

Garavellite, FeSbBiS_4 , a new mineral from the Cu-Fe deposit of Valle del Frigido in the Apuane Alps, northern Tuscany, Italy

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SUMMARY. Garavellite occurs in polished sections, as small aggregates, up to 200 μm across, of anhedral crystals, usually in direct contact with tetrahedrite, Sb-rich bismuthinite, chalcocopyrite, and siderite. Chemical formula $\text{Fe}_{0.80}\text{Cu}_{0.02}\text{Sb}_{1.13}\text{Bi}_{0.78}\text{As}_{0.01}\text{S}_4$ on the basis of $S = 4$, or ideally FeSbBiS_4 .

The mineral has an orthorhombic unit cell with $a = 11.439$, $b = 14.093$, $c = 3.754$ Å, $Z = 4$; calculated density 5.64 gm/cm³. Important diffraction lines are 14.00 (m) 010, 7.08 (m) 020, 3.62 (vs) 230, 3.49 (m) 040, 3.34 (m) 320, 3.20 (vs) 121, 3.10 (m) 201, 2.98 (s) 240, 2.89 (s) 221, 2.63 (vs) 311, 2.51 (vs) 250, 2.16 (m) 421, 1.677 (m) 312. In reflected light it is grey with a brown-olive tint similar to that of tetrahedrite. Birefractance is distinct and anisotropism is also strong, from yellowish-green to bluish grey. Vickers hardness (50 g load) 212-22 kg/mm². Reflectance in air: 470 nm $R_1 = 33.5$ -34.7%, $R_2 = 40.5$ -42.8%; 546 nm 32.8-34.7%, 40.2-42.0%; 589 nm 32.6-33.7%, 39.3-41.0%; 650 nm 32.4-34.6%, 38.4-41.0%.

The mineral and name have been approved before publication by the Commission on New Minerals and Mineral Names, IMA.

Frigidite, the so-called nickel-bearing variety of tetrahedrite found at this locality, is shown to be an intergrowth of tetrahedrite and Ni-bearing minerals.

DURING a detailed mineralogical study of the deposit of Valle del Frigido (Apuane Alps, Tuscany), a mineral with the ideal formula FeSbBiS_4 has been found. We have named this mineral garavellite in honour of Professor C. L. Garavelli in recognition of his contribution to the field of mineralogy of Tuscan ore deposits. The mineral and name have been approved by the Commission on New Minerals and Mineral Names of the I.M.A.

The deposit of Valle del Frigido is located 1 km

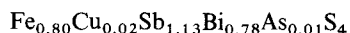
eastward from the city of Massa, along the banks of the stream Frigido and it was intensively mined till the third decade of this century. The orebodies are formed of spathic siderite with disseminated chalcocopyrite. Other minerals present in minor to trace quantities include tetrahedrite, pyrrotine, pyrite, marcasite, galena, sphalerite, meneghinite, ullmannite, pentlandite, vaesite, bismuthinite, chalcocopyrite, and quartz. Garavellite appears in polished sections, as small aggregates, up to 200 μm across, of anhedral crystals, usually in direct contact with tetrahedrite, Sb-rich bismuthinite— $(\text{Bi}_{0.75}\text{Sb}_{0.25})_2\text{S}_3$ —, chalcocopyrite, and siderite. The deposit of Valle del Frigido is particularly known in the mineralogical literature for two varieties of tetrahedrite pointed out by Bechi and by d'Achiardi (1881) at the end of the last century (Manasse, 1906; Palache *et al.*, 1944). Bechi's variety, called coppite, is a quite usual Fe-rich tetrahedrite, while d'Achiardi's variety was considered to be a Ni-rich tetrahedrite, and named frigidite. We have electron-probed several areas of this tetrahedrite and we detected no Ni content over the limit of detectability, 0.07 wt%. This fact linked to the presence, never reported before, of ullmannite, pentlandite, and vaesite strictly associated with tetrahedrite suggests that the so-called frigidite is an intergrowth of tetrahedrite and the above-mentioned Ni-bearing minerals.

