

Coquandite, $\text{Sb}_6\text{O}_8(\text{SO}_4)\cdot\text{H}_2\text{O}$, a new mineral from Pereta, Tuscany, Italy, and two other localities

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Abstract

Coquandite, a new antimony oxy-sulphate hydrate, occurs as spheroidal knobs of silky fibres or, rarely, as tiny transparent colourless lamellar crystals on stibnite at the Pereta mine, Tuscany, Italy; it is associated with klebelsbergite, peretaite, valentinite, sulfur, gypsum, stibiconite, and senarmontite. Coquandite is triclinic $P\bar{1}$, with a 11.434(7), b 29.77(4), c 11.314(4) Å, α 91.07(7)°, β 119.24(3)°, γ 92.82(1)°. It has a cell volume of 3352(5)Å³ with $Z = 12$ and a calculated density of 5.78 g cm⁻³. The crystals, elongated along [001] and flattened on {010}, display polysynthetic twinning with (010) as the twin plane. Optically, they are biaxial (+) with $z \approx c$, $2V \gg 60^\circ$, $n = 2.08(5)$. The strongest lines of the X-ray powder pattern are [d in Å, (I), (hkl)] 14.84(50)(020), 9.27(41)(111, 110), 6.81(67)130, 3.304(93)(090), 3.092(100)(330).

Coquandite has also been found at the Cetine mine, Tuscany, Italy, and at the Lucky Knock mine, Tonasket, Okanogan County, Washington, USA. 22 microprobe chemical analyses (elemental microanalysis for H) gave Sb_2O_3 88.91, SO_3 8.35, CaO 0.04, Na_2O 0.03, H_2O 1.43, total 98.76 wt.%, corresponding to the empirical formula $(\text{Sb} + \text{S} = 7) \text{Sb}_{5.98}\text{Ca}_{0.01}\text{Na}_{0.01}\text{O}_{7.96}(\text{SO}_4)_{1.02}\cdot 0.78\text{H}_2\text{O}$, and to the idealised formula $\text{Sb}_6\text{O}_8(\text{SO}_4)\cdot\text{H}_2\text{O}$. The I.R. spectrum, which confirms the presence of water in the formula, is given.

A partial structural arrangement is also given: the Sb polyhedra lie in nine layers perpendicular to [010] and form 'hexagonally' shaped groups surrounded by SO_4 tetrahedra.

Keywords: coquandite, new mineral, Sb oxy-sulphate, Pereta, Tuscany, Italy.

Introduction

COQUANDITE, ideally $\text{Sb}_6\text{O}_8(\text{SO}_4)\cdot\text{H}_2\text{O}$, is a new mineral that was first encountered during the characterisation of oxidation minerals collected in the seventies in the abandoned Pereta stibnite mine, Tuscany, Italy. Two other antimony-bearing species, klebelsbergite (Cipriani *et al.*, 1980a) and peretaite (Cipriani *et al.*, 1980a,b), were also found in this mine. Coquandite is the third naturally occurring antimony oxy-sulphate

known, after klebelsbergite, redefined by Nakai and Appleman (1980), and peretaite.

The new mineral has been named coquandite in honour of the French scientist Henri Coquand (1811–81), Professor of geology and mineralogy, who carried out extensive studies of the antimony deposits of Tuscany between 1842 and 1849. Both the mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (ref. 91-024). Type material is preserved

at the National Museum of Natural History, Smithsonian Institution in Washington, and at Museums of Natural History of the Universities of Florence and Pisa (catalogue numbers 1761/RI and 8800, respectively).

During the characterisation of the coquandite from Pereta, the same species was identified in some specimens collected at Cetine, Tuscany, Italy, and also in a specimen from the Lucky Knock mine, Tonasket, Okanogan County, Washington, U.S.A.

Occurrence and paragenesis

The main geological formations outcropping in the area near Pereta are, from bottom to top, the 'Calcare Cavernoso' limestone, the 'Macigno' sandstone, and sands and clays of the 'Neoautotono Toscano'. A stibnite vein with quartzitic gangue fills a fracture in the limestone, which appears to be thoroughly silicified. Coquandite usually occurs as white powdery masses embedded between the needles of columnar stibnite, or as thin crusts with a pearly lustre. It appears sometimes as spheroidal knobs of feathery aggregates of silky fibres, and, rarely, as tiny flexible lamellar crystals on stibnite and quartz in cavities in the limestone. Coquandite is strictly associated with klebelsbergite and peretaite, and is also associated with valentinite, senarmontite, sulfur, gypsum, and stibiconite. Like klebelsbergite and peretaite, the mineral was probably formed by the action of sulphuric acid on stibnite.

