

Eu(III) interactions with calcium carbonate

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Understanding the interactions of radionuclides with mineral phases is important for the long-term storage safety of nuclear waste deposits which depends strongly on their interactions with the minerals. Calcite is a candidate mineral for use in nuclear waste repositories. Model studies involve nonradioactive trivalent lanthanides. In the present work Eu(III) interactions with calcite were investigated using two crystallization techniques which could yield complementary information. Counter-diffusion of (Ca^{2+} , Eu^{3+}) and (Na^+ , CO_3^{2-}) ions was achieved through a porous silica hydrogel [1] in a U-shaped tube and aqueous solutions supersaturated with respect to calcite were prepared by mixing equimolar CaCl_2 and Na_2CO_3 solutions. The range of Eu(III) concentration was 10^{-2} –50 mM. In the case of gels, Eu(III) was introduced into the sodium silicate solution used for the preparation of the silica gel to avoid formation of Eu(III) oxides. Crystals of calcium carbonate polymorphs in the presence of Eu(III) were formed in less than a month in the silica gel. Crystal growth proceeded and was finalized past a time period of one year. Additional crystallization experiments were carried out by vapor diffusion using the sitting drop crystallization method on a 'crystallization mushroom' [2]. Calcium carbonate precipitated in droplets containing CaCl_2 : $(\text{NH}_4)_2\text{CO}_3$ ratio of 2.5 in the presence of Eu(III) concentration of 4–10 mM. The calcium carbonate polymorphs formed in the presence of Eu(III) were examined by Scanning Electron Microscope (SEM-EDS) and with electron microprobe (EMP) analysis. The extent of incorporation of Eu(III) into the calcium carbonate crystal structure is discussed in the perspective of using this mineral as a host for radionuclide disposal.

[1] Prieto M. Fernández-González A. Putnis A. & Fernández-Díaz L. (1997) *Geochim. Cosmochim. Acta* **61**, 3383–3397.

[2] Hernández-Hernández A. Rodríguez-Navarro A.B. Gómez-Morales J. Jiménez-Lopez C. Nys Y. & García-Ruiz J.M. (2008) *Cryst. Growth Design* **8**, 1495–1502.

Bacterial and fungal communities colonizing mercury sulfide surfaces

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Soils and sediments, where mercury (Hg) can exist as Hg sulfide minerals (HgS), represent major reservoirs of Hg in aquatic environments. Due to their low solubility, primary and authigenic HgS (e.g. cinnabar and metacinnabar) have historically been considered insignificant sources of soluble Hg(II) to the environment. Recently however, the solubility of HgS was shown to be greatly enhanced in the presence of a natural microbial consortium [1]. The mechanisms for this enhanced solubility have yet to be assessed. Moreover, bacteria and fungi capable of colonizing HgS surfaces in the environment have not been identified, yet their proximity and association with the mineral makes them likely key players in effecting chemical changes that can impact dissolution.

To this end, we assessed the microbial diversity on HgS surfaces in the Hg-contaminated sediments and floodplain soils of the East Fork Poplar Creek in Oak Ridge, TN. Cinnabar and metacinnabar mineral sections were incubated at various depths, and hence redox conditions, in the creek channel, bank, and floodplain. Other metal sulfides, namely pyrite (FeS_2) and sphalerite (ZnS), were also incubated to distinguish the host metal effects on the colonizing community composition. Composition and diversity were determined after 6 weeks of incubation, via pyrosequencing using bacterial (16S rRNA) and fungal (ITS) primers.

Our results reveal a high diversity of microorganisms colonizing all the metal sulfide surfaces. The microbial community composition and phylogenetic diversity vary as a function of the host metal within the sulfide, as well as between the HgS polymorphs, cinnabar and metacinnabar. Oxidation rinds are observed on metacinnabar surfaces, the extent of which decreases with depth within the sediment. These communities have been cultivated and are being investigated for their ability to solubilize HgS. The results from this study will have large implications on the role that microbial communities play in the dissolution of HgS phases and hence mobility of Hg within the environment.

[1] Jew A.D. *et al.* (2007) AGU Fall Meeting.