Oxidation Zones of Volcanogenic Massive Sulphide Deposits in the Troodos Ophiolite, Cyprus: Targeting Secondary Copper Deposits

Submitted by Daniel Bijan Parvaz to the University of Exeter as a thesis for the degree of Doctor of Philosophy in Earth Resources C, March 2014.
Abstract

Gossans, the brightly coloured oxidation products of sulphide mineralised rocks, have acted as an exploration target for base and precious metals and sulphur for thousands of years. They are easily identified from remote sensing and field-based reconnaissance, and once found may be drilled to determine the character of mineralisation below. The number of targets drilled could potentially be reduced if gossans overlying significant mineralisation can be discriminated from their field relations, mineralogy and geochemistry. Previous such studies have focussed on porphyry-type systems, with less attention on the generally much lower tonnage volcanogenic massive sulphide (VMS) deposits. However, VMS continue to provide an economically important source of metals in Europe and elsewhere. The Troodos Massif in Cyprus was chosen for this study as it hosts a currently active Cu mine along with historically worked VMS, is little deformed and has a relatively well understood geological framework. Of particular interest are secondary Cu deposits (SCUD) which form due to weathering of primary massive sulphides (PMS). These can be worked at relatively lower financial and environmental cost, and at much lower grades (down to around 0.1 % Cu). The only currently mined SCUD in Cyprus is the Phoenix ore body at Skouriotissa, which lies immediately adjacent to, and structurally below the Phoukasa PMS.

The questions addressed in this study are: 1) Do Cypriot PMS that were mined for Cu show original Cu enrichments, or is their elevated Cu content a result of supergene enrichment to form an SCUD? This was addressed by comparing the mineralogical, chemical and S isotopic compositions of PMS mined for Cu with those mined for pyrite only from across the Troodos; 2) Do gossans formed from Cu-rich sulphides show distinctive mineralogical and chemical signatures? The characteristics of gossans known to overlie prospective sulphide bodies were compared with those from barren PMS; 3) What circumstances promote the formation of SCUDs? In particular, did sulphide oxidation occur on the sea floor or in a terrestrial environment? It was considered likely that SCUD formation may require sea floor oxidation because this will result in limited Cu dispersion, due to both sharp pH and redox gradients and limited fluid flow when compared with terrestrial weathering, where the depth to the water table can be considerable. The question was addressed by comparing the field relations, chemistry and S and O isotope compositions of gossans thought to have formed on the sea floor (Skouriotissa - Phoenix) with those generated in a terrestrial setting (Kokkinopezoula, Mathiati and Sia).

The remnants of primary VMS deposits mined for Cu in Cyprus (Phoukasa, Sia and Troulli) almost exclusively contain primary Cu sulphides such as chalcopyrite. Secondary Cu sulphides, mainly chalcocite and covellite, are only present in significant concentrations at Phoukasa and Troulli, with Cu oxides being found in Phoenix. At Phoukasa, secondary Cu sulphides have a mean δ^{34}S = 3.69±0.08 ‰ similar to primary pyrite and chalcopyrite (mean δ^{34}S = 3.78±0.08 ‰) suggesting formation from Cu-rich fluids that scavenged S from primary sulphides. Sulphide material collected from copper mines has Cu = 840 to > 10,000 ppm at Phoukasa; 167 to 3573 ppm at Sia; 288 to > 10,000 ppm at Troulli, while the Cu-barren deposits have generally lower Cu grades (Cu = 170 to 433 ppm at Kokkinopezoula; 327 to 1303 ppm at Mathiati north). There are no systematic differences in the S isotope compositions of pyrite between deposits mined for Cu and those not (average δ^{34}S = 1.68, 3.74 and 7.1 ‰ for Cu-rich Sia, Lysos and Phoukasa, and 5.03 and 3.70 ‰ for Cu-poor Kokkinopezoula and Mathiati North sulphides, respectively).
No consistent chemical differences (including chalcophile elements) could be identified between gossans overlying Cu-rich as opposed to barren PMS. Gossans overlying the Lysos and Sia Cu-rich PMS, however, show an enrichment in Pb and Zn not observed in other gossans, and umbers, which are chemical sediments associated with VMS systems, often overlying gossans, show strong Cu enrichments in the vicinity of Cu-rich PMS. Umber samples from near the Cu-rich Phoukasa sulphide body contain > 10,000 to 35,400 ppm Cu, while those around Cu-poor Mathiati North contain 669 to 819 ppm Cu. There were no differences in the S isotope compositions of gypsum from sulphide bodies which were Cu-rich (δ^{34}S = 5.9 to 6.9 ‰ for Sia, Phoukasa and Troulli) and Cu-poor (δ^{34}S = 5.0 to 7.3 ‰ for Kokkinopezoula, Mathiati North).

