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Reederite-(Y), a new sodium rare-earth carbonate mineral with a unique fluorosulfate anion

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Abstract

Reederite-(Y), ideally, $(Na,Mn,Fe)_{15}(Y,REE)_2(CO_3)_9(SO_3F)Cl$, is a new mineral from Mont-Saint-Hilaire, Quebec. It occurs as blocky, yellow to orange-brown grains up to 2 mm. Associated minerals include trona, shortite, petersenite-(Ce), catapleiite, minor analcime, and manganotychite. The mineral has a vitreous luster and white streak. It is soft (Mohs hardness 3–3.5) and brittle, with a conchoidal fracture and perfect {001} cleavage. Reederite-(Y) is uniaxial negative, $\omega = 1.548(1)$ and $\epsilon = 1.537(1)$. It is hexagonal, space group $P\bar{6}$, $a = 8.773(1)$, $c = 10.746(2)$ Å, and $Z = 1$. The strongest X-ray powder diffraction lines are [d (Å), I, (hkl)] 2.532, 100, (212); 4.39, 80 (102); 2.774, 80, (113); 2.240, 80, (213); 6.20, 40, (101); 1.657, 40 (116,314,322,410); and 2.067, 30, (105,303). The infrared spectrum is given. An electron microprobe analysis gave Na_2O 34.04, CaO 0.70, MnO 1.23, Al_2O_3 1.31, Y_2O_3 10.24, La_2O_3 1.39, Ce_2O_3 3.54, Nd_2O_3 1.99, Er_2O_3 1.19, Dy_2O_3 1.39 (plus minor amounts of Fe, Pr, Sm, Gd, and Yb oxides), SO_3 5.07, CO_2 (calc) 31.91, F 1.86, and Cl 2.05, $-O \equiv F + Cl$ 1.24, total 99.14 wt%. $D_{meas} = 2.91$ g/cm³, $D_{calc} = 2.85$ g/cm³. The structure has been refined to $R = 3.2\%$. The carbonate layers are thick slabs accommodating $(CO_3)^{2-}$ groups oriented perpendicular to the {001} layering, the large cation polyhedra, and the Cl^- and $(SO_3F)^-$ anions. The Na atoms adopt a variety of distinct coordinations. This is the first reported natural occurrence of a fluorosulfate anion.

Introduction

Mont-Saint-Hilaire is well known for its diversity of mineral species. This diversity is due to the complex chemistry of this geological formation, and the new mineral species described in this study is yet another example of this complexity. At this locality 39 carbonate minerals have been identified (Horváth and Gault, 1990), as well as approximately ten unknown minerals (Chao et al., 1990). Of the identified carbonates, 16 contain rare-earth elements as essential elements: ancylite-(Ce), bastnäsite-(Ce), calcio-ancylite-(Ce), calcioburbankite (Van Velthuizen et al., 1995), cordylite-(Ce), daqingshanite-(Ce), donnayite-(Y), kainosite-(Y), mckelveyite-(Y), parisite-(Ce), petersenite-(Ce) (Grice et al., 1994), reederite-(Y) (this study), remondite-(Ce), shomiokite-(Y), synchysite-(Ce), and tundrite-(Ce).

The new mineral described here, reederite-(Y), found originally in the Poudrette quarry, Mont-Saint-Hilaire, Rouville County, Quebec, is named in honor of Richard J. Reeder, who is currently coeditor of the *American Mineralogist,* for his significant contributions on carbonate mineralogy. The new mineral and the name were unanimously approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association. Cotype material is housed in the collection of the Canadian Museum of Nature under catalogue no. 81520.

Occurrence

Mont-Saint-Hilaire is an alkaline intrusive complex and one of the ten Monteregian Hills, which are aligned along the Saint Lawrence Valley for almost 150 km eastward from Oka to Megantic.

The cotype specimens were collected in 1992 by G. Haineault, a private collector. At present, reederite-(Y) is considered a very rare mineral because only approximately 40 mg is known to exist. The specimen was collected in the Poudrette quarry from a sodalite xenolith in syenite. Reederite-(Y) occurs as an inclusion in a vug filled by trona and is associated with shortite, petersenite-(Ce), catapleiite, minor analcime, and manganotychite. This mineral assemblage is thought to be a late-stage hydrothermal infilling.

