Eur. J. Mineral.
1993, **5**, 1167-1174

Rosenbergite, $AlF[F_{0.5}(H_2O)_{0.5}]_4.H_2O$, a new mineral from the Cetine mine (Tuscany, Italy): description and crystal structure

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Abstract: Rosenbergite is a new aluminium fluoride mineral from the Cetine mine, Tuscany, Italy. It occurs as radiating tufts of slender tetragonal crystals, elongated parallel to [001], in cavities in a highly silicified limestone. The crystals are colourless and transparent, with a vitreous lustre. Associated minerals are gypsum, fluorite, elpasolite, ralstonite and onoratoite. Electron microprobe analysis (water by difference) gives $Al_{1.02}F_{2.98}.2.99H_2O$ (simplified formula $AlF_3.3H_2O$). Optically uniaxial (-) with $\epsilon = 1.403$ and $\omega = 1.427$; VHN_{15} microhardness 103; $d_{calc} = 2.111$ g/cm^3; $d_{meas} = 2.10(1)$g/cm^3. The unit cell is tetragonal $a = 7.715(1)$, $c = 3.648(1)$Å, space group $P4/n$ and $Z = 2$. The strongest lines in the X-ray Gandolfi pattern are (d_{obs}, I, hkl) 5.47(100)(110), 2.439(72)(130), 2.027(70)(131), 1.775(78)(012), 1.725(85)(240), 1.306(70)(142). The IR spectrum is also given. The mineral is named for P.E. Rosenberg of Washington State University, U.S.A.

The crystal structure was refined to an R index of 0.0186, using a set of 245 observed (16 σ) reflections ($R = 0.0276$ for all 316 collected reflections). The structure consists of chains of corner-linked $Al[F_4(H_2O)_2]$ octahedra running parallel to [001] and isolated water molecules. A dense network of hydrogen bonds strongly connects the Al-F chains. The structural formula is $AlF[F_{0.5}(H_2O)_{0.5}]_4.H_2O$.

Key-words: rosenbergite, new mineral, aluminium fluoride, crystal structure, Cetine mine (Italy).

Introduction

The existence of a synthetic crystalline form of aluminium trifluoride trihydrate has been known for many years (Ehret & Frere, 1945). Recently, the corresponding natural phase has been identified in volcanogenic encrustations at Mount Erebus, Antarctica, among other aluminium fluorides (Rosenberg, 1988): the poor quality of the crystals prevented a complete description of the mineral.

During visits to the Cetine mine, the mineral collectors A. Rossellini and, at a later date, V. Santoni found a few specimens of an unknown mineral, which they brought to our attention. This mineral has the same powder diffraction pattern and the same chemical composition as Rosenberg's mineral.

We are pleased to name the new mineral rosenbergite in honour of Prof. P.E. Rosenberg of Washington State University, U.S.A., in recognition of his first description of the species. The new mineral and name have been approved by the I.M.A. Commission on New Minerals and Mineral Names. A type specimen is preserved at the Museum of Natural History of the University of Florence, under the catalogue number 1934/RI.

A single-crystal structure refinement of rosenbergite, based on the structure determined

0935-1221/93/0005-1167 $ 1.75

by Teufer (1964) for the analogous $FeF_3.3H_2O$ compound, was also carried out as a contribution to the crystal chemistry of aluminium fluoride minerals.

Occurrence

The Cetine mine is located approximately 20 km southwest of Siena, on the far eastern flank of the Colline Metallifere. It is an antimony deposit described as an epigenetic mineralization related to a late phase of the Pliocene-Pleistocene Apennine magmatism. At its base, the local geological succession comprises quartzitic/phyllitic terrains of the so-called Tuscan basement, which are Paleozoic to Triassic in age. These are overlain by a strongly weathered Triassic evaporite formation known as the "Calcare Cavernoso". The ore at the Cetine mine consists of stibnite in small pods disseminated within this highly silicified limestone.

