U(VI) stability in Fe(III)-reducing soils

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The solubility, mobility, and bioavailibility of U in the near surface environment is largely controlled by ambient redox conditions and microbial processes. It is generally accepted that soluble U(VI) reduction to insoluble U(IV) occurs under microbially mediated Fe(III)-reducing conditions. This mechanism is often invoked to remediate U contaminated sites [1] and may potentially limit U(VI) migration in the deep subsurface impacted by geological disposal of radioactive waste [2]. Study of U behaviour at natural analogue sites that are contaminated with U gives long-term insight into the potential for such reactions to limit U migration. Here, we present results from the Needle's Eye natural analogue site in Scotland, UK, where weathering of a local pitchblend vein yields elevated concentrations of U in organic rich sediments and groundwater. We took cores from this site under anoxic conditions and used bulk geochemical measurements coupled with microfocus-XRF mapping, -XANES, and -EXAFS of resin embedded sediment to probe U biogeochemistry. Bulk analysis shows high U concentration (>1000 mg kg^{-1}) and strongly reducing conditions (70 – 100% Fe(II) in solids). Micro-focus measurements show that U is present at its highest concentration when stable as U(VI), despite robust Fe(III)-reducing conditions. Groundwater concentrations of U in this section of the core are also elevated (~200 µg L^{-1}). Bulk EXAFS analysis show that sediment U(VI) is complexed by organic matter. This zone of sediment appears stable until, at increased depth, the U concentration in the sediment and porewater decreases (to ~200 mg kg^{-1} and 75 µg L^{-1}) and sediment U speciation changes from U(VI) to U(IV) across a narrow transistion zone. Here, EXAFS analysis suggests the formation of monomeric U(IV) rather than uraninite.

[1] Brookshaw *et al.* (2012) *Min. Mag* **76**, 777-806
[2] Williamson *et al.* (2014) *Env. Sci. Technol.* **22**, 13549-13556