Orthowalpurgite, (UO2)Bi4O4(AsO4)2·2H2O, a new mineral from the Black Forest, Germany

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Abstract: The new mineral orthowalpurgite was found associated with preisingerite, quartz and anatase on a specimen from the dump of the Schmiedestollen, Wittichen, Black Forest, Germany. It forms transparent, yellow, orthorhombic crystals with $2/m$ symmetry up to 0.3 mm, tabular ‖ {010}, elongated ‖ [100]; crystallographic forms are {010}, {010}, {104}, and {100}; Mohs' hardness 4½, density(calc.) = 6.51 g cm^{-3}. The crystals are brittle, show a conchoidal fracture, and an indistinct cleavage parallel to {001}. Orthowalpurgite is biaxial negative, $n_x = 1.91(2)$, $n_y = 2.00(2)$ and $n_z = 2.05$ (calculated), $2V_x = 70(3)°$ ($\lambda = 589$ nm); orientation: X ‖ c, Y ‖ a, and Z ‖ b. Neither pleochroism nor dispersion were observed. Electron-microprobe analyses gave UO_3 17.86 wt.%, Bi_2O_3 64.21 wt.%, As_2O_5 16.11 wt.%, H_2O (calculated from the idealized formula) 2.43 wt.%, Σ 100.61 wt.%; this yielded the empirical formula (based on 16 oxygen atoms) $(UO_2)_{0.92}Bi_{4.06}O_{3.89}(AsO_4)_{2.07}\cdot1.99H_2O$, ideally $(UO_2)Bi_4O_4(AsO_4)_2\cdot2H_2O$. The cell parameters are $a = 5.492(1)$ Å, $b = 13.324(2)$ Å, $c = 20.685(3)$ Å, $V = 1513.6$ Å^3, space group $Pbcm$, $Z = 4$. A crystal structure investigation was performed using single-crystal X-ray data. The refinement converged at $R = 0.080$ and $R_w = 0.031$ for 999 reflections with sin θ/λ ≤ 0.6 Å^{-1} [$F_o > 2\sigma(F_o)$] and 68 variable parameters. The coordination polyhedra around the $Bi^{[4+2]}$ and $Bi^{[5+2]}$ atoms are edge- and corner-connected to Bi_8O_8 layers. The layers are interconnected *via* $(UO_2)(AsO_4)_2$ chains to form a three-dimensional network. The name orthowalpurgite was chosen to express the structural relationship to the triclinic polymorph walpurgite.

Key-words: orthowalpurgite, (UO2)Bi4O4(AsO4)2·2H2O, new mineral, Wittichen (Black Forest, Germany), crystal structure, walpurgite.

Introduction

During sampling of minerals in June 1980 on the dump of the Schmiedestollen, Wittichen, Black Forest, Germany, a single specimen was found with very small yellow crystals that were preliminary assigned to walpurgite. The true identity of this material remained unknown, until in 1993, chemical analyses (main constituents by EDX: Bi, U, As) and X-ray diffraction powder

work proved the crystals to be similar but definitely not identical with walpurgite. In particular it was not possible to refine the cell metric from the observed powder data on the basis of the walpurgite cell. More detailed studies on this material showed it to be an orthorhombic polymorph of walpurgite with a closely related atomic arrangement.

Walpurgite was described and named 'Walpurgin' after the 'Walpurgis' vein of the mine

'Weißer Hirsch' at Schneeberg-Neustädtel, Saxony, Germany by Weisbach (1871). The spelling of the mineral name was modified already by Brush (1872) to 'walpurgite'. Up to now the two spellings are retained at least in German and English, respectively. Further investigations were performed by Schrauf (1872), Winkler (1873) and Weisbach (1873, 1877), cf. also Frondel (1958). Fischer (1945, 1948) carried out a detailed morphological study and a microchemical analysis which yielded an almost correct chemical formula. First X-ray investigations were performed by Evans (1950). A careful structure determination by Mereiter (1981, 1982) confirmed the results of Fischer (1948), except for the water content, which turned out to be two water molecules instead of three. Therefore the correct chemical formula of walpurgite is $(UO_2)Bi_4O_4(AsO_4)_2 \cdot 2H_2O$.

Obviously, walpurgite was first named waltherite (Vogl, 1856; Bertrand, 1881; Dana, 1882; cf. also Frondel, 1943 and Kirchheimer, 1963); however, Fischer (1955) pointed out the identity of waltherite and walpurgite. Walpurgite is a rare mineral, up to now only a few occurrences have been reported. Besides the type locality (Weisbach, 1871; Gebhard, 1982) walpurgite has been described from the Geistergang, Eliaszeche, Joachimsthal, Czech Republic. Mostly due to the activities of mineral collectors, walpurgite was mentioned from several localities in the Schneeberg area, Saxony, Germany (Schlegel et al., 1991, 1992; Martin & Schlegel, 1992), and from the Black Forest (Walenta, 1972, 1980; Markl, 1992). One of the most famous localities for well formed walpurgite crystals is the dump of the Schmiedestollen near Wittichen, Black Forest, Germany. Recently walpurgite was found in a similar mineralization near Dalbeattie, South Scotland (Braithwaite & Knight, 1990).

The present paper is part of investigations of bismuth(III) oxo-salts (Krause et al. 1993, and in print; Effenberger et al., 1994) and deals with the description and characterization of the new mineral orthowalpurgite. In addition the atomic arrangement is presented and compared with that of walpurgite. Structural data on walpurgite used in the present paper refer to Mereiter (1982).

The name of the new mineral was chosen to show the relationship to walpurgite. The mineral and mineral name were approved by the Commission of New Minerals and Mineral Names (I.M.A.) prior to publication (#94-024). Type material including the crystal used for investiga-

tion of the crystal structure is deposited in the collection of the Institut für Mineralogie, Ruhr-Universität Bochum, Germany.

Occurrence

Orthowalpurgite occurs as transparent yellow crystals on the dump of the Schmiedestollen, Wittichen, Black Forest, Germany. The veins in the area of Wittichen belong to the Co-Ni-Ag-Bi-U-formation; in the 18th century they were famous for the occurrence of native silver, and of cobalt and nickel bearing ore minerals. The dump of the Schmiedestollen is well known for its great variety of secondary minerals, predominantly arsenates and uranyl-arsenates of copper, bismuth, cobalt, nickel, iron, barium, magnesium, and calcium. Nearly 150, in part very rare, minerals have been found there, amongst them also well formed walpurgite crystals. For the description of the paragenesis of the deposit see e.g. Wimmenauer (1952), and for a survey of the minerals see Walenta (1987) or Steen (1989) and references therein.

On the type-specimen orthowalpurgite is associated with preisingerite spherules, quartz, and very small tabular anatase crystals, which are embedded in loose aggregates of a non-crystallized, white, powdery material with main constituents Al and Si (according to an EDX-analysis). Up to now the type-specimen is the only known sample of orthowalpurgite. The total amount of material reaches about 2 to 3 milligrams. Orthowalpurgite may have formed by weathering of emplectite, wittichenite or other Bi-bearing ore minerals.

Description

Morphology and physical characterization

Crystals of orthowalpurgite are tabular on {010} with maximum dimensions up to 0.3 mm; they are often elongated parallel to [100], mostly they form fan-shaped aggregates up to 1 mm. The crystals are orthorhombic holohedral, the crystallographic forms {010}, {001}, {104} (rare), and {100} have been observed. Alternations of most probably {104} and {001} result in
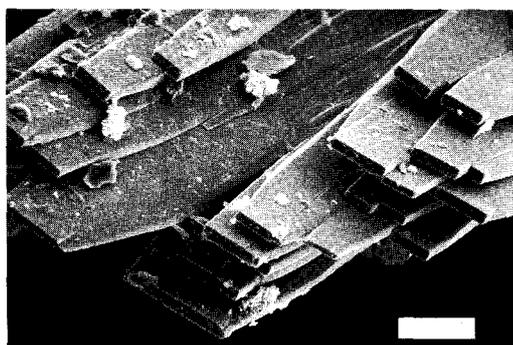
Fig. 1. SEM micrograph of orthowalpurgite; scale bar is 20 μm.

a rounded shape (Fig. 1); discernible edges between these faces have rarely been observed. In contrast to walpurgite, twinning was not observed for orthowalpurgite. The pale yellow crystals do not exhibit any zoning as known for walpurgite, which often shows brownish to greenish or cloudy rims due to alteration. The streak is pale yellow, the lustre is adamantine; Mohs' hardness is 4½, Vickers microhardness VHN_{25} is 330 kg mm^{-2}. Orthowalpurgite is non-fluorescent. The crystals are brittle, show a conchoidal fracture and an indistinct cleavage parallel to {001}. Due to lack of material the density could not be determined experimentally; the X-ray density is 6.51 g cm^{-3}. Orthowalpurgite is soluble in warm dilute HCl without effervescence.

