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Rollandite, $Cu_3(AsO_4)_2 \cdot 4H_2O$, a new mineral: its description and crystal structure

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Abstract: Rollandite, $Cu_3(AsO_4)_2 .4H_2O$, was found in the old copper mines of Roua (Alpes-Maritimes, France), associated with olivenite, conichalcite, clinotyrolite, cornubite, kolfanite, pharmacosiderite, gerhardtite, atacamite, gilmarite, wallkilldellite-Fe, cuprite, domeykite, algodonite and native copper. It forms aggregates (1mm diameter) consisting of perfect crystals (0.5 x 0.15 x 0.1 mm maximum dimension). The bottle-green crystals are elongated along **a**, slightly flattened on {010}, and have a good cleavage on {001}. They are not twinned. The mineral is orthorhombic, *Pnma*, $a = 5.6906(4)$, $b = 17.061(1)$, $c = 9.732(1)$ Å, $V = 944.9(1)$ Å^3, $Z = 4$, $D_{meas} = 3.9(1)$ and $D_{calc} = 3.84$ g/cm^3. The strongest lines in the X-ray powder diffraction pattern (d_{obs} in Å, (hkl), I_{vis}) are: 8.52, (020), 100; 3.721, (131), 60; 3.221, (141) (051), 90; 3.102, (132), 40; 2.817, (103)(033), 35; 2.795, (142), 35; 2.350, (143) (053), 25; 2.133, (080) (251), 25. Mohs' hardness is 4-4.5. Luster is vitreous transparent, streak is very light green; crystals are biaxial (-) with $\alpha = 1.745(5)$, $\beta = 1.755(5)$, $\gamma = 1.760(5)$ at 590 nm; $2V_{obs} = 71(2)°$, $2V_{calc} = 70.1(4)°$. Non pleochroic. The crystal structure was solved by direct methods (Mo$K\alpha$ radiation) and refined using 1407 observed unique reflections to $R = 0.086$, $R_w = 0.046$. The structure of rollandite is formed by (020) sheets of $Cu1O_6$ octahedra and [100] chains of $Cu2O_5$ square pyramids linked by AsO_4 tetrahedra. The water molecule $O6H_2$ is bonded by hydrogen bonds in the channels running along [100].

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

Introduction

Rollandite, $Cu_3(AsO_4)_2 \cdot 4H_2O$, is a new mineral discovered in samples collected by Danielle Mari, Gilbert Mari and Pierre Rolland in the old copper mines of Roua, which are situated in the northwestern part of the Alpes-Maritimes department (France).

The mineral name honours Pierre Rolland (1940 -), an eminent mineral collector of the Roua mines who works in the well-known Oceanographic Museum of the principality of Monaco. 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. 447.008

Occurrence

The new mineral described occurs in the Roua

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copper occurrences (South group) in the upper part of the Var valley (the Daluis gorge) at the western margin of the Barrot Dome. The metallogeny and geology of this Dome have been studied by Vinchon (1984) and Mari (1992). In the Roua 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 and native silver. Detailed mineralogical study of this ore deposit produced several secondary, rare and unknown mineral species (Sarp *et al.*, 1994, 1995, 1996). The new mineral described here occurs in small geodes in association with olivenite, conichalcite, clinotyrolite, cornubite, kolfanite, pharmacosiderite, gerhardtite, atacamite, gilmarite (Sarp & Černý, 1999), wallkilldellite-Fe (Sarp *et al.*, 1999), cuprite, domeykite, algodonite and native copper.

Physical and optical properties

Rollandite occurs as aggregates of maximum size 1mm in diameter, which are formed by perfect crystals of maximum size 0.5 x 0.15 x 0.1 mm. The crystals are elongated parallel to **a**, slightly flattened on {010} and have one good {001} cleavage; they are not twinned. The most developed forms are {010}, {011}, {101} and {001} (Fig. 1). The crystals are bottle-green, transparent, with vitreous lustre and very light green streak. The mineral is very brittle with conchoidal fracture. The Mohs' hardness is 4-4.5. The density, measured by flotation in heavy liquid, is 3.9 (1) g/cm^3 and the calculated density is 3.84(1) (based on the empirical formula) and 3.80 g/cm^3 (based on the ideal formula). The mineral is soluble in HCl. It is nonfluorescent and nonpleochroic. Rollandite is biaxial negative, with α = 1.745(5), β = 1.755(5), γ = 1.760(5) (determined at 590 nm), $2V_{obs}$ = 71(2)° and $2V_{calc}$ = 70.1(4)°. The dispersion ($r < v$) is strong. The optical orientation is: O.A.P.//{001}, α = **a**, β = **c**, γ = **b**.

