SORPTION OF AQUEOUS FE(II) ON GOETHITE INVESTIGATED WITH STABLE OXYGEN ISOTOPES

A Thesis Presented

By

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This thesis work is aimed at examining the oxygen atom mixing between common iron(III) oxides and Fe(II)$_{aq}$ solution during the sorption process. First, $^{18}$O labeled iron(III) minerals were used in batch sorption reactors to study the exchange of oxygen atom within the Fe(II)$_{aq}$ – iron(III) oxide system. Results showed a much lesser extent of oxygen mixing than reported Fe mixing from previous studies, even when dissolved Fe(II) is present. The oxygen mixing extents are 3.95 % more for goethite and 9.66 % more for ferrihydrite than their respective controls within 14 days.

A consecutive atom exchange kinetic study indicated that O exchange is not inhibited by surface Fe sorptive site saturation, and that after 40d sorption experiment, the maximum O exchange is 54.96 % across reactors with different initial solid loadings and Fe(II)$_{aq}$ levels. The second part of this work examined the influence of aqueous Fe(II) on the sorption of selenium oxyanions (selenite and selenate) in Fe(II)$_{aq}$ – iron(III) systems. It was found that Fe(II)$_{aq}$ promotes selenium oxyanion sorption, and potential electron transfer occurred at the interface of goethite and selenite.

Iron exists in nature in various forms including minerals in underground formations, freshwater and seawater sediments and in almost any living organisms. The diverse electrochemical properties of elemental Fe and its compounds have found way in many environmental applications; for example, Fe powder is used in permeable reactive barriers for groundwater remediation; Ferrate (+6 valent iron, FeO$_4^{2-}$) is used as an environmentally-friendly disinfectant for water and wastewater treatment. In recent decades, sorption of iron(III) oxides in reducing, Fe(II)-rich environment was extensively studied, with the advancement of spectroscopic techniques, researchers have found that the presence of aqueous Fe(II) changes the surface sorption activity of Fe minerals. Evidence of heavy metal incorporation and release, electron transfer between phases and through bulk solids, and the observation of recrystallization on the surface of the substrate mineral structures have positively confirmed the catalytic effects of aqueous Fe(II) on mineral-water interactions. More recent studies with $^{57}$Fe isotope tracers found near-complete mixing of structural Fe atoms with bulk solution dissolved Fe(II).
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Chapter 1. Introduction

1.1 Iron in the environment

Iron is ubiquitous in the environment; it is the fourth most abundant element in the Earth’s crust by weight and the sixth most common element in the universe. Naturally occurring forms of iron are mostly iron oxides, which may contain iron in many different oxidation states. The Earth has a huge reservoir of iron-bearing rocks (iron ores) and these are usually found in the forms of hematite ($\text{Fe}_2\text{O}_3$) or magnetite ($\text{Fe}_3\text{O}_4$). Many of the environmentally relevant iron (hydr)oxides are present within soils, rocks, freshwater sediments, atmospheric dust, ocean sediments, and organisms. Iron (hydr)oxides is very important in regulating the speciation and flux of pollutants and nutrients among different phases and domains. Vertebrates rely on iron-containing hemoglobin to transport oxygen through the body. Certain animals such as pigeons or insects like honeybees use the inherent magnetic property of iron oxides (especially magnetite) for navigation\textsuperscript{1}.

Fe exists in many oxidation states, the most common being elemental (zero-valent), ferric (trivalent) and ferrous (divalent) iron. The varied oxidation states are good indicators of the redox condition of the Fe containing environment. For example, ferrous iron forms are prevalent in subsurface environments with little to no oxygen, such as anoxic aquifers and cave seepage channels\textsuperscript{2}, and most ferrous species are soluble; however, in open channel systems like watershed or mine drainage, ferric iron is typically the dominant form. The redox chemistry of iron is complex and plays a key role in a great many of geochemical and biological processes. Iron may act as the both electron donor and acceptor in microbial metabolisms. This dual property has also enabled Fe redox chemistry to mediate the nutrient cycling and contaminant transformation in many abiogenic conditions.
Iron is present in various natural aquatic environments. Fe\(^{2+}\) and Fe\(^{3+}\) ions may freely dissolve under acidic conditions, and precipitate as hydroxides when pH is more basic. When concentration is relatively low, Fe\(^{2+}\) can stay dissolved at pH less than 8. Ferric iron starts to precipitate and form a yellow/orange compound around pH = 3.5. Ferrous iron is easily oxidized in neutral or basic solutions when exposed to oxygen or other oxidants. In circumneutral water, Fe(III) is much less soluble than Fe(II) and forms iron (hydr)oxides more readily. By creating sorbents through the formation of Fe(III) oxides, precipitation of Fe\(^{3+}\) is commonly used for the treatment of iron pollution and the sequestration/immobilization of other metals that are active in Fe redox chemistry. The dissolution and precipitation of iron (hydr)oxides depend heavily on pH, redox potential (E\(_{\text{h}}\)) and water chemistry. The respiration of subsurface microorganisms can also significantly influence the mobility of relevant Fe species. Together with other geogenic (e.g. weathering), anthropogenic processes (e.g. air sparging), iron takes so many forms and exist in a vast range of aqueous systems.

1.2 Goethite

Goethite is widely present in natural soils and also commonly found in swampy headwater areas, cave floors, and river or lake sediments. It is normally formed through weathering of other iron minerals (e.g. pyrite, magnetite) under oxidizing conditions. Goethite belongs to the orthorhombic crystal family, it has needle-like crystal structure and its chemical formula is \(\alpha\)-FeO(OH). Normally, goethite is synthesized in the laboratory via two methods; one is thermal conversion of ferrihydrite slurry at alkaline pH, and the other is the oxidation of Fe(II) by O\(_2\) when bicarbonate is present.

1.3 Surface sorption and desorption of iron oxides/minerals in anoxic water environment.

Iron minerals have been shown to sorb various metals and natural organic matter (NOM) as well as Fe(II) cations within Fe(II)-rich environments. Studies have demonstrated metal cation incorporation and surface adsorption of oxyanions such as selenate\(^{3-}\). Iron oxides also have great
sorption capacity for phosphate, silicate and other environmentally relevant anions. One study found that Cu$^{2+}$ in the solution increase the sorption of organic matter by forming inner-sphere complexes with goethite surface. The robust uptake of metal cations had been frequently attributed to (i) electrostatic interactions between the positively charged cations and the negatively charged surface oxygen groups and (ii) surface complexation reactions that involve bond formation at surface sites, usually directly with surface oxygen groups. For oxyanions which contain oxygen atoms surrounding a central metal atom, one oxygen atom, either from the oxyanion or the iron oxide, must be removed prior to a new metal-O-Fe bond forms. One study looked at the surface ligand exchange of selenite sorption onto goethite using stable oxygen isotope tracing technique, and the result suggested a mixed mechanism of bond breaking; the oxygen released may come from the break of i) O-H bonds at goethite surface and ii) Se-O bond of selenite oxyanion. Sorption process is influenced by factors including solution pH, surface charge of the substrate and the charge of the sorbate itself. Metal cations may form direct bonds with surface oxygen groups in an inner-sphere configuration, but loose associations with the surface in outer-sphere configurations are also possible. Furthermore, iron oxides in the environment are rarely pure and often contain metal impurities, and the release of pre-incorporated metals from metal-substituted goethites can be possible during atom cycling reactions between dissolved Fe(II) and goethite. This led to the investigation of the factors that influence the rate and extent of metal cycling between the aqueous and solid phase using isotopic signature, which will be the focus of discussion below.

