

## U(VI) sorptive reduction on magnetite nanoparticles

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The release of uranium into the environment through anthropogenic induced geochemical perturbations (e.g. mining activities or nuclear waste repository sites) is a potential threat to eco- and biosphere due to the uranium chemo- and radiotoxicity. It is therefore of great importance to gain insight into the various chemical and physical processes governing uranium migration behavior. The heterogeneous reduction of U (VI) to U (IV) by ferrous iron is believed to be a key process influencing the fate and transport of U in the environment. Magnetite as stainless steel corrosion product will be one of the main Fe (II) containing mineral phases present when spent fuel corrosion occurs.

Thus, an extensive laboratory program under anoxic conditions and exclusion of CO<sub>2</sub> as function of pH and contact time has been conducted to study the interaction of uranium with a synthetic nanoparticulate (size distribution 30-300nm) magnetite (Fe<sup>II</sup>Fe<sup>III</sup>O<sub>4</sub>) applying spectroscopic techniques (XPS, XAFS) to verify the presence and amount of reduced uranium on the magnetite surface.

U (VI) sorption kinetic studies revealed a fast initial sorption with > 90% magnetite associated U after 24 hours within the pH range 5-11. In contrast to earlier studies [1] neither an uranium association at pH < 3 nor a decrease in the magnetite associated U at pH ≥ 9 could be observed. Redox speciation on one year reacted samples by XPS and U L<sub>3</sub>-edge XANES revealed for samples within pH 5.4 to 9.7 40-60% tetravalent U. Thermodynamic calculations based on the experimentally determined pe/pH values corroborate the spectroscopic findings and predict U (IV) as the predominant redox state. XAFS measurements to clarify the coordination environment and identify the potential presence of U (V), as documented by Ilton and co-workers [2], were additionally performed and will be presented.

[1] Missana *et al.* (2003) *GCA* **67**, 2543–2550. [2] Ilton *et al.* (2010) *ES&T* **44**, 170–176.

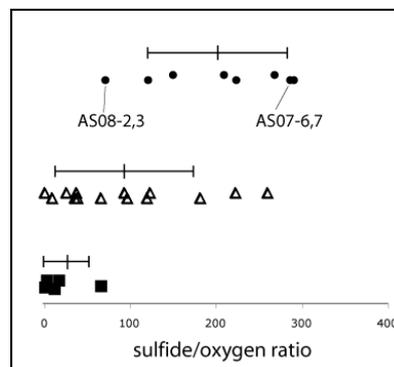
## Sulfur-oxidizing biofilms in terrestrial subsurface hot springs

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Many sulfidic groundwaters host chemosynthetic microbial communities and are therefore important model ecosystems for sulfur biogeochemistry in both modern and ancient environments. Here we present the first description of conspicuous microbial biofilms inhabiting near-neutral, moderately thermophilic (35-50°C) waters inside the Rio Garrafo caves near Acquasanta Terme, Italy. Biofilms were collected from waters with 400-830 micromolar sulfide, <10 micromolar O<sub>2</sub>, pH 6.3 to 6.7, and conductivity 8.5-10.5 mS/cm. Based on rRNA methods, lithoautotrophic Gamma- and Epsilonproteobacteria are the principle biofilm architects. Deltaproteobacterial sequences retrieved from the biofilms have <90% 16S rRNA similarity to their closest relatives in public databases, and may represent novel sulfate reducing bacteria. Multivariate analyses of 16S rDNA clone libraries show that Acquasanta biofilms share few species in common with Frasassi cave biofilms (13°C, 80 km distant), but are strongly similar when compared at the level of clades sharing 85-90% 16S rDNA similarity. We also show that a simple ecological niche model [1] predicts the taxonomy of the dominant sulfur oxidizing populations in the Acquasanta biofilms, despite strong variations in temperature, conductivity, and sulfide concentrations among biofilms included in the model.



**Figure 1:** Chemical and physical controls on the taxonomic identity of biofilm-forming sulfur oxidizers. Closed circles, Epsilonproteobacteria-dominated; open triangles, *Beggiatoa*-dominated; closed squares, *Thiothrix*-dominated.

[1] Macalady (2008) *ISME J.* **2**, 590–601.