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Cossaite, $(Mg_{0.5},\square)Al_6(SO_4)_6(HSO_4)F_6\cdot 36H_2O$, a new mineral from La Fossa crater, Vulcano, Aeolian Islands, Italy

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ABSTRACT

Cossaite, ideally $(Mg_{0.5},\square)Al_6(SO_4)_6(HSO_4)F_6\cdot 36H_2O$, was found in the altered pyroclastic breccia of an active fumarole (T about 350ºC) located at the rim of the La Fossa crater, Vulcano Island, Aeolian archipelago, Sicily, Italy. Cossaite is trigonal, space group $R\bar{3}$, with a = 22.010(2), c = 9.238(1) Å, V = 3875.6(6) Å^3, Z = 3. It forms stout prismatic hexagonal crystals up to 100 μm in size, terminated by rhombohedral faces, and is associated with thermessaite, vlodavetsite, sassolite and salammoniac. Cossaite is colourless to white, the streak is white and the lustre vitreous. It is not fluorescent in either long-wave or short-wave ultraviolet radiation. The calculated density is 2.075 g cm^{-3}. The mean refractive index n_{obs} is 1.49(1) (589 nm). Chemical analysis gave MgO 1.4, Al_2O_3 19.5, SO_3 34.7, F 5.7, (H_2O 40.85, from structure refinement), O=F −2.4, total 99.75 wt.%, corresponding to the empirical formula $Mg_{0.56}Al_{6.19}S_{7.01}H_{73.37}F_{4.85}O_{65.15}$ calculated on the basis of 70 oxygen plus fluorine atoms. The strongest six lines in the X-ray powder diffraction pattern [d_{obs}(Å) (I) (hkl)] are: 4.15 (100) (140), 3.87 (70) ($3\bar{2}2$), 11.00 (50) (110), 4.58 (25) (131), 2.770 (20) ($\bar{3}33$), 2.166 (20) ($\bar{1}\bar{8}1$). The crystal structure was refined to a final R index of 0.0349. It contains octahedral $[Al(H_2O)_5F]^{2+}$ cations and sulphate anions interacting via hydrogen bonds to form channels running along [001], where disordered $[Mg(H_2O)_6]^{2+}$ cations and hydrogensulphate anions are hosted.

KEYWORDS: cossaite, new mineral, crystal structure, Vulcano Island, Aeolian Islands, Italy.

Introduction

THE fumaroles at La Fossa crater, Vulcano, Aeolian Islands have proved to be an important source of new mineral species, including several sulphates (Demartin *et al.*, 2008; Demartin *et al.*, 2010*a*,*b*,*c*; Campostrini *et al.*, 2011). During systematic sampling carried out in 2009, the new mineral cossaite, $(Mg_{0.5},\square)Al_6(SO_4)_6(HSO_4)F_6\cdot 36H_2O$, was discovered. The properties and crystal structure of the mineral are reported here.

The mineral name honours Alfonso Cossa (1833−1902), an Italian chemist and mineralogist who was the author of a number of publications about the minerals of Vulcano, including descriptions of new species such as hieratite (Cossa, 1881, 1882). The mineral and the mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification of the IMA; proposal 2009-031. The holotype specimen (no. 2009-1) is deposited in the Reference Collection of the Dipartimento di Chimica Strutturale e Stereochimica Inorganica at the Università degli Studi di Milano. The name cossaite was used previously for a potassium-bearing variety of paragonite found at Fenestrella near Borgofranco, Valle del Chisone, Torino, Italy (Schaller and Stevens, 1941); this is not a valid mineral species.

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Occurrence and physical properties

Cossaite was found on altered pyroclastic breccia at the F5AT medium-temperature fumarole (T ~350ºC), which is located at the rim of La Fossa crater. It is associated with thermessaite, vlodavetsite, sassolite and salammoniac. Only two translucent crystals, up to 100 μm in size, were present on the single specimen that was recovered; one of these crystals was removed and used to characterize the mineral. The crystals are stout prismatic in habit and terminated by rhombohedral faces (Fig. 1). They are colourless, the streak is white and the lustre vitreous. No fluorescence was observed under either short-wave or long-wave ultraviolet radiation. The tenacity is brittle and the fracture is uneven. The calculated density is 2.075 g cm^{-3} (from the empirical formula and the unit-cell data reported below); the density measured by flotation in a toluene-methylene iodide mixture is 2.08(1) g cm^{-3}. The mean value of the refractive index [n_{obs} = 1.49(1) (589 nm)] was measured by immersion methods in a kerosene-monochloronaphthalene mixture; n_{calc} = 1.516 (Gladstone–Dale). The Gladstone–Dale compatibility index, 1 – (K_P/K_c), calculated using the empirical formula and n_{av}, is 0.052 which is 'good' (Mandarino, 1981).