1.4 Fe(II)-catalyzed recrystallization of iron oxides (also interpreted as surface growth and dissolution)

The redox reaction between Fe(II) and Fe(III) species, both dissolved and solid, is quite dynamic during both biotic and abiotic processes and has been widely acknowledged as a critical reaction in biogeochemical Fe cycling. The reactions between dissolved Fe(II) and Fe(III) oxide surfaces
have been recently explored to better understand interfacial Fe(II)-Fe(III) sorption and electron transfer processes in common iron oxides. After sorption of dissolved Fe(II) onto Fe(III) oxides, the unrecoverable aqueous Fe(II) and spectroscopic observations of newly-formed surface adsorbed Fe(III) species have confirmed the interfacial redox activity resulting in oxidation of sorbed Fe(II) to Fe(III), and some studies have provided spectroscopic evidence for interfacial Fe(II)-Fe(III) electron transfer. As a concurrent process, atom exchange between the solid and liquid phases have been demonstrated to be prominent. The sorption and oxidation of dissolved Fe(II) to surface Fe(III) may reduce structural Fe(III) to soluble Fe(II) which may be released back to solution, creating ongoing atom exchange processes. With electron transfer and atom exchange (ETAE), Fe cycling is believed to influence micro and micro-nutrient availability, transformation of contaminants and other biogeochemical processes.

The ETAE process has been examined for goethite, hematite, and magnetite, and extensive recrystallization and atom exchange of Fe between Fe minerals and aqueous Fe(II) has been observed. In an effort to study the mechanism of atom exchange between aqueous Fe(II) and iron(III) oxides, Handler et. al found near-complete mixing of Fe between solid and liquid phases but no significant physical changes to goethite crystals. A model of coupled growth and dissolution at different surface sites linked via bulk solid electron transfer has been established as an attempt to account for the fast kinetic of recrystallization. Another study by Gorski et al. has also found extensive exchange (54-71%) for magnetite, and bulk electron conduction not the rate-limiting step of the Fe mixing. Among other studies with common iron(III) oxides, the extent of Fe atom exchange differs significantly. While ~100% Fe mixing were found for both ferrihydrite and goethite as a result of Fe(II)-catalyzed ETAE, very negligible mixing was observed for hematite (<1%). It is very likely that the degree of exchange depends on both the oxide properties and the reaction solution conditions. Though the degree of Fe mixing may be subjected to the effects of multiple processes (e.g. Fe uptake, formation of surface-sorbed species,
and the bulk solid conduction and diffusion of electron and Fe atoms), for a certain type of oxide, some processes stand out to be the rate and extent limiting ones.

Despite the extensive Fe atom exchange, negligible morphology change was observed for the studied oxides. The most recent hypothesis is presented in the Redox Driven Conveyor Belt model and the process relies on bulk electron conduction and the topotactical reformation of the crystal structure. Solid-state diffusion of Fe atoms in the crystal lattices and pore diffusion of Fe atoms in the oxide structure are also invoked to explain this phenomenon for some Fe oxides. Among all the possible mechanisms, the driving force of Fe(II)$_{aq}$-catalyzed ETAE were sought.

These prior studies that examine the pathway of atomic mixing have mostly relied on Fe isotopic tracing techniques to quantify atom exchange. Many other isotopic studies that focus on geochemical Fe fractionation among different phases have also shed light on Fe cycling in the laboratory Fe(II)$_{aq}$-iron(III) system. A study with hematite has suggested reduction by dissimilatory iron reducing bacteria (DIRB) to remain the most efficient process in nature that varies Fe isotopic fractionation$^{14}$. It is also found Fe cycling between dissolved Fe(II) and the Fe oxides ferrihydrite, hematite and goethite is also influenced by both the equilibrium and kinetic isotopic effects$^{14-16}$. The results of the fractionation studies, especially the insights of the isotopic effects on Fe cycling, provide important context for interpreting the results of the tracer studies.

Finally, the possibility of the release of structurally-incorporated trace metals during Fe ETAE has been examined. The studies with trace metal substituted Fe(III) oxides showed the release of the structurally incorporated metal atoms into the solution when Fe(II)$_{aq}$ is present to drive ETAE$^{8,9,11,17}$. The release of structurally incorporated trace metals have been observed for hematite, magnetite and goethite. The release of trace metals from iron oxides are linked to Fe(II) catalyzed recrystallization and may be influenced by factors including the radius and valent of the incorporated metals. Studies with Ni- and Zn-doped goethite and hematite found 3 – 9 % atom
Another study with Co-substituted magnetite measured approximately 7% of the structural Co release within 1 day of exposure to aqueous Fe(II) $^{11}$.

In order to assess the role of ETAE in biogeochemical cycling of Fe, it is necessary to understand the factors that might impact the rate and extent of the contributing processes. Many studies adopted relatively simpler reaction conditions and pure lab-synthesized Fe(III) oxides as an attempt to isolate the interaction between Fe(II)$_{aq}$ and Fe(III) oxides.

### 1.5 Objectives, hypotheses, and overview

In this thesis work, two sets of experiments were carried out. The objective of the first experiment, which is presented in Chapter 2, is to demonstrate the mixing of oxygen atoms between the solid phase (iron oxides) and solution. The experiment is designed to examine if O is exchanged as well as Fe in the process of Fe(II)$_{aq}$-catalyzed recrystallization and if yes, how fast the mixing takes place, and if steady state can be achieved after a certain length of reaction. Also, quantitative analysis of the Fe and O mixing can be informed by monitoring the Fe(II) in the solid and liquid phases. As a hypothesis, mixing of O is expected, and the degree of mixing depends on the stoichiometry of Fe and O in the substrate crystal.

In the second part of the thesis work, we investigated the influence of aqueous Fe(II) on the sorption of oxyanions (selenate and selenite) onto goethite. This part of work is aimed at examining the influence of Fe(II)-catalyzed ETAE on the sorption capacity and redox transformation of oxyanions. Our hypothesis is that aqueous Fe(II) promotes the sorption of both selenate and selenite, and a portion of selenate will be reduced to selenite through the acquisition of electron from the oxidative precipitation of aqueous Fe(II) on goethite.

The sorption experiments were all carried out in batch reactors to ensure identical conditions. By varying the concentration of ratio of sorbent to sorbate, and the concentration of other species in concern, and measuring the concentration of targeted species in the solid and liquid phases,
valuable information of the reaction rate and extent can be obtained. As a complementary set of
eperiment, four more groups of sorption reactors were ran with $^{18}$O-enriched goethite, and
longer kinetic study results were obtained from the added sampling time points and the four sets
of sorbent : sorbate ratios applied to the sorption reactors. In the first part of our work (Chapter 2),
we used stable isotope tracing techniques to reveal the rate and extent of oxygen mixing. In the
2nd part of our work, selenate/selenite sorption test is performed to detect possible redox reactions
happening in aqueous Fe(II)-goethite system. As a preliminary attempt, this redox pair was
chosen to reveal the potential reduction and oxidation processes occurring in the interaction
between aqueous ferrous iron and goethite. The role Fe(II) plays in the sorption and possible
redox interactions was revealed by the contrast of the control group without initial aqueous Fe(II).
Finally, a summary of the experiment results and conclusions in relation to the objectives, and a
brief discussion of the implications are provided at the end of Chapter 2 and Chapter 3.

