

## Precipitation of pentavalent uranium on magnetite

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Remediation of uranium-contaminated environments often relies on the reduction of the soluble uranyl ion ( $U(VI)O_2^{2+}$ ) to sparingly soluble  $U(IV)$  phases by gaining two electrons. Heterogeneous reduction of  $U(VI)$  to  $U(IV)$  on mineral surfaces is often considered a one-step two-electron process. However, stabilized  $U(V)$  found in recent studies indicates that mineral surfaces can retard the  $U(VI)$  reduction under certain conditions [1]. We investigated the reduction pathways of uranium (one-step two-electron, two-step one-electron, or one-electron followed by  $U(V)$  disproportionation,  $2U(V) \rightarrow U(VI) + U(IV)$ ) by reducing  $U(VI)$  electrochemically on a magnetite electrode at pH 3.4. The one-electron reduction of  $U(VI)$  was first confirmed using electrochemical methods [2]. Precipitation of nano-size uranium phases on magnetite under reducing potentials and dissolution of the solids at oxidizing potentials were observed by *in situ* electrochemical-AFM. XPS and XANES analysis of the magnetite electrodes polarized in uranium solutions at voltages from -0.1 to -0.9 V ( $E^0_{U(VI)/U(V)} = -0.135V$  vs. Ag/AgCl) show the presence of only  $U(V)$  and  $U(VI)$ . EXAFS analysis identified uranyl type coordination in the uranium precipitates with the longest average  $U-O_{axial}$  distance of  $2.05 \pm 0.01$  Å. The results show that the electrochemical reduction of  $U(VI)$  on magnetite only yields  $U(V)$ , even at a potential of -0.9 V, indicating the high kinetic barrier for the two-electron reduction from  $U(VI)$  to  $U(IV)$ . Thus,  $U(IV)$  is likely to be eventually generated through the disproportionation of  $U(V)$ .  $U(V)$  does not disproportionate in the present study but stabilized on magnetite through precipitation of mixed-valence state  $U(V)/U(VI)$  solids.

[1]Ilton, Boily, Buck, Skomurski, Rosso, Cahill, Bargar & Felmy (2010), *Environmental Science & Technology* **44**, 170-176. [2]Yuan, Renock, Ewing & Becker (2015), *Geochimica et Cosmochimica Acta*. **156**, 194-206.