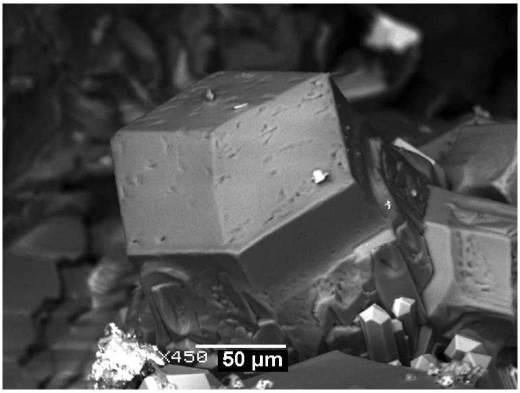

FIG. 1. Scanning electron microscope image of a cossaite crystal (from the type specimen) associated with thermessaite (bottom right).

Chemical data

The sample was damaged significantly under a high intensity electron beam, probably due to dehydration; therefore a low intensity beam was used for analysis. A JEOL JSM 5500 LV scanning electron microscope was used with an IXRF EDS 2000 electron microprobe under the following experimental conditions: accelerating voltage 20 kV, beam current 10^{-11} A, beam diameter 2 μm. The water content could not be determined by thermogravimetry due to the minute amount of material available; it was calculated stoichiometrically from the results of the single-crystal structure analysis. The mean analytical results are reported in Table 1. The empirical formula calculated on the basis of 70 oxygen plus fluorine atoms is $Mg_{0.56}Al_{6.19}S_{7.01}H_{73.37}F_{4.85}O_{65.15}$. The simplified formula obtained from structure refinement is $(Mg_{0.5},\square)Al_6(SO_4)_6(HSO_4)F_6{\cdot}36H_2O$, which requires MgO 1.25, Al_2O_3 19.00, SO_3 34.80, F 7.08, H_2O 40.85, O=F –2.98, total 100.00 wt.%. The lower fluorine content in the empirical formula in comparison to the simplified

TABLE 1. The chemical composition of cossaite.

Constituent	Wt.%*	Theoretical wt.% $^\$$	Range	Probe standard
MgO	1.4	1.25	1.1–2.1	almandine garnet
Al_2O_3	19.5	19.00	19.0–19.9	albite
SO_3	34.7	34.80	32.8–35.9	synthetic anhydrite
F	5.7	7.08	5.6–8.8	KF
$H_2O^\dagger$	40.85	40.85		
O=F	–2.40	–2.98		
Total	99.75	100.00		

* Average of 6 analyses.
$^\$$ Calculated from the simplified formula $(Mg_{0.5},\square)Al_6(SO_4)_6(HSO_4)F_6{\cdot}36H_2O$.
† From structure refinement.

formula is probably due to partial substitution of OH for F.

X-ray data and refinement of the structure

X-ray powder diffraction data were obtained with a Gandolfi camera (114.6 mm in diameter; Cu-$K\alpha$ radiation, λ = 1.5418 Å) from the same crystal fragment (0.08 × 0.06 × 0.04 mm) used for the final structure determination (Table 2). A least-squares fit of these data provided the following unit-cell parameters: a = 22.002(3), c = 9.232(2) Å, V = 3870.5(9) Å^3.

