ALUMINOCOQUIMBITE, AlFe(SO$_4$)$_3$•9H$_2$O, A NEW ALUMINUM IRON SULFATE FROM GROTTA DELL'ALLUME, VULCANO, AEOLIAN ISLANDS, ITALY

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Abstract

Aluminocoquimbite, AlFe(SO$_4$)$_3$•9H$_2$O, is a new mineral species formed as a product of low-temperature (<100°C) fumarolic activity at Grotta dell'Allume (Alum Grotto), Vulcano, Aeolian Islands, Sicily, Italy. It occurs as colorless to pale pink tabular or short prismatic crystals up to 0.5 mm in size in association with alunogen, coquimbite, krausite, tamarugite, voltaite, pertlikite, yavapaiite, pickeringite and metavoltine. The mineral is trigonal, space group $P\bar{3}1c$ (no. 163), with *a* 10.7065(7), *c* 17.3077(11) Å, *V* 1718.2(2) Å^3 and *Z* = 4. The strongest six reflections in the X-ray powder-diffraction pattern [d_{obs} in Å(*I*)(*hkl*)] are: 9.251(100)(010), 5.310(83)(110), 3.152(43)($\bar{2}$24), 4.087(33)(022), 1.765(20)($\bar{5}$53), and 2.112(17)($\bar{2}$51). Chemical analyses yielded the empirical formula Al$_{1.07}$Fe$_{0.92}$S$_{2.92}$H$_{18.49}$O$_{21}$. The simplified formula is AlFe(SO$_4$)$_3$•9H$_2$O. The measured density is 2.03(1) g/cm^3, and the calculated density is 2.044 g/cm^3. The mineral is uniaxial (+), with ω = 1.53 and ε = 1.56 (589 nm). Using single-crystal diffraction data, the structure was refined to a final *R(F)* = 0.0218, and *wR*2 = 0.0685. The structure of aluminocoquimbite is different from that of coquimbite, and contains isolated Al(H$_2$O)$_6$ octahedral units and infinite [Fe(SO$_4$)$_3$]$_\infty$ columns running along [001], consisting of octahedrally coordinated iron atoms and sulfate ions, similar to those observed in ferrinatrite, Na$_3$(H$_2$O)$_3$[Fe(SO$_4$)$_3$]. Interstitial H$_2$O molecules are arranged in a cyclohexane-like chair conformation held together by hydrogen bonding, as in the structure of coquimbite.

Keywords: aluminocoquimbite, new mineral species, crystal structure, coquimbite, iron sulfates, Vulcano island, Italy.

Sommaire

L'aluminocoquimbite, AlFe(SO$_4$)$_3$•9H$_2$O, est une nouvelle espèce minérale formée à faible température (<100°C) suite à une altération fumerollienne à Grotta dell'Allume (grotte d'alum), Vulcano, îles Aéoliennes, en Sicile, Italie. Elle se présente en cristaux incolores ou rose pâle, tabulaires ou prismatiques trappus, atteignant 0.5 mm. Lui sont associées alunogène, coquimbite, krausite, tamarugite, voltaïte, pertlikite, yavapaïte, pickeringite et métavoltine. Il s'agit d'un minéral trigonal, groupe spatial $P\bar{3}1c$ (no. 163), avec *a* 10.7065(7), *c* 17.3077(11) Å, *V* 1718.2(2) Å^3 et *Z* = 4. Les six raies les plus intenses du spectre de diffraction (méthode des poudres) [d_{obs} en Å(*I*)(*hkl*)] sont: 9.251(100)(010), 5.310(83)(110), 3.152(43)($\bar{2}$24), 4.087(33)(022), 1.765(20)($\bar{5}$53), et 2.112(17)($\bar{2}$51). Les analyses chimiques ont donné la formule empirique Al$_{1.07}$Fe$_{0.92}$S$_{2.92}$H$_{18.49}$O$_{21}$. La formule simplifiée est AlFe(SO$_4$)$_3$•9H$_2$O. La densité mesurée est égale à 2.03(1) g/cm^3, et la densité calculée, 2.044 g/cm^3. Le minéral est uniaxe (+), avec ω = 1.53 et ε = 1.56 (589 nm). En utilisant les données obtenues sur monocristal, la structure a été affinée jusqu'à un résidu final *R(F)* de 0.0218 (*wR*2 = 0.0685). La structure de l'aluminocoquimbite diffère de celle de la coquimbite; elle contient des octaèdres Al(H$_2$O)$_6$ isolés et des colonnes [Fe(SO$_4$)$_3$]$_\infty$ infinies parallèles à [001] contenant des atomes de fer en coordination octaédrique et des groupes sulfate, semblables à ceux rencontrés dans la ferrinatrite, Na$_3$(H$_2$O)$_3$[Fe(SO$_4$)$_3$]. Des molécules de H$_2$O interstitielles définissent une conformation en chaise rappelant le cyclohexane; elles sont interliées par liaisons hydrogène, tout comme dans la structure de la coquimbite.