The area is a known site for mineral collectors, because numerous sulphate minerals (such as uklonskovite, jurbanite, rostite, tamarugite, ferrinatrite, sideronatrite), as well as an interesting suite of rare stibnite alteration minerals (such as cetineite, peretaite, klebelsbergite, onoratoite), occur in the mine. Sabelli & Brizzi (1984) have provided detailed information on the underground workings and the mineral assemblages of the mine.

Rosenbergite seems to be very rare at this locality. Despite a careful examination of numerous specimens under a stereomicroscope, only small amounts of the new mineral were found in a few specimens. Rosenbergite occurs in cavities of the "Calcare Cavernoso" limestone, in association with gypsum, fluorite, elpasolite, ralstonite, and onoratoite. The crystals occur as more or less slender tetragonal prisms, up to 0.25 mm in length, grouped as small aggregates (Fig. 1).

The rosenbergite found at Cetine may have formed through the action of F-rich water solutions during the intense hydrothermal activity that affected the locality.

X-ray crystallography

The X-ray powder diffraction pattern of rosenbergite, given in Table 1, was obtained by means of a Gandolfi camera (114.6 mm diameter) using Cu*K*α radiation in the 16-105° 2θ range. Indexing was performed taking the intensities of reflections collected for the structural study into account. The data are in good agreement with those obtained by Ehret & Frere (1945) and Freeman (1956) on synthetic β-$AlF_3.3H_2O$, and in excellent agreement with those given by

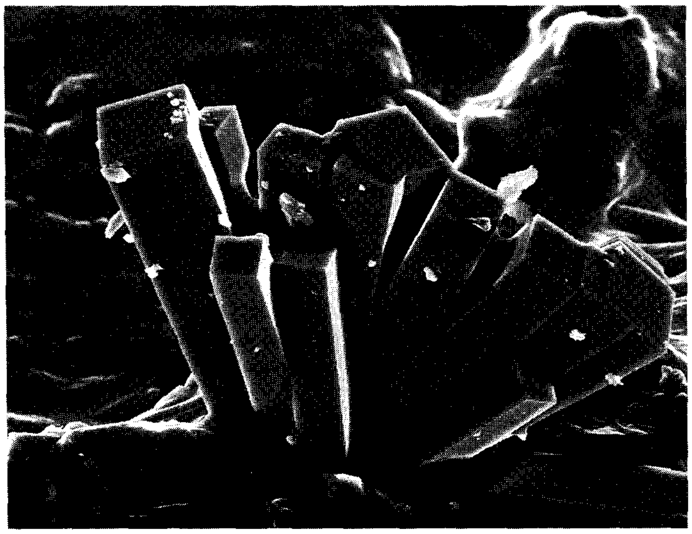

Fig. 1. Electron micrograph of a tuft of tetragonal crystals (length 0.2 mm) of rosenbergite.

Table 1. X-ray powder diffraction data for rosenbergite.

h k l	d_{calc}	d_{obs}	I/I_o
1 1 0	5.455	5.47	100
2 0 0	3.857	3.86	60
0 0 1	3.648	3.65	45
0 1 1	3.298	3.30	63
1 1 1	3.032	3.03	62
2 2 0	2.728	2.728	63
2 0 1	2.651	2.647	57
2 1 1	2.507	2.506	58
1 3 0	2.440	2.439	72
2 2 1	2.185	2.185	36
3 0 1	2.102	2.102	17
1 3 1	2.028	2.027	70
4 0 0	1.929	1.928	60
2 3 1	1.846	1.845	55
3 3 0	1.818	1.820	38
0 1 2	1.775	1.775	78
2 4 0	1.725	1.725	85
1 4 1	1.665	1.665	42
3 3 1	1.627	1.626	10
1 2 2	1.613	1.613	50
2 4 1	1.560	1.559	30
5 1 0	1.513	1.513	43
3 0 2	1.488	1.487	13
1 3 2	1.461	1.460	18
3 4 1	1.421	1.420	15
5 1 1	1.398	1.397	10
2 3 2	1.388	1.388	65
4 4 0	1.364	1.362	10
5 2 1	1.334	1.333	47
5 3 0	1.323	1.323	25
1 4 2	1.306	1.306	70
3 3 2	1.288	1.290	15
6 0 0	1.286		
5 3 1	1.244	1.244	29
6 2 0	1.220	1.221	60
1 0 3	1.201	1.198	15
6 1 1	1.198		
5 0 2	1.178	1.178	55
3 4 2	1.178		
6 2 1	1.157	1.156	10
5 2 2	1.127	1.127	65
6 3 1	1.097	1.096	12
3 1 3	1.088	1.089	15
6 4 0	1.070	1.070	25
2 3 3	1.057	1.057	8
6 1 2	1.041	1.041	28
3 7 0	1.013	1.013	18
2 4 3	0.994	0.994	25
6 3 2	0.973	0.973	35

