RADOVANITE, $Cu_2Fe^{+3}(As^{+5}O_4)(As^{+3}O_2OH)_2H_2O$, A NEW MINERAL: ITS DESCRIPTION AND CRYSTAL STRUCTURE

BY

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ABSTRACT

Radovanite, $Cu_2Fe^{+3}(As^{+5}O_4)(As^{+3}O_2OH)_2H_2O$, a new mineral: its description and crystal structure. - Radovanite, $Cu_2Fe^{+3}(As^{+5}O_4)(As^{+3}O_2OH)_2H_2O$, occurs at the old copper mines of Roua (Alpes-Maritimes, France), associated with cuprite, native copper, malachite, trippkeite, olivenite and algodonite. It forms aggregates (2mm in diameter) formed by small equidimensional crystals or slightly elongated crystals along a or b (0.15 x 0.08 x 0.02 mm maximum dimension). The megascopic color is green pistachio. The mineral is not twinned and has no cleavage. It is orthorhombic, Pnma, a=9.585(1), b=13.143(1), c=8.0884(7) Å, V=1018.9(2) Å^3, Z=4, d_{meas}=3.9(1) and d_{calc}=3.83(1) g/cm^3. The strongest lines in the X-ray powder diffraction pattern (d_{obs} in Å, (hkl), I_{vis}) are : 6.88, (011), 25; 6.179, (101), 90; 3.241, (122), 40; 3.090, (202), 100; 2.710, (240) (321), 25; 2.214, (251) (223), 25. Mohs' hardness could not be measured because of the small grain size. Luster is vitreous transparent, streak is green; crystals are biaxial (-) with α =1.80(1), β =1.84(1). γ = 1.86(1) at 589 nm; $2V_{obs}$ = 65(5)°, $2V_{calc}$ = 70(3)°. It is pleochroic with γ = green pistachio, β = yellow green, α = light green to colorless. The optical orientation is a = β, b = γ and c = α. The crystal structure was solved by direct methods (MoKα radiation) and refined using 1027 observed unique reflections to R = 0.059, R_w = 0.023. The structure of radovanite is formed by a three-dimensional network formed by pairs of edge-sharing CuO_5 square pyramids and FeO_6 octahedra interconnected by AsO_4 tetrahedra and AsO_3 triangles. The water molecul is fixed in a structure cavity by hydrogen bonds of its two hydrogen atoms and of the OH group which is shared between the CuO_5 square pyramid and AsO_3 triangle.

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

INTRODUCTION

Radovanite, $Cu_2Fe^{+3}(As^{+5}O_4)(As^{+3}O_2OH)_2H_2O$, is a new mineral discovered in samples collected by Danielle Mari, Gilbert Mari and Pierre Rolland in the old copper mines of Roua, wich are situated in the northwestern part of the Alpes-Maritimes department (France).

The mineral name honours Dr. Radovan Černý, crystallograph at the University of Geneva, Switzerland.

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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. 478.004.

OCCURRENCE

The new mineral described occurs in the Roua copper deposits 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, native gold and native silver. Detailed mineralogical study of this ore deposit produced several secondary, rare and unknown mineral species (SARP *et al.*, 1999, 2000, 2001). The new mineral described here forms aggregates, associated with cuprite, native copper, malachite, trippkeite, olivenite and algodonite.

PHYSICAL AND OPTICAL PROPERTIES

Radovanite occurs as aggregates of maximum size 2 mm in diameter, wich are formed by small equidimensional crystals or slightly elongated crystals along a or b of maximum size 0.15 x 0.08 x 0.02 mm (Fig.1). The most developed forms are (101), (011), (001), (010), (hk0) and (hkl). The mineral is not twinned and has no cleavage. The crystals are green pistachio, transparent, with vitreous luster and green streak. The mineral is brittle with conchoidal fracture. The Mohs' hardness could not be measured. The density measured by flotation in heavy liquid, is 3.9(1) g/cm^3 and the calculated density is 3.83(1) g/cm^3 (based on the ideal formula) and 3.79(1) g/cm^3 (based on the empirical formula). The mineral is very slowly soluble in HCl. It is nonfluorescent and has medium pleochroism: γ = green pistachio, β = yellow green, α = light green to colorless. Radovanite is biaxial negative, with α = 1.80(1), β =1.84(1), γ = 1.86(1) (determined at 589 nm), $2V_{obs}$ = 65(5)° and $2V_{calc}$ = 70(3)°.

