Volatilization of Hg from HgS minerals mediated by the coupled activity of thiosulfate and a sulfur-oxidizing bacterium

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Soils and sediments, where mercury (Hg) can exist as the Hg sulfide mineral metacinnabar (β-HgS), represent major Hg reservoirs in aquatic environments. Due to its low solubility, metacinnabar has historically been considered an insignificant source of Hg to the aqueous environment. Our previous work has shown that bacterial colonization of metacinnabar incubated in the shallow sediments of the Hg-contaminated East Fork Poplar Creek (Oak Ridge, TN) is dominated by genera known to use reduced sulfur compounds as electron donors during growth. Based on 16S rRNA pyrosequencing, *Thiobacillus thioparus*, an obligate autotrophic neutrophilic sulfur oxidizer, is among the most abundant colonizers.

Here we show that *T. thioparus* incubated aerobically in the presence of metacinnabar and thiosulfate (0.1-20 mM) results in substantial metacinnabar dissolution and release of Hg. Upon reaction, sulfate concentrations are higher than can be attributed to oxidation of thiosulfate alone, yet aqueous Hg(II) concentrations remain below detection limit. We show that in the presence of live cultures of *T. thioparus* aqueous Hg(II) released following HgS dissolution is rapidly volatilized forming Hg(0). In control incubations (media with thiosulfate and metacinnabar, and no viable cells) thiosulfate concentrations correlate with levels of dissolved Hg(II), suggesting that thiosulfate, a strong Hg-binding ligand, abiotically induces HgS dissolution. *T. thioparus* posseses genes involved in the Mer detoxification pathway, and we are currently investigating *mer* expression in this system.

These findings have important implications for environmental Hg cycling, highlighting the unappreciated potential of Hg release from assumed permanent solid-phase Hg sinks. It further introduces new pathways for solid-phase Hg to enter the global atmospheric mercury pool.

Role of deep carbides in the formation of hydrocarbons?

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Whether hydrocarbons in rocks are inorganic or organic in origin might be evaluated by considering carbides as precursors in the formation of deep hydrocarbons and a range of volatile compounds, since carbide may constitute >2 wt% of the Earth's core [1].

Low pressure carbides can be (a) *Interstitial* (Ti, V, Cr, Zr, Nb, Hf, Ta, W) (b) *Covalent* (B, Si): (c) *Intermediate* (Ti, V, Cr, Mn, Fe, Co,Ni): or (d) *Salt-like* (Groups I, II, and III). In the absence of high-P experimental data, groups (a) (b) and (c) should be included as candidates for carbides found in the inner core, because they are stable at high-T; they also react with water and/or oxygen to form hydrocarbons and CO or CO_2 respectively. Carbides can be described as 'reactive minerals' [2] and react with water to yield hydrocarbons. Hydrocarbon pathways from CH_4 at high-P have started to be explored [3].

Siderophile element carbides (Cr, Fe, Ni, V, Mn, Co) hydrolise with water to yield "organic matter"[4]. We propose similar reactions based on carbides of Ca and Al for the formation of methane hydrate. The reactions are expected to be of the general type: M_xC_y +nH_2O where M is the metal = Hydrocarbons such as CH_4 +$M(OH)_2$. In the presence of oxygen such hydrocarbons would react to form CO and ultimately CO_2. Similar reactions could occur with nitrides, sulphides and silicides. These compounds are stable at high-T and would react with water and oxygen at lower temperatures.

Methane hydrates are common in continental shelf sediments and in deep arctic permafrost and occur at depths of around 500m [5]. Methane is found under lakes such as Lake Kivu [6]. It is generally assumed that such deposits are of biological origin. However, no explanation is given as to how complex molecules form organic deposits. Synthesis routes at high-T are well known, but we propose experiments to high-P conditions to test whether deep carbides [7] act as possible precursors in the abiotic synthesis of hydrocarbons and methane hydrates.

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