Single-crystal diffraction data were collected on a Bruker Apex II CCD diffractometer with Mo-$K\alpha$ radiation (λ = 0.71073 Å) using a one min. frame time and 0.3º frame width. A total of 12,951 diffraction intensities up to 2θ = 61.3º were collected; 2541 are unique. The unit-cell dimensions obtained from the single crystal were refined by least-squares methods using 4238 reflections with $I > 5\sigma(I)$; their values are given in Table 3, together with other details concerning the data collection and refinement. The diffraction data were reduced using the Bruker program *SAINT*, and were corrected for Lorentz and polarization factors, and background. No violations of the systematic absences of the space group $R\bar{3}$ were observed. An absorption correction using the *SADABS* program (Sheldrick, 2000) was applied (maximum and minimum transmission factors 1.000 and 0.905, respectively). The structure was solved by direct methods using *SHELXS* and refined using the *SHELXL97* program (Sheldrick, 2008) implemented in the *WinGX* suite (Farrugia, 1999). All the hydrogen atoms, with the exception of those of Ow6 and of the hydrogensulphate anion, were detected in a difference Fourier map and included in the final refinement. The occupancies of the Mg and Ow6 sites were refined and converged to a value not significantly different from 0.5; therefore they were kept fixed at this value in the subsequent stages of the refinement. The final R is 0.0349 for 1926 observed reflections [$I > 2\sigma(I)$]. A list of the coordinates and displacement parameters of the atoms is reported in Table 4.

Results and discussion

On April 2009, we submitted a proposal for the new mineral to the CNMNC. This proposal (approved in July 2009) included the simplified chemical formula $NaAl_6(SO_4)_6(SO_3F)F_6{\cdot}36H_2O$, derived from chemical analysis and preliminary

TABLE 2. X-ray powder diffraction data for cossaite.

I/Io[†]	d_{obs} (Å)	d_{calc} (Å)*	$h\ k\ l$
50	**11.00**	**11.00**	**1 1 0**
25	**4.58**	**4.59**	**1 3 1**
100	4.15	**4.16**	**1 4 0**
70	**3.87**	**3.89**	**3 $\bar{2}$ 2**
15	2.960	2.966	$\bar{3}$ $\bar{4}$ 1
20	**2.770**	**2.769**	**$\bar{3}$ 3 3**
15	2.472	2.474	1 4 3
17	**2.345**	**2.345**	**0 7 2**
20	**2.166**	**2.168**	**$\bar{1}$ $\bar{8}$ 1**
15	2.008	2.008	1 8 2
15	1.893	1.893	3 6 3
15	1.761	1.760	3 5 4
15	1.531	1.529	3 9 3

[†] Determined densitometrically from a Gandolfi camera film.

* Calculated from the unit cell a = 22.002(3), c = 9.232(2) Å, obtained from least-squares refinement from the above data using the program *UNITCELL* (Holland and Redfern, 1997).

TABLE 3. Single-crystal data and refinement parameters for cossaite.

Crystal system	Trigonal
Space Group	$R\bar{3}$
a (Å)	22.010(2)
c (Å)	9.238(1)
V (Å^3)	3875.6(6)
Z	3
Radiation	Mo-$K\alpha$
μ (mm^{-1})	0.589
D_{calc} (g cm^{-3})	2.075
Measured reflections	12,951
Independent reflections	2541
Observed reflections [$I > 2\sigma(I)$]	1926
Refined parameters	175
*Final R and $wR2$	0.0349, 0.1111
[§]Goodness-of-fit (GoF)	1.008

*$R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$.
$wR2 = \{\Sigma[w(F_o^2-F_c^2)]/\Sigma[w(Fo^2)^2]\}^{1/2}$.
The weighting scheme used is $w=1/[\sigma^2(F_o^2)+(0.0705k)^2]$ where $k = (\mathrm{Max}(F_o)^2 + 2F_c^2)/3$ as defined by *SHELX-97* (Sheldrick, 2008).
[§]$\mathrm{GoF} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ where n = no. of reflections, p = no. of refined parameters.

TABLE 4. Coordinates of the atoms and displacement parameters [*U*eq/*U*(i,j)] for cossaite.

