

Cu isotope geochemistry in the unusual Las Cruces supergene copper deposit

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The Las Cruces deposit (17 Mt @ 6.7% Cu) is the last on-going mine of the Iberian Pyrite Belt (IPB). The ore deposit consists of an unusual supergene copper enrichment zone of a common late Devonian VMS. This is located below the Guadalquivir river Basin, which hosts an aquifer on its base that is still interacting with the deposit nowadays. Late Alpine faults crosscut the deposit and act as fluid pathways related to the latest enrichment process; thus, three Cu-sulphides generations are identified: granular non-cemented Cu-sulphides formed during the weathering process, chalcocite related to late calcite-quartz veins, and euhedral chalcocite crystals grown over calcite veins. Textures and isotope geochemistry suggest a critical influence of microbial activity during the enrichment processes.

The primary sulphides show enrichment on $\delta^{65}\text{Cu}$ ($1.96 \pm 0.70\text{‰}$) in comparison to other primary sulphides worldwide [1]. The secondary Cu-sulphides are largely depleted on $\delta^{65}\text{Cu}$ and they show consecutively steeply enrichment on $\delta^{65}\text{Cu}$ in the three Cu-sulphides mineralization generations: $\delta^{65}\text{Cu} = -6.39 \pm 0.10\text{‰}$ in granular non-cemented Cu-sulphides, $\delta^{65}\text{Cu} = -5.36 \pm 0.19\text{‰}$, in chalcocite related to late calcite-quartz veins and $\delta^{65}\text{Cu} = -3.77 \pm 0.17\text{‰}$ in euhedral chalcocite crystals. These would show the three steps of the evolution of a mineralizing fluid, which is also enhanced by biogenic activity [2]. Finally, the gossan samples show a very large variation in $\delta^{65}\text{Cu}$, including both positive and negative values ($\delta^{65}\text{Cu} = -7.79\text{‰}$ & 3.84‰).

The $\delta^{65}\text{Cu}$ composition of the Las Cruces ore deposit present unusual values in comparison with studies developed on other VMS and gossan related.

[1] Larson *et al.* (2003) *Chem. Geol.* **201**, 337–350.

[2] Mathur *et al.* (2005) *Geochim. Cosmochim. Acta* **69**, 5233–5246.

The nanoscale structure of complex perovskite-type oxides with superb dielectric properties

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The perovskite (ABO_3) structure type is an outstanding example of how chemical variations can tune the nanoscale atomic arrangements and thus influence the properties of complex oxide materials. Thanks to V. M. Goldschmidt who formulated the relation between the chemical composition and the structural stability, the perovskite-type crystals are nowadays key functional materials used in a number of technological applications. Pb-based relaxors are advanced ferroelectrics with remarkable dielectric, electromechanical and electrooptic responses. The exceptional properties of relaxors are due to their structural inhomogeneities. At ambient conditions, the average structure is pseudocubic but rich in ferroic nanoregions too small to be directly studied by conventional diffraction analysis. However, combining *in situ* temperature and pressure diffraction and Raman scattering allows us to resolve the structural complexity of relaxors. Due to the different length and time scales of sensitivity, diffraction probes the long-range order, i.e. the structure averaged over time and space, while Raman spectroscopy can detect local structural deviations from the average structure via the anomalous Raman activity of the phonon modes that, when the symmetry of the average structure is considered, should not generate Raman peaks. Hence, the combined analysis of the long-range order induced at low temperatures or high pressures and of the phonon anomalies enhanced on temperature decrease or pressure increase can reveal the energetically preferred structural nanoclusters existing at ambient conditions. The structural analysis of series of model compounds, namely stoichiometric and A-site doped (Ba^{2+} , Bi^{3+} , La^{3+} , Sr^{2+}) $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ and $\text{PbSc}_{0.5}\text{Na}_{0.5}\text{O}_3$ as well as solid solutions with three cationic types on the B-site showed that at ambient conditions, on the mesoscopic scale, polar order coexists with antiferrodistortive order, which may be the key reason for the relaxor behaviour. Chemically-induced local elastic fields influence the nanoscale atomic clustering more strongly than chemically-induced local electric fields do.