(Traduit par la Rédaction)

Mots-clés: aluminocoquimbite, nouvelle espèce minérale, structure cristalline, coquimbite, sulfates de fer, île de Vulcano, Italie.

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Introduction

The fumaroles located at La Fossa crater at Vulcano, Aeolian Islands, Italy, are a source of many interesting and new minerals, mainly halides (fluorides, chlorides) and bismuth sulfides and sulfosalts, together with abundant native sulfur and boric acid (see, for instance, Demartin *et al.* 2010a, 2010c, 2010d, and references therein). There are, however, other sites on this island, which are instead especially rich in sulfates, a few of them being very rare. Among these sites, close to the harbor and near the "Faraglione di Levante", there is Grotta dell'Allume (Alum Grotto), a cavity whose walls are completely encrusted by sulfates, and which partially collapsed in the 1940s. Here, as a result of our systematic investigation of the mineralogical species from Vulcano, a new aluminum iron sulfate related to coquimbite but with a different crystal-structure was found. The new species, named *aluminocoquimbite* after the composition and structural relationships to coquimbite, $Fe_2(SO_4)_3 \cdot 9H_2O$, is described in the present work. The mineral and the mineral name were approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2009–095). The holotype material is deposited in the Reference Collection of the Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università degli Studi di Milano, specimen number 2009–03.

Occurrence, Chemical Data and Physical Properties

Aluminocoquimbite occurs as a product of low-temperature (<100°C) fumarolic activity. It forms colorless to pale pink tabular or short prismatic crystals up to 0.5 mm in size (Fig. 1), in association with alunogen, coquimbite, krausite, tamarugite, voltaite, pertlikite, yavapaiite, pickeringite and metavoltine. The prevailing forms of the crystals are the pinacoid and hexagonal prisms of first and second order. No twinning is apparent. The *c:a* ratio calculated from the unit-cell parameters is 1.617. The mineral is not hygroscopic and is stable in open air. The streak is white, and the luster is vitreous. The cleavage is imperfect on {101}. No fluorescence was observed both under short-wave and long-wave ultraviolet radiation.

The density measured by flotation in a toluene–CH_2I_2 mixture is 2.03(1) g/cm³; that calculated corresponding to the empirical formula and to the X-ray data is 2.044 g/cm³. The mineral is uniaxial (+) with $\omega = 1.53$ and $\varepsilon = 1.56$ (589 nm); the average index of refraction calculated using Mandarino's constants (1981) is 1.540, leading to a compatibility index $[1 - (K_P/K_C)] = -0.039$ (excellent).

A micro-FTIR spectrum was acquired (64 accumulations) by means of a Jasco IRT–3000 spectrometer, after placing the sample in a compression diamond cell; the spectrometer has a resolution of 4 cm^{-1}. The sampled area was 50×50 μm². The spectrum shows clear features at 1149, 1096, 1034 and 943 cm^{-1} related to the SO_4^{2-} stretching modes; other absorptions at 1660, 867 and 705 cm^{-1} might be related to H_2O bending modes. Absorptions at 3040, 3388, 3675 cm^{-1} are consistent with H_2O stretching modes; a broad band at about 2530 cm^{-1} could be related to the presence of strong hydrogen bonds (Petch *et al.* 1956).