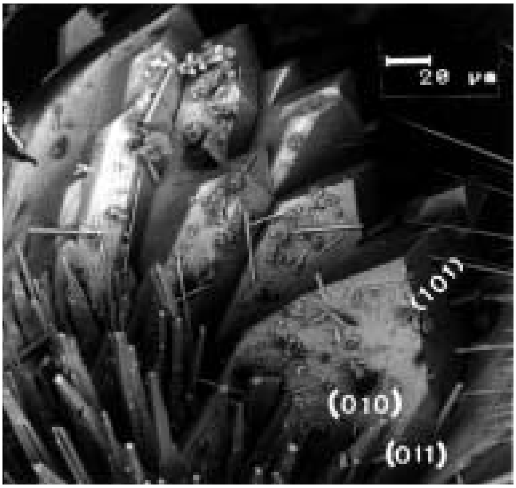

Fig. 1. SEM image of rollandite crystals, elongated parallel to **a**, and slightly flattened on {010}. Acicular crystals are olivenite.

Chemical composition

Rollandite was analyzed with a Cameca electron microprobe, using operating voltage of 15 kV, beam current of 15 nA, and a beam size of 10 µm. Qualitative examination showed only Cu and As. For quantitative analysis, trippkeite (Cu, As), copper metal (Cu) and arsenic metal (As) were used as standards. The results are given in Table 1.

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

	Average of 10 analysis	Range of 10 analysis	Standard deviation	Ideal formula
CuO	44.87	43.98-45.95	0.6	44.15
As_2O_5	42.44	40.35-43.75	1.0	42.53
H_2O*	12.69			13.32

*By difference

The H_2O was estimated by difference due to insufficient sample. The empirical formula based on 12 oxygen atoms is: $Cu_{3.09}As_{2.02}H_{7.71}O_{12}$ and the idealized formula, $Cu_3(AsO_4)_2.4H_2O$, 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 0.188 and 0.189 respectively. The value of Kp, calculated using the average index of refraction (1.753), and the calculated density from the empirical formula, is 0.196. For the same average index of refraction and the calculated density from the idealized formula, Kp is 0.198. The compatibility index is -0.043 for the empirical formula, and -0.048 for the idealized formula, indicating good compatibility (Mandarino, 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 Cu*K*α radiation). The relative intensities of the reflections were estimated visually. A single-crystal of rollandite 0.128 x 0.032 x 0.016 mm in size was examined by the precession

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

(*hkl*)	*d*(calc).	*d*(obs.)	*I*(vis.)	(*hkl*)	*d*(calc).	*d*(obs.)	*I*(obs.)
020	8.531	8.520	100	204	1.849 ¦		
002	4.866	4.865	5	064	1.849 ¦		
111	4.720	4.723	10		}	1.847	5
040	4.265	4.271	<5	182	1.847 ¦		
131	3.717	3.721	60	173	1.843 ¦		
112	3.614	3.612	<5	115	1.831	1.829	5
141	3.221			321	1.819		
	}	3.221	90		}	1.817	5
051	3.220			271	1.818		
132	3.100	3.102	40	331	1.769 ¦		
103	2.818			191	1.769 }	1.765	5
	}	2.817	35	302	1.767 ¦		
033	2.818			234	1.758 ¦		
	2.794	2.795	35	164	1.758 }	1.759	10
142							
201	2.731	2.732	5	312	1.758 ¦		
220	2.699	2.701	<5	322	1.730		
221	2.601	2.603	10		}	1.731	5
230	2.544	2.543	<5	272	1.730		
231	2.462			280	1.706 ¦		
	}	2.462	5	341	1.706 }	1.704	5
161	2.461			0.10.0	1.706 ¦		
004	2.433			174	1.648	1.647	5
	}	2.434	5	303	1.637 ¦		
212	2.431			093	1.637 ¦		
240	2.367			351	1.634 }	1.634	10
	}	2.366	20	342	1.633 ¦		
071	2.364			313	1.630 ¦		
143	2.351			282	1.610		
	}	2.350	25		}	1.610	5
053	2.351			0.10.2	1.610		
232	2.255			225	1.579		
	}	2.255	10		}	1.574	5
162	2.254			290	1.578		
250	2.185			264	1.550		
	}	2.184	<5		}	1.550	10
171	2.183			1.10.2	1.549		
124	2.164	2.165	<5	075	1.521	1.519	5
080	2.133			245	1.503	1.504	10
	}	2.133	25	353	1.476		
251	2.132				}	1.473	10
134	2.082	2.081	<5	324	1.473		
233	2.002			255	1.453	1.452	5
	}	2.003	10	400	1.423		
163	2.002				}	1.425	5
181	1.956			0.12.0	1.422		
	}	1.954	10				
082	1.953						
243	1.922	1.922	<5				
301	1.862 ¦						
091	1.861 }	1.860	10				
262	1.859 ¦						

