

Mercury stable isotope variations in a Bolivian watershed: Evidence for mass-independent fractionation

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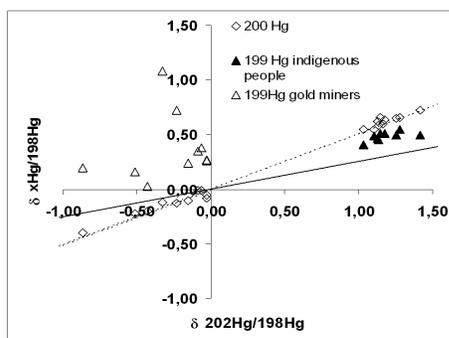
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Mercury contamination is an environmental problem of increasing concern in the Amazon basin. In Bolivia, indigenous people have elevated methylmercury hair concentrations. This highly toxic molecule originates in the release of inorganic Hg from chemical and physical weathering and from human activities. The aim of our study is to trace the sources and the processes involved in the cycle of Hg, in the Beni River watershed, through variations in Hg isotopic compositions. Three types of samples are studied: sediments, liquid Hg⁰ from gold mining and hair from gold miner and indigenous populations. Hg isotopic compositions were analyzed on a Thermo-Finnigan *Neptune* MC-ICP-MS at Trent Univ. and at the LMTG after sample digestion by *aqua regia* at 120°C (Foucher and Hintelmann, 2006).

The $\delta^{202/198}\text{Hg}$ values (relative to NIST 3133) are significantly different with respect to the external precision of 0.05-0.2 ‰ (2σ): -0.34 ± 0.02 ‰ for liquid mercury, -1.05 ± 0.14 ‰ for sediments, -0.44 ± 0.20 ‰ for miner hair (n=9), $+1.18 \pm 0.10$ ‰ for indigenous people hair (n=12). Mass-independent isotope fractionation was observed for odd isotope ratios in all hair samples (Figure 1): $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ anomalies of up to 1.16 and 0.98 ‰ respectively were observed, and were more pronounced for miners than indigenous communities. Preliminary data on fresh and oxidized black shale samples show up to 2 ‰ variation.

Figure 1: Mass-independent fractionation observed for $\delta^{199/198}\text{Hg}$ for gold-miner and indigenous people hair samples. Lines represent mass dependent fractionation.



Reference

Foucher D. and Hintelmann H. (2006), *ABC*. **384** 1470-1478

First steps in the feasibility study of CO₂ geological storages monitoring through noble gas geochemistry

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Since noble gases are relatively inert, and for some of them lighter than CO₂, they migrate faster. Thus they are potential precursors to survey the integrity of CO₂ storages. By monitoring the surrounding aquifers, it could be possible to detect these precursors (e.g.: Helium (He) or Argon from spikes or air-pollution), and then to properly survey the trapping efficiency of a storage. In order to study the noble gases dissolved in brines, we have developed a new fully automated line, linked to a quadrupole mass spectrometer QMS200 by *Balzers*. We extract our water samples in gas phase, trap the water vapor on cold traps, and then purify the residual gas phase to analyze noble gases with our QMS. Gas aliquots can be sampled in order to analyze isotopic ratios using our glass-made mass spectrometers Aresibo.

As preliminary step, we chose to validate our new line with a simple analogue of CO₂ storages: the Pavin lake, in the French Massif Central. Pavin lake is a crater lake (max. depth 90 m), aged of about 6 000 years and resulting from a magmato-phreatic eruption. The water column of this lake is stratified in two major layers, isolating the lower one which accumulates biogenic or magmatic gases like CO₂ or He.

We collected water samples in mechanically sealed copper tubes, and analyzed them using our system. Our results enable to plot dissolved ⁴He concentration profiles. Whereas the upper layer presents ⁴He concentrations around 7.81e⁻⁸ cm³STP/g of water at -40 m, the lower layer presents higher ⁴He concentrations with 5.64e⁻⁶ cm³STP/g at -80 m.

We focused our study on the water layer with the highest ⁴He concentration gradient (between -60 m to -70 m) to compare our results with those obtained by Aeschbach-Hertig *et al.* (1999). Our results between 2.49e⁻⁷ cm³STP/g at -60 m and 1.77e⁻⁶ cm³STP/g at -70 m are in accordance with those published in 1999. Helium isotopic ratios are also similar to the value obtained by Aeschbach-Hertig *et al.* (1999), i.e. the subcontinental mantle ratio (6.5 Ra).

The accordance of our results with those published by Aeschbach-Hertig *et al.* (1999) validates our new extracting-purifying-analyzing line and completes the preliminary step of our work. Our aim is now to test on a CO₂ natural accumulation in France, the feasibility of the monitoring methodology we suggest.

Reference

Aeschbach-Hertig *et al.* (1999), *Geochim. Cosmochim. Acta* **63**, 3357-3372.