

Hg(II) adsorption and speciation on bacterial surfaces

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Complexation of Hg with cysteine residues in dissolved organic matter (DOM) is widely believed to control the bioavailability of Hg in aquatic systems, affecting the rate and extent of Hg-methylation. Despite indirect evidence for the binding of Hg to biomass, Hg-biomass interaction remains a largely overlooked aspect. In light of recent studies elucidating the binding of chalcophilic metal cations (Cd and Zn) with sulfhydryl functional groups on biomass, we investigated the interaction of Hg (II) with bacterial cell surfaces.

Our results show Hg (II) reacts with bacterial surface and forms stable complexes which change dramatically at very low Hg:biomass ratios. At environmentally relevant Hg:biomass ratios, a very strong and stable complex Hg (cysteine)₃ is formed on bacterial surface, perhaps as a pathway to reduce toxicity in the vicinity of the cell. At higher yet relevant Hg concentrations, Hg-(cysteine)₃ complexes formed on bacterial cell walls are less stable and smaller in size. These surface bound Hg complexes likely control the rate and extent of the transfer of Hg (II) into the cell cytoplasm of methylating bacteria for Hg-methylation. These results have strong implications on our longstanding view of the role of DOM in controlling Hg-methylation in natural and contaminated systems.

For non-methylators, surface bound Hg (II) could either stay as Hg-cysteine complexes until cysteine is oxidized and released back into aqueous phase or it would convert into inorganic Hg-sulfide nanoparticles with time. Implications of these results on methylation, speciation, mobility, and bioavailability of Hg will be discussed.

Seawater Lithium isotope evolution during the Cenozoic

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We present the first high-resolution long term Cenozoic (65 Ma) ⁷Li/⁶Li record of seawater as measured in triple-cleaned planktonic forams. Seawater $\delta^7\text{Li}_{\text{SW}}$ (~31.0‰) reflects a balance between input sources [chemical weathering of the silicate continents ($\delta^7\text{Li}_{\text{Riv}}$ ~23‰) and hydrothermal weathering of seafloor silicate basalts ($\delta^7\text{Li}_{\text{HT}}$ ~5.6‰)], and removal by reverse weathering into authigenic clays in sediments plus low-temperature seafloor basalt weathering ($\delta^7\text{Li}_{\text{SED}}$ ~15‰). $\delta^7\text{Li}$ fractionation on removal from seawater ($\Delta_{\text{SW-SED}}$ ~16‰) drives seawater isotopically heavy. This $\delta^7\text{Li}_{\text{SW}}$ preserved in marine planktonic foraminifera provides a unique time tracer of changes in the global silica cycle [1.2].

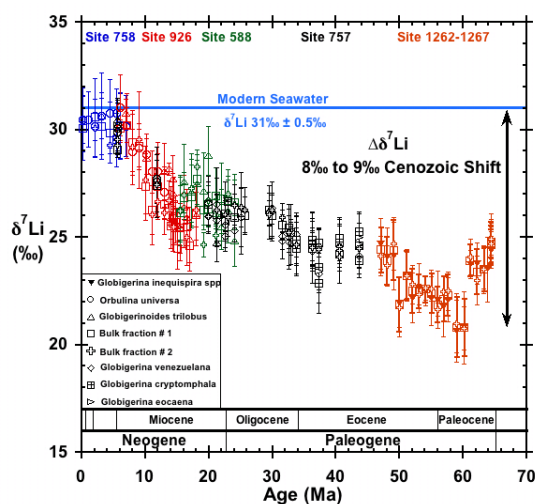


Figure 1: $\delta^7\text{Li}$ of Cenozoic Seawater.

$\delta^7\text{Li}_{\text{SW}}$ shows an enormous 8-9‰ rise from 60Ma (22‰) to present (30.5‰). This requires massive increases in either silicate weathering fluxes ($F_{\text{RIV}} +350\%$) and weathering intensity ($\delta^7\text{Li}_{\text{RIV}} +18\%$), dramatic changes in the Li silicate reverse weathering sink ($\Delta_{\text{SINK}} +8\%$), or both, suggesting an increase in both $[\text{Li}]_{\text{ocean}}$ and τ_{Li} during the Cenozoic.

[1] Hathorne & James (2006) *EPSL*. **246**, 393–406. [2] Misra & Froelich (2009) *JAAS*. **24**, 1524–1533.