method (Ni-filtered Cu*K*α) and the same crystal was measured on an Enraf-Nonius CAD4 diffractometer with monochromatized Mo*K*α radiation in θ/2θ scanning-mode with limits $-7 < h < 7$, $-23 < k < 23$, $-13 < l < 13$. A total of 3246 reflections was measured up to θ = 30°. Lattice parameters were refined on the basis of 25 reflections with 8.5° < θ < 29.5° using a program CELDIM (Enraf-Nonius, 1989): a = 5.6906(4), b = 17.061(1), c = 9.732(1) Å, V = 944.9(1) Å^3, a: b: c = 0.3335: 1: 0.5704. Data reduction was done using the programs REFCAL and SORTRF and analytical absorption correction using LSABS from the *Xtal*3.2 package (Hall *et al.*, 1992). The structure was solved in the space group *Pnma* by direct methods with program GENTAN from the *Xtal*3.2 package. The structure (without hydrogen atoms) was refined on F^2 with program LSLS from the *Xtal*3.2 package using all 1407 observed unique reflections (R_{int} = 0.085) weighted $1/\sigma^2$. The secondary-extinction correction was done according to Becker & Coppens (1974) with the extinction parameter g = 6004(538). The refinement converged to R = 0.086, R_w = 0.046 and *Goof* = 1.06 with 83 parameters, including anisotropic-displacement parameters. The largest residuals in the difference-Fourier map are -3.81 and 4.17 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

Table 3. Atom positions and displacement parameters for rollandite.

Atom	x	y	z	U_{eq} (Å^2)
Cu1	0.4264(2)	0.51379(6)	0.3510(1)	0.0099(3)
Cu2	0.0230(3)	1/4	0.2214(2)	0.0072(4)
As	0.3649(2)	0.10323(5)	0.10043(9)	0.0061(2)
O1	0.019(1)	0.1463(4)	0.5231(6)	0.013(2)
O2	0.024(1)	0.0351(3)	0.3188(6)	0.009(2)
O3	0.116(1)	0.0611(3)	0.0365(6)	0.010(2)
O4 (H_2O)	0.275(1)	0.5962(3)	0.2386(7)	0.011(2)
O5	0.280(1)	0.1745(3)	0.2150(6)	0.008(2)
O6 (H_2O)	0.214(2)	1/4	0.823(1)	0.025(3)
O7 (H_2O)	0.360(2)	1/4	0.4847(8)	0.011(2)

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

Table 4. Selected interactomic distances (Å) for rollandite.

Cu1-O2	1.933(6)	Cu2-O5	1.951(6)
Cu1-O4 (H_2O)	1.979(6)	Cu2-O5	1.951(6)
Cu1-O3	1.993(6)	Cu2-O5	1.988(6)
Cu1-O3	2.000(6)	Cu2-O5	1.988(6)
Cu1-O2	2.458(6)	Cu2-O7 (H_2O)	2.211(9)
Cu1-O4 (H_2O)	2.582(6)		
		As-O1	1.659(6)
		As-O2	1.670(6)
		As-O3	1.704(6)
		As-O5	1.719(6)
Range of edges within CuO_6 octahedron:	2.571(8) - 3.532(9)		
Range of edges within $Cu2O_5$ square pyramid:	2.576(8) - 3.341(10)		
Range of edges within AsO_4 tetrahedron:	2.729(9) - 2.774(9)		
$O_h4\cdots O1$	2.551(9)	$O_h4\cdots O6$	2.751(7)
$O_h6\cdots O1$ (× 2)	2.897(11)	$O_h7\cdots O1$ (× 2)	2.652(9)

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

	Cu1	Cu2	As	H1	H2	H3	H4	$\Sigma_{\text{excluding Hs}}$	$\Sigma_{\text{including Hs}}$
O1			1.34	0.26		0.16	0.21	1.34	1.97
O2	0.50 0.12		1.30					1.92	1.92
O3	0.43 0.42		1.18					2.03	2.03
O4 (H_2O)	0.44 0.09			0.74	0.80			0.53	2.07
O5		2×0.48 2×0.43	1.14					2.05	2.05
O6 (H_2O)					0.20×2	0.84×2		0	2.08
O7 (H_2O)		0.24					0.79×2	0.24	1.82
Σ	2.00	2.06	4.96	1	1	1	1		

The bond valences for hydrogen atoms were fixed to 1.
Left and right multipliers refer to equivalent bonds for cations and oxygens, respectively.

