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Mineralogical and chemical evolution of ochreous precipitates formed during Acid Mine Drainage processes at the Roşia Montană gold mine (Romania)

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The Roşia Montană gold mine (Apuseni Mountains, Romania) is characterized by active and intense Acid Mine Drainage (AMD) processes that cause the widespread circulation of Acid Sulphate Waters (ASW; pH $\leq$ 3), containing very high levels of Potentially Toxic Elements (PTE) deriving not only by the sulphide mineralizations but also from host rocks and gangue minerals (such as Zn, Cr, Cu, Ni, As, and Pb) [1].
The studied area is located within the Roşia Montană mining site, which is a hydrothermal gold deposit hosted in andesites and dacites of Neogene age, piercing the prevolcanic sedimentary basement [2]. In this study a mineralogical and geochemical characterization of the ochreous precipitates and associated waters forming within the Roşia river was carried out in order to evaluate the mineralogical variations starting from the lowest adit of the "Sf. Cruci din Orlea" gallery up to the confluence between Roşia and Abrud rivers; the partitioning of PTE between contaminated waters and secondary minerals was also investigated. The mineralogy of the precipitates was determined by means of XRPD, whereas the bulk chemistry by ICP-MS. Some selected samples, representative of the main mineralogical assemblages, were further analyzed by means of trasmission electron microscopy (TEM) and microanalysis (EDX). Temperature, pH and Eh were measured in situ, whereas the chemical analysis on mine waters were made by means of ICP-OES, AAS and chromatography.
Ochreous precipitates are characterized by high concentrations of PTE (in particular V, Zn, Cd, As, Pb) and consist of a mixture, in variable proportion, of K-jarosite and schwertmannite, which represent the stable secondary minerals along the investigated transect of Roşia river. Moreover a positive correlation between Fe and S with As, V and Pb suggests an effective control of schwertmannite and jarosite on the mobility of specific PTE. Waters flowing from "Sf. Cruci din Orlea" gallery (ASW) are characterized by the lowest pH values (2.7-3.1) and the highest Eh (460-484 mV), SO4 (688-4800 mg/L) and PTE contents (Zn, Cr, Cu, Ni, Co, Cd). A remarkably different hydrochemistry is evident at the confluence between Roşia and Abrud rivers, being characterized by a significant increase in pH (6.3-7), decrease in Eh ($\approx$ 300 mV), and a general reduction of dissolved SO4 and metal load.
The results indicate that the role of secondary minerals as "mitigating agents" can be limited because even minor pH-Eh oscillations would cause mineralogical transformations, via dissolution-reprecipitation or solid-state transformation that could lead to trace elements mobilization in the environment. Positive correlation with more stable minerals could suggest a permanent storage within the solid phases.

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