According to Monetti (1924) and Capuzzi and Carriero (1973), the deposit of Valle del Frigido has a lenticular vein form, 0.40-2 m thick, concordant with the embedding quartz-sericite schist described by Manasse (1906). The wall rocks belong to the upper part of a complex of detritic sediments,

Triassic in age, which represent the basement of the so-called 'Paraautoctono Apuano'. The basement was affected by the alpine tectonism and it is characterized by a low grade of metamorphism corresponding to the greenschist facies, dated by K/Ar method at 14 Ma (Giglia and Radicati di Brozolo, 1970; Trevisan *et al.*, 1971; Dallan Nardi and Nardi, 1975).

Carmignani *et al.* (1972, 1975), to whom the reader is referred for a detailed description of the deposits of the Apuane Alps, pointing out the tectonically undisturbed character of the deposit of Valle del Frigido and of its minerals, suggest an epigenetic post-tortonian age of emplacement with magmatic affiliation linked to an inferred deeply located acid pluton.

Composition. The chemical composition of garavellite has been determined by electron-probe analyses performed on five different grains apparently free from contamination. The Philips-Norelco AMR/3 electron-probe of the Institute of Mineralogy of Florence operated at 20 kV was used (Tanelli, 1970; Corsini and Tanelli, 1974). Standards were pure Fe, Cu, As, Sb, Bi, and synthetic bismuthinite. Each element in each point was counted three times and the measured concentrations were corrected for atomic number, absorption, and fluorescence using the programme of Duncumb and Jones (1969), slightly modified. The results of the analyses are summarized in Table I, and in fig. 1 some X-ray images of garavellite are shown. On the basis of $S = 4$ the average composition yields the formula



or ideally FeSbBiS_4 . The analyses reveal that Sb:Bi atomic ratio ranges, at constant sum, from

1.57 to 1.30, apparently to indicate a diadochy of these elements in garavellite. The formula of garavellite appears to be close to that of berthierite FeSb_2S_4 , with a slightly different Fe:S ratio, which

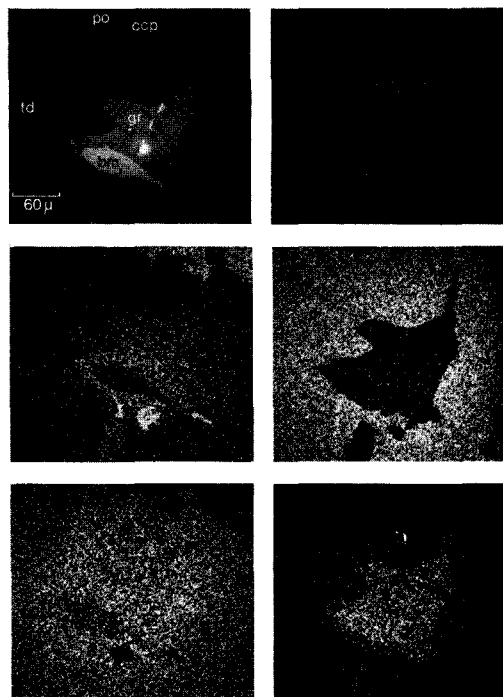


FIG. 1. Electron-probe secondary electrons image (top left) and X-ray images of a typical association of garavellite (gr = garavellite, ccp = chalcopyrite, td = tetrahedrite, bm = bismuthinite, po = pyrrhotine). Top right, Ni; middle left, Fe; middle right, Cu; bottom left, Sb; bottom right, Bi.