Chapter 2. Oxygen isotope tracer study of the Fe(II)$_{aq}$ –goethite and
Fe(II)$_{aq}$–ferrihydrite sorption system

2.1 Introduction

2.1.1 The Fe(II)$_{aq}$ – Iron (III) oxide system
Iron is the most abundant redox-active metal on earth, and it exists in both dissolved phase and
solid phase across different formations. One major goal of geochemistry is to study how
environmental conditions affect mineral transformation. Iron oxides and hydroxides are
frequently used as representative minerals for mineralogical studies. Past studies have made
observations of the incorporation of metals into Fe oxides when aqueous Fe(II) is present, and it
is yet unclear the role the integration process plays in the sequestration of toxic metals or
metalloids such as Pb and As. More recently, remarkable Fe atom mixing was observed when
thermodynamically stable Fe oxides (goethite, hematite, magnetite, etc) are exposed to aqueous Fe(II), and yet, the recrystallized Fe oxides exhibited no noticeable change in the size, form and structural properties, as revealed by spectroscopic observations.

Amidst the observations of Fe oxide/hydroxide reacting with aqueous Fe(II), the extent of Fe mixing is scattered. Yet it is difficult to attribute the difference to the variations in experimental conditions. The phenomenon has been unique to Fe oxide reaction with Fe(II) and could be present in Fe(II)$_{aq}$-rich environment such as reduced sediment and anoxic early Earth.

Though the pathway of the atomic mixing in Fe(II)$_{aq}$ – Iron(III) oxide system is yet unclear, the extent of Fe mixing has pointed to the possibility of complete mineral structural cycling induced by Fe(II)$_{aq}$ – catalyzed recrystallization. Recrystallization, sometimes also known as homoeptaxial mineral growth, is the growth of crystalline material on the surface of existing mineral, and the new crystal is of identical composition as underlying crystals (goethite grow on goethite, hematite grow on hematite, etc). The Fe atom exchange observed for stable iron oxides involves no secondary mineral transformation and thus suggested to be caused by Fe(II)-catalyzed recrystallization. Heretofore there hasn’t been a universal model to explain the observation. Many hypotheses have been suggested that invokes a certain pathway as facilitator of the exchange process. One model by Handler et. al., based on study with goethite, invokes the coupled growth and dissolution of Fe(III) mineral in a conveyor-belt fashion; aqueous Fe(II) is reduced at one site and the electron is conducted through the mineral lattice; at another site, solid-bound Fe(III) atom acquires electron and becomes soluble reduced Fe, creating a cycling process that exchanges Fe atoms in the entire solid phase. The driving force proposed in this model is the electro-potential difference between different types of crystallographic faces.
2.1.2 Isotope Tracing Approach

Iron isotope tracing has been a most commonly used tool for studying the redox cycling of Fe in the Fe(II)\textsubscript{aq}/Fe(III)\textsubscript{aq}-Fe oxide interactions. In some of those works, laboratory synthesized iron oxides labeled with isotopic Fe were reacted with isotopically normal Fe\textsuperscript{2+} solution\textsuperscript{19}; others investigated the fractionation of isotopic Fe in which normal Fe iron oxides were exposed to \textsuperscript{57}Fe\textsuperscript{2+} enriched solution\textsuperscript{13}. In goethite – Fe\textsuperscript{2+} system experiment, Fe atom pools of bulk solution and solid mix almost completely\textsuperscript{13}. But much less release of bulk solid Fe atoms was observed for another experiment\textsuperscript{19}. Some minor variations in the solution condition and the oxide itself can cause a very significant difference in the extent of Fe atom mixing.

2.1.3 Overview of \textsuperscript{18}O tracer study

In the collective results of some previous studies, the binary solid-liquid reaction is actually quite dynamic and could include many processes like inter-phasic electron transfer, topotactic Fe precipitation and dissolution, epitaxial crystal growth, and the collateral fractionation of other metal atoms. The generic process of electron transfer and atom exchange (ETAE) is therefore regulated by factors controlling the abovementioned processes, and it may be hard to study an individual process since they happen simultaneously. In our study, instead of looking in depth into the factors that control the rate and extent of Fe mixing, we used oxygen signature to monitor the mixing of bulk solid oxygen into water. As another important element in goethite, oxygen mixing will provide important clues on how the bond between Fe and O atom breaks when Fe is mixing, and that whether the entire solid structure cycles.

2.2 Experimental Methods

2.2.1 \textsuperscript{18}O-enriched goethite and ferrihydrite synthesis

\textsuperscript{18}O-enriched goethite was produced in batches from a hydrothermal synthesis recipe modified from a Schwertmann and Cornell method\textsuperscript{20}. One gram of \textsuperscript{18}O-enriched water (97 atom \%,
Cambridge Isotopes Lab) and 9 ml of DI water was added to a Teflon-lined centrifuge tube to a total volume of about 10 ml. After shaking up until complete homogenization, 610 mg KOH pellets were added and dissolved. The tube now contained all added O atoms and was capped and allowed to equilibrate for an hour. A mass of 390 mg anhydrous FeCl₃ powder was then added to the KOH solution, and the tube was shaken on a vortex mixer. In the tube, a dark brown and thick suspension of ferric hydroxide formed. In order to break down clusters of precipitates and to ensure dissolution of all ferric chloride salt, the tube was ultrasonicated for 10 minutes. The suspension was aged in a 68°C oven for 4 days. At the end of synthesis, the precipitate turned into yellow-ochre colored solid. The solid was centrifuged, freeze-dried, ground, and sieved through 45 micron standard sieve. Normal distilled water washing was omitted to preclude unknown factors that may possibly change the oxide’s morphological and isotopic properties. A total of 138 mg ¹⁸O-enriched goethite was produced with yield slightly above 60%, this was unexpected as the yield in previous practice and later synthesis runs all reached 93%. The loss was most likely due to the author’s inexperience with grounding and sieving as some mass was noticed to have escaped as a result of electrostatic repulsion. Supernatant was decanted after centrifugation and preserved for later use in ferrihydrite synthesis. The pH of supernatant after synthesis was 13. Subsequent enriched goethite syntheses for later experiments produced approximately 95% yield of goethite mass.

¹⁸O-enriched ferrihydrite synthesis followed a Schwertmann and Cornell method²⁰. In brief, dissolved Fe(III) salt was precipitated with alkali until the pH falls between 7 and 8. In this study, the ¹⁸O-enriched water supernatant from the above synthesis was reused as the alkali solution, and Fe(III) salt was added incrementally while being continuously agitated. The pH dropped from 13 to 7.5 and the precipitate was immediately centrifuged, freeze-dried, ground, and sieved (with 106 micron standard sieve). In total, 154 mg of anhydrous FeCl₃ salt was added to approx. 10 ml supernatant, and this synthesis yielded 54.6 mg ¹⁸O-enriched ferrihydrite. The percentage yield
was 68.2% based on the empirical ferrihydrite formula of $\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$. Apart from the variables that contributed to the low yield, it was presumed that a portion of the Fe salt wasn’t dissolved and formed aggregates with the hydrolyzed Fe(III) content. The solubility of Fe(III) salt is pretty low in the upper pH ranges.

The goethite produced for the second experiment were quickly washed with small amount of DI water to reduce the salt content. After adding a small amount of DI to the goethite paste, the vessel was capped and agitated briefly on vortex mixer, and brought into centrifuge. The exposure of $^{18}\text{O}$-enriched goethite to water or air were kept at minimum, as we yet don’t know if $^{18}\text{O}$ will exchange with ambient $^{16}\text{O}$.

