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Surface Catalysed Reduction of uranium(VI) by Iron (II) in the Presence of Carbonate

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Hexavalent uranium as uranyl ions (UO_2^{2+}) and its complexes is relatively mobile in aqueous environments. Tetravalent uranium on the contrary has a low solubility and forms precipitates such as uraninite. The reduction of uranium from U(VI) to U(IV) is therefore an important process controlling the environmental behaviour of uranium. Recently it was shown by Liger et al. (1999) that Fe(II) is a powerful reductant of U(VI) in the presence of catalysing mineral surfaces. Hence they proposed that heterogeneous reduction of U(VI) is a major pathway for uranium immobilisation in natural environments. In their experiments, dissolved carbonate was excluded. In natural environments, carbonate may affect the surface catalysed reduction by competing for mineral surface sites, and by complexing Fe(II) and U(VI) at the surface and in solution. Thermodynamic calculations, based on literature equilibrium constants, predict that heterogeneous uranyl reduction rates should decrease significantly at pH values above 7, in systems at equilibrium with atmospheric carbon dioxide relative to CO_2-free systems. By taking into account carbonate adsorption and formation of aqueous Fe(II) and U(VI) complexes, plus ternary surface U(VI)-carbonate complexes, the reduction rate constants should decrease by a factor of about 2 and 5 at pH 7.5 and 8.5, respectively. In the calculations it was assumed that the reduction rate of ternary U(VI)-carbonate surface complexes is negligible.

The predicted effects were checked by measuring the disappearance of U(VI) in the presence of Fe(II) and hematite in batch experiments, at fixed pH and variable carbonate concentrations. The experimental effect of dissolved carbonate on the U(VI) reduction was significantly smaller than predicted. Thus, either the adsorption and complexation of carbonate was overestimated, or the assumption that the reduction rate of ternary U(VI)-carbonate surface complexes is negligible is wrong.

Surface titration and adsorption experiments are being performed to evaluate the influence of carbonate on the adsorption of Fe(II) and U(VI) onto iron(hydr-)oxides and to optimise equilibrium constants for describing carbonate adsorption and complexation. The results in combination with a kinetic study, should allow us to constrain the role of ternary U(VI)-carbonate surface complexes in the heterogeneous U(VI) reduction by Fe(II).

Liger E, Charlet L, Van Cappellen P, *Geochim. Cosmochim. Acta*, **63**, 2939-2955, (1999).