Rosenberg (1988) for the Antarctic mineral. The unit cell of rosenbergite is tetragonal with a = 7.715(1) and c = 3.648(1) Å, derived from the Gandolfi data by means of least squares calculations; these values are slightly smaller than those given by Freeman (1957) and Rosenberg (1988). The systematic extinctions ($hk0$, $h + k = 2n + 1$) and the Laue group $4/m$ derived from single crystal data lead to the space group $P4/n$ (the space group $P4/ncc$ reported in the JCPDS card 35-827 is due to the doubled c parameter adopted for indexing the pattern).

Chemical, physical and optical properties

Rosenbergite was analyzed with a Jeol JXA-8600 electron microprobe (operating conditions: 6 kV accelerating voltage, 10 nA beam - Faraday cup - current, and 20 μm diameter defocused beam). Elpasolite, K_2NaAlF_6, was used as a standard. Elements other than Al and F were not detected in a preliminary energy-dispersion scan. The results of analyses (five different spots on two grains) are Al 19.94 and F 41.05 wt.%. Because the amount of material available was insufficient for a direct determination, a value of H_2O 39.01 wt.% was assigned by difference. On the basis of Al + F = 4, the formula is $Al_{1.02}F_{2.98}.2.99H_2O$, which is in accordance with that derived from the crystal structure determination: $AlF[F_{0.5}(H_2O)_{0.5}]_4.H_2O$. The infrared absorption spectrum (Fig. 2) was recorded on a Perkin Elmer FTIR 1760X spectrophotometer in the region 550-4000 cm^{-1} using a KBr micropellet. The absorptions in the 3400/3100 and 1700 cm^{-1} regions indicate the presence of structural water in the mineral.

The crystals are colourless and transparent, and have a vitreous lustre and good (001) cleavage. They have a hardness of VHN 103 (average of 5 determinations with a 15-g indentor; range 92-113; standard deviation 7). The observed density, determined by the sink-float method in a mixture of tetrabromoethane and 1:2-dibromopropane, is 2.10(1) g/cm^3; the calculated density is 2.111 g/cm^3. The mineral does not fluoresce under long- or short-wave ultraviolet light.

Optically, rosenbergite is uniaxial negative, and has low dispersion. The refractive indices, ϵ = 1.403 and ω = 1.427, were measured by immersion in H_2O diluted glycerol, with an Eickhorst gemmological refractometer. The Gladstone-Dale relationship gives Kp = 0.1985 and