Optical properties

The optical behaviour seems to be the most

proper aid for a quick distinction between walpurgite and orthowalpurgite, because only the latter shows a straight extinction. The optical parameters were determined on a spindle stage (λ = 589 nm). Crystals of orthowalpurgite are optically biaxial negative with n_x = 1.91(2), n_y = 2.00(2), n_z = 2.05 (calculated), and $2V_x$ = 70(3)°. The optical orientation is X ‖ c, Y ‖ a, and Z ‖ b. Neither pleochroism nor dispersion were observed.

Chemical data

A preliminary EDX analysis of the new mineral showed Bi, U and As to be the main constituent elements. The chemical formula of orthowalpurgite was derived by means of an electron-microprobe analysis (Table 1) and a single-crystal structure investigation. A light yellow transparent and homogeneous crystal chip of walpurgite from Joachimsthal, Czech Republic, was used as internal standard; its chemical composition was checked prior to the investigation by in-house standards. Besides P (less than 0.1 wt.%) no elements with atomic number greater than 8 were detected in orthowalpurgite. The little scatter among the individual analyses is in agreement with the observed optical homogeneity of the crystals. Due to lack of material the water content could not be determined experimentally, and therefore the empirical formula is based on the theoretical value of 2.43 wt.% H_2O calculated from the idealized formula.

Based on the empirical formula, the mean refractive index of 1.987, and the calculated density of 6.51 g/cm^3, the compatibility (1-Kp/Kc) = 0.007 is superior (Mandarino, 1981).

Table 1. Results of electron-microprobe analyses for orthowalpurgite (operating voltage 15 kV, beam current 10 nA, diameter of electron beam 1 μm).

constituent	weight-%*	range	standards	theoretical
UO_3	17.86	17.54 — 18.40	walpurgite, uraninite	19.28
Bi_2O_3	64.21	63.50 — 65.39	walpurgite, Bi_2S_3	62.80
As_2O_5	16.11	15.83 — 16.24	walpurgite, arsenopyrite	15.49
H_2O	2.43 †			2.43
total	100.61			100.00

* mean of 8 analyses	† calculated from the idealized formula

Empirical formula based on O = 16: $(UO_2)_{0.92}Bi_{4.06}O_{3.89}(AsO_4)_{2.07} \cdot 1.99H_2O$
Idealized formula: $(UO_2)Bi_4O_4(AsO_4)_2 \cdot 2H_2O$

Table 2. Observed and calculated powder diffraction pattern for orthowalpurgite.

h	k	l	d_{calc}	I_{calc}	d_{obs}	I_{obs}	h	k	l	d_{calc}	I_{calc}	d_{obs}	I_{obs}
0	0	2	10.342	100	10.354	94	2	3	4	2.129	3	2.125	2
0	2	0	6.662	12	6.659	29	0	6	3	2.114	5	2.113	14
0	2	1	6.341	4	6.348	6	1	1	9	2.093	5	2.093	8
0	2	2	5.601	34	5.610	40	2	4	2	2.076	6 }		
1	0	0	5.492	5	5.495	4	1	5	5	2.074	3 }	2.071	12
0	0	4	5.170	7	5.171	9	1	3	8	2.069	4 }		
1	1	0	5.078	7	5.073	4	0	4	8	2.042	2	2.042	9
1	1	1	4.931	20	4.935	11	2	4	3	2.026	14	2.024	11
1	2	0	4.238	4	4.239	3	0	2	10	1.975	3	1.974	5
0	2	4	4.084	9	4.086	12	0	6	5	1.957	10	1.957	13
1	0	4	3.764	13	3.768 ·	13	2	3	6	1.934	4	1.935	4
1	1	4	3.623	14 }	3.621	21	2	2	7	1.925	5	1.926	5
1	2	3	3.610	6 }			1	3	9	1.913	3	1.913	4
1	3	0	3.453	21 }	3.452	34	2	4	5	1.886	4	1.886	3
0	0	6	3.447	7 }			0	6	6	1.867	6 }	1.864	13
1	3	1	3.406	3	3.406	2	1	5	7	1.862	13 }		
1	2	4	3.277	5 }	3.277	56	2	5	3	1.843	7	1.843	6
1	3	2	3.276	41 }			2	3	7	1.832	6	1.832	5
1	1	5	3.207	78	3.208	100	2	2	8	1.811	11 }		
0	4	2	3.171	18	3.168	15	0	2	11	1.809	8 }	1.810	17
1	3	3	3.088	72	3.088	76	2	4	6	1.805	3 }		
0	4	3	2.999	22	2.999	50	1	7	0	1.799	12	1.798	13
1	2	5	2.960	6	2.958	15	1	7	2	1.772	5 }	1.772	5
1	3	4	2.872	3 }	2.852	46	3	2	0	1.765	3 }		
1	1	6	2.852	36 }			2	1	9	1.747	12	1.747	11
0	4	4	2.800	3	2.800	13	1	7	3	1.740	12 }	1.741	14
2	0	0	2.746	21 }	2.747	24	2	5	5	1.736	4 }		
1	4	2	2.746	5 }			3	0	4	1.726	7	1.726	7
0	2	7	2.701	9 }	2.701	19	3	2	3	1.710	5 }	1.704	5
2	1	0	2.690	5 }			2	2	9	1.704	6 }		
2	1	1	2.667	5 }	2.661	13	2	6	3	1.675	4	1.675	2
2	0	2	2.654	3 }			3	2	4	1.671	4	1.669	4
2	1	2	2.603	5 }	2.596	12	1	5	9	1.659	15	1.660	10
0	4	5	2.594	5 }			3	3	3	1.644	6	1.644	4
1	1	7	2.554	2	2.553	7	1	1	12	1.632	7	1.631	5
2	2	2	2.466	4	2.466	3	3	2	5	1.624	4	1.623	3
0	2	8	2.410	10	2.409	12	2	5	7	1.605	7 }	1.605	5
0	4	6	2.395	3	2.392	4	3	1	6	1.605	4 }		
1	5	1	2.382	4	2.380	5	2	6	5	1.594	5	1.593	3
2	3	1	2.321	5	2.322	3	3	4	2	1.586	9	1.586	3
1	1	8	2.304	5	2.302	5	3	2	6	1.571	3	1.572	2
2	2	4	2.279	4 }	2.278	7	2	6	6	1.544	3	1.544	3
2	3	2	2.278	3 }			1	1	13	1.518	7 }		
2	1	5	2.255	9	2.255	6	3	2	7	1.515	3 }	1.517	5
0	6	1	2.208	4	2.208	10	2	2	11	1.511	5 }		
0	2	9	2.172	11 }	2.172	26	2	7	4	1.497	4	1.497	2
0	6	2	2.171	6 }			1	5	11	1.479	18	1.479	9
2	0	6	2.148	6	2.148	2							

The powder diffraction pattern was calculated with program LAZY PULVERIX (Yvon *et al.*, 1977) according to the results of the structure refinement. The observed pattern was taken with a Philips PW1710 diffractometer (Cu$K\alpha$-radiation; internal standard Si); reflections with $I_{calc} \geq 3$ are listed. I is normalized to 100.