### 2.2.2 Batch sorption test

Batch sorption reactors have the advantage of sampling consistency, as the reactor content has been constantly stirred to maintain uniform solid and dissolved material concentrations within the reactor throughout the experiment time span. In our experiment, either goethite or ferrihydrite powder was suspended in the reactor solution. Upon any partial change of $\delta^{18}\text{O}$ of oxides (i.e. change of relative amount of $^{18}\text{O}$ to $^{16}\text{O}$ as a result of the release of $^{18}\text{O}$ from oxide to solution or the incorporation of $^{16}\text{O}$ from water into the oxide structure), the changed portion got dispersed and mixed within the rest of the reactor content, and thus the measurements of $\delta^{18}\text{O}$ can be reliably presented as a time series.

### 2.2.3 Oxygen Isotope Analysis

Oxygen has three stable isotopes, $^{16}\text{O}$, $^{17}\text{O}$ and $^{18}\text{O}$, and they are the composition of natural occurring oxygen. The most abundance isotope is $^{16}\text{O}$, which accounts for 99.762% of all. In our experiment, we synthesized iron oxides (goethite and ferrihydrite) with $^{18}\text{O}$-enriched water, and thus labeled the oxides with isotopic oxygen $^{18}\text{O}$. With the Liquid Water Isotope Analyzer, the relative content of $^{18}\text{O}$ (tracer) compared to $^{16}\text{O}$ (normal) is analyzed and expressed as $\delta^{18}\text{O}$ in per...
mil (parts per thousand, ‰). It is an indicator of isotopic fractionation and is widely used in fields like geochemistry, paleoclimatology and paleoceanography. The formula is as follows:

\[
\delta^{18}O = \left( \frac{\frac{^{18}O}{^{16}O}_{\text{sample}}}{\frac{^{18}O}{^{16}O}_{\text{standard}}} - 1 \right) \times 1000 \cdot \%e
\]

where the standard has a known isotopic composition, such as Vienna Standard Mean Ocean Water (VSMOW).

2.3 Experimental Set-up

All experiments were carried out in an anaerobic glovebox filled with mixed nitrogen (about 98%) and hydrogen gas (about 2%) unless otherwise indicated. The solutions were made with deoxygenated DI water inside the glovebox and allowed to equilibrate with glovebox atmosphere for at least 24 hours before use. All other materials and instruments introduced into glovebox were degassed overnight prior to the experiment. The sorption reactors were all covered with aluminum foil to prevent any photochemical reactions.

In the first part of sorption experiments, the mass of \(^{18}\text{O}\) enriched goethite and ferrihydrite oxides were halved to allow for equal amounts of oxides within both a variable and a control reactor. The desired amounts of oxide were weighed out on a microbalance and in vessels of microcentrifuge tubes. One tube contained the mass of iron oxide for one sorption reactor. The tubes were brought into the glovebox, opened, and allowed to deoxygenate for 24 hours.

The stock Fe(II) solution was prepared by dissolving Fe(0) metal powder in diluted HCl acid; after sitting overnight while sitting on the magnetic stirrer, the solution was filtered through 0.2 micron nylon filter to remove insoluble particles. The concentration of the stock solution was
about 300 mM, samples were taken to determine the stock Fe(II) concentration with colorimetical method with 1,10-phenanthroline.  

The buffer and salt solution was prepared in the glovebox by weighing the required mass of MOPS buffer and KBr powder and dissolving them in DI water. Then the solution pH was adjusted to 7.5 using dilute NaOH and HCl solutions (both approx. 0.1M).

A series of four sorption reactors (A) goethite + dissolved Fe$^{2+}$ (B) goethite control (C) ferrihydrite + dissolved Fe$^{2+}$ and (D) ferrihydrite control were set up for the experiment. Reactor A and C contained aqueous Fe(II) while reactors B and D were without Fe(II) so as to demonstrate the effect of aqueous Fe(II) in the sorption and the potential liquid-solid atom exchange process, to be revealed by oxygen isotope tracing. The reactor solution of A & C were prepared by spiking a certain volume of stock Fe(II)$_{aq}$ into the buffer and salt solution to get 1mM initial Fe(II) concentration. After Fe(II) addition, the vial was agitated and the pH re-adjusted to 7.5 by adding some dilute NaOH. The stock solution was allowed to equilibrate for 12 hours and then filtered to remove precipitates that may form. Initial Fe-containing reactor stock solution was sampled for both aqueous $^{18}$O and aqueous Fe(II). Throughout this experiment, 3 or 4 parallel samples were taken for Fe(II)$_{aq}$ so the concentrations could be averaged later.

The pH of buffer and salt solution was re-adjusted to 7.5 before the start of sorption experiment, and this was stock solution for control reactors B & D. samples were taken from both reactor stocks for analyzing initial aqueous $^{18}$O. About 1.5ml solution was required for each $^{18}$O sample.

Right at the beginning of the sorption experiment, aliquots of 15 ml appropriate reactor stock solution were pipetted into 25 ml crimp-top glass vials labeled A, B, C and D. Iron oxides were added to the reactors in pre-weighed portions contained in the microcentrifuge tubes, and some reactor solution was pipetted back to the tubes to retrieve the remaining mass. The reactors were then wrapped and placed on an end-over-end rotator and allowed to mix for half a month. The $^{18}$O
samples were taken at 1d, 7d and 14d, and Fe(II) samples at times of 10min, 30min, 1h, 3h, 1d, 7d and 14d (Table 1).

The above procedures was followed by another sorption experiment, in which the sorption kinetics were observed over a longer period of time. The experiment consisted of four groups of sorption reactors, each contained a different ratio of goethite mass to bulk aqueous Fe(II) concentration. The conditions are detailed in Table 3. Each group contained 11 reactors; the first 8 were sorption reactors with goethite suspended in Fe(II)-containing solution, and the remaining 3 were goethite controls with no Fe(II) added. One (or more) reactor were taken off at the sampling time(s). Additionally, 2 sets of Fe(II) controls, consisting of 1.5 mM and 0.4 mM Fe(II) reactor stock solutions, were set alongside the sorption reactors.

Only $^{18}$O-enriched goethite was used; three batches of such goethite were synthesized. Group A and B were assigned their own batches, and group C and D divided up a third batch. Unlike the preceding experiment, goethite was pre-weighted into small portions each containing the mass needed for one reactor. The goethite portions were allowed to deoxygenate for 24 hours before sorption experiment. Reactor stock solutions were prepared by dissolving calculated mass of MOPS buffer and NaCl in deoxygenated DI water, and then spiking concentrated Fe(II) stock solution to get the desired initial Fe(II)$_{aq}$ levels. After pH adjustment to around 7.2, the stock was filtered through 0.2 $\mu$m PTFE filters so that small precipitates can be removed. A portion of buffer and salt solution was reserved for running goethite control reactors without spike of dissolved Fe(II). The Fe(II)$_{aq}$-spiked stock solutions were allowed to equilibrate for longer than 12 hours. Before starting the sorption reaction, the reactor stock solutions were filtered one more time and pH checked.

To start the sorption experiment, 7 ml aliquots of filtered stock were transferred to labeled glass vials and then the pre-weighted goethite mass were added. The starting times were staggered; the
sequence to start the reactors can be arbitrary, as reactors were individually timed. Reactors were sacrificed after running for the designated length of time on an end-over-end rotator.

