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Clinocervantite, β-Sb_2O_4, the natural monoclinic polymorph of cervantite from the Cetine mine, Siena, Italy

RICCARDO BASSO [1], GABRIELLA LUCCHETTI [1], LIVIO ZEFIRO [1]
and ANDREA PALENZONA [2]

[1] Dipartimento di Scienze della Terra dell'Università, Corso Europa 26, I-16132 Genova, Italy
e-mail: mineral@dister.unige.it
[2] Dipartimento di Chimica e Chimica industriale dell'Università,
Via Dodecaneso 31, I-16146 Genova, Italy

Abstract: Clinocervantite occurs at the Cetine di Cotorniano mine associated with valentinite, tripuhyite, bindheimite and rosiaite. Clinocervantite, appearing generally as aggregates of single prisms elongated along [001] or twinned on {100}, is colourless, transparent, with vitreous lustre, biaxial, with the lowest measured refractive index $\alpha' = 1.72$ and the highest one $\gamma' = 2.10$. The strongest lines in the powder pattern are $d_{111} = 3.244$ Å and $d_{31\bar{1}} = 2.877$ Å. The crystal structure, space group *C2/c* with $a = 12.061(1)$ Å, $b = 4.836(1)$ Å, $c = 5.383(1)$ Å, $\beta = 104.60(4)°$ and $Z = 4$, has been refined to $R = 0.020$, confirming the new mineral to be the natural analogue of the synthetic β-Sb_2O_4 already known. The structures of clinocervantite and cervantite may be regarded as built up by stacking layers of nearly identical structure and composition accounting for both polytypism in the Sb_2O_4 compound and twinning of the clinocervantite crystals.

Key-words: clinocervantite, crystal-structure refinement, cervantite, twinning.

Introduction

During the study of rosiaite (Basso *et al.*, 1996), an associated new mineral was found in material from the Cetine mine, central Tuscany, Italy. It is the natural Sb^{3+} Sb^{5+} oxide, corresponding to the synthetic compound β-Sb_2O_4 (Rogers & Skapski, 1964; Amador *et al.*, 1988). The new mineral is the monoclinic modification of cervantite, α-Sb_2O_4, (Gopalakrishnan & Manohar, 1975; Thornton, 1977; Amador *et al.*, 1988). Both mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (ref. 97–017). Type material is preserved at the Dipartimento di Scienze della Terra, Sezione di Mineralogia, Università di Genova, Italy.

Occurrence, physical properties and chemical composition

Clinocervantite occurs in little cavities of a rock fragment found in the debris derived from mining operations, associated with valentinite, Sb_2O_3, tripuhyite, $FeSb_2O_6$, bindheimite, $Pb_2Sb_2O_6$-(O,OH) and rosiaite $PbSb_2O_6$. Clinocervantite appears as aggregates of crystals, elongated along [001], with prismatic habit. The crystals do not exceed 0.2 mm in length and often reveal polycrystalline twins. Clinocervantite crystals show slightly variable morphologies, the most common one being represented by the dominant prism {110} combined with subordinated {122} and {$\bar{2}11$} prisms (Fig. 1). The twin law corresponds to twin and composition plane {100}.

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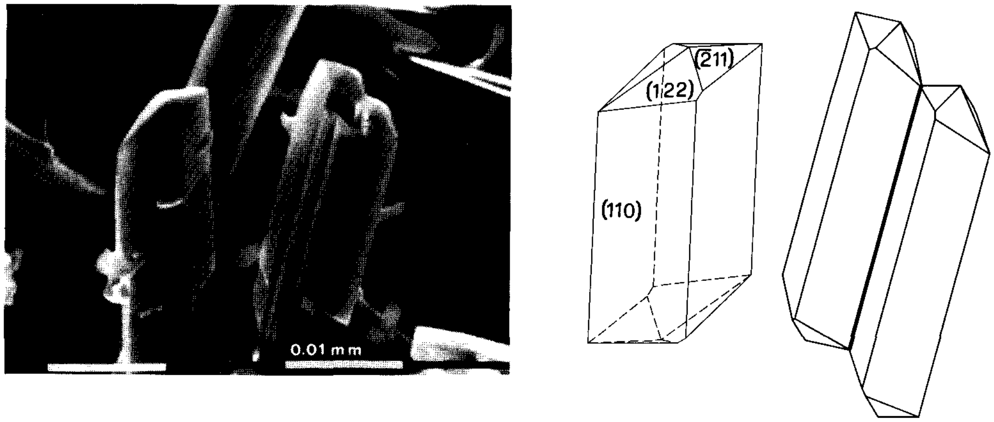


Fig. 1. Morphology of clinocervantite: a) SEM image; b) idealized drawing.

