 ROBL-CRG	Experiment title: Uranium sorption onto natural iron colloids in mine waters	Experiment number: 20-01-632
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Report:

We applied Fe K-edge EXAFS spectroscopy to elucidate the molecular structure of ferrihydrite contributing by ~65% to colloids of an abandoned uranium mine (# M2) [1]. Ferrihydrite reference samples were prepared in a N₂ flushed glove box ($p_{\text{CO}_2} < 0.2 \text{ Pa}$) both in the absence (# FhN₂) and in the presence of 50 μM UO₂(NO₃)₂ (# FhUN₂) by rising the pH of a 1 mM Fe(NO₃)₃·9H₂O solution with NaOH up to 5.5. EXAFS spectra of the frozen pastes were collected in transmission mode using a He cryostat (30 K).

Results.

The first peak of the Fourier transform (FT) corresponds to five or six oxygen atoms coordinated to the absorbing Fe atom by two different atomic distances (R) (Fig. 1a). Up to three O-atoms were found to be coordinated with $R_{\text{Fe-O1}} \sim 1.94 \text{ \AA}$ and $R_{\text{Fe-O2}} \sim 2.06 \text{ \AA}$, respectively. The second FT peak fits to three Fe-Fe shells with $R_{\text{Fe-Fe1}} = 2.89\text{-}2.96 \text{ \AA}$, $R_{\text{Fe-Fe2}} \sim 3.07 \text{ \AA}$, and $R_{\text{Fe-Fe3}} = 3.37\text{-}3.45 \text{ \AA}$. Including a fourth Fe shell with $R_{\text{Fe-Fe4}} = 3.92\text{-}4.00 \text{ \AA}$ improved the fit of oscillations at higher k values and explained the third FT peak. Neither the EXAFS of sample FhUN₂ nor the calculated difference with spectrum FhN₂ give evidence on the adsorbed U(VI).

Discussion.

The splitting of the O-shell into two subshells is due to Fe-O and Fe-OH bonds, confirming the formation of octahedral clusters by deprotonation [2]. Although the Fe-Fe distance of 2.89 Å suggests face sharing octahedra in M2, the structural data do not support hematite, but instead a highly polymerized intermediate stage on the transition from ferrihydrite to hematite [3]. The Fe-Fe₁ distance of ~2.95 Å cannot be unequivocally attributed to either face sharing or edge sharing linkage. Therefore, the calculated distances of 3.00±0.07 Å and ~3.45 Å are explained by edge sharing and double-corner sharing linkage, respectively [4]. Two Fe octahedra sharing a single corner exhibit an Fe-Fe distance of 3.92-4.00 Å [5]. The type and number of linkages were combined to a representative basic unit (indicated by dashed circle in Fig. 1b) which consists of six Fe(O,OH)₆ octahedra in planar arrangement; four of them are coordinated by edges, and two octahedra are linked to this tetrameric unit by sharing double-corners. Each basic unit representing a section of the homogenous network is linked to two other units of the same type by sharing a single corner (modified from [4]).

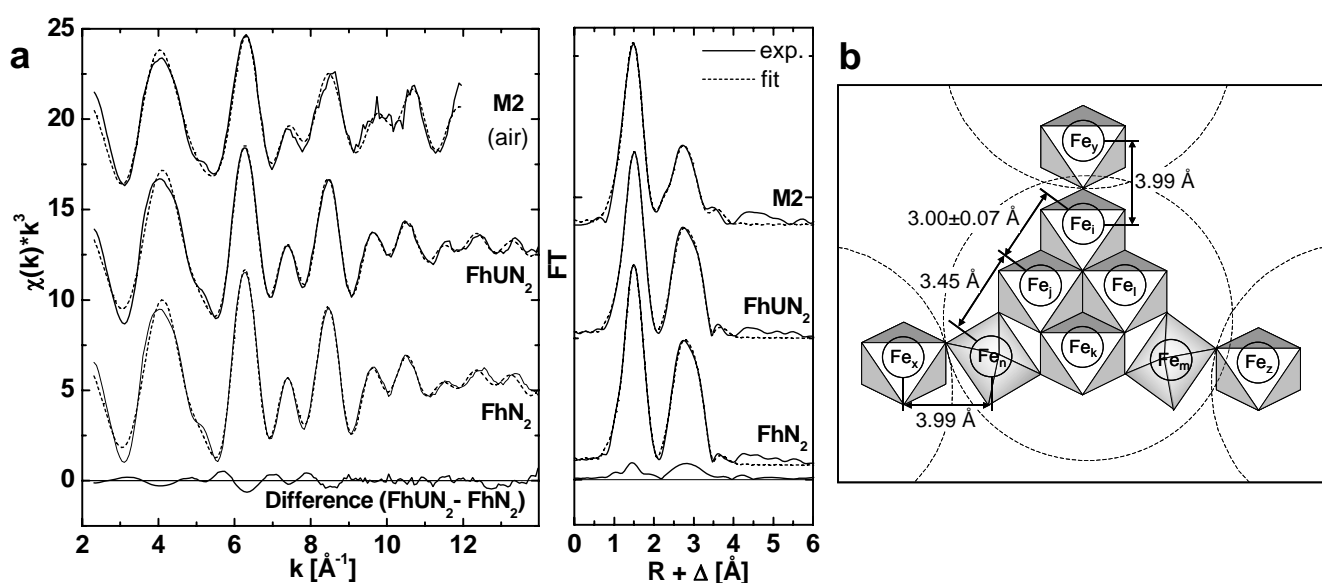


Fig. 1a. Fe K-edge EXAFS spectra and FTs of ferrihydrite (M2: mine water colloid sample; FhUN₂ and FhN₂: samples prepared with and without U(VI) at $p_{CO_2} < 0.2$ Pa). **b.** Molecular topology of ferrihydrite fundamental unit fitting these EXAFS data.

References

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