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GRUMIPLUCITE, A NEW MERCURY – BISMUTH SULFOSALT SPECIES FROM THE LEVIGLIANI MINE, APUAN ALPS, TUSCANY, ITALY

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ABSTRACT

Grumiplucite, ideally $HgBi_2S_4$, is a new mercury – bismuth sulfosalt species. It occurs as submillimetric prismatic, grey-black metallic crystals, together with mercury, cinnabar and mercurian sphalerite, in cavities of quartz – carbonate veins in the small mercury deposit of Levigliani, Apuan Alps, Tuscany, Italy. Crystals are elongate according to [010] axis and ubiquitously twinned on (001). Grumiplucite has a monoclinic symmetry, space group *C2/m*, with unit-cell dimensions *a* 14.164(5), *b* 4.053(1), *c* 13.967(3) Å, β 118.28(3)°, *V* 706.1(6) Å^3, *Z* = 4. The strongest five reflections of the X-ray powder-diffraction pattern [*d* in Å(I)] are: 3.05(s), 2.914(ms), 2.865(ms), 3.86(m), and 3.55(m). Grumiplucite is the natural analogue of the synthetic compound $HgBi_2S_4$. In reflected light, it is creamy white (parallel polars) with low bireflectance; under crossed polars, the mineral is distinctly anisotropic (bluish grey to yellowish grey). The calculated density is 7.02 g/cm^3. It formed at a low temperature in a low-$f(S_2)$ environment.

Keywords: grumiplucite, new mineral species, mercury – bismuth sulfosalt, Levigliani mine, Apuan Alps, Italy.

SOMMAIRE

Nous décrivons ici la grumiplucite, de composition idéale $HgBi_2S_4$, nouvelle espèce de sulfosel à mercure et bismuth. Elle se présente en cristaux submillimétriques prismatiques, de couleur gris-noir et d'aspect métallique. On la trouve en présence de mercure, cinnabre et sphalérite enrichie en mercure dans des cavités dans des veines de quartz – carbonate du petit gisement de mercure de Levigliani, dans les Alpes apouennes, en Toscane, Italie. Les cristals sont allongés selon [010] et invariablement maclés sur (001). La grumiplucite possède un symétrie monoclinique, groupe spatial *C2/m*, et les paramètres réticulaires *a* 14.164(5), *b* 4.053(1), *c* 13.967(3) Å, β 118.28(3)°, *V* 706.1(6) Å^3, *Z* = 4. Les cinq raies les plus intenses du spectre de diffraction (méthode des poudres) [*d* en Å(I)] sont: 3.05(s), 2.914(ms), 2.865(ms), 3.86(m), et 3.55(m). La grumiplucite est l'analogue naturel du composé synthétique $HgBi_2S_4$. En lumière réfléchie, elle est blanc crémeux (nicols parallèles) avec une faible biréflectance; avec les nicols croisés, elle montre une anisotropie distincte, du gris bleuâtre au gris jaunâtre. La densité calculée est égale à 7.02 g/cm^3. Le milieu de formation en est un de faible température et faible fugacité de soufre.

(Traduit par la Rédaction)

Mots-clés: grumiplucite, nouvelle espèce minérale, sulfosel de mercure et bismuth, mine Levigliani, Alpes apouennes, Italie.

INTRODUCTION

We have undertaken a re-examination of the large group of sulfosalts from the ore deposits of the Apuan Alps in Tuscany, Italy. This project entailed a careful study of the Hg–Zn–Fe sulfide assemblage from the Levigliani mercury mine. The presence of peculiar compositions of sulfides such as mercurian sphalerite and zincian metacinnabar associated with cinnabar and native mercury at Levigliani was reported by Dini *et al.* (1995). In the course of the present study at Levigliani, we discovered a new Hg–Bi sulfosalt, corresponding to the synthetic phase $HgBi_2S_4$ (Brower *et al.* 1973). In this paper, we define the new mineral. We named it *grumiplucite* after the group of amateur mineralogists called **Gruppo Mineralogico e Paleontologico Lucchese**, members of which provided the specimens for study. The specimens were found by Luigi Pierotti, Ugo Quilici and Moreno Romani.