Physical and optical properties

Reederite-(Y) occurs as irregular tabular to blocky grains up to 2 mm. The mineral is transparent yellow to orange-brown with a white streak and vitreous luster. It is brittle, with a conchoidal fracture and perfect {001} cleavage. The mineral is relatively soft (Mohs hardness 3–3.5) and does not fluoresce. The density, measured by suspension in bromoform, is 2.91 ± 0.03 g/cm³, which is high compared with the calculated density of 2.85 g/cm³. This discrepancy can be attributed to minor volatilization of Na

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TABLE 1. Chemical composition of reederite-(Y)

Oxide	wt%	Atomic proportions*	Theoretical wt%**
Na_2O	34.04	Na 13.63	38.588
CaO	0.70	Ca 0.16	
MnO	1.23	Mn 0.22	
FeO	0.42	Fe 0.07	
Al_2O_3	1.31	Al 0.32	
Y_2O_3	10.24	Y 1.13	18.74
La_2O_3	1.39	La 0.11	
Ce_2O_3	3.54	Ce 0.27	
Pr_2O_3	0.36	Pr 0.03	
Nd_2O_3	1.99	Nd 0.15	
Sm_2O_3	0.52	Sm 0.04	
Gd_2O_3	0.80	Gd 0.06	
Er_2O_3	1.19	Er 0.08	
Dy_2O_3	1.39	Dy 0.09	
Yb_2O_3	0.37	Yb 0.02	
SO_3	5.07	S 0.79	6.64
CO_2†	31.91	C 9.00	32.86
F	1.86	F 1.22	1.58
Cl	2.05	Cl 0.72	2.94
Sum	100.38	O 30.51	101.33
O ≡ F + Cl	−1.24		−1.33
Total	99.14		100

* Based on 32 anions.
** For ideal formula $Na_{15}Y_2(CO_3)_9(SO_3F)Cl$.
† Calculated from stoichiometry and crystal-structure analysis.

under the electron beam and to the combined effects of undetected REEs.

Reederite-(Y) is uniaxial negative, $\omega = 1.548(1)$ and $\epsilon = 1.537(1)$ (for $\lambda = 589$ nm). Some grains were observed to be biaxial negative with $2V$ up to 15°. It is nonpleochroic. A Gladstone-Dale calculation gives a compatibility index of 0.014, which is regarded as superior (Mandarino, 1981).

CHEMICAL COMPOSITION

Chemical analyses were performed on a JEOL 733 Superprobe using the wavelength-dispersive mode. A conventional ZAF correction routine was used for data reduction. The operating voltage was 15 kV, the beam current was 0.020 μA, and the beam was defocused to 40 μm to minimize decomposition and Na migration, which were severe effects in reederite-(Y). To reduce these effects further, ten spots were used for the reported analysis (Table 1) after first checking the sample for chemical homogeneity using the BSE detector. REE analyses were corrected for peak overlaps. Standards used were albite (Na$K\alpha$), YIG (yttrium iron garnet) (Y$L\alpha$), synthetic (REE)PO_4 set (La$L\alpha$, Ce$L\alpha$, Pr$L\beta$, Nd$L\alpha$, Sm$L\alpha$, Gd$L\alpha$, Er$L\alpha$, Dy$L\beta$, Yb$L\alpha$), calcite (Ca$K\alpha$), almandine (Fe$K\alpha$, Al$K\alpha$), rhodochrosite (Mn$K\alpha$), celestine (S$K\alpha$), scapolite (Cl$K\alpha$), and synthetic La(CO_3)F (F$K\alpha$). The presence of $(CO_3)^{2-}$ was established by crystal-structure analysis and infrared spectroscopy. The empirical formula based on 32 anions is: $(Na_{13.63}Al_{0.32}Mn_{0.22}Ca_{0.16}Fe_{0.07})_{14.40}(Y_{1.13}Ce_{0.27}Nd_{0.15}La_{0.11}Dy_{0.09}Er_{0.08}Gd_{0.06}Sm_{0.04}Pr_{0.03}Yb_{0.02})_{1.90}(CO_3)_9(SO_3F)_{0.79}(Cl_{0.72}F_{0.43})_{1.15}O_{1.14}$.

