

# Fluorcalciroméite, $(\text{Ca},\text{Na})_2\text{Sb}_2^{5+}(\text{O},\text{OH})_6\text{F}$ , a new roméite-group mineral from Starlera mine, Ferrera, Grischun, Switzerland: description and crystal structure

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## ABSTRACT

Fluorcalciroméite,  $(\text{Ca},\text{Na})_2\text{Sb}_2^{5+}(\text{O},\text{OH})_6\text{F}$ , is a new roméite-group, pyrochlore-super-group mineral (IMA 2012-093), from Starlera mine, Ferrera, Hinterrhein district, Grischun, Switzerland. The intimately associated minerals are: braunite, hematite, calcite, quartz and, rarely, wallkilldellite-(Mn). It occurs as euhedral octahedra, untwinned, from 0.1 to 1 mm in size. The crystals are yellow to orange and translucent; the streak is white, and the lustre is vitreous to resinous. It is non-fluorescent under ultraviolet light. Mohs' hardness is  $\sim 5\frac{1}{2}$ , tenacity is brittle. Cleavage is not observed; fracture is conchoidal. The calculated density is  $5.113 \text{ g/cm}^3$ . The mineral is isotropic,  $n_{\text{calc.}} = 1.826$ . The Raman spectrum is dominated by bands of Sb–O octahedral bond stretching and O–Sb–O bending modes. The chemical composition ( $n = 13$ ) is (by wavelength-dispersive spectroscopy (WDS),  $\text{H}_2\text{O}$  calculated by difference, wt.%): Na<sub>2</sub>O 4.11, CaO 15.41, MnO 0.54, CuO 0.01, ZnO 0.01, PbO 0.02, Al<sub>2</sub>O<sub>3</sub> 0.10, FeO 0.50, Y<sub>2</sub>O<sub>3</sub> 0.07, SiO<sub>2</sub> 0.04, TiO<sub>2</sub> 0.01, UO<sub>2</sub> 0.01, Sb<sub>2</sub>O<sub>5</sub> 76.18, WO<sub>3</sub> 0.78, F 2.79, H<sub>2</sub>O 0.59, O = F –1.17, total 100.00. The empirical formula, based on 2 cations at the B site, is  $(\text{Ca}_{1.16}\text{Na}_{0.56}\square_{0.22}\text{Fe}_{0.03}\text{Mn}_{0.03})_{\Sigma 2.00}(\text{Sb}_{1.98}\text{Al}_{0.01}\text{W}_{0.01})_{\Sigma 2.00}\text{O}_6[\text{F}_{0.62}(\text{OH})_{0.28}\text{O}_{0.06}\square_{0.04}]_{\Sigma 1.00}$ . The strongest eight X-ray powder-diffraction lines [ $d$  in Å( $I$ )( $hkl$ )] are: 5.934(81)(111), 3.102(20)(311), 2.969(100)(222), 2.572(6)(400), 1.979(7)(333), 1.818(8)(440), 1.551(15)(622), and 1.484(5)(444). The crystal structure refinement ( $R_I = 0.0106$ ) gave the following data: cubic,  $Fd\bar{3}m$ ,  $a = 10.2987(8) \text{ \AA}$ ,  $V = 1092.31(15) \text{ \AA}^3$ ,  $Z = 8$ . Unit-cell parameters refined from the powder data are:  $a = 10.284(2)$ ,  $V = 1087.7(7) \text{ \AA}^3$ ,  $Z = 8$ .

**KEYWORDS:** fluorcalciroméite, new mineral, Starlera mine, Ferrera, Grischun, Switzerland, pyrochlore supergroup, roméite group, crystal structure.

## Introduction

THE roméite group of minerals, consisting of one valid species (hydroxycalciroméite) and four species that need to be completely described in order to be approved as valid species (“fluor-natroroméite”, “fluorcalciroméite”, “oxycalciroméite” and “oxyplumboroméite”), became part

of the pyrochlore supergroup of minerals when its new nomenclature system (Atencio *et al.*, 2010) was introduced. This paper presents the complete description of the new species fluorcalciroméite,  $(\text{Ca},\text{Na})_2\text{Sb}_2^{5+}(\text{O},\text{OH})_6\text{F}$ , approved by IMA-CNMNC (IMA number 2012-093).

