Gilmarite, Cu$_3$ (AsO$_4$) (OH)$_3$, a new mineral: its description and crystal structure

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Abstract: Gilmarite, Cu$_3$ (AsO$_4$) (OH)$_3$, occurs at the old copper mines of Roua (Alpes-Maritimes, France), associated with cuprite, posnjackite, langite, clinotyrolite, connellite, brochantite, malachite, vesignieite, cornubite, olivenite, trippkeite, domeykite and djurleite. It forms rosettes (0.3 mm diameter) or isolated crystals (0.1 × 0.04 × 0.02 mm maximum dimension). The green-blue crystals are elongated along [101] or [100], flattened on {010} and have a good cleavage on {010}. They are not twinned. The mineral is triclinic, $P\bar{1}$, a = 5.445 (4), b = 5.873 (3), c = 5.104 (3) Å, α = 114.95 (3), β = 93.05 (5), γ = 91.92 (4)°, V = 147.5 (2) Å^3, Z = 1, D$_{meas}$ = 4.2 (1) and D$_{calc}$ = 4.28 g/cm^3. The strongest lines in the X-ray powder diffraction pattern (d$_{obs}$ in Å, (hkl), I$_{vis}$) are: 4.613, (001), 100; 4.580, (01$\bar{1}$), 50; 3.390, (101), 60; 2.713, (200), 40; 2.543, (01$\bar{2}$) (12$\bar{1}$), 40. Mohs' hardness is ~3. Luster is vitreous transparent, streak is bluish green; crystals are biaxial (–) with α = 1.760 (5), β = 1.80 (1), γ = 1.83 (1) at 589 nm; 2 V$_{obs}$ = 77 (4)°, 2 V$_{calc}$ = 80 (1)°. Pleochroism is weak with γ = green; , α, β = light green. The crystal structure was solved by direct methods (Mo$K\alpha$ radiation) and refined using 1640 observed unique reflections to R = 0.062, R_w = 0.041. Gilmarite is a polymorph of clinoclase, their structures are quite different. The structure of gilmarite is formed by infinite chains of CuO$_6$ octahedra and CuO$_5$ square pyramids extending along the **b** axis. These chains are connected *via* CuO$_5$ square pyramids to form sheets parallel to (001). The sheets are connected *via* AsO$_4$ tetrahedra.

Key-words: gilmarite, new mineral, powder pattern, crystal structure, arsenate, copper, hydrogen bonding.

Introduction

Gilmarite, Cu$_3$ (AsO$_4$) (OH)$_3$, is a new mineral discovered in samples collected by Danielle Mari, Gilbert Mari and Pierre Rolland in the old copper mines of Roua (North group, municipality of Guillaumes) which are situated NW of the Alpes-Maritimes department (France), about 50 km as the crow flies from Nice. This mineral is a polymorph of clinoclase.

The mineral name honours Gilbert Mari (1944-), mineralogist, University of Nice-Sophia Antipolis, president of the Association of Naturalists of Nice and the Alpes-Maritimes, for the remarkable work he has done with his wife Danielle and Pierre Rolland on the old copper mines of this area (Mari, 1992). The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

Type material is preserved in the Department of Mineralogy of the Natural History Museum of Geneva, Switzerland, under reference no. 477.006.

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. This Dome consists of a small massif formed by an anticline, in which the Permian
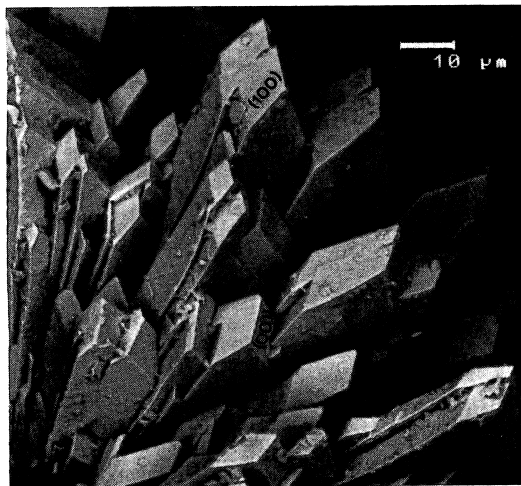
Fig. 1. SEM image of gilmarite crystals, elongated in the [101] direction, and flattened on {010}. Bar scale is 10 μm.

series are particularly well developed, and is surrounded by deformed and folded Mesozoic and Cenozoic formations. The Barrot Dome forms the south-west end of the Argentera-Barrot basin in which a continental Permian series was deposited in a distentional graben (Vinchon, 1984).