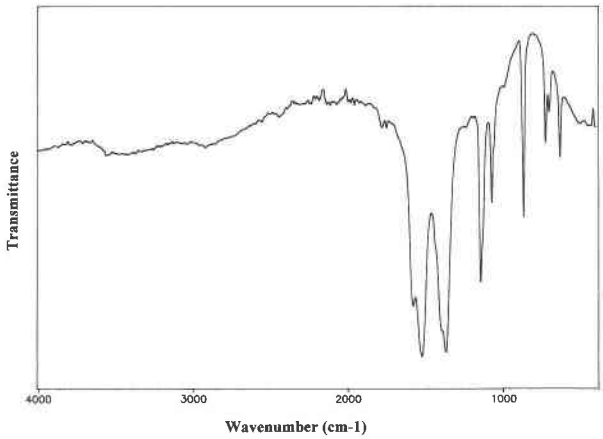

Fig. 1. Infrared spectrum of reederite-(Y).

INFRARED ANALYSIS

The infrared spectrum (Fig. 1) of reederite-(Y), which is relatively complex, was obtained using a Bomen Michelson MB-120 Fourier transform infrared spectrometer with a diamond-anvil cell microsampling device. The absence of a peak in the 3560 cm^{-1} region, the O-H stretching frequency, is significant because it indicates a lack of either OH^- anions or H_2O molecules. Peaks in the 1380–1580 cm^{-1} region are assigned to ν_3 asymmetric stretching mode of $(CO_3)^{2-}$; 1070–1140 cm^{-1} are ν_1 symmetric stretching of $(CO_3)^{2-}$; 870 cm^{-1} is ν_2 out-of-plane bending of $(CO_3)^{2-}$; and 700–725 cm^{-1} could be ν_4 in-plane bending of $(CO_3)^{2-}$. Vast and Deporcq-Stratmains (1977) gave IR data for $Na(SO_3F)$. They attributed 1095 cm^{-1} to ν_1 symmetric S-O stretching, 785 cm^{-1} to ν_2 symmetric S-F stretching, and 565 cm^{-1} to ν_3 O-S-O bending. These frequencies also probably contribute to the peaks 1072, 724 or 700, and 633 cm^{-1} in Figure 1.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE DETERMINATION

Precession camera photographs show reederite-(Y) to be hexagonal with possible space group choices $P6/m$, $P\bar{6}$, and $P6$. X-ray powder diffraction data, obtained using a 114.6 mm Debye-Scherrer camera and Cu$K\alpha$ (Ni-filtered) radiation, are given in Table 2.

For the intensity-data measurements, a crystal fragment of cotype reederite-(Y) was used. A Siemens, fully automated, four-circle diffractometer operated at 50 kV and 30 mA was used for the data collection. Information relevant to the data collection and structure determination are given in Table 3. Reduction of the intensity data, structure determination, and structure refinement were accomplished by means of the SHELXTL (Sheldrick, 1990) package of computer programs.

The phasing of a set of normalized structure factors gives a mean value $|E^2 - 1|$ of 0.692, indicative of a noncentrosymmetric space group. The combined figure of merit (CFOM) for several space groups in both the trigonal

