Zeitschrift: Archives des sciences et compte rendu des séances de la Société

Herausgeber: Société de Physique et d'Histoire Naturelle de Genève

**Band:** 54 (2001)

Heft: 1

**Artikel:** Theoparacelsite, Cu3(OH)2As2O7, a new mineral: its description and

crystal structure

Autor: Sarp, Halil / erný, Radovan

**DOI:** https://doi.org/10.5169/seals-740511

### Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Mehr erfahren

#### **Conditions d'utilisation**

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. En savoir plus

#### Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. Find out more

**Download PDF: 20.11.2025** 

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

Archs Sci. Genève Vol. 54 Fasc. 1 pp. 7-14 Mai 2001	
---	--

# THEOPARACELSITE, Cu<sub>3</sub>(OH)<sub>2</sub>As<sub>2</sub>O<sub>7</sub>, A NEW MINERAL: ITS DESCRIPTION AND CRYSTAL STRUCTURE

BY

## Halil SARP<sup>1</sup> & Radovan ČERNÝ<sup>2</sup>

#### **ABSTRACT**

Theoparacelsite, Cu<sub>3</sub>(OH)<sub>2</sub>As<sub>2</sub>O<sub>7</sub>, a new mineral: its description and crystal structure. -Theoparacelsite, Cu<sub>3</sub>(OH)<sub>2</sub>As<sub>2</sub>O<sub>7</sub>, was found in the old copper mines of Roua (Alpes-Maritimes, France), associated with olivenite, cornubite, clinotyrolite, connellite, brochantite, malachite, trippkeite, pharmacosiderite, strashimirite, gilmarite, native copper, cuprite, algodonite and domeykite. It forms aggregates in geodes of cuprite (1mm diameter) formed by xenomorph crystals (0.2 x 0.1 x 0.05 mm maximum dimension), rectangular elongated crystals (90 x 10 x 5 µm), perfect little rectangular crystals (10 x 7 x 2 µm), equidimentional crystals blunted at their extremities (20 µm), pseudomorphs after thin acicular crystals of olivenite, or finally in very fine grained aggregates. The dark pistachio green rectangular crystals are elongated along b, flattened on {001}, and have a perfect cleavage on {001}. They are not twinned. The mineral is orthorhombic, Pmma, a = 8.3212(8), b = 2.9377(3), c = 4.6644(5)Å, V = 114.02(2) Å<sup>3</sup>, Z = 2/3, and  $D_{calc}$  = 4.72 (1) g/cm<sup>3</sup>. The strongest lines in the X-ray powder diffraction pattern ( $d_{obs}$  in Å, (hkl),  $I_{vis}$ ) are: 3.104, (201), 100; 2.486, (011), 70; 2.400, (210), 25; 1.672, (212), 30; 1.596, (411), 25; 1.330, (601)(221), 25. The Mohs' hardness could not be measured. Luster is vitreous to adamantin, streak is yellowish green; crystals are biaxial (+) with  $\alpha = 1.81(1)$ ,  $\beta =$ 1.82(1),  $\gamma = 1.86(1)$  at 590 nm;  $2V_{obs} = 57(3)^{\circ}$ ,  $2V_{calc} = 54(1)^{\circ}$ . Pleochronism is moderate with  $\gamma =$  dark green pistachio,  $\beta =$  olive green,  $\alpha =$  light olive green. The crystal structure was solved by direct methods (Mo $K\alpha$  radiation) and refined using 207 observed unique reflections to R = 0.063,  $R_w = 0.064$ . The structure of theoparacelsite is disordered and formed by (001) sheets of CuO<sub>6</sub> octahedra with the composition  $CuO_3$ . The sheets are linked in the c direction by chains of  $AsO_4$  tetrahedra parallel to b and occupied from 2/3 giving so the composition As<sub>2/3</sub>O<sub>3</sub>.

Key-words: theoparacelsite, new mineral, powder pattern, crystal structure, arsenate, copper.