The intention of the authors, in naming the new mineral grumiplucite, is to acknowledge amateur mineralogists all over the world for their contribution to

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the development of regional and systematic mineralogical studies, for providing specimens, and for invaluable field observations. The mineral and mineral name were approved by the Commission on New Minerals and Mineral Names of IMA. The type material is preserved in the Museo di Storia Naturale e del Territorio, University of Pisa (#4262).

GEOLOGICAL SETTING AND OCCURRENCE

The small mercury deposit of Levigliani, located near the homonymous small village in the Apuan Alps, is hosted within phyllitic and metavolcanic rocks of Middle to Upper Ordovician age, which were intensely deformed and metamorphosed to the greenschist facies (about 3–4 kbar and 350°–370°C) during both the Hercynian and Tertiary Apenninic orogenies (Carmignani & Kligfield 1990). With respect to typical epithermal mercury deposits, Levigliani is somewhat peculiar, because it is hosted in metamorphic rocks, and it reached the present structural arrangement during a syntectonic and synmetamorphic process of mineralization. In spite of its metamorphic setting, Levigliani probably represents a pre-Hercynian concentration of mercury sulfide, which survived through Hercynian and Alpine tectonometamorphic events (Dini 1992, Lattanzi *et al.* 1994). Deformation and partial remobilization during the tectono-metamorphic processes involved the circulation of metamorphic fluids.

The process of mineralization led to sulfide disseminations and quartz–carbonate veins that developed in a multistage process spanning the entire Tertiary tectonometamorphic event (Dini 1992, Dini *et al.* 1995). Specifically, veins began to form in the stage of early compression (D_1) and were progressively folded and deformed, with axial planes parallel to the main schistosity (S_1). Local gentle folding and thickening of the veins occurred (D_2 stage) during the development of a crenulation cleavage S_2. The discrete (millimetric) clots and patches of Hg–Zn–Fe sulfides are deformed and aligned along S_1.

A unique mineralogical situation exists in the "Cavetta" tunnel, where some decimetric to metric quartz veins occur at the hinge of a late-stage (D_2) gentle fold (Dini 1992). These veins contain widespread cavities completely or partially filled by native mercury, with the walls of the cavities covered by millimetric crystals of cinnabar, pyrite and mercurian sphalerite. Usually their size does not exceed a few millimeters, but during the exploitation in the 18th century (Targioni Tozzetti 1777), some very large cavities (containing about 1 t of native mercury) were found.

Ore minerals at Levigliani are mainly cinnabar and pyrite, subordinate zincian metacinnabar, mercurian sphalerite, native mercury, chalcopyrite, and minor galena. Gangue minerals include mainly quartz, with Mg-rich siderite, Fe-rich dolomite and calcite. Stibnite, tentatively reported by Carmignani *et al.* (1972) on the basis of reflected light microscopy only, was not observed in our specimens, but it could in fact be the grumiplucite specimens reported in our study.

Grumiplucite was found in cavities of the quartz veins in the "Cavetta" tunnel. Grumiplucite is very rare, and less than ten specimens have been collected so far. Usually the crystals are emplaced on cinnabar and mercurian sphalerite; in some cases, they float and

