

Iodargyrite (AgI) in supergene zones of argentiferous Cu deposits in the Atacama Desert, Chile: Involvement of I-rich waters?

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We document the occurrence of inclusions of a (Ag,I)-rich mineral in supergene chalcocite from the Mantos de la Luna argentiferous stratabound Cu deposit in the Coastal Range of northern Chile. In this deposit, located 30 km south of Tocopilla, Cu mineralization occurs preferentially in the lower levels of amygdaloidal and porphyritic horizons. Mineral paragenesis is simple and composed exclusively of Ag-bearing supergene chalcocite (digenite), atacamite, and chrysocolla.

EMPA observations reveal the presence of discrete, micron-sized (1-10 μm) inclusions of a Ag iodide mineral in supergene chalcocite. The inclusions were identified as iodargyrite by means of EDS and WDS elemental mapping. The Ag concentrations in the inclusions vary from 1.0-67.6 wt% and they are contaminated by Cu and S from chalcocite. The small size and the beam-sensitivity of the Ag-I inclusions precluded the precise description of its chemical formula. However, the Ag and I elemental maps strongly correlate with the inclusions, whereas the WDS maps of Cu and S correlate well with the chalcocite sulfide host.

The occurrence of iodargyrite inclusions in supergene chalcocite suggests the involvement of iodine-rich waters during supergene enrichment at the Mantos de la Luna Cu deposit. Considering the fact that the occurrence of iodargyrite is restricted to extremely arid environments [1], our observations strongly suggest the prevalence of hyperarid conditions during the latest stages of supergene enrichment of the Mantos de la Luna argentiferous Cu deposit in northern Chile. This suggests that supergene enrichment processes of Cu deposits in the hyperarid Atacama Desert are dynamic in nature and do not exclusively require the presence of meteoric water. Further studies are needed not only to address the isotopic signature (and age) of iodine-rich waters involved in supergene enrichment of these deposits (e.g. deep formation waters), but also to constrain the origin of iodine in the extensive nitrate deposits occurring in the eastern flank of the Coastal Range.

[1] Boyle (1997) *Can. Mineral.* **35**, 23-34.

Vacuum extraction of volatile organic compounds from water for compound-specific stable carbon isotope analysis at the sub- $\mu\text{g/L}$ level

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A new method (VacEx) for the vacuum extraction of volatile organic compounds (VOCs) from water samples was developed. Following protocols for noble gas analysis (1) allowed determination of carbon isotopic compositions of VOCs, increasing the sensitivity of compound-specific stable carbon isotope analysis (carbon-CSIA) to the sub-microgram per liter level. VacEx was developed to extract and pre-concentrate VOCs for later carbon-CSIA by the standard extraction technique purge-and-trap (2). The $\delta^{13}\text{C}$ signatures determined by using the new VacEx-P&T-mass spectrometry (MS) and the standard P&T-MS were in good agreement (<1‰). Limits of detection for carbon-CSIA are now for *trans*-DCE and *cis*-DCE 0.21 $\mu\text{g/L}$, for TCE 0.24 $\mu\text{g/L}$, for MTBE 0.02 $\mu\text{g/L}$, for benzene 0.15 $\mu\text{g/L}$, for toluene 0.03 $\mu\text{g/L}$, for ethylbenzene and m-p-xylene 0.06 $\mu\text{g/L}$ and for o-xylene 0.03 $\mu\text{g/L}$.

Using noble gas analytical protocols in water allowed, for the first time, to determine VOCs isotopic compositions at the very low typical concentrations in natural waters. This analytical development brings carbon-CSIA closer to field applications in assessing *in situ* VOCs transformation.

[1] Beyerle *et al.* (2000) *Environ. Sci. Technol.* **34**, 2042-2050.

[2] Zwank *et al.* (2003) *Anal. Chem.* **75**, 5575-5583.