

Hg stable isotopes in human hair as a tracer for dietary Hg exposure

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Since mercury (Hg) and methylmercury (MMHg) toxicity for humans is known, scientists try to evaluate its impacts on health. Dietary MMHg exposure, *via* food consumption of marine and freshwater fish, can be evaluated by hair Hg analysis. However, populations exposed to elevated atmospheric Hg⁰ levels, such as goldminers, may have important respiratory Hg uptake. In addition inorganic Hg⁰ can also be adsorbed at the hair surface. In this study, we use speciation analysis to evaluate inorganic Hg and MMHg concentrations in hair and isotopic analysis of Hg to trace sources of MMHg. Different people from the Beni River basin in Bolivia were studied: native gold-miners, alluvial gold-miners and indigenous people. Native gold-miners do not eat fish while alluvial gold-miners and indigenous people do. For comparison, hair of European colleagues with a dominant marine fish MMHg exposure were also analyzed.

Hg speciation analysis, by species-specific isotope dilution GC-ICPMS show that the percentage of MMHg in human hair varies between 60 and 90% in native people and Europeans and between 10 and 93% in gold-miners. These results show presence of inorganic Hg adsorbed on hair surface. Variations in total Hg stable isotopic composition measured by cold-vapor MC-ICPMS reveal large variations in $\delta^{202}\text{Hg}$ (relative to NIST 3133) and $\Delta^{201}\text{Hg}$ respectively between -0.87‰ and $+0.19\text{‰}$ and $+0.04\text{‰}$ and $+0.99\text{‰}$ for gold-miners hair. Native people hair have homogenous isotopic signatures; $\delta^{202}\text{Hg}=+1.18\pm 0.24\text{‰}$ (2SD, n=10) and $\Delta^{201}\text{Hg}=+0.25\text{‰}$ close to average $\Delta^{201}\text{Hg}$ of the Beni basin fish. Europeans hair present $\delta^{202}\text{Hg}$ between $+1.87\text{‰}$ and $+2.59\text{‰}$ and $\Delta^{201}\text{Hg}$ between $+0.55\text{‰}$ and $+1.02\text{‰}$ which is close to published marine fish $\delta^{202}\text{Hg}$ and $\Delta^{201}\text{Hg}$. Previously we showed that absorption of MMHg *via* fish consumption is followed by metabolic MDF of $+2\text{‰}$ of $\delta^{202}\text{Hg}$ for hair [1].

Three types of Hg exposure for gold-miners can be deduced from combined MDF/MIF signatures: Hg adsorbed on hair surface from vapor Hg (0), MMHg from local Beni basin fish consumption and MMHg from imported marine fish. Combined Hg isotopic and speciation analysis emerges as a powerful tool to trace sources of human Hg exposition.

[1] Laffont, L. *et al.* (2009) Environmental Science & Technology **43**, 8985–8990.

Influence of CO₂ on New Albany Shale composition and pore structure

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To determine the possible influence of CO₂ on the pore structure and mineralogy of the New Albany Shale (Devonian-Mississippian), experiments were conducted utilizing Indiana shale samples of varying total organic carbon content under various conditions. After the shale samples were heated as high as 150°C in Teflon-lined high-pressure reaction cells with either distilled water or NaCl brine and CO₂, the reaction products were characterized by mesopore and micropore analysis, X-ray diffraction and scanning electron microscope analysis of the shale residue, and fluid chemistry analysis of the reactant brine. Results from CO₂-saturated shale and distilled water showed no changes in shale pore structure relative to shale samples without CO₂ surface saturation. A second series of experiments was run at 80°C, using 50,000 ppm NaCl brine, 60-mesh ground shale (2:1 by mass), and varying amounts of solid CO₂ (dry ice). The pressure in the reaction cells was controlled by the partial pressure of CO₂ and ranged from 100 to 3500 psi (0.69 to 24.13 MPa). Post-reaction brine samples showed up to thousands of ppm of K, Mg, and Ca in solution. The concentration of Ca and Mg in the brine tended to increase in proportion to the increasing partial pressure of CO₂. The same experiments using chips of shale from the New Albany Shale showed lower concentrations of the cations in solution, but displayed a similar pattern of elevated increasing Ca and Mg with increasing CO₂ pressure. Scanning electron microscope examination of the shale chips confirmed the dissolution of carbonate-mineralized biogenic structures in the shale.