

# High-Resolution Mineralogical Characterization and Biogeochemical Modeling of Uranium Reduction Pathways at the NABIR Field-Research Site

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In our proof-of-concept work, we have extensively studied two samples from Area 3 (FWB103-00-40E, 39.5 ft depth, and FWB103-00-42D, 42 ft) using a electron microprobe analy (EMPA) and variety of transmission electron microscopy (TEM) methods: conventional TEM amplitude-contrast imaging, high-resolution (HRTEM) imaging, selected-area electron diffraction (SAED), convergent-beam electron diffraction (CBED), energy-dispersive X-ray emission spectroscopy (EDS), electron energy-loss spectroscopy (EELS), and chemical mapping by energy-filtered TEM (EFTEM). Since we have already published this work in the premier journal *Environmental Science and Technology* (Stubbs et al., 2006), only a brief summary of this work will be given here.

The primary conclusion of our study was that there are at least three, distinct mineralogical hosts for uranium in the Area 3 core samples we studied: (1) iron oxides (including oxyhydroxides), (2) mixed Mn-Fe oxides; and (3) a discrete uranium phosphate mineral having

U:P  $\approx$  1:1 (consistent with minerals in the autunite and meta-autunite groups). As shown in Figures 1 and 2, the Fe oxides occur as two texturally different forms: pseudomorphs after pyrite (FeS<sub>2</sub>) within weathered shale and free-floating particles in the very fine-grained

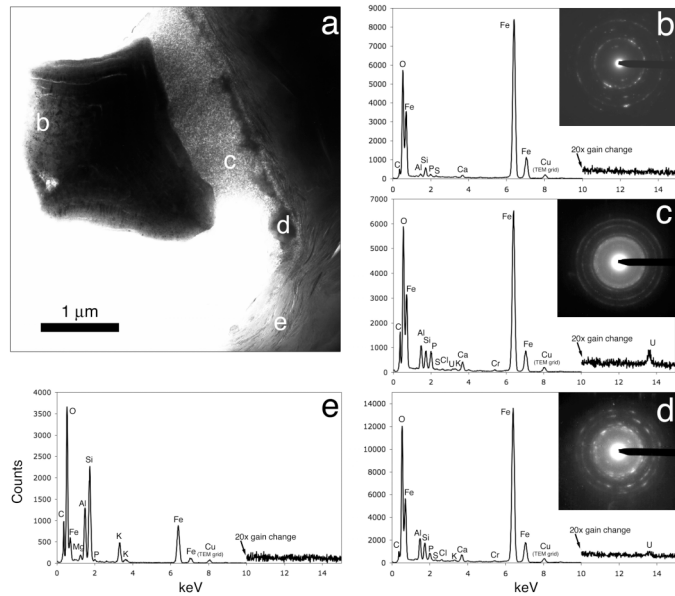
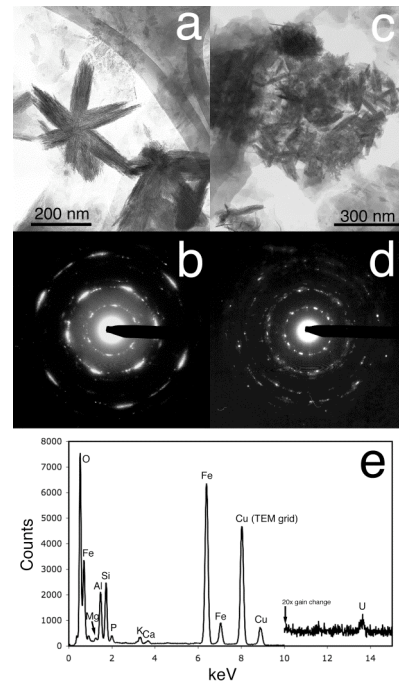


Figure 1. (a) Bright-field TEM image of iron oxide pseudomorph occurring within shale. (b-e) SAED and EDS collected from (b) hematite core with no detectable U; (c) ferrihydrite rim, which contains appreciable U and P, as well as Cr; (d) goethite halo containing lesser amounts of U and P, as well as Cr; and (e) surrounding clay matrix with no detectable U (Stubbs et al., 2006a).

Figure 2. BFTEM image and SAED from (a) and (b) star-shaped goethite twin, and (c) and (d) mass of uranium-bearing goethite. Centermost ring in each SAED ( $\sim 4.5$  Å) is contributed by clay. (e) EDS from center of goethite star shows these twins host U, P and possibly Ca. EDS also shows Al, Si, Mg and K from clay. EDS from goethite mass (not shown) is similar (Stubbs et al., 2006a).