TABLE 2. X-ray powder diffraction data for reederite-(Y)

hkl	d_{calc}* (Å)	d_{meas} (Å)	*I*	*hkl*	d_{calc}* (Å)	d_{meas} (Å)	*I*
001	10.745	10.76	10	205	1.8705	1.870	15
100	7.597	7.59	10	223	1.8704		
101	6.203	6.20	40	313	1.8162	1.815	15
002	5.372	5.37	15	006	1.7909	1.790	<5
102	4.386	4.39	80	402	1.7907		
110	4.386			106	1.7431	1.742	10
200	3.7988	3.801	20	320	1.7430		
201	3.5815	3.580	15	215	1.7206	1.721	5
112	3.3978	3.401	10	224	1.6989	1.698	5
103	3.2398	3.244	15	403	1.6780	1.678	5
202	3.1018	3.103	15	116	1.6580		
210	2.8716	2.872	20	314	1.6579	1.657	40
113	2.7743	2.774	80	322	1.6579		
211	2.7742			410	1.6579		
004	2.6863	2.686	5	305	1.6385	1.639	5
203	2.6060	2.606	20	206	1.6199	1.620	5
104	2.5327			412	1.5842	1.584	<5
212	2.5325	2.532	100	323	1.5672	1.567	<5
300	2.5325			007	1.5350	1.535	<5
301	2.4650	2.452	10	225	1.5350		
302	2.2908	2.289	5	216	1.5196	1.520	5
213	2.2404	2.240	80	315	1.5046		
204	2.1933	2.194	<5	413	1.5045	1.505	15
220	2.1932			501	1.5045		
310	2.1072	2.108	5	306	1.4622		
105	2.0679	2.067	30	324	1.4622	1.462	10
303	2.0678			330	1.4621		
222	2.0305	2.028	<5	420	1.4358	1.436	<5
312	1.9617	1.962	15	405	1.4232	1.423	5
115	1.9299	1.930	10				

* Calculated on the basis of refined unit-cell parameters: a = 8.773(1), c = 10.746(2) Å.

and hexagonal crystal systems indicated a preference for space group $P3$. The phased-normalized structure factors were used to give an E-map that correctly located the two REE sites and 17 lighter element sites. The first least-squares refinement gave R = 21%. From this initial model it took several sets of refinements to locate the 26 atoms in the final model and to assign to them the correct scattering curves. In $P3$, with isotropic temperature factors, the structure refined to R = 5.5%, and with anisotropic temperature factors to R = 3.2 and R_w = 3.1%. The structure was checked for higher symmetry with the computer program MISSYM (LePage, 1987), which indicated a possible $\bar{6}$ symmetry axis. $P\bar{6}$, in fact, is the true symmetry of reederite-(Y) for the X-ray intensity data, but, as will be discussed later, $P3$ symmetry has some desirable features in the detailed crystal chemistry.

TABLE 4. Positional coordinates (× 10^4), U_{eq} (× 10^3), and bond valences* for reederite-(Y)

Atom	*x*	*y*	*z*	U_{eq} (Å²)	B.V. (vu)
Y	0	0	1781(1)	10(1)	3.26
Na1	6667	3333	1983(3)	18(1)	1.29
Na2	3525(3)	9032(3)	2615(2)	22(1)	1.04
Na3	6137(6)	9633(7)	0	46(3)	1.06
Na4	4434(4)	1209(4)	5000	22(1)	1.14
Na5	0	0	5000	24(1)	1.06
Cl	3333	6667	0	270(15)	1.04
C1	7140(10)	6463(10)	0	13(1)	4.06
C2	3203(7)	2521(6)	6997(4)	13(1)	3.97
O1	9089(6)	3455(6)	8977(3)	32(2)	2.06
O2	8327(7)	8105(7)	0	22(2)	2.02
O3	8885(5)	5304(5)	6543(3)	19(2)	2.02
O4	8645(4)	7725(5)	6596(3)	16(1)	2.13
O5	460(5)	7481(5)	7901(3)	18(1)	2.03
O6	1934(11)	4930(10)	5000	97(6)	2.13
S	3333	6667	5000	18(1)	6.36
F**	3333	6667	3533(10)	15(4)	1.00

* Calculated using parameters of Brese and O'Keeffe (1991).
** Occupancy in this site is 0.5.

