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Heavy Metal Incorporation During Goethite Oriented Attachment

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Nucleation and growth of iron (oxyhydr)oxides in natural environments often occur in mixed cation systems, where minor and trace elements co-precipitate with abundant phases. Less well understood is whether these elements can be incorporated into host minerals by non-classical growth pathways. For example, goethite can grow by oriented attachment (OA) of co-aligned precursor nanoparticles. As a result, the composition of the mineral is a function of both 1) element compatibility and 2) growth mechanism. To discern between these two competing controls on incorporation, this study focuses on the incorporation of U(VI) and W(VI) during the growth of goethite by OA.

Measurements of U(VI) incorporation into goethite by ICP-OES, XRD, and TEM showed that U(VI) additions early in the OA process hindered crystallization [1]. However, the amount of sorbed U(VI) was highest when added early during OA and decreased over time, eventually converging to similar values for both early and late additions of U(VI). Evidence from scanning transmission electron microscopy (STEM) indicated a portion of the acid resistant sorbed U(VI) was likely associated with grain boundaries between aggregating particles, not nanopores. These features – and the associated U(VI) – were annealed out with increasing reaction time. Further evidence that U(VI) was not incorporated into the structure of goethite was acquired by time elapsed imaging of U atom diffusion and extended X-ray absorption fine structure spectra (EXAFS). Quantification *by ab initio* molecular dynamics informed EXAFS showed an upper solubility limit of only U/Fe ~0.02 atom% in goethite where U(VI) was added early in the process.

To determine the effect of heavy metal coordination chemistry, we are comparing and contrasting the incorporation of W(VI) and U(VI) into goethite during OA under identical conditions. Unlike uranyl(VI), tungsten(VI) does not have unreactive uranyl oxygens that were shown to impede U(VI) incorporation into goethite during OA. Further, addition of U(VI) or W(VI) during the formation of ferrihydrite – the metastable OA precursor – may further constrain the solubility of these elements in the final goethite structure.

[1] Soltis, J.A., et al. (2019) *Environmental Science: Nano* **6**(10), 3000-3009.