Geophysical Research Abstracts, Vol. 8, 04345, 2006
SRef-ID: 1607-7962/gra/EGU06-A-04345

Gold, silver and rare accessory minerals in hydrothermal volcanic massive sulfide deposits of the Northern-Apennine ophiolites (Italy)

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A number of massive sulfide deposits occur associated with Jurassic ophiolites in the Northern Apennine of Eastern Liguria and Emilia Romagna (Italy). These deposits, characterized by Cu- to Zn-Cu-rich mineral assemblages typical of ophiolite-associated deposits worldwide, have been a main source of copper since the Bronze age, although they are not active any more. Based on field observations, morphology and stratigraphic position, the deposits can be grouped into: 1) stratiform ore located at the top of serpentinite or pillow lava units, 2) stratabound deposits inside the pillow lavas; 3) stockwork veins, cutting across various units of the ophiolite sequence, including serpentinite, massive gabbro, and pillow basalts. Sporadic information reported in ancient and recent documents indicate that silver and gold were occasionally recovered in some copper mines of Eastern Liguria. Our preliminary bulk-ore analyses indicated the existence of sensible concentrations of Au, Ag, and U in samples from the stratiform and the stratabound ores, whereas all of the stockwork veins were found to be depleted in these metals. The investigation “in situ” by optical and electronic microscopes and electron microprobe analyses of selected ore samples from four mining localities allowed the discovery of the mineral carriers of Au and Ag such as native gold, acanthite or argentite (Ag2S), and freibergite (Ag,Cu,Fe)12(Sb,As)4S13. These minerals form a complex assemblage of microscopic to sub-microscopic ($<$ 10 ìm) accessory minerals, including uraninite, barite, galena, smithsonite, siderite, a La-Ce-carbonate and a Sn-hydroxide, attributable to the rare mineral hydroromarchite Sn3O2(OH)2. The textures of the sulfide host, mostly composed of chalcopyrite, pyrite and sphalerite, are indicative of metal deposition in a range of conditions,

starting from precipitation from hot, metal-charged solutions (syngenesis), followed by post-depositional replacement of biological material and clastic re-sedimentation, at low temperature (epigenesis). Syngenetic gold is enriched in Ag and occurs with uraninite in Fe-Cu rich ore. Fineness of native gold becomes higher by loss of Ag into secondary Ag2S during seafloor weathering of the sulfides. Genesis of freibergite is related with re-crystallization of sphalerite in massive Zn-Fe ore. Hydroromarchite was found in massive Zn-Fe ore, closely related with late deposition of siderite and secondary pyrite, possibly related to the action of neutral to basic and reducing waters flushing through the ore in the initial stages of seafloor diagenesis. The widespread evidence for seafloor re-sedimentation and biogenic-driven reworking of the sulfides, indicates a transition from proximal VMS to a more distal-type of deposit formed by re-sedimentation processes in a dynamic tectonic environment. This would be in agreement with the interpretation of the Jurassic Ligurian ocean as a narrow basin in the early stage of its opening, having its modern analogue in the Red Sea.