

Sb-rich routhierite from Monte Arsiccio mine (Apuan Alps, Tuscany, Italy): occurrence and crystal structure

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Routhierite, $\text{Tl}(\text{Cu},\text{Ag})(\text{Hg},\text{Zn})_2(\text{As},\text{Sb})_2\text{S}_6$, is a rare sulfosalt first described from Jas Roux (France), in association with pierrotite, stibnite, smithite, sphalerite, realgar, orpiment, pyrite, baryte, and chabournéite [1]. Routhierite was later described from the Hemlo gold deposit, Ontario, Canada [2] and from Vorontsovskoye, Middle Urals, Russia [3]. The crystal structure of routhierite was recently solved using a specimen from the type locality [4].

During the study of the sulfosalt assemblages of the baryte-pyrite-iron oxides ore deposits from Southern Apuan Alps, Tuscany, Italy, routhierite was identified at the Monte Arsiccio mine. It occurs as anhedral grains, up to 1 mm in size, strictly associated with aktashite, baryte, boscardinite, cymrite, protochabournéite, pyrite, realgar, Hg-rich sphalerite, and stibnite, in small veinlets embedded in pyrite-rich dolostones. In this occurrence, routhierite in some cases seems to replace aktashite. More rarely, routhierite was also found in quartz veins, as euhedral crystals, dark red in color, associated with boscardinite. Preliminary identification was achieved through X-ray powder diffraction and qualitative EDS chemical analysis, which shows the presence of Tl, Cu, Ag, As, Sb, and S as the only elements with $Z > 9$.

The crystal structure of routhierite from Monte Arsiccio was solved in the space group $I-42m$, with a 9.9780(5), c 11.3764(7) Å. It was refined up to $R_1 = 3.00\%$ for 960 observed reflections. In the crystal structure of routhierite, $(\text{Cu},\text{Ag})\text{S}_4$ and HgS_4 tetrahedra share corners to form a framework with channels parallel to **c**. These channels host TlS_6 and $(\text{As},\text{Sb})\text{S}_3$ polyhedra, sharing corners and edges with the tetrahedra. All the geometrical features are in agreement with those reported by [4]. The relatively short Tl – Tl distance of 3.33 Å could indicate some Tl – Tl interaction, as proposed by previous authors for routhierite [4] and its Zn analogue, staldierite [5].

The crystal structure study of Italian routhierite points to the formula $\text{Tl}(\text{Cu}_{0.84}\text{Ag}_{0.16})\text{Hg}_2(\text{As}_{1.28}\text{Sb}_{0.72})\text{S}_6$, $Z = 4$. The $\text{Sb}/(\text{As}+\text{Sb})_{\text{at.}}$ ratio is 0.36, to be compared with the value 0.11-0.12 for routhierite from Jas Roux [1]; the highest $\text{Sb}/(\text{As}+\text{Sb})_{\text{at.}}$ ratio was measured on routhierite from Hemlo, giving 0.60 and 0.80 [2], and corresponding to the Sb analogue of routhierite.

The Sb-rich nature of routhierite from Monte Arsiccio mine agrees with the usual richness in antimony of the sulfosalts from the Apuan Alps ore district. Actually, protochabournéite [6] and boscardinite [7], first discovered at this locality, are the Sb-rich member of the chabournéite series and a Tl-Sb homeotype of baumhauerite, respectively. Finally, routhierite is the eighth Hg sulphide described from the baryte-pyrite-iron oxides ore deposits from Apuan Alps.

Ref. [1] Johan *et al.* (1974): *Bull. Soc. fr. Minéral. Cristallogr.*, **97**, 48-53; [2] Harris (1989): *Geol. Surv. Canada, Econ. Geol. Rep.*, **28**, 88 pp.; [3] Pekov (1998): Ocean Pictures, Moscow, 369 pp.; [4] Bindi (2008): *Acta Crystallogr.*, **C64**, i95-i96; [5] Graeser *et al.* (1995): *Schweiz. Mineral. Petrogr. Mitt.*, **75**, 337-345; [6] Orlandi *et al.*: *Can. Mineral.*, submitted; [7] Orlandi *et al.*: *Can. Mineral.*, in press.