X-ray investigation

The powder diffraction pattern of orthowalpurgite is given in Table 2. Because of the poor quality of the JCPDS pattern No. 8-324 (walpurgite), a sample of walpurgite from the dump of the Schmiedestollen was used to obtain new powder data (Table 3). These data are in good agreement with the theoretical pattern given by Mereiter (1982). Refinement of the cell parameters leads to $a = 7.138(2)$, $b = 10.447(5)$, $c = 5.502(3)$ Å, $\alpha = 101.58(4)$, $\beta = 111.02(3)$, $\gamma = 88.21(3)°$, and $V = 374.8(2)$ Å^3; for Mereiter's (1982) data see Table 4. Similarities of the X-ray powder patterns of walpurgite and orthowalpurgite are evident, but the distinction

Table 3. Observed and calculated powder diffraction pattern for walpurgite from Wittichen, Black Forest, Germany.

h	k	l	d_{calc}	I_{calc}	d_{obs}	I_{obs}	h	k	l	d_{calc}	I_{calc}	d_{obs}	I_{obs}
0	1	0	10.224	100	10.257	41	3	2	-2	2.013	13 }	2.013	8
1	0	0	6.657	13	6.670	12	1	1	2	1.998	5 }		
1	-1	0	5.696	27	5.706	18	3	-1	-2	1.985	5	1.984	5
1	1	0	5.468	14	5.478	9	2	-4	-1	1.957	4	1.957	3
0	2	0	5.112	6	5.117	7	1	5	0	1.931	13	1.930	11
0	0	1	5.029	4	5.024	4	3	-3	-1	1.903	3 }	1.898	11
1	0	-1	4.962	28 }	4.961	12	3	-3	0	1.899	12 }		
0	1	-1	4.926	6 }			3	3	-2	1.881	5	1.882	4
1	-2	0	4.145	5	4.150	4	2	-3	-2	1.863	12 }	1.863	7
0	2	-1	4.016	17	4.023	6	2	3	1	1.855	6 }		
1	2	0	3.970	5	3.971	5	1	2	2	1.837	3	1.840	3
1	0	1	3.458	6 }	3.454	14	1	5	-2	1.812	3 }		
1	-1	1	3.451	14 }			3	-1	1	1.811	7 }		
0	3	0	3.408	8 }	3.400	23	2	1	-3	1.809	6 }	1.809	9
2	0	-1	3.394	17 }			3	0	1	1.804	3 }		
2	1	-1	3.313	7 }			1	-4	2	1.801	5 }		
1	-2	-1	3.296	15 }	3.268	32	4	0	-1	1.783	6 }		
0	2	1	3.268	58 }			3	4	-1	1.781	8 }	1.782	12
2	-1	-1	3.136	47 }			0	5	1	1.773	3 }		
1	1	1	3.125	8 }			0	5	-2	1.772	12 }	1.774	9
2	1	0	3.124	39 }	3.128	100	4	1	-1	1.764	5	1.763	8
1	-2	1	3.109	54 }			3	1	1	1.745	6	1.745	7
1	-3	0	3.090	4 }			1	3	-3	1.733	5	1.732	2
1	3	-1	3.058	58	3.059	38	3	4	-2	1.721	3	1.722	2
2	2	-1	2.955	3	2.951	8	1	-1	-3	1.700	5 }		
1	1	-2	2.744	29 }	2.739	26	3	-4	-1	1.697	4 }		
2	2	0	2.734	12 }			4	0	-2	1.697	3 }		
0	3	1	2.588	9	2.587	7	4	2	-1	1.696	6 }	1.696	12
0	0	2	2.514	9 }	2.513	9	2	-1	-3	1.696	6 }		
2	1	-2	2.509	5 }			1	-4	-2	1.693	5 }		
0	4	-1	2.492	4	2.490	3	3	-3	-2	1.681	3 }	1.678	2
0	2	-2	2.463	3	2.463	2	0	0	3	1.676	3 }		
1	4	-1	2.445	6 }			2	-5	1	1.668	3 }		
1	-4	0	2.422	24 }	2.421	19	2	1	2	1.664	7 }		
2	-1	1	2.412	7 }			3	0	-3	1.654	6 }	1.655	5
3	1	-1	2.333	3 }	2.331	2	2	4	1	1.648	4 }		
2	3	0	2.330	3 }			0	3	-3	1.642	6 }		
1	3	1	2.251	5	2.251	3	0	4	2	1.634	5 }	1.634	6
1	-2	-2	2.209	10	2.211	5	1	6	0	1.633	4 }		
3	-1	0	2.189	10 }	2.188	20	2	4	-3	1.610	6	1.608	2
2	3	-2	2.188	9 }			3	5	-1	1.586	4	1.587	2
1	0	2	2.114	10	2.112	6	4	-2	-2	1.568	3 }		
3	-2	0	2.069	9	2.070	12	4	2	0	1.562	3 }	1.563	4
							2	-4	2	1.555	6 }		

The powder diffraction pattern was calculated with program LAZY PULVERIX (Yvon *et al.*, 1977) according to the results of the structure refinement (Mereiter, 1982). The observed pattern was taken with a Philips PW1710 diffractometer (Cu$K\alpha$-radiation; internal standard Si); reflections with $I_{calc} \geq 3$ are listed. I is normalized to 100.

between the two mineral species is possible by careful investigation of the patterns.

Weissenberg film investigations on a crystal fragment of orthowalpurgite clearly showed orthorhombic symmetry. Systematic extinctions are consistent with the space groups $Pbc2_1$ and $Pbcm$, structure analysis proved the centric one to be relevant to orthowalpurgite. Finally a small crystal chip was selected for X-ray data collection (for details see Table 5); it was mounted with its longest dimension parallel to the Φ axis

of the four-circle diffractometer to minimize absorption effects.

The atomic parameters of U and Bi were derived by direct methods, As and O atoms were located from Fourier maps. The H atoms were not located experimentally, but crystal chemical considerations and bond strength calculations give a clear allocation for the H2O molecule. Extinction was found to be negligible. Anisotropic displacement parameters were used for the atoms U, Bi, and As, whereas oxygen atoms were re-

Table 4. Comparison between walpurgite and orthowalpurgite.

	walpurgite *	orthowalpurgite †
a	7.135(2) Å	5.492(1) Å
b	10.426(4) Å	13.324(2) Å
c	5.494(1) Å	20.685(3) Å
α	101.47(2)°	90°
β	110.82(2)°	90°
γ	88.20(2)°	90°
V	374 Å³	1513.6 Å³ = 4 × 378.4 Å³
space group	P1̄ (no. 2)	Pbcm (no. 57)
cell content	1×{(UO₂)Bi₄O₄(AsO₄)₂·2H₂O}	4×{(UO₂)Bi₄O₄(AsO₄)₂·2H₂O}
	* data from Mereiter (1982)	† from powder data

Table 5. Summary of crystal data, X-ray data collection, and structure refinement of orthowalpurgite.

$a = 5.492(1)$ Å	crystal dimensions: 0.08 x 0.03 x 0.04 mm³
$b = 13.324(2)$ Å	$2\vartheta/\omega$ scan mode, scan speed 0.45 to 0.90° min⁻¹
$c = 20.685(3)$ Å	scan width: 1.05° (increased for α_1-α_2 dispersion)
$V = 1513.6$ Å³	3 standard reflections each 120 min
space group Pbcm	maximal variation of intensity ±2.45%
$Z = 4$	range of data collection: 3° < 2ϑ < 50°
$R_{int} = 0.038$	9384 total measured reflections (+h, ±k, ±l)
$R = 0.080$	1372 unique reflections
$R_w = 0.031$	999 reflections with $F_o > 2\sigma(F_o)$ for refinements
$w = 2.096 [\sigma(F_o)]^{-2}$	$\mu(MoK\alpha) = 614$ cm⁻¹
68 variable parameters	empirical absorption correction (ψ scans)
max $\Delta/\sigma \leq 0.001$	transmission factors from 0.238 to 0.426

Philips PW1710 powder diffractometer (CuKα radiation) for lattice parameters, STOE AED2 four-circle diffractometer (Mo tube, graphite monochromator) for data collection. Data were corrected for Lorentz and polarization effects, neutral complex scattering functions from International Tables for Crystallography (1992).

fined isotropically. Final atomic parameters are given in Table 6[1]. Calculations were performed with programs SHELX76 (Sheldrick, 1976) and SDP (Frenz & Associates, 1992). For convenience throughout the paper, oxygen atoms belonging to the arsenate anion and to the water molecule are denoted as O_a and O_w, whereas O_o is used for the oxo-oxygen atom and O_u for the oxygen atoms of the (UO₂) group.

