Nanoscale study of exopolymeric substance-mediated uranium biomineralization

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Bacterially-mediated biogenic reduction of soluble hexavalent uranium U(VI) into a less-soluble U(IV) product is among the planned bioremediation strategies at uranium-contaminated sites in the U.S. The primary product of this reduction is thought to be uraninite (UO_2), a highly insoluble crystalline nanoparticulate. While uraninite forms under certain conditions, recent research has shown formation of another U(IV) species under different conditions. *Shewanella oneidensis* MR-1, an intensely studied bacterium for its remediation properties, produces UO_2 under simple aqueous solutions (sodium bicarbonate). In the presence of moderate or high concentrations of alkaline earth cations such as Ca^{2+}, the same bacterium will form U(IV) diffusely distributed on cell biomass and biopolymers, termed monomeric U(IV) [1].

There is electron microscopy evidence that exopolymeric substances (EPS) play a role in the formation of UO_2 [2]. Moreover, EPS-deficient mutants appear to produce less UO_2 than the wild-type, confirming that prediction.

Here, we present a combined microscopic and spectroscopic approach to address the changes in U biomineralization as a function of medium. Using scanning transmission X-ray microscopy (STXM) coupled to near edge X-ray absorption fine structure (NEXAFS), we acquired carbon speciation and actinide elemental maps of *S. oneidensis* wild-type and mutant each generating either UO_2 or monomeric U(IV). In concert, we also provide cryo-preserved, low-dose transmission electron microscope (TEM) images of the reducing bacteria thin-sectioned to display ultrastructure features. The specificity of the association of UO_2 and monomeric U(IV) with biomolecules was demonstrated with these approaches suggesting the importance of individual biomolecules in controlling biomineralization products.

[1] Bernier-Latmani *et al.* (2010) *Environ. Sci. Technol.* **44**, 9456–9462. [2] Marshall *et al.* (2006) *PLoS Biol.* **4**, 1324–1333.

Modelling the free energy of adsorption of persistent organic pollutants at clay mineral-water interfaces

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Clay minerals represent a cheap alternative for the remediation of pollutants. The clay mineral bentonite has been shown experimentally to adsorb organic pollutants [1] and heavy metal ions [2]. Here we applied computational techniques to model the adsorption of a range of organic molecules, more specifically polyhalogenated compounds (PHCs), on the clay minerals montmorillonite and pyrophyllite. Montmorillonite, a dioctahedral smectite, is the principal constituent of bentonite, while pyrophyllite is the template for all dioctahedral smectites.

The CLAYFF [3] and GAFF [4] force fields were applied to the clay surface and organic molecules, respectively. The interatomic potentials were derived using simple mixing rules and TIP3P/FS [5] water was used in solvated systems. DFT-D2 calculations using the VASP code [6] were carried out to confirm the potential model. PMF free energy calculations were undertaken using the DL_POLY_2.0 code [7]. Further free energy calculations, steered molecular dynamics, umbrella sampling and metadynamics used the PLUMED software plug-in [8].

Our results show that the simple model for the interatomic potentials had good agreement with DFT-D2 calculations. Adsorption energies for montmorillonite were dependent on the counter ions. The free energy techniques all gave comparable results. However, metadynamics was both consistently accurate and less computationally demanding than the other methods. In general, for similarly structured PHCs the adsorption energy increased with the number of chlorine substituents. Even in simple systems the differences are significant, for example the free energies of adsorption for benzene and hexachlorobenzene on the surface of pyrophyllite were -9.6 and -38.6 $kJmol^{-1}$, respectively.

[1] Hassanien *et al.* (2010) *J. Haz. Mat.* **178**, 94–100. [2] Hamidpour *et al.* (2010) *J. Haz. Mat.* **181**, 686–691. [3] Cygan *et al.* (2004) *J. Phys. Chem. B* **108**, 1255–1266. [4] Wang *et al.* (2004) *J. Comp. Chem.* **25**, 1157–1174. [5] Wu *et al.* (2006) *J. Chem. Phys.* **124**, 024503. [6] Kresse & Furthmuller (1996) *Phys. Rev B* **54**, 11169–11186. [7] Smith & Forester (1996) *J. Mol. Graph.* **14**, 136–141. [8] Bonomi *et al.* (2009) *Comp. Phys. Comm.* **180**, 1961–1972.