2)	Ca1-F2	2.33(1)	Ca2-F1	2.43(1)	Ca3-F3	2.44(1)
Na-O3	2.46(2)	Ca1-O5	2.54(2)	Ca2-O1	2.46(1)	Ca3-O4	2.47(2)
Na-O5	2.58(2)	Ca1-O2	2.55(2)	Ca2-O5	2.52(2)	Ca3-O1	2.50(2)
Na-O2	2.61(1)	Ca1-O6	2.56(2)	Ca2-O4	2.54(2)	Ca3-O2	2.52(2)
Na-O4	2.68(2)	Ca1-O4	2.57(2)	Ca2-O2	2.59(2)	Ca3-O5	2.59(2)
Na-O1	2.70(2)	Ca1-O3	2.59(1)	Ca2-OW	2.66(2)	Ca3-O3	2.65(2)
⟨Na-Φ⟩	2.509	Ca1-O1	2.59(2)	Ca2-O6	2.67(2)	Ca3-OW	2.72(2)
		⟨Ca1-Φ⟩	2.476	⟨Ca2-Φ⟩	2.489	⟨Ca3-Φ⟩	2.487
		C1 triangle				C2 triangle	
C1-O2	1.23(2)	O1-O2	123(1)	C2-O4	1.25(3)	O4-O5	122(1)
C1-O1	1.31(2)	O1-O3	115(1)	C2-O5	1.29(3)	O4-O6	121(1)
C1-O3	1.32(2)	O2-O3	121(1)	C2-O6	1.32(2)	O5-O6	117(1)
⟨C1-O⟩	1.287	⟨O-O⟩	120	⟨C2-O⟩	1.287	⟨O-O⟩	120

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of sheldrickite has four large-cation sites, but only two distinct types of polyhedra. The Na polyhedron, with 8-fold coordination, fits a compressed octahedron modified by the removal of one edge (Fig. 3a). The compressed axis corresponds to the Na–F bonds, whereas the removed edge results in the four longer bonds within the polyhedron (Table 4). Each of the three *Ca* sites has a similar stereochemistry and a similar polyhedron, with nine-fold coordination. The polyhedron fits within an irregular trigonal prism (Fig. 3b), with the three F atoms defining the equatorial plane and the other six ligands, the upper and lower face of the prism.

The crystal structure of sheldrickite is layered on (001) (Fig. 2). The layering of the *REE* carbonates was described in detail by Grice *et al.* (1994). In sheldrickite, there are two layers of different composition: (1) $Na(CO_3)_2 \cdot H_2O$, and (2) CaF. In Figure 2, the pseudo-*m* planes are positioned through the

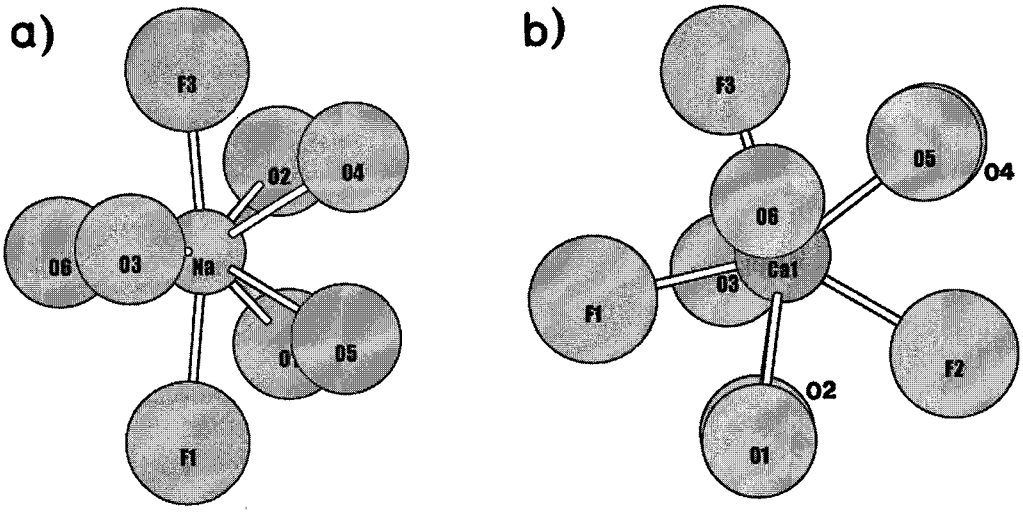

FIG. 3. The large-cation polyhedra in sheldrickite: a) (Na–φ_8) and b) (Ca1–φ_9).

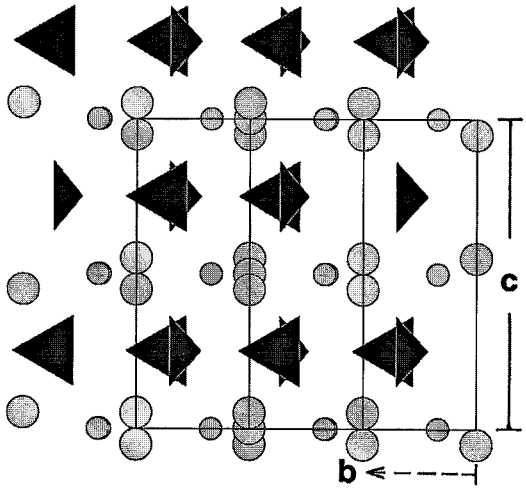

FIG. 4. The structure of bastnäsite-(Ce) projected along [100]. Dark triangles represent (CO_3) polyhedra, large light-shaded circles, F atoms, and smaller dark-shaded circles, Ce atoms.