Discussion

General outline

The new mineral orthowalpurgite is a poly-

morph of walpurgite, the crystal structures of the two phases are closely related, even though topological differences can be seen clearly. The crystal system changes from triclinic in walpurgite to orthorhombic in orthowalpurgite, and the cell content is quadrupled. The U atoms are on special positions and show point symmetry 1̄ in walpurgite and m in orthowalpurgite, whereas the two Bi atoms, the AsO₄ tetrahedron and the water molecule are on general positions in both minerals. Larger differences occur for the O_u and O_o atoms: the single O_u position in walpurgite splits into two independent positions with site symmetry m in orthowalpurgite; instead of two general O_o positions in walpurgite there are one general position and two positions on the twofold axis in orthowalpurgite. Despite the change of point symmetry for the corresponding atomic positions, the shape of their coordination polyhe-

[1] The list of F_o—F_c data is available upon request from the Editorial Office of the European Journal of Mineralogy or from the authors.

Table 6. Structural parameters (e.s.d.'s in parentheses) for orthowalpurgite.

atom	site symmetry	Wyckoff letter	x	y	z	U_{eq}/U_{iso}
U	m	$4(d)$	0.6850(4)	-0.0150(1)	¼	0.020
Bi(1)	1	$8(e)$	0.6754(2)	0.10257(9)	0.03039(5)	0.012
Bi(2)	1	$8(e)$	0.2199(2)	0.30468(9)	0.07715(5)	0.012
As	1	$8(e)$	0.2014(6)	0.0033(2)	0.1292(1)	0.014
$O_u(1)$	m	$4(d)$	0.804(7)	-0.147(2)	¼	0.045(9)
$O_u(2)$	m	$4(d)$	0.560(6)	0.121(2)	¼	0.031(9)
$O_o(1)$	1	$8(e)$	0.399(3)	0.434(1)	0.0352(9)	0.015(5)
$O_o(2)$	2	$4(c)$	0.484(5)	¼	0	0.010(6)
$O_o(3)$	2	$4(c)$	0.005(5)	¼	0	0.018(7)
$O_a(1)$	1	$8(e)$	0.335(4)	0.111(1)	0.1009(7)	0.012(4)
$O_a(2)$	1	$8(e)$	0.397(3)	-0.064(1)	0.3250(9)	0.021(5)
$O_a(3)$	1	$8(e)$	0.103(3)	-0.071(1)	0.0672(8)	0.012(5)
$O_a(4)$	1	$8(e)$	-0.053(3)	0.033(1)	0.1708(8)	0.018(5)
O_w	1	$8(e)$	0.762(4)	0.246(2)	0.1459(8)	0.037(6)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	0.0154(9)	0.0266(11)	0.0187(8)	-0.0019(9)	0	0
Bi(1)	0.0067(5)	0.0120(6)	0.0162(6)	0.0000(5)	-0.0015(5)	-0.0001(2)
Bi(2)	0.0091(6)	0.0123(6)	0.0141(5)	-0.0011(5)	0.0006(5)	0.0000(2)
As	0.012(2)	0.016(2)	0.014(1)	-0.003(1)	0.001(1)	0.0004(4)

Anisotropic displacement parameter: $\exp [-2 \pi^2 \Sigma_{i=1}^{3} \Sigma_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j]$
U_{eq} after Fischer & Tillmanns (1988)

dra is maintained. Bond lengths and bond angles for orthowalpurgite are compiled in Table 7, the crystal structure is depicted in Fig. 2.

The uranyl group

The U atom is [2 + 4] coordinated by two O_u and by four O_a atoms as found in walpurgite. The axial U—O_u bonds are shorter than the equatorial U—O_a bonds, which is characteristic for the uranyl group. The O—U—O angles are very regular; deviations from rectangularity are less than 5.5°. The equatorial U—O_a bond lengths are practically the same in the two minerals. Surprisingly in orthowalpurgite the axial U—O_u bond lengths turned out to be very long (mean value 1.91 Å) by contrast with those in walpurgite (1.78 Å). Such long axial U—O bonds are rather the exception than the rule for an uranyl group; it should be mentioned that the displacement parameters of the atoms U and O_u are large. Due to site symmetry $\bar{1}$ of the U atom in walpurgite both U—O_u bond lengths are equal by symmetry, whereas in orthowalpurgite U—$O_u(1)$ seems to be shorter than U—$O_u(2)$, which might be caused by the hydrogen bonding scheme.

The Bi atoms

The coordination of the two Bi(III) atoms is characterized by the stereochemically active lone-pair electrons. Bi(1) and Bi(2) have five and four one-sided arranged oxygen atom ligands with Bi—O bonds from 2.10 to 2.43 Å; as in walpurgite the three nearest neighbours are O_o atoms, next nearest neighbours are O_a atoms. The five ligands belonging to the Bi(1) atom form a tetragonal pyramid, the Bi atom lies outside the coordination figure. The Bi(2) atom forms with its four neighbours a tetragonal pyramid with the Bi atom at the apex. Most striking are the distortions caused by the connection over each two edges: these O—O edges (2.54 to 2.63 Å) and the corresponding O—Bi—O angles (70.7 to 73.5°) are the shortest and smallest within these polyhedra. The coordinations are completed by two additional ligands at distances of 2.71 to 3.09 Å; further O atoms are excluded from the discussion because their Bi—O distances are above 3.38 Å. The O_o atoms are bound exclusively to Bi atoms in [3], [4] and [2 + 2] coordinations with approximate trigonal planar and tetrahedral arrangements. In walpurgite the two O_o atoms are [3] and [3 + 1] coordinated.

The AsO₄ tetrahedron

The arsenate group forms a regular tetrahedron which shares only corners with other coordination polyhedra. The average <As—O> bond length is 1.70 Å, the O—O edges vary from 2.69 to 2.82 Å, the O—As—O angles from 104.8 to 111.5°. The O_a atoms are [2] or [3] coordinated: like in walpurgite two of the four O_a atoms [$O_a(1)$ and $O_a(3)$] are ligands around two Bi atoms. $O_a(2)$ and $O_a(4)$ are the equatorial ligands of the $(UO_2)O_4$ group; $O_a(2)$ additionally acts as an acceptor of one of the two hydrogen bonds from the water molecule. In walpurgite the coordination of the O_a atoms is slightly different: both O_a atoms involved in the $(UO_2)O_4$ coordination are acceptors of hydrogen bonds and one participates in a 'long' Bi—O bond.

The H₂O molecule

The O_w atom is weakly connected to two Bi atoms at approximately 3 Å. Most probable acceptors of the hydrogen bonds are the atoms $O_a(2)$ and $O_u(2)$ with $O_w\cdots O$ distances of 2.75(3) and 2.94(3) Å and a suitable angle $O_a\cdots O_w\cdots O_u$ of 104.0(9)°. Further $O_w\cdots O$ distances are ≥ 3.03(3) Å, the corresponding $O\cdots O_w\cdots O$ angles are less suitable. This is a striking difference to walpurgite: Mereiter (1982) found that both hydrogen bonds have most probable O_a atoms as their acceptors with $O_w\cdots O$ distances of 2.77 and 2.88 Å, respectively.

Connection scheme and comparison walpurgite/orthowalpurgite

Both minerals have complex structures with layers parallel (010)/(001) (in the following it is referred to walpurgite/orthowalpurgite, respectively). The coordination polyhedra around the Bi(*III*) atoms are connected to form a two-dimensional net-work, the AsO₄ tetrahedra are

Table 7. Bond lengths (Å) and bond angles (°) for orthowalpurgite.