The general formula of the pyrochlore-super-group minerals is  $A_{2-m}B_2X_{6-w}Y_{1-n}$ , where  $m = 0-1.7$ ,  $w = 0-0.7$ ,  $n = 0-1$  (Lumpkin and Ewing, 1995). The X site is dominated by O. In the roméite group, the B site is dominated by  $\text{Sb}^{5+}$ . In

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fluorcalcioroméite, the *A* site is dominated by Ca, and the *Y* site is dominated by F. Chemical analyses that correspond to fluorcalcioroméite were previously recorded from Fianel, Val Sterla and Starlera mines, Ferrera, Switzerland, by Brugger *et al.* (1997); from Prašivá granitic pegmatites, Slovakia by Uher *et al.* (1998); and again from Starlera mines, Ferrera, Switzerland, by Brugger and Gieré (1999).

Type material is deposited in the collections of the Museo Regionale di Scienze Naturali, Sezione di Mineralogia, Petrografia e Geologia, via Giovanni Giolitti 36, I-10123 Torino, Italy, registration number M/15925. Cotype samples are deposited in the RRUFF project, registration number R120140, and in the Museu de Geociências, Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080 - São Paulo, SP, Brazil, specimen number DR745.

### Occurrence

Fluorcalcioroméite occurs at Starlera mine (46°31'24" N, 9°27'37"E), Ferrera, Hinterrhein district, Grischun, Switzerland. The Starlera Mn deposit of Val Ferrera belongs to the Middle Penninic domain of the Swiss Alps (Brugger *et al.*, 1997, 2002). The most exhaustive description of the geology of the Val Ferrera Fe-Mn deposits was made by Brugger and Gieré (2000). According to them, the Starlera mine (Suretta nappe) is the only deposit of the province that was exploited for Mn. This deposit is characterized by a complicated palaeogeographic and structural position. The ore is hosted in dolomitic marbles, but may be in direct contact with the augen gneiss of the underlying basement. In the vicinity of Starlera, the basal quartzite exhibits large variations in thickness, from >20 m at Bergwiesen to zero at Starlera. These variations in thickness might represent a Triassic palaeogeography (trough) that favoured ore deposition at Starlera. The present thickness of the ore, up to 12 m, also reflects doubling of the sequence by folding. Breccias with a matrix rich in magnesioriebeckite asbestos are abundant and characteristic of the Starlera deposit. According to Brugger *et al.* (1997), the Starlera Mn deposit is most likely of syndimentary exhalative origin.

The intimately associated minerals are: braunite, hematite, calcite, quartz and, rarely, wallkilldellite-(Mn). Hematite, calcite and quartz were confirmed by Raman spectroscopy.

### Habit and physical properties

Fluorcalcioroméite occurs as octahedra from 0.1 to 1 mm across (Fig. 1). No twinning is observed. The crystals are yellow to orange, with a white streak. The lustre is vitreous to resinous. The mineral is translucent. It is non-fluorescent under ultraviolet light. Mohs' hardness was not measured, but it is probably  $\sim 5\frac{1}{2}$  by analogy with hydroxycalcioroméite (Hussak and Prior, 1895). The tenacity is brittle. Cleavage and parting were not observed; fracture is conchoidal. Density could not be measured because of lack of sufficient pure material. The calculated density is 5.113 g/cm<sup>3</sup> based on the empirical formula and unit-cell parameters obtained from the single-crystal XRD data.

The mineral is isotropic. The refractive index calculated from the Gladstone-Dale relationship based on the empirical formula is  $n_{\text{calc.}} = 1.826$  (higher than that of available immersion liquids).

### Composition of fluorcalcioroméite

The composition of fluorcalcioroméite was determined using a Cameca SX100 electron microprobe (WDS mode, 25 kV, 20 nA, and electron beam diameter <1  $\mu\text{m}$ ). Back-scattered electron images showed no significant dishomogeneity in the studied crystals (Fig. 2). H<sub>2</sub>O was calculated by difference. Analytical data from 13 points are given in Table 1. The empirical formula, based on 2 cations at the *B* site



FIG. 1. Fluorcalcioroméite with hematite, calcite and quartz from Starlera mine, Ferrera, Hinterrhein district, Grischun, Switzerland.