The mineral is colourless and transparent; it has vitreous lustre, white streak and does not show any evident cleavage. It is brittle with uneven fracture. Due to the small size of the crystals, it was impossible to measure density and hardness. The calculated density is 6.72 g/cm^3. The mineral does not fluoresce under short- and long-wave ultraviolet light. Clinocervantite is biaxial, with $\alpha' = 1.72$ and $\gamma' = 2.10$ measured using monochromatic Na-light ($\lambda = 589$ nm) at 25 °C.

The chemical composition of clinocervantite was determined by an electron microprobe (PHILIPS SEM 515 electron microscope equipped with EDAX PV9100 spectrometer) in energy dispersive mode, with an accelerating voltage of 15 kV and a beam current of 2.10 nA. Spot analyses show neither significant variations nor compositional zoning in the single crystals. Nine microprobe analyses, performed on different crystals, give an Sb average content of 79.19 ± 0.01 wt%, corresponding to the empirical formula $Sb_{2.000}O_4$, calculated on the basis of four oxygen atoms. Elements other than Sb are below their detection limits.

X-ray powder diffraction

The powder pattern (Table 1) was obtained by a Guinier STOE camera using graphite-monochromatized Cu$K\alpha$ radiation and silicon as internal standard. The relative intensities of the reflections were estimated visually and the indices were in-

Table 1. X-ray powder-diffraction data for clinocervantite (*d* in Å).

			Calculated		Measured					Calculated		Measured	
h	*k*	*l*	*d*	*I*	*d*	*I*	*h*	*k*	*l*	*d*	*I*	*d*	*I*
1	1	0	4.468	6	4.472	W	2	2	$\bar{2}$	1.783	21	1.782	W
1	1	1	3.240	100	3.244	VS	1	1	$\bar{3}$	1.674	19	1.674	W
3	1	0	3.031	4	3.036	VVW	2	2	2	1.620	14)	1.619	M
4	0	0	2.918	33	2.920	M	7	1	$\bar{1}$	1.619	17)		
3	1	$\bar{1}$	2.877	68	2.877	S	1	3	0	1.597	2	1.597	VVW
2	0	$\bar{2}$	2.639	23	2.640	W	5	1	$\bar{3}$	1.519	11)	1.519	W
0	2	0	2.418	14	2.416	VW	7	1	$\bar{2}$	1.518	1)		
4	0	$\bar{2}$	2.244	1	2.245	VVW	1	3	1	1.512	10	1.511	W
2	0	2	2.182	15	2.183	VW	3	3	0	1.489	1	1.488	VVW
2	2	1	1.985	2	1.985	VVW	3	3	$\bar{1}$	1.470	10	1.469	VW
4	2	0	1.862	21	1.861	W	8	0	0	1.459	5	1.459	VVW
5	1	1	1.812	20	1.811	W	6	2	$\bar{2}$	1.439	10	1.438	VVW
6	0	$\bar{2}$	1.790	11	1.789	W							

ferred from the pattern calculated by the LAZY PULVERIX program (Yvon *et al.*, 1977), using the structural model resulting from the single-crystal X-ray diffraction study as input data. The powder pattern reported for synthetic β-Sb_2O_4 in the JCPDS card 17-620 (Powder Diffraction File, 1994) is in agreement with that of clinocervantite. The unit cell parameters refined from the powder data are a = 12.060(5) Å, b = 4.832(2) Å, c = 5.384(3) Å and β = 104.60(2)°.

Table 2. Crystal structure data for clinocervantite.

Formula used for refinement	Sb_2O_4
Space group	*C2/c*
Z	*4*
a(Å)	12.061 (1)
b(Å)	4.836 (1)
c(Å)	5.383 (1)
β (°)	104.60 (4)
V(Å^3)	303.83 (4)
μ (Mo*K*α, mm^{-1})	17.73
Measured reflections ($-19 \leq h \leq 19$, $0 \leq k \leq 7$, $-8 \leq l \leq 8$)	1396
Unique reflections	668
Observed reflections ($I > 3\sigma_I$)	613
R (observed)	0.020
R (all)	0.023
Extinction parameter (× 10^3)	5.5 (2)

Refinement of the crystal structure

A clinocervantite prismatic fragment, measuring 0.15 × 0.075 × 0.038 mm, was used for the single-crystal X-ray diffraction study. The data collection was performed by means of an ENRAF-NONIUS CAD-4 automatic diffractometer. The cell parameters were determined and refined using 25 reflections within the angular range 27° < θ < 31°. The

Table 3. Atomic coordinates and equivalent isotropic temperature factors (Å^2) (Hamilton, 1959) for clinocervantite.