Regarding the environment of formation of SCUDs, an initial submarine oxidation of the Phoukasa VMS is considered likely as it is immediately overlain by marine pelagic sediments, while all other deposits studied are overlain by volcanics. In addition, volcanics in the vicinity of Phoukasa show large negative Ce anomalies (Ce/Ce* = 0.90 to 0.38, average = 0.71), consistent with sea floor alteration, compared with other localities such Kokkinopezoula (Ce/Ce* = 0.89 to 1.08, average = 0.97) and Sia (Ce/Ce* = 0.92 to 1.03, average = 0.99). Unfortunately, the S isotope composition of gypsum could not be used to determine the nature of the gossan-forming environment. Gypsums from all locations (average δ^{34}S = 6.74±0.08 ‰) have δ^{34}S values similar to, but slightly ^{34}S enriched compared with their associated sulphides (average δ^{34}S = 2.9±0.08 ‰) which indicates that their S isotope signature largely reflects that of S released during sulphide oxidation, as opposed to evaporation of sulphate-rich waters or direct precipitation from a similar solution (i.e., seawater). However, the oxygen isotope composition of gypsum (average δ^{18}O = 6.2 ‰) from Sia (average δ^{18}O = 2.4 ‰) reflects a mixture of atmospheric O (δ^{18}O = 23.6 ‰) and Mediterranean meteoric water O (δ^{18}O =-5.0 ‰), indicating a terrestrial environment of formation. Gypsum from Skouriotissa has an average δ^{18}O = 6.6 ‰ which most likely indicates a combination of seawater and seawater-dissolved O (δ^{18}O =23.5 ‰), despite some overlap with the composition of meteoric water and atmospheric O.

In summary, it is proposed that the currently unique nature of Skouriotissa as hosting the only major SCUD in Cyprus is due largely to initial sea water alteration of the Phoukasa PMS resulting in limited Cu dispersion and localised Cu enrichment within the primary ore body. Subsequent uplift and alteration of the Phoukasa PMS led to the formation of a relatively high grade SCUD in the Phoenix deposit.

The main outcomes of the study are a series of models for the development of gossans and associated lithologies in terrestrial and seafloor weathering environments in Cyprus. These incorporate a new term (retali) for acid leached volcanics in the footwall of PMS, and exploration-relevant field, mineralogical and chemical criteria for their discrimination from gossans, which overlie PMS. In agreement with an existing model, the formation of the Phoenix SCUD is interpreted as having been due to the downward migration of Cu-bearing acid fluids from the seafloor oxidation of the upper parts of the Phoukasa deposit. Secondary Cu mineralisation is thought to have taken place within the relatively reducing environment below the water table in lavas stratigraphically below the Phoukasa deposit. That the formation of SCUDs may require seafloor sulphide oxidation, and that this can be recognised in the mineralogical and chemical compositions of associated volcanics and gossans, provides new exploration criteria for SCUDs. However, it should be noted that the Phoenix deposit was the only SCUD examined in this study, and that this model should therefore be tested elsewhere.