

Plutonium coprecipitation with calcite

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For the long-term performance assessment of nuclear waste repositories, knowledge about the interactions of actinide ions with minerals is imperative. Plutonium (Pu) is a highly toxic, long lived radionuclide characterized by complex chemical and physical properties and much attention has been paid to understanding its behavior in order to guarantee its safe handling and long-term storage. The mobility of Pu in the subsurface is affected by Pu-mineral interactions such as adsorption-desorption and structural incorporation. Calcite (CaCO_3) is the thermodynamically stable calcium carbonate polymorph under typical environmental conditions, and is a common secondary phase in near surface environments, making it a major component of many rocks and soils. Furthermore, in geological repositories, calcite is expected to form as an alteration product of cement-based materials. The reactivity of the calcite surface and its ability to tolerate significant variations in its chemical composition through substitution of Ca for other cations make calcite a potentially important sink for environmental contaminants. The goal of this work is to understand the fate of Pu during growth and crystallization of calcite single crystals. We provide laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and extended x-ray absorption fine structure spectroscopy of Pu(VI) and (IV) coprecipitated with calcite. These data are used to identify the likely structure of Pu incorporated into calcite and provide insight into the potential for Pu sequestration in calcite precipitates. Overall, the EXAFS and LA-ICP-MS data clearly support the coprecipitation of plutonyl in the bulk calcite, though the exact nature of the complex is difficult to elucidate. The coprecipitated plutonyl could be either incorporated in distorted Ca lattice sites or in defect sites. The LA-ICP-MS additionally shows that the coprecipitation of Pu(VI) is favored over the coprecipitation of Pu(IV). We provide evidence to suggest that Pu(VI) is reduced to Pu(V) during calcite synthesis and that Pu resides in a distorted Ca position in calcite. Our results suggest that Pu sequestration in calcite may provide one mechanism that can immobilize Pu and isolate it from groundwater interactions in contaminated environments and nuclear waste repositories. LLNL-ABS-819892