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 > 1.84. The optical orientation is: a = β, b = γ, c = α.

CHEMICAL COMPOSITION

Crystals of radovanite were chemically analysed with a Cameca electron microprobe, using a beam size of 12 µm, an operating voltage of 15kV, and a beam current of 30 nA. Qualitative examination showed only Cu, As, Fe, Al and P. For quantitative analysis, FeAsS (Fe,As), CuO (Cu), pyroxene (Al) and apatite (P) were used as standards.

The results are given in Table I. The H_2O content was estimated by difference due to insufficient sample. The empirical formula based on 11 oxygen atoms is: $Cu_{1.93}$ $Fe^{+3}_{0.92}Al_{0.01}P_{0.02}As^{+5}_{1.01}As^{+3}_{2.01}H_{4.15}O_{11}$ and the idealized formula, Cu_2Fe^{+3}
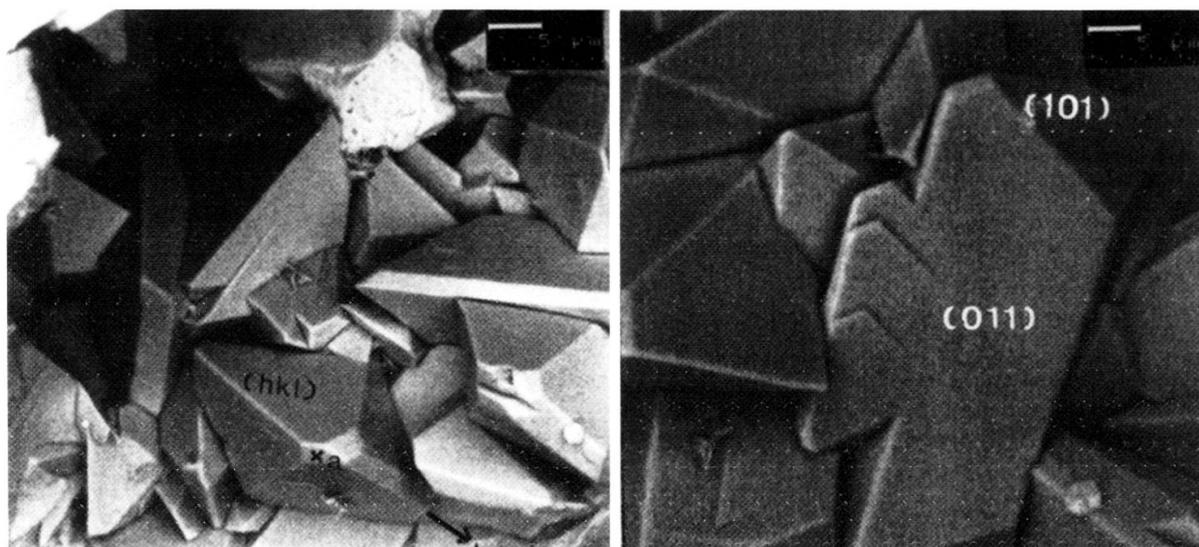
FIG. 1.
SEM images of radovanite crystals, a) equidimensional crystals, b) elongated crystals along a axis.

$(As^{+5}O_4)$ $[As^{+3}O_2(OH)]_2H_2O$, was confirmed by structure determination. In some crystals, the Al_2O_3 content increases and there is a remplacement between Fe^{+3} and Al giving the following formula: $Cu_2(Fe^{+3}_{0.5}Al_{0.5})(As^{+5}O_4)(As^{+3}O_2OH)_2H_2O$. This last formula will represent radovanite-Al. The only ferrous end-member has been studied in detail.