Table 4 contains the final positional and equivalent isotropic displacement parameters; Table 5, anisotropic displacement coefficients; Table 6, observed and calculated structure factors; and Table 7, the selected interatomic distances and angles.[1]

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of reederite-(Y) is layered on {001} (Fig. 2). The layering of REE carbonates is described in detail by Grice et al. (1994). In reederite-(Y) there are three layers of differing composition: (1) $Na_3(CO_3)_3Cl$; (2) $Na_4Y(CO_3)_3$; and (3) $Na_4(SO_3F)$. Figure 2 shows that the m planes pass through layers 1 and 3, thus layer 2 is the only one doubled in the c-period. Each slab is of approximately equal thickness (i.e., 10.74 ÷ 4 = 2.68 Å), and each is of the mixed-layer type (Grice et al., 1994), wherein the CO_3 groups are not in a separate layer but are mixed with other cation and anion polyhedra. Slabs thick enough to accommodate these other polyhedra are rendered by

[1] A copy of Tables 5 and 6 may be ordered as Document AM-95-596 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 3. Structure-analysis data for reederite-(Y)

Ideal formula	$Na_{15}Y_2(CO_3)_9(SO_3F)Cl$	a = 8.763(1) Å
Space group	$P\bar{6}$	c = 10.736(2) Å
Crystal size	0.52 × 0.27 × 0.20 mm	V = 714.1(2) Å³
		Z = 1
Rad./Mon.	Mo/graphite	Total *I*s 3399
μ	6.21 mm⁻¹	F unique 1214
ψ merge, before/after	0.11/0.03	$F_o > 4\sigma$ 1200
Min. trans.	0.46	R (equivalent *I*s) 1.9%
Max. trans.	0.97	Final R = 3.2%, R_w = 3.1%
$R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/\Sigma wF_o^2]^{1/2}$		
$w = (\sigma_{F_o}^2)^{-1}$		

TABLE 7. Selected interatomic distances (Å) and angles (°) in reederite-(Y)

Y-O2	2.476(3) × 3	O2-O2a	66.7(1) × 3	O4-O4a	75.4(1) × 3
Y-O4	2.460(3) × 3	O2-O4	96.9(1) × 3	O4-O5	53.4(1) × 3
Y-O5	2.458(3) × 3	O2-O5	79.2(2) × 3	O4a-O5	74.1(1) × 3
⟨M-O⟩	2.465	O2-O5a	76.9(2) × 3	O5-O5a	118.1(1) × 3
Na1-O1	2.313(6) × 3	O1-O1a	101.7(1) × 3	O1-O3	82.4(1) × 3
Na1-O3	2.431(4) × 3	O1-O3a	92.3(1) × 3	O3-O3a	82.2(1) × 3
⟨M-O⟩	2.372				
Na2-F	2.224(6)	F-O3	95.7(2)	O1-O3	84.0(2)
Na2-O1	2.228(4)	F-O4	127.1(3)	O1-O4	82.3(1)
Na2-O3	2.440(5)	F-O5	91.9(1)	O1-O5	96.0(2)
Na2-O4	2.543(6)	F-O6	50.1(3)	O4-O5	73.8(2)
Na2-O5	2.391(4)	O3-O4	90.8(1)	O4-O6	79.8(1)
Na2-O6	2.663(3)	O3-O6	80.4(2)	O5-O6	94.3(2)
⟨M-O⟩	2.453				
Na3-Cl	2.532(4)	Cl-O1	87.7(2) × 2	O1-O5	83.6(1) × 2
Na3-O1	2.571(7) × 2	Cl-O5	97.4(2) × 2	O2-O5	74.6(1) × 2
Na3-O2	2.770(7)	O1-O1a	50.6(2)	O5-O5a	140.1(3) × 2
Na3-O5	2.398(4) × 2	O1-O2	118.1(2) × 2		
⟨M-O⟩	2.540				
Na4-O3	2.577(5) × 2	O3-O3a	79.2(2) × 2	O3a-O6	86.3(2)
Na4-O3a	2.433(4) × 2	O3-O3b	80.0(2)	O4-O4a	87.9(20
Na4-O4	2.470(5) × 2	O3a-O3b	85.8(2)	O4-O6	86.3(2)
Na4-O6	2.388(9)	O3-O4	52.5(1) × 2	O4a-O6	86.9(1) × 2
⟨M-O⟩	2.478	O3-O4a	106.5(2) × 2		
Na5-O4	2.440(3) × 6	O4-O4a	76.1(1) × 6	O4a-O4b	89.2(2) × 3
		O4-O4b	138.3(1) × 6		
C1-O1	1.276(5) × 2	O1-O1a	118.9(6)		
C1-O2	1.287(8)	O1-O2	120.6(3) × 2		
C2-O3	1.263(6)	O3-O4	121.8(5)		
C2-O4	1.294(6)	O3-O5	121.8(4)		
C2-O5	1.305(7)	O4-O5	116.4(4)		
S-F	1.575(11)	F-O6	90 × 3		
S-O6	1.398(6) × 3	O6-O6a	120 × 3		