According to their stratigraphic positions, the ore showings have been divided into four groups. In the past, only the stratiform mineralization at the contact between the Permian and Triassic formations was considered of economic interest. The Cerisier ore deposit, at the southern flank of the massif, was in production from 1860 to 1886, producing around 2500 tons of copper extracted from chalcocite and bornite.

The metallogeny of the Barrot Dome has been studied by Vinchon (1984). The new mineral described here occurs in the Roua copper occurrences in the upper part of the Var valley (the Daluis gorge) at the western margin of the Dome. These ore occurrences outcrop in the upper part of the cliffs, some 250 m above the left bank of the river. They occur in two distinct zones 400 m apart, a northern and a southern zone lying, respectively, in the districts of Guillaume and Daluis.

The Roua ore deposit occurs in a peculiar stratigraphic position. The cupriferous mineralization is hosted in a gangue formed by subvertical dolomite and calcite veinlets, with accessory aragonite. The veinlets crosscut the Permian

pelites and red sandstones of the Cians Formation. Their thickness varies from a few mm to a few cm. They are oriented ENE-WSW in the northern group, and ESE-WNW in the southern group. The veins have been worked since the Chalcolithic period. There are numerous short galleries (15 in the northern group, 21 in the southern one) with a total length of 210 m. Between the 17th and the 19th centuries, the most mineralized veinlets were mined out again by explosives. The last attempt to mine this area ended in 1864.

The cupriferous mineralization at Roua consists of flake-shaped native copper, sometimes several tens of cm in size with irregular contours, and up to 3.5 cm thick, and small nodules. This copper occurs in the central part of the veinlets, and is always associated with cuprite, copper arsenides (domeykite, algodonite, koutekite), and, more rarely, native silver. The composition of the native copper varies from pure copper to an alloy with an arsenic content of up to 12 wt.%.

In the course of a detailed mineralogical study, several secondary, rare and unknown mineral species have been recognized (Sarp et al., 1994, 1996). The new mineral described here occurs in small geodes in association with cuprite, posnjackite, langite, clinotyrolite, connelite, brochantite, malachite, vesignieite (Sarp et al., 1995), cornubite, olivenite, trippkeite, domeykite and djurleite.

Physical and optical properties

Gilmarite forms rosettes of maximum size 0.3 mm in diameter or isolated crystals of maximum size $0.1 \times 0.04 \times 0.02$ mm. The crystals are elongated along [101] or [100], flattened on {010} and have one good cleavage parallel to {010}; they are not twinned. The most developed forms are {100}, {010}, {001} and {101} (Fig. 1). The crystals are green blue, transparent, with vitreous lustre and blue-green streak. The mineral is brittle with uneven irregular fracture. The Mohs' hardness is ~ 3. The density, measured by flotation in heavy liquid, is 4.2(1) g/cm^3 and the calculated density is 4.21 g/cm^3 (based on the empirical formula) and 4.28 g/cm^3 (based on the ideal formula). The mineral is soluble in HCl. It is nonfluorescent and has weak pleochroism : γ = green; α and β = light green. Gilmarite is biaxial negative, with α = 1.760 (5), β = 1.80 (1), γ =1.83 (1) (determined at 589 nm), 2 V_{obs} = 77(4)° and 2 V_{calc} = 80(1)°. The index of refraction γ had 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 > υ) is weak. The optic orientation is as follows: on {010} α ∧ c = 33°, β ∧ a = 37.1°; on {001} β ∧ a = 34.3°, γ ∧ b = 30.1°; on {101} γ' ∧ b = 44° and β' ∧ [101] = 36.5°.