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 identical Kc values of 0.220. The value of Kp, calculated using the average index of refraction (1.833), and the calculated density from the empirical formula, is 0.220. For the same average index of refraction and the calculated density from the idealized formula, Kp is 0.217. The compatibility index is 0.000 for the empirical formula, and 0.014 for the idealized formula, indicating superior compatibility index (MANDARINO, 1981) between the physical and chemical data.

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

		Average of 4 analyses	Range of 4 analyses	Standard deviation	Ideal formula
	CuO	26.3	24.5 – 27.2	1.0	27.08
Fe (8.9)			8.8 – 9.0	0.3	
	Fe_2O_3*	12.7			13.59
	Al_2O_3	0.04	0.03 – 0.04		
	P_2O_5	0.3	0.2 – 0.3		
As (39.0)			38.7 – 39.3	0.4	
	As_2O_5**	19.93			19.55
	As_2O_3**	34.32			33.66
	H_2O***	6.41			6.12

* In the structure, Fe is +3
** Calculated in relation with structural formula
*** By difference

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

(hkl)	d(calc.)	d(obs.)	I(vis.)	(hkl)	d(calc.)	d(obs.)	I(vis.)
011	6.889	6.88	25	240	2.710		
020	6.572	6.56	10		}	2.710	25
101	6.182	6.179	90	321	2.708		
111	5.594	5.585	<5	042	2.550	2.551	20
200	4.793	4.789	5	302	2.507	2.510	<5
201	4.123	4.119	5	400	2.396	2.395	5
002	4.044	4.041	<5	251	2.217		
211	3.934	3.924	<5		}	2.214	25
220	3.872	3.871	20	223	2.213		
102	3.726	3.725	5	060	2.191	2.190	<5
112	3.585	3.584	5	152	2.148	2.148	5
221	3.493	3.489	<5	162	1.888	1.890	5
022	3.444	3.443	<<5	432	1.865		
122	3.241	3.241	40		}	1.864	5
202	3.091	3.090	100	501	1.865		
301	2.972	2.973	5	253	1.752	1.751	10
141	2.901 }			502	1.732	1.733	5
		2.897	15	452	1.622	1.621	10
311	2.898						

X-RAY CRYSTALLOGRAPHY

Powder-diffraction data (Table II) were obtained using a Gandolfi camera (114.6 mm in diameter, Ni-filtered CuKα radiation). The relative intensities of the reflections were estimated visually. A single-crystal of radovanite, 0.038 x 0.031 x 0.019 mm in size, was examined by the precession method (Ni-filtered CuKα) and the same crystal was measured on a Stoe IPDS diffractometer with monochromatized MoKα radiation and image plate detector in φ-oscillation scanning-mode with limits -11 < h < 11, -16 < k < 13, -9 < l < 9. A total of 4818 reflections (1027 unique, R_{int} = 0.085) was measured up to Θ = 25.6°. Lattice parameters were refined on the basis of 2000 reflections with 3° < Θ < 25.5°: a = 9.585(1), b = 13.143(1), c = 8.0884(7) Å, V = 1018.9(2) Å^3, a : b : c = 0.7293 : 1 : 0.6154. Data reduction and analytical absorption correction were done using the program X-RED (STOE & CIE, 1999). The structure was solved in the space group Pnma by direct methods with program GENTAN from the Xtal3.7 package (HALL et al., 2000), and refined on F^2 (without hydrogen atoms) with program LSLS from the Xtal3.7 package using all 1027 unique reflections weighted 1/σ^2. The refinement converged to R = 0.059, R_w = 0.023 and Goof = 0.81 with 86 parameters, including anisotropic-displacement parameters of all atoms. The largest residuals in the difference-Fourier map were −1.87 and 1.88 e/Å^3.