Quantitative chemical analyses (11) were carried out in an energy-dispersion mode (EDS) using a JEOL JSM 5500 LV scanning electron microscope equipped with an IXRF EDS 2000 detector at an excitation voltage of 20 kV, a beam current of 10 pA, and a beam diameter of 2 μm. Element concentrations were measured using the $K\alpha$ lines for Fe, Al, and S. The mean analytical results are reported in Table 1. We estimated the H_2O content by difference, as no thermogravimetric methods could be used, owing to the scarcity of the material available. The empirical formula (based on 21 O atoms) is $Al_{1.07}Fe_{0.92}S_{2.92}H_{18.49}O_{21}$; the simplified formula is $AlFe(SO_4)_3 \cdot 9H_2O$, which requires Fe_2O_3 14.98, Al_2O_3 9.58, SO_3 45.04, H_2O 30.40, total 100.00 wt%.

X-Ray Data and Crystal Structure of Aluminocoquimbite

The X-ray powder-diffraction data were obtained using a Philips PW1100 diffractometer (Cu$K\alpha$; Table 2) under the following conditions: step width 0.02°, time per step 5 s, divergence slit 0.25°, Soller slit 0.04 rad, antiscatter slit 0.5°. The unit-cell parameters, refined from the powder data (Holland & Redfern 1997), are *a* 10.7078(7), *c* 17.3033(18) Å and *V* 1718.1(2) Å³; they compare well with those obtained from the single crystal: *a* 10.7065(7), *c* 17.3077(11) Å, *V* 1718.2(2) Å³. The symmetry is trigonal, space group $P\bar{3}1c$ (no. 163).

The crystal structure of aluminocoquimbite was solved and refined from single-crystal X-ray data to a final *R* and *wR*2 (all data) of 0.0218 and 0.0685, respectively; these results are reported in Demartin *et al.* (2010b), together with a detailed discussion on the structure. It is different from that of coquimbite and paracoquimbite (Robinson & Fang 1971, Fang & Robinson 1970, 1974, Majzlan *et al.* 2006, 2010), as it contains two independent octahedrally coordinated

TABLE 1. CHEMICAL COMPOSITION OF ALUMINOCOQUIMBITE

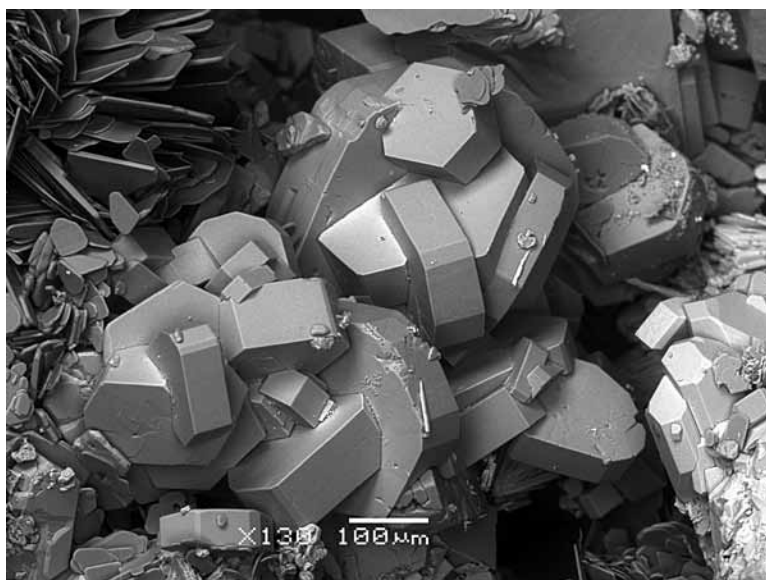| Constituent	wt.%	Range	e.s.d.	Probe standard
Fe_2O_3	13.96	13.49 – 14.30	0.1	coquimbite
Al_2O_3	10.30	9.80 – 10.78	0.2	coquimbite
SO_3	44.24	43.13 – 45.72	0.2	coquimbite
H_2O	31.50*			
Total	100.00			

* By difference.

