Role of Nano-Goethite in Controlling U(VI)

Sorption-Desorption in Subsurface Soil

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Abstract

Iron oxide nanoparticles in natural soils and sediments can be nanoporous due to the aggregation of nanoparticles. Nanopores can greatly affect the sorption-desorption as well as reduction-oxidation behavior of U(VI) because of their high internal surface area and nanopore confinement effects. Batch U(VI) sorption-desorption experiments were conducted to understand the role of nano-goethite in controlling U(VI) sorption-desorption behavior in saprolite subsoil from Oak Ridge Field Research Center (ORFRC), Tennessee, a premier field research site for environmental remediation. The subsoil samples from ~6.5-8.5 m depth were nearly homogeneous in mineral composition (quartz, illite and smectite) and particle size distribution. The subsoil samples were characterized by a range of dithionite-citrate-bicarbonate (DCB) extractable Fe(III) oxide content (127-404 $\mu\text{M/g}$), BET surface area (25-38 m^2/g), and nanoporosity (pore size < 10 nm; 16-30 $\mu\text{L/g}$). Transmission electron microscopy (TEM) imaging and X-ray energy dispersive spectroscopy (EDS) analyses revealed that aggregated goethite nano-crystals were poorly crystalline and nanoporous, and U(VI) sorption was dominantly associated with those nanoporous goethite aggregates rather than clay minerals. U(VI) sorption to the saprolite subsoils at circumneutral pH increased with higher amount of nanoporous goethite in the presence of a range of Ca^{2+} and HCO_3^- . Sequential extraction of U(VI) pre-sorbed to saprolite subsoils with NaHCO_3 (1, 10, and 100 mM) exhibited more resistant U(VI) desorption from soils containing higher amount of nanoporous goethite. This study suggests that nano-crystalline goethite with nanoporous structure may exert a significant role in controlling the mobility and transport of U(VI) in subsurface environment where nanoporous minerals are ubiquitous and abundant.

Keywords: Uranium, Nanopores, Goethite, Sorption, Saprolite

1. Introduction

Subsurface soil/sediment and groundwater have been contaminated with uranium at numerous uranium mining and nuclear weapons manufacturing sites, posing a human health and environmental threat (Lottermoser and Ashley, 2005; McKinley et al., 2007; Neiva et al., 2014). In natural environments, uranium occurs mainly in the form of U(IV) and U(VI) depending on redox state (Langmuir, 1997). U(VI) is the dominant species in oxic aquifers, and its mobility is governed by sorption-desorption processes. The mobility of U(VI) increases with U(VI) complexation by carbonate species and calcium (Dong et al., 2005; Fox et al., 2006; Wazne et al., 2003), which are common chemical components in groundwater.

Uranium mobility and transport have been investigated by numerous batch and column experiments using synthetic Fe or Al oxides, as well as natural sediments and soils (Barnett et al., 2002; Barnett et al., 2000; Davis et al., 2004; Hsi and Langmuir, 1985; Sylwester et al., 2000). However, mechanistic understanding of uranium sorption-desorption behavior in subsurface environments is complicated by the chemical and physical heterogeneity of subsurface materials. Thus, results from laboratory sorption experiments using pure synthetic minerals may not properly represent the chemical reactions occurring in natural systems. For instance, although nanopores are ubiquitous in porous geologic media and provide the most reactive surface area, the role of nanopores in controlling the mobility of inorganic and organic contaminants remains poorly understood (Hochella, 2008; Wang et al., 2003) because most of laboratory batch or column sorption experiments have been conducted using non-nanoporous materials. A strong time-dependence of sorption and non-reversible desorption behavior, as well as partial and incomplete redox reaction that are frequently observed in natural soil or sediment, have been attributed to the effect of nanopores or micropores (Hochella, 2008; Jeon et al., 2004;

Pignatello and Xing, 1996; van Beinum et al., 2005). Ferric iron oxides (e.g., ferrihydrite, goethite, and hematite), which are widely thought to be the most important sorbents for U(VI) under circumneutral pH, are likely nanoporous in natural sediments/soils due to the aggregation of nanoparticles (Banfield et al., 2000; Gilbert et al., 2009; van der Zee et al., 2003). Nanopores can greatly affect the sorption-desorption or reduction-oxidation behavior of U(VI) because of their high internal surface area and nanopore confinement effects (Jung et al., 2012; Senapati and Chandra, 2001; Wang, 2014; Wang et al., 2003).

