

A comparative study of calcite dissolution in the presence of aqueous sulphate: Batch and AFM experiments

AIKATERINI I. VAVOURAKI^{1,2,3*}, CHRISTINE V. PUTNIS³,
ANDREW PUTNIS³, ERIC H. OELKERS⁴
AND PETROS G. KOUTSOUKOS^{1,2}

¹Department of Chemical Engineering, University of Patras, Greece

(*correspondence: kvavouraki@chemeng.upatras.gr)

²Institute of Chemical Engineering & High Temperature Chemical Processes, Patras, Hellas (pgk@iceht.forth.gr)

³Institut für Mineralogie, Universität Münster, Germany (putnisc@uni-muenster.de)

⁴Géochimie et Biogéochimie Expérimentale, LMTG/CNRS Université Paul Sabatier, Toulouse, France (oelkers@lmtg.obs-mip.fr)

An exhaustive number of studies have been performed to characterize carbonate mineral reactivity due to its importance in the global carbon cycle, biologic activity, and waste immobilization, etc. [1]. Despite these studies, there are still large differences in dissolution rates obtained from macroscale versus nanoscale studies. In an attempt to understand these differences, rates were measured using both *in situ* AFM on the calcite (10 $\bar{1}$ 4) surface and mixed-flow reactors on calcite powders. Calcite dissolution rates in 0.1 M NaCl and 0.1 M NaHCO₃ were measured using both techniques at pH= 8.4 and 25 °C. Resulting rates are comparable to previous studies [2, 3]. In the presence of aqueous sulphate corresponding rates show that this anion inhibits calcite dissolution. In all cases surface-normalized calcite dissolution rates obtained from the AFM are significantly faster than those obtained from mixed-flow reactor experiments. AFM dissolution rates were measured in a relatively flat calcite surface with few defects compared to high step and kink densities of calcite grains used in measuring 'bulk' dissolution rates. The differences in dissolution rates may be attributed to the relative distribution and reactivity of morphologic features on the calcite surface.

[1] Morse J.W., Arvidson R.S. & Lüttge A. (2007), *Chem. Rev.* **107** 342-381. [2] Cubillas P., Köhler S., Prieto M., Chairat C. & Oelkers E.H. (2005), *Chem. Geol.* **216** 59-77. [3] Shiraki R., Rock P.A. & Casey W.H. (2000), *Aquat. Geochem.* **6** 87-108.

Manganese incorporation into biogenic uraninite affects its oxidative stability

HARISH VEERAMANI¹, JONATHAN O. SHARP¹,
ELENA I. SUVOROVA¹, ELEANOR SCHOFIELD²,
KAI-UWE ULRICH³, APURVA MEHTA,
DANIEL E. GIAMMAR³, JOHN R. BARGAR²
AND RIZLAN BERNIER-LATMANI¹

¹Environmental Microbiology Laboratory, École Polytechnique Fédérale de Lausanne, Switzerland (rizlan.bernier-latmani@epfl.ch)

²Stanford Synchrotron Radiation Lightsource, CA, USA

³Department of Energy, Environmental and Chemical Engineering, Washington University, MO, USA

The remediation of sites contaminated with uranium is proposed through the stimulation of microbial U(VI) reduction to produce the relatively insoluble biogenic mineral uraninite (UO₂). The long-term stability of biogenic uraninite hinges on its resistance to environmental oxidants such as oxygen. Geological sedimentary uraninites often contain structural cation impurities that have been shown to increase their resistance to oxidation. If biogenic uraninite could analogously incorporate ground water cations, its stability might be enhanced. The work presented herewith evaluates the effect of soluble Mn²⁺, a common groundwater cation, on the formation, structure and reactivity of biogenic uraninite synthesized by *Shewanella oneidensis* MR1. The structure of the biogenic uraninite was investigated using electron microscopy, synchrotron based EXAFS and SR-PD. Its reactivity was assessed using batch and continuous-flow dissolution studies.

Synchrotron based analytical techniques indicated that up to 4.4 weight percent Mn(II) substitutes at the U site within the uraninite lattice. Mn incorporation was associated with a decrease in average particle size and an overall reduction in local and intermediate-range structural order. Despite the smaller particle size and presumably greater surface area, both solubility and dissolution rates of Mn-reacted uraninite were substantially lower than those of unreacted biogenic uraninite.

We conclude that incorporation of Mn(II) into biogenic uraninite lattice lowers the material's reactivity with respect to oxidative dissolution. This finding has important environmental implications since bioreduction of U(VI) and presumable precipitation of UO₂ would unavoidably occur in the presence of groundwater cations (Mn²⁺, Ca²⁺, Mg²⁺, etc), which can likely incorporate into the structure and thus enhance the oxidative stability of biogenic uraninite in the environment.