Chemical composition

Crystals of gilmarite were chemically analyzed with a Cameca electron microprobe, using a beam size of 14 μm, an operating voltage of 15 kV, and a beam current of 6.5 nA. Qualitative examination showed only Cu and As. For quantitative analysis, chalcopyrite (Cu) and arsenic metal (As) were used as standards. The results are given in Table 1. The H_2O was estimated by difference due to insufficient sample. The empirical formula based on 7 oxygen atoms is: $Cu_{3.00}As_{0.98}H_{3.10}O_7$ and the idealized formula, $Cu_3 (AsO_4) (OH)_3$, was confirmed by structure determination. The Gladstone-Dale constants of Mandarino (1981) along with the oxide proportions, determined from the electron-micropobe data and from the crystal structure, lead to identical Kc values of 0.180. The value of Kp, calculated using the average index of refraction (1.797), and the calculated density from the empirical formula, is 0.189. For the same average index of refraction and the calculated density from the idealized formula, Kp is 0.186. The compatibility index is −0.050 for the empirical formula, and −0.033 for the idealized formula, indicating good and excellent compatibility (Man-

Table 1. Chemical analysis [wt.%] of gilmarite.

	Average of 5 analysis	Range of 5 analysis	Standard deviation	Ideal formula
CuO	63.0	62.67-63.32	0.2	62.68
As_2O_5	29.64	29.21-30.56	0.5	30.22
H_2O^*	7.36			7.10*

* By difference

darino, 1981) between the physical and chemical data.

X-ray crystallography

Powder-diffraction data (Table 2) were obtained using a Gandolfi camera (114.6 mm diameter, Ni-filtered CuKα). The relative intensities of the reflections were estimated visually. A single- crystal of gilmarite 0.048 × 0.024 × 0.020 mm in size was examined by the precession method (Ni-filtered CuKα) and the same crystal was measured on a Stoe Stadi-4 diffractometer with monochromatized MoKα radiation in a θ/2θ scanning-mode with limits −7 < h < 7, −8 < k < 8, −7 < l < 7. A total of 1724 unique reflections was measured up to θ = 30°. Lattice parameters were refined on the basis of 30 reflections with 5.9° < θ < 20.5° using Stoe DIF4 software (Stoe & Cie, 1988): a = 5.445(4), b = 5.873(3), c = 5.104(3) Å, α = 114.95(3), β = 93.05(5), γ = 91.92(4)°, V = 147.5(2) Å³, $a : b : c$ = 0.9271 : 1 : 0.8691. Data reduction was done using the programs REFCAL
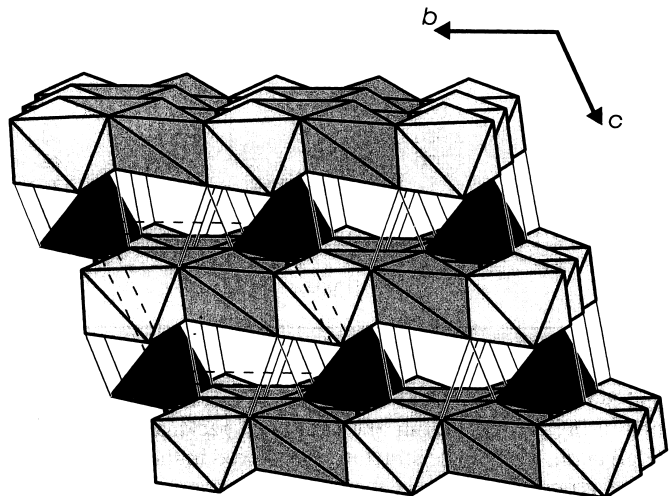

Fig. 2. The structure of gilmarite viewed approx. down [100]. The Cu3 octahedra are shaded light grey, the Cu1 and Cu2 square pyramids medium grey and the As tetrahedra dark grey. Hydrogen bonds are shown as thin lines, the outlines of the unit cell are dashed.

Table 2. X-ray powder diffraction data for gilmarite (d in Å).