having CO_3 groups oriented perpendicular to the layering plane rather than lying flat.

REE and Na polyhedra

The coordination polyhedra of reederite-(Y) are unusual and interesting. The REE site, with ninefold coordination, is a truncated trigonal dipyramid, and each of the five Na sites has a unique stereochemistry. Na1-O_6 is a regular trigonal antiprism. In the structure refinement this site has a scattering power greater than Na (i.e., 12.1 e^-), with a bond valence of 1.29 vu and a short ⟨M-O⟩ bond length of 2.37 Å. This suggests that the Na1 site is partially occupied by the transition metals present in the chemical analysis (Table 1). Na2-(O_5F) is a distorted trigonal antiprism. The distortion is a result of the short bond lengths Na2-F and Na2-01 of 2.22 and 2.23 Å, respectively. Na3-(O_5Cl) is a distorted polyhedron resembling a bifurcated tetragonal pyramid. The base of the pyramid is lozenge shaped because the Na3-Cl and Na3-O2 bond lengths are considerably longer than the two Na3-O5 bonds. Na4-O_7 is the only Na atom that is not sixfold coordinated. It has the general form of a tetragonal bipyramid with one pyramid bifurcated. Na5-O_6 is a regular trigonal prism. This ability of Na atoms to adopt variable stereochemistries is another factor that gives rise to the large chemical diversity within REE carbonate mineral species (Grice et al., 1994).

The $(SO_3F)^-$ polyhedron

The fluorosulfate anion, $(SO_3F)^-$, is of particular interest because this is the first reported occurrence of it in nature. This anion is a stable constituent of synthetic salts, and fluorosulfuric acid, HSO_3F, is one of the strongest of pure liquid acids. As an acid it is useful as a solvent for high-oxidation-state species and as a convenient laboratory fluorinating agent (Cotton and Wilkinson, 1980; Purcell and Kotz, 1977). An ideal $(SO_4)^{2-}$ anion would have molecular symmetry T_d, whereas ideally the isolated $(SO_3F)^-$ anion would belong to the C_{3v} symmetry group. Depending on how each of the O atoms interacts with surrounding cations in a crystal structure, the symmetry of $(SO_3F)^-$ could be lowered to that of C_s or C_1 (Vast and Deporcq-Stratmains, 1977). Figure 3 shows that the $(SO_3F)^-$ species in reederite-(Y) apparently has D_{3h} molecular symmetry. In fact, the F atomic site refines to one-half occupancy in each of the two symmetry-related positions; thus, the molecule is a trigonal pyramid having C_{3v} symmetry and statistically oriented half of the time up and half of the time down with a spatial average configuration of a dipyramid (Fig. 3). The large displacement parameter along [001] for the O6 atom (Table 6) supports this model. This indicates the "discomfort" of O6 on an m plane. In fact, O6 may be refined as a split site, in which case it lies on either side of m by 0.33(1) Å. This latter adjustment to the model does not affect the symmetry of the $(SO_3F)^-$ anion, but it does lower the space group symmetry of the crystal to $P3$. The occupancy of each atom in the $(SO_3F)^-$ anion refines to approximately 0.9 atoms.