At the end of the run, reactor was taken off and the content filtered. An extra 6 ml of DI water was used to moisturize filter tip and rinse off the solids sticking to the interior of the vial. Samples of aqueous Fe(II) and $\delta^{18}$O were taken from the filtrate, the sampling procedures are described in section 2.4. Goethite control reactors 9 to 11 were processed in the same manner as regular reactors. For reactor 9 ($t = 0$), time for goethite contact with stock solution was kept minimum; after a short agitation on a vortex mixer, the goethite suspension was immediately filtered and the filtrate sampled for aqueous Fe(II) and $\delta^{18}$O.

All three stock solutions (1.5 mM Fe, 0.4 mM Fe and no Fe) were sampled for aqueous Fe(II) at day 0 and day 40. The Fe(II) controls without goethite were also rotated in the same way as regular reactors and the Fe(II)$_{aq}$ measured at day 15 and day 30.

### 2.4 Sampling method

#### 2.4.1 Aqueous Fe(II)

Aqueous Fe(II) was tested colorimetrically with 1,10-phenanthroline method. The concentration can be measured reliably between about 20 to 300 micromolar. In this experiment, 100 µl of a filtered sample was added into 1ml DI water for 11-fold dilution, which brought the concentration a little below 100 micromolar. After acidification and dilution with dilute HCl (about 0.5 M), aliquots of 200 µl 1,10-phenanthroline and 200 µl ammonium acetate buffer solution were added to samples. An orange-red complex forms by 1,10-phenanthroline complexed with Fe(II). The absorbance was measured at 510 nm in a spectrophotometer and the Fe(II)$_{aq}$ concentration calculated based on the standard curve prepared with Fe(II) standards in the same approach.
2.4.2 $^{18}$O balance calculations

Liquid Water Isotope Analyzer (LWIA, Pennsylvania State University) was used to measure the $\delta^{18}$O values in liquid samples. One sample run required at least 5ml of the $^{18}$O-containing water. The isotope analyzer detects the relative abundance of $^{18}$O (tracer atom) versus $^{16}$O (normal) of the liquid samples, and the results are calibrated with a standard curve drawn from the analysis of a set of standards with known $^{18}$O/$^{16}$O values. The final results are in units of per mil (parts per thousand, ‰).

The $\delta^{18}$O values can be used to calculate the percentage of oxygen that exchanged between the solid and liquid phases. The calculation is based on the mass balance of $^{18}$O atoms within the system boundary. The solid and liquid phase can be viewed as two pools of oxygen-18 atoms that mix upon contact. The increase of the $\delta^{18}$O of water indicates the flux of $^{18}$O atoms through mineral-water interface. The higher the $\delta^{18}$O of water, the more $^{18}$O is released from goethite structure. If steady-state at each sampling point and uniform $^{18}$O site distribution in the goethite is assumed, the $\delta^{18}$O of water at any point can be expressed as

$$
\delta^{18}O_{mix} = \frac{n_{O_{water}} \delta^{18}O_{water} + n_{O_{goethite}} \delta^{18}O_{goethite} \times EX(\%)}{n_{O_{water}} + n_{O_{goethite}} \times EX(\%)}
$$

Where $n_O$ is the total moles of O atoms in either water or goethite mass, which can be calculated with the molecular weight and stoichiometry; $EX(\%)$ is the percentage exchange of O atoms.

With $\delta^{18}O_{mix}$ measured from this experiment, the percentage exchange of O between goethite and water can be calculated using this formula.

The $\delta^{18}$O values of both the oxide (goethite or ferrihydrite) and the stock solution were required for the above calculation. In an effort to determine the $^{18}$O content of the lab-synthesized goethite and ferrihydrite, several methods were tried out to dissolve goethite and ferrihydrite samples; first, dithionite ($Na_2S_2O_4$) solution with citrate ($Na_3C_6H_5O_7\cdot2H_2O$) and bicarbonate ($NaHCO_3$) was...
used, this is a common alternative method to acid dissolution used in soil analysis. Dithionite is a reductant and citrate serves as a complexant that forms soluble chelated Fe species. Solutions that may dissolve Fe(III) oxides either has concentrated $\text{H}^+$ ions, or has weakly acidic anions that are good complexants (such as citrate or EDTA). The result was not satisfactory, no significant dissolution was observed for goethite or ferrihydrite even with dithionite loading of 25 g/l, given the fixed solids concentration of 1 g/l. One study by Rueda et al. suggested citrate is less effective than EDTA when used with dithionite, because dithionite is more rapidly depleted at lower pH ($\text{pH} < 4$), and thus less Fe(III) could be reduced$^{22}$. Traditional acid method was resorted to in the end, results showed that 5M HCl is an appropriate solvent to completely dissolve both goethite and ferrihydrite with some heating. DI water samples, together with acid-dissolved goethite samples, were analyzed for the initial $^{18}$O compositions.

2.5 Results and discussions

In this study, we used $^{18}$O isotope as the tracer to indicate the potential oxygen cycling within the aqueous Fe(II) - iron(III) oxide system. The main goal is to examine if structural oxygen is capable of leaving the solid lattice and then mixing with bulk solution. Previous studies have already demonstrated near complete Fe exchange within 30 days under circumneutral conditions, demonstrating the extensive mixing occurring between the two Fe reservoirs$^{13}$. If $^{18}$O also displays the trend of near complete mixing, then it will be apparent that the atom exchange between oxide and Fe(II) solution is complete and the entire Fe oxide structure cycles. If the extents of O and Fe differs, then we know the two follows different pathways towards equilibrium, and it would be necessary to look at factors that govern the process of Fe(II)-catalyzed atom exchange equilibration.
Aqueous Fe$^{2+}$ remained relatively stable after the initial Fe$^{2+}$ uptake (Figure 1). Within 24 hours, dissolved Fe$^{2+}$ concentration in bulk solution decreased from ~ 1.1 mM to ~0.5 mM. Sample sacrificed at day 14 showed a slight increase of aqueous Fe$^{2+}$ concentration, though due to the sparseness of sample points, we cannot induce the time of the increase. Similar trends were observed for ferrihydrite (Figure 1), though the initial Fe$^{2+}$ uptake spanned only few hours, indicating a much faster kinetic than the goethite uptake. The faster uptake is most likely due to the relatively lower crystallinity and higher specific surface area of ferrihydrite compared to goethite. Neither goethite nor ferrihydrite control showed observable Fe$^{2+}$ in bulk solution phase; and given that no Fe$^{2+}$ were spiked at the beginning, the possibility of net dissolution and reduction of oxide-bound Fe(III) in the Fe(II)$_{aq}$ – absent environment is ruled out. All filtered liquid were colorless and remained transparent across all sampling points. Similar sorption trends were observed by Handler et al. in their experiment with $^{57}$Fe solution and isotopically normal goethite.$^{23, 24}$

In the goethite + dissolved Fe$^{2+}$ reactor, $\delta^{18}$O value increased from -5.55 ‰ to -2.79 ‰ within 14 days (Figure 2). The control reactor showed no change of $\delta^{18}$O value at all, which confirms the role of aqueous Fe$^{2+}$ as the catalyzer to the process of atom exchange, and that no O atoms from goethite spontaneously mixes with O from water. According to Handler et al., the isotopic Fe mixing continues even when dissolved Fe$^{2+}$ in the aqueous phase reached steady state. Our observation that $\delta^{18}$O of water kept increasing without net uptake or release of aqueous Fe$^{2+}$ indicates that oxygen also partake the solids-water mixing in the same manner as structural Fe.