CRYSTAL STRUCTURE

Atom coordinates, standardized by the program STRUCTURE TIDY (GELATO & PARTHE, 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. The structural projections along three crystallographic axes are given in the Fig. 2.

TABLE III. Atom positions and displacement parameters for radovanite.

Atom	x	y	z	U_{eq} (Å²)
Cu	0.2535(1)	0.13718(9)	0.7512(2)	0.0142(5)
Fe	0	0	1/2	0.0083(9)
As1	0.0095(2)	1/4	0.5392(2)	0.0070(6)
As2	0.29252(9)	0.06939(8)	0.3001(1)	0.0123(4)
O1	0.0039(8)	0.1455(5)	0.4230(7)	0.013(3)
O2	0.1147(6)	0.0308(4)	0.702(1)	0.012(3)
O3	0.3248(6)	0.0264(5)	0.8747(9)	0.017(4)
O4 - OH	0.3997(7)	0.0814(6)	0.483(1)	0.026(4)
O5	0.3806(8)	1/4	0.818(2)	0.018(6)
O6 - H₂O	0.078(1)	1/4	0.024(2)	0.035(7)
O7	0.1653(8)	1/4	0.635(1)	0.011(5)

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

TABLE IV. Selected interatomic distances (Å) for radovanite.

Cu-O3	1.894(7)	Fe-O3	1.992(6)
Cu-O7	1.947(6)	Fe-O3	1.992(6)
Cu-O2	1.969(6)	Fe-O1	2.012(6)
Cu-O5	1.994(6)	Fe-O1	2.012(6)
Cu-O4	2.683(8)	Fe-O2	2.013(7)
		Fe-O2	2.013(7)
As1-O1	1.665(6)		
As1-O1	1.665(6)	As2-O2	1.775(6)
As1-O7	1.684(9)	As2-O3	1.793(7)
As1-O5	1.69(1)	As2-O4	1.810(7)

Range of edges within CuO₅ square pyramid:		2.450(9) - 3.51(1)	
Range of edges within FeO₆ octahedron:		2.774(9) - 2.917(9)	
Range of edges within As1O₄ tetrahedron:		2.69(1) - 2.77(1)	
Range of edges within As2O₃ triangle:		2.450(9) - 2.722(9)	
O4···O6	2.80(1)	O6···O4	2.80(1)

Atom coordination and bond valences were analysed by the program IVTON (BALIC ZUNIC & VICKOVIC, 1996). There are one Cu, one Fe and two As sites in the structure. The geometry of polyhedral coordination around Cu is a square pyramid, around Fe an octahedron, around As1 a tetrahedron, and around As2 a triangle. 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 (see Table V). Valence sums for cations are in good agreement with their corresponding ionic charges. The sum for O6 (0) indicates the presence of a water molecule not included in the coordination of cations. The sum for O4 (1.02) indicates the presence of OH group. The sums for all other oxygen atoms range from 1.83 to 2.21, thus

TABLE V. Bond valence (vu) table for radovanite.

	Cu	Fe	As1	As2	H1	H2	H3^a	H3^b	$\Sigma_{\text{excluding H's}}$	$\Sigma_{\text{including H'}}$
O1		2 x 0.51	2 x 1.32						1.83	1.83
O2	0.46	2 x 0.50		1.04					2.00	2.00
O3	0.56	2 x 0.53		0.99					2.08	2.08
O4-OH a	0.07			0.95	0.20		0.80		1.02	2.02
O4-OH b	0.07			0.95		0.20		0.80	1.02	2.02
O5	0.43 x 2		1.23						2.09	2.09
O6-H2O					0.80	1		0.20	0	2.00
O7	0.48 x 2		1.25						2.21	2.21
Σ	2.00	3.08	5.12	2.98	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.

