ACCESSORY MINERALS IN VOLCANIC MASSIVE SULFIDE DEPOSITS OF THE NORTHERN-APENNINE OPHIOLITES (ITALY): THEIR PETROGENETIC SIGNIFICANCE

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INTRODUCTION

The recent development of electronic microscopy techniques in mineralogy allows us to seek answers in the accessory phases that accompany the major mineral assemblage of rocks, but generally escape identification with optical microscopy due to their scattered occurrence and submicroscopic size. In many cases, however, careful analysis and characterization of these accessory minerals can be used to determine chemical and physical conditions controlling the formation of the host rocks.

Mineralogical investigation of VMS deposits associated with the Tethyan ophiolites of the Northern Apennine (Italy) was performed at the Department of Earth Sciences and the Instrumental Center (CIGS) of the University of Modena and Reggio Emilia, using traditional optical microscopy and the systematic scanning of polished sections under high-magnification electronic microscope. A suite of previously unreported accessory minerals was discovered, some of which are very rare in nature, or are unusual for the metallogenic environment where they are found. The main goal of this contribution is to illustrate the petrogenetic role of these accessory minerals, giving emphasis to their significance as indicators of the palaeo-geographic environment and physical-chemical conditions of the ore deposition.

GEOLOGICAL SETTING AND MAIN MINERALOGY OF THE SULFIDE DEPOSITS

Based on morphology and structural relationships with the host rocks, Ferrario and Garuti (1980) and Garuti and Zaccarini (2005) have recognized three types of sulfide deposits associated with the Northern Apennine ophiolites (Figure 1):

1) Stratiform ore consisting of high-grade and massive sulfide bodies set concordant with litho-stratigraphic joints a) at the top of pillow lava, covered with pelagic sediments (cherts, palombini shale), or b) inside the ophiolitic breccia at the top of serpentinite, systematically covered with pillow lava.
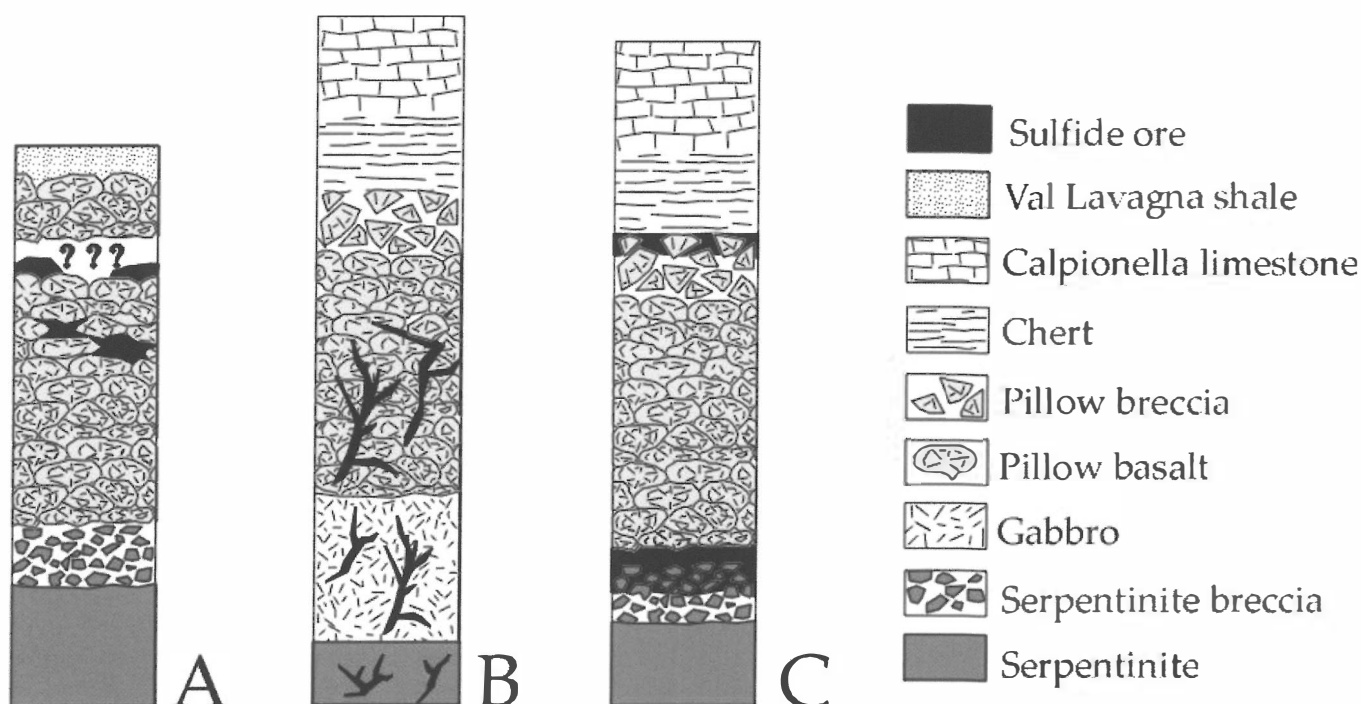

Figure 1: Geological setting of stratabound (A), stockwork veins (B) and stratiform (C) sulfide deposits in typical stratigraphic sequences of the Northern Apennine ophiolites.