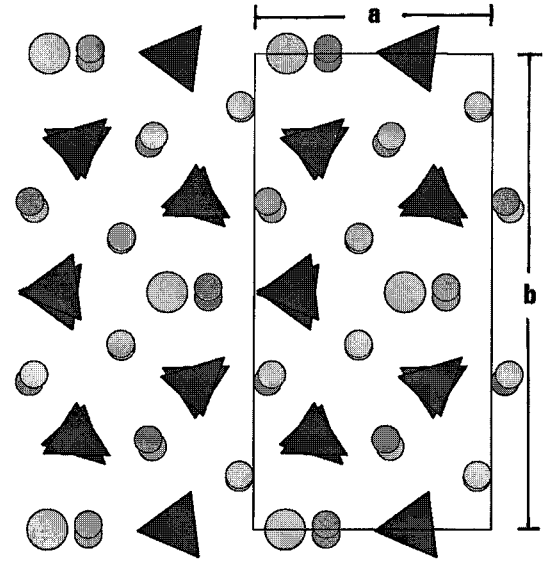

FIG. 6. The structure of rouvilleite projected along [001]. Dark triangles represent (CO_3) polyhedra, large light-shaded circles, F atoms, small light-shaded circles, Na atoms, and small dark-shaded circles, Ca atoms.

$Na(CO_3)_2 \cdot H_2O$ layers, and the pseudo-2-fold axis along [100] is at 0,0,0. The carbonate layer is of the "mixed-layer" type (Grice *et al.* 1994), wherein the "standing-on-end" (CO_3) groups (Grice *et al.* 1994) are not in a separate layer but occur with the cations and H_2O groups.

In general, the *REE*-fluorocarbonate minerals are layered, have "standing-on-end" (CO_3) groups, and are of two distinct types. The members of the bastnäsite – parisite – röntgenite – synchysite group are syntactic intergrowths of various stacking combinations of *REE*, F, alkaline earths and (CO_3) groups. The bastnäsite-(Ce) structure (Fig. 4) (Ni *et al.* 1993) is an example of this group, with two types of layer, a CeF layer and a "standing-on-end" (CO_3) layer. Similar syntactic intergrowths occur in the Ba fluorocarbonates cebaite-(Ce), huanghoite-(Ce) and kukharenkoite-(Ce). Figure 5 shows the structure of cebaite-(Ce) (Yang 1995), with mixed layers of "standing-on-end" (CO_3) sharing the slab with the larger Ba, Ce and F atoms. The sheldrickite structure is a combination of these two extremes, the bastnäsite-(Ce) structure with segregated large-cation layers and (CO_3) layers, and the cebaite-(Ce) structure with integrated large-cation and (CO_3) groups in the same layer. Thus, sheldrickite has a segregated large-cation layer and an integrated large cation – (H_2O) – (CO_3) layer. Interestingly, the structure of rouvilleite (Yamnova *et al.* 1991), which is similar in composition to sheldrickite, does not have the distinct layering that other fluorocarbonates exhibit; it has layering on (210), with alternating layers of Na–Ca–(CO_3) groups and a Ca–Na–F layer (Fig. 6) comparable in type and composition to sheldrickite, but not as well layered.

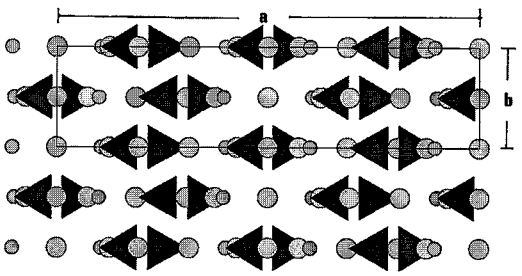

FIG. 5. The structure of cebaite-(Ce) projected along [001]. Dark triangles represent (CO_3) polyhedra, large dark-shaded circles, Ba atoms, large light-shaded circles, F atoms and smaller dark-shaded circles, Ce atoms.

PARAGENESIS OF SHELDRICKITE

Sheldrickite occurs in a marble xenolith in the nepheline syenite intrusive unit. Although no work has been done to assess the origins of this or other marble xenoliths in the quarry, it seems likely that they were blocks of Paleozoic limestone caught up in the rising silica-undersaturated syenitic magma. The limestone

was a rich source of Na, $CaCO_3$ and F, the F being evident in such minerals as carletonite, fluorapatite, fluorapophyllite, fluorite, leucophanite, polylithionite, taeniolite and zeophyllite (Horváth & Gault 1990). All of these minerals result from hydrothermal reworking of the Ordovician limestone into which the nepheline syenite of Mont Saint-Hilaire was emplaced.

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