(hkl)	d(calc.)	d(obs.)	I(vis.)	(hkl)	d(calc.)	d(obs.)	I(obs.)
100	5.427	5.430	10	012	1.849		
010	5.315	5.321	15			1.848	<5
001	4.615	4.613	100	220	1.843		
01̄1	4.577	4.580	50	032̄	1.830		
1̄10	3.920	3.923	5			1.830	5
110	3.689	3.690	10	202̄	1.826		
101̄	3.652	3.654	20	21̄2	1.811		
111̄	3.534	3.535	15	300	1.809	1.810	10
1̄11	3.464	3.470	15	121	1.807		
101	3.393	3.390	60	1̄12̄	1.795	1.795	5
011	2.924	2.930	10	030	1.772	1.773	10
021̄	2.895	2.892	<5	222̄	1.767	1.764	5
200	2.713	2.713	40	1̄32	1.736		
11̄1	2.666			22̄2	1.732	1.734	5
		2.663	10	132̄	1.731		
020	2.657			112	1.709	1.706	<5
1̄21	2.576	2.579	10	202	1.697	1.696	5
012̄	2.548			310	1.681		
		2.543	40			1.681	<5
12̄1	2.532			013̄	1.680		
111	2.491	2.491	5	22̄1	1.656		
1̄20	2.447	2.445	30			1.656	<5
201̄	2.419	2.420	5	130	1.654		
210	2.358			123̄	1.620	1.620	5
211̄	2.355	2.357	10	12̄3	1.582	1.582	10
112̄	2.355			32̄1	1.549	1.550	10
120	2.330	2.331	<5	32̄0	1.540	1.541	10
2̄11	2.313			003	1.538		
		2.310	10			1.537	10
002	2.307			221	1.538		
022̄	2.288	2.289	10	32̄1	1.520	1.520	10
201	2.267			311	1.485	1.485	<5
		2.271	15	302̄	1.478		
1̄12	2.261					1.480	<5
102̄	2.183	2.186	<5	133̄	1.477		
122̄	2.124	2.125	20	041̄	1.451		
12̄2	2.093	2.096	<5			1.450	5
21̄1	2.075			042̄	1.447		
		2.075	5	230	1.443		
102	2.069					1.442	<5
2̄21	2.000	2.000	5	1̄22	1.441		
021	1.970			1̄42	1.406	1.406	<5
		1.966	5	131	1.384		
2̄20	1.960			122	1.384	1.384	10
211	1.913	1.914	5	203̄	1.383		
212̄	1.908						
		1.904	10				
12̄1̄	1.899						

and SORTRF and an analytical absorption correction using LSABS from the Xtal 3.2 package (Hall *et al.*, 1992). The structure was solved in the space group $P\,1$ by direct methods with program GENTAN from the Xtal 3.2 package. The struc- ture (without hydrogen atoms) was refined on F^2 with program LSLS from the Xtal 3.2 package using 1640 observed reflections (weighted $1/\sigma^2$) with $F^2_{obs} > 0\ \sigma\ (F^2_{obs})$. The secondary-extinction correction was done according to Becker & Cop-

Table 3. Atom positions and displacement parameters for gilmarite.

Atom	x	y	z	$U_{eq}(\text{Å}^2)$
Cu1	0.0492(2)	0.6036(2)	0.3224(2)	0.0098(4)
Cu2	0.5489(2)	0.3631(2)	0.3568(2)	0.0099(4)
Cu3	0.5723(2)	0.8811(2)	0.3869(2)	0.0099(4)
As	-0.0013(1)	0.0003(1)	0.0001(1)	0.0089(4)
O1	0.1620(10)	0.2710(10)	0.0710(10)	0.0150(20)
O2	0.1880(109	0.8050(10)	0.0740(10)	0.0180(20)
O3(OH)	0.7030(10)	0.5420(10)	0.1540(10)	0.0100(20)
O4	0.7430(9)	0.0600(10)	0.1860(10)	0.0130(20)
O5(OH)	0.3710(10)	0.6730(10)	0.5380(10)	0.0090(20)
O6(OH)	0.4830(10)	0.2230(10)	0.6300(10)	0.0130(20)
O7	0.9050(10)	0.8680(10)	0.6530(10)	0.0160(20)

The equivalent isotropic atomic displacement parameters are expressed as
$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

Table 4. Selected interatomic distances (Å) for gilmarite.

