

Is plutonium being incorporated by magnetite under anoxic conditions?

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Magnetite, which forms under anoxic conditions on the surface of corroding steel containers, is able to reduce a range of elements, including radionuclides of high relevance in the context of nuclear waste disposal, e.g. Se, Tc, U, Np, Pu [1]. Aqueous Pu(V) is rapidly reduced by nanoparticulate magnetite to Pu(III), which then forms stable, tridentate sorption complexes on the {111} faces of magnetite [2]. Trivalent lanthanides have been shown to substitute for Fe(III) in magnetite, although their ionic radii are about 1.4 times larger than that of Fe(III) (1.15-1.17 vs. 0.79 Å in six-fold coordination) [3]. To investigate if such an incorporation is also possible for Pu(III) with a similar ionic radius as the lanthanides, we conducted coprecipitation experiments with two Pu loadings of 1000 and 3500 ppm. UV-VIS spectroscopy showed an immediate reduction of Pu(V) to Pu(III) in the initial Fe(II)/Fe(III) chloride solution. After formation of the black magnetite precipitate, Pu(III) concentration in solution was below 10⁻⁹ M. X-ray Absorption Near-Edge Structure (XANES) spectroscopy confirmed the trivalent oxidation state of solid phase-associated Pu. Extended X-ray Absorption Fine-Structure (EXAFS) spectroscopy was then used to investigate the molecular structure of incorporated Pu(III) in the fresh precipitate as well as after Fe(II)-induced aging [4]. The EXAFS spectra revealed two different spectral components. The first component represents the tridentate Pu(III) sorption complex also observed during sorption experiments. The second component represents Pu(III) in a highly distorted magnetite Oh site. The proportion of the incorporated Pu(III) decreased from about 75% to 40% with Fe(II)-induced aging, while the proportion of sorbed Pu(III) increased correspondingly. Our results suggest, therefore, that Pu can be incorporated by magnetite, but will convert to sorbed species on the long time scales relevant for nuclear waste disposal.

[1] Scheinost *et al.* (2008) *J. Contam. Hydrol.* **102**, 228-245.

[2] Kirsch *et al.* (2011), *Environ. Sci. Technol.* **45**, 7267–

7274. [3] Moon *et al.* (2007) *Extremophiles* **11**, 859-867. [4]

Boland *et al.* (2011) *Environ. Sci. Technol.* **45**, 1327-1333.

Mineralogy and geochemistry of natural porcelanites

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Natural porcelanites from Filipestii de Pădure, Romania, were analyzed from mineralogical, radiometric and geochemical point of view. These artifacts resulted from the *in situ* ignition of the relic coal in the sterile wastes issued from the mining activity, as well as from the burning of the clay formations in the couch and roof of the coal layers.

The mineralogical associations inferred by X-ray powder diffraction analyzes of 10 samples of porcelanite consist in gypsum, anhydrite, bassanite, quartz, sanidine, tridymite, mullite, cordierite, hematite, spinel, cristobalite, illite, spinel. Cell parameters for the most representative species were obtained by least squares refinement of X-ray power data.

Anhydrite and gypsum are particularly abundant, reaching up to 45 % of the porcelanite volume. FTIR study shows in all the samples the group of bands in the 1000-1160 cm⁻¹ region materializing stretching motions of the (SO₄)²⁻ group, as well as bands characteristic to the vibrations of molecular water. SEM photos show that in some cases anhydrite postdates gypsum, pseudomorphs of anhydrite after gypsum conserving the (010) perfect cleavage of gypsum.

ICP-MS analysis pointed out the presence of a large spectrum of REE (e.g. Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Zb, Lu), as well as of U and Th.

The gamma-energy spectrum radiometric measurements showed the presence of the following natural radionuclides (in order of the decreasing abundance): Ra-226, U-238, K-40 and Th-232.