Garavellite, $\text{FeSbBiS}_4$, a new mineral from the Cu–Fe deposit of Valle del Frigido in the Apuane Alps, northern Tuscany, Italy

**F. Gregorio, P. Lattanzi, and G. Tanelli**

Istituto di Mineralogia, Petrografia e Geochimica
Università di Firenze, Via La Marmora 4, 50121 Firenze, Italy
Centro CNR per la Mineralogia e Geochimica dei sedimenti

**F. Vurro**

Istituto di Mineralogia e Petrografia
Università di Bari, Palazzo Ateneo, 70100 Bari, Italy

**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, chalcopyrite, and siderite. Chemical formula $\text{Fe}_{0.60}\text{Cu}_{0.02}\text{Sb}_{1.13}\text{Bi}_{0.75}\text{As}_{0.25}\text{S}_4$ on the basis of $S = 4$, or ideally $\text{FeSbBiS}_4$. 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/cm$^3$. Important diffraction lines are $14.00$, $3.70$, $2.30, 3.49$ (m) $000, 3.34$ (m) $020, 2.98, 2.89$ (s) $221, 2.63$ (s) $311, 2.51$ (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. Bireflectance is distinct and anisotropism is also strong, from yellowish-green to bluish grey. Vickers hardness (50 g load) 21.2–22.2 kg/mm$^2$. 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 $\text{FeSbBiS}_4$ 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 orehodies are formed of spastic siderite with disseminated chalcopyrite. Other minerals present in minor to trace quantities include tetrahedrite, pyrrhotite, pyrite, marcasite, galena, sphalerite, meneghninite, uillmannite, pentlandite, vaesite, bismuthinite, chalcocite, 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—($\text{Bi}_{0.75}\text{Sb}_{0.25})\text{S}_3$—, chalcopyrite, 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’Achirardi (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’Achirardi’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 uillmannite, 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 detritite 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 Brozzolo, 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

\[
\text{Fe}_{0.80}\text{Cu}_{0.01}\text{Sb}_{1.13}\text{Bi}_{0.78}\text{As}_{0.01}\text{S}_4
\]

or ideally \(\text{FeSbBiS}_4\). 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 \(\text{FeSb}_2\text{S}_4\), 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.](image)

**TABLE I. Microprobe analyses of garavellite**

<table>
<thead>
<tr>
<th>Analysis number</th>
<th>Weight %</th>
<th>Atoms % (normalized to 100.00)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Cu</td>
</tr>
<tr>
<td>1a</td>
<td>9.41</td>
<td>0.30</td>
</tr>
<tr>
<td>1b</td>
<td>9.40</td>
<td>0.30</td>
</tr>
<tr>
<td>2a</td>
<td>9.30</td>
<td>0.51</td>
</tr>
<tr>
<td>2b</td>
<td>9.30</td>
<td>0.51</td>
</tr>
<tr>
<td>3a</td>
<td>9.34</td>
<td>0.05</td>
</tr>
<tr>
<td>3b</td>
<td>9.33</td>
<td>0.05</td>
</tr>
<tr>
<td>4a</td>
<td>9.49</td>
<td>0.29</td>
</tr>
<tr>
<td>4b</td>
<td>9.49</td>
<td>0.29</td>
</tr>
<tr>
<td>5a</td>
<td>9.24</td>
<td>0.28</td>
</tr>
<tr>
<td>5b</td>
<td>9.24</td>
<td>0.28</td>
</tr>
</tbody>
</table>

a. Standards: pure Fe, Cu, As, Sb, Bi, and Bi$_2$S$_3$ for sulphur.
b. Standards: pure Fe, Cu, As, Sb, and Bi$_2$S$_3$ 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.
TABLE II. X-ray powder diffraction data for garavellite