Cu1-O1	1.973(6)	Cu3-O4	1.993(7)
Cu1-O7	1.975(5)	Cu3-O3 (OH)	2.018(6)
Cu1-O3 (OH)	1.987(6)	Cu3-O5 (OH)	2.020(7)
Cu1-O2	2.208(8)	Cu3-O7	2.228(6)
Cu1-O5 (OH)	1.956(6)	Cu3-O6 (OH)	1.958(6)
		Cu3-O2	2.471(6)

Cu2-O6 (OH)	1.936(8)	As-O7	1.647(5)
Cu2-O3 (OH)	1.960(7)	As-O1	1.682(6)
Cu2-O5 (OH)	1.974(6)	As-O4	1.689(6)
Cu2-O4	1.989(6)	As-O2	1.711(7)
Cu2-O1	2.406(6)		

Range of shared edges between
CuO$_6$ and CuO$_5$ polyhedra :   2.581(8) - 2.920(10)

Range of edges within
AsO$_4$ tetrahedron :   2.676(8) - 2.848(8)

O$_h$3···O$_h$6	2.716(7)	O$_h$5···O2	2.765(9)
O$_h$6···O1	2.852(9)		

Table 5. Bond valence (vu) table for gilmarite.

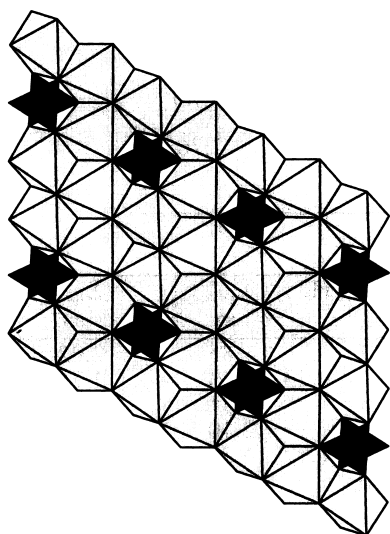|	Cu1	Cu2	Cu3	As	H1	H2	H3	$\Sigma_{excluding}$ H'S	$\Sigma_{including}$ H'S
O1	0.45	0.14		1.26		0.17		1.85	2.02
O2	0.24		0.12	1.17			0.23	1.53	1.76
O3 (OH)	0.44	0.47	0.40		0.76			1.31	2.07
O4		0.43	0.43	1.24				2.10	2.10
O5 (OH)	0.47	0.45	0.40				0.77	1.32	2.09
O6 (OH)		0.50	0.47		0.24	0.83		0.97	2.04
O7	0.45		0.23	1.38				2.06	2.06
Σ	2.05	1.99	2.05	5.05	1	1	1		

The bond valences for hydrogen atoms were fixed to 1.
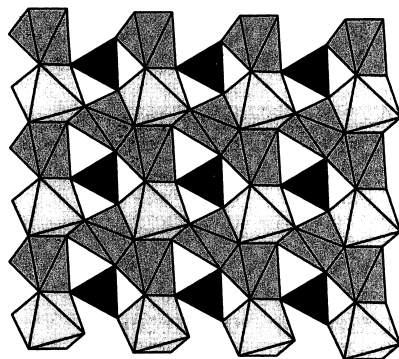
a. Gilmarite
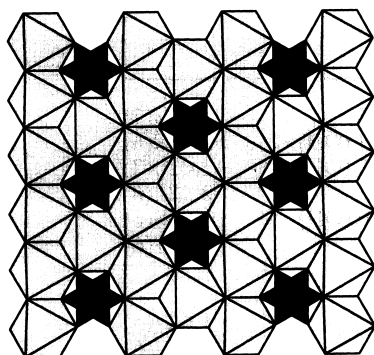
b. Vesignieite

c) Cornubite

pens (1974) with the extinction parameter g = 923(78). The refinement converged to R = 0.062, R_w = 0.041 and Goof = 1.59 with 102 parameters, including anisotropic-displacement parameters. The refined value of the Flack (1983) parameter is −0.03(3). The largest residuals in the difference-Fourier map are −2.22 and 2.22 e/Å^3.