TABLE I. Microprobe analyses of garavellite

Analysis number	Weight %						Atoms % (normalized to 100.00)						
	Fe	Cu	As	Sb	Bi	S	Total	Fe	Cu	As	Sb	Bi	S
1a	9.41	0.30	0.16	29.90	33.28	27.43	100.48	11.73	0.33	0.15	17.10	11.10	59.60
1b	9.40	0.30	0.16	29.92	33.70	27.41	100.89	11.71	0.33	0.15	17.10	11.22	59.49
2a	9.30	0.51	0.14	29.77	31.91	26.67	98.30	11.85	0.57	0.13	17.40	10.86	59.18
2b	9.30	0.51	0.14	29.78	32.28	26.66	98.67	11.84	0.57	0.13	17.38	10.98	59.10
3a	9.34	0.05	0.22	27.49	35.91	26.93	99.94	11.87	0.05	0.21	16.03	12.20	59.63
3b	9.33	0.05	0.22	27.50	36.30	26.91	100.31	11.85	0.05	0.21	16.02	12.33	59.55
4a	9.49	0.29	0.17	28.48	35.02	26.25	99.70	12.16	0.32	0.16	16.74	11.99	58.62
4b	9.49	0.29	0.17	28.48	35.18	26.25	99.86	12.16	0.32	0.16	16.74	12.04	58.58
5a	9.24	0.28	0.17	28.80	34.10	27.36	99.95	11.61	0.31	0.15	16.60	11.45	59.88
5b	9.24	0.28	0.17	28.80	34.24	27.35	100.08	11.61	0.31	0.15	16.59	11.49	59.84

a. Standards: pure Fe, Cu, As, Sb, Bi, and Bi_2S_3 for sulphur.

b. Standards: pure Fe, Cu, As, Sb, and Bi_2S_3 for bismuth and sulphur.

Average composition (at. %): Fe 11.84-Cu 0.31-As 0.16-Sb 16.77-Bi 11.57-S 59.35.

could be imputed either to a deficiency of iron or to an excess of sulphur.

To our knowledge, in the Fe-Sb-Bi-S system there are neither natural nor synthetic strictly quaternary phases, and none of the S-bearing ternary phases, synthetic FeBi_4S_7 (Craig *et al.*, 1971; Sugaki *et al.*, 1972), gudmundite (FeSbS), and berthierite (FeSb_2S_4), enlarge their compositional field in the quaternary system (Palache *et al.*, 1944; Ramdohr, 1969; Nowacki, 1969; Clark, 1966; Craig and Barton, 1973). In particular berthierite, which is stable at very low sulphur activity and at temperatures up to 563 °C, according to Barton (1971), is characterized by a composition matching the ideal formula very well, and a Bi-bearing berthierite has never been reported.

X-ray powder diffraction data. The small grain size and occurrence of garavellite as fine polycrystalline aggregates preclude single-crystal investigations. We have tried to synthesize garavellite at 300 and 500 °C, but our attempts, by dry synthesis in silica vessels, were unsuccessful. X-ray powder-diffraction data were obtained using both Debye and Gandolfi cameras. After microprobe analyses and optical investigations, the grains of garavellite were gouged out with the point of a needle, picked up on a glass fibre coated with silicon grease, and mounted in the camera.

In Table II the X-ray powder-diffraction pattern of garavellite, collected using a 114.6-mm Debye camera, Straumanis film mounting, and iron-filtered cobalt radiation, is reported. Additional reflections of contaminant siderite were also recorded.

The pattern of garavellite is similar to that of berthierite as reported by Berry and Thompson (1962) and Barton (1971), but includes such lines as 14.00 and 3.77 Å, indexed as 010 and 001 respectively, which violate the space group requirement of *Pnam* assigned to berthierite (Buerger and Hahn, 1955). The orthorhombic cell dimensions, obtained by the least-squares method, are: $a = 11.439$ Å, $b = 14.093$ Å, $c = 3.754$ Å.

By analogy with the powder-diffraction data, garavellite is presumed to have a defective berthierite-type structure, with one of the two Sb sites of berthierite occupied by bismuth. The calculated densities of FeSbBiS_4 and $\text{Fe}_{0.83}\text{Cu}_{0.02}\text{As}_{0.01}\text{Sb}_{1.17}\text{Bi}_{0.81}\text{S}_{4.15}$, for $Z = 4$ as for berthierite, are respectively 5.64 gm/cm³ and 5.40 gm/cm³.