Atom	Wyckoff notation	Occupancy	*x*/*a*	*y*/*b*	*z*/*c*	*U*eq (Å^2)
Al	18*f*	1	0.37501(1)	0.87307(1)	0.35346(2)	0.01662(5)
Mg	3*b*	0.5	⅓	⅔	7⁄6	0.0840(9)
S1	18*f*	1	0.21195(1)	0.95870(1)	0.16739(2)	0.01769(4)
S2	6*c*	0.5	⅓	⅔	0.69198(6)	0.0211(2)
F	18*f*	1	0.32848(2)	0.79736(2)	0.24892(5)	0.0319(1)
Ow1	18*f*	1	0.45582(2)	0.90169(3)	0.23929(6)	0.0263(2)
Ow2	18*f*	1	0.34841(2)	0.92446(3)	0.23172(5)	0.0272(1)
Ow3	18*f*	1	0.42288(3)	0.95598(2)	0.46392(5)	0.0241(2)
Ow4	18*f*	1	0.40817(3)	0.82981(3)	0.48384(7)	0.0368(2)
Ow5	18*f*	1	0.29490(2)	0.84390(3)	0.47033(6)	0.0258(2)
Ow6	18*f*	0.5	0.34139(6)	0.74857(6)	1.0290(1)	0.0382(3)
O1	18*f*	1	0.14732(3)	0.95419(3)	0.22260(7)	0.0351(2)
O2	18*f*	1	0.24997(3)	1.02178(3)	0.07647(6)	0.0380(2)
O3	18*f*	1	0.19434(3)	0.89589(2)	0.08023(6)	0.0250(1)
O4	18*f*	1	0.25714(3)	0.96364(3)	0.28903(6)	0.0287(2)
O5	6*c*	0.5	⅓	⅔	0.8511(3)	0.0560(8)
O6	18*f*	0.5	0.30686(6)	0.71231(5)	0.6401(2)	0.0349(3)
H1a	18*f*	1	0.4606(3)	0.8681(2)	0.1844(7)	0.067(4)
H1b	18*f*	1	0.4992(3)	0.9437(3)	0.241(1)	0.063(4)
H2a	18*f*	1	0.3579(6)	0.9368(6)	0.1326(5)	0.106(5)
H2b	18*f*	1	0.3107(2)	0.9327(3)	0.247(1)	0.095(5)
H3a	18*f*	1	0.4316(5)	0.9653(5)	0.5639(4)	0.060(3)
H3b	18*f*	1	0.4218(3)	0.9988(2)	0.454(1)	0.073(4)
H4a	18*f*	1	0.3722(4)	0.7927(4)	0.5360(9)	0.110(6)
H4b	18*f*	1	0.4516(2)	0.8311(4)	0.474(1)	0.121(6)
H5a	18*f*	1	0.2577(4)	0.7973(3)	0.461(1)	0.054(3)
H5b	18*f*	1	0.2925(4)	0.8632(3)	0.5596(5)	0.057(3)

Table 4. (*contd.*).

	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{23} (Å^2)	U_{13} (Å^2)	U_{12} (Å^2)
Al	0.0141(1)	0.0188(1)	0.0161(1)	0.0005(1)	−0.0001(1)	0.0075(1)
Mg	0.0455(7)	0.0455(7)	0.161(3)	0	0	0.0228(3)
S1	0.0189(1)	0.0191(1)	0.0168(1)	−0.0014(1)	−0.0022(1)	0.0108(1)
S2	0.0195(1)	0.0195(1)	0.0241(5)	0	0	0.0098(1)
F	0.0272(2)	0.0239(2)	0.0378(3)	−0.0094(2)	0.0023(2)	0.0078(1)
Ow1	0.0207(2)	0.0250(2)	0.0290(3)	−0.0016(2)	0.0092(2)	0.0082(2)
Ow2	0.0369(2)	0.0428(2)	0.0160(2)	0.0043(2)	0.0021(2)	0.0304(2)
Ow3	0.0280(2)	0.0224(2)	0.0163(2)	−0.0017(2)	−0.0021(2)	0.0085(2)
Ow4	0.0262(2)	0.0502(2)	0.0410(3)	0.0229(2)	0.0059(2)	0.0242(2)
Ow5	0.0178(2)	0.0326(2)	0.0215(2)	0.0006(2)	0.0052(2)	0.0086(2)
Ow6	0.0480(5)	0.0469(5)	0.0315(6)	−0.0120(5)	−0.0096(5)	0.0326(4)
O1	0.0236(2)	0.0408(2)	0.0463(3)	−0.0154(2)	−0.0024(2)	0.0202(2)
O2	0.0471(3)	0.0205(2)	0.0273(3)	0.0042(2)	−0.0099(3)	0.0026(2)
O3	0.0372(2)	0.0232(2)	0.0190(2)	−0.0032(2)	0.0017(2)	0.0185(2)
O4	0.0318(2)	0.0483(2)	0.0164(2)	−0.0053(2)	−0.0056(2)	0.0279(2)
O5	0.0667(10)	0.0667(10)	0.0344(13)	0	0	0.0334(5)
O6	0.0359(5)	0.0337(4)	0.0431(7)	0.0063(5)	0.0044(5)	0.0233(3)