Atom	*x/a*	*y/b*	*z/c*	*Beq*
Sb1	1/4	1/4	0	0.26
Sb2	0	0.2851 (1)	1/4	0.53
O1	0.1918 (2)	0.0517 (6)	0.6746 (6)	0.55
O2	0.0939 (2)	0.4122 (6)	0.0949 (6)	0.51

Table 4. Selected interatomic distances (Å) and angles (°) for clinocervantite.

	M–O distance		O–O distance	O–M–O angle
Sb^{5+}O$_6$ octahedron				
2 Sb1–O1	1.959 (3)	2 O1–O1*	2.738 (1)	88.48 (6)
2 –O1	1.965 (3)	2 –O1	2.811 (3)	91.52 (6)
2 –O2	2.004 (3)	2 –O2*	2.651 (4)	96.03 (12)
		2 –O2	2.794 (4)	89.48 (12)
		2 –O2	2.819 (4)	90.52 (12)
		2 –O2	2.946 (4)	96.03 (12)
Average	1.976		2.793	92.01
Sb^{3+}O$_8$ dodecahedron				
2 Sb2–O1	2.940 (3)	2 O1–O1*	2.738 (1)	54.56 (5)
2 –O1	3.030 (3)	2 –O1**	4.561 (6)	99.63 (7)
2 –O2	2.026 (3)	–O1	4.895 (6)	112.71 (11)
2 –O2	2.212 (3)	2 –O2*	2.651 (4)	59.99 (10)
		2 –O2	2.953 (4)	68.15 (10)
		2 –O2	3.764 (4)	90.41 (9)
		2 –O2	3.786 (4)	97.66 (10)
		2 O2–O2**	2.535 (5)	73.33 (12)
		–O2	2.800 (6)	87.43 (17)
		2 –O2	2.822 (2)	83.40 (9)
Average	2.552		3.295	80.80

* Octhedron-dodecahedron shared edges. ** Dodecahedron-dodecahedron shared edges.

diffraction intensities were measured up to $\theta = 35°$, using graphite-monochromatized MoKa radiation and operating in the ω–θ scan mode. A semi-empirical absorption correction was applied using the ψ scan method (North *et al.*, 1968).

The crystal structure was refined in the space group *C2/c* starting with the coordinates resulting from the structural analysis of the corresponding synthetic compound (Amador *et al.*, 1988). Refinements were carried out by a modified version of the ORFLS program (Busing *et al.*, 1962), using the scattering factors for neutral atoms from the International Tables for X-ray Crystallography, vol. IV (1974). Total site occupancy was fixed for all atoms; scale factor, secondary extinction coefficient, positional and thermal parameters were simultaneously derived. Final refinements were carried out with anisotropic temperature factors for all atoms. Tables 2, 3 and 4 summarize the experimental details and the results of the crystal structure refinement. The structure refinement confirms clinocervantite to be the natural analogue of synthetic β-Sb_2O_4.

According to Rogers & Skapski (1964) and Amador *et al.* (1988), the coordination polyhedron of the pentavalent Sb atom is a slightly distorted octahedron. For the trivalent Sb, with a stereochemically active lone pair of electrons, only four short Sb-O bonds are generally considered by many authors, for both α- and β-Sb_2O_4, leading to a one-sided four-fold coordination. The polyhedron is described as a near tetragonal pyramid made by four basal oxygen atoms and an apical vertex at which the nonbonded electron pair is pointing (Roger & Skapski, 1964; Gopalakrishnan & Manohar, 1975; Thornton, 1977). A similar coordination is reported by Kennedy (1994) also for the trivalent Bi in synthetic $BiSbO_4$, isostructural with clinocervantite. Amador *et al.*, (1988) suggest, for α and β forms of Sb_2O_4, a very distorted octahedral coordination of trivalent Sb, taking into account two additional bonds with longer Sb-O distances. An eight-fold coordination is attributed to the trivalent Bi in the mixed valent oxide Bi_2O_4 (Kumada *et al.*, 1995), isostructural with clinocervantite. In the present study the eight-fold coordination leads to a bond-valence sum value of 3.04 for the trivalent Sb, using the parameters of Brese & O'Keeffe (1991); it becomes 2.93 disregarding the two longer bonds and goes down to 2.78 if the pyramidal coordination is assumed.