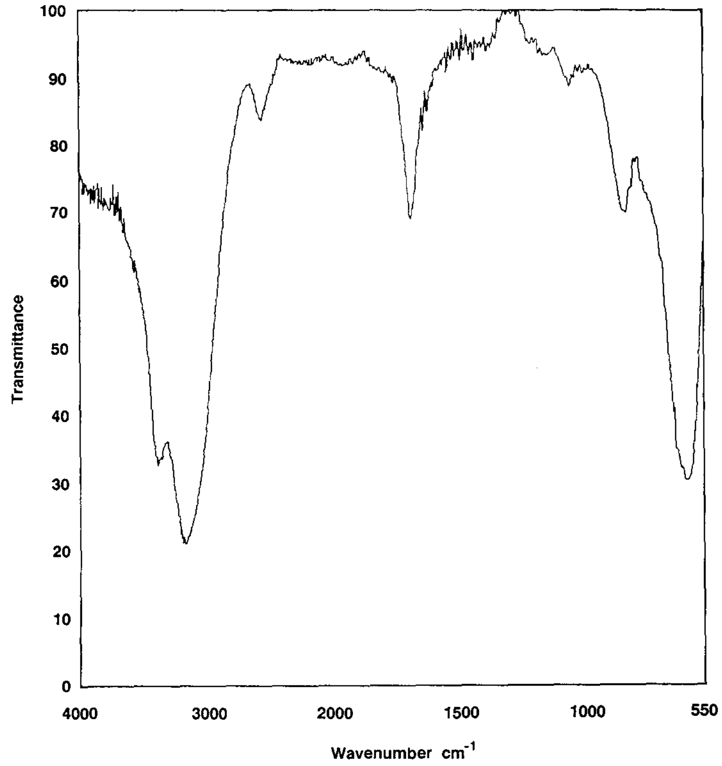

Fig. 2. Infrared absorption spectrum of rosenbergite.

Kc = 0.1976 (K values for fluorides from Pauly, 1982), with a superior compatibility index 1 - (Kp/Kc) = - 0.0045 (Mandarino, 1981).

Crystal structure refinement and discussion

A crystal not exceeding 0.2 mm in length was chosen for data acquisition using an Enraf Nonius CAD-4 diffractometer, with graphite-monochromatized Mo$K\alpha$ radiation. 1445 reflections were measured in the range $2° < \theta < 30°$, using the ω - θ scan technique. From a total of 316 independent reflections, 245 were considered observed on the basis of $Fo > 16\sigma(Fo)$. The R-factors from the counting statistics (after merging) were 0.026 and 0.031 for observed and all reflections, respectively. Semi-empirical absorption (North *et al.*, 1968) and Lp corrections were applied. Neutral atomic scattering factors were taken from the International Tables for X-ray Crystallography (1974).

The structure determined by Teufer (1964) for the synthetic $FeF_3.3H_2O$ was used as a starting point for the location of the Al, F, and O atoms in rosenbergite. The program used for least-squares refinement was a local version of ORFLS (Busing *et al.*, 1962). The refinement with isotropic temperature factors converged to a R index (defined as $R = \Sigma \mid \mid Fo \mid - \mid Fc \mid \mid / \Sigma \mid Fo \mid$) of 0.075. A weight $w = 1/\sigma^2(Fo)$ was given to the observed reflections (zero weight for "unobserved" ones). A difference electron density map calculated at this stage gave an indication of the positions in which the H atoms might be expected and also of the variation in site occupancies. The introduction of the H atoms and the site occupancies into the anisotropic refinement (isotropic for H atoms) lowered the R index to a value of 0.0167 for the observed reflections. Despite the excellent convergence reached by the full refinement, the freely refined hydrogen positions were not entirely reliable. For this reason the hydrogen atoms were placed in calculated positions (with fixed B = 3 Å^2), at about 0.9 Å

Table 2. Fractional atomic coordinates and anisotropic thermal parameters (isotropic for hydrogen atoms). Bond distances and angles.

	Occ.	x	y	z	$B_{eq.}$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	1.0	1/4	1/4	0.1396(2)	0.88	404(6)	404	1336(40)	0	0	0
F	1.0	1/4	1/4	0.6384(3)	1.98	1099(16)	1099	1328(86)	0	0	0
O(1)	1.0	3/4	1/4	1/2	1.41	537(17)	537	3145(130)	0	0	0
O(2)	0.5	0.4652(1)	0.3484(1)	0.1366(2)	1.91	553(12)	776(13)	4833(67)	-145(9)	-312(24)	692(24)
H(1)	0.5	0.655	0.283	0.379	3.00						
H(2)	0.5	0.488	0.449	0.046	3.00						
H(3)	0.5	0.560	0.315	0.258	3.00						

Octahedral bond distances		Hydrogen bridges		Water angles	
Al-F	1.819(1) and 1.828(1) Å	O(1)-O(2)	2.675(1) Å	O(2)-O(1)-O(2)"	104.21(2)°
Al-O(2) (x4)	1.825(1) Å	O(2)-O(2)'	2.600(1) Å	O(1)-O(2)-O(2)'	106.01(4)°