structure refinement. On this basis, cossaite would have been the second mineral containing the fluoro-sulphate anion; the first is reederite-(Y) (Grice *et al.*, 1995). The results, with a reasonable value (0.054) of the *R* index, were acceptable and sufficient for the preliminary characterization of the mineral, although some structural details remained to be clarified. In particular some of the components of the structure, including the supposed fluorosulphate ion, SO_3F^-, the Na^+ ion and its surrounding water molecules, appeared to be disordered and required further experimental work. We recently succeeded in obtaining improved X-ray data from an additional crystal fragment of better quality. The new data (i.e. those reported in the present work) prompted us to reconsider the earlier chemical analyses, which underestimated the Mg content and wrongly estimated the Na content. The error in the Na content was due to contamination by a Na-bearing admixed phase, which was not detected in the backscattered electron images. Unfortunately, our efforts to justify the presence of a site containing significant amounts of Na resulted in an incorrect interpretation of the corresponding portion of the crystal structure. The new interatomic distances and bond-valence calculations (see below) unquestionably show that the supposed Na site is occupied by Mg; the difference between the two is undetectable in electron density maps because Mg^{2+} and Na^+ are isoelectronic. Furthermore, the new and improved structure refinement allowed us to rule out the presence of a disordered fluorosulphate ion (see below), in favour of a hydrogensulphate ion, leading to the revised formula $(Mg_{0.5},\square)Al_6(SO_4)_6(HSO_4)F_6{\cdot}36H_2O$.

On the basis of this new interpretation, the structure of cossaite contains octahedral $[Al(H_2O)_5F]^{2+}$ and $[Mg(H_2O)_6]^{2+}$ cations, and sulphate and hydrogensulphate anions, arranged as shown in Fig. 2. The $[Al(H_2O)_5F]^{2+}$ cations are located in a general position of the unit cell, with an average Al−Ow distance of 1.887 Å; of these distances the longest is to Ow4 (1.8933(7) Å) i.e. with the water molecule more involved in hydrogen bonding. All the hydrogen atoms of the $[Al(H_2O)_5F]^{2+}$ cation have been unambiguously located and refined, so that the hydrogen bond pattern among different symmetry-related $[Al(H_2O)_5F]^{2+}$ cations and that of the same cations with the surrounding sulphate and hydrogensulphate anions is clearly established (Figs 3 and 4;

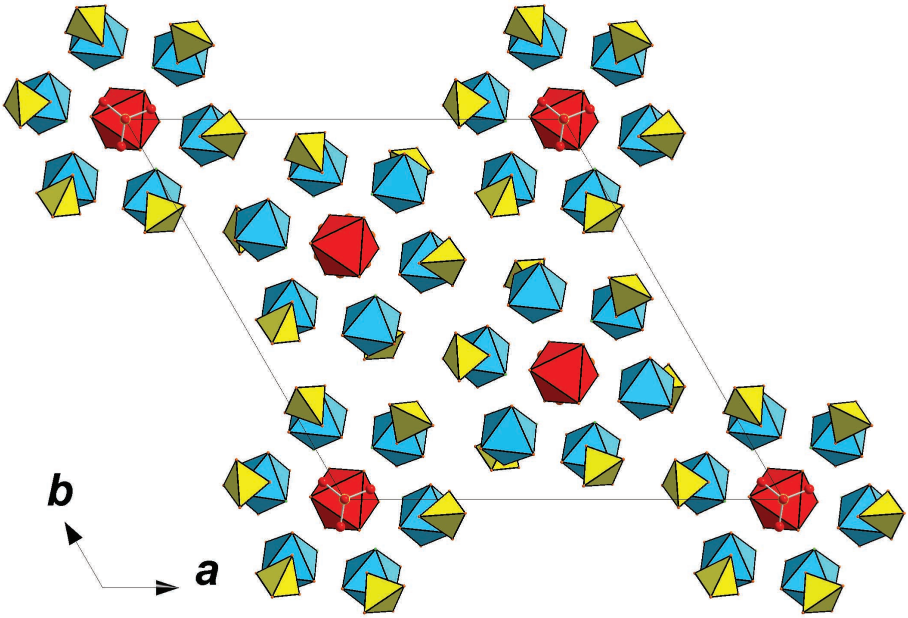

FIG. 2. A projection of the crystal structure of cossaite along [001]. The Al-centred polyhedra are shown in sky blue, the Mg-centred polyhedra in red and the sulphate ions in yellow. The hydrogensulphate anions (above or below the Mg polyhedra) are represented using sticks and balls (S is yellow, O is red).