Also of interest in the $(SO_3F)^-$ anion are the bond lengths. The mean S-O bond length in the sulfate mineral schairerite (Fanfani et al., 1975), $Na_{21}(SO)_4F_6Cl$, is 1.47 Å, whereas in the sulfite minerals gravegliaite (Basso et al.,

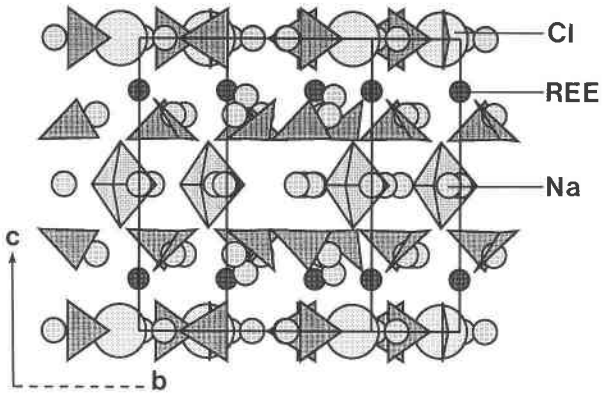

Fig. 2. The reederite-(Y) structure projected on (100) and rotated 10° about [001]. Dark triangles represent CO_3 polyhedra, light-shaded trigonal dipyramids SO_3F polyhedra, large circles represent Cl atoms, small light-shaded circles Na atoms, and small dark-shaded circles REE atoms.

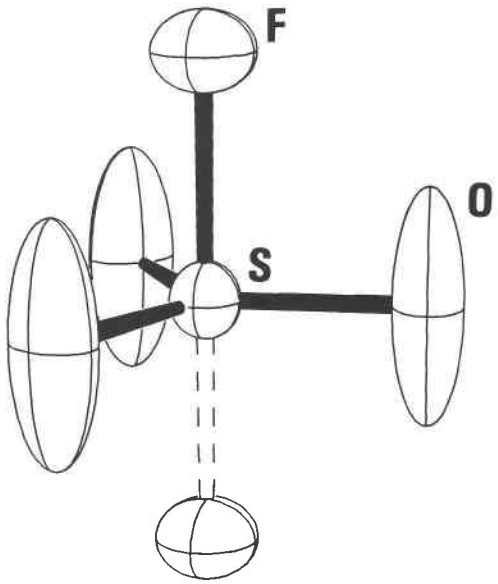

Fig. 3. The SO_3F molecule in reederite-(Y). The F-atom site is one-half occupied, hence statistically oriented one-half of the time up and one-half of the time down.

1991), $MnSO_3 \cdot 3H_2O$, and scotlandite (Pertlik and Zemann, 1985), $PbSO_3$, it is 1.53 Å. In reederite-(Y) the mean S-O bond length is 1.40 Å (Table 7) for the refinement of O6 fixed on the *m* plane and 1.447(8) Å when O6 is allowed to refine off the *m* plane. In schairerite the mean O-S-O bond angle is 109° compared with 115.0(4)° in reederite-(Y) when O6 is off the *m* plane. The slightly shorter S-O bond lengths and larger bond angles in reederite-(Y) compared with a regular sulfate anion are to be expected because the S-F bond is longer and F^- has a smaller ionic radius than O^{2-}.

More complex molecules of oxyfluorides of S have been reported with the $(SO_3F)^-$ group as an essential constituent (Wells, 1975). For example, the nuclear magnetic resonance spectra of $(SO_3F_2)^{2-}$ indicates that the additional F atom bonds to O, not S, giving a tail to the fluorosulfate group and no longer having a configuration like that in Figure 3.

The Cl^- atom

In the reederite-(Y) crystal structure the Cl^- atom, like O6, has a large displacement parameter parallel to [001] (Table 6). It also can be refined as a split atomic site 0.41(1) Å on either side of the *m* plane. This has the effect of increasing the Na3-Cl bond length to 2.576(5) Å (compare Table 7). There is no apparent reason for this, but it is another indication that the true symmetry may be *P*3. In fact, the symmetry may be even lower given that some crystals are optically biaxial.