Calculations based on mass balance (Section 2.4.2) has shown that with initial aqueous Fe(II), 3.99 % of the O atoms in goethite has been mixed with all water; the control showed only 0.04 % exchange. The presence of dissolved Fe(II) has promoted 3.95 % more O mixing from goethite solid within 14 days, indicating the release of a significant amount of solid-bound O atoms.
The $\delta^{18}O$ of ferrihydrite + Fe$^{2+}$ reactor has increased from -5.55 ‰ to -0.43 ‰ in 14 days. (Figure 2) Control reactor displayed a minute increase of $\delta^{18}O$ from -6.4 ‰ to -5.39 ‰. Like goethite, the $\delta^{18}O$ of ferrihydrite also followed an increasing trend, and dissolved Fe$^{2+}$ significantly affected the rate and extent of ferrihydrite O mixing. The influence of existing Fe$^{2+}$ seemed to have a stronger effect on ferrihydrite O mixing than on goethite (Figure 3 and 4), and pre-existing Fe$^{2+}$ has caused 4-fold increase in the mixing of ferrihydrite structural O (Table 2).

As observed for both goethite and ferrihydrite, even with the presence of initial Fe$^{2+}$, the percentage of oxygen atom mixing is very low. This contrasts to our hypothesis that all solid-associated atoms, including Fe and O, equally participate in the solid-liquid atom mixing through the Fe(II)-catalyzed recrystallization process. Since Fe atoms were not isotopically labeled in this study, no direct reference to Fe atom mixing is available, and we could not know the rate and extent of Fe fractionation. In the context of our experimental conditions and the results, there are two possibilities: the first is the entire oxide structure does not completely mix, and oxygen fractionation takes a different approach from iron fractionation. The other possibility is that the entire oxide does mix, but O quickly re-precipitates due to its strong affinity to solid Fe(III) phase.

The second experiment is very similar to the first one; however, instead of multiple extractions from the stirring goethite suspension in a single big reactor, samples were taken from individual reactors with designated sampling times.

Results of this experiment are shown in Fe(II)$_{aq}$ and O exchange time plots. (Figure 5) Aqueous Fe(II) in reactor Group A decreased slightly from 1.46 mM to around 1.26 mM in the first 15 minutes, initial uptake was followed by a steady period over the 30 day experiment. In Figure 5, the 40d data of reactor group A is missing because sample broke during processing. Reactor group B showed stronger initial Fe(II)$_{aq}$ uptake pattern comparing to group A, while negligible decrease is observed for group C or D. It seems that for C and D, measured concentration is
oscillating about the initial Fe(II)$_{aq}$ level during the sorption process. The change of Fe(II)$_{aq}$ is also presented in Figure 6 as the change of sorbed Fe concentration, which is the statistical value of micromoles of Fe(II) removed from solution by sorption normalized to the mass of goethite (grams) in reactor. The variance of sorbed Fe concentration is lowest in group B (with the highest solids to initial Fe(II)$_{aq}$ ratio) and highest in group D (with the lowest solids to initial Fe(II)$_{aq}$ ratio). Given same initial Fe(II)$_{aq}$ concentration of A, C and D (1.5 mM), it is apparent that when solid : Fe(II) ratio is less than 1.6 (the ratio in A: 2.4 g/l solid to 1.5 mM initial Fe(II)$_{aq}$), surface site availability becomes the more limiting factor for how much Fe sorbs. Similarly, B exhibited near complete uptake of Fe(II)$_{aq}$ because of the abundance of sorption sites. It is noteworthy that in Figure 6, the absolute values of y axis (sorbed Fe concentration) bear no physical meanings; if millimole instead of micromole is used, the values will shrink by 1000 fold. Control reactors containing 1.5 mM and 0.4 mM reactor Fe(II) stocks showed no Fe(II)$_{aq}$ changes.

The percentage of O atom exchange is based on the exchange between 7 ml DI water of -9.53 ‰ (mean measured) $\delta^{18}$O and the added goethite mass of 42,892 ‰ (calculated) $\delta^{18}$O. (goethite $\delta^{18}$O calculation is based on $^{18}$O mass balance and the assumption that goethite batches produced from same recipe have identical $^{18}$O contents) The percentage mixing of goethite structural oxygen displayed very weak trend of increase, with a consistent upward trend within the first 7 days of reaction. Within 30 days, an overall exchange of 16.12 % is observed from Group A, while Group B, C, and D have overall exchange of 10.52 %, 6.17 % and 45.6 %, respectively.

Several factors are potentially influencing the extent of O atom mixing; here, two factors are taken into account as an attempt to correlate the percentage O mixing with the reactor initial conditions and/or the extent of Fe uptake. The initial solid to Fe(II)$_{aq}$ ratio is in the decreasing order of B, A, C and D. It can be observed from Figure 5 that aqueous Fe(II) in Group B approached zero within the first 15 minutes, and the below-limit detection nullifies Group B Fe(II) data from reactors running longer than 15 minutes. For reactors C and D, surface sites are nearly
saturated due to the high Fe(II)\textsubscript{aq} to solid ratio, as a result, very negligible percentage of initial Fe(II)\textsubscript{aq} is sorbed onto goethite surface. The minor changes of sorbed Fe (in µmoles) in C and D caused great variations in sorbed Fe ratio, given the denominator of grams goethite. This precludes sorbed Fe ratio of C and D groups as a reliable source of data. After the exclusions, it can be seen that lower initial goethite Fe(II)\textsubscript{aq} ratio and higher sorbed Fe ratio is associated with more O atom exchange. The previous sorption experiment data is used here for comparison (Reactor labeled P in Table 4), and due to previous study only lasted for 14 days, only the 15 day data from reactors A, B, C and D are used for general trend analysis.

Despite the identical initial Fe(II)\textsubscript{aq} concentration and the near-saturated nature of surface sorption sites, a much higher overall O exchange was observed for D than C. Thus the oxygen mixing is not merely a function of how much Fe is sorbed. Smaller solids loading and higher fraction of unsorbed Fe are also promoting extra mixing of structural O atoms. The extent of mixing keeps increasing even when surface site is near saturation, and that higher unsorbed Fe brings about more O exchange is implying that the O exchange is not inhibited by surface Fe saturation. There’re two possible reasons, one is that Fe(II)\textsubscript{aq} precipitation and structural Fe dissolution happen at differential surface sites from oxygen cycling; the other possibility is that the potential gradient contributed to the formation of outer-sphere configured Fe(II)-Fe(III) species, which though redox-active, do not participate in bulk solid electron conduction, and allows the surface detached oxygen atoms to freely diffuse through.

2.6 Environmental Implications

The sorption studies performed for the first part of the thesis provided some important conclusions that helps to further the understanding of the pathway of the sorption between dissolved Fe(II) and common iron oxides. The rate and extent of oxygen exchange does not follow Fe exchange reported by a previous study\textsuperscript{29}. Oxygen atoms appear to not cycle out of goethite to the same extent as Fe atoms. Therefore, it is expected that the entire goethite crystal
does not dissolve and re-precipitate. The conveyor belt model proposed by Handler et al.\textsuperscript{23} may need to be reconsidered for. Oxygen mixing does not seem to be inhibited by surface site saturation caused by Fe uptake, and higher sorbed Fe on the same amount of solids appears to promote higher extent of oxygen mixing. Therefore, it is expected that for more reducing environment, pollutant assimilation induced at the mineral-water surface by redox activity, or the atom exchange process, will be much more efficient than more oxidative environments.