Although numerous studies have investigated the role of Fe(III) oxides in controlling U(VI) sorption or desorption using synthetic minerals or natural soil/sediments (Barnett et al., 2002; Barnett et al., 2000; Curtis et al., 2004; Fox et al., 2006; Hsi and Langmuir, 1985; Kohler et al., 2004; Waite et al., 1994), few studies have focused on the mechanistic role of Fe(III) oxide nanoparticles in natural subsurface soil/sediment. In order to understand the role of natural Fe(III) oxide nanoparticles in regulating U(VI) sorption-desorption behavior in subsurface soil, we conducted batch sorption and desorption experiments with natural saprolite subsoils from Oak Ridge Field Research Center (ORFRC), which contained various amounts of nano-goethite. Nanoporous structure of nano-goethite in the saprolite subsoils was investigated by high resolution transmission electron microscopy (TEM) imaging.

2. Material and methods

2.1. Samples Preparation

Subsurface soil cores (5 cm diameter) were collected at the Area 2 site of Oak Ridge Field Research Center (ORFRC), Tennessee as previously described (Moon et al., 2006). The soil core tubes were sealed with plastic caps immediately after sample collection and stored at 4°C. The

ORFRC was established within the Y-12 National Security Complex area on the Department of Energy's Oak Ridge Reservation in Oak Ridge, TN to serve as a premier field research site for environmental remediation (Moon et al., 2006).

Materials were retrieved from ca. 90-cm lengths of native saprolite at 6.5-9 m depth below the ground surface. The core sections were air-dried, sieved through a 2 mm sieve, and thoroughly homogenized. A portion of sample was extracted with 10% nitric acid (1.6 N) (Fisher, trace metal grade) for 2 days to determine total solid phase U, and with the dithionite-citrate-bicarbonate (DCB) to determine the amount of Fe(III) oxides (e.g., goethite, ferrihydrite) (Jackson, 1986). For the DCB extraction, 2.5 g of the sieved saprolite soil was reacted with 20 mL of 0.3 M sodium citrate solution, 2.5 mL of 1 M sodium bicarbonate solution and 0.5 g sodium dithionite at 80 °C for 15 minutes with vigorous stirring. After the supernatant was collected, the same extraction was repeated. The DCB extractable Fe is the sum of the first and second extractions.

Based on DCB extractable Fe, three samples (GP-4-5-00, GP-4-4-25, and GP-3-5-00 at ~6.5-8.5 m depth) containing background levels of U ($< 0.01 \mu\text{M/g}$ by 10% HNO_3 for 2 days) and a range of Fe(III) oxide content (7138, 11161, and 22582 mg/kg Fe) were selected, and will be referred to as low Fe(III) soil, medium Fe(III) soil, and high Fe(III) soil, respectively (Table 1). Specific surface area and pore size distribution were determined using a surface area and pore size analyzer (NOVA e4200, Quantachrome Instruments) by BET (Brunauer-Emmett-Teller) method and BJH (Barrett-Joyner-Halenda) method, respectively. The standard reference material (Quantachrome Instruments; $108 \text{ m}^2/\text{g}$) confirmed that the analytical error is less than $\pm 5\%$.

2.2. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis

X-ray diffraction analyses were carried out using a Rigaku Rapid II X-ray diffraction system with a 2-D image plate (Mo K α radiation). The two-dimensional images were integrated to produce conventional 2 θ -I patterns using Rigaku's 2DP software. Mineral identification was conducted using JADE software (Materials Data Inc., Livermore, CA) with a database published by the Joint Committee on Powder Diffraction Standards (International Center for Diffraction Data, Newtown Square, PA). TEM and SAED (Selected Area Electron Diffraction) measurements were carried out using a FEI Titan 80-200 FEG-TEM/STEM microscope equipped with an X-ray EDS (Energy Dispersive Spectroscopy) analyzer and Gatan Image Filtering (GIF) system to provide a high resolution image of goethite nano-crystals. All the TEM samples were prepared by dropping solid suspension drops onto holey carbon-coated TEM copper grids and dried in air. After reacting saprolite subsoil samples (0.2 g) with 0.1 M NaNO₃ solution containing 150 μ M U(VI) and 1 mM NaHCO₃ at pH 6.8 buffered by 10 mM PIPES (1,4-piperazinediethanesulfonic acid) for 1 week, the U(VI) sorbed on goethite nanoparticles and clays was analyzed by TEM-EDS.

