U(^{VI}) Reduction by Biotic and Abiotic Green Rusts

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Green rust (GR) is a mixed Fe^{II}-Fe^{III} mineral with high reactivity. It is ubiquitous in anoxic soils, sediments, and groundwater[1] and plays an important role in the fate and transformation of redox-active contaminants[2]. GR can be formed via various biotic and abiotic processes[3], which can lead to different morphological and/or surface properties that are likely to affect the relative reactivity of biotic vs. abiotic GRs with respect to redox transformations of contaminants[3]. Although biotic and abiotic GRs have been shown to reduce U^{VI}, the speciation and the stability of the resulting U^{IV} phases are poorly understood. This study investigated the products of U^{VI} reduction by biotic and abiotic GRs in batch experiments, using carbonate extractions and synchrotron x-ray spectroscopy to characterize the solids. The results show that both biotic and abiotic GRs rapidly remove U^{VI} from synthetic groundwater via reduction to U^{IV}. The initial (1h) products in the abiotic GR system are individual U^{IV} atoms associated with the solids. Over time (16-32d) the proportion of nano-particulate uraninite increases, leading to a dramatic decrease in the extractability of U^{IV} by carbonate. In contrast, the solid-phase U^{IV} atoms in the biogenic GR system remain as relatively extractable, non-uraninite U^{IV} species over the entire reaction period of 32 days. The presence of carbonate and calcium during U^{VI} reduction by GR affected the extractability of U^{IV} in the system with biogenic GR. These data provide new insights into the fate and stability of U^{IV} under anoxic conditions in the presence of carbonate and calcium, and have major implications for designing approaches for the remediation of uranium contaminated groundwater.

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[1] Christiansen et al. (2009) Environ. Sci. Technol. **43**, 3436-3441. [2] Latta et al. (2015) Curr. Inorg. Chem. **5**, 156-168. [3]Zegeye et al. (2014) J Phys. Chem. C, **118**, 5978-5987.