

Supergene Processes in the Copper Mineralization at the Kraljičin Zdenac on the Medvednica Mt.

Danijela Šmajgl, Ladislav A. Palinkaš, Danijela Mavrić, Vladimir Bermanec

Faculty of Sciences, Geology department, University of Zagreb, Croatia (lpalinkas@geol.pmf.hr)

Supergene leaching, oxidation and chalcocite enrichment is a common process which takes place in the weathering environment of copper mineralisation. Penetration of oxygen rich water under the earth surface, is a beginning of a new geochemical scenario which changes hypogene parageneses into a garden of numerous supergene minerals, with an astonishing lush of flashing colours.

Eh-pH diagram of the stability fields of common supergene sulphide and oxide minerals in the system Cu-C-S-H₂O (Fig.1) shows possible paths followed by solution descending from the oxidized zone, generating enrichment, and infiltrating into hypogene ore or protore. The facies are defined by hydrologic regimes in the vadose zone, in the zone of capillary fringes and in the saturated zone.

Sulphide oxidation takes place above the water table as an electrochemical process mediated by acidophilic, Fe- and S-oxidizing bacteria. Prevailing acidic condition facilitates leaching of Cu, which is transferred downward to the reduced environment, beneath the water table, where sulphide enrichment takes place. Enrichment is primarily an abiotic cation-exchange reaction of Cu, which substitutes more electronegative metals. The required S is inherited from the replaced sulphide minerals. Bacteria also play a role in the enrichment process by facilitating metal adsorption.

Primary mineralization consists of stratabound ore body within a parametamorphic rock series. The ore layer is "sandwiched" between hangingwall metadolostone and the silicified layer of protomarl as a footwall. Primary minerals are chalcocopyrite, pyrite, and eventually primary bornite. The gangue minerals are anhedral quartz, carbonates, and barite.

The shape of the secondary copper mineralization at Kraljičin Zdenac is a pseudo-layer approximately 1 m thick, with (A) pyrite and (B) chalcocopyrite-pyrite rich area.

Supergene processes in this restricted space, developed a faint zonation that could hardly be compared with the standard architecture of the supergene oxidation and enrichment zones above a primary Cu mineralization above an appreciable ore deposit. The common zoning in an ideally developed supergene cover, from the top to bottom is: leached cappings (gossan cap), oxidized Cu ore, and chalcocite-enriched ore (cementation zone, Sillitoe, 2005). The ore outcrop at the Medvednica Mt. contains three assemblages, characteristic of the oxidizing supergene process: (i) Mild oxidation stage; primary ore containing chalcocopyrite and pyrite, and bornite mildly oxidized into covellite (ii) Moderate oxidation stage; moderately oxidized ore containing chalcocite, covellite, and copper oxides, and native copper (iii) Intensive oxidation stage; intensely oxidized ore containing chrisocolla, azurite, malachite and goethite.

Chemical thermodynamics invoked geochemistry as an unavoidable tool in quantitative interpretation of complex natural systems. Among various thermodynamic stability field diagrams the Eh-pH ones have been found most convenient for describing mineral-solution equilibria in near-surface environments. Their

accuracy greatly depends on the consistency of standard free energy data. There is no easy guide to estimate their validity. Their estimation goes far back in the middle of the past century. Some useful criteria to choose reliable ones is the frequency of their use, and persistently similar values coming from different sources. The Eh-pH diagram, constructed for use in this research, is a rectification of the earlier ones (Garrels, 1954; Garrels & Christ, 1965; Sikka *et al.*, 1991, Sato, 1992) (Fig. 1.). The oral presentation brings a thermodynamically up-to-date Eh-pH diagram of copper species in the system Cu-S-C-H₂O.

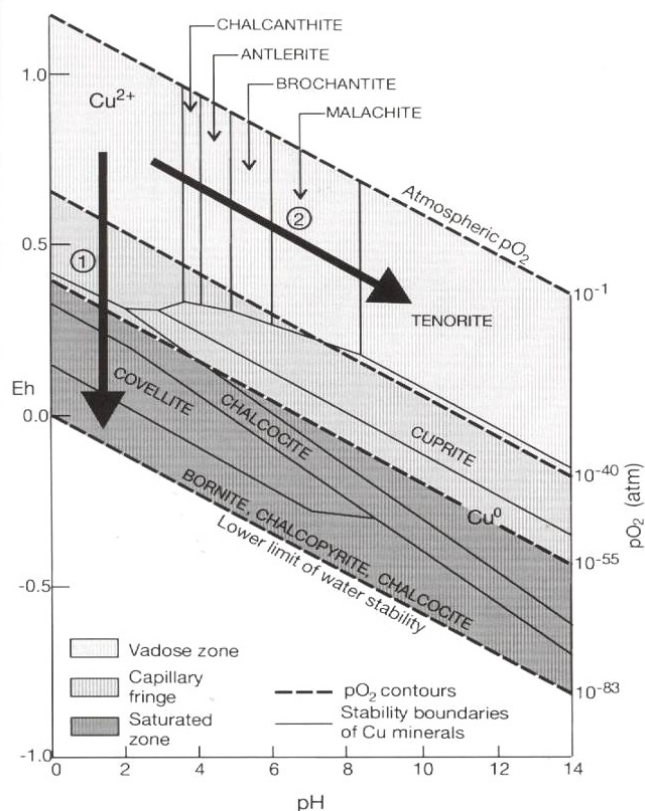


Fig. 1.: Eh-pH diagram for supergene copper mineral species in the weathering environment (Garrels, 1954; Garrels & Christ, 1965; Sikka *et al.*, 1991, Sato, 1992).

Garrels, R. M. (1954): *Geochim et Cosmochim Acta*, 5: 153-168

Garrels, R. M., Christ C. M. (1965): *Solutions, minerals and equilibria*, Harpers Geosci Ser, New York: pp. 450.

Sikka, D. B., Petruk, W., Nehru, C. E., Zhang, Z. (1991): *Ore Geol Rev*, 6: 257-290

Sato, M. (1992): *Geochim Cosmochim Acta*, 56/8: 3133-3156.

Sillitoe, R. H. (2005): *Econ Geol 100th Ann Vol*, 723-768