Structural relationships between cervantite and clinocervantite: polytypism and twinning

In the structure of clinocervantite sheets of corner-sharing $Sb^{5+}O_6$ octahedra alternate with sheets of

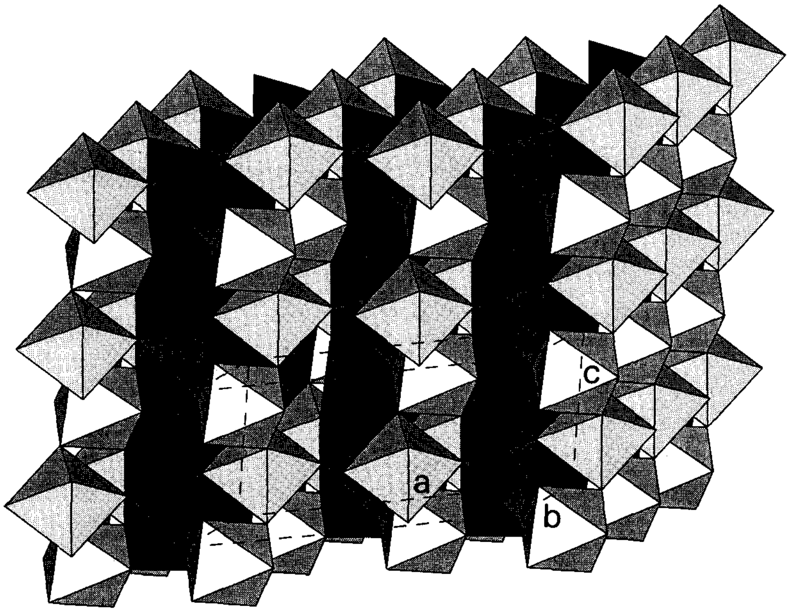


Fig. 2. Sheets of corner-sharing $Sb^{5+}O_6$ octahedra alternating with sheets of edge-sharing $Sb^{3+}O_8$ dodecahedra in the structure of clinocervantite.

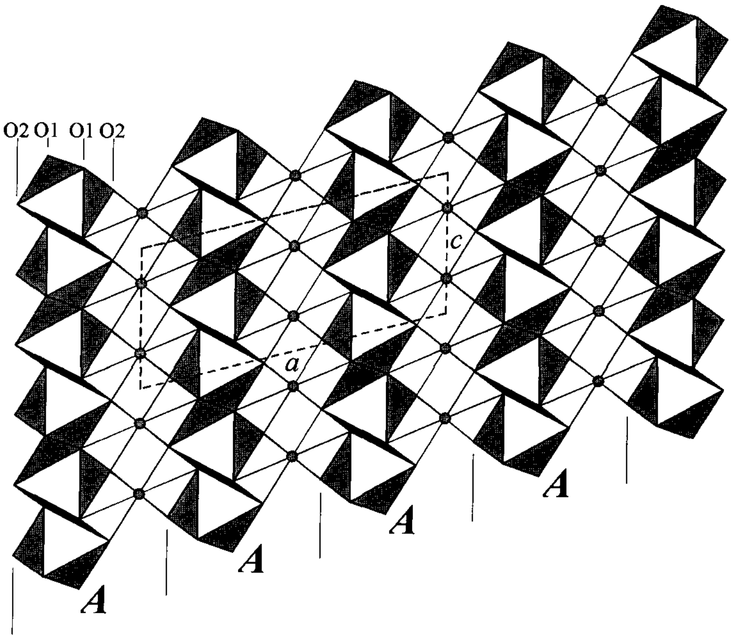
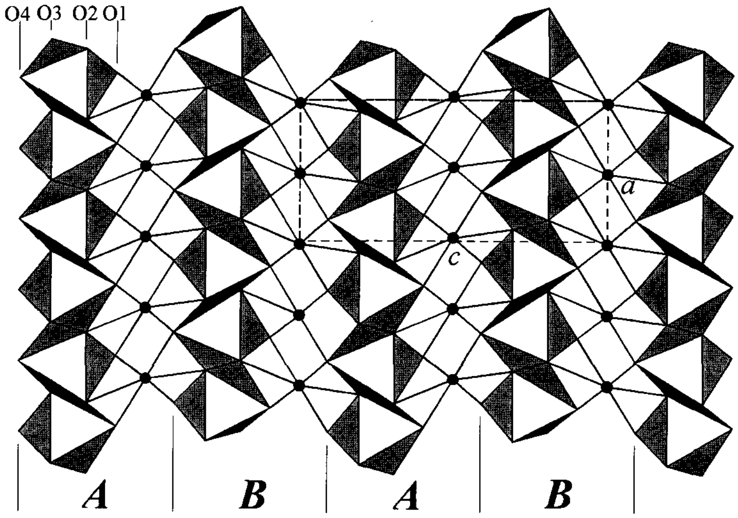