Legend:
- Sulfide ore
- Val Lavagna shale
- Calpionella limestone
- Chert
- Pillow breccia
- Pillow basalt
- Gabbro
- Serpentinite breccia
- Serpentinite

	Au	Ag	U	Hyd	Ilm	Chr	Mgt	Hem	Ba,Ca	Zrc	REE
Ore in basalt and basalt breccia											
stockwork veins					X			X		X	
stratiform	X	X	X	X					X		X
stratabound	X	X	X		X			X	X		
Ore in serpentinite											
stockwork veins						X	X			X	X
stratiform	X		X			X	X			X	

Abbreviations: Au = gold, electrum Ag = argentite, freibergite, U = uraninite, Hyd = hydroromarchite, Ilm = ilmenite, Chr = chromite, Mgt = magnetite, Hem = hematite, , Ba,Ca = barite, anhydrite, Zrc = zircon, REE = rare earth elements bearing minerals.

Table 1: Distribution of the relevant accessory minerals in sulfide deposits of the Northern Apennine

2) Stratabound ore composed of high-grade and massive sulfide inside pillow lava.
3) Stockwork ore consisting of low-grade disseminated sulfides in quartz-calcite veins cutting across different units of the ophiolite sequence: serpentinite, gabbro, or pillow basalt.

All of the deposits are characterized by the Cu-Fe to Cu-Fe-Zn assemblages typical of hydrothermal ophiolite-hosted VMS deposits worldwide (Galley & Koski 1999). Pyrite, chalcopyrite, sphalerite, and pyrrhotite are dominant phases, usually associated with a gangue of quartz and calcite accompanied by chlorite, epidote, and titanite, in variable proportions. There are however differences depending on geological setting of the ore deposits. According to Garuti & Zaccarini (2005), the stratiform deposits originally formed by accumulation of sulfide precipitating from metal charged hydrothermal solutions venting at the sea floor (proximal hydrothermal stage). Post-depositional reworking by submarine debris flow at the sea floor produced a hydrothermal-sedimentary mixed ore (distal re-sedimentation stage). As a consequence, ore and gangue minerals were transformed into a poorly sorted clastic sediment in which biologic remnants, replaced by sulfide (microfossil shells, algae filaments), occur embedded in a matrix of chlorite and clay minerals. The stratabound sulfide ore probably formed by deposition of sulfide at the sea water-basalt interface, as a result of hydrothermal activity, syngenetic with the emplacement of the host pillow-lava, with very limited or no post-depositional reworking. Deposition of stockwork ores occurred at variable depth below the sea floor. In some cases hydraulic breccia formed by adiabatic-boiling and explosion of super-heated uprising hydrothermal fluids. With a few exceptions, no genetic relationships between stockwork and stratiform deposits could be established.

THE ACCESSORY MINERALS

The identified accessory minerals are native metals (gold, electrum), sulfides and sulfosalts (millerite, linneite, galena, argentite or achantite, freibergite), oxides and hydroxides (ilmenite, rutile, hematite, magnetite, chromite, uraninite, limonite, hydroromarchite), silicates (zircon), sulfates (barite, anhydrite), carbonates (smithsonite, siderite, un. La-Ce-CO$_3$), phosphates (apatite, monazite). Minerals formed in the supergene conditions were not considered in this work. Distribution and frequency of relevant accessory minerals is presented in Table 1.