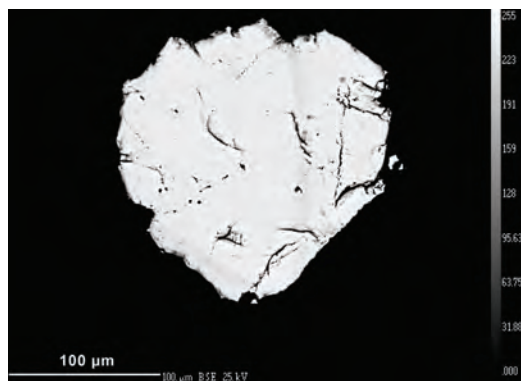


FIG. 2. BSE image of fluorcalcioroméite from Starlera mine, Ferrera, Hinterrhein district, Grischun, Switzerland.

is  $(\text{Ca}_{1.16}\text{Na}_{0.56}\square_{0.22}\text{Fe}_{0.03}^{2+}\text{Mn}_{0.03}^{2+})_{\Sigma 2.00}$   
 $(\text{Sb}_{1.98}\text{Al}_{0.01}\text{W}_{0.01})_{\Sigma 2.00}\text{O}_6[\text{F}_{0.62}(\text{OH})_{0.28}$   
 $\text{O}_{0.06}\square_{0.04}]_{\Sigma 1.00}$ . The simplified formula is  
 $(\text{Ca},\text{Na})_2\text{Sb}_2^{5+}\text{O}_6(\text{F},\text{OH})$ . The charge-balanced,  
 endmember variant of this formula is  
 $(\text{Ca}_{1.50}\square_{0.50})\text{Sb}_2^{5+}\text{O}_6\text{F}$ .

### Raman data

The Raman spectra of fluorcalcioroméite (Fig. 3) were collected on a randomly oriented crystal

from 15 scans of 30 s each, and 100% power per scan using a Thermo Almega microRaman system, with a solid-state laser (532 nm) and a thermoelectrically cooled CCD detector. The laser is partially polarized and spectra were collected with a  $4\text{ cm}^{-1}$  resolution and a spot size of  $\sim 1\ \mu\text{m}$ . A tentative assignment of observed Raman modes for fluorcalcioroméite based on previous studies on pyrochlore supergroup minerals (Bahfenne and Frost, 2010; Frost and Bahfenne, 2010) is as follows. Peaks ( $\text{cm}^{-1}$ ) were observed at 827, 790 (weak, broad) overtones, 518 (relatively strong, sharp) Sb–O stretching, 468 (weak, shoulder) Sb–O stretching, and 302 (weak, sharp) O–Sb–O bending. Also, in the region of the stretching vibrations of OH groups, there are two well resolved bands centred at  $3630\text{ cm}^{-1}$  and  $3686\text{ cm}^{-1}$ .

### Crystal structure determination

A yellow to orange crystal of dimensions  $0.09\text{ mm} \times 0.08\text{ mm} \times 0.08\text{ mm}$  was selected for single-crystal XRD study on a Bruker X8 APEX2 CCD diffractometer with graphite-monochromated  $\text{MoK}\alpha$  ( $\lambda = 0.71073\ \text{\AA}$ ) radiation. Data were collected up to  $65^\circ$  in  $2\theta$  and gave the following results: cubic, space group  $Fd\bar{3}m$ ,  $a = 10.2987(8)\ \text{\AA}$ ,  $V = 1092.3(2)\ \text{\AA}^3$ , and  $Z = 8$ . Final

TABLE 1. Chemical analyses of fluorcalcioroméite ( $n = 13$ ).

