

## High Cd concentrations in Bajocian carbonates in the Swiss Jura Mountains: Evidences for hydrothermal input

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Anomalous high Cd concentrations (up to 16 mg/kg) in certain soils of the Swiss and French Jura Mts. are related to underlying Cd-enriched (up to 21.4 ppm) carbonate rocks of Middle-Late Jurassic age. The aim of this study is to understand the processes controlling Cd incorporation into carbonate rocks of Bajocian age and to develop a predictive tool to identify potentially contaminated top soils of Cd-enriched carbonate rocks. The geochemical approach includes thin-section microscopy, ICP-MS, ion microprobing, sulphur isotope analysis, and Rb-Sr/Pb-Pb isotopic dating and tracing.

Cd distribution in the carbonate rocks is heterogeneous, ranging from 0.03 to 12 ppm within few centimeters. Cd does not correlate with other trace elements, excepting Zn. High Cd concentrations in carbonate rocks are commonly related to the presence of subordinate, Cd-rich (up to 2%) sphalerite mineralization.  $\delta^{34}\text{S}$  values of sphalerites ( $-22.3$  to  $-5.3\text{‰}$ ) suggest that intraformational bacterial sulfate reduction was the main source of reduced sulfur, with S-contributions from the degradation of diagenetic Fe sulfides and organo-S-compounds. Sphalerite Pb isotope signatures are uniform, indicating isotopically well-homogenized fluid systems. Comparative isotope patterns may point to extraformational lead sources located in the crystalline basement. Rb-Sr dating of sphalerites indicates a Middle-Late Jurassic, post-Bajocian mineralization event at c. 162 Ma.

We argue that sphalerite mineralization and Cd enrichment in the Bajocian carbonate rocks reflects multistage tectonic and hydrothermal periods in the region related to the opening of the Atlantic and Alpine Tethys oceans, which led to the reactivation of Variscan basement faults. Tertiary (Oligocene) tectonic activity related to the opening of the Rhine graben may have triggered some remobilisation of sulfides and redistribution of Cd.

## Fractionation of Cl isotopes during precipitation of NaCl from a nearly pure NaCl brine

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The natural spring 'Fonte da Pipa' in Rio Maior (Central Portugal) is unique as it contains about 137 grams of dissolved NaCl per litre and this salt is extracted and marketed as table salt by a local Cooperative. The salt content from this spring probably originates from dissolving salt from a shallow diapir in this area. Water extracted from the spring is pre-concentrated in large basins until it contains about 250 grams NaCl per litre. It is then transferred to shallow concrete basins and left until all water is evaporated. This latter procedure takes place at air temperatures above 25 °C and requires about one week to complete. In a first approach to study the saline spring we sampled water from the spring and several evaporation basins to study the Cl isotope compositions of the brine and the precipitated NaCl. As the springwater is a nearly pure (98%) NaCl brine we expected it to have a large (potential) Cl isotope variation. This is unlike fractionation of Cl isotopes precipitating from seawater. As the Cl isotope fractionation factor for NaCl is much larger than for KCl and MgCl<sub>2</sub>, in seawater a minimum  $\delta^{37}\text{Cl}$  of about  $-0.5\text{‰}$  is expected [1]. Indeed we found values regularly decreasing from  $-0.2\text{‰}$  for the saline spring to as low as  $-1.1\text{‰}$  in the most evaporated brine. The NaCl precipitate in all cases had more positive  $\delta^{37}\text{Cl}$  values compared to the co-existing brine, and decreased from  $0.0\text{‰}$  in the first precipitate to  $-0.5\text{‰}$  in the last stage.

We believe it is important that this unique saline spring and its hydrological environment be studied in detail as the spring is located in an area heavily used for agricultural purposes. The extraction of freshwater from wells as close as 100 meters from the saline spring implies that a sharp boundary exists between the saline and fresh groundwater; pumping of freshwater for agricultural purposes may therefore disturb the equilibrium between these two water systems and cause an unwanted rise in salinity of this valuable freshwater resource.

[1] Eggenkamp, Kreulen & Koster van Groos (1995) *Geochimica et Cosmochimica Acta* **59**, 5169–5175.