### **INTRODUCTION**

Theoparacelsite, Cu<sub>3</sub>(OH)<sub>2</sub>As<sub>2</sub>O<sub>7</sub>, is a new mineral discovered in samples collected by Danielle Mari, Gilbert Mari and Pierre Rolland in the old copper mines of Roua (North and South group, municipality of Guillaumes and Daluis respectively), which are situated NW of the Alpes-Maritimes department (France), about 50 km from Nice.

The mineral name honors Philippus Theophrastus Aureolus Bombastus von Hohenheim, called Paracelse (1493-1541). The name Paracelse is a Greek-roman translation of Hohenheim which means «close to the sky». He was an important Swiss

Département de Minéralogie du Muséum d'histoire naturelle de la Ville de Genève, 1 route de Malagnou, CP 6434, CH-1211 Genève 6, Suisse.

<sup>&</sup>lt;sup>2</sup> Laboratoire de Cristallographie, Université de Genève, 24 quai Ernest-Ansermet, CH-1211 Genève 4, Suisse.

physician, chemist, alchemist and doctor who also worked in mineralogy (*De Mineralibus*, *De Elemento Aquae & Fructibus eius*). He is often misunderstood by people ignoring vocabulary, customs and difficulties encountered by scientists of the XVI<sup>th</sup> century. The history learns us that his purposes were warped! Even now, some contemporary journals criticized him wrongly. Nowadays, he is known in toxicology for having said: «All is poison, nothing is poison, it is the dosage which makes the poison».

The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

The type material is preserved in the Department of Mineralogy of the Natural History Museum of Geneva, Switzerland, under reference no. 447.010.

#### **OCCURRENCE**

The Barrot Dome, in the north-eastern part of the Alpes-Maritimes area (France), is characterized by the presence of numerous showings of cupriferous ore. The metallogeny and geology of this Dome has been studied by VINCHON (1984) and MARI (1992). The new mineral described occurs in the Roua copper occurrences (North and South group) in the upper part of the Var valley (the Daluis gorge) at the western margin of the Barrot Dome. In this ore deposit, the cupriferous mineralisation is hosted in a gangue formed by dolomite, calcite and aragonite, and consists of native copper, cuprite, domeykite, algodonite, koutekite, native gold and native silver. Detailed mineralogical study of this ore deposit produced several secondary, rare and unknown mineral species (SARP et al., 1994, 1995, 1996, 1999). The new mineral described here occurs in small geodes of cuprite in association with olivenite, cornubite, clinotyrolite, connelitte, brochantite, malachite, trippkeite, pharmacosiderite, strashimirite, gilmarite (SARP & ČERNÝ, 1999), native copper, cuprite, algodonite and domeykite.

#### PHYSICAL AND OPTICAL PROPERTIES

Theoparacelsite occurs as aggregates found in geodes of cuprite (1 mm diameter) which are formed by: xenomorph crystals of maximum size  $0.2 \times 0.1 \times 0.05$  mm, rectangular elongated crystals of maximum size  $90 \times 10 \times 5$  µm, perfect little rectangular crystals ( $10 \times 7 \times 2$  µm), equidimentional crystals blunted at their extremities ( $\sim 20$  µm), pseudomorphs after thin acicular crystals of olivenite (Fig. 1) and finally in powder. The rectangular crystals are elongated parallel to b, flattened on  $\{001\}$ , and have one perfect  $\{001\}$  cleavage; they are not twinned. The most developed forms are  $\{001\}$ ,  $\{010\}$ ,  $\{100\}$ ,  $\{110\}$  and  $\{101\}$ . The crystals are dark pistachio green, translucent, with vitreous to adamantine lustre and yellowish green streak. The mineral is brittle with conchoidal fracture. The Moh's hardness could not be measured. The density could not be determined owing to the small quantity of the mineral. It sinks rapidly in Clerici solution. The calculated density is 4.72(1) g/cm<sup>3</sup> based on the ideal formula. The mineral is soluble in HCl. It is nonfluorescent and has medium pleochroism:  $\gamma = \text{dark green pistachio}$ ;  $\beta = \text{olive green}$ ;  $\alpha = \text{light olive green}$ . Theoparacelsite is biaxial

