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## Methods

Samples for this study were collected in the Sant'Olga level (524 m a.s.l.), one of the lowermost adits of the Monte Arsiccio mine. Several polished sections were investigated with a reflected light optical microscope and with a scanning electron microscope (Philips XL 30 operating at 20 kV) coupled with an energy-dispersive X-ray fluorescence spectrometer at the Pisa University's Dipartimento di Scienze della Terra.

Bulk chemical analyses of these samples were performed at Actlabs (Ancaster, Ontario, Canada) and at Pisa University's Dipartimento di Scienze della Terra using a variety of instrumental methods (ICP-AES, ICP-MS, XRF, INAA, FIMS) and sample preparation techniques (acid dissolution, lithium metaborate/tetraborate fusion, sodium peroxide sintering, pressed powder pellets, etc.).

Mineral phases were identified and studied through X-ray diffraction studies, using both single-crystal and powder techniques at Pisa University's Dipartimento di Scienze della Terra. Single-crystal data were collected through a Bruker Smart Breeze single-crystal diffractometer equipped with an air-cooled CCD and graphitemonochromated Mo  $K\alpha$  radiation. Powder patterns were collected using a 114.6 mm Gandolfi camera with Ni-filtered Cu  $K\alpha$  radiation.

Chemical analyses of mineral phases were carried out with a CAMEBAX SX 50 electron-microprobe at the BRGM-CNRS-University common laboratory, Orléans, France, using the following analytical conditions: accelerating voltage 20 kV, current 20 nA. Emission lines are  $K\alpha$  for Cu, Zn, Fe, S, and Cl;  $L\alpha$  for Ag, Cd, As, and Sb,  $M\alpha$  for Tl and Hg.



**Figure DR1**. Optical microscope images of country rocks and ores from the Monte Arsiccio mine. A: Microcrystalline barite ore showing polygonal texture with 120° triple junctions (transmitted light, crossed polars). B: Partially recrystallized pyritebearing dolostone (transmitted light, crossed polars). Abbreviations: Brt, barite; Dol, dolomite; Py, pyrite.



**Figure DR2**. Backscattered electron images of Tl-Hg-As-Sb-Ag-Pb sulfosalts showing melt-related textures in the barite + pyrite ore. A: Interstitial pocket (laffittite, protochabournéite and realgar) within the barite crystal matrix B: Interstitial protochabournéite within the barite crystal matrix (note the rounded barite crystals at the contact with protochabournéite). C: Interstitial pocket consisting of protochabournéite and "Ag-routhierite". D: Two protochabournéite blebs connected by a small "Ag-routhierite" "drop". E: Two interconnected pockets of "Ag-routhierite" containing small blebs of realgar. F: Tiny interstitial pocket showing an intergrowth of protochabournéite and "Ag-routhierite". Abbreviations: Ag-Rou, "Ag-routhierite"; Brt, barite; Laf, laffittite; Pc, protochabournéite; Rlg, realgar.



**Figure DR3**. Backscattered electron images of Tl-Hg-As-Sb-Ag-Cu-Pb sulfosalts showing melt-related textures in the dolostone. A: Interstitial pocket consisting of aktashite overgrown by routhierite and protochabournéite. B: Interstitial mass consisting of protochabournéite, routhierite and an unidentified Ag-Sb-As sulfosalt (labeled Ag,Sb,As,S) within the pyrite + dolomite crystal matrix. C: Complex vein of sulfosalts in the dolostone. D: Detail of the upper right portion of image C showing the sharp sinuous contact between stibnite and routhierite. E: Sharp sinuous contact between stibnite in a sulfosalt vein. F: Association of stibnite and boscardinite in a vein within the dolostone. Abbreviations: Akt, aktashite; Brt, barite; Bsc, boscardinite; Cym, cymrite; Dol, dolomite; Pc, protochabournéite; Py, pyrite; Rou, routhierite; Twn, twinnite.