Noteworthy, accessory minerals of Au-Ag-U along with hydroromarchite Sn$_3$O$_2$(OH)$_3$, and Ba-Ca sulfates appear to be restricted to the stratiform and stratabound deposits, and seem absent in subseafloor stockwork veins (Figure 2). Gold initially precipitated as Au-Ag alloy in the high temperature hydrothermal stage (stratabound ores), but is concentrated up to the ppm level as pure Au by sea-floor weathering of stratiform ores. In fact, gold was found to be particularly abundant in sulfide ores characterized by debris flow texture (Garuti and Zaccarini, 2005). Similarly to pure gold, the Ag minerals do not appear to be high-temperature hydrothermal minerals. They mostly occur in Zn-Fe rich facies of some stratiform deposits, and represent unmixed phases during recrystallization of sphalerite at low temperature (Garuti and Zaccarini, 2005). Uranium is believed to have been removed by the sea water at the seafloor venting sites, by reaction with reducing hydrothermal solutions (Klinkhammer and Palmer, 1991). Hydroromarchite is a rare mineral in nature, having been reported to be a common product of submarine corrosion of pewter items (Ramik et al., 2003; Dunkle et al., 2003). In the investigated deposits, it is found as either thin coats replacing marcasite and pyrite or minute idiomorphic crystals in a complex assemblage consisting of sphalerite, siderite, , smithsonite, barite and an unidentified Fe-Ca sulfate. If an anthropogenic origin of hydroromarchite is excluded, the mineral must have formed at low temperature by reaction between the ore and the sea water. Barite and anhydrite are common constituents of modern sea-floor «black smoker» sulfide chimneys, precipitating by reaction of sea water with the buoyant hydrothermal solution.

A second group of accessory minerals occur exclusively in ore deposits associated with serpentinite and serpentinite breccia (Figure 3), being they of stratiform or stockwork type. Significantly, these minerals were not observed in the sulfide ores hosted in basalt. The most common accessory minerals of this type are chromite and the product of its hydrothermal alteration (ferrian chromite and magnetite). Chromite does not pertain to the hydrothermal assemblage, but represents a detrital
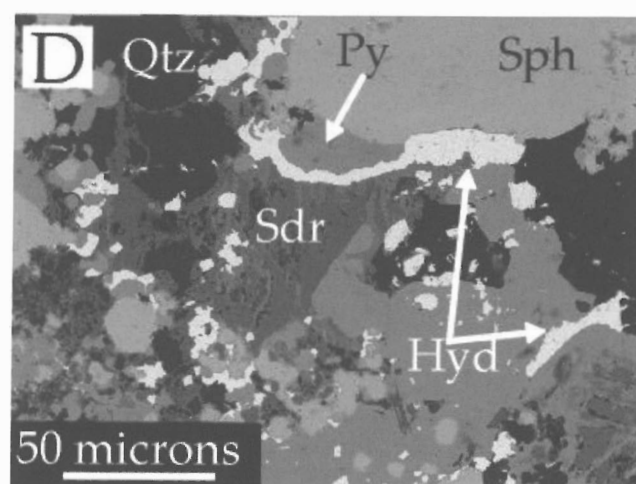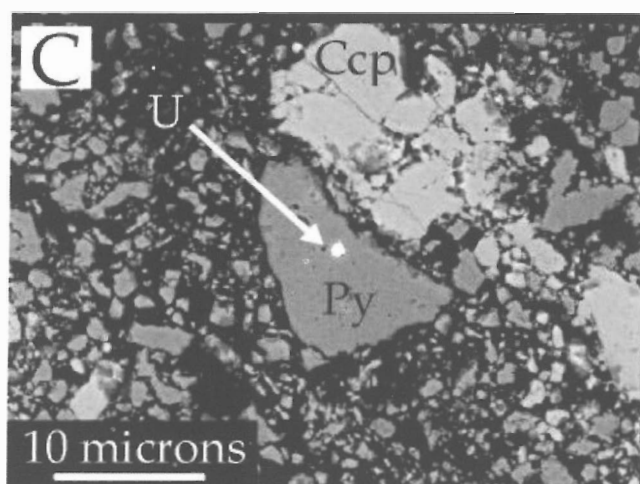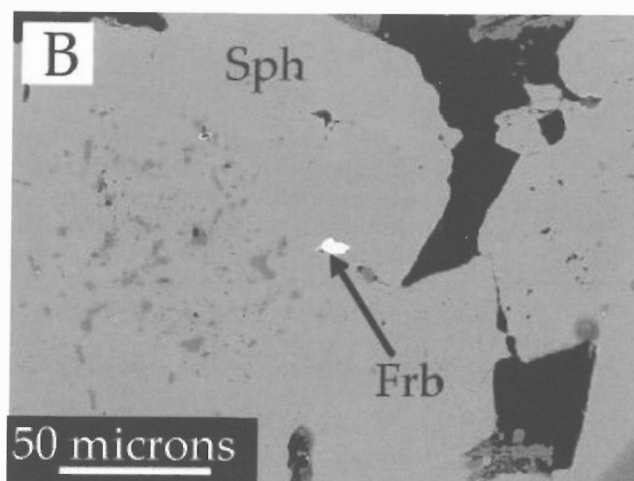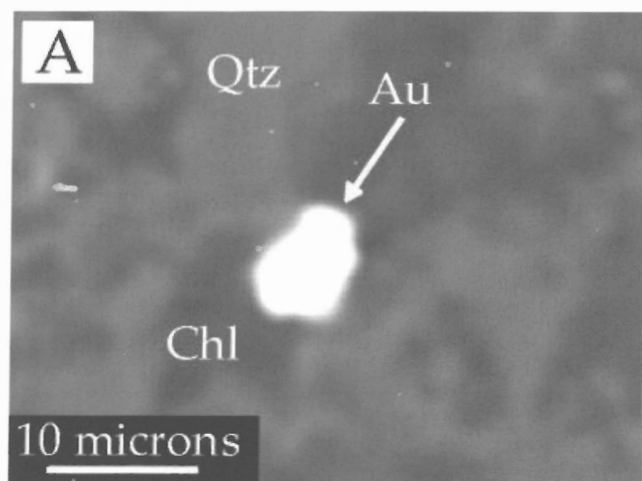
Figure 2: BSE images of accessory minerals from stratiform sulfide deposits of the Northern Apennine ophiolites. Abbreviations: Qtz = quartz, Chl = chlorite, Au = gold, Sph = sphalerite, Frb = freibergite, U = uraninite, Ccp = chalcopyrite, Py = pyrite, Sdr = siderite, Hyd = hydroromarchite.