Constituent	Wt.%	Range	Standard deviation	Probe standard
$\text{Na}_2\text{O}$	4.11	3.75–4.44	0.23	Albite
$\text{CaO}$	15.41	15.14–16.05	0.26	Wollastonite
$\text{MnO}$	0.54	0.43–0.67	0.08	Rhodonite
$\text{CuO}$	0.01	0.00–0.03	0.01	Chalcopyrite
$\text{ZnO}$	0.01	0.00–0.03	0.01	Gahnite
$\text{PbO}$	0.02	0.00–0.10	0.03	Wulfenite
$\text{Al}_2\text{O}_3$	0.10	0.03–0.26	0.05	BAS498-s (basalt glass)
$\text{FeO}$	0.50	0.41–1.11	0.21	BAS498-s (basalt glass)
$\text{Y}_2\text{O}_3$	0.07	0.01–0.15	0.05	YAG garnet
$\text{SiO}_2$	0.04	0.02–0.12	0.03	Wollastonite
$\text{TiO}_2$	0.01	0.00–0.03	0.01	Rutile
$\text{UO}_2$	0.01	0.00–0.03	0.01	$\text{UO}_2$
$\text{Sb}_2\text{O}_5$	76.18	73.39–77.18	0.93	Stibnite
$\text{WO}_3$	0.78	0.61–1.80	0.32	Scheelite
F	2.79	2.40–3.07	0.23	$\text{MgF}_2$
$\text{H}_2\text{O}$	0.59			
O=F	–1.17			
Total	100.00			

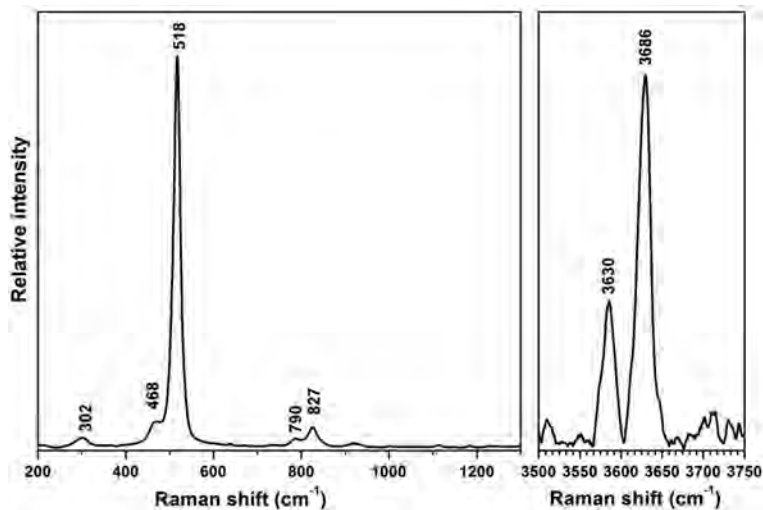


FIG. 3. Raman spectrum of fluorcalcioroméite.

unit-cell parameters were based on 505 reflections with index ranges  $-12 \leq h \leq 11$ ,  $-13 \leq k \leq 12$ ,  $-3 \leq l \leq 15$ . The structure was solved with the program *SHELXS-97* (Sheldrick, 2008) and the final model was refined on  $F^2$  by full-matrix least-squares procedures with *SHELXL-97* (Sheldrick, 2008), using anisotropic thermal displacement parameters for all atoms. The  $\theta$  range for data collection was 3.4 to 32.6°. A total of 774 reflections were collected. The X-ray absorption correction of the intensity data was

calculated using the program *SADABS* from Bruker.

The general formula of pyrochlore supergroup minerals is  $A_{2-m}B_2X_{6-w}Y_{1-n}$  ( $m = 0$  to 2),  $w = 0$  to 0.7,  $n = 0$  to 1) (Atencio *et al.*, 2010). The standard pyrochlore structures have all atoms occupying special positions ( $A = 16d$ ,  $B = 16c$ ,  $X = 48f$  and  $Y = 8b$ ) in  $Fd\bar{3}m$  (Subramanian *et al.*, 1983). The  $A$  cation site (16d) is eight coordinated and  $B$  cation site (16c) is six coordinated. The  $X$  (48f) and  $Y$  (8b) are 4-coordinated anion sites. The

TABLE 2. Crystal data and details of structure refinement.