indicating that they probably do not act as proton acceptors in H···O bonds. This result and the analysis of interatomic distances between oxygen atoms show that possible hydrogen bonds can occur only between O6 and O4 atoms. However, it would means two hydrogen bonds between two oxygen atoms. We therefore prefer a model where one hydrogen atom does not participate in any hydrogen bond. 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 in Table V possible hydrogen bonds. The water molecule oxygen O6 and the hydroxyl group oxygen O4 each yield one O-H and accept one H···O bond. The hydrogen bonds form a zig-zag chain along b-axis (see Fig. 2a,2c). This model requires that the true symmetry of the structure is lower, when the hydrogen atoms are included, which stays to be confirmed. The second hydrogen of the water molecule is not localized in this model, which again stays to be confirmed. The most probable candidate as an acceptor for this hydrogen bond is O1, which is slightly undersaturated (Table V). However, the distance O1-O6 is 3.58(1) Å, which is too long to attribute any energy to that hydrogen bond. The topology of the framework structure of radovanite can be described as $M_1=T_2-M_1=M_1-M_2-T_1-M_1$ according to the classification of EBY & HAWTHORNE (1993), where M_1 is CuO_4OH square pyramid, M_2 is FeO_6 octahedron, T_1 is $As1O_4$ tetrahedron and T_2 is $As2O_2OH$ triangle. Important structural motifs of radovanite (Fig. 2), Cu_2Fe (AsO_4) $(AsO_2 OH)_2$ H_2O, are similar as those in liroconite, $Cu_2Al(AsO_4)(OH)_4$ H_2O (BURNS et al., 1991): linear $[Fe(As1O_4)\varphi_4)]$ chain ($\varphi4$ = unspecified ligand) extending along [010], and edge-sharing dimmer $[Cu_2O_6(OH)_2]$ formed from two CuO_4OH square pyramids. In liroconite this dimmer is formed from two $CuO_2(OH)_2(H_2O)_2$ octahedrons, and Al substitutes Fe. The cross linkage between the chains and the dimmers is the same in radovanite and in liroconite with one important difference: the cross linkage of dimmers by $As2O_2OH$ triangles in radovanite is absent in liroconite. In the place of missing apical oxygen atom, which transform CuO_6 octahedron in liroconite to CuO_5 square pyramid in radovanite, there is a large cavity where the water molecule is fixed only by hydrogen bonds (Fig. 2a.). The structural similarity of the orthorhombic radovanite and pseudo-orthorhombic (monoclinic angle $\beta=91.32°$) liroconite can be seen also by similarity of lattice parameters: $a_{\text{radovanite}} \sim c_{\text{liroconite}}$, $b_{\text{radovanite}} \sim a_{\text{liroconite}}$, $c_{\text{radovanite}} \sim b_{\text{liroconite}}$.
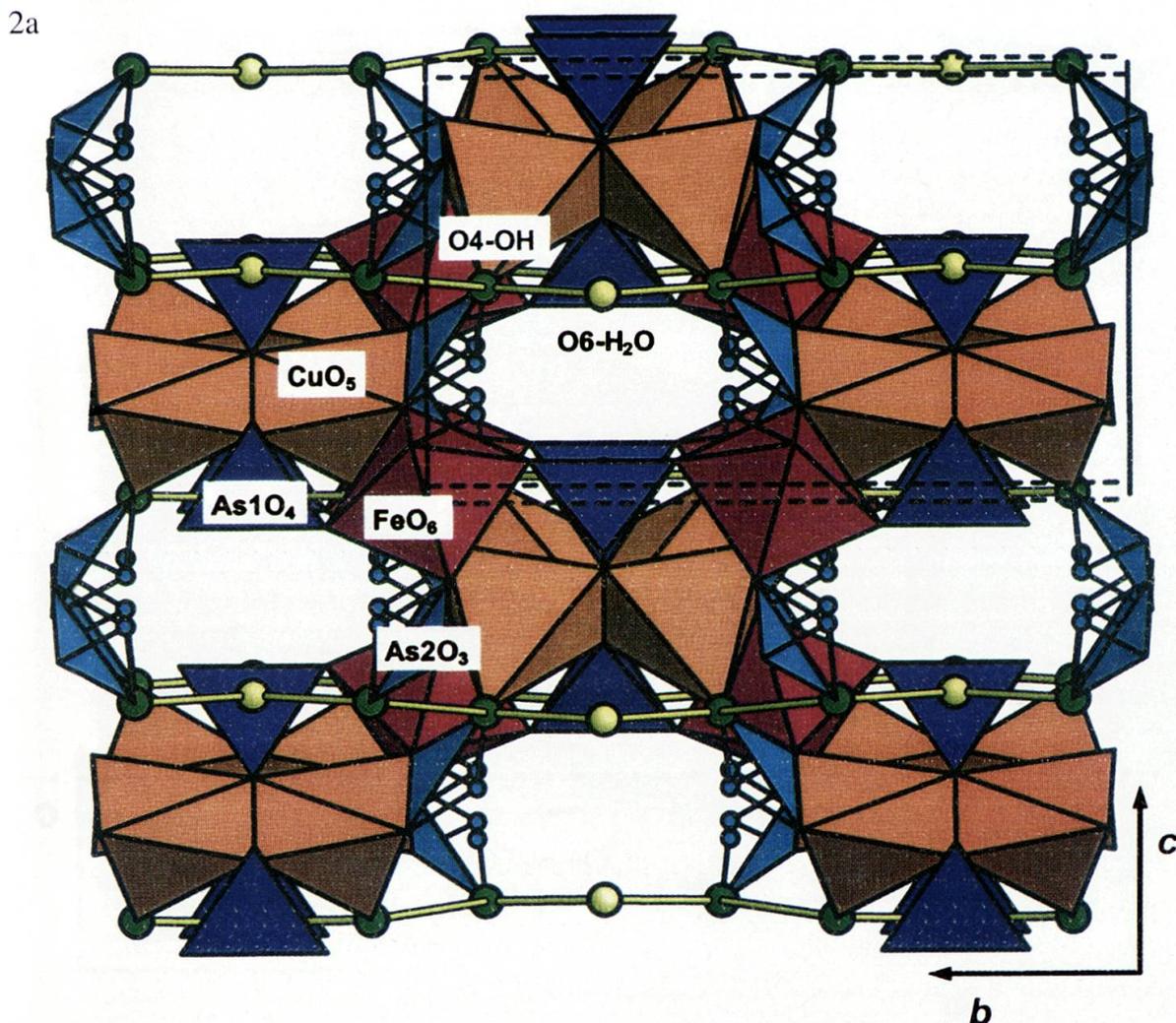
2a