Anisotropic temperature factors (x 10^5) are in the form $\exp-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)$.
$B_{eq.}$ ($Å^2$) = $4/3\ \Sigma_i\Sigma_j\beta_{ij}a_ia_j$.

from their donors. With hydrogens in these positions, the final *R* index for the observed reflections is 0.0186 (*R* = 0.0276 for all data). Final atomic parameters, together with bond distances and angles, are given in Table 2. A list of observed and calculated structure factors may be obtained on request from the authors or through the E.J.M. Editorial Office.

The [001] projection of the structure of rosenbergite is given in Fig. 3. The $Al[F_4(H_2O)_2]$ octahedra are corner-linked in chains along the 4-fold axes, perpendicular to the figure. The free water molecule has the O(1) oxygen in the $\bar{4}$ position. Because of the symmetry, the four surrounding H(1) hydrogens, present at a 50% occupancy level, assume a tetrahedral arrangement around the O(1) donor. The O(2) structural site is a disordered site because it is calculated as being occupied by the oxygen of the ligand water molecule and by a fluorine atom in equal proportions. According to this, the refinement indicates occupancies of 50% also for the H(2) and H(3) sites. The network of hydrogen bonds provides a strong connection among the Al-F chains. The projection shown in Fig. 4 gives two Al-F chains and the free water molecules.

In the Al-octahedron, there are two Al-F distances, 1.819 and 1.828 Å (which fall within the typical range of 1.80-1.86 Å for the Al-F bond), and four Al-O(2) bond distances of 1.825 Å. This last value is very close to the previous Al-F bond values, even though water oxygens are statistically present in the O(2) sites at a 50% occupancy level. Because the Al atom is 0.01 Å out of the four O(2) plane, the octahedral bond angles differ slightly from 90 and 180°.

As already mentioned, the refined positions of the H atoms were not entirely satisfactory. Indeed, only H(3) was 0.95 Å away from its donor O(2), an acceptable O-H distance for a

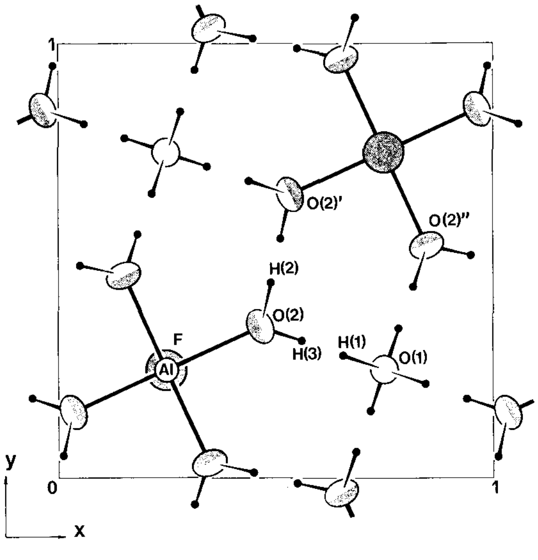

Fig. 3. [001] projection of the structure of rosenbergite. The black-and-white O(2) sites indicate 0.5 F + 0.5 H_2O occupancy. Ellipsoids are scaled at the 50% probability level.