|			
Bi(1)—O_o(1)	2.10(2)	O_o(1)—Bi(1)—O_o(1)	70.7(7)
Bi(1)—O_o(1)	2.28(2)	O_o(1)—Bi(1)—O_o(2)	72.1(6)
Bi(1)—O_o(2)	2.32(1)	O_o(1)—Bi(1)—O_a(1)	80.6(6)
Bi(1)—O_a(1)	2.38(2)	O_o(1)—Bi(1)—O_a(3)	77.4(6)
Bi(1)—O_a(3)	2.39(2)	O_o(1)—Bi(1)—O_o(2)	139.9(7)
Bi(1)—O_o(3)	2.75(2)	O_o(1)—Bi(1)—O_a(1)	82.9(6)
Bi(1)—O_w	3.09(2)	O_o(1)—Bi(1)—O_a(3)	87.4(6)
		O_o(2)—Bi(1)—O_a(1)	76.7(6)
		O_o(2)—Bi(1)—O_a(3)	98.7(5)
		O_a(1)—Bi(1)—O_a(3)	157.9(6)
Bi(2)—O_o(3)	2.11(2)	O_o(3)—Bi(2)—O_o(1)	103.0(5)
Bi(2)—O_o(1)	2.17(2)	O_o(3)—Bi(2)—O_o(2)	73.5(8)
Bi(2)—O_o(2)	2.28(2)	O_o(3)—Bi(2)—O_a(3)	76.4(6)
Bi(2)—O_a(3)	2.43(2)	O_o(1)—Bi(2)—O_o(2)	71.7(5)
Bi(2)—O_a(1)	2.71(2)	O_o(1)—Bi(2)—O_a(3)	75.8(6)
Bi(2)—O_w	2.99(2)	O_o(2)—Bi(2)—O_a(3)	128.5(5)
U—O_u(1)	1.88(3)	O_u(1)—U—O_u(2)	180.0(9)
U—O_u(2)	1.94(3)	O_u(1)—U—O_a(4)	92.4(9) 2×
U—O_a(4)	2.27(2) 2×	O_u(1)—U—O_a(2)	88.6(9) 2×
U—O_a(2)	2.31(2) 2×	O_u(2)—U—O_a(4)	87.9(8) 2×
		O_u(2)—U—O_a(2)	91.1(8) 2×
		O_a(4)—U—O_a(4)	92.4(6)
		O_a(4)—U—O_a(2)	91.6(6) 2×
		O_a(4)—U—O_a(2)	175.9(6) 2×
		O_a(2)—U—O_a(2)	84.5(6)
As—O_a(4)	1.69(2)	O_a(4)—As—O_a(2)	111.5(9)
As—O_a(2)	1.69(2)	O_a(4)—As—O_a(1)	109.5(9)
As—O_a(1)	1.71(2)	O_a(4)—As—O_a(3)	104.8(9)
As—O_a(3)	1.71(2)	O_a(2)—As—O_a(1)	111.3(9)
		O_a(2)—As—O_a(3)	108.3(9)
		O_a(1)—As—O_a(3)	111.5(9)
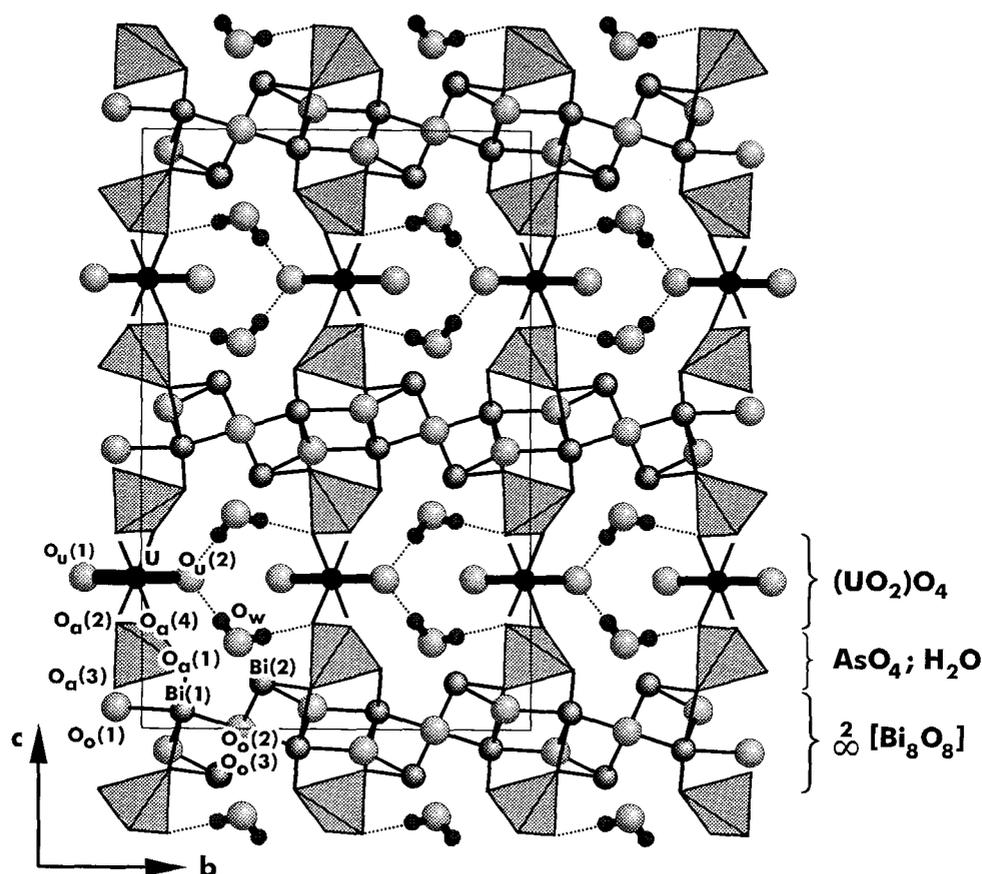
Fig. 2. The crystal structure of orthowalpurgite in a projection on (100) (program ATOMS, Dowty, 1991).

branched, the H_2O molecules are weakly bound to these layers. The tetragonal dipyramids $(UO_2)O_4$ link these $[Bi_4O_4(AsO_4)_2·2H_2O]_n$ (n = 1/2) layers. On the other hand the structures may be described by $[Bi_4O_4]/[Bi_8O_8]$ layers linked by $[(UO_2)(AsO_4)_2]$ chains running parallel [001]/[100]; the water molecule fills the remaining space within the framework.

The $[Bi_4O_4]/[Bi_8O_8]$ layers in walpurgite/ orthowalpurgite are formed as follows: edge-connection of the Bi(1)O5 and Bi(2)O4 polyhedra results in chains parallel [101]/[010]. Neighbouring chains are identical by translation in [001]/[100]. In walpurgite a sequence of four Bi atoms in [101] define slabs (indicated by m, n, o, and p in Fig. 3a; the atoms labelled m and p are Bi(2)[4] atoms, those labelled n and o are Bi(1)[5] atoms

related by a centre of symmetry). As can be seen from Fig. 3b the sequence m_1, n_1, o_1, and p_1 of Bi atoms in orthowalpurgite define slabs which are practically equivalent to those in walpurgite. Whereas in walpurgite these slabs repeat by translation, in orthowalpurgite the sequence is interrupted by a second slab (indicated by p_2, o_2, n_2, and m_2 in Fig. 3b) which is symmetry-related to the former by the twofold axis in $(x\frac{1}{4}0)$. In orthowalpurgite the atoms labelled with n_1, n_2, o_1, and o_2 are still Bi(1)[5] atoms, those labelled m_1, m_2, p_1, and p_2 are Bi(2)[4] atoms; only the pairs m_1-p_1, n_1-o_1, m_2-p_2, n_2-o_2 are related by $\overline{1}$ symmetry, but not m_1-p_2, m_2-p_1, n_1-o_2, n_2-o_1. The slabs have orthorhombic symmetry in orthowalpurgite but they are triclinic distorted in walpurgite.

The different connection schemes cause topologically different linkages between neighbouring Bi_4O_4/Bi_8O_8 rows in the two mineral species. Each two BiO_4 pyramids and BiO_5 polyhedra form by sharing a common edge double polyhedra of point symmetry $\bar{1}$ (in walpurgite both types of double polyhedra, in orthowalpurgite only BiO_5) or 2 (BiO_4 in orthowalpurgite). These double polyhedra are mutually linked via pairs of shared edges to form chain-like structures in both minerals. While the mutual linkage of the double polyhedra in walpurgite is trans for both kind of polyhedra, in orthowalpurgite it is trans for the BiO_5 double polyhedra but of a cis-type for the BiO_4 double polyhedra. The Bi—O bonds within the Bi_4O_4/Bi_8O_8 rows are stonger than those between them: the linkage to neighbouring rows is realized by the longest of the 'short' Bi—O bonds. The 'long' $Bi(1)^{[5+2]}$—O_o is within the Bi_8O_8 row, the $Bi(2)^{[4+2]}$—O_a bond is between the rows in walpurgite and in orthowalpurgite; the other 'long' Bi—O bonds are formed with O_w atoms.

The sequence of the $[Bi_4O_4]/[Bi_8O_8]$ or even $[Bi_4O_4(AsO_2)_2 \cdot 2H_2O]_n$ (n = 1/2) layers may be described roughly as an ···AA··· and an ···ABAB··· stacking in walpurgite and orthowalpurgite, respectively. However, they cannot be described exclusively as stacking variants, because the layers in the two compounds are definitely different.