**Chapter 3. Selenate/selenite speciation in Fe(II)\textsubscript{aq} –goethite system**

### 3.1 Introduction

#### 3.1.1 Selenium in the Environment

Selenium is an important micronutrient for human and other mammals, but it has a really narrow concentration band between the necessary and toxicity level. While selenium induces bio-toxicity through many different mechanisms, ingestion of selenium-polluted drinking water has the greatest impact and it has raised widespread public health concern. Soluble selenium species consists of selenate (+6, Se(VI), SeO\textsubscript{4}\textsuperscript{2-}), selenite (+4, Se(IV), SeO\textsubscript{3}\textsuperscript{2-}) and hydroxyselenite (+4, Se(IV), HSeO\textsubscript{3}[-]), all of which are oxyanions; other forms of selenium include the elemental selenium (solid) and selenide minerals (solid) and selenide gas (-2, Se(-II), H\textsubscript{2}Se). Four common valent states of Se are +6, +4, 0, and -2. Selenium oxyanions have high solubility and mobility in water, and due to increased anthropogenic activities, a threatening amount of selenium is introduced to water bodies through farm drainage (selenium in pesticides) and oil refinery effluents. The speciation and oxidation states of Se affect its partitioning and mobility within and across compartments in nature. Due to the high affinity of Se oxyanions to porous surfaces, adsorption is frequently used to remove selenite and selenate in drinking water treatment.
3.1.2 Sorption of Oxyanions onto Iron Oxides

Earlier equilibrium and macroscopic studies have shown extent of irreversibility in the sorption of selenium oxyanions on iron minerals. This observation has begged for the question of the variation of sorption mechanisms, and with the advance of spectroscopic and molecular tracing techniques, laboratory kinetic studies were made possible to reveal the specific binding pathways associated with selenium oxyanions. In the kinetic study of selenate/selenite sorption on goethite-water interface by Zhang and Sparks, the measured intrinsic equilibrium constants for selenite was a close match to the modeled parameters based on ligand-exchange hypothesis. Based on the triple layer model (TLM) proposed by Zhang and Sparks (1990), selenite sorption happens in two stages; the first is the formation of outer-sphere complex by electrostatic attraction, and the second stage is the replace of surface hydroxyl group with selenium oxyanions with ligand exchange and the formation of inner-sphere complexes. Studies by Saeki et al utilized stable oxygen isotope tracers to further probe the surface ligand-exchange pathway, their results revealed the a mixed mechanism of mono-dentate and bi-dentate complexation. Studies with green rust (Fe(II)/Fe(III) hydroxides), a relatively more redox-active iron mineral, has shown that selenate can be reduced to selenite and elemental Se by structural Fe(II) and the electron transfer is the rate-limiting step in the sorption process. The differential sorption capacity of selenium oxyanions to goethite suggests that oxidation states of Se is an important factor that affects sorbate affinity to surface sorption sites and the rate and extent of sorption. Due to the fast kinetics of initial uptake, adsorption can be used to remove selenium from drinking water. Commonly used sorbents include ferrihydrite, ferrous hydroxide, activated carbon and activated alumina. Limitations exist for most adsorption techniques, for example, ferrihydrite and alumina are ineffective for selenate removal; the ferrous hydroxide has high reagent requirements, and produces a lot of sludge. Groundwater selenium pollution control also relies on the sequestration and immobilization by biological or chemical reduction of selenium species to elemental Se or by sorption of redox-active materials.
3.1.3 Rationale, Goal and Experiment Overview

Since there’s research evidence that electron transfer is pretty robust and is potentially mediating the redox cycling and recrystallization processes, it has led us to wonder the importance it can have on contaminant transformation in redox-active natural water environments. In our study, we have used selenite (SeO$_4^{2-}$) and selenate (SeO$_3^{2-}$), a pair of redox active selenium oxyanions, as representative pollutants. The goal of this study is to examine the influence of aqueous Fe(II) on the sorption of selenate/selenite on iron(III) oxide, and if there’s any redox changes to the selenium species during the oxide-oxyanion interactions.

As a preliminary attempt, this redox pair was chosen to reveal the potential reduction and oxidation processes occurring in the interaction between aqueous ferrous iron and goethite. The role Fe(II) plays in the sorption and possible redox interactions will be revealed by the comparison to the control group without initial aqueous Fe(II).

3.2 Experimental Methods

3.2.1 Isotopically Normal Goethite Synthesis

Normal goethite was synthesized in a similar approach as the $^{18}$O-enriched goethite of the previous chapter (Schwertmann and Cornell, 2000). A Teflon-lined tube with O-ring was used as the reaction vessel. Instead of diluted $^{18}$O water, 10 ml of DI water was added to dissolve a mass of 610 mg KOH pellets. This solution was then allowed to equilibrate for 20 min before a pre-weighed mass of 390 mg anhydrous FeCl$_3$ was added. Thick red-brown slurry of ferrihydrite formed immediately. The tube was vortexed and ultrasonicated for about 20 minutes to dissolve all Fe salt and achieve complete homogeneity. The slurry was held at 68°C oven for 4 days. During the heating process, the red brown suspension of ferrihydrite was converted to a compact, yellow-ochre precipitate of goethite. The vessel was removed from oven and centrifuged at $\times10,000$ g. To reduce background electrolyte, the solid was washed with DI water three times.
The supernatant was carefully decanted and discarded after each wash cycle consisting of agitation and centrifugation. After the final decantation, solid was freeze-dried, ground with mortar and pestle, and finally passed through 106-micron standard sieve. In this effort, 200.6 mg solid was produced and the yield was 93.7 %.

3.2.2 Experimental Set-up

All experiments were carried out in an anoxic glovebox filled with nitrogen (about 97 %) and hydrogen (3 %). All the glass and plastic ware, powdered materials were allowed to sit in the glovebox and degassed for at least 24 hours before use. All solutions used in the glovebox were made inside the glovebox with deoxygenated DI water (DO-DI). Chemicals were all reagent grade.

The reactor was also monitored for dissolved Fe(II) in bulk liquid phase. Solid loading for both groups were approx. 1.1 g/L. The designed initial Fe(II) concentration in experimental group was 2 mM. Both reactors had a circumneutral pH of 7.1±0.1, and this was maintained by manual adjustments at various points in the experiment. No buffer and salt solution was added, as this would interfere with the ICP-MS-based analysis of Se(IV)/Se(VI).

Two batches of normal goethite (one from a previous practice) made with same recipe were combined to get enough mass for this sorption experiment. The oxide was uniformly dry-mixed on an end-over-end rotator for an hour. On the microbalance, two portions of goethite, each 132 mg, were weighed into microcentrifuge tubes, and brought into the glovebox. Tube was opened up in glovebox and allowed to deoxygenate for at least 24 hours. A calibrated pH meter was brought into the glovebox for pH adjustments. The pre-weighed goethite was added separately into two glass jars each containing 120 ml DI-DO water. The solid suspension was mixed with a stir bar and magnetic stirrer for 5 minutes. After the agitation, pH were adjusted to 7.1±0.1 by adding small volumes (about 20 µL at a time) of 0.1 M HCl or 0.1 M NaOH solutions. The
volumes of each adjustment were recorded. After 4 hours of stirring, a small volume of stock Fe(II) solution was spiked into the experiment bottle to reach 2 mM initial aqueous Fe(II). Fe(II) stock solution was prepared by dissolving Fe(0) metal powder with dilute HCl acid, the procedures were described in Section 2.3. The spiked volume was estimated based on the approximate Fe(II) stock concentration, not considering the ensuing interactions between oxides and aqueous Fe(II) after the spike. Samples were taken to determine Fe(II) stock concentration. After Fe(II) addition, pH of both jars were re-adjusted and the suspensions stirred for another 24 hours. During this time, Fe(II)$_{aq}$ - goethite pair underwent the initial phase of fast kinetic changes and reach a plateau, where bulk solution Fe(II) concentration is supposed to be constant.