Genesis of reederite-(Y)

Because reederite-(Y) has a unique chemistry, its formation is indicative of the conditions of crystallization. It occurs in an alkaline, highly agpaitic rock. This type of occurrence favors the presence of large or low valence cations having weak Lewis acid strengths (i.e., REE and Na atoms), which stabilize weak Lewis bases such as $(HSiO_4)^{3-}$, $(HPO_4)^-$, $(HCO_3)^-$, Cl^-, and F^-. This set of criteria explains the stabilization of silicophosphate minerals at Mont-Saint-Hilaire (Grice and McDonald, 1993). In the present case, reederite-(Y) occurs in a late stage vug with the bicarbonate mineral trona. An $(HCO_3)^-$ anion has an average Lewis base strength of 0.17 vu on each O^{2-}. The $(FSO_3)^-$ anion has Lewis base strength of 0.03 vu, which is considerably lower than that of F^- [0.21 vu (Brown, 1981)], $(SO_4)^{2-}$ (0.17 vu), and $(HSO_4)^-$ (0.11 vu). Thus, the fluorosulfate anion forms in response to the stabilization of this highly sodic carbonate mineral.

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References cited

Basso, R., Lucchetti, G., and Palenzona, A. (1991) Gravegliaite, $MnSO_3 \cdot 3H_2O$, a new mineral from Val Graveglia (Northern Apennines, Italy). Zeitschrift für Kristallographie, 197, 97–106.

Brese, N.E., and O'Keeffe, M. (1991) Bond-valence parameters for solids. Acta Crystallographica, B47, 192–197.

Brown, I.D. (1981) The bond-valence method: An empirical approach to chemical structure and bonding. In M. O'Keeffe and A. Navrotsky, Eds., Structure and bonding in minerals, p. 1–30. Academic, New York.

Chao, G.Y., Conlon, R.P., and Van Velthuizen, J. (1990) Mont Saint-Hilaire unknowns. Mineralogical Record, 21, 363–368.

Cotton, F.A., and Wilkinson, G. (1980) Advanced inorganic chemistry (4th edition), 1396 p. Wiley, New York.

Fanfani, L., Nunzi, A., Zanazzi, P.F., Zanzari, A.R., and Sabelli, C. (1975) The crystal structure of schairerite and its relationship to sulpholite. Mineralogical Magazine, 40, 131–139.

Grice, J.D., and McDonald, A.M. (1993) Silicophosphate minerals: Crystal chemistry and genetic significance. Geological Association of Canada Annual Meeting: Program and Abstracts, 18, 47.

Grice, J.D., Van Velthuizen, J., and Gault, R.A. (1994) Petersenite-(Ce), a new mineral from Mont Saint-Hilaire, and its structural relationship to other REE carbonates. Canadian Mineralogist, 32, 405–414.

Horváth, L., and Gault, R.A. (1990) The mineralogy of Mont Saint-Hilaire, Québec. Mineralogical Record, 21, 284–360.

LePage, Y. (1987) Computer derivation of the symmetry elements implied in a structure description. Journal of Applied Crystallography, 20, 264–269.

Mandarino, J.A. (1981) The Gladstone-Dale relationships: IV. The compatibility concept and its application. Canadian Mineralogist, 19, 441–450.

Pertlik, F., and Zemann, J. (1985) The crystal structure of scotlandite, $PbSO_3$. Tschermaks Mineralogisch-Petrographische Mitteilungen, 34, 289–295.

Purcell, K.F., and Kotz, J.C. (1977) Inorganic chemistry, 1116 p., Saunders, Philadelphia, Pennsylvania.

Sheldrick, G.M. (1990) SHLXTL, a crystallographic computing package, revision 4.1. Siemens Analytical X-Ray Instruments Inc., Madison, Wisconsin.

Van Velthuizen, J., Gault, R.A., and Grice, J.D. (1995) Calcioburbankite, a new mineral from Mont Saint-Hilaire, Québec and its relationship to the burbankite group of minerals. Canadian Mineralogist, 32, in press.

Vast, P., and Deporcq-Stratmains, M. (1977) Interaction entre anion et cation dans des sels d'ion sulfate monosubstitué: Cas des fluorosulfates. Revue de Chimie Minérale, 13, 20–32.

Wells, A.F. (1975) Structural inorganic chemistry (4th edition), 899 p. Clarendon, Oxford, U.K.

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