(Balić Žunić & Vicković, 1996). There are two Cu and one As sites in the structure. Cu1 is coordinated by a distorted octahedron, Cu2 by a square pyramid and As by a tetrahedron.

No hydrogen atoms were detected in the difference-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 calculate the bond valences for all non-hydrogen atoms (Table 5). The sums for O4 (0.53) and O7 (0.24) indicate the presence of water molecules. The sum for O6 (0) indicates the presence of a water molecule not included in the coordination of cations. The sums for all other oxygen atoms range from 1.34 to 2.05, 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 & Altermatt (1985) we propose possible hydrogen bonds. The results are given in Table 5. The water molecule O6 yield two O-H and accept two H···O bonds. The water molecules O4 and O7 yields two O-H bonds each. The atom O1 accepts three H···O bonds. From the six hydrogen bonds one is intralayer, and five are inter-layer.

Discussion of the structure

The structure of rollandite (Fig. 2) belongs to the group of M = M-T framework structures 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 half of the cations (every second cation pair is missing). The resulting (020) sheet of $Cu1O_6$ octahedra in rollandite can be seen

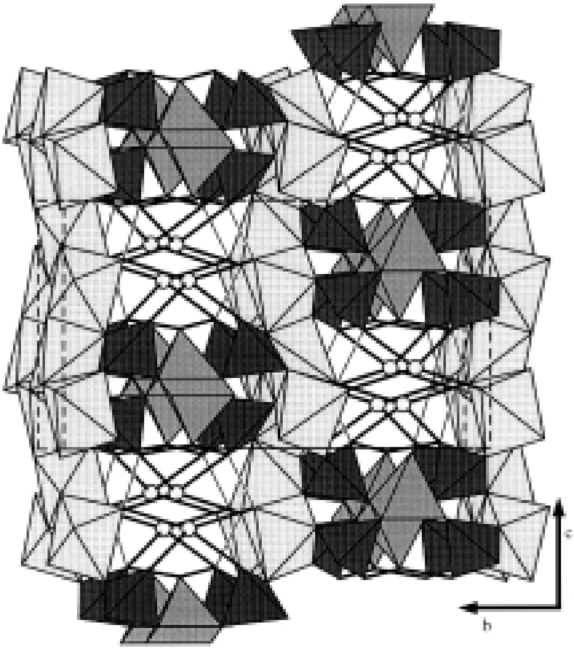

Fig. 2. The structure of rollandite viewed approx. down [100]. The Cu1 octahedra are light grey, the Cu2 square pyramids are medium grey and the As tetrahedra are in dark grey. Hydrogen bonds are shown as black thick lines, the outlines of the unit cell are dashed.

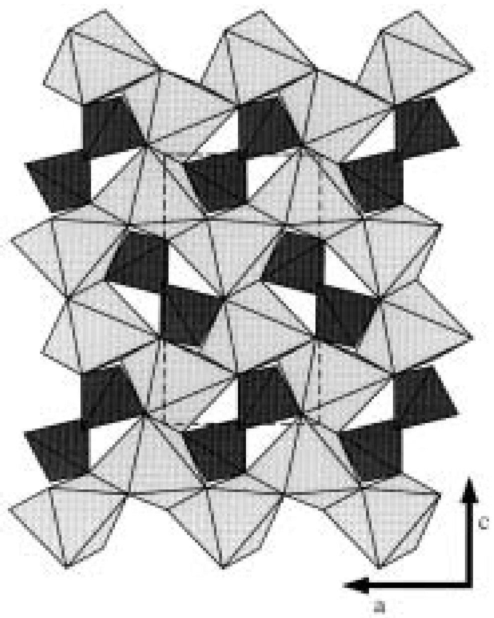

Fig. 3. The sheets of edge-sharing octahedra which are the basic building units of rollandite parallel to (020). The grey scale of the coordination polyhedra corresponds to Fig. 2.

in Fig. 3. Opposing the empty cation pair site, alternatively on both sides of the sheet, there are two AsO_4 tetrahedra which share two vertices each with the sheet. The tetrahedra cross-link sheets *via* the infinite chains of $Cu2O_5$ square pyramids extending along the **a**-axis by sharing one vertex with the chain (Fig. 2). The sheets are additionaly cross-linked by hydrogen bonds and by the interstitial water molecule $O6H_2$ situated in the channels running along the **a**-axis.

The powder pattern of rollandite visually resemble that of a synthetic compound $Cu_3(AsO_4)_2{\cdot}4H_2O$ (Mas, 1949) whose structure, however, was not determined.

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