Table 5). With the exception of O1, which is also hydrogen bonded to Ow6 (O1···Ow6 = 2.513(1) Å), all the remaining oxygen atoms of the sulphate anions are exclusively hydrogen bonded to the $[Al(H_2O)_5F]^{2+}$ cations. The resulting structure contains channels running along [001], where the $[Mg(H_2O)_6]^{2+}$ cations and the hydrogensulphate anions are hosted in a disordered manner. The former are located on $\bar{3}$ symmetry axes (Wyckoff position 3*b*) with an average occupancy of 0.5, so that these positions and their symmetry equivalents are either occupied or vacant along the channel. Due to partial occupancy and disorder, the (half) hydrogen atoms of the water molecule could not be located in the difference Fourier map. In addition to the O1···Ow6 hydrogen bond (see above), the short Ow6···F and Ow4···Ow6 distances (Table 5) indicate the presence of significant hydrogen bond interactions with the $[Al(H_2O)_5F]^{2+}$ cations, where Ow6 behaves as the donor atom. The Mg–Ow6 distance, 2.140(6) Å, is comparable to that in hydrated phyllosilicates such as talc (2.06–2.11 Å) and is much shorter than the shortest Na–O bond lengths observed in ionic compounds such as Na_2O (2.40 Å), showing that sodium is not present in significant amounts at the site. A bond valence calculation using the parameters reported by Brese and O'Keeffe (1991) produces a value of 1.80 v.u., which is reasonably close to the value expected for a divalent cation.

Contrary to our previous interpretation, the presence of a fluorosulphate anion was ruled out because the equivalent atomic displacement parameter of the O5 atom is reasonable and in line with those of the other atoms of the anion (Table 4). In the refinement where this atom was interpreted as being fluorine, the corresponding atomic displacement parameter was unusually large.

The hydrogensulphate anion is located close to a $\bar{3}$ symmetry element (Wyckoff position 3*a*) and disordered, the model of disorder consisting of

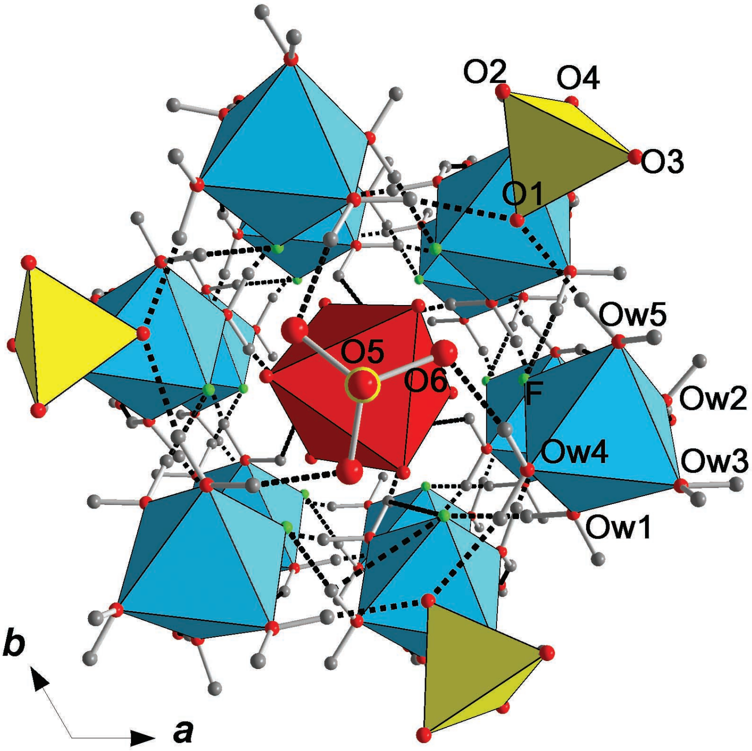

FIG. 3. A projection of the crystal structure of cossaite along [001] showing the channel containing the Mg^{2+} and HSO_4^- ions. The hydrogen bonds involving the hydrogen atoms located in the structure determination are shown as black dashed lines.