FIG. 2.

The structure of radovanite viewed approx. Down to a) [100], b) [010] and c) [001]. CuO_5 square pyramids are in orange, FeO_6 octahedra in red, $As2O_3$ triangles in sky blue and $As1O_4$ tetrahedra in blue. The As2 atoms in AsO_3 triangles are shown as small spheres, the oxygen atoms O4-OH and O6-H_2O participating in the hydrogen bonds as larger spheres. Hydrogen bonds are shown as thick lines, the outlines of the unit cell are dashed.

RÉSUMÉ

RADOVANITE, $Cu_2Fe^{+3}(As^{+5}O_4)(As^{+3}O_2OH)_2 H_2O$,
UN NOUVEAU MINÉRAL: SA DESCRIPTION ET SA STRUCTURE CRISTALLINE

Radovanite, $Cu_2Fe^{+3}(As^{+5}O_4)(As^{+3}O_2OH)_2 H_2O$, 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 de l'Association Internationale de Minéralogie (I.M.A). Le minéral est orthorhombique, son groupe d'espace est Pnma. Les paramètres de la maille élémentaire sont a = 9,585(1), b = 13,143(1), c = 8,0884(7) Å. Il est optiquement biaxe (-) avec α = 1,80(1), β = 1,84(1), γ = 1,86(1). La structure atomique a été affinée en utilisant 1027 réflections uniques observées jusqu'à R = 0.059, R_w = 0.023.