2.3. Batch Sorption-Desorption Experiments

One gram of dry soil was placed in a 15 mL plastic centrifuge tube (Fisher Scientific), and 10 mL of a solution containing U(VI)-acetate (50-95 μ M), NaHCO₃ (0.1–5 mM), and Ca(NO₃)₂ (0–10 mM) was added. Ca²⁺ and HCO₃⁻ have a significant impact on the aqueous speciation of U(VI), and consequently, on the sorption and mobility of U(VI) in aquifers because of the formation of uranyl calcium carbonate and uranyl carbonate species (Fox et al., 2006). The concentration range of Ca²⁺ and HCO₃⁻ were selected to represent typical fresh groundwater compositions. The solution pH was initially adjusted to 6.3 by adding 0.1 N HNO₃ or 0.1 N

NaOH and using a pH meter (Accumet XL20, Fisher Scientific). For sorption kinetics experiments, the tubes were shaken at 250 rpm for 20 minutes to 2 days in the presence of 95 μM U(VI), 1 mM HCO_3^- and 0-10 mM Ca^{2+} . Additional sorption kinetics experiment was conducted by reacting 50 μM U(VI) with the soil samples (1 g) in 0.1 M NaNO_3 solution (10 mL) containing 2.5 mM Ca^{2+} and 5 mM HCO_3^- at equilibrium pH of ~ 6.5 -7.0 for 2 weeks. For sorption equilibrium experiments, the tubes were shaken at 250 rpm for 2 days in the presence of 90 μM U(VI) and 0.1-5 mM HCO_3^- or for 7 days in the presence of 95 μM U(VI), 1 mM HCO_3^- , and 0-10 mM Ca^{2+} (3 replicate sets) at equilibrium pH of ~ 6.5 -7.0. For all experiments, ionic strength was adjusted to 0.1M with NaNO_3 . After reaction, the supernatant was collected by centrifugation at 3000 rpm for 10 minutes and analyzed as described below. The final pH was measured using a pH meter (Accumet XL20, Fisher Scientific).

After 2-day sorption experiments of 90 μM U(VI), the soil samples were rinsed twice with deionized water, and then subjected to sequential desorption by 10 mL of 1, 10, and 100 mM NaHCO_3 . Each desorption step lasted 24 hrs. A set of soil samples exposed to 95 μM U(VI) in the presence of Ca^{2+} and HCO_3^- for 1 week were extracted with 10 mM NaHCO_3 for 30 minutes to 1 week. Subsamples (100 μL) were taken for U(VI) analysis after centrifugation at 3000 rpm for 10 minutes. Dissolved U(VI) concentrations for sorption and desorption experiments were determined using a kinetic phosphorescence analyzer (KPA-11) (ChemChek Instruments, Richland, WA) (Brina and Miller, 1992). Analytical error was less than $\pm 5\%$. Sorbed U(VI) was determined by the difference between the initial and final aqueous U(VI) concentrations.

3. Results

3.1. Mineralogy of saprolite subsoils and nanoporous structure of goethite

XRD analysis showed that the < 2 mm fraction of all three saprolite subsoils (low, medium and high Fe(III) soils: 7138, 11161, and 22582 mg/kg Fe) is composed mainly of quartz, illite and smectite, while a minor peak of calcite was identified in the low Fe(III) soil (Fig. 1). Nano-goethite was observed in all three soils by TEM (Fig. 2). The goethite was closely associated with illite/smectite (I/S), and exhibited nanocrystalline and nanoporous structures, particularly in the medium and high Fe(III) soils (Fig. 2). Goethite in the high Fe(III) soil was dominated by aggregates of nano-crystals with an average size of ~5 nm. Very broad diffraction rings (insert in lower-right corner of Fig. 2A) indicate the goethite nano-crystals in the high Fe(III) soil are poorly crystalline. A high-resolution TEM image (Fig. 2B) displayed nanopore space between the goethite nano-crystals. The structural state of goethite in the high and medium Fe(III) soils is between ideal goethite and ferrihydrite (Fig. 2A-2C). The goethite may be formed through oriented aggregation of its precursor ferrihydrite nano-crystals, as suggested by Banfield et al (Banfield et al., 2000). Therefore the amount of Fe(III) oxides determined by the DCB extraction represents both goethite and ferrihydrite. Goethite nano-crystals are fewer in the low Fe(III) soil (Fig. 2D) than in the medium and high Fe(III) soils, which resulted in less nanopore surfaces in low Fe(III) soil. Quantitative X-ray energy-dispersive spectroscopy (EDS) analyses showed that all the goethite nano-crystals contained small amounts of Al (13-16 mole % Al) (Fig. 2E).

