Mineralogical and geochemical investigation of the Ermioni VMS supergene alteration zone, Argolis, Greece

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Ore deposit geology, exploitation history and production

The Ermioni volcanogenic massive sulfide ore, with pyrite and minor chalcopyrite and sphalerite, was a target of exploitation from the early 20th century for the production of sulfuric acid for fertilizers. Outcrops of the massive, stockwork and disseminated ore have suffered extensive supergene alteration resulting in the formation of iron caps that were used in the past as indicators of the sub-surface primary ore (Aronis, 1951). Small-scale exploitation took place namely prior World War II (Aronis, 1951; Mousoulos, 1958), whereas after the war, production dropped significantly until the cease of the Ermioni mines in the late 70s (Sideris and Skounakis, 1987).

Sampling – Analytical methods

The present study was focused on the most important mine sites, Karakasi and Roro. Samples were collected from locations where outcrops of the supergene alteration zones are still preserved, and from abandoned mine wastes. Sampling included massive to semi-massive oxidized ore samples, and oxidized samples from both the stringer and leached ore zones from Karakasi and Roro. Mineralogy was determined by combination of transmitted and reflected light optical microscopy, Raman Spectroscopy, X-ray Diffractometry and Scanning Electron Microscopy. Primary and secondary ore samples were commercially analyzed by ICP-AES for determination of Au grades.

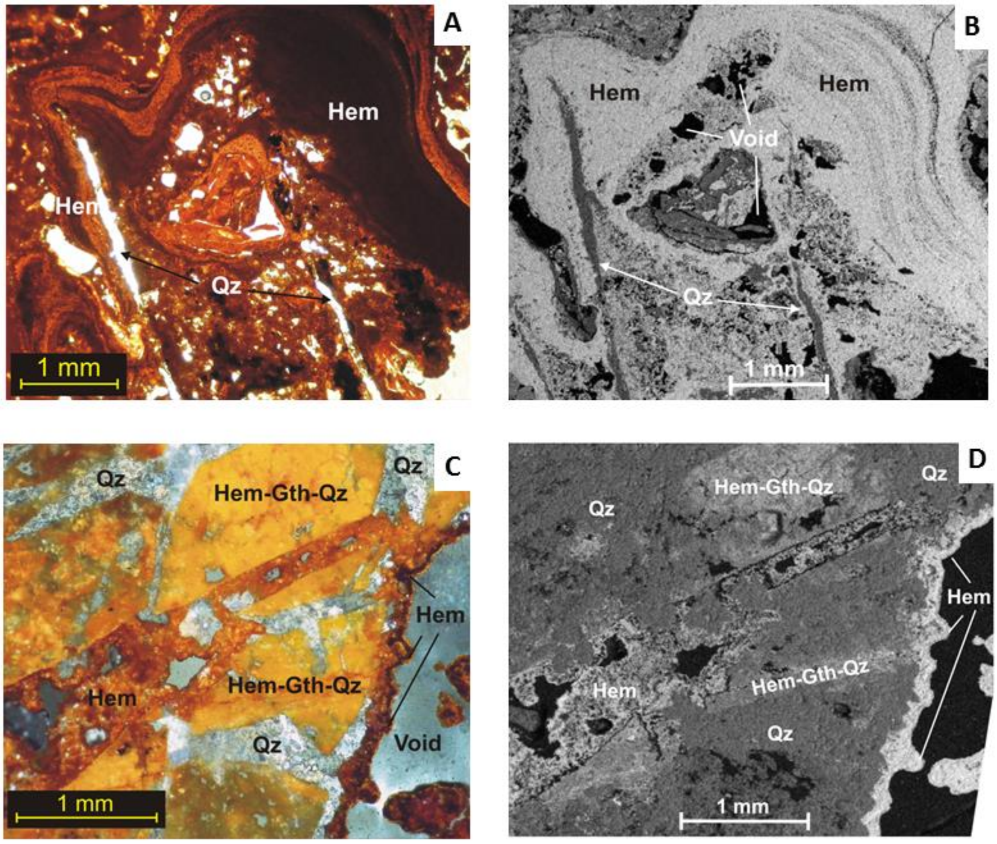

Figure 1. Optical and Backscattered Electron Microscopy images of the Ermioni supergene alteration zone. A-B. Roro oxidation zone. Extensive hematite colloform banding (Hem) is observed with minor quartz (qz) fragments and quartz veinlets. The highly porous texture of the rock is observed. C-D. Karakasi oxidation zone. Primary quartz stockwork is preserved, providing the highly cohesive character to the rock. Primary ore phases are pervasively altered and replaced by hematite (Hem) with minor goethite (Gth). Occasionally, colloform bands and porous veinlets of predominant hematite are developed between hematite-goethite-quartz masses. Abbreviations after Whitney and Evans (2010).

