

Neptunium(V) incorporation into calcite

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A multi method approach has been applied in order to study structural neptunyl (NpO_2^+) incorporation into calcite. Highly doped (~1.2 %) NpO_2^+ containing calcite, synthesized in a mixed flow reactor, has been studied using low temperature EXAFS spectroscopy, Raman spectroscopy, and XRD. Analysis of the Np-L_{III} low temperature EXAFS data reveals the same result as shown in a previous study¹, i.e. NpO_2^+ incorporated into calcite is coordinated by four monodentate bound carbonate ions. In the Raman spectrum the NpO_2^+ containing calcite shows an additional band compared to pure calcite at 753 cm^{-1} . This band is assigned to the symmetric O=Np=O stretching vibration, ν_1 , and is, as expected, shifted to lower frequencies compared to ν_1 of the NpO_2^+ aquo ion at 767 cm^{-1} ². For aqueous neptunyl(V) carbonate complexes this band is observed between 762 cm^{-1} and 756 cm^{-1} ². Rietveld refinement of the XRD powder patterns shows that incorporation of NpO_2^+ into calcite causes a slight decrease in the unit cell parameters. From a Williamson-Hall plot of the NpO_2^+ containing calcite and the calcite seed material we can show that the average crystal size and the local strain in the crystal lattice is increased by the co-precipitation of NpO_2^+ containing calcite onto the seed crystals.

Evaluation of data from seven mixed flow reactor experiments allows the description of the NpO_2^+ uptake by calcite in terms of a simple thermodynamic solid-solution model. In accordance with the EXAFS results a complex coupled substitution mechanism has been proposed where three CaCO_3 are exchanged for one $\text{Ca}_{0.5}\text{NpO}_2\text{CO}_3$ and 1.5 vacant calcium sites. The system may be described as a regular solid-solution with one Guggenheim Parameter, $a_0 \approx 2$, up to a content of 3.6% of the hypothetical neptunium endmember ($\log_{10} K_{sp} \approx -13$).

[1] Heberling, F., Denecke, M.A. & Bosbach, D. (2008) *Environ. Sci. Technol.* **42**(2), 471-476. [2] Clark, D.L., Conradson, S.D., Ekberg, S.A., Hess, N.J., Janecky, D.R., Neu, M.P., Palmer, P.D. & Tait, C.D. (1996) *New J. Chem.* **20**(2), 211-220.

Phototrophic Fe(II) oxidizing bacteria – To encrust or not to encrust

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Bacteria can oxidize Fe(II) to Fe(III) either phototrophically or chemotrophically with nitrate as electron acceptor. Fe(III) is poorly soluble at neutral pH and usually precipitates as a Fe(III) (hydr)oxide mineral. Bacteria catalyzing the oxidation of Fe(II) to Fe(III) therefore face the challenge of how to deal with an insoluble product. Thus, neutrophilic Fe(II)-oxidizing cells must receive electrons from Fe(II) without acting as a nucleation site for the $\text{Fe(III)}_{\text{aq}}$ themselves, leading to cell surface Fe(III) mineral precipitation. Fe(III) mineral precipitation at the cell surface would limit metabolism and ultimately cause cell death. In laboratory cultures, we have established that cell encrustation indeed results in a higher number of dead cells, proving that encrustation avoidance is essential for cell survival, but it is unknown by which mechanism cells hinder encrustation.

Several strategies are plausible: i) modification of the cell surface; ii) acidification of the cell vicinity; iii) production of Fe(III)-chelating ligands. We evaluate these strategies and present models how neutrophilic Fe(II)-oxidizing bacteria could avoid encrustation and compare differences between encrusting to non-encrusting strains.