For the low, medium, and high Fe(III) soil samples, BET specific surface area was 25, 29, and 38 m²/g, respectively, while nanoporosity was 1.5, 2.0, and 1.9 μ L/g for pore size < 2 nm, and 16.3, 18.4, and 30.4 μ L/g for pore size < 10 nm, respectively (Table 1, Fig. 3). BJH pore volume for larger pores with size between 10 nm and 120 nm are 19.1, 20.1, and 56.4 μ L/g for low, medium and high Fe(III) soil samples, respectively. The particle size distribution by weight

determined by sieving with a 0.063 mm sieve was similar for all 3 soil samples, showing ~80% sand and ~20% silt and clay.

3.2. Dominant role of nano-goethite in U(VI) sorption

The low, medium, and high Fe(III) soils sorbed 3.4, 6.3, and 7.0 $\mu\text{mol U(VI)/g}$, respectively, when 0.2 g of soil was exposed to 10 mL of 0.1 M NaNO_3 solution containing 150 $\mu\text{M U(VI)}$ and 1 mM NaHCO_3 at pH 6.8 for 1 week. TEM-EDS analysis revealed that most of the sorbed U(VI) was associated with nano-goethite clusters, displaying distinct U peaks in their EDS spectra, whereas U peaks from clay minerals (e.g., illite, smectite) were low, and not distinctive from background peaks (Fig. 4). The U peak for nano-goethite clusters was relatively higher in the high and medium Fe(III) soils than the low Fe(III) soil, consistent with approximately 2-fold higher concentrations of sorbed U(VI) in the high and medium Fe(III) soils than the low Fe(III) soil. Although clays are much more abundant than goethite in FRC saprolite soils, TEM-EDS results indicate that the nano-goethite crystals play the dominant role in controlling U(VI) sorption. This is also consistent with a previous TEM-EDS study that identified iron oxyhydroxides as a distinct solid phase hosts for uranium in U(VI) contaminated FRC soils from Area 3 (Stubbs et al., 2006). Besides goethite and trace amount of Mn oxides (Table 1), no other secondary oxide minerals that are likely to affect U(VI) sorption were identified from the saprolite subsoil by our TEM or XRD analyses.

3.3. U(VI) sorption behavior in saprolite subsoils

Sorption of 90-95 $\mu\text{M U(VI)}$ to all three soils in 0.1M NaNO_3 solution was rapid, regardless of the presence of HCO_3^- (1 mM) or Ca^{2+} (0-10 mM). In the medium and high Fe(III) soils, the

U(VI) sorption rapidly increased to 66-73% and 74-89%, respectively in 20 minutes, and then slowly increased to 72-82% and 86-95%, respectively in 48 hours (Fig. 5). In the low Fe(III) soil, the U(VI) sorption increased rapidly to 42-56% in 20 minutes, but remained relatively constant at 41-52% in 48 hours. After two days of sorption reaction, pH increased slightly from 6.3 to 6.5 in the medium and high Fe(III) soil suspensions, while pH increased from 6.3 to 7.0 in the low-Fe(III) soil suspension likely due to dissolution of minor amount of calcite (Fig. 1). Given that U(VI) sorption to Fe(III) oxyhydroxides (e.g., ferrihydrite and goethite) in the presence of HCO_3^- is the highest at circumneutral pH between 6 and 8 (Hsi and Langmuir, 1985; Waite et al., 1994; Wazne et al., 2003), the pH increase from 6.3 to 6.5 or 7.0 is likely to have an insignificant effect on U(VI) sorption to goethite in saprolite subsoils. Sorption of 50 μM U(VI) to the soils in the presence of 2.5 mM Ca^{2+} and 5 mM HCO_3^- at circumneutral equilibrium pH of ~ 6.5 -7.0 for 2 weeks also showed initially rapid U(VI) sorption with 16, 27, and 50% sorption to low, medium, and high Fe(III) soils in 2 days, respectively. Then the U(VI) sorption to low, medium, and high Fe(III) soils increased slowly to 22, 40, and 66% in 1 week, and subsequently to 32, 51, and 73% in 2 weeks, respectively (Fig. 5).

The 2-day sorption of 90 μM U(VI) to the saprolite soils in 0.1M NaNO_3 solution decreased markedly with increasing HCO_3^- concentration from 0.1 mM to 5 mM because of increased formation of uranyl-carbonato species (Wazne et al., 2003; Davis et al., 2004): 47% to 14% for the low Fe(III) soil, 84% to 29% for the medium Fe(III) soil, and 99% to 36% for the high Fe(III) soil (Fig. 6A). PHREEQC modeling (Parkhurst and Appelo, 1999) predicted the speciation of 90 μM U(VI) at equilibrium pH of 6.5-7.0 using the databases from Bernhard et al (2001) and Guillaumont et al (2003), as well as the LLNL.dat database (a database file in PHREEQC) (Bernhard et al., 2001; Guillaumont et al., 2003). Uranyl-carbonato species (e.g.,

$\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$) account for 0-1%, 24-26% and 95-98% of total U(VI) in the presence of 0.1, 1 and 5 mM HCO_3^- , respectively.

