Microbial methylation of mercury sulfides: Comparison between dissolved Hg-sulfides, nanoparticulate and bulk scale HgS

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Mercury (Hg) contamination in soils and sediments poses a hazard if converted to methylmercury (MeHg), the more toxic and bioaccumulative form of the metal. Methylation of mercury in the environment occurs primarily by anaerobic microorganisms such as sulfate-reducing bacteria. MeHg production rates generally depend on the growth of these anaerobic organisms and also on the amount of inorganic Hg that is available for uptake into these bacteria. The objective of our research was to identify the chemical forms of Hg that are bioavailable to methylating bacteria, and thus, susceptible to methylation in sediments. Our overall goal was to develop a new model that links the chemistry of Hg to methylation potential, a model that considers the kinetics of HgS precipitation in anaerobic porewater of sediments. We hypothesized that bioavailable Hg concentration is related to the kinetics of Hg-sulfide precipitation, and not necessarily to equilibrium speciation of Hg in sulfidic porewater. Nanoparticles of HgS (size less than ~10 nm) are the first formation products during metacinnabar formation, and were expected to be more bioavailable than larger, more crystalline (and less soluble) metacinnabar particles. We performed methylation experiments with a pure culture of *Desulfobulbus propionicus*, a sulfate-reducing bacterium known to take up and methylate Hg. The bacteria cultures were exposed to three different forms of Hg-sulfides (dissolved Hg-bisulfide complexes, nanoparticulate HgS, and bulk scale metacinnabar), formulated to represent three different 'aging' states of mercury in sulfidic sediments. Our results indicate that methylation rate (normalized to cell density) was greatest with the dissolved Hg-sulfide treatment. In the treatments with HgS nanoparticles, mercury methylation was observed at a rate that, while slower than the dissolved Hg-sulfide treatment, was faster than the bulk scale metacinnabar treatment. These results suggest that a fraction of inorganic mercury associated with HgS nanoparticles is bioavailable to methylating bacteria, possibly due to higher solubility and specific surface area of nanoparticles over micro-scale particles. Future work will investigate how nanoparticles deliver mercury to bacteria cells and assess metal uptake rates as a function of particle solubility and surface area.

Potentially habitable ancient environments in Gusev crater, Mars

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Habitable environments must sustain liquid water at least intermittently and also provide both chemical building blocks and useful sources of energy for life. Observations by Spirit rover indicate that conditions have probably been too dry to sustain life, at least since the emplacement of the extensive basalts that underlie the plains around the Columbia Memorial Station landing site. Local evidence of relatively minor aqueous alteration [1] probably occurred under conditions where the activity of water was too low to sustain biological processes as we know them.

In contrast, multiple bedrock units in West Spur and Husband Hill in the Columbia Hills have been extensively altered. Patterns of elemental abundances are consistent with aqueous processes involving migrating fluids [2]. Fe in several of these units has been extensively oxidized [3]. Conceivably any microbiota present during the aqueous alteration of these rocks might have obtained energy from Fe oxidation. Spirit discovered olivine-rich ultramafic rocks during her descent from Husband Hill southward into Inner Basin. Alteration of similar ultramafic rocks on Earth can yield H_2 that can provide both energy and reducing power for microorganisms.

Spirit's discovery of deposits rich in ferric sulfate is consistent with the aqueous dissolution and/or alteration of olivine under acidic conditions [2] such as those associated with hydrothermal activity. The oxidation of iron and sulfur that can accompany such activity can be an energy source for life. Hydrothermal systems on Earth that sustain either acidic [4] or neutral to alkaline fluids [5] have been shown to provide this energy. Collectively the observations by Spirit rover are consistent with the possibility that habitable environments existed in Gusev crater at least intermittently in the distant geologic past.

[1] Haskin *et al*. (2005) *Nature* **436**, 66–69. [2] Ming *et al*. (2008) *JGR* **113**, E12S39, doi:10.1029/2008JE003195. [3] Morris *et al*. (2008) *JGR* **113**, E12S42, doi:10.1029/2008JE003201. [4] Innskeep & McDermott (2005) In *Geothermal Biology & Geochemistry in Yellowstone*, N. P. Montana State Univ., pp.143–162. [5] Shock *et al*. (2005) In *ibid*., 96–109.