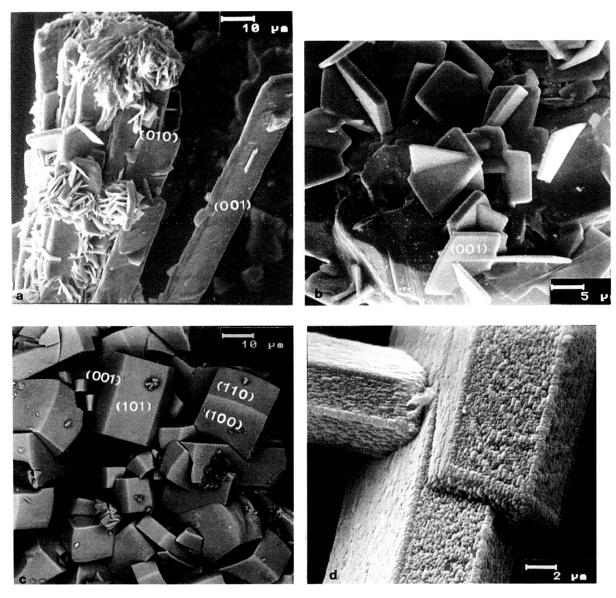


Fig. 1.

SEM images of the different morphologies of theoparacelsite crystals, a) rectangular crystals elongated in the b axis direction; aggregates of small crystals are cornubite, b) perfect little rectangular crystals, c) equidimentional crystals blunted at their extremities, d) pseudomorphs after olivenite crystals.

positive, with  $\alpha = 1.81(1)$ ,  $\beta = 1.82(1)$ ,  $\gamma = 1.86(1)$  (determined at 589 nm),  $2V_{obs} = 57(3)^{\circ}$  and  $2V_{calc} = 54(1)^{\circ}$ . The index of refraction was to be measured rapidly due to the fact that the mineral is attacked by Cargille's liquids of refractive index > 1.80. The dispersion (r>v) is moderate. The optical orientation is:  $\alpha = a$ ,  $\beta = c$ ,  $\gamma = b$ .

## CHEMICAL COMPOSITION

Theoparacelsite was chemically analyzed with a Cameca electron microprobe, using a beam size of 10 µm, operating voltage of 5kV, and a beam current of 11 nA. Qualitative examination showed only Cu and As. For quantitative analysis, trippkeite

(Cu, As), arsenic metal (As) and copper metal (Cu) were used as standards. The results are given in Table I. The H<sub>2</sub>O content was estimated by difference due to insufficient quantity of the material. The empirical formula based on 9 oxygen atoms is: Cu<sub>2.99</sub>As<sub>2.02</sub>H<sub>1.92</sub>O<sub>9</sub> and the idealized formula, Cu<sub>3</sub>(OH)<sub>2</sub>As<sub>2</sub>O<sub>7</sub>, was confirmed by structure determination. The Gladstone-Dale constants of Mandarino (1981) along with the oxide proportions, determined from the electron-microprobe data and from the crystal structure, lead to Kc values of 0.172 and 0.170, respectively. The value of Kp (Mandarino, 1981), calculated using the average index of refraction (1.83), and the calculated density from the empirical formula, is 0.175. For the same average index of refraction and the calculated density from the idealized formula, Kp is 0.204. The compatibility index is -0.017 for the empirical formula, and -0.035 for the idealized formula, indicating superior and excellent compatibility (Mandarino, 1981) between the physical and chemical data.

	Average of 5 analyses	Range of 8 analyses	Standard deviation	Ideal formula
CuO	48.77	47.90-49.69	0.6	49.05
$As_2O_5$	47.68	46.43-49.57	1.0	47.25
$As_2O_5$ $H_2O^*$	3.55			3.70

TABLE I. Chemical analysis [wt.%] of theoparacelsite.