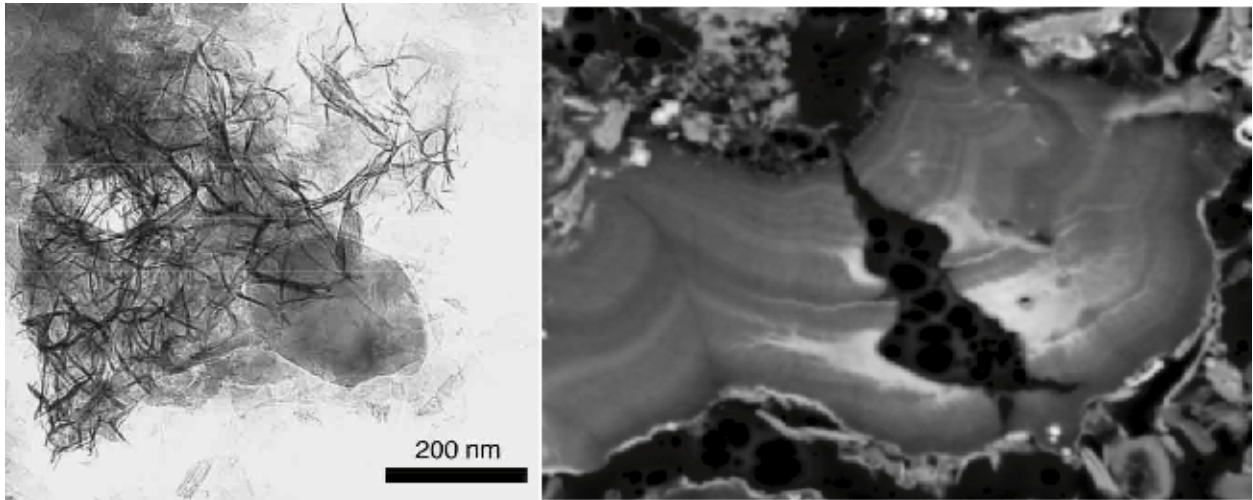


Figure 3. Uranium-containing Mn-Fe oxides. Left: Bright-field TEM image of a small particle from fines, containing U, Ba, and Pb. Right: Backscattered electron image of botryoidal, vein-filling morphology in coherent shale, containing U and Ba.

unconsolidated portions of the samples. Similarly, the mixed Mn-Fe oxides occur as both free particles and vein fillings in coherent shale (Fig. 3). Morphologically, most of the loose particles are consistent with a phyllo-manganate, whereas the vein-filling materials are probably chain and tunnel structured oxides. Perhaps the most interesting mineral host for uranium is the discrete U-phosphate mineral that occurs within coherent pieces of shale (Fig. 4). As noted above, its chemical composition is consistent with a mineral of the autunite or meta-autunite groups, and its morphology is also consistent with these uranyl phosphate layer minerals (Suzuki et al., 2005).

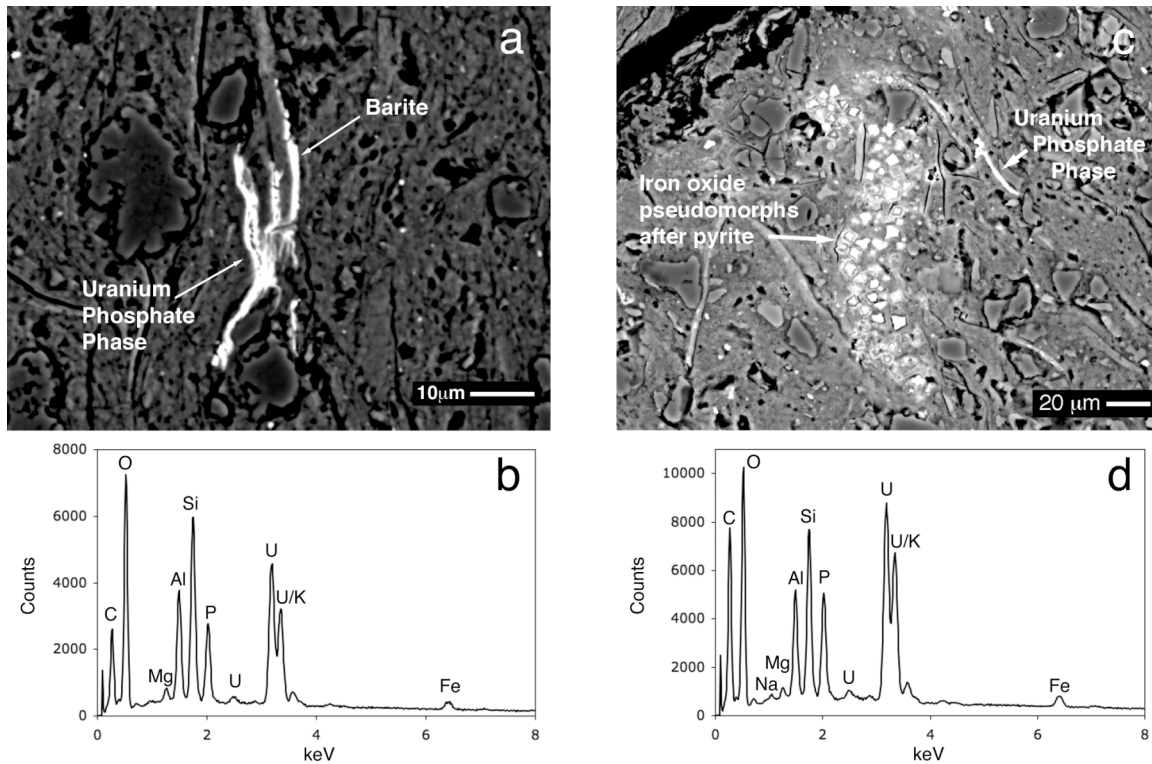


Figure 4. (a) and (c) BSE showing uranium phosphates. (b) and (d) EDS of uranium phosphates. Other peaks in spectra may result from difficulty in isolating phases under the beam (Stubbs et al., 2006a).

It is interesting to note, and perhaps very significant, that in all of these different hosts uranium is always associated with phosphate. Immobilization of uranium by phosphorus has been observed previously in nature (Jerden and Sinha, 2003; Jerden et al., 2003; Murakami et al., 2005) and could also be an important process at the Oak Ridge FRC.

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