

Isotope Geochemistry of Native Sulfur, a Tracer of Microbial Activity in Secondary Ore Deposits

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The Las Cruces mine (Iberian Pyrite Belt) is a VMS deposit with an unusual secondary zone, displaying high Cu grades in the cementation blanket but with a gossan that has been reduced to uncommon mineral assemblages (Conde et al., 2007). This singularity is related with the flourishing of deep microbial communities from the Messinian (Tornos et al., 2017), when the former gossan was transformed into siderite- and sulfide-rich assemblages.

Microbial activity at Las Cruces has been traced via microbiological techniques (Tornos et al., 2019) and biomarkers (Rey-Samper et al., 2022). In this late study, we detected elemental sulfur related to organic remnants. Native sulfur is an unusual mineral in these systems but potentially can be formed by microbial sulfate reduction. Elemental sulphur was extracted from 160 g of grinded sample for 12 hours using a Soxhlet extraction apparatus with a mixture of dichloromethane and methanol (8:1 ratio). Samples were then concentrated by evaporation until elemental sulphur crystallized, which was recovered and analysed by means of MC-ICPMS.

$\delta^{34}\text{S}_{\text{sulfur}}$ (CDT) is close to +12.2‰ (CDT). This result could be interpreted in two different ways: 1) the elemental sulphur was deposited as a by-product of the reduction of aqueous sulfate in underground water when reaching the gossan— $\delta^{34}\text{S}$ of aquifer water range between -8.9 to +20.4 ‰ (Scheiber et al. 2015)—or 2) the elemental sulfur is a consequence of the microbial reduction of the gossan—reduced rocks have $\delta^{34}\text{S}$ values of +12.3 to +22.9‰ (Tornos et al., 2017). Either way, the microbial-driven sulfate reduction could explain the formation and preservation of elemental sulfur in the modified gossan. This study shows that the presence of elemental sulfur in secondary assemblages can track the presence of microbial processes that are otherwise undetectable.

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