Optical features. In reflected light garavellite is grey with a brown-olive tint similar to tetrahedrite. Bireflectance is distinct and more evident in air than in oil. Anisotropy is strong, but not as strong as for bismuthinite, with colours in 45° positions from yellowish grey to bluish grey. Polishing hardness is higher than bismuthinite, slightly

TABLE II. X-ray powder diffraction data for garavellite

<i>hkl</i>	d_{obs}	d_{calc}	<i>I</i>	<i>hkl</i>	d_{obs}	d_{calc}	<i>I</i>
010	14.0 Å	14.092 Å	m	112	1.831 Å	1.837 Å	vw
020	7.08	7.05	m	531	1.803	1.804	vw
130}	4.39	{4.35 4.44}	w	370}	1.779	{1.780 1.774}	w
220}				071}			
001	3.77	3.68	w	550}	1.756	1.753	w
230}	3.62	{3.63 3.63}	vs	171}			
011}				601	1.677	{1.672 1.677}	m
040}	3.49	{3.52 3.46}	m	312}	1.655	{1.653 1.657}	vw
111}				640}			
320	3.34	3.35	m	621}	1.560	1.560	vw
121	3.20	3.18	vs	042}			
201	3.10	3.14	m	380}	1.505	{1.507 1.502}	w
211	3.07	3.06	vw	631}			
240}	2.98	{3.00 2.96}	s	412	1.401	{1.401 1.399}	vw
330}				471}			
221	2.89	2.87	s	252}	1.361	1.363	w
131	2.83	2.84	vw	561}			
311}	2.63	{2.63 2.61}	vs	810}	Orthorhombic—(calculated		
231}				522}	1.401	on 59 reflections):	
250}	2.51	{2.53 2.51}	vs	262}	$a = 11.439$ Å		
141}				820}	1.401	$b = 14.093$ Å	
160	2.29	2.30	w	291}	$c = 3.754$ Å		
510}	2.25	{2.26 2.25}	w	1.10.0}	1.399		
051}				661}	1.377		
411}	2.25	2.25	w	490}	1.374		
151	2.21	2.21	w	741}	1.379		
421	2.16	2.16	m	172	1.363		
431	2.04	2.05	w				
450}	2.00	{2.01 2.00}	w				
360}				600	1.908	1.907	m
610}	1.892	{1.889 1.899}	w				
270}				261}	1.876	{1.881 1.817}	vw
002}	1.876	1.817	vw	002}	1.855	1.840	vw

higher than chalcopyrite and slightly lower than tetrahedrite. Reflectance and microindentation measurements were made using the Vickers apparatus of the Institute of Geological Sciences of the United Kingdom in London (diamond paste and Texmet final polishing, standard SiC Zeiss 157, Schott continuous interference Li-Ne filter). The maximum and minimum values for R_1 and R_2 at the four principal wavelengths are listed in Table III. The microindentation hardness (VHN) is between 212 and 222 kg/mm² using a 50-g load.

TABLE III. Reflectance measurements in air of garavellite

λ	R_1	R_2
470 nm	33.5-34.7	40.5-42.8
546	32.8-34.7	40.2-42.0
589	32.6-33.7	39.3-41.0
650	32.4-34.6	38.4-41.0

In reflected light the qualitative features of garavellite easily distinguish it from berthierite, in particular the pink tint of the latter mineral (sample from Braunsdorf, Saxony; polished-section collection of IGS). According to the reflectance and microindentation hardness reported in Ramdohr (1969), Uytendogaardt and Burke (1971), and Caye and Padeloup (1976), garavellite is a little harder and darker than berthierite.

Preservation of type material. Garavellite-bearing samples mounted in polished section have been deposited at the mineralogical museums of the Universities of Florence and Bari.

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