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 3, and a list of selected interatomic distances is given in Table 4. Atom coordination and bond valences were analyzed by the program IVTON (Balić Žunić & Vicković, 1996). There are three Cu and one As sites in the structure. Cu1 and Cu2 are co-ordinated by a square pyramid, Cu3 by a distorted octahedron, and As by a tetrahedron. The structure is formed by infinite chains of $Cu3O_6$ octahedra and $Cu2O_5$ square pyramids extending along the **b**-axis (Fig. 2, 3a) sharing edges O3-O5 and O4-O6. These chains are connected *via* $Cu1O_5$ square pyramids by sharing edges O2-O5, O1-O5 and O3-O7, forming sheets parallel to (001). These sheets are connected *via* AsO_4 tetrahedra (Fig. 2).

No hydrogen atoms were detected in the dif-ference-Fourier map, therefore the concept of bond valences (Brown & Kang Kun Wu, 1976) was used to locate the hydrogen bonds. The data of Brese & O'Keeffe (1991) were used to calcu-late the bond valences for all non-hydrogen atoms (see Table 5). The sums for O3 (1.31), O5 (1.32) and O6 (0.97) indicate the presence of OH groups. The sums for all other oxygen atoms range from 1.53 to 2.10, thus indicating that some of them may act as proton acceptors in H...O bonds. Valence sums for cations are in good agreement with their corresponding ionic charges.

Based on the dependence of H...O bond valence on O...O distance (assuming stretched O-H...O bond angles) according to Brown & Alter-matt (1985) we propose possible hydrogen bonds. The results are given in Table 5. Two OH groups

← Fig. 3. The sheets of edge-sharing octahedra which are the basic building units of a) gilmarite, parallel to (001), b) vesignieite, parallel to (001) and c) cornubite parallel to (0$\bar{1}$1). The grey scale of the coordination polyhedra corresponds to Fig. 2.

(O3 and O5) yield one O-H bond each. The OH group O6 yields one O-H and accepts also one H...O bond. Two atoms (O1 and O2) accept one H...O bond each. All three hydrogen bonds bridge between the octahedral layers.

Discussion of the structure

Gilmarite, $Cu_3(AsO_4)(OH)_3$, is a polymorph of monoclinic clinoclase (Eby & Hawthorne, 1990). The structure of clinoclase contains two sets of $Cu_2(OH)_4O_4$ dimer groups, each formed by two square pyramids; there is no dimer group in gilmarite.

The structure of gilmarite belongs to the group of infinite sheet structures with M = M-T type of sheets according to the classification of Eby & Hawthorne (1993). It can be derived from a sheet of edge-sharing octahedra (as observed in brucite) by removal of one quarter of the cations (every second cation in every second chain is missing). Opposing the empty cation site, on one side of the sheet, there is an AsO_4 tetrahedron (see Fig. 3a) which links adjacent sheets. The Cu1 and Cu2 octahedra are changed to square pyramids by removal of one oxygen atom per Cu1-Cu2 pair.

Similar sheets occur in the structures of vesignieite, $Cu_3Ba(VO_4)_2(OH)_2$, (Ma *et al.*, 1990) and cornubite, $Cu_5(AsO_4)_2(OH)_4$, (Sieber *et al.*, 1984). In vesignieite, one quarter of the octahedral sites are vacant. In their place, there are two VO_4 tetrahedra, one on each side of the sheet (see Fig. 3b). Adjacent sheets are linked by VO_4 tetrahedra and BaO_6 octahedra. In cornubite, one sixth of the octahedral sites are vacant. In their place are two AsO_4 tetrahedra, one on each side of the sheet (Fig. 3c).

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