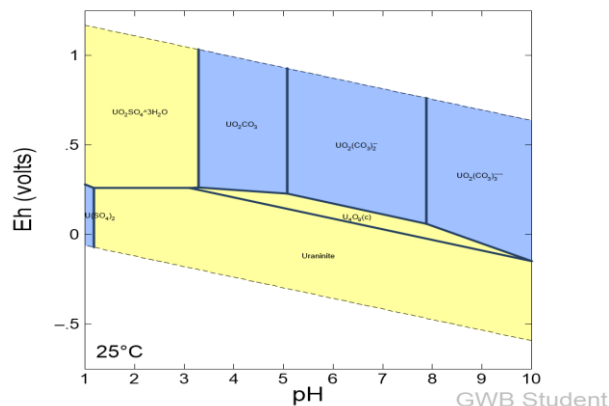


Introduction

Uranium (U) is a naturally occurring radionuclide that poses serious health risks owing to its chemical and radiological toxicity. The main route of U exposure towards humans is drinking (ground)water. The mobility of U is essentially driven by its speciation, where U(VI) is present as relatively mobile species and U(IV) as largely immobile in the environment. Hence, many U remediation strategies are targeted towards biotic or abiotic reduction of U(VI) to immobile U(IV) species. However, success of such remediation processes is dependent on biogeochemical conditions caused by interactions between dissolved species, mineral surfaces, and local microbial activity (1). Protecting water quality thus requires better understanding of the biogeochemical factors that control U stability in the subsurface environment; one such factor is the presence of organic ligands (2).

We therefore tested, using flow-through sediment column experiments under anoxic conditions and geochemical modelling, the processes that lead to U bio reduction in an aquifer and U remobilization induced by organic ligands of the same sediment in batch.

Synthetic Groundwater and U



This Eh/pH diagram shows the expected speciation of uranium in our synthetic groundwater solution. Mineral species are yellow, and dissolved species blue. Groundwater composition: U 25 μM , CaCl_2 2 mM, NaHCO_3 7 mM, Na_2SO_4 3.24 mM. pH was adjusted to 7.1. It is expected for U to reduce and acquire a solid phase even at low oxidizing or slightly reducing conditions.

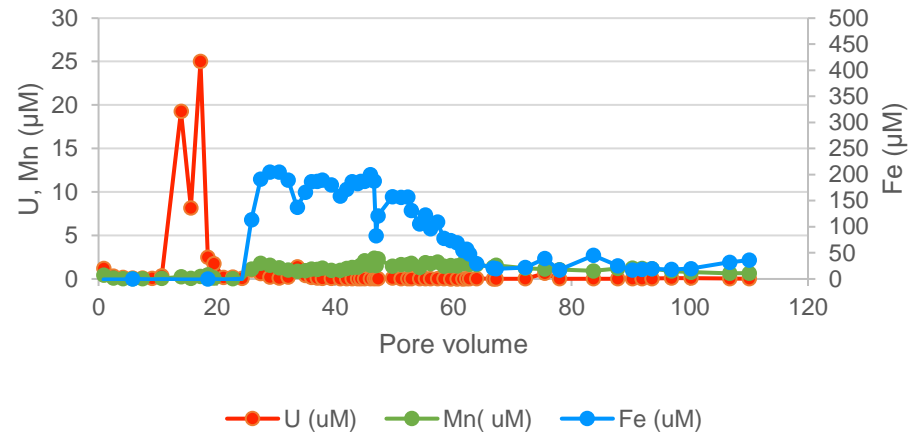
U Bioreduction

We used a reductive immobilization process designed to mimic under laboratory conditions the process of bio-reductive immobilization of dissolved uranium that would happen in an anoxic aquifer (5).

Two 15 cm long, 25mm diameter glass columns were filled with natural anoxic sediment from an aquifer and flushed with 100 Pore Volumes (approx. 4 weeks) of anoxic synthetic groundwater solution and glucose as a reductant.

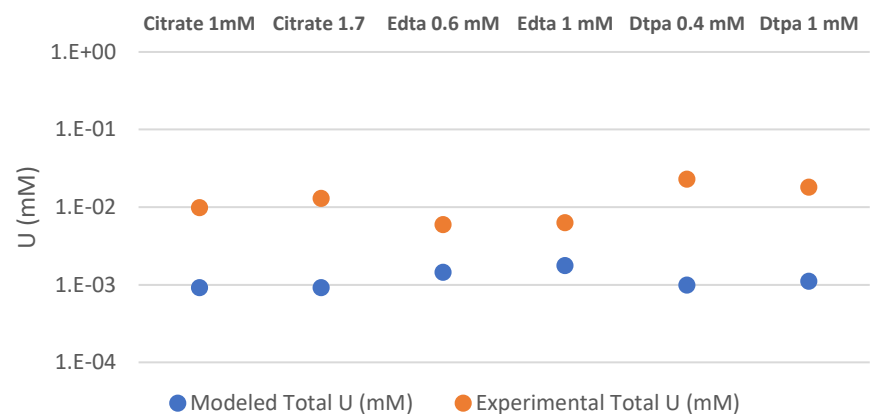
In PhreeqC (3) we have used a similar solution composition and used Ethanol as reductant. Sediment XRD data was used to model the solid phase. Experimental and modeled outcomes gave comparable results.

Column Effluent Concentration



Ligand-induced Remobilization

We tested the U-remobilization with the ligands Citrate, Edta and Dtpa in batch experiments, using 1g of the previously bioreduced sediment in 44ml of ligand solution. Mobilized U was measured over time and compared to modelled results in PhreeqC. Control (synthetic groundwater without ligand) showed no significant remobilization in both setups.



Laboratory and modelled results consistently are within approximately one order of magnitude of each other, with the model underestimating the extent of mobilization seen experimentally. This, and the high Fe concentrations in solution, indicate that observed lab U-remobilization results could be explained not only by direct U-ligand complexation, but by several other complex processes. One of them being the model not including the variety of U(IV) species that would be present in natural systems, and the indirect U-remobilization due to ligand-induced dissolutions of iron- and other minerals that have U(IV) adsorbed to their surfaces (1,4).

Conclusions

The presence of organic chelates has been shown to effectively remobilize reduced uranium and bring it to a concentration that exceeds the safety guidelines for U in drinking water ($30\mu\text{g L}^{-1}$). Nonetheless, the impact of chelates in U-remobilization of such sediment environments is complex and additionally needs to consider indirect remobilization processes and dissolution of minerals that provide surfaces for U(IV) adsorption which contributes to the overall release of uranium in environmental systems. This work highlights the need for further investigation into the effects of organic chelates on U in environmentally relevant systems.

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