<table>
<thead>
<tr>
<th>hkl</th>
<th>d_{obs}</th>
<th>d_{calc}</th>
<th>l</th>
<th>hkl</th>
<th>d_{obs}</th>
<th>d_{calc}</th>
<th>l</th>
</tr>
</thead>
<tbody>
<tr>
<td>010</td>
<td>14.0 A</td>
<td>14.092 m</td>
<td>112</td>
<td>1.831 A</td>
<td>1.837 A</td>
<td>vw</td>
<td>020</td>
</tr>
<tr>
<td>130</td>
<td>4.39 A</td>
<td>4.435 w</td>
<td>77</td>
<td>1.780</td>
<td>001</td>
<td>3.77 A</td>
<td>3.68 w</td>
</tr>
<tr>
<td>230</td>
<td>3.62 A</td>
<td>3.535 vs</td>
<td>171</td>
<td>1.750</td>
<td>040</td>
<td>3.49 A</td>
<td>3.352 m</td>
</tr>
<tr>
<td>013</td>
<td>3.65 A</td>
<td>3.650 m</td>
<td>601</td>
<td>1.655</td>
<td>020</td>
<td>3.20 A</td>
<td>3.18 vs</td>
</tr>
<tr>
<td>121</td>
<td>3.10 A</td>
<td>3.14 m</td>
<td>380</td>
<td>1.597</td>
<td>220</td>
<td>4.44 A</td>
<td>4.44 w</td>
</tr>
<tr>
<td>021</td>
<td>3.07 A</td>
<td>3.06 vs</td>
<td>631</td>
<td>1.598</td>
<td>240</td>
<td>2.98 A</td>
<td>3.06 s</td>
</tr>
<tr>
<td>330</td>
<td>2.89 A</td>
<td>2.87 s</td>
<td>252</td>
<td>1.595</td>
<td>131</td>
<td>2.83 A</td>
<td>2.84 vs</td>
</tr>
<tr>
<td>311</td>
<td>2.63 A</td>
<td>2.63 vs</td>
<td>510</td>
<td>1.423</td>
<td>231</td>
<td>2.61 A</td>
<td>2.61 vs</td>
</tr>
<tr>
<td>250</td>
<td>2.51 A</td>
<td>2.53 vs</td>
<td>820</td>
<td>1.401</td>
<td>141</td>
<td>2.51 A</td>
<td>2.51 vs</td>
</tr>
<tr>
<td>160</td>
<td>2.39 A</td>
<td>2.30 w</td>
<td>293</td>
<td>1.398</td>
<td>150</td>
<td>2.26 A</td>
<td>2.26 vs</td>
</tr>
<tr>
<td>510</td>
<td>2.25 A</td>
<td>2.25 w</td>
<td>661</td>
<td>1.377</td>
<td>411</td>
<td>2.25 A</td>
<td>2.25 w</td>
</tr>
<tr>
<td>421</td>
<td>2.16 A</td>
<td>2.16 m</td>
<td>172</td>
<td>1.361</td>
<td>431</td>
<td>2.04 A</td>
<td>2.05 w</td>
</tr>
<tr>
<td>450</td>
<td>2.00 A</td>
<td>2.01 w</td>
<td>174</td>
<td>1.379</td>
<td>450</td>
<td>2.00 A</td>
<td>2.01 w</td>
</tr>
<tr>
<td>600</td>
<td>1.90 A</td>
<td>1.907 m</td>
<td>341</td>
<td>1.379</td>
<td>610</td>
<td>1.89 A</td>
<td>1.894 w</td>
</tr>
<tr>
<td>270</td>
<td>1.89 A</td>
<td>1.894 w</td>
<td>661</td>
<td>1.377</td>
<td>261</td>
<td>1.88 A</td>
<td>1.881 w</td>
</tr>
<tr>
<td>002</td>
<td>1.87 A</td>
<td>1.871 vs</td>
<td>661</td>
<td>1.377</td>
<td>620</td>
<td>1.85 A</td>
<td>1.840 w</td>
</tr>
</tbody>
</table>

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 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 Tomax final polishing, standard Sic Zeiss 157, Schott continuous interference Li-Ne filter). The maximum and minimum values for R₁ and R₂ 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

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>R₁</th>
<th>R₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>470</td>
<td>33.5-34.7</td>
<td>40.5-42.8</td>
</tr>
<tr>
<td>546</td>
<td>32.8-34.7</td>
<td>40.2-42.0</td>
</tr>
<tr>
<td>589</td>
<td>32.6-33.7</td>
<td>39.3-41.0</td>
</tr>
<tr>
<td>650</td>
<td>32.4-34.6</td>
<td>38.4-41.0</td>
</tr>
</tbody>
</table>
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), Uytenbogaardt and Burke (1971), and Caye and Pasdeloup (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.

Acknowledgements. The authors are pleased to thank Dr. A. Kato, Chairman of IMA Commission on New Minerals and Mineral Names, Professor I. Kostov of the National Natural History Museum of Bulgaria, Dr. P. B. Barton, Jr., of the United States Geological Survey, Professor M. Franzini of Pisa University, and Professors G. P. Bernardini, C. Cipriani, S. Menchetti, and C. Sabelli of the Florence University for their helpful criticism. We are grateful to Dr. S. H. U. Bowie and Mr. P. R. Simpson of the Institute of Geological Sciences, London, and Dr. N. F. M. Henry of the University of Cambridge for suggestions and assistance with the reflectance determinations.

REFERENCES

Barton (P. B., Jr.), 1971. Econ. Geol. 66, 121-32.
Capuzzi (Q.) and Carriero (M.), 1973. Il Frantoio, 11, 3-7.
Duncumb (P.) and Jones (E. M.), 1969. Tube Investments, Techn. report, n. 260.
Palache (C.), Berman (H.), and Frondel (C.), 1944. Dana's system of mineralogy, 7th edn, 1, Wiley & Sons, Inc., NY, London.
Sugaki (A.), Shima (H.), and Kitakaze (A.), 1972. Synthetic sulfide minerals (IV), Technology Report Yamaguchi Univ., 1, 76-85.
Trevisan (L.), Dallan (L.), Federici (P. R.), Giglia (G.), Nardi (R.), and Raggi (G.), 1971. Note illustrative Carta Geol. d'Italia, foglio 96, Serv. Geol. It. Roma.
Uytenbogaardt (W.) and Burke (E. A.), 1971. Tables for microscopic identification of ore minerals, Elsevier Publ., Amsterdam.

[Manuscript received 9 August 1978]