Mots-clés: radovanite, nouveau minéral, diagramme de poudre, structure cristalline, arseniate-arsenite, cuivre, fer, liaison d'hydrogène.
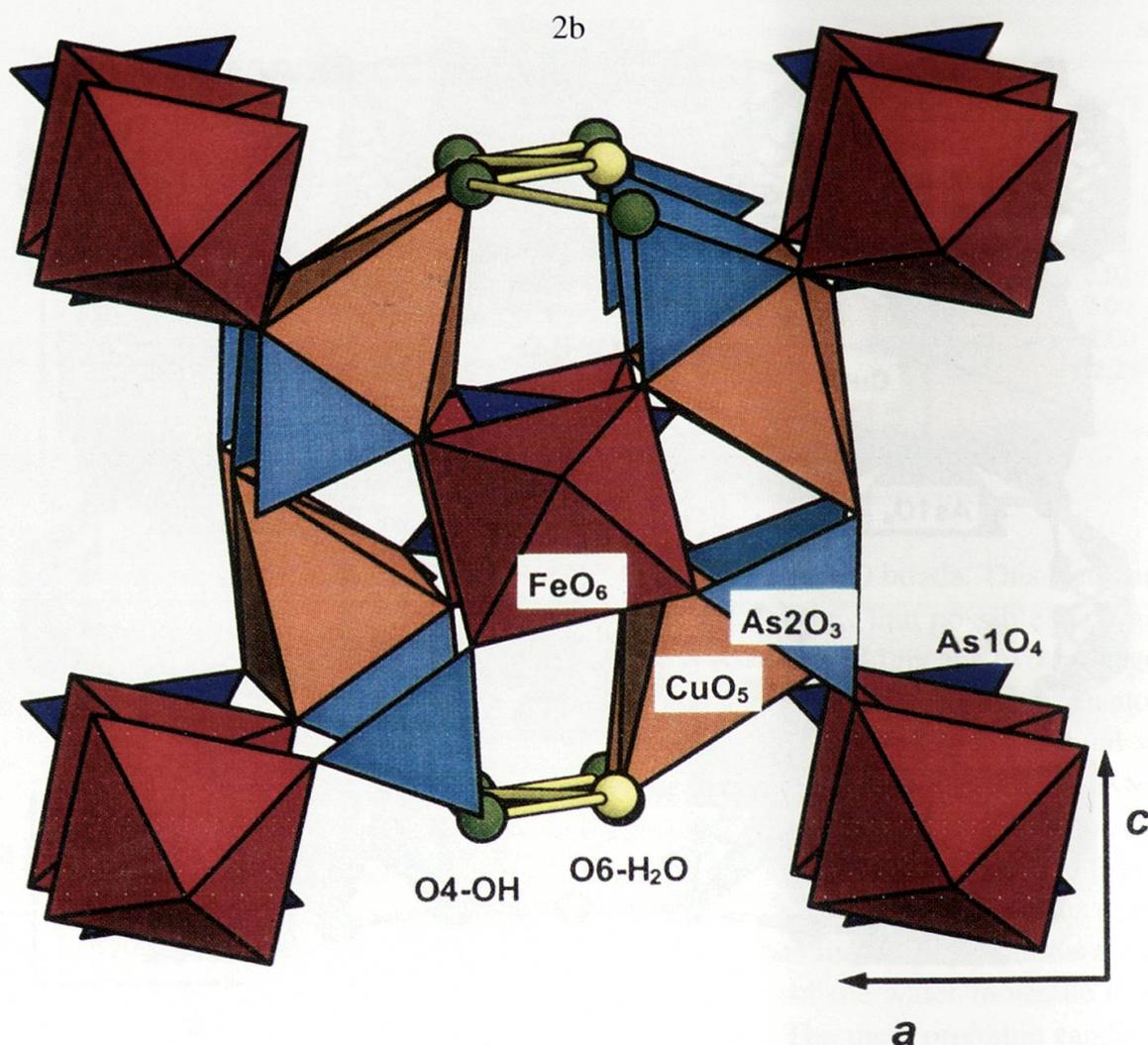
2b