The equatorial ligands around the U atom belong to four arsenate groups. Linkage of the uranyl groups with the arsenate tetrahedra form $[(UO_2)(AsO_4)_2]$ chains parallel $[001]/[100]$ in walpurgite/orthowalpurgite. Due to the different space groups their ribbon symmetries are $p\bar{1}/p1m$, which for walpurgite causes a twisting of the tetragonal dipyramids $(UO_2)O_4$, and a different orientation of the arsenate tetrahedra (Fig. 4).

The similarity of the atomic arrangements necessitates some remarks on the cell parameters (see Table 4). The base vectors c (walpurgite) and a (orthowalpurgite) are equal within limits of error; they give the translation periods between the Bi_4O_4/Bi_8O_8 rows within the $[Bi_4O_4]/[Bi_8O_8]$ layers. Due to the different stacking sequence of the $[Bi_4O_4]/[Bi_8O_8]$ layers c (orthowalpurgite) is approximately twice as large as b (walpurgite). The translation period parallel to the Bi_4O_4/Bi_8O_8 rows in walpurgite (t_{101} = 7.326 Å) is definitely larger than in orthowalpurgite (b/2 = 6.662 Å) due to the fact that the orthorhombic modification of $(UO_2)Bi_4O_4(AsO_4)_2 \cdot 2H_2O$ has more buckled chains. This allows the Bi_4O_4 rows in walpurgite to fit into one another better than the Bi_8O_8 rows in orthowalpurgite: $d_{10\bar{1}}$ (walpurgite) is only 4.962 Å as compared to a (orthowalpurgite) = 5.492 Å. Both compounds show their crystals to be elongated parallel to the
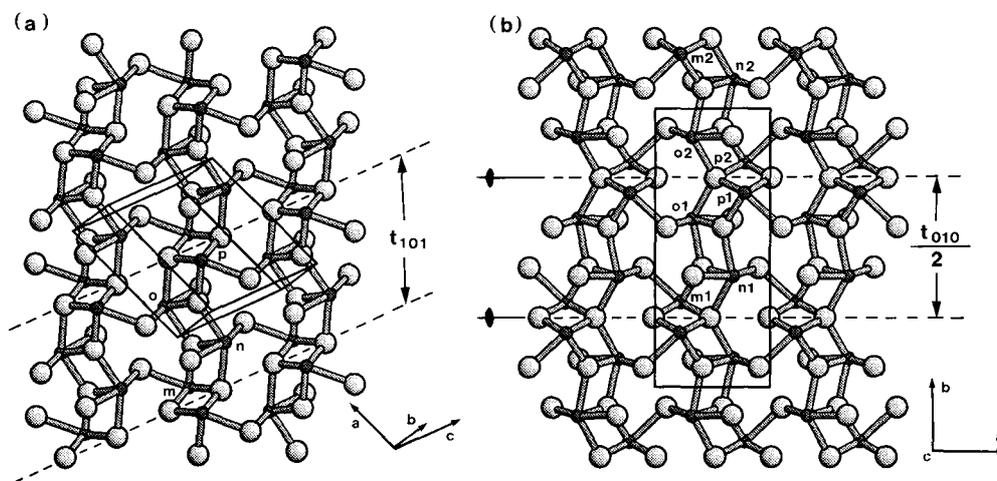

Fig. 3. The layers (a) $[Bi_4O_4]$ in walpurgite and (b) $[Bi_8O_8]$ in orthowalpurgite: The identity period t_{101} in walpurgite and the analogous part of the structure in orthowalpurgite $1/2 \cdot t_{010}$ are marked. The doubling of the translation period in orthowalpurgite by the two-fold axes is indicated. The topologically different linkage of the chains is shown (program ATOMS, Dowty, 1991).
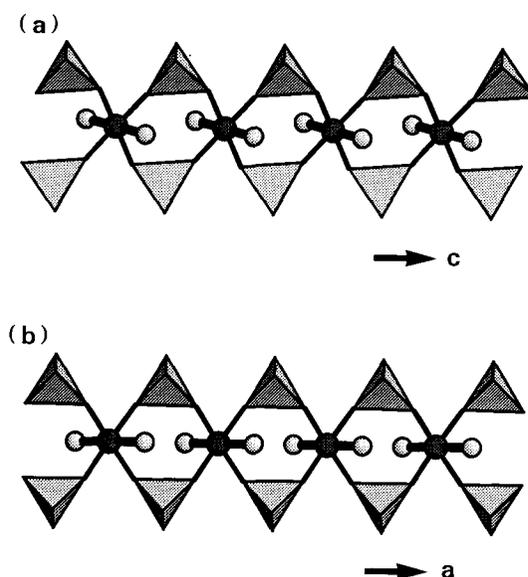
(a)

(b)

Fig. 4. The $[(UO_2)(AsO_4)_2]$ chains in (a) walpurgite and (b) orthowalpurgite (program ATOMS, Dowty, 1991).

$[(UO_2)(AsO_4)_2]$ chains. Walpurgite is flattened parallel to the $[Bi_4O_4]$ layers, whereas orthowalpurgite is flattened perpendicular to the Bi_8O_8 rows, but parallel to the $[(UO_2)(AsO_4)_2]$ chains.

Conclusion

The crystal structures of walpurgite and orthowalpurgite are similar with respect to the coordination polyhedra and to the connection schemes. The main differences concern (i) the differences between the Bi_4O_4/Bi_8O_8 rows, (ii) the topologically different linkage between the Bi_4O_4/Bi_8O_8 rows to layers, (iii) the torsion of the AsO_4 tetrahedra combined with the twisting of the tetragonal dipyramids $(UO_2)O_4$ within the $[(UO_2)(AsO_4)_2]$ chains, (iv) details in the coordination of the oxygen atoms, and (v) the acceptors of the hydrogen bonds of the water molecule. These points justify the description of two distinct mineral species.

Due to the fact that walpurgite and orthowalpurgite are polymorphs with similar atomic arrangements, their physical properties do not differ very much. Therefore the hitherto existing investigations on walpurgite were checked for misidentification, but no evidence could be found

yet. This is of particular interest, because walpurgite and orthowalpurgite have been found at the same deposit. All investigations on walpurgite published up to now give no evidence for the violation of triclinic symmetry, even if twins are very common. The twin plane in walpurgite usually observed is (010). Therefore the $[Bi_8O_8]$ layer of orthowalpurgite cannot be described as a simple multiple twinning according to the twin-law observed for walpurgite.

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Sabelliite, a new copper-zinc arsenate-antimonate mineral from Sardinia, Italy

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Abstract: Sabelliite, ideally $(Cu,Zn)_2Zn[(As,Sb)O_4](OH)_3$, is a new mineral from Is Murvonis Mine, Domusnovas, Sardinia. It occurs as intergrown aggregates or isolated crystals in a compact quartzitic matrix, in an outcrop close to worked fluorite veins of an old mine. The platy {001} disk-shaped emerald-green crystals are transparent with adamantine lustre. Associated minerals are theisite, malachite, azurite, and tetrahedrite. Electron microprobe analyses give: Cu 34.80, Zn 15.65, Si 0.33, As 15.04, Sb 4.96, O 28.00, H 0.67 (calculated), total 99.45 wt%. Optically, sabelliite is nonpleochroic, uniaxial negative, with $\omega = 1.802(2)$ and $\varepsilon = 1.797(2)$. VHN_{15} microhardness = 386. Density (calc.) = 4.65 g/cm^3. The unit cell is trigonal with $a = 8.201(1)$, $c = 7.315(1)$ Å, $V = 426.07(9)$ Å^3, space group $P\bar{3}$, and $Z = 3$. The strongest lines in the Gandolfi X-ray pattern are ($d_{obs}.I,hkl$) 2.522(100)(121), 2.166(88)(122), 1.805(92)(123), 1.550(100)(410), 1.513(85)(124). The IR spectrum is also given. The mineral is named after Dr. Cesare Sabelli, researcher of the C.N.R.. Sabelliite belongs to a proposed mineral family that includes spangolite, schulenbergite, namuwite, and theisite.

Key-words: sabelliite, new mineral, copper-zinc arsenate-antimonate, Is Murvonis Mine (Sardinia, Italy).