mineral derived from the ultramafic country rock. When included in the quartz matrix of the stockwork veins chromite is partially corroded and altered into ferrian-chromite and magnetite as a result of reaction with the hot hydrothermal fluids. In contrast, detrital chromite in stratiform ores is unaltered and occurs as large crystals included in massive sulfide ore. Some ore deposits associated with serpentinite contain abundant authigenic magnetite and hematite within the sulfide ground-mass. Zircon is particularly abundant in the stockwork ores, occurring in the quartz matrix of the veins, although one large grain was found in the calcite gangue of a stratiform ore. The REE-bearing minerals form a minute dissemination in stockwork veins as well as in stratiform

ores. They are more abundant in zircon rich samples suggesting affinity among these minerals.

CONCLUDING REMARKS

1) The stratiform and stratabound ores contain accessory Au and U minerals which are indicators of the deposition of the sulfide ore as a result of the reaction between the sea-water and hydrothermal fluids venting at the sea-floor. Other minerals, such as the Ag-compounds formed by post-depositional equilibration of silver bearing sphalerite, or break down of electrum under sea-floor weathering conditions (Garuti and Zaccarini, 2005). Sea-floor

Figure 3: Reflected-light images of accessory oxide minerals from the stockwork veins deposits. A = partially corroded crystal of chromite, rimmed by ferrian-chromite and magnetite. B = lamellae of hematite. Qtz = quartz.
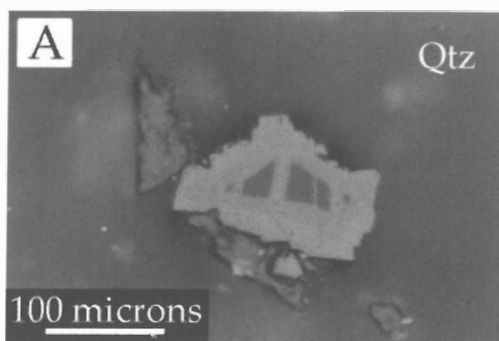
weathering appears to be a controlling-factor for the deposition of rare minerals such as hydroromarchite during diagenetic reworking of the ore. The fact that these phases are absent in the stockwork veins suggests that processes leading to the concentration of these metals occurred exclusively in the submarine environment. Therefore the interaction with the sea water was the «condicio sine qua non» for the formation of these accessory minerals, thus making them important indicators of the palaeo-geographic environment of formation of their host sulfide deposits.

2) The accessory chromite and related minerals, are distinctive of sulfide ore hosted in serpentinite. Chromite is detrital in origin. In stockwork veins, the mineral was probably extracted from the country rock and trasported by uprising hydrothermal fluids. In stratiform deposits, chromite is derived by the erosion of adjacent serpentinite and incorporated in the sulfide ore as it deposited. A further influence of the ultramafic nature of some host rocks is the abundance of Fe oxides that accompany the sulfide ores. This indicates that the parent solution of these ores became Fe-rich by leaching of the ultramafic country rocks.

3) Detailed mineralogical study of the sulfide deposits of the Northern Apennine ophiolites indicates that the accessory minerals are useful petrogenetic indicators. From one hand, they can be used to identify the palaeo-geographic environment of ore deposition, distinguishing between seafloor and sub-seafloor conditions. To the other, they allow to assess the geochemical-mineralogical influence of the lithological association in which the ore deposits occur: mafic versus ultramafic host rocks.

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