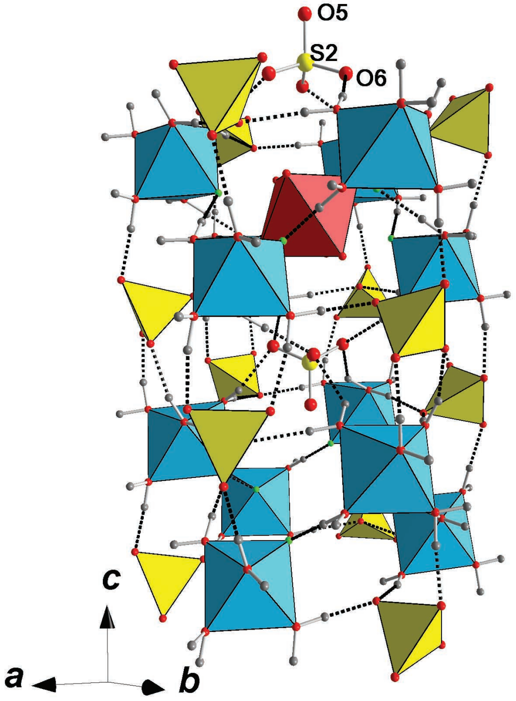

FIG. 4. A perspective view of the channel containing the Mg^{2+} and HSO_4^- ions. The hydrogen bonds involving the hydrogen atoms located in the structure determination are shown as black dashed lines.

two alternative orientations having an occupancy 0.5 is shown in Fig. 5*a*, with the S2 sulphur atom displaced from the 3*a* position by about 0.23 Å. If the S2 atom were placed exactly in the 3*a* position, unusual bond angles and anomalous anisotropic displacement parameters would result (Fig. 5*b*), clearly suggesting that the sulphur atom should be split into two positions. Of the two alternative orientations of the hydrogensulphate anion, only the one with the O5 atom pointing away from the $[Mg(H_2O)_6]^{2+}$ cation is acceptable (Fig. 4), otherwise too short a distance between O5 and Ow6 would result (2.379(2) Å). The HSO_4^- anion is hydrogen bonded to Ow4 with O···O distances of 2.824(1) and 2.623(1) Å. The electron density corresponding to the positions of the disordered (half) H atom belonging to the HSO_4^- anion is too weak to show up in the difference Fourier maps. Moreover, the interatomic S2–O5 and S2–O6 distances (Table 5) are not indicative of where protonation occurs. Although in ordered HSO_4^- anions the distance corresponding to the S–OH bond is longer than the other S–O bonds, typical values being close to 1.51–1.52 Å, compared to 1.44 Å for the unprotonated ones (Catti *et al*., 1979; Ferraris and Ivaldi, 1984; Hawthorne *et al*., 2000); in cossaite all four distances have an intermediate value of about 1.47 Å. This suggests that the proton of the HSO_4^- anion is disordered over four positions; the result of this disorder is that the observed S–O