The extent of U(VI) sorption was higher with increasing soil Fe(III) oxide content, regardless of HCO_3^- concentration. Distribution coefficient (K_d) for U(VI) in the presence of 0.1-5 mM HCO_3^- increased from 2-9 mL/g for the low Fe(III) soil to 4-52 mL/g for the medium Fe(III) soil and 6-850 mL/g for the high Fe(III) soil (Fig. 6B). The dominant role of soil Fe(III) oxides in U(VI) sorption has also been documented for materials from other DOE sites (the Savannah River and Hanford sites) (Barnett et al., 2002; Barnett et al., 2000).

The 1-week sorption of 95 μM U(VI) to the saprolite subsoils (3 replicate sets) in 0.1M NaNO_3 solution with 1 mM HCO_3^- was lower only slightly in the presence of 5 or 10 mM Ca^{2+} than in the absence of Ca^{2+} (Fig. 6C). As Ca^{2+} concentration increased from 0 mM to 5 mM and 10 mM, the extent of U(VI) sorption decreased from 46% to 42% and 32% for the low Fe(III) soil, from 83% to 78% and 70% for the medium Fe(III) soil, and from 93% to 87% and 85% for high Fe(III) soil. This result is consistent with the minor effect of Ca on U(VI) sorption onto a saprolite soil collected from 1 to 1.5 m depth at the Melton Branch Watershed on the Oak Ridge Reservation (Gadelle et al., 2001). The distribution coefficient (K_d) increased with higher soil Fe(III) oxide content: from 5-9 mL/g for the low Fe(III) soil to 23-51 mL/g for the medium Fe(III) soil and 56-143 mL/g for the high Fe(III) soil (Fig. 6D). Based on the PHREEQC modeling for the speciation of 95 μM U(VI) at equilibrium pH of 6.5-7.0, uranyl-calcium-carbonato ternary species account for 0%, 36-60% and 63-83% of total U(VI) in the presence of 0, 5 and 10 mM Ca^{2+} with 1 mM HCO_3^- , respectively. Uranyl-carbonato species compose 23-25%, 9-16%, and 4-9% of total U(VI) in the presence of 0, 5 and 10 mM Ca^{2+} with 1 mM HCO_3^- .

, respectively at pH of 6.5-7.0, while uranyl-hydroxyl-carbonato species (e.g., $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$) are 66-68%, 26-42% and 10-23% of total U(VI), respectively.

3.4. U(VI) desorption behavior in saprolite subsoils

Estimation of the labile fraction of U(VI) that participates in sorption-desorption processes, as well as any non-labile fraction (Phillips et al., 1995) that is resistant to desorption, is critical for predicting the mobility and transport of U(VI) in subsurface environments. Sodium bicarbonate (NaHCO_3) extraction at varying concentration has been used to selectively remove U(VI) from natural soils and sediments (Elias et al., 2003; Gadelle et al., 2001; Kohler et al., 2004; Mason et al., 1997; Zhou and Gu, 2005). Soils exposed to 90 μM U(VI) for two days in the presence of varying HCO_3^- concentration (0.1, 1, or 5 mM) were extracted sequentially (24 hours per extraction) at a range of NaHCO_3 concentrations (1, 10, and 100 mM). The combined proportion of U(VI) released from the saprolite soils by 1 mM and 10 mM NaHCO_3 [relatively more labile U(VI) fraction] decreased with increasing amount of Fe(III) oxides: 54-67% for the low Fe(III) soil, 34-52% for the medium Fe(III) soil, 28-31% for the high Fe(III) soil (Fig. 7). Correspondingly, the less labile U(VI) fraction [U(VI) released by 100 mM NaHCO_3 + undesorbed U(VI)] was greater with increasing amount of Fe(III) oxides: 33-46% for the low Fe(III) soil, 48-66% for the medium Fe(III) soil, and 69-72% for the high Fe(III) soil. The sequential desorption of U(VI) sorbed to the saprolite subsoils indicates that U(VI) sorption tends to be more irreversible in the presence of higher amount of nanoporous goethite.