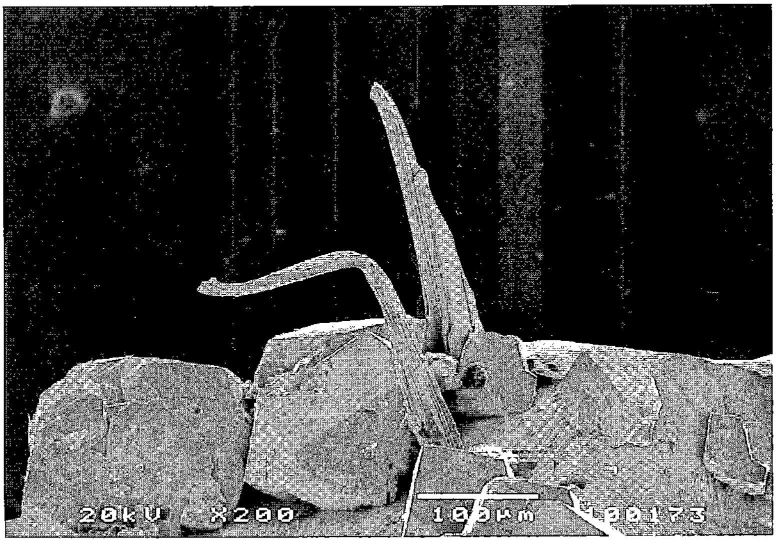

FIG. 1. Long prismatic crystals of grumiplucite on mercurian sphalerite, associated with rhombohedral crystals of cinnabar (SEM photo). Scale bar: 100 µm.

TABLE 1. REFLECTANCE DATA (R_1 AND R_2) IN AIR AND OIL FOR GRUMIPLUCITE

λ nm	Air		Oil	
	*R*1	*R*2	*R*1	*R*2
400	33.9	36.1	21.2	24.0
420	34.4	36.6	21.8	24.2
440	35.1	37.2	22.5	24.8
460	35.6	37.7	23.0	24.9
470	*35.7*	*37.8*	*23.2*	*25.0*
480	35.9	38.0	23.3	25.1
500	35.9	38.0	23.5	25.2
520	35.5	37.6	23.3	25.1
540	35.4	37.5	23.1	25.0
546	*35.4*	*37.5*	*23.0*	*25.0*
560	35.3	37.4	22.6	24.7
580	35.2	37.3	22.2	24.2
589	*34.9*	*37.0*	*22.0*	*24.0*
600	34.7	36.8	21.8	23.7
620	34.2	36.2	21.0	23.3
640	33.9	35.9	20.5	22.8
650	*33.9*	*35.8*	*20.4*	*22.7*
660	33.8	35.7	20.2	22.7
680	33.8	35.6	20.2	22.7
700	33.9	35.6	20.2	22.6

Note: Standard used was SiC 47 42 51, number 097 (Carl Zeiss); measurements in oil were carried out at 20°C, with oil having an index of refraction of 1.5150.

protrude from millimetric drops of native mercury. Pyrite is ubiquitous. In some cases, grumiplucite crystals are partially covered by small crystals of cinnabar and mercurian sphalerite and by very small drops of native mercury.

PHYSICAL AND OPTICAL PROPERTIES

Grumiplucite occurs as very slender grey-black prismatic crystals (1 mm long and 0.1 mm across), with a metallic luster and almost micaceous (001) cleavage (Fig. 1). All the specimens show long, prismatic crystals elongate according to [010] and ubiquitously twinned on (001). Only three small acicular crystals were available for the crystal-chemical characterization. Crystallographic, chemical and optical data were collected on the same crystal, whereas further crystallographic investigations and semiquantitative chemical analyses were carried out on the other two crystals.

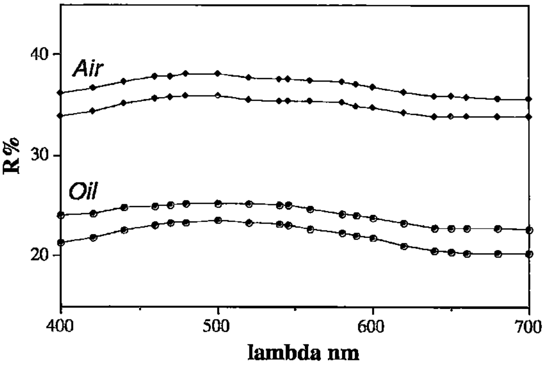

FIG. 2. The reflectance spectra of grumiplucite in air and in oil (data from Table 1).

In reflected light, grumiplucite is creamy white (parallel polars) with low bireflectance. Values of reflectance R_1 and R_2 in air and in oil are reported in Table 1 and in Figure 2. Under crossed polars, the mineral is distinctly anisotropic (bluish grey to yellowish grey).

Density was not determined owing to the small size of the crystals; the calculated density is 7.02 g/cm^3 for $Z = 4$.

