Isotopic analysis of sulfide captured on photographic film: Laboratory and field experiments

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Sulfide is formed in sediment pore waters or in the water column of stagnant water bodies by the action of anaerobic sulfate-reducing bacteria. Sampling of free sulfide in natural environments has typically been done using syringes (for water column) or cores (for pore water). Yet the resolution of these approaches is often too coarse to capture steep environmental (e.g., redox) or ecological gradients in microbially dominated sediments.

We seek a means to capture a continuous record of ambient sulfide for subsequent stable isotope ($\delta^{34}S$) analysis. Previous work highlighted the potential of sulfide capture on metallic silver disks [e.g., 1-3]. However, this is not suitable for frequent deployments, particularly covering areas greater than a few cm^2. Here we build upon previous work for capturing atmospheric sulfide [e.g., 4,5], via reaction with the silver compound embedded in photographic film to form silver sulfide, which can then be quantified. This technique has the potential to capture a continuous $\delta^{34}S$ record across a wide range of environments and has the advantages of being inexpensive, readily available, rapidly deployable, and can be used *en masse* for sampling [4]. Here we test the reliability of photographic film to accurately capture the $\delta^{34}S$ signature of aqueous sulfide in laboratory experiments as well as in a natural setting.

In laboratory experiments, strips of photographic film were immersed in dissolved sulfide solutions with pH spanning 7–11 in closed systems and in contact with the atmosphere. No isotopic offset was detected for films immersed in high pH solutions. However, at pH ~7 films were consistently depleted by 1–2‰ relative to fluids, which we attribute to fractionation between sulfide species within the solution.

The method was also tested at a field site. Mahoney Lake in British Columbia, Canada, has sulfide present in the water column below ~7 m depth. Photographic film was lowered into the water alongside syringes for sulfide collection and a comparison made between the isotopic composition of sulfide from the film and the syringes. As with the laboratory experiments, the film sulfide was depleted by 1–2‰ compared to the aqueous sulfide under circumneutral pH.

[1] Visscher *et al*. (2000) *Geology* **28**, 919-922. [2] Fike *et al*. (2008) ISME J. **2**, 749 – 759. [3] Fike *et al*. (2009) *GCA* **73**, 6187 – 6204. [4] Horwell *et al*. (2004) *J. Environ. Monit.* **6**, 630 – 635. [5] Horwell *et al*. (2005) *J. Volcanol. Geoth. Res.* **139**, 259 – 269.

Complexation of Neptunium(V) with *Bacillus subtilis* endospores and their exudates

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Biological media may affect the movement of neptunyl ions, a highly toxic and potentially mobile radionuclide, in the environment. Most previous investigations of neptunyl-microbial interactions have focused on interactions with vegetative bacterial cells. However, endospores are known to comprise up to ca. 50% of the total bacterial populations in some environments and reserachers have identified endospore counts in soils as high as ca. 10^5 CFU/g of soil. Despite endospores being important biological media in the environment, neptunyl-endospore interactions have been ignored. Thus, we investigated neptunyl ion interactions with *Bacillus subtilis* endospore surfaces and their exudates.

B. subtilis endospore exudates are dominated by dipicolinic acid, which is a ligand that strongly binds neptunyl ions. *B. subtilis* endospores contain a large reservoir of dipicolinic acid in their cortex that can be released during germination or changes in permeability of the endospore coat, the latter being the most likely form of release in this work. Spectrophotometric investigations of the chemical form of neptunyl ion in endospore exudate solutions were consistant with the formation of neptunyl-dipicolinate complexes. Due to the strength of the 1:1 neptunyl-dipicolinate complex, neptunyl speciation in these experimental systems was heavily influenced by exudate complexation and controlled the extent surface adsorption. Neptunyl ions weakly adsorbed onto the endospore surface and sorption decreased with increasing pH, which corresponds to increasing aqueous complexation by dipicolinate.

Using spectrophotometric measurements of neptunyl-dipicolinate complexes and neptunyl-endospore adsorption data, we determined thermodynamic stability constants for both species. With stability constants determined in this work, we compared controls on neptunyl partitioning in simulated systems with *B. subtilis* vegetative and sporulated cells, (at dipicolinc acid concentrations corresponding to the extent of sporulation), and generic natural organic matter. Neptunyl complexation by dipicolinic acid exerted the greatest biological control in the simulated systems. This work highlights the importance of considering radionuclide complexation by microbial exudates when trying to understand the fate and transport of radionuclides in the environment.