

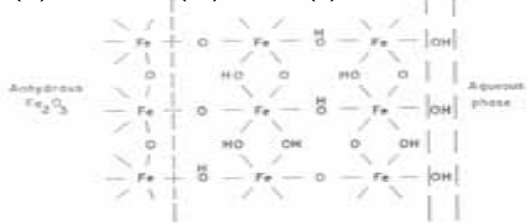
Hydrous Ferric Oxide (HFO) vs. Hematite

• Thermodynamically distinctive bulk phases, but the surfaces could be similar due to hydration of the interface.

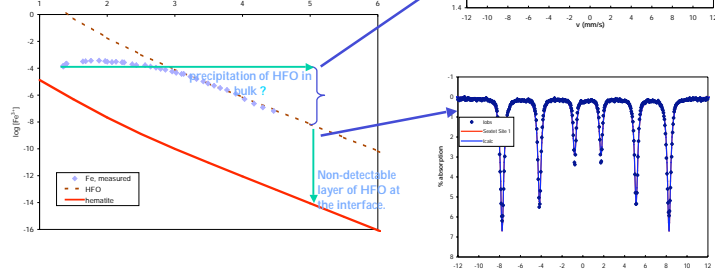
• **Hypothesis** → The surface of HFO is energetically similar to the surface of hematite.

• **Objective** → Compare the reactions of HFO and hematite with U(VI) and Fe(II).

• **Experimental** → The reactions of interests were (1) preparation of sub-micron hematite, (2) sorption of U(VI), and (3) redox of U(VI) and Fe(II) with HFO or hematite.



Evidence 1: Solubility of Fe(III)

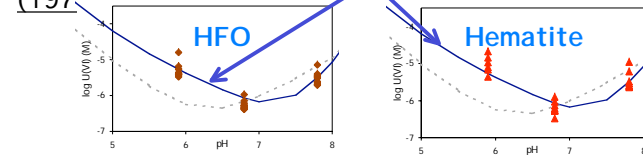
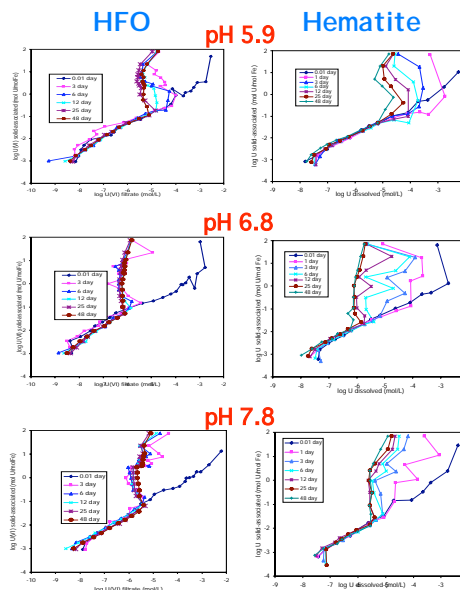


Preparation of sub- μ m hematite

- Thermal-forced hydrolysis of FeCl₃ solution, followed by dilution to pH 5 or filtration through 10kDa membrane until pH 5 reached.
- Mossbauer spectroscopy showed hematite with an HFO impurity for diluted sample, and pure hematite for the membrane-cleaned sample.
- However, [Fe(III)]_{dissolved} measured while cleaning was in equilibrium with HFO.
- Therefore, surface of hematite consists of HFO-like layers

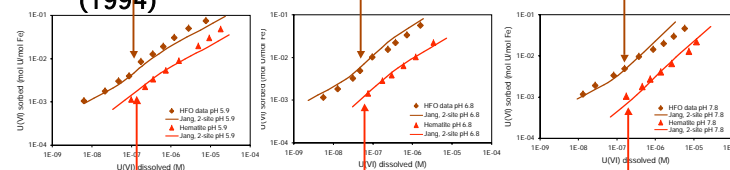
Evidence 2: Sorption & Precipitation of U(VI)

Solubility of UO₃ in the presence of both HFO and hematite was consistent with hydrolysis and solubility constants in Langmuir (1970)



After accounting only for differences in pH_{ZPC} and surface area, U(VI) sorption to both phases was well modeled using same surface complexes (>FeOUO₂⁰, >FeOUO₂⁺, >FeOUO₂CO₃⁻², >FeO(UO₂)₃(OH)₅⁰, and >FeO(UO₂)₂(OH)₂⁰).

HFO data modeled with modifications to Waite et al. (1994)



Hematite data modeled using the same sorption constants & species

Evidence 3: Redox reactivity of Fe(III)/Fe(II) toward U(VI)

- 2 sorption conditions (pH 6.8): Low and high U(VI)_T, corresponding to 0.5 and 5.0 U/nm².
- Reduction occurred with low U(VI)_T, but no reduction was observed at high U(VI)_T experiment even with higher thermodynamic driving force.
- For both HFO and hematite, final redox of low U(VI)_T was consistent with goethite solubility.
- Mossbauer analysis confirmed that both HFO and hematite were partially converted to goethite, i.e. more goethite was formed than due to oxidation of Fe(II) by U(VI).
- Goethite from hematite showed wider magnetic splitting than from HFO, which is consistent with wider magnetic splitting of hematite than HFO. Therefore, goethite is present intact with the initial surfaces, not as discrete particles.

