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Pu(IV) interaction with iron(III) (oxyhydr)oxide minerals

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Pu is a key risk-driving radionuclide in many natural and engineered environments including contaminated land, in the treatment of radioactive effluents, and the long-term management of nuclear materials such as the geodisposal of radioactive wastes. Important controls on Pu mobility in these environments include sorption, incorporation, and recrystallization reactions, especially with common mineral Fe(III) bearing phases such as ferrihydrite, goethite (FeO(OH)), and hematite (Fe_2O_3). Given this importance it is critical to gain a mechanistic understanding of Pu interactions with iron (oxyhydr)oxide mineral phases.

Following on from previous work [1], we present Pu L_3-edge extended x-ray absorption fine structure (EXAFS) spectroscopic data (among other techniques) collected from a series of Pu(IV) containing Fe(III) mineral samples obtained from sorption, coprecipitation, and recrystallization experiments. At higher loadings Pu-Pu atom pairs can be clearly identified in the data strongly indicating the formation of $Pu(IV)O_2$ nanoparticles in ferrihydrite and goethite systems. Interestingly, a splitting in the oxygen environment is observable in ferrihydrite systems with two coordination shells at ~2.2 and ~2.4 Å. At lower concentrations in all samples studied multiple (>4) Fe scatterers can be identified confirming the formation of polynuclear complexes associated with the Fe(III) minerals. Furthermore, in several goethite samples clear splitting in the Pu-Fe shells can be observed at ~3.2 and ~3.5 Å indicating a complex binding mechanism as the overriding mechanism of sequestration in these systems.

[1] Smith et al, *ACS Earth Space Chem.*, 2019, **3**, 2437-2442.