

Mercury bioaccumulation in coastal and migratory foodwebs in the Gulf of Mexico

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We combined N, C, and Hg stable isotope approaches to i) identify the factors that most strongly predict MeHg accumulation in northern Gulf of Mexico (nGOM) fish; and ii) determine if coastal species residing in the Mississippi River plume (MRP) and migratory offshore species derive their MeHg from the same sources. MeHg concentrations in the coastal fish species (menhaden, anchovy, speckled trout, red drum, red snapper, grey snapper) ranged over two orders of magnitude and were weakly correlated ($r^2=0.44$) with $\delta^{15}\text{C}$ (-24.7 to -15.6). However, MeHg concentrations were well-explained by $\delta^{15}\text{N}$ ($r^2=0.84$), with minimal improvement in r^2 after adding $\delta^{13}\text{C}$ in a multivariate model ($r^2=0.85$), indicating that trophic position was the dominant driver of MeHg levels. Yellowfin and blackfin tuna caught offshore of the MRP span approximately two trophic positions and fall on a comparably good ($r^2=0.77$) but parallel MeHg vs. $\delta^{15}\text{N}$ line. The different baseline N values suggest largely disconnected food webs and, therefore, different MeHg sources. Hg stable isotope data provide further support for this assertion. The coastal fish had $\delta^{202}\text{Hg}$ values of 0 to -1.0‰ and $\Delta^{199}\text{Hg}$ values of ~0.5‰, whereas offshore migratory tunas had higher $\delta^{202}\text{Hg}$ values of 0.2 to 0.5‰ and $\Delta^{199}\text{Hg}$ values of ~1.5‰. Coastal fish $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values were consistent with our isotopic measurements of total Hg in marine sediments but require either a small degree of photochemical reduction of Hg^{2+} prior to methylation or photochemical demethylation of MeHg prior to uptake into the foodweb. The higher $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values for offshore fish are most easily explained by a MeHg source that has undergone substantial demethylation (>~50%) before entering the base of the foodweb. Thus, the Hg stable isotope results offer further confirmation of disconnected foodwebs, and support the idea that MeHg was either advected from coastal environments and demethylated before entering the foodweb, or that MeHg was sourced and methylated in the open ocean.

Role of sulfur in hydrothermal metal fractionation and the formation of porphyry-type ore deposits

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Sulfur plays essential roles in hydrothermal ore-forming processes [1], which calls for precise quantitative sulfur determination in fluid inclusions. Feasibility test for sulfur quantification by comparing data from both LA- Quadrupole (Q) -ICP-MS and LA- High Resolution (HR) -ICP-MS show that reliable sulfur quantifications in the fluid inclusions is possible [2], provided that a very careful baseline definition is applied.

We measured sulfur together with copper and other ore metals in the cogenetic brine and vapor inclusions (“boiling assemblages”) hosted by quartz in various types of ore deposits, to check the metal transporting capabilities of sulfur in the two fluids. Clear compositional correlations of sulfur with copper and gold (correlational vapor partitioning behaviors along with S relative to Na and other chloride-complexed cations), with a molar S/Cu ratio commonly close to 2, indicates sulfur-complexed metal transportation in the high-temperature hydrothermal vapor, and probably in some of the brines as well. Vapor inclusion in the boiling assemblages from magmatic-hydrothermal ore deposits and granitic intrusions generally show an excess of sulfur over ore metals. This allows efficient sulfide ore precipitation in high-temperature porphyry-type deposits, and complexation of gold by the remaining sulfide down to lower temperatures.

The results demonstrating that S, Cu and Au are highly enriched in vapor-like magmatic fluids implies that such low-salinity fluids are the key agent for the formation of rich porphyry copper and epithermal gold deposits [3].

[1] Heinrich *et al.* (1999) *Geology*. [2] Guillong *et al.* (2008) *J. Anal. At. Spectrom.* [3] Seo *et al.* (2009) *Earth Planet. Sci. Lett.* in review.