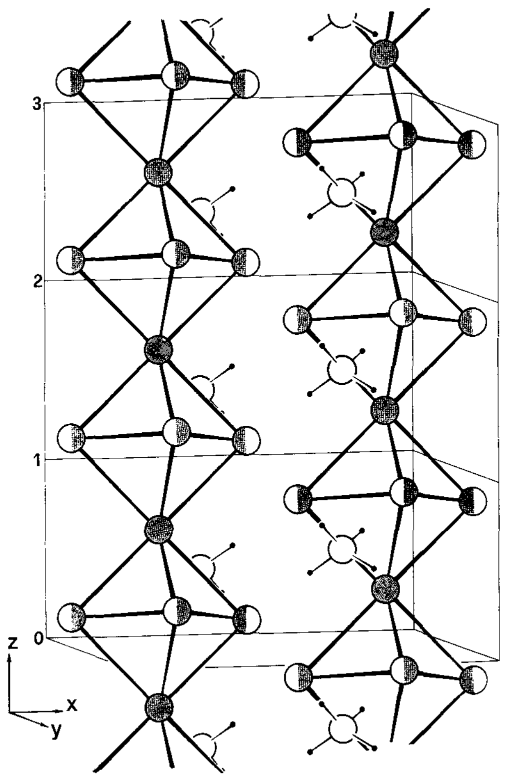

Fig. 4. A projection of the structure of rosenbergite through three unit-cells. For clarity, the H atoms of the ligand water molecules are not shown.

water molecule (Chiari & Ferraris, 1982), whereas H(1) and H(2) were much too close, about 0.7 and 0.8 Å, from O(1) and O(2), respectively.

The hydrogen atoms H(2) and H(3) are clearly present only when their oxygen donor in the O(2) site is also present (at 50% occupancy); in this case O(1) and fluorine in the O(2)' site are acceptors (Fig. 3). Alternatively, when the fluorine atom occupy the O(2) site, H(1) and the centrosymmetric equivalent of H(2) are present at that moment, the fluorine atom becomes an acceptor, while the O(1) and O(2)' water oxygens act in their turn as donors. In such a way, in agreement with the refinement results, all the hydrogen sites are 50% occupied. This H-bond pattern is supported by the valence balance (Table 3), computed according to Brown & Altermatt (1985) for Al-O bonds and to Ferraris & Ivaldi (1988) for H bonds.

The two water angles (Table 2, Fig. 3) are 104.21° for the O(1) water molecule (whose acceptors are both O + F atoms), and 106.01° for the O(2) molecule (with one O and one O + F as acceptors atoms). These values are in accordance with those reported in the review of water molecule geometry by Chiari & Ferraris (1982). Indeed, the smaller value found in rosenbergite is close to the 103.6° average value that, according to these authors, characterizes the molecules with F acceptors, while the greater value approximates 108.3°, the average value given for O acceptors.

On the basis of the classification of the aluminofluoride minerals by Hawthorne (1984), rosenbergite represents, from a topological point of view, the first known example of a corner-linked chain mineral. The good (001) cleavage observed would seem in contrast with the atomic arrangement of the structure. Evidently, the cleavage is due to the presence of very strong hydrogen bonds, which provide a solid connection of the chains to one another. Therefore, the structure, which topologically appears to be a chain structure, can actually be considered as a sheet structure.

The structural arrangement of rosenbergite differs from that of ralstonite ($Na_xMg_xAl_{2-x}(F,OH)_6.H_2O$, cubic with a = 9.91Å), which is an associated mineral in both the Cetine mine and

Table 3. Electrostatic valence balance for rosenbergite.

		Al	H(1)	H(2)	H(3)	Sum
O(1)	100% H_2O	-	0.38	-	0.12	0.50 (x4)
O(2)	50% H_2O	0.50	-	0.34	0.38	0.97
	50% F		0.12	0.14	-	0.51
F		0.51+0.49	-	-	-	1.00

the Antarctic encrustations (Rosenberg, 1988). Due to the lower grade of hydration, the structure of ralstonite, which is built on an Al-F corner-sharing framework (Effenberger & Kluger, 1984), is clearly more condensed. A similar framework might characterize the structure of the aluminium fluoride monohydrate (also found with rosenbergite and ralstonite in Antarctica), which could be regarded as a ralstonite-like mineral. At Cetine, ralstonite and rosenbergite probably represent two different sets of conditions during the intense hydrothermal activity that affected the locality.

Acknowledgements: We would like to thank A. Rossellini and V. Santoni, two mineral collectors of the A.M.F. mineralogical group in Florence, for providing the specimens of rosenbergite for investigation, and M.Camaiti for the IR spectrum at the CNR-Centro di studio sulle cause di deperimento e sui metodi di conservazione delle Opere d'Arte, Florence.

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Received 18 March 1993
Accepted 23 June 1993