CHEMICAL COMPOSITION

Qualitative SEM–EDS chemical analyses of grumiplucite showed abundant mercury, bismuth and sulfur, with no other element having Z greater than 11. Quantitative analyses were done with a JEOL JXA 8600 electron microprobe at the C.N.R. – Centro di Studi per la Minerogenesi e la Geochimica Applicata in Florence, with an acceleration potential of 15 kV, and a beam current (monitored on a Faraday cup) of 10 nA. A spot size of 10 μm was used to avoid devolatilization effects. The following standards were used: cinnabar (provided by Astimex Sci. Ltd., Toronto) for Hg (86.2 wt% Hg, 13.8 wt% S), and synthetic Bi_2S_3 for Bi and S. The raw data were reduced using the φ(ρz) correction program provided by Tracor Northern (Bastin *et al.* 1987).

The chemical data for grumiplucite (Table 2) are in good agreement with those of the ideal composition $HgBi_2S_4$. The empirical formula, calculated on the basis of S = 4, is $Hg_{0.94}Bi_{2.04}S_4$.

TABLE 2. GRUMIPLUCITE: ELECTRON-MICROPROBE ANALYTICAL DATA

element		range	ideal $HgBi_2S_4$
Hg wt%	25.4	24.21 - 26.12	26.86
Bi	57.6	56.63 - 58.54	55.97
S	17.4	16.79 - 17.97	17.17
Total	100.4		

The composition quoted is the mean of 12 datasets.

X-RAY CRYSTALLOGRAPHY

Rotation, Weissenberg and precession photographs indicate that grumiplucite is monoclinic, with *C2/m*, *C2*, *Cm* as possible space-groups. The unit-cell parameters obtained through least-squares fit of 25 high-2θ reflections collected with a four-circle diffractometer are: *a* 14.164(5), *b* 4.053(1), *c* 13.967(3) Å, β 118.28(3)°, *V* 706.1(6) Å^3. These data are in good agreement with the crystal-structure study of Mumme & Watts (1980) on synthetic $HgBi_2S_4$. These authors indicate *C2/m* as the correct space-group.

TABLE 3. X-RAY POWDER PATTERN OF GRUMIPLUCITE AND SYNTHETIC $HgBi_2S_4$*

Grumiplucite				Synthetic $HgBi_2S_4$	
I_{obs}	d_{obs} (Å)	d_{calc} (Å)	*h k l*	d_{obs} (Å)	I/I_o
w	6.18	6.17	0 0 2	6.17	75
mw	4.75	4.743	2 0 1	4.740	20
mw	4.58	4.566	$\bar{2}$ 0 3	4.570	16
m	3.86	3.871	1 1 0	3.860	18
mw	3.62	3.617	2 0 2	3.610	95
m	3.55	3.547	1 1 1		
		3.544	$\bar{4}$ 0 2	3.540	75
mw	3.50	3.498	$\bar{2}$ 0 4	3.490	100
w	3.37	3.372	$\bar{4}$ 0 3		
vw	3.13	3.125	4 0 0		
			0 0 4	3.080	80
s	3.05	3.051	$\bar{3}$ 1 2		
		3.050	$\bar{1}$ 1 3	3.040	85
ms	2.914	2.9116	$\bar{3}$ 1 0	2.905	25
ms	2.865	2.8676	2 0 3		
		2.8639	$\bar{3}$ 1 3	2.861	40
			$\bar{2}$ 0 5	2.786	12
			4 0 1	2.735	6
m	2.644	2.6449	3 1 1	2.639	25
			1 1 $\bar{4}$	2.598	16
w	2.356	2.3576	2 0 4	2.356	50
w	2.324	2.3229	$\bar{5}$ 1 2	2.320	9
w	2.305	2.3020	$\bar{2}$ 0 6	2.300	45
w	2.253	2.2572	$\bar{5}$ 1 1	2.253	30
		2.2558	1 1 4		
mw	2.236	2.2349	$\bar{6}$ 0 1		
		2.2334	$\bar{1}$ 1 5	2.231	35
w	2.179	2.1782	$\bar{6}$ 0 5	2.177	10
mw	2.130	2.1301	$\bar{5}$ 1 0	2.127	14
w	2.083	2.0745	3 1 3	2.072	16
w	2.059	2.0618	4 0 3		
		2.0552	0 0 6	2.054	70
			0 2 0	2.028	35
vw	2.014	2.015	$\bar{6}$ 0 6	2.014	8
vw	1.996	1.9945	2 0 5	1.993	16
			$\bar{4}$ 0 7	1.988	16
w	1.954	1.9543	1 1 5	1.951	50
vw	1.941	1.9365	$\bar{1}$ 1 6	1.933	25
m	1.913	1.9138	$\bar{5}$ 1 6	1.911	25
m	1.805	1.8083	4 0 4	1.8070	14
			5 1 2	1.8000	30
vw	1.786	1.7922	$\bar{3}$ 1 7	1.7900	25
			2 2 2	1.7690	14
vw	1.762	1.7634	$\bar{8}$ 0 3	1.7630	16
			$\bar{2}$ 2 4	1.7540	20
w	1.747	1.7444	$\bar{8}$ 0 5	1.7430	14
			1 1 6	1.7130	9