## X-RAY CRYSTALLOGRAPHY

Powder-diffraction data (Table II) were obtained using a Gandolfi camera (114.6 mm diameter, Ni-filtered  $CuK\alpha$  radiation). The relative intensities of the reflections were estimated visually. A single-crystal of the oparacelsite 0.083 x 0.083 x 0.035 mm in size was examined by the precession method (Ni-filtered Cu  $K\alpha$ ) and the same crystal was measured on a Philips PW1100 diffractometer with monochromatized Mo  $K\alpha$ radiation in  $\Theta/2\Theta$  scanning-mode with limits -11 < h < 11, -4 < k < 4, -6 < 1 < 6. A total of 1548 reflections was measured up to  $\theta = 30^{\circ}$ . Lattice parameters were refined on the basis of 23 reflections with  $6.6^{\circ} < \Theta < 24^{\circ}$  using a program LATCON from the *Xtal*3.2 package (Hall et al., 1992): a = 8.3212(8), b = 2.9377(3), c = 4.6644(5) Å, V =114.02(2) Å3, a:b:c=1:0.3530:0.5605. Data reduction was done using the programs REFCAL and SORTRF and analytical absorption correction using LSABS from the Xtal3.2 package. The structure was solved in the space group Pmma by direct methods with program GENTAN from the Xtal3.2 package. The structure (without hydrogen atoms) was refined on F2 with program LSLS from the Xtal3.2 package using all 207 observed unique reflections ( $R_{int} = 0.074$ ) weighted  $1/\sigma^2$ . The occupancy of the As site was refined to 2/3 and fixed to that value in the final refinement. The secondaryextinction correction was done according to BECKER & COPPENS (1974) with the extinction parameter g = 381(67). The refinement converged to R = 0.063,  $R_w = 0.064$  and

<sup>\*</sup>By difference

(hkl)	d(calc).	d(obs.)	I(vis.)	(hkl)	d(calc).	d(obs.)	I(vis)
001	4.660	4.658	5	411	1.595	1.596	25
200	4.161	4.162	5	003	1.553		
101	4.066	4.065	15		}	1.552	10
201	3.104	3.104	100	402	1.552		
010	2.938	2.940	<5	103	1.527		
011	2.485	2.486	70		}	1.526	<5
210	2.400	2.400	25	312	1.525		
301	2.384			020	1.469	1.470	<5
	}	2.384	10	203	1.455	1.455	<5
111	2.381			013	1.373		
002	2.330	2.330	15		}	1.372	5
211	2.134	2.136	<5	412	1.372		
400	2.081	2.080	10	303	1.355		
012	1.826	1826	<5	113	1.355 }	1.353	<5
302	1.784 I			502	1.354		
	}	1.783	<5	601	1.329		
112	1.783 Î				}	1.330	25
410	1.698	1.699	<5	221	1.328		
212	1.672	1.672	30	610	1.254	1.255	10

TABLE II. X-ray powder diffraction data for theoparacelsite (d in Å)

Goof = 1.99 with 20 parameters, including anisotropic-displacement parameters. The largest residuals in the Fourier-difference map are -1.28 and 1.23 e/Å<sup>3</sup>.

## **CRYSTAL STRUCTURE**

Atom coordinates, standardized by the program STRUCTURE TIDY (GELATO & PARTHÉ, 1987), and equivalent isotropic-displacement parameters for non-hydrogen atoms are given in Table III, and a list of selected interatomic distances is given in Table IV. Atom coordination was analyzed by the program IVTON (BALIC ŽUNIČ & VICKOVIČ, 1996). The structure of theoparacelsite is disordered. There is one Cu and one As site in the structure. Cu is coordinated by a distorted octahedron, which forms trans[CuO<sub>4</sub>] chains parallel to b. The chains are cross-linked by apical vertices with other chains and form (001) sheets of CuO<sub>3</sub>. The site of As is coordinated by a slightly distorted tetrahedron. The tetrahedra AsO<sub>4</sub> are cross-linked with other tetrahedra by sharing the oxygen O2 and form chains parallel to b. However, the As site is occupied only by 2/3. The As<sub>2/3</sub>O<sub>3</sub> chains cross-link the CuO<sub>3</sub> sheets in the c-axis direction. The partial occupancy of the As site and high values of all displacement parameters U means that the structure is disordered. A possible inversion twinning in the non-centrosymmetric sub-groups was checked and excluded (using the inversion-distinguishing power of As and MoKα radiation). By a careful inspection of the precession photographs hk0 and 0kl very weak lines of diffuse intensity were observed at k = 2/3, 5/3. It means probably a local ordering on the As site occupied in our model by 2/3. No long range order showing a superstructure peaks was, however, observed. Further investi-

Atom	x	у	z	$U_{\rm eq}({\rm \AA}^2)$	Occ.
Cu	0	0	0	0.0197(2)	1
As	1/4	1/2	0.5443(2)	0.0263(3)	2/3
O1	0.0876(3)	1/2	0.7798(5)	0.0212(7)	1
O2	1/4	0	0.368(2)	0.102(3)	1

TABLE III. Atom positions and displacement parameters for theoparacelsite.