Introduction

In 1990, during field work in Southern Sardinia for an ongoing study of copper alteration minerals, a few specimens were found of an unknown mineral. A preliminary investigation of the material, which was collected in the abandoned Is Murvonis Mine (Domusnovas, Iglesias district), suggested the mineral might be a new species (Brizzi et al., 1993). Shortly thereafter, a mineral showing similar morphological and chemical characteristics was found at mine dumps near Schwaz, Austria (Dillen, 1993, pers. comm.).

A full mineralogical study confirms that the Is Murvonis mineral really is a new species. We are pleased to name the new mineral sabelliite in honour of Dr. Cesare Sabelli, of the Consiglio Nazionale delle Ricerche (C.N.R.), in recognition of his important work with the copper alteration minerals of Sardinia. The new mineral and name have been approved by the I.M.A. Commission on New Minerals and Mineral Names. A type specimen is kept at the Museum of Natural History of the University of Florence, under catalogue number 2053/RI.

The crystal structure of sabelliite was determined by Olmi et al. (1995).

Occurrence

Geologically, the Iglesiente region (S-W Sardinia) consists of a Cambrian-Silurian succession (Carmignani et al., 1986). The Domusnovas area offers a good example of the geology of the region; the main formations comprise a limestone known as the "Calcare Ceroide" as well as poly-

genic Ordovician conglomerates and coarse sand-stones with interbedded shales. During Hercynian deformation, the area underwent low-grade metamorphism with the formation of a complex system of faults. Karst phenomena later developed, and hydrothermal fluids subsequently deposited fluorite vein-like bodies along the faults and karst rims occurring in the dark-gray limestone. Only one body of economic interest has been mined in this century. The green or blue fluorite always contains traces of copper (Uras, 1958).

The fluorite is frequently accompanied by sul-phides and sulphosalts (galena, sphalerite, chal-copyrite, tetrahedrite-tennantite), and by copper-zinc alteration minerals (aurichalcite, malachite, azurite, brochantite, rosasite, hemimorphite). Sabelliite occurs in a quartzitic outcrop as rare minute crystals often overgrown on foliated aggregates of theisite, to which it is closely re-lated from a chemical and physical standpoint. Both minerals are believed to be weathering pro-ducts of sulphides and sulphosalts. Sabelliite is probably the last-formed mineral of the oxidation process.

Physical properties

Sabelliite has a highly characteristic appear-ance: its crystals are tabular {001} and cylindri-cal, thus resembling small coins (no crystal form other than the basal pinacoid has been recog-nized) (Fig. 1 and 2). The diameter of intergrown disk-shaped crystals rarely exceeds 400 μm, while isolated single crystals can be up to 200 μm in diameter and 15 μm in thickness. They are

transparent and emerald-green, having an ad-amantine lustre and a light-green streak. The crystals are brittle, with no cleavage, and have a micro-hardness of VHN = 386 (average of 20 determinations with 15 g indentor: range 322-469), which corresponds to a calculated Mohs' hardness of about 4.5.

The mineral's density is too high to be measured using floatation techniques, and not enough material was available for the pycnome-ter (density bottle) method. The calculated den-sity is 4.65 g/cm^3, on the basis of the experimen-tal chemical composition and assuming three formula units in the unit-cell. The mineral does not fluoresce under long- or short-wave ultravio-let radiation.

Sabelliite is optically nonpleochroic, uniaxial negative, with ω = 1.802(2) and ε = 1.797(2). Refractive indices were measured in Na gel-fil-tered light by immersion in mixtures of Cargille oils and sulphur saturated methylene iodide. Since the high values of the indices prevented the use of an Abbé refractometer, the indices of the mixtures were determined on an Eickhorst Modul 1 gemmological refractometer (Hurlbut, 1984).

Calculation of the Gladstone-Dale relationship gives Kp = 0.1720 and Kc = 0.1753, which indi-cate a "superior" compatibility index 1-(Kp/Kc) of 0.019 (Mandarino, 1981).

Chemistry and infrared study

Sabelliite was analysed with a JEOL JXA-8600 electron microprobe (15 kV accelerating voltage, 10 nA beam current- Faraday cup, 5 μm defo-
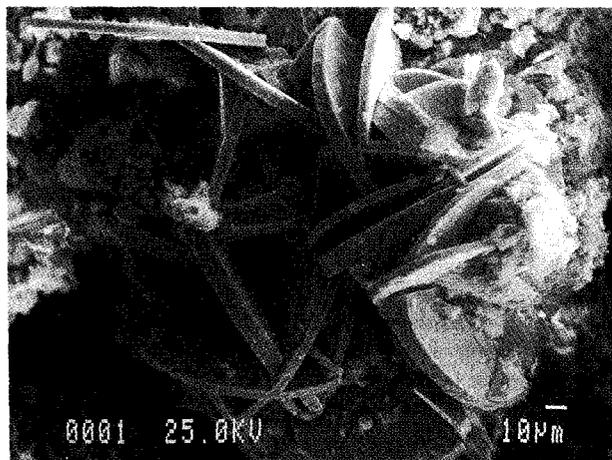

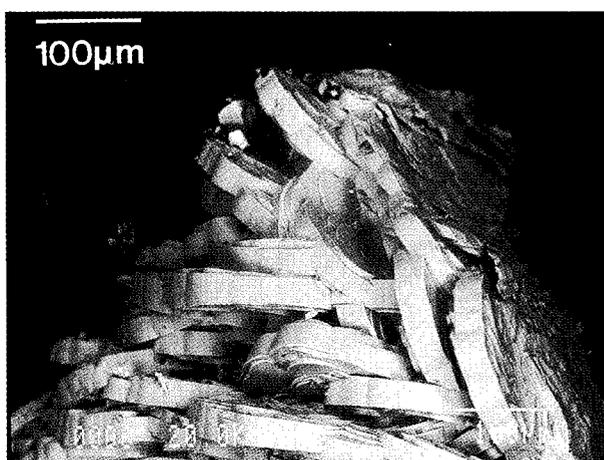Fig. 1. Electron micrograph of some disk-shaped sabelliite crystals.

Fig. 2. Electron micrograph of an aggregate of strongly intergrown sabelliite crystals.

cused beam) equipped with a Tracor-Northern Series II system. No elements (with Z > 9) other than those reported here were detected by a preliminary 300s-energy-dispersive scan. The standards used were: cuprite (Cu$K\alpha$), willemite (Zn$K\alpha$,Si$K\alpha$), arsenolite (As$L\alpha$) and senarmontite (Sb$L\alpha$). The dearth of pure material prevented the quantitative determination of the H_2O content. For this reason, the oxygen content was also measured by electron microprobe with a LDE1 crystal, which is a layered synthetic dispersion lattice (Nash, 1992) manufactured by the Jeol Company, using quartz as standard (McGuire et al., 1992). The raw data were reduced using a $\varphi(\rho z)$ correction routine (Bastin et al., 1987). The results of the analyses (twenty different spots on four crystals) are given in Table 1. The empirical formula, calculated on

Table 1. Electron microprobe analytical results.

	1			2	3
Cu	34.80	(32.44–37.26)	CuO	43.56	40.61
Zn	15.65	(13.91–17.34)	ZnO	19.48	20.77
Si	0.33	(0.19– 0.49)	SiO_2	0.71	–
As	15.04	(13.42–16.32)	As_2O_5	23.07	23.46
Sb	4.96	(4.10– 6.15)	Sb_2O_5	6.59	8.26
O	28.00	(26.94–29.20)	H_2O	6.05	6.90
	98.78			99.46	100.00
H	0.67				
	99.45				

1 – Atomic wt.% (ranges in parenthesis), including the
    O content, experimentally determined.
    The 0.67 wt% H amount was calculated to compensate
    the excess of negative charge.
2 – Converted oxide percentages.
3 – Calculated oxide percentages for the idealized
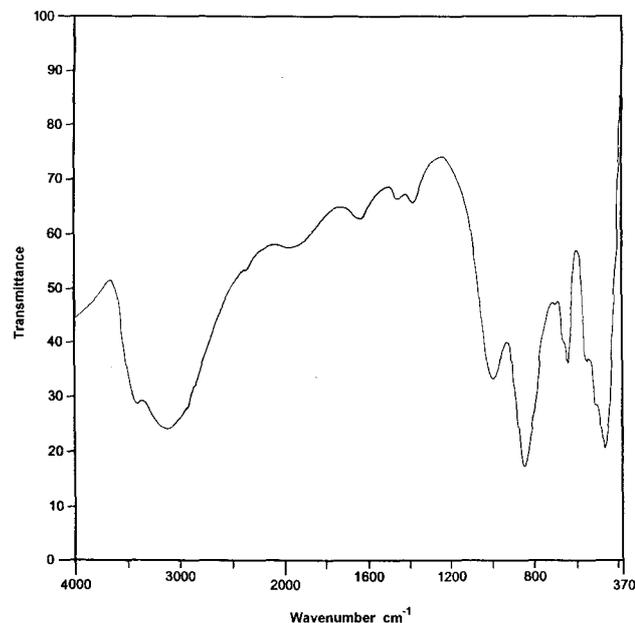   formula, with Cu/Zn=2 and As/Sb=4.