Temperature (K)	293(2)
Crystal colour	orange
Crystal size (mm)	0.09 × 0.08 × 0.08
Crystal system	Cubic
Space group	$Fd\bar{3}m$ (#227, origin at 16c, $-3m$ )
Unit-cell dimension $a$	10.2987(8) Å
Unit-cell volume $V$	1092.31(15) Å <sup>3</sup>
$Z$	8
Density (calculated)	5.135 g/cm <sup>3</sup>
Absorption coefficient	11.20
$F(000)$	1526
Reflections collected/unique	774/123
Parameters	14 ( $R_{\text{int}} = 0.015$ )
Goodness-of-fit on $F^2$	1.186
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0106$ , $wR_2 = 0.0318$
Largest diff. peak	0.57 e.Å <sup>-3</sup> at (0.3750, 0.3750, 0.1059), 0.34 Å from O (48f)
Largest diff. hole	-0.38 e.Å <sup>-3</sup> at (0.2543, 0.4957, -0.0043), 1.93 Å from O (48f)

FLUORCALCIOROMÉITE, A NEW ROMÉITE-GROUP MINERAL

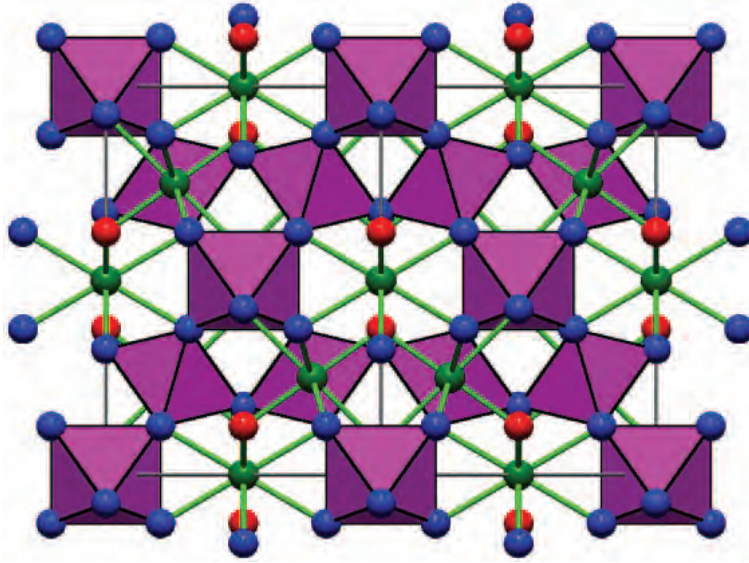


FIG. 4. Crystal structure of fluorcalcioroméite. Purple: Sb–O octahedra; green: (Ca,Na,Mn) atoms; blue: O1, and red: F1.  $\text{SbO}_6$  octahedra share corners to form a three-dimensional framework, with (Ca,Na,Mn) atoms eight-coordinated occupying the cavities in the framework.

*B* site is used as the origin. The initial structure refinement model was constrained by the results from the microprobe analysis. For simplicity, the *B* site was set to full occupancy (Sb = 2 a.p.f.u.). The amount of Fe was treated as Mn at the *A* site due to their similar X-ray scattering power. Trace elements such as Al and W were ignored, due to their negligible effects on the final results. During the refinement, the site occupancies of the major cations at the *A* site, Ca and Na, were allowed to vary. The final model was refined with anisotropic displacement parameters for all atoms and converged to  $R_1 = 0.011$ ,  $wR_2 = 0.032$ . The O and OH contents of the *X* (48*f*) position and *Y* (8*b*)

were calculated from charge-balance requirements.

The positional parameter *x* of the 48*f* site position is 0.3233(2), which is close to the value of 0.3125 in the ideal pyrochlore structure (Subramanian *et al.*, 1983). This result shows that the oxygen environment around *B* cations has an approximate octahedral array and *A* cations are located within distorted cubes.