The equivalent isotropic atomic displacement parameters are expressed as

 $U_{\text{eq}} = (1/3) \sum_{i} \sum_{j} U_{ij} \alpha_i * \alpha_j * \mathbf{a}_i . \mathbf{a}_j.$ 

TABLE IV. Selected interactomic distances (Å) for theoparacelsite.

Cu-O1 (x 4) 1.935(2) As-O2 (\* 2) 1.684(4)

Cu-O2 (x 2)

AsO<sub>4</sub> tetrahedron:

2.697(5)

As-O1 (\* 2)

1.742(3)

Range of edges within CuO<sub>6</sub> octahedron: Range of edges within

2.519(3) - 3.244(3) 2.703(4) - 2.9377(7)

gation of the diffuse intensity is currently undergone.

No hydrogen atoms were detected in the Fourier-difference map. For this reason and, because of the disordered structure, we have not performed the calculations of the bond valence sums.

## DISCUSSION OF THE STRUCTURE

The sum formula of theoparacelsite,  $CuAs_{2/3}O_3$ , corresponds to Z = 2. If we suppose the usual cationic charges  $As^{5+}$  and  $Cu^{2+}$ , the charge equilibrium needs 2/3 of a hydrogen atom giving so a probable formula  $CuO_{1/3}[AsO_3OH]_{2/3}$ . To get a stoichiometric formula we need to suppose Z = 2/3 and the formula becomes  $Cu_3(OH)_2As_2O_7$ . It indicates a probable 3-fold superstructure if the structure were ordered. This corresponds to the observed diffuse intensity in the reciprocal space with k = 2/3, 5/3. The final conclusion about the stoichiometric formula can be done, however, only after the complete analysis of the diffuse intensity.

The structure of theoparacelsite, CuO<sub>1/3</sub>[AsO<sub>3</sub>OH]<sub>2/3</sub>, (see Fig. 2) belongs to the group of M=M-T framework structures according to the classification of EBY & HAWTHORNE (1993). The arrangement of the CuO<sub>4</sub> and AsO<sub>3</sub> chains resembles that in olivenite, Cu<sub>2</sub>AsO<sub>4</sub>(OH) (ToMAN, 1977). However, in olivenite the AsO<sub>4</sub> tetrahedra do not form chains, but they are isolated, because each second tetrahedron is missing. Consequently each second CuO<sub>4</sub> chain is replaced by isolated pairs of trigonal bipyramid Cu<sub>2</sub>O<sub>8</sub>.

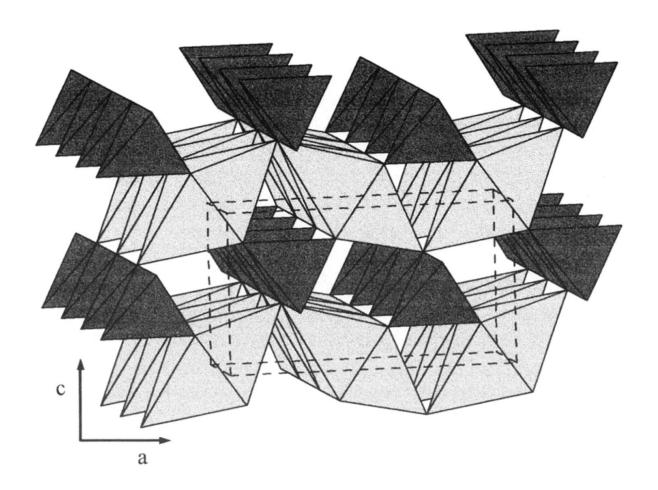


Fig. 2.