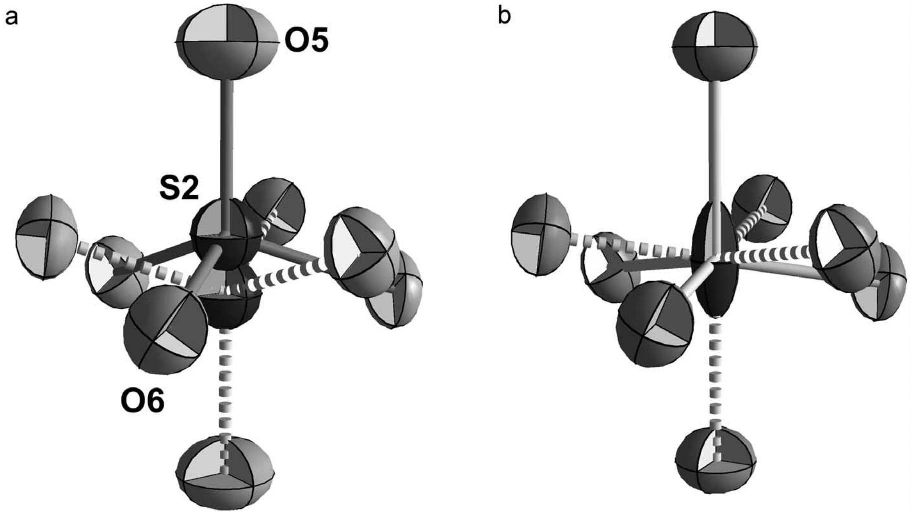

FIG. 5. The two orientations of the HSO_4^- anion: (*a*) S2 atom split into two positions; (*b*) S2 atom located on the 3*a* ($\bar{3}$) Wyckoff axes.

TABLE 5. Selected interatomic distances (Å) and angles (º) for cossaite.

Al−F	1.7468(5)	Al−Ow3	1.8865(5)
Al−Ow1	1.8848(6)	Al−Ow4	1.8933(7)
Al−Ow2	1.8840(6)	Al−Ow5	1.8853(6)
<Al−Ow>	1.887		
Mg−Ow6 ×6	2.140(1)		
S1−O1	1.4672(7)	S1−O3	1.4745(6)
S1−O2	1.4736(6)	S1−O4	1.4682(6)
<S1−O>	1.471	<O−S1−O>	109.47
S2−O5	1.470(3)	S2−O6 ×3	1.471(1)
		<O−S2−O>	109.47
Hydrogen bonds involving the H atoms located in the structure			
Ow1···O3^{i}	2.691(1)	Ow1−H1b···O3^{i}	160.9(6)
Ow1···F^{i}	2.696(1)	Ow1−H1a···F^{i}	176.5(5)
Ow2···O4	2.606(1)	Ow2−H2b···O4	167.5(5)
Ow2···O4^{ii}	2.640(1)	Ow2−H2a···O4^{ii}	175.6(4)
Ow3···O2^{iii}	2.696(1)	Ow3−H3b···O2^{iii}	166.0(4)
Ow3···O3^{iv}	2.629(1)	Ow3−H3a···O3^{iv}	169.0(4)
Ow4···O1^{v}	2.818(1)	Ow4−H4b···O1^{v}	168.3(5)
Ow5···O2^{iv}	2.708(1)	Ow5−H5b···O2^{iv}	160.7(5)
Ow5···O1^{vi}	2.690(1)	Ow5−H5a···O^{vi}	177.3(5)
Ow4···O6	2.824(1)	Ow4−H4a···O6	172.7(7)
Ow4···O6^{vii}	2.623(1)	Ow4−H4a···O6^{vii}	129.2(6)
Other proposed hydrogen bonds			
Ow6···F^{viii}	2.381(1)	Ow6···F^{ix}	2.804(1)
Ow6···F^{vii}	2.399(1)	Ow6···Ow4^{ix}	2.635(2)
Ow6···O1^{iv}	2.513(1)		

Symmetry codes: i = y−1/3, −x+y+1/3, −z+1/3; ii = −y+4/3, x−y+5/3, z−1/3; iii = −x+y−1/3; −x+4/3, z+1/3; iv = −y+4/3, x−y+5/3, z+2/3; v = x−y+4/3, x+2/3, −z+2/3; vi = −x+1/3, −y+5/3, −z+2/3; vii = y−1/3, −x+y+1/3, −z+4/3; viii = x, y,1+z; ix = x−y+2/3, x+1/3, 4/3−z.

distance is the weighted average of three S−O distances and one S−OH distance.

In spite of the strongly acid fluorine-rich environment in which cossaite crystallized, it is not a fluorosulphate, but rather a rare example of a mineral containing the hydrogensulphate ion. Other minerals which contain this group include mercallite [$KHSO_4$] (Payan and Haser, 1976), matteuccite [$NaHSO_4{\cdot}H_2O$] (Carobbi and Cipriani, 1952), letovicite [$(NH_4)_3H(SO_4)_2$] (Leclaire *et al.*, 1985) and probably misenite [$K_8(HSO_4)_6SO_4$] (Strunz and Nickel, 2001). It is worthwhile emphasizing that a satisfactorily low value of the *R* index does not guarantee that all of the essential details of a crystal structure involving light atoms are correct.

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