FeO₆ As2O₃ As1O₄ CuO₅

O4-OH O6-H₂O

c

a

ACKNOWLEDGEMENTS

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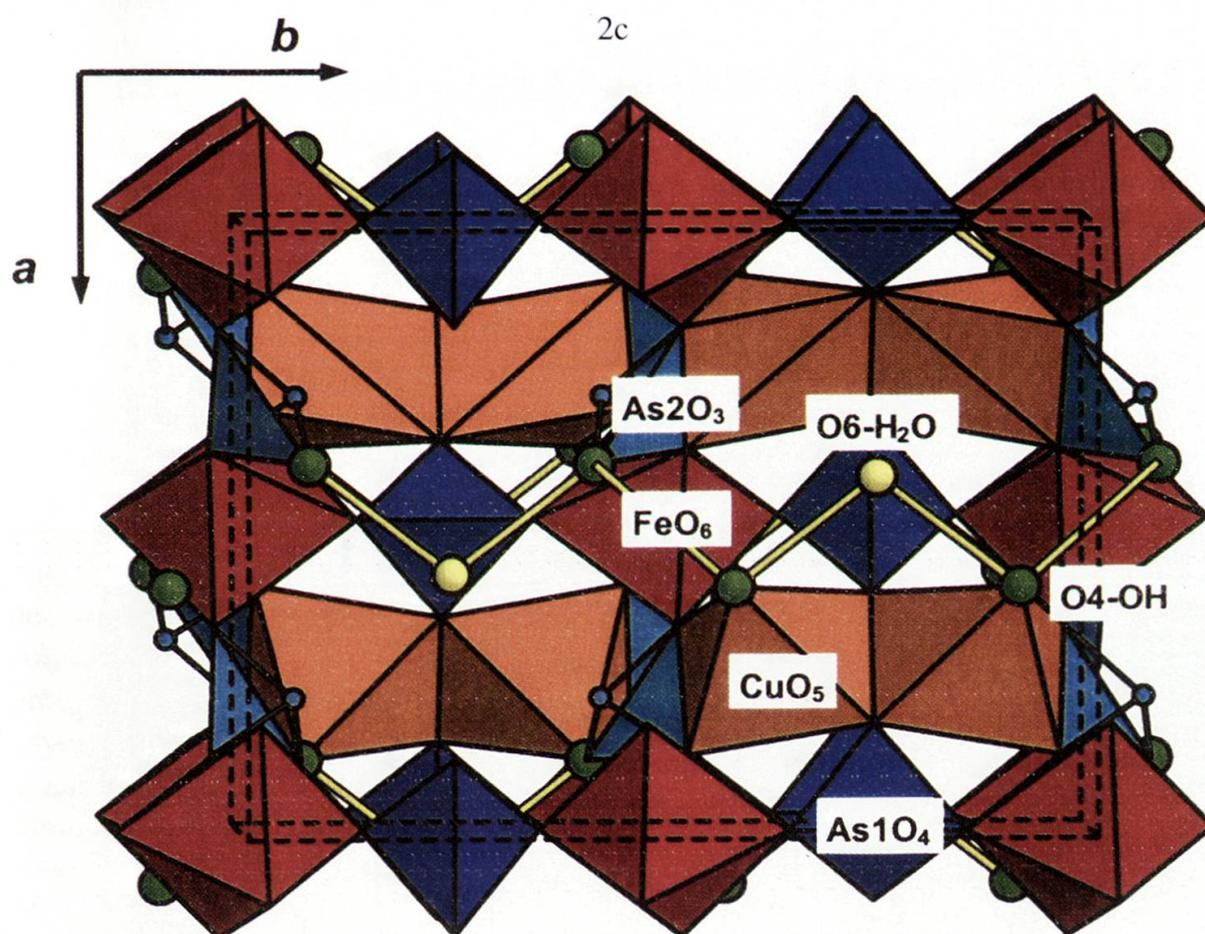
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