Fig. 3. (a) Building layers A in the structure of clinocervantite viewed along [010].



(b) Building layers A and B in the structure of cervantite viewed along [0$\bar{1}$0].

edge-sharing $Sb^{3+}O_8$ dodecahedra, both parallel to the *b c* plane (Fig. 2). The symmetry $2_1/c$ repeats each octahedral sheet into itself as the symmetry $2/c$ does for the dodecahedral sheet. Furthermore, octahedral sheets are equivalent each other by diad axes, glide planes and centres of symmetry as well as dodecahedral sheets, accounting for the overall symmetry of the clinocervantite structure described in the space group *C2/c*. Because a six-fold coordination was ascribed to Sb^{3+} in cervantite, unlike the eight-fold assigned in clinocervantite, the two structures may be homogeneously described in terms of alternating Sb^{3+} and octahedral Sb^{5+} sheets.

As shown in Fig. 3a, a unique type of building layer A, made by two adjacent octahedral Sb^{5+} and Sb^{3+} sheets, may be recognized in the structure of clinocervantite. Each layer, with composition Sb_2O_4, is transformed into the adjacent one, with which shares the boundary oxygen atoms, applying the lattice vector $(\boldsymbol{a} + \boldsymbol{b})/2$ of the *C* centred cell. Thus, the structure of clinocervantite may be described in terms of an AA... stacking sequence.

In the structure of cervantite the octahedral Sb^{5+} sheets, alternating with the Sb^{3+} sheets parallel to the a b plane, exhibit a pseudo-symmetry equal to the symmetry of the corresponding sheet in clinocervantite, taking into account that the glide plane a of cervantite corresponds to the glide plane c of clinocervantite. Also the dimensional features of the corresponding sheets in the two structures are nearly equal being $c_o \approx a_m \sin\beta$, $b_o \approx b_m$ and $a_o \approx c_m$, where the subscripts o and m refer to orthorhombic (cervantite) and monoclinic (clinocervantite) phases, respectively. On the other hand, in the cervantite structure (Fig. 3b) adjacent octahedral Sb^{5+} sheets are repeated by a screw axis 2_1 perpendicular to the sheets as well as adjacent Sb^{3+} sheets. Because of the absence of mirror or glide planes parallel to these sheets, the elements of pseudo-symmetry are no long symmetry operators for the whole structure in agreement with the space group $Pna2_1$.

In the structure of cervantite two types of layer may be recognized: a layer A, corresponding to that of clinocervantite, alternating with a layer B, equivalent to layer A by the 2_1 screw axis. Thus, the structure of cervantite may be described as an ABAB... stacking sequence.

Considering in the two structures only the oxygens shared between adjacent layers, it may be observed that the arrangement of the oxygens O2, placed in planes parallel to (100), of the layer A in clinocervantite can be almost perfectly superimposed with the arrangement of the oxygens O4, placed in planes parallel to (001), of both layers A and B in cervantite. The above considerations outline the polytypic relationship between cervantite and clinocervantite.

As a consequence, the twinning of the clinocervantite crystals can be explained in terms of occasional stacking fault. A sequence AA... leads to a single crystal of clinocervantite as well as a sequence BB..., where the second crystal is rotated by a two-fold axis, parallel to [001], with respect to the first one. A stacking sequence like AA..ABB..B leads to a twin, composed by two single crystals, with composition and twin plane {100}.

In the studied sample twinned crystals, composed only by two or few single crystals, were observed. The previously described stacking fault, if frequently repeated, would lead to a polysynthetic twinning not observed in the clinocervantite crystals. Conversely, polysynthetic twinning has been reported by Rogers & Skapski (1964) for synthetic β-Sb_2O_4.

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