The structure of theoparacelsite viewed approximatively down [010]. The Cu octahedra are in light grey and the As tetrahedra are in dark grey.

#### **RESUME**

## THEOPARACELSITE, Cu<sub>3</sub>(OH)<sub>2</sub>As<sub>2</sub>O<sub>7</sub>, UN NOUVEAU MINÉRAL: SA DESCRIPTION ET SA STRUCTURE CRISTALLINE

Theoparacelsite, Cu3(OH)2As2O7, un nouveau minéral, a été découvert dans les mines de cuivre de Roua (Alpes-Maritimes, France). Le minéral et son nom ont été homologués par la Commission internationale des nouveaux minéraux. Le minéral est orthorombique, son groupe d'espace est Pmma. Les paramètres de la maille élémentaire sont a = 8,321(8), b = 2,9377(3), c = 4,6644(5) Å. Il est optiquement biaxe (+) avec  $\alpha = 1,81(1)$ ,  $\beta = 1,82(1)$ ,  $\gamma = 1,86(1)$ .

Mots-clés: theoparacelsite, nouveau minéral, diagramme de poudre, structure cristalline, arseniate, cuivre.

## **ACKNOWLEDGEMENTS**

We thank C. de Jong Bozkurt for typing the manuscript and J. Wuest for the scanning electron microscope photographs.

#### **REFERENCES**

- BALIC ŽUNIČ, T. & I. VICKOVIĆ. 1996. IVTON program for the calculation of geometrical aspects of crystal structures and some crystal chemical applications. *J. Applied Cryst.*, 29, 305-306.
- BECKER, P.J. & P. COPPENS. 1974. Extinction within the limit of validity of the Darwin transfer equations. II. Refinement of extinction in spherical crystals of SrF<sub>2</sub> and LiF. *Acta Cryst.*, A30, 148-153.
- EBY, R.K. & F.C. HAWTHORNE. 1993. Structural relations in copper oxysalt minerals. I. Structural hierarchy. *Acta Cryst.*, B49, 28-56.
- GELATO, L.M. & E. PARTHÉ. 1987. STRUCTURE TIDY a computer program to standardize crystal structure data. J. Applied Cryst., 20, 139-143.
- HALL, S.R., H.D. FLACK & J.M. STEWART. 1992. Eds. Xtal3.2. Reference Manual. Universities of Western Australia, Geneva and Maryland.
- Mandarino, J.A. 1981. The Gladstone-Dale relationship: part IV. The compatibility concept and its applications. *Can. Mineral.*, 19, 441-450.
- MARI, G. 1992. Les anciennes mines de cuivre du Dôme de Barrot (Alpes-Maritimes). Ed. Serre, Nice, 112 p.
- SARP, H., G. MARI, D. MARI & P. ROLLAND. 1994. Contribution à l'étude minéralogique des indices cuprifères de Roua (Daluis, Alpes-Maritimes, France). *Riviéra Scientifique*, Nice, 47-56.
- SARP, H., G. MARI, D. MARI & P. ROLLAND. 1995. Sur la présence de vésigniéite dans les indices cuprifères de Roua (Daluis et Guillaumes, Alpes-Maritimes, France). Riviéra Scientifique, Nice, 45-48.
- SARP, H., G. MARI, D. MARI & P. ROLLAND. 1996. Données nouvelles sur la minéralogie des indices cuprifères de Roua (Daluis et Guillaumes, Alpes-Maritimes, France). *Riviéra Scientifique*, Nice, 27-36.
- SARP, H. & R. ČERNÝ. 1999. Gilmarite, Cu<sub>3</sub>(AsO<sub>4</sub>) (OH)<sub>3</sub>, a new mineral: its description and crystal structure. *Eur. J. Mineral.*, 11, 549-555.
- TOMAN, K. 1977. The symetry and crystal structure of olivenite. Acta Cryst., B33, 2628-2631.
- Vinchon, C. 1984. Sédimentogenèse et métallogénèse du Permien du Dôme de Barrot (Alpes-Maritimes). Thèse d'Etat. *Document B.R.G.M.*, no. 70, 445 p.