Fig. 1. SEM–BSE image of crystals of aluminocoquimbite, associated with tamarugite (platy crystals, top left) and yavapaiite (light gray crystals, right).

iron atoms exclusively linked to the oxygen atoms of the sulfate ions, $Al(H_2O)_6$ isolated units and interstitial H_2O molecules. The site-occupancy refinement shows that the two iron positions are occupied exclusively by this element, and the Al site, by aluminum only. Iron-centered octahedra are connected to the sulfate tetrahedra by corner-sharing and alternate to form infinite columns along [001], similar to those observed in ferrinatrite, $Na_3(H_2O)_3[Fe(SO_4)_3]$ (Scordari 1977, Scordari & Ventruti 2009) and in pyracmonite (Demartin *et al.* 2010d). These columns are joined through hydrogen-bond interactions with the octahedral $Al(H_2O)_6$ units, which are located at about $z = 0, 1/2, 1$. As a result, the structure displays cages centered at about $z = \frac{1}{4}$ and $\frac{3}{4}$, which are occupied by six H_2O molecules arranged in a cyclohexane-like chair held together by hydrogen bonds. Additional hydrogen bonds involving these H_2O molecules are formed with the surrounding sulfate ions, whose oxygen atoms are lone-pair donors, and with the Al-coordinated H_2O molecules, whose hydrogen atoms are lone-pair acceptors.

CONCLUSIONS

The chemical composition of coquimbite can deviate significantly from the traditional formula $Fe_2(SO_4)_3 \cdot 9H_2O$ because of appreciable concentration of aluminum at the *2b* site, with Al/(Al + Fe) values at least up to 0.25 (Robinson & Fang 1971, Fang & Robinson 1970, Majzlan *et al.* 2006, Demartin *et*

TABLE 2. X-RAY POWDER-DIFFRACTION DATA
FOR ALUMINOCOQUIMBITE

I/Io	d_{obs}	d_{calc}*	h	k	l	I/Io	d_{obs}	d_{calc}*	h	k	l
100	9.251	9.273	0	1	0	4	2.509	2.515	$\bar{3}$	3	4
13	8.710	8.652	0	0	2	5	2.451	2.463	1	2	5
83	5.310	5.354	1	1	0	5	2.442	2.449	$\bar{2}$	2	6
9	4.550	4.553	1	1	2	4	2.285	2.276	$\bar{2}$	$\bar{2}$	4
5	4.350	4.326	0	0	4	4	2.222	2.227	1	2	6
33	4.087	4.087	0	2	2	5	2.196	2.181	0	2	7
9	3.638	3.614	0	2	3	17	2.112	2.111	$\bar{2}$	5	1
13	3.365	3.365	$\bar{2}$	1	4	4	1.965	1.962	$\bar{2}$	4	6
4	3.509	3.505	$\bar{1}$	3	0	3	1.819	1.812	$\bar{2}$	5	5
43	3.152	3.163	$\bar{2}$	2	4	3	1.807	1.807	0	4	6
2	3.051	3.043	$\bar{3}$	3	1	5	1.783	1.782	1	3	7
3	3.011	3.091	0	3	0	20	1.765	1.766	$\bar{5}$	5	3
7	2.876	2.884	0	0	6	6	1.727	1.718	$\bar{6}$	2	2
6	2.753	2.754	0	1	6	3	1.700	1.705	0	5	4
10	2.732	2.724	0	3	3	4	1.686	1.686	$\bar{1}$	3	9
11	2.530	2.539	$\bar{1}$	2	6	4	1.678	1.677	$\bar{2}$	6	3
						3	1.626	1.624	2	4	4

* Calculated from the unit-cell: *a* 10.7078(7), *c* 17.3033(18) Å, obtained from least-squares refinement from the above data using the program UNITCELL (Holland & Redfern 1997).

al. 2010b). However, to attain a higher Al content, a structural rearrangement must occur, leading to the new mineral *aluminocoquimbite*, in which this ratio is 0.5 (Demartin *et al.* 2010b). Structural changes related to a variation in composition at the octahedral sites have also been observed for other sulfates of ferric iron, such

as those in the copiapite group (Majzlan & Michallik 2007), and can also be expected in other open structures.

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