The refined charge-balanced formula is  $(\text{Ca}_{1.22}\text{Na}_{0.54}\text{Mn}_{0.06})_{\Sigma 1.82}\text{Sb}_{2.00}^{5+}\text{O}_6[\text{F}_{0.62}(\text{OH})_{0.28}\text{O}_{0.10}]_{\Sigma 1.00}$ . The crystal-structure data and characteristics of the XRD study are given in Table 2. The structure is shown in Fig. 4. Atom

TABLE 3. Atomic coordinates and displacement parameters ( $\text{\AA}^2$ ) for fluorcalcioroméite.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ca1	½	½	½	0.0114(3)	0.0114(3)	0.0114(3)	0.0114(3)	−0.0017(3)	−0.0017(3)	−0.0017(3)
Na1	½	½	½	0.0114(3)	0.0114(3)	0.0114(3)	0.0114(3)	−0.0017(3)	−0.0017(3)	−0.0017(3)
Mn1	½	½	½	0.0114(3)	0.0114(3)	0.0114(3)	0.0114(3)	−0.0017(3)	−0.0017(3)	−0.0017(3)
Sb1	0	0	0	0.0030(1)	0.0030(1)	0.0030(1)	0.0030(1)	−0.00026(5)	−0.00026(5)	−0.00026(5)
O1	¼	0.3233(2)	¼	0.0066(4)	0.0071(6)	0.0056(9)	0.0071(6)	0	0.0059(8)	0
F1	¾	¾	¾	0.0097(9)	0.0097(9)	0.0097(9)	0.0097(9)	0	0	0
OH	¾	¾	¾	0.0097(9)	0.0097(9)	0.0097(9)	0.0097(9)	0	0	0

TABLE 4. Selected bond lengths and bond valences for fluorcalciroméite.

Bond	Bond length	BV (v.u.)	$\Sigma$	Valence from EMPA
$A(16d)-X(48f)$	2.5742(15)	0.155 ( $\times 6$ )	0.930	
$A(16d)-Y(8b)$	2.2297(2)	0.282 ( $\times 2$ )	0.564	
$\Sigma$			<b>1.494</b>	<b>1.450</b>
$B(16c)-X(48f)$	1.9708(8)	0.856 ( $\times 6$ )	5.136	
$\Sigma$			<b>5.136</b>	<b>4.960</b>
$X(48f)-A(16d)$	2.5742(15)	0.155 ( $\times 2$ )	0.310	
$X(48f)-B(16c)$	1.9708(8)	0.856 ( $\times 2$ )	1.712	
$\Sigma$			<b>2.022</b>	
$Y(8b)-A(16d)$	2.2297(2)	0.282 ( $\times 4$ )	1.128	
$\Sigma$			<b>1.128</b>	

coordinates are given in Table 3 and selected bond lengths and bond valences in Table 4. The empirical bond-valences of the simplified refined model were calculated using only the parameters published by Brown and Altermatt (1985). However, the results for the *B* site were excessively high, 5.550 (v.u.). This problem was solved using the bond valence parameters obtained by Mills *et al.* (2009) for Sb cations and the final results are similar to the valences calculated from microprobe analysis. A CIF file with structure data of fluorcalciroméite can be downloaded from the

Inorganic Crystal Structure Database at FIZ Karlsruhe, Germany (CSD number 425866).

Powder XRD data were obtained using a Siemens D5000 diffractometer using  $\text{CuK}\alpha$  radiation and 40 kV and 40 mA (Table 5). Unit-cell parameters refined from the powder data (*CellCalc* program, Miura, 2003) in the same space group  $Fd\bar{3}m$  obtained by single-crystal XRD as follows:  $a = 10.284(2)$ ,  $V = 1087.7(7) \text{ \AA}^3$ , and  $Z = 8$ . The calculated X-ray powder diffraction pattern was obtained from the determined structure model using the *XPOW* program by Downs *et al.* (1993).

TABLE 5. X-ray powder-diffraction pattern for fluorcalciroméite.

$d_{\text{obs.}} (\text{\AA})$	$I_{\text{obs}}$	$d_{\text{calc.}} (\text{\AA})$	$I_{\text{calc}}$	$hkl$
5.934	81	5.946	100	111
		3.641	6	220
3.102	20	3.105	29	311
2.969	100	2.973	77	222
2.572	6	2.575	2	400
2.100	4	2.102	11	422
1.979	7	1.982	15	333
1.818	8	1.821	54	440
1.739	4	1.741	12	531
1.571	4	1.571	6	533
1.551	15	1.553	29	622
1.484	5	1.487	5	444
1.439	4	1.442	2	711
1.439	4	1.442	11	551
		1.341	10	731
		1.287	6	800
		1.214	3	822

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