The cell parameters, refined by the least-squares method from X-ray powder-diffraction data, are as follows: *a* 14.185(5), *b* 4.071(7), *c* 13.995(5) Å, β 118.22(3)°, *V* 712(1) $Å^3$. Gandolfi camera, diameter 114.6 mm, Cu*K*α radiation, λ = 1.54178 Å. Intensities are given as follows: s strong, ms medium strong, m medium, mw medium weak, w weak, vw very weak. * JCPDS 26-880.

Results of a crystal-structure analysis of grumiplucite (S. Merlino, pers. commun.) confirm *C2/m* as the correct space-group and the formula $HgBi_2S_4$, and point to an OD character of the new mineral.

In Table 3, X-ray powder-diffraction data for grumiplucite, collected with a Gandolfi camera with diameter of 114.6 mm and Cu*K*α radiation, are compared with those for the synthetic analogue (Brower *et al.* 1973).

PARAGENETIC CONSIDERATIONS

Some qualitative observations can now be made about the physicochemical conditions at Levigliani during the formation of grumiplucite. Dini *et al.* (1995) described the existence at Levigliani of two main mineral assemblages. The earlier assemblage of cinnabar I + pyrite + zincian metacinnabar (7.3 mol.% ZnS, 1.4 mol.% FeS) probably formed under conditions not far from the peak of metamorphism (T about 350°–370°C, P 3–4 kbar). The later assemblage of cinnabar II + pyrite + mercurian sphalerite (25.3 mol.% HgS, 6.4 mol.% FeS) ± chalcopyrite ± galena overprinted and partially replaced the earlier assemblage at $T \approx 200°C$, $P \approx 1.5$ kbar.

The absence of the relatively high-temperature zincian metacinnabar and the presence of mercurian sphalerite (19.7 mol.% HgS and 20 mol.% FeS, determined in this work) and cinnabar associated with grumiplucite constrain our assemblage to the same range of P and T as that suggested by Dini *et al.* (1995) for their retrograde assemblage. Moreover, the presence of native mercury, so far found only in "Cavetta" veins, confirms this interpretation. In fact, the coexistence of cinnabar with native mercury in the field of pyrite is restricted to a narrow range of $f(S_2)$ and T conditions at the low-T side of the $f(S_2)$-T diagram (Fig. 3), just a little above the pyrite–pyrrhotite curve.

Thus, at Levigliani two mineral assemblages (B and C in Fig. 3) containing mercurian sphalerite (assemblage C including grumiplucite and native mercury) were formed by late-stage synmetamorphic processes at temperatures around 200°–300°C, pressure ≈ 1.5 kbar and at low sulfur fugacity [$-12 < \log f(S_2) \approx -16$ atm]. This environment is well demonstrated by the textural and structural relationship with respect to the earlier zincian metacinnabar assemblage (A in Fig. 3), formed at higher temperature (370°–390°C), pressure ≈ 3.5 kbar and relatively higher fugacity of sulfur [$-6 < \log f(S_2) \approx -8$ atm]. The new mercury–bismuth sulfosalt grumiplucite crystallized at a late stage of the synmetamorphic ore processes at Levigliani, as a result of very peculiar low values of T and $f(S_2)$ attained in the late-stage "Cavetta" veins.