After sorption experiments with 95 μM U(VI) in the presence of Ca^{2+} and HCO_3^- (Fig. 6), time course experiments of U(VI) desorption from a set of saprolite soils by 10 mM NaHCO_3 over 1 week generally exhibited two-step desorption behavior (Fig. 8): an initial fast desorption

step during the first 24 hrs, followed by slow desorption step lasting several days. Multiple steps of U(VI) desorption over days or weeks have been also reported from 20 mM carbonate extraction of natural sediments of former U mill tailings sites at Naturita and Rifle, CO (Hyun et al., 2009; Kohler et al., 2004). During the first 24-hour desorption period, sorbed U(VI) concentration rapidly decreased from 0.29-0.41 $\mu\text{M/g}$ to 0.18-0.30 $\mu\text{M/g}$ for the low Fe(III) soil, from 0.64-0.74 $\mu\text{M/g}$ to 0.21-0.25 $\mu\text{M/g}$ for the medium Fe(III) soil, and from 0.75-0.83 $\mu\text{M/g}$ to 0.42-0.58 $\mu\text{M/g}$ for the high Fe(III) soil (Fig. 8). Between 24-hour desorption and 7-day desorption, sorbed U(VI) concentration continued to decrease to 0.04-0.19 $\mu\text{M/g}$ for the low Fe(III) soil, to 0.09-0.30 $\mu\text{M/g}$ for the medium Fe(III) soil, and to 0.29-0.46 $\mu\text{M/g}$ for high Fe(III) soil (Fig. 8). In general, the 1-week U(VI) desorption% was lower for soil with higher amount of Fe(III) oxides: 61-86% for the low Fe(III) soil, 50-84% for the medium Fe(III) soil, 44-59% for the high Fe(III) soil.

4. Discussion

The results show that the ORFRC saprolite soils contain nano-goethite with nanoporous structure, which provides the reactive surfaces for U(VI) sorption. U(VI) sorption to the saprolite soils is mainly attributed to poorly crystalline nanoporous goethite, which was probably transformed from ferrihydrite, not to isolated individual well-crystalline goethite. The U(VI) sorption to the ORFRC saprolite soils at circumneutral pH increased with higher amount of nano-goethite in the presence of HCO_3^- and Ca^{2+} . The sorption of 95 μM U(VI) increased rapidly, reaching near equilibrium in less than 1 hour, but a slower sorption process continued in the medium and high Fe(III) soils (Fox et al., 2006; Waite et al., 1994). The sorption of 50 μM U(VI) sorption for 2 weeks also showed a similar kinetic behavior: a rapid initial sorption

followed by slower sorption. The time-dependence of U(VI) sorption is attributed to rapid sorption onto external surfaces of goethite, followed by intraparticle diffusion and sorption onto interior surface sites of the nanoporous goethite (Axe and Anderson, 1997; Trivedi and Axe, 2000; van Beinum et al., 2005).

The U(VI) desorption from the saprolite soils by 10 mM NaHCO_3 over 1 week displayed two-step desorption behavior (Fig. 8). The two-step U(VI) desorption behavior suggests that the initial fast desorption of U(VI) from the soils is attributed to release of U(VI) bound to external surfaces of goethite, while the subsequent slower desorption step was associated with internal nanoporous surfaces of goethite (Wang et al., 2003). The less extensive U(VI) desorption by 1 or 10 mM NaHCO_3 from the medium and high Fe(III) soils compared to the low Fe(III) soil (Fig. 7) is also attributable to the higher abundance of nanoporous goethite in the medium and high Fe(III) soils than the low Fe(III) soil (Fig. 2). U(VI) release from the medium and high Fe(III) soils was slower and more irreversible than U(VI) desorption from the low Fe(III) soil perhaps because of slower diffusion of ions in and out of nanopores or kinetically-hindered release of U(VI) due to strong U(VI) binding to internal nanoporous surfaces. Ion diffusivity is significantly reduced in nanopores compared to bulk water (Kerisit and Liu, 2009; Nagumo et al., 2008), posing mass transfer limitation on rates of U(VI) desorption. Due to slow diffusion of HCO_3^- into the nanopores of goethite and slower diffusion of U(VI) out of the nanopores of goethite, U(VI) desorption rate can decrease significantly. In addition, the presence of nanoporous domains may increase the intrinsic binding strength and decrease the desorbability of U(VI) through solvation energy effects. The solvation energy of charged ions is reduced in nanopores because of the lower dielectric constant of solvent water in nanopores than in bulk solution, which reduces the affinity for metal hydration in aqueous solution, thus increasing the

tendency for inner sphere complexation and mineral precipitation (Senapati and Chandra, 2001; Wang, 2014; Wang et al., 2003). It has been also reported that the surface charge density on nanoparticles is significantly higher than that on non-nanoparticles under same chemical conditions (Abbas et al., 2008; Barisik et al., 2014; Wang, 2014; Wang et al., 2003; Wang et al., 2002).