Upon completion of 24 hour stirring, pH was checked and re-adjusted if necessary. Aliquots of 20 ml were transferred to 25 ml clean crimp-top glass vials using pipette and bulb. During extraction, the suspension was being vigorously stirred to equalize oxide concentration in each aliquot. These glass vials were all batch sorption reactors with controlled initial conditions and identical operation parameters. Four reactors were prepared in each group, with labels A~D for experimental group and E~H for control group. Take samples from the remaining of both jars to determine the aqueous Fe(II) concentrations with colorimetical approach. The procedure was described in Section 2.4.1.

Reactors A to H were spiked with either selenite or selenate stock to get to the designed initial Se(IV) or Se(VI) concentrations. The organization of the reactors is shown in Table 5 with initial Se(IV)/Se(VI) concentrations. The time for adding Se stock solutions should be as short as possible. These doped reactors were subsequently crimped and shook up vigorously, wrapped in aluminum foil and placed on an end-over-end rotator inside the glovebox. After 24 hours of rotation in the dark, these reactors were taken off and sampled for Se(IV), Se(VI) and aqueous Fe(II).
The same volume of Fe(II) stock was spiked into an equivalent volume of DI (120ml + increments from pH adjustment) to determine the pre-sorption Fe(II) level. Fe(II) samples from Fe(II) stock needed to be diluted as the concentration was beyond the range of reliable measurement (20 ~ 300 µM) by 1,10-phenanthroline method.

3.3 Sampling method
All sampling were carried out inside the glovebox; aqueous Fe(II) samples were immediately acidified with dilute HCl solution (~0.1 M), and selenate or selenite samples were kept in microcentrifuge tubes inside the glovebox until the time of ICP-MS analysis. In this study, only aqueous samples were collected. After 24 hours of agitation on an end-over-end rotator, suspensions in reactors A to H were extracted with syringe and needle, and filtered with 0.2 micron nylon filters into 8 ml clean glass vials. A total volume of 5 ml liquid sample is required for each reactor. A ten-fold dilution was needed for the experimental group Fe(II)aq samples to bring down the concentration to the range of 100 ~ 200 µM (i.e. 2 mM). Aqueous Fe(II) was measured with 1,10 – phenanthroline method (see 2.4.1). Two aliquots of 2 ml liquid selenate/selenite samples were prepared for each reactor. Right before performing LC-ICP-MS analysis, the samples were spiked with 100 µL EDTA solution (as the complexation agent) to block the Fe interference with the analysis.

3.4 Analysis of selenium species (ICP-MS)
The analyses of aqueous selenate/selenite can be performed in many a ways. ICP-MS is the more and more used for its superior speed, precision and sensitivity. In our test, liquid samples were first injected into a Dionex ion exchange column attached to a Varian liquid chromatography unit and washed through with eluent (citric acid 20 mM, free acid form of EDTA (ethylenediaminetetraacetate) 5 mM, pH 6.0 ~ 6.5 adjusted with ammonium hydroxide). Components with different retention times were then separated and forced out of the column. The
analytes were then detected by an inductively coupled plasma mass spectrometer (Bruker Aurora M90) and quantified to standard solutions of known selenate or selenite concentrations.

3.5 Results and discussions

The aqueous Fe(II) concentrations prior to the addition of selenate/selenite is 1423 uM, as determined by the sample taken when aliquots of goethite suspension were transferred to separate reactors. In the 24 hours of equilibration of goethite suspension after Fe(II) is spiked, the dissolved Fe(II) in the solution phase dropped from 1826 µM to 1423 µM, indicating about 20% of initial Fe(II) uptake. Figure 7 and 8 shows the dissolved Fe(II) concentration of experimental and control groups respectively. The Fe(II) analysis of reactors E, F, G and H were non-effective (below 20 µM detection limit); and due to the lack of initial aqueous Fe(II), control group reactors cannot provide useful information about the sorption kinetics between selenium oxyanions and goethite, other than no generation of aqueous Fe(II) in that sorption process.

The loss of Fe(II)\textsubscript{aq} from reactor A and C are 23% and 24% respectively, and 14% and 13% from reactors B and D. (Table 6) Higher percentage losses are associated with high concentrations of selenium oxyanions, and the correlation is not linear. Compared with the vast uptake (loss from bulk solution phase) of selenate (Figure 9, reactors A to D), the continued uptake of Fe from solution showed great inhibition. It is possible that in the first 24 hours of sorption, Fe(II) sorptive sites might have reached saturation.

From the chart of bulk solution selenate and selenite (Figure 9), we can see that the presence of aqueous Fe(II) greatly promoted additional sorption of selenate (e.g. reactor A vs. E, reactor B vs. F) and selenite (reactor C vs. G). For selenate reactors A, B, E and F, more oxyanion removal were observed in A and E, indicating sorption kinetic dependence on substrate concentrations. The presence of aqueous Fe(II) promoted complete uptake of selenite by goethite (reactor C and D), while only half oxyanion was sorbed in reactor G. The extremely low level of selenate
detected in selenite reactors may be indicative of possible surface redox reaction between selenite and oxide crystal, that selenite is more redox-active in the interaction system of Fe(II)-iron(III). It is possible that some selenite was oxidized and the donated electrons become integrated in the Fe redox cycling and electron shuttling processes. By the comparison of either A and C or E and G, it can be seen that goethite has much higher affinity for selenite than for selenate.

In the previous chapter, the aqueous Fe(II) and iron oxide systems were explored. In addressing the goal of this specific study, the presence of Fe(II) in solution change the sorption capacity of goethite for both selenite and selenate. Although the pathway is not yet understood, the altered sorptive activity is most probably a concomitant process in surficial redox activities. One possible scenario is the incorporation of Se oxyanions into goethite crystal structure via Fe(II)-catalyzed recrystallization. Another likely scenario is that Fe(II), Fe(III) and Se oxyanion make a new mineral or solid solution at the surface of goethite.

3.6 Environmental implications

Sorption of in surface and subsurface environment plays an important role in the fate and transport of selenium pollutant. Evidence by many previous studies have revealed the dynamic nature of the interfacial interactions between selenium oxyanions and common iron oxides, and with sorbate-specific pathway, selenium species in nature are subject to multiple processes that changes its toxicity and mobility. There’s a pressing demand to find better treatment technologies for selenium removal, and that is only possible with a clearer understanding of the sorption process itself.
Figures

Figure 1. Bulk solution aqueous Fe(II) concentration in batch reactors A(red), B(blue), C(green) and D(yellow); with shared experiment conditions: 15 ml liquid volume, 25 mM MOPS buffer, 25 mM KBr, initial pH 7.5; reactor A: 4 g/L goethite, