Uranium(V) incorporation mechanisms and stability in Fe(II)/Fe(III) (oxyhydr)oxides

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Abstract
Understanding interactions between radionuclides and mineral phases underpins site environmental clean-up and waste management in the nuclear industry. Transport and fate of radionuclides in many subsurface environments are controlled by adsorption, redox and mineral incorporation processes. Interactions of iron (oxyhydr)oxides with uranium have been extensively studied due to the abundance of uranium as an environmental contaminant and ubiquity of iron (oxyhydr)oxides in engineered and natural environments. Despite this, detailed mechanistic information regarding the incorporation of uranium into Fe(II) bearing magnetite and green rust is sparse. Here, we present a co-precipitation study where U(VI) was reacted with environmentally relevant iron(II/III) (oxyhydr)oxide mineral phases. Based on diffraction, microscopic, dissolution and spectroscopic evidence, we show the reduction of U(VI) to U(V) and stabilisation of the U(V) by incorporation within the near-surface and bulk of the particles during co-precipitation with iron (oxyhydr)oxides. U(V) was stable in both magnetite and green rust structures and incorporated via substitution for octahedrally coordinated Fe in a uranate-like coordination environment. As the Fe(II)/Fe(III) ratio increased, a proportion of U(IV) was also precipitated as surface associated UO\textsubscript{2}. These novel observations have significant implications for the behaviour of uranium within engineered and natural environments.
Introduction

Uranium is a problematic contaminant at nuclear sites, and is the dominant radionuclide by mass in radioactive wastes destined for geological disposal. Groundwater conditions under both scenarios range from mildly acidic to alkaline, and oxic to anoxic.\textsuperscript{1-4} The oxidation state of uranium is a significant control on its mobility. Under oxic conditions, soluble and environmentally mobile U(VI) dominates; under anaerobic conditions, uranium is typically reduced to poorly soluble U(IV). During biological and abiotic reduction of U(VI), U(V) reportedly forms as a transient species.\textsuperscript{5-7} Recent work has also suggested that U(V) can be stabilized at mineral surfaces\textsuperscript{8-12} and via incorporation into environmentally relevant iron (oxyhydr)oxide phases such as goethite ($\alpha$-FeOOH) and magnetite (Fe$^{II}$/Fe$^{III}$$_2$O$_4$).\textsuperscript{13-21} Indeed, establishing the extent of U(V) stability on interaction with Fe (oxyhydr)oxides is essential in underpinning predictive models for U behavior in environmental systems which currently do not recognise the presence of U(V). To achieve this, U speciation needs to be determined at a molecular scale which is a key step in defining the significance of U(V) in environmental systems and in developing realistic models to predict the environmental fate of uranium.

Fe(II)/Fe(III) bearing (oxyhydr)oxide minerals such as magnetite and green rust\textsuperscript{22} (e.g. [Fe$^{II}$/Fe$^{III}$]$_3$(OH)$_4$[Cl,nH$_2$O]) are ubiquitous in anoxic subsurface environments (e.g. soils, and sediments), forming via a variety of biogeochemical processes\textsuperscript{23,24} and during the anaerobic corrosion of steel, a significant component in contaminated, engineered environments and geological disposal facilities.\textsuperscript{25-27} Recent studies have suggested possible pathways of how U(VI) reduction occurs at the magnetite surface.\textsuperscript{8,10,11,28} Some studies suggest U(VI) is reduced to directly form U(IV)\textsuperscript{29}, whereas other studies show U(VI) is reduced to U(V) via a one electron transfer process, and then disproportionate to form U(IV).\textsuperscript{28,30} Previous spectroscopic studies have suggested that U(V) can be stabilized via its incorporation into magnetite within the octahedral sites in a distorted uranate-like coordination, although the exact structural site has not been conclusively determined, and no information on U(V) stabilisation in other Fe(II)/Fe(III) (oxyhydr)oxides (e.g. green rust) is currently available.\textsuperscript{8,16,19} Theoretical simulations of U incorporation into iron (oxyhydr)oxide minerals have provided information on the U(VI) and U(V) coordination environment when substituted for octahedrally coordinated Fe within the magnetite structure.\textsuperscript{21,31} Recently, advances in spectroscopic techniques have also demonstrated that U(IV), U(V) and U(VI) can be distinguished using high energy resolution fluorescence detected-X-ray absorption near edge structure (HERFD-XANES) techniques.\textsuperscript{19} Ultimately, if U(V) is incorporated into the structure of Fe(II)/Fe(III) (oxyhydr)oxides after U(VI) reduction, this could prevent disproportionation and lead to long term immobilisation of U(V). However, the pathway and mechanism of U(V) incorporation into magnetite and green rust are either poorly defined or yet to be determined.

Here, we synthesised both magnetite and green rust with U(VI) via a co-precipitation process. We then gained detailed molecular scale insights into the speciation and atomic-scale mechanisms of incorporation of U within the mineral structures using state-of-the-art HERFD-XANES spectroscopy in combination with extended X-ray absorption fine structure (EXAFS) spectroscopy. Synchrotron analysis unequivocally confirmed the reduction of U(VI) to stabilized, octahedrally coordinated U(V) which is incorporated within both magnetite and green rust. This facile stabilization of U(V) within these bulk mineral phases may have
important implications for the fate of U in engineered and natural environments where U(VI) has typically been considered transient.

**Methods**

**Mineral synthesis and characterisation** Uranium bearing magnetite and green rust were synthesized using a direct co-precipitation method with experiments performed at room temperature in an anaerobic chamber. In brief, solutions of 0.1 M FeCl₂, 0.2 M FeCl₃, 0.3 M HCl and 0.0126 M U(VI)Cl₆ were mixed for 24 hours before mineral precipitation was induced by introduction of the Fe(II)/Fe(III) solution into a N₂ sparged 28-30% w/v NH₄OH solution (pH 11) under continuous stirring over 15 minutes to a final pH of 9. This led to the instantaneous co-precipitation of the uranium doped minerals. Four different starting Fe(II)/Fe(III) ratios were used to form magnetite and green rust:

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x = \frac{Fe(II)}{Fe(III)} = 0.5, 0.6, 0.8 \text{ or } 2.0
\]

After reaction, the solid samples were analyzed by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) to characterize the structure, particle size and morphology. The distribution of uranium within the iron (oxyhydr)oxides particles was determined using acid dissolution performed as a function of [H⁺] in solution.

**X-ray Absorption Spectroscopy (XAS)** Uranium L₃ edge XAS spectra were collected on wet mineral pastes at Diamond Light Source, beamline B18 in a liquid N₂ cryostat in fluorescent mode using a Ge detector. Analysis of the EXAFS spectra was performed in Artemis and Athena with details given in the SI. U M₄ edge HERFD XANES spectra were collected at European Synchrotron Radiation Facility, beamline ID26 through the use of a X-ray emission spectrometer and analysed using iterative transformation factor analysis to determine the proportion of U(IV), U(V) and U(VI) in the samples.

**Results and Discussion**

Co-precipitation experiments were performed to determine the speciation of uranium following co-precipitation with either magnetite or green rust. The Fe(II)/Fe(III) (oxyhydr)oxides were co-precipitated with U(VI) at starting Fe(II)/Fe(III) ratios of 0.5/0.6 to synthesise magnetite and 0.8/2.0 to synthesise green rust (Figure S1). Additionally, transmission electron microscopy showed the magnetite was nanoparticulate, with particle sizes ranging from 1 to 20 nm (Figure S2). Green rust was present as pseudo-hexagonal plates of approximately 50 - 600 nm, and energy dispersive X-ray analysis showed chloride was present, indicating green rust chloride formed (Figure S3).

**Reduction of U(VI) to stable U(V).** Uranium M₄ edge HERFD XANES spectra were used to determine the oxidation state of U associated with the Fe(II)/Fe(III) (oxyhydr)oxide phases (Figure 1). The energy of the XANES peak position showed a systematic decrease with increasing Fe(II)/Fe(III) ratio (Figure S4) from 3726.5 eV (at 0.5 Fe(II)/Fe(III)) to 3726.3 eV (at 2.0 Fe(II)/Fe(III)). Comparison with the peak position of the U oxidation state standards (U(VI) = 3726.95 eV, U(V) = 3726.4 eV and U(IV) = 3725.2 eV) suggests that U(V) dominated in all of the samples. Furthermore, there were no indications of the higher energy peaks (3728.7 eV and 3732.0 eV) which are typical of U(VI). However, in the Fe(II)/Fe(III) = 2.0
spectra, the small shoulder on the low energy side of the XANES spectrum confirms the presence of U(IV) (Figure 1). Iterative transformation factor analysis (ITFA) of the HERFD-XANES data identified the three main component present in the samples (Figure S5) and indicated that at Fe(II)/Fe(III) = 0.5 – 0.8, 87-96 % of U was present as U(V), with the remainder contributing from U(VI) for Fe(II)/Fe(III) = 0.5 and U(IV) for Fe(II)/Fe(III) = 0.6 and 0.8 (Table S1). At Fe(II)/Fe(III) = 2.0, U(V) still dominated but the amount of U(IV) had increased to approximately 28 % in this sample. The L3-edge XANES also supports stabilisation of U(V) with XANES edge positions for all the samples (17171.2 eV – 17169.6 eV) between those of U(VI) (17173.4 eV) and U(IV) (17170.3 eV). Additionally, shifts in the U L3-edge XANES post-edge resonance features to a lower energy relative to the uranyl U(VI) standard indicate the formation of a uranate-like coordination consistent with the reported U coordination within magnetite (Figure S6).

**Figure. 1:** U M₄ edge HERFD-XANES of U co-precipitated with magnetite (Fe(II)/Fe(III) = 0.5 and 0.6) and green rust (Fe(II)/Fe(III) = 0.8 and 2.0) with standards U(IV)O₂, U(IV)₂U(V)₂O₉ and U(VI) adsorbed to ferrihydrite. Grey arrows indicate characteristic U(V) features.

**U incorporation within magnetite and green rust.** U L₃ edge EXAFS spectra (Figure S7, Table S2) were analysed to determine the molecular scale speciation of U associated within the magnetite and green rust mineral phases. For U associated with magnetite (Fe(II)/Fe(III) = 0.5 and 0.6), the best fits confirm 4-4.5 oxygen backscatterers at 2.17(1)Å, indicative of uranate-like coordination, which is consistent with our interpretation of the L₃ edge XANES spectra. The lower U-O coordination number than would be predicted for an octahedral site (i.e. <6), is due to the presence of a proportion of U(IV)O₂ or U(VI) within the samples. The fitting of Fe shells to the EXAFS was then informed assuming that U incorporation into magnetite occurred by substituting U for Fe at an octahedrally coordinated Fe site. The fits confirmed the presence of two U-Fe shells at 3.20(2) Å and 3.72(2) Å for Fe(II)/Fe(III) = 0.5 and 3.15 (2) Å and 3.69 (3) Å for Fe(II)/Fe(III) = 0.6, showing a systematic and significant increase in the interatomic distance relative to the Fe-Fe
distances in magnetite (2.97 Å and 3.48 Å respectively\(^{38}\)). In Fe(II)/Fe(III) = 0.6, the additional
U-O and U-U backscattering shells observed at 2.42(3) Å and 3.89(2) Å respectively, reflect
the presence of U(IV) supporting the HERFD-XANES data, and assuming an error of ±1 on the
coordination number, the proportions of U(IV) are within error (i.e. 4-20% U(IV)). Finally,
the presence of oxygen backscatters at 1.81(2) and 2.43(2) Å in the fit for the Fe(II)/Fe(III)
= 0.5 sample suggests a modest contribution from U(VI) in uranyl dioxygenyl coordination as
confirmed by the ITFA analysis, and has previously been attributed to U(VI) adsorbed to
magnetite.\(^{8,15}\)

For samples Fe(II)/Fe(III) = 0.8 and 2.0, the U-O coordination environment in green rust
showed differences when compared to the magnetite system, with U-O distances at
approximately 1.90(6) Å and 2.17(1) Å again indicative of uranate-like coordination. Similar
to the magnetite systems, additional U-O and U-U shells at 2.46(2) Å and 3.89 (1) Å confirm
the presence of U(IV)O\(_2\) which is consistent with the HERFD -XANES analysis and previous
studies.\(^{25,48}\) Similar to the magnetite system, fitting of additional Fe shells was informed by
the green rust structure and assumes direct substitution of octahedrally coordinated Fe by
U. The best fits include 6 Fe at 3.09(1) Å and 3.28(2) Å with an additional shell of 4 Fe at
5.25(3) Å. These fits are consistent with the Fe-Fe distances in green rust, which are 3.19 Å
and 5.52 Å respectively. The dissolution experiments for the Fe(II)/Fe(III) = 0.5, 0.6 and 0.8
samples (Figure S8) show an initial release of 35 - 40% of U with minimal Fe dissolution,
followed by congruent diss
olution of U and Fe. This suggests that 60-65% of the U is distributed within the
magnetite/green rust particles with the remaining present as discrete U phases (i.e. UO\(_2\)) or
near-surface associated U(V)/U(VI).

Overall, the EXAFS and dissolution data confirm that U(V) is incorporated within octahedral
sites in the Fe(II)/Fe(III) (oxyhydr)oxide phases in a uranate-like coordination environment.
This is consistent with several recent experimental and theoretical reports showing U can
directly substitute for octahedrally coordinated Fe in iron (oxyhydr)oxide mineral
phases.\(^{8,15,16,19,31}\) The current work extends these observations to systems where U(V) is the
dominant species during direct precipitation of magnetite and green rust for the first time.

Mechanism of U(V) incorporation into magnetite and green rust.

Our results show that direct co-precipitation of U(VI) with magnetite and green rust leads to
reduction of U(VI) to U(V) and subsequent stabilization within the bulk structure of both
minerals. The stabilization of U(V) via incorporation into Fe(II)/Fe(III) bearing iron
(oxyhydr)oxides has been hypothesised in several systems\(^{8,15,16}\) with very recent work
postulating U(V) stabilisation via incorporation into magnetite.\(^{19}\) For the current work, in
both systems U(V) is incorporated into the mineral structures via direct substitution of U for
octahedrally coordinated Fe. In magnetite the average U(V)-O bond length is 2.17(1)
(Fe(II)/Fe(III) = 0.5 and 0.6) consistent both with U(V) in uranate-like coordination\(^{19,47}\) and
also with recent atomistic simulations which predict a U-O distance of 2.08 Å for this
system.\(^{19,31,49}\) The U-Fe interatomic distances derived from the EXAFS data (i.e. 3.15-3.20 Å
and 3.69-3.72 Å) are consistent with those previously published.\(^{19}\) The U-Fe distances are ≈
0.2 Å longer than the Fe-Fe distances in magnetite, but the distance between the two Fe
shells matches that of pure magnetite (≈ 0.5 Å, Table S2). Again these values are consistent
with U(V) incorporation simulations for the first Fe shell (3.15 Å) in magnetite.\(^{31}\) The reason
for the increased interatomic distances is unlikely to be the size of the incorporated U(V)
(the octahedral crystal radius for U(V) is 0.9 Å, and for Fe(II) / Fe(III) are 0.92 / 0.785 Å);
rather increased repulsive electrostatic interactions between U(V) and the Fe(II/III) atoms pushed the iron out.\textsuperscript{31} The low coordination numbers of the U-Fe shells relative to pure magnetite (2 vs. 6), are likely due to the nanoparticulate nature of magnetite which leads to a proportion of the U being near-surface associated.\textsuperscript{50} This is consistent with the dissolution data which shows (Figure S8) 35-40\% of U is released with minimal Fe dissolution, suggesting this fraction is near-surface associated U(V)/U(VI) and UO\textsubscript{2}, with the remaining U distributed evenly throughout the particles. The presence of U(IV) at the (near-)surface of the particles is likely due to the presence of Fe(II) which provides strong reducing conditions resulting in the reduction of sorbed U to U(IV) surface complexes which can transform to UO\textsubscript{2} particles.

The incorporation of U(V) into green rust (Fe(II)/Fe(III) 0.8 and 2.0) again occurs via direct substitution for octahedrally coordinated Fe within the sheet structure of the layered double hydroxide. In addition, the dissolution data indicates that 35-40\% of U is present as a discrete phase or is near-surface associated, which is consist with the presence of UO\textsubscript{2} in the XAS, formed via the process stated above, and some near-surface associated U(V). The EXAFS data indicate that the U(V) local coordination is different to that observed in magnetite (Figure S7). Indeed, the best fit for these samples confirmed 2 oxygens at ≈1.9 Å, and a shell of 4 equatorial oxygens at 2.17 Å, again consistent with uranate-like coordination environment (Table S2). This difference in the U(V)-O coordination relative to magnetite is presumably due to the layered structure of the green rust similar to that seen for U(V) incorporation into other layered iron (oxyhydr)oxides (i.e. lepidocrocite).\textsuperscript{51} Here, incorporation of U(V) within isolated octahedral sheets evidently provides significantly less steric constraint on the U(V)-O octahedron relative to U(V) in the highly constrained cubic spinel structure of magnetite. The variation in the axial and equatorial U-O bond lengths in the U(V) incorporated within green rust clearly leads to local distortion of the green rust octahedral sheet and splitting of U-Fe distances relative to the Fe-Fe distances in green rust (Table S2). Overall, the best fit indicates three to four Fe-O octahedra adjacent to the short (1.9 Å) U-O axial oxygens, and approximately two Fe-O octahedra adjacent to the long (2.17 Å) U-O equatorial oxygens (Figure 2). This is consistent with the U(V) being present in a distorted octahedral environment and is presumably due to the enhanced flexibility of the octahedral sheet in green rust compared to octahedral sites within cubic magnetite.

The novel incorporation of U(V) in green rust is in contrast to previous sorption studies where U(IV) surface complexes or UO\textsubscript{2}(s) were observed as the reaction end products.\textsuperscript{25,48,52}

\textbf{Figure 2:} (a) Magnetite structure showing Fe-Fe distances\textsuperscript{38} and U-Fe distances obtained from EXAFS of Fe(II)/Fe(III) = 0.6; (b) Green rust structures showing Fe-Fe distances\textsuperscript{40} and U-
Fe distances obtained from EXAFS of Fe(II)/Fe(III) = 2.0. Yellow lines indicate shorter U-O distances (1.9 Å) and white lines indicate longer U-O distances (2.17 Å).

The observed energy shift of the U(V) M4 edge HERFD-XANES main peak position (Figure 1) for different Fe(II)/Fe(III) ratios (Figure S4) from 3726.5 eV (Fe(II)/Fe(III) = 0.5) to 3726.3 eV (Fe(II)/Fe(III) = 2.0) may relate to different strengths of the covalent bond between the U and neighbouring atoms.53 Electronic structure calculations (Figure S9) show a clear difference in the distribution of density of states for U incorporated into the octahedral site of magnetite relative to green rust. The hybridization between U f-states and Fe d-states above the Fermi level are much stronger for U incorporated into green rust relative to magnetite. This may be associated with a stronger, more covalent, U bond in green rust compared to the U bond in the magnetite structure.

**Mechanism of U(V) stabilization.** Our results suggest that U(V) incorporation during magnetite and green rust formation occurs via a two-step process (abstract art). Firstly, we suggest that U(VI) is adsorbed to the surface of the growing Fe(II)/Fe(III) (oxyhydr)oxide nanoparticles and undergoes reduction to U(V) via one electron transfer. Secondly, during rapid crystal growth the U(V), which is compatible with the Fe octahedral site in both magnetite19 and green rust, becomes incorporated within the structure. These steps are consistent with those proposed for U(V) incorporation during goethite formation14, however further research is required to determine the exact nature of each step in the process.

Recent work has highlighted that disproportion of U(V) can occur on the magnetite surface, implying that stabilization of structural U(V) may only occur during rapid crystal growth rates.10 Under these conditions, isolation of U(V) within the mineral structure may prevent its disproportionation to U(IV) and U(VI). Indeed, U(V) is reportedly stable for up to 550 days suggesting that incorporated U(V) may be stable over extended time periods.15 Furthermore, steric constraints seem likely to favour U(V) stabilisation in these systems as U(IV) strongly prefers larger coordination environments (e.g. n = 8).8,13,20 Indeed, steric constraints may be the most crucial factor in stabilising U(V) as both magnetite and green rust are electrically conductive54 and therefore physical isolation of U(V) alone seems unlikely to prevent disproportionation.

**Implications for U speciation and fate in the environment**

Here, we have shown the reduction of U(VI) to U(V) followed by incorporation into both magnetite and green rust is the dominant process during the direct precipitation of these mineral phases. The potential for U(V) incorporation processes to be dominant in these environmentally relevant phases is certainly highlighted in this and other very recent work19 and has important, and as yet not fully explored implications for understanding and predicting U mobility in engineered and natural environments. Clearly, the extent of U(V) incorporation into Fe(II)/Fe(III) (oxyhydr)oxides forming under contaminated land and geodisposal conditions needs to be fully quantified. Incorporation of U(V) into mineral phases commonly present in contaminated environments may offer a more resilient species to oxidative remobilisation compared to uraniumite and adsorbed U(IV) which are readily oxidised to soluble U(VI) in many environmental systems.16,55 The incorporation of U(V) in magnetite and green rust offers a promising prospect to optimise its incorporation in a range of engineered settings whilst the stability of U(V) in these systems clearly warrants further investigation.
Supporting Information Available: Additional figures and tables showing XRD patterns, TEM images and EDS analyses, HERFD-XANES data and fitting results, EXAFS fitting parameters, dissolution data and a description of the EXAFS fitting process.

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