Results and discussion

Mineralogical investigation of Ermioni oxidized massive ore samples revealed the high degree of supergene alteration with hematite and minor goethite being the major secondary phases identified, whereas only traces of pyrite and chalcopyrite relicts are still present. SEM studies revealed that both hematite and goethite from Karakasi and Roro show no enrichment in other metals. Minor jarosite is also observed by XRD and SEM studies in the partially altered stockwork ore at Karakasi and Roro. At Roro, rock samples from the oxidation zone are both porous and brittle, and extensive hematite colloform banding is observed (Figure 1A, 1B). The supergene alteration zone at Roro is occasionally rich in secondary Cu phases (azurite and malachite) as a result of weathering of primary ore rich in chalcopyrite. At Karakasi, the samples from the supergene alteration zone show higher silica content relative to Roro. Hematite forms fine-grained aggregates between quartz stockwork, whereas occasional colloform bands are observed around voids (Figure 1C, 1D). In contrast to Roro, the Karakasi iron cap samples are very cohesive although highly porous, an observation that is related to the siliceous nature of the Karakasi primary ore (Mousoulos, 1958). The supergene alteration zones at Karakasi and Roro are characterized by very limited Au enrichment that is related to both the small size of the primary ore bodies, and the very low Au content in the primary ore (Table 1). The higher Au grades are identified in samples collected from Roro, whereas at Karakasi, the Au content of the supergene alteration zone is even lower (Table 1).

Table 1: Au grades (in gr/t) from the Ermioni massive ore and supergene alteration zones at Karakasi and Roro locations.

Sample type	Au grade
Roro massive sulfide ore	0.431
Roro massive sulfide ore	0.504
Roro massive sulfide ore	0.548
Roro oxidized ore	0.727
Roro oxidized ore	0.744
Roro oxidized ore	0.722
Karakasi oxidized ore	0.002
Karakasi oxidized ore	0.110
Karakasi oxidized ore	0.113
Karakasi oxidized ore	0.104
*Karakasi primary ore	0.2
*Roro primary ore	0.4
*Data from Mousoulos (1958)	

Concluding, hematite predominates in the Ermioni oxidation zone followed by lower amounts of goethite. Their formation is directly related to the presence of pyrite in the primary ore, but also to the predominant physicochemical conditions of the near-surface environment. Typical secondary phases Fe in oxidation zones include ferrihydrite, schwertmannite, jarosite, goethite and hematite, and the stability of those minerals depends on the gradually evolving physicochemical conditions of the surface environment. Newbrough and Gammons (2002) and Fukushi et al. (2003) state that with increasing pH and decreasing sulfate load the series of replacement are as follows:

Jarosite → schwertmannite → ferrihydrite → goethite → hematite

Hematite and goethite are the most stable secondary Fe(III) phases in mildly acidic to alkaline and oxidative conditions (Nordstrom & Alpers, 1999). It is therefore reasonable to assume that as supergene alteration phenomena progressed, the geochemical environment of the Ermioni oxidation zone gradually changed from highly oxidative with increased sulfate load, to mildly acidic and oxidative with very low sulfate content.

References

Aronis, G., 1951. Research on the iron-pyrite deposits in the Hemioni mining district, Geological and geophysical surveys, Subsurface Research Department, Ministry of Coordination, Athens, 153-188.

Mousoulos, L., 1958. Les gisements pyriteux du district minier d'Hermione. Étude sur leur gèologie et minéralogie. Le problème de leur genèse, Ann. Géol. Pays Hellén., 9, 119-164.

Fukushi, K., Sasaki, M., Sato, T., Yanase, N., Amano, H., Ikeda, H., 2003. A natural attenuation of arsenic in drainage from an abandoned arsenic mine dump. Applied Geochemistry, 18, 9, 1267-1278.

Newbrough, P., Gammons, C.H., 2002. An experimental study of water-rock interaction on acid rock drainage in the Butte mining district, Montana. Environmental Geology, 41, 705-719.

Nordstrom, D.K., Alpers, C.N., 1999. Geochemistry of acid mine waters, in: Plumlee, G.S., Logsdon, M.J., (Eds.), Reviews in Economic Geology, 6A. The Environmental Geochemistry of Mineral Deposits. Part A: Processes, Techniques, and Health Issues, Society of Economic Geologists, 133-160.

Sideris, C., Skounakis, S., 1987. Metallogeny in the Basic Rocks of a Paleosubduction Area – The Case of Ermioni Cu-bearing Pyrite Mines (East Peloponnesos, Greece). Chem. Erde, 47, 93-96.

Whitney, D.L., Evans, B.W., 2010. Abbreviations for names of rock-forming minerals. American Mineralogist, 95, 185-187.