A limited, partial desorption of U(VI) by 10-100 mM HCO_3^- from U(VI) contaminated sediment/soil has been previously reported (Curtis et al., 2004; Gadelle et al., 2001; Kohler et al., 2004; Phillips et al., 1995). The mass of labile U(VI) in U-contaminated aquifer sediments from a former U mill tailings site at Naturita, CO, was estimated by the sodium bicarbonate/carbonate extraction of 20 meq/L alkalinity, which accounted for approximately 10-40% of total sediment U (Curtis et al., 2004; Kohler et al., 2004). In contrast, nearly all solid phase U(VI) was successfully removed from contaminated soils from the Fernald Environmental Management Project (FEMP) site near Fernald, OH and from the field research center (FRC) in Oak Ridge, TN using sodium bicarbonate of 0.5-1 M (Mason et al., 1997; Zhou and Gu, 2005). The extraction effectiveness of ~0.1 M sodium bicarbonate varied from 20 to 94% of total sorbed U(VI), depending on the types of soil (Gadelle et al., 2001; Phillips et al., 1995). In this study, the sequential extraction of U(VI) sorbed to the ORFRC saprolite subsoils by 1 to 10 and 100 mM HCO_3^- resulted in only partial desorption of U(VI): 67-80% desorption from the low Fe(III) soil, 54-68% desorption from the medium Fe(III) soil, 65-70% desorption from the high Fe(III) soil. It is likely that the bioavailability of U(VI) sorbed on nanoporous goethite is significantly reduced because nanoporous domains of Fe(III) oxides are highly effective at stabilizing U(VI) against desorption (Chevallier et al., 2010; Zachara et al., 2016). Microorganisms with a typical size of micrometers cannot directly access U(VI) inside nanopores, which also effectively

reduces the bioavailability of U(VI) (Wang, 2014). Although many details remain unclear (e.g., the relative importance of mass transfer vs. intrinsic binding strength effects related to nanopores; the correlation between nanopore abundance and the presence of various Fe(III) oxide and other mineral phases), our experimental data for natural subsurface soils from ORFRC suggest that nanopores within nano-crystalline Fe(III) oxides may exert a significant role in regulating the sorption-desorption behavior, and hence the mobility and transport of U(VI) in subsurface environments where such phases are abundant.

5. Conclusions

The U(VI) sorption-desorption behavior in ORFRC saprolite subsurface soils was investigated. The saprolite subsoils were essentially homogeneous in mineral composition and particle size distribution, but were characterized by a range of DCB extractable Fe(III) oxide content and different pore size distributions. Key conclusions from this study include:

1. TEM imaging revealed that nanopores were formed between aggregated nano-goethite crystals, particularly in the medium and high Fe(III) saprolite subsoils.
2. TEM-EDS analysis exhibited that U(VI) sorption occurred predominantly on nano-goethite crystals rather than clay minerals, and higher U peaks were detected on nanoporous goethite clusters in the medium or high Fe(III) soils than on crystalline goethite clusters in the low Fe(III) soil.
3. A higher extent of U(VI) sorption at variable Ca^{2+} and HCO_3^- concentrations and a lower extent of U(VI) desorption by 1-100 mM NaHCO_3 took place in the soil with higher quantity of nanoporous goethite.

4. The initial fast desorption of U(VI) from the ORFRC saprolite subsoils (24-hour time scale) seems to result from release of U(VI) from external surfaces of goethite, while the subsequent slower desorption phase was attributed to slower diffusion of HCO_3^- and U(VI) in and out of nanopores of goethite or kinetically-hindered release of U(VI) from internal nanoporous surfaces of goethite due to strong U(VI) binding to nanoporous surfaces.

Overall, the results of this study shed light on the role of nano-goethite in enhancing the sorption and retention of U(VI) in subsurface ORFRC soil. This phenomenon has thus far been poorly recognized because numerous previous laboratory studies of U(VI) sorption by natural soil or sediment have not focused on nanoporous or nanocrystalline minerals. Our findings imply that understanding of sorption-desorption behavior of U(VI) on nanoporous mineral surfaces will be critical to better predict the mobility and transport of U(VI) in subsurface environment where nanoporous minerals are ubiquitous and abundant.

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Table 1. Summary of chemical, physical, and mineralogical characteristics of ORFRC saprolite subsoils. Prior to sorption-desorption experiments, background U concentration in saprolite soils was determined by 10% HNO₃ extraction for 2 days. Fe(III) content was determined by DCB extraction. BET specific surface area and nanoporosity were analyzed by a surface area and pore size analyzer; Minerals were identified using XRD and TEM (Qz, Ill, Sm, and Cal represent quartz, illite, smectite, and calcite, respectively).