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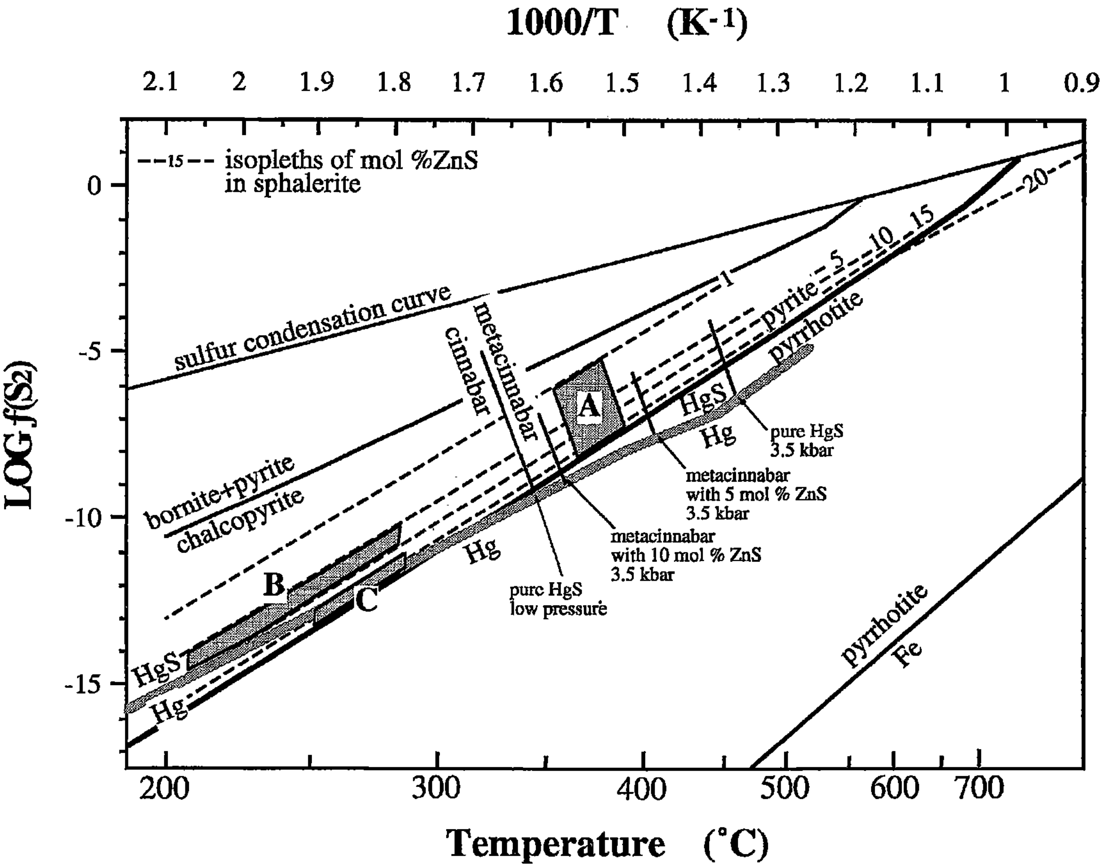

FIG. 3. Temperature – sulfur fugacity diagram in the system Hg–Zn–Fe–S at low pressure (modified after Barton & Skinner 1979, Potter & Barnes 1978, Scott 1983). The curves for the cinnabar – zincian metacinnabar assemblage at 3.5 kbar have been extrapolated after Dini *et al.* (1995). Plotting of the relatively high-pressure mineral assemblages of Levigliani on this diagram is not strictly correct, but the uncertainty introduced can be considered unimportant for our purposes. In fact, the effect of pressure on the diagram is to raise all buffer curves and isopleths to higher values of $f(S_2)$, resulting in changes in the absolute values, but not in the relative positions.

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