Fig. 3. Infrared absorption spectrum of sabelliite.

the basis of O = 7, is $Cu_{2.19}Zn_{0.96}(As_{0.80}Sb_{0.16}Si_{0.05})_{\Sigma 1.01}O_{4.31}(OH)_{2.69}$. The crystal structure refinement (Olmi et al., 1995) shows that the Zn atoms are coordinated both octahedrally (as are the Cu atoms) and tetrahedrally. Further occurrences of sabelliite may display some variation in cationic content. Owing to this possibility, the simplified formula $(Cu,Zn)_2Zn[(As,Sb)O_4](OH)_3$ was adopted.

For the IR study, a very small amount of material was examined with a FTIR Perkin-Elmer SYS 2000 spectrophotometer. Several IR spectra (which were reproducible to ± 4 cm^{-1} in the 4000-2000 cm^{-1} region, and to ± 2 cm^{-1} in the 2000-370 cm^{-1} region) were recorded in the 4000-370 cm^{-1} range, using a KBr micropellet. The spectrum (Fig. 3) confirms the absence of structural H$_2$O (Olmi et al., 1995), as there is simply a broad intense band in the 3500-3000 cm^{-1} region. The weak peak at 1636 cm^{-1} may be attributed to water adsorbed by the KBr micropellet (Braithwaite, 1983), or to a harmonic of lower-frequency fundamentals (Sumin de Portilla, 1974; Hill, 1976). As discussed in the structural study, the presence of one ascertained OH group and of an additional disordered hydroxyl appears confirmed by the two bands at 3420 and

3126 cm^{-1}, which are within the region of the stretching vibrations of the hydroxyl groups (Braithwaite & Ryback, 1988). The spectrum is more complex in the region with frequencies lower than 1000 cm^{-1}. The strong absorption bands at 844 and 457 cm^{-1}, with shoulders at 795 and 504 cm^{-1}, are due to the stretching and bending vibrations of the AsO$_4^{3-}$ group (Farmer, 1974). The absorption at 993 cm^{-1} is probably due to the deformation of OH groups bonded to Cu atoms (Braithwaite, 1983; Sumin de Portilla, 1974), while the absorption at 545 cm^{-1} can be related to stretching vibrations of Zn-O and Cu-O bonds (Tarte & Preudhomme, 1970; Sumin de Portilla, 1974; Sumin de Portilla et al., 1981; Braithwaite, 1983 and 1987).

X-ray crystallography and related species

Single-crystal X-ray studies (Weissenberg camera and single-crystal diffractometer) show that sabelliite is trigonal. The space group, from the crystal stucture analysis, is $P\bar{3}$.

The X-ray powder diffraction data given in

Table 2. X-ray powder diffraction pattern for sabelliite (114.6 mm Gandolfi camera, Ni-filtered CuKα radiation, photometrically measured intensities).

hkl	$d_{calc.}$ (Å)	$d_{obs.}$ (Å)	I/I_0	hkl	$d_{calc.}$ (Å)	$d_{obs.}$ (Å)	I/I_0
001	7.314	7.33	42	412	1.427	1.427	54
100	7.102	7.15	7	224	1.365	1.364	12
101	5.096	5.11	18	025	1.353	1.352	8
110	4.101	4.11	55	240	1.342	1.341	23
002	3.657	3.66	52	241	1.320	1.320	55
111	3.577	3.58	49	413	1.308	1.308	13
102	3.252	3.25	31	125	1.285	1.284	25
201	3.195	3.20	46	242	1.260	1.260	16
112	2.729	2.726	29	512	1.204	1.204	9
120	2.684	2.688	29	414	1.182	1.183	22
022	2.548	2.548	15	243	1.176 } 1.175		31
121	2.520	2.522	100	315	1.175		
030	2.367	2.369	26	405	1.129	1.129	8
031	2.252	2.253	28	216	1.110	1.109	23
122	2.164	2.166	88	244	1.082	1.082	26
113	2.096	2.096	25	415	1.064	1.064	24
220	2.050	2.054	12	440	1.025	1.025	7
221	1.974	1.974	18	530	1.015 } 1.014		17
311	1.902	1.901	18	070	1.015		
004	1.829	1.828	7	531	1.005 } 1.005		31
123	1.805	1.805	92	701	1.005		
132	1.734	1.733	23	245	0.989	0.989	12
041	1.725	1.725	23	532	0.978 } 0.978		18
114	1.670	1.670	26	702	0.978		
204	1.626	1.626	18	703	0.937 } 0.937		23
321	1.590	1.591	22	533	0.937		
223	1.569	1.569	9	360	0.895	0.895	15
410	1.550	1.550	100	361	0.888 ⌐		
313	1.532	1.532	8	704	0.887 ⊦ 0.888		27
124	1.511	1.513	85	534	0.887 ⌐		
322	1.488	1.489	17	705	0.834 } 0.834		15
005	1.463	1.462	11	535	0.834		
034	1.447	1.448	16				

Table 2 were obtained using a Gandolfi camera (114.6 mm diameter) with Ni-filtered CuKα radiation. Indexing was performed on the basis of single-crystal data, taking account of the intensities of the reflections collected for the structural study. The unit-cell parameters, refined by means of a least-squares calculation from the powder data, are: $a = 8.201(1)$, $c = 7.315(1)$ Å, $V = 426.07(9)$ Å^3.

The chemical composition, unit-cell parameters and symmetry of sabelliite are fairly similar to those of several other copper minerals, which are listed in Table 3. The powder patterns of all these species also show significant similarities. The lattice parameters of sabelliite are practically identical to those of schulenbergite (Hodenberg et al., 1984). The chemical variability assumed for sabelliite is actually observed in schulenbergite: its Zn-analogue, indeed, has a highly variable Cu/Zn ratio, whose lowest value is 0.34 (Livingstone et al., 1992), compared with the value of 1.33 found in schulenbergite. Spangolite

Table 3. Formulae and lattice parameters of related minerals.

Mineral	Chemical formula	Cell parameters (Å)		Symmetry
Spangolite	$Cu_6Al(SO_4)(OH)_{12}Cl.3H_2O$	$a=8.274$	$c=14.371$	$P31c$
Namuwite	$(Zn,Cu)_4(SO_4)(OH)_6.4H_2O$	$a=8.29$	$c=10.50$	hexagonal
Schulenbergite	$(Cu,Zn)_7(SO_4,CO_3)_2(OH)_{10}.3H_2O$	$a=8.249$	$c= 7.183$	$P3$ or $P\bar{3}$
Theisite	$Cu_5Zn_5[(As,Sb)O_4]_2(OH)_{14}$	$a=8.223$	$c=15.019$	trigonal
Sabelliite	$(Cu,Zn)_2Zn[(As,Sb)O_4](OH)_3$	$a=8.201$	$c= 7.315$	$P\bar{3}$

(Merlino *et al.*, 1992), whose *a* parameter is the same and *c* parameter is twice that of sabelliite or schulenbergite, exhibits dense octahedral sheets, as does sabelliite (Olmi *et al.*, 1995). Namuwite (Bevins *et al.*, 1982) and theisite (Bonazzi & Olmi, 1989), whose structures are still unknown, show the same *a* parameter and a closely similar symmetry.

From the above considerations, and from the structural analogies discussed by Olmi *et al.* (1995), the grouping of these species in the same mineral family appears quite reasonable, following also the suggestion by Hodenberg *et al.* (1984) who have pointed out that schulenbergite is closely related to spangolite and namuwite.

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