Sample ID	U conc.	Fe(III) conc.	Specific surface area	Nanoporosity (μL/g)		Mineralogy	
	μM/g	mg/kg		< 2 nm	< 10 nm	XRD	TEM
Low Fe(III)	0.0068	7138	25	1.5	16.3	Qz, Ill, Sm, Cal	Goethite, Mn oxide (minor)
Medium Fe(III)	0.0015	11161	29	2.0	18.4	Qz, Ill, Sm	Goethite
High Fe(III)	0.0016	22582	38	1.9	30.4	Qz, Ill, Sm	Goethite

Fig. 1. X-ray diffraction patterns for ORFRC saprolite subsoils with low (GP-4-5-00), medium (GP-4-4-25), and high (GP-3-5-00) Fe(III) oxide content. Mineralogy in all samples is dominated by quartz (Q), illite (I), and smectite (S). The low Fe(III) subsoil shows a distinct 104 diffraction peak for calcite (C).

Fig. 2. TEM images showing nano-sized goethite in the high Fe(III) saprolite subsoil (A, B), as well as twined goethite (V-shape) consisting of oriented aggregation of goethite nano-crystals in the medium Fe(III) saprolite soil (C) and the low Fe(III) saprolite soil (D). I/S and G in TEM images indicate illite/smectite clay and goethite, respectively. X-ray EDS spectrum (E) shows small amount of Al in the goethite. Cu peak is from Cu grid holding the specimen. Si peak is from florescence peak of Li-drifted Si detector.

Fig. 3. Top: BJH cumulative pore volume in the low to high Fe(III) soils as a function of pore size. **Bottom:** BJH cumulative surface area (squares) as a function of pore size and BJH surface area distribution (circles) for the low to high Fe(III) soils.

Fig. 4. TEM-EDS showing U(VI) concentrations sorbed on goethite nanoparticles (A: the high Fe(III) soil, B: the medium Fe(III) soil, C: the low Fe(III) soil) and clays (D: the high Fe(III) soil, E: the medium Fe(III) soil, F: the low Fe(III) soil). TEM images of nano-goethite clusters in the high (G), medium (H), and low (I) Fe(III) soils. Soil samples (0.2 g) were reacted with 0.1 M NaNO_3 solution containing 150 μM U(VI) and 1 mM NaHCO_3 at pH 6.8 for 1 week.

Fig. 5. Top: Sorption kinetics of 95 μM U(VI) to ORFRC soils (1 g) with various Fe(III) oxide content in 0.1 M NaNO_3 solution (10 mL) containing 1 mM HCO_3^- and a range of Ca^{2+} (0, 5, and 10 mM) at equilibrium pH of $\sim 6.5-7.0$ for 48 hours. **Bottom:** Sorption kinetics of 50 μM U(VI) to ORFRC soils (1 g) in 0.1 M NaNO_3 solution (10 mL) containing 2.5 mM Ca^{2+} and 5 mM HCO_3^- at equilibrium pH of $\sim 6.5-7.0$ for 2 weeks. Error bars represent standard deviation of replicates (N=2).

Fig. 6. U(VI) sorption to the low, medium, and high Fe(III) soils at circumneutral pH of ~6.5-7.0 at various HCO₃⁻ and Ca²⁺ concentration. **A** and **B**: Sorption percentage and distribution coefficient (Kd) of 90 μM U(VI) in 0.1M NaNO₃ solution containing 0.1, 1, or 5 mM HCO₃⁻ for 2 days. **C** and **D**: Sorption percentage and distribution coefficient (Kd) of 95 μM U(VI) in 0.1M NaNO₃ solution containing 1 mM HCO₃⁻ with 0, 5 or 10 mM Ca²⁺ for 7 days. Error bars represent standard deviation of replicates (N=3).

Fig. 7. U(VI) desorption from the low, medium, and high Fe(III) subsoils by sequential extraction with 1, 10, 100 mM NaHCO_3 after sorption of 90 μM U(VI) in 0.1M NaNO_3 solution containing 0.1, 1, and 5 mM HCO_3^- . Each extraction was conducted for 24 hrs.

Fig. 8. Desorption kinetics of U(VI) (left) and U(VI) remaining on the solid phase (right) during 1-week extraction with 10 mM NaHCO₃. The soils were exposed to 95 μM U(VI) in 0.1M NaNO₃ solution containing 1 mM HCO₃⁻ with 0, 5, or 10 mM Ca²⁺ for one week prior to conduction of the desorption experiment.