The environment in which coquandite was found at Cetine is similar to that of Pereta. The ore at the Cetine mine consists of stibnite in small pods disseminated within the highly silicified limestone of the 'Calcare Cavernoso' formation. Coquandite, which is very rare in this locality, occurs as minute tabular crystals on stibnite or quartz, in small cavities in the limestone. The associated minerals are the same as observed at Pereta. In the specimen from the Lucky Knock mine, coquandite appears as silky fibres or small platelets implanted on stibnite or stibiconite needles.

Physical, optical and crystallographic properties

Coquandite crystals from Pereta occur as tiny transparent to translucent colourless individuals, elongated along [001] and flattened on (010); they do not exceed 0.01 mm in thickness, have an adamantine lustre, and a white streak. They are flexible and often display an onion-skin aspect (Fig. 1). The forms observed with a two-circle goniometer are {010} major and {001}, {2 $\bar{1}$ 0},



Fig. 1. Scanning electron photomicrograph of a tuft of coquandite crystals from Pereta.

and $\{1, \bar{1}, 2, 0\}$ minor (Fig. 2), with no evident cleavage. The crystals are too small to allow an accurate determination of hardness, and the material available is insufficient for its density to be determined with the Berman balance. The calculated density is 5.78 g cm^{-3} . No fluorescence effects were observed with either short-wave or long-wave ultraviolet radiation.

Due to the small size of the crystals and their high indices of refraction, it was impossible to completely determine their optical data. The following data were obtained from the same crystal used for the morphological study: biaxial (+), mean n 2.08(5) (white light) by minimum deviation, birefringence low, $2V$ (meas.) $\gg 60^\circ$. Orientation: length slow with $z \approx c$, axial plane parallel to [001], parallel extinction on {010}. Nonpleochroic.

The X-ray single-crystal study (Weissenberg and precession methods) indicates triclinic symmetry and polysynthetic twinning with (010) as the twin plane. The space group inferred from the crystal structure analysis is $P\bar{1}$. The X-ray powder diffraction data obtained on a 114.6 mm diameter Gandolfi camera, using Fe- $K\alpha$ radiation, are given in Table 1. Intensities were estimated visually by comparison with a calibrated intensity scale. Indexing was performed on the basis of single-crystal data, taking into account the intensities of reflections collected for the structural study. The unit-cell parameters, determined from powder data by means of least-square calculations, are: a 11.434(7), b 29.77(4), c 11.314(4) Å, α 91.07(7)°, β 119.24(3)°, γ 92.82(1)°, vol 3352(5)Å³.

The powder diffraction patterns obtained on the coquandite samples from Cetine and Lucky Knock are very similar to that reported for the Pereta material.

Table 1. X-ray powder diffraction data for coquandite from Pereta (d in Å).

$d_{\text{meas.}}$	I/I_0	$d_{\text{calc.}}$	$h\ k\ l$
14.84	50	14.851	0 2 0
9.27	41	9.268; 9.253	1 1 $\bar{1}$; 1 1 0
8.59	25	8.537	$\bar{1}$ 2 0
8.01	34	8.035; 8.024	0 2 1; 1 2 0
6.81	67	6.796	1 3 0
5.70	14	5.706	1 $\bar{1}$ 1
4.63	14	4.627	2 2 0
3.765	19	3.763	2 0 1
3.690	15	3.701; 3.693	2 0 $\bar{3}$; 3 1 $\bar{1}$
3.580	14	3.587	3 2 $\bar{1}$
3.440	20	3.453; 3.442	1 8 $\bar{1}$; 3 3 $\bar{1}$
3.304	93	3.300	0 9 0
3.200	39	3.205; 3.193	$\bar{3}$ 2 3; 3 2 0
3.138	24	3.144	1 9 1
3.092	100	3.085	3 3 0
3.052	16	3.062	0 $\bar{4}$ 3
2.842	32	2.846	$\bar{3}$ 6 0
2.813	16	2.818	0 5 3
2.712	32	2.707	3 6 $\bar{3}$
2.575	13	2.569	3 7 $\bar{3}$
2.268	6	2.265; 2.262	3 9 0; 4 7 $\bar{3}$
2.097	4	2.097	2 9 2
1.989	5	1.987	5 8 2
1.918	16	1.916	0 3 5
1.865	4	1.865; 1.866	6 4 3; 5 9 1
1.754	3	1.756	2 5 4
1.685	4	1.684	6 9 3
1.655	5	1.656	3 8 3
1.626	2	1.625	0 2 6
1.590	6	1.591	6 4 $\bar{6}$

Chemistry

A preliminary qualitative electron-probe scan showed that the only cations present in significant amounts are Sb and S. Traces of Ca and Na were detected. Quantitative chemical analyses were carried out with a wavelength dispersive ARL-SEM-Q electron microprobe. Running conditions were: 15 kV accelerating voltage, 20 nA specimen current, 10–20 μm electron beam size. Reference standards of natural valentinite, baryte, and albite were used for Sb, S, and Na respectively; a synthetic silicate was used for Ca. The raw data were corrected on-line by the Ziebold and Ogilvie (1964) method, using the Albee and Ray (1970) correction factors. The water content was determined only on the Lucky Knock specimen (owing to the small quantity of material, the Pereta and Cetine coquandites were not examined) using the Carlo Erba 1104 elemental micro-analyser on about 1 mg of substance.

The results of the analyses of the coquandite from Pereta, Cetine and Lucky Knock are shown in Table 2. The oxide percentages calculated for the ideal compound $\text{Sb}_6\text{O}_8(\text{SO}_4)\cdot\text{H}_2\text{O}$, as well as the averaged values, are also reported. The atomic ratios were derived from the latter values on the basis of $\text{Sb} + \text{S} = 7$. The total general percentage of 98.76 is somewhat unsatisfactory.

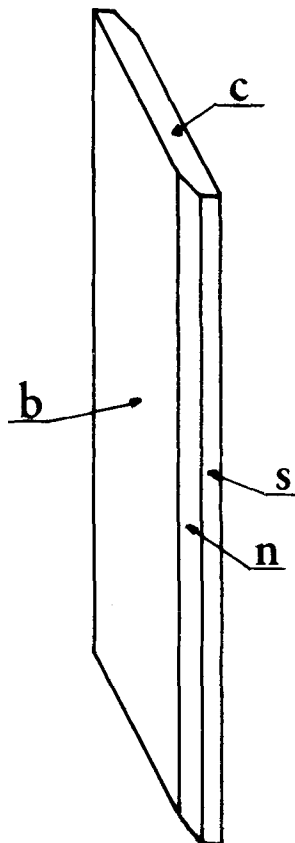


Fig. 2. Typical habit of a coquandite crystal from Pereta. Forms are: b {010}, c {001}, s {210}, n {1,1 $\bar{2}$,0}.

A better total, 99.86, was obtained from the Lucky Knock analyses, which are more reliable, probably due to the larger sizes of the crystals from this locality.

An infrared absorption spectrum was recorded over the wavenumber range 4000 to 450 cm^{-1} in a Perkin Elmer FTIR 1760X spectrophotometer (Fig. 3), using a KBr pellet heated beforehand to 110°C for 12 hours. The peaks at 3423 and 1646 cm^{-1} can be reasonably attributed to water of crystallisation. The main peaks in the 1200–500 cm^{-1} region are due to absorption by the sulphate ion and Sb–O bonds.

Structure analysis

For the X-ray structure analysis small, very thin crystals were taken from the Cetine and Lucky Knock samples. Weissenberg photographs revealed the triclinic symmetry and a faint

Table 2. Chemical data for coquandite from the three localities.

	Pereta		Cetine		Lucky Knock	
	wt. % ¹	range	wt. % ²	range	wt. % ³	range
Sb ₂ O ₃	88.25	(86.01-89.70)	88.53	(87.54-89.71)	89.96	(88.14-90.96)
SO ₃	8.35	(8.16-8.55)	8.33	(8.12-8.59)	8.38	(8.10-8.55)
CaO	0.04	(0.01-0.06)	0.04	(0.02-0.05)	0.04	(0.03-0.05)
Na ₂ O	0.02	(0.00-0.05)	0.02	(0.00-0.03)	0.05	(0.00-0.11)
H ₂ O	-		-		1.43 ⁴	(± 0.27)

	Sb ₆ O ₈ (SO ₄)·H ₂ O		average	
	wt. %	wt. %	wt. %	atoms ⁵
Sb ₂ O ₃	89.92	88.91	Sb	5.98
SO ₃	8.23	8.35	S	1.02
CaO	-	0.04	Ca	0.01
Na ₂ O	-	0.03	Na	0.01
H ₂ O	1.85	1.43	H	1.56
			O	12.82
Sums	100.00	98.76		

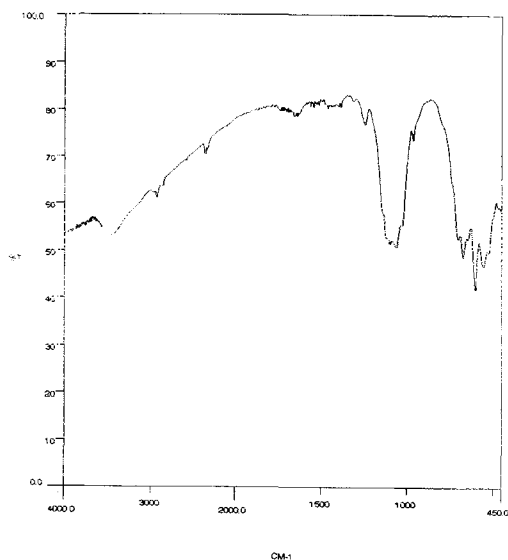
¹mean of 10 analyses on 3 grains²mean of 4 analyses on 2 grains³mean of 8 analyses on 7 grains⁴water by elemental microanalysis⁵number of atoms on the basis of Sb+S=7

Fig. 3. Infrared absorption spectrum of coquandite from Lucky Knock.

doubling of some reflections along the b^* direction, which denotes the presence of polysynthetic twinning with (010) as the twin plane. Totals of about 7000 (Cetine) and 6500 (Lucky Knock) independent reflections were measured on a Philips PW 1100 four-circle diffractometer, using graphite-monochromated Mo- $K\alpha$ radiation and the ω - 2θ scan technique. The unit-cell dimensions, determined from 25 reflections on the Lucky Knock crystal, which gave the best set of intensity data, are a 11.449(3), b 29.846(5), c 11.337(4) Å, α 91.16(3)°, β 118.88(3)°, γ 92.49(2)°.

By means of both direct and Patterson methods, most of the Sb + S atomic positions were determined. They are approximately arranged in layers perpendicular to [010] and form dense nets in each layer, with interatomic distances of 3.5–3.8 Å. The layers (nine in the whole unit-cell) are between 3.3 and 3.5 Å from one another, so the general three-dimensional arrangement of Sb + S atoms approximates close-packing. During subsequent isotropic refinements, which gave better results ($R = 0.13$) in the space group $P\bar{1}$, many oxygen atoms were detected by means of a series of Fourier syntheses. The finding of anions makes understand-

ing the connection of polyhedra possible. Considering the oxygens and the *E* lone pairs, the Sb-polyhedra show both the characteristic trigonal bipyramidal arrangement SbO_4E and the tetrahedral SbO_3E , as is usually found in $\text{Sb}^{3+}\text{-O}$ compounds. Within each layer, groups of seven Sb-polyhedra are closely linked to each other in the shape of centred hexagons, surrounded by SO_4 tetrahedra. These large units, which are more evident in the first and fourth layers, are directly interconnected in the *y* direction to form a three-dimensional framework.

Unfortunately, it was not possible to detect the whole set of atoms ($36\text{Sb} + 6\text{S} + 78\text{O}$) in the structure. Only $33\text{Sb} + 6\text{S} + 63\text{O}$, belonging mainly to the first four layers (and their symmetry-related layers), were positioned. The remainder of the structure, namely the layer at the middle of the unit-cell, is not well defined, and Sb-O or S-O polyhedra are not recognisable in this region. This confused slice of the structure probably represents the boundary between the two individuals of the twin, and/or a problematic structural disorder. Obviously, the lack of some atomic positions makes any further refinement impossible, and prevents the complete and precise definition of the structural arrangement of coquandite. In spite of the 'hexagonal' disposition of Sb-polyhedra within the layers and the particular unit-cell geometry, a trigonal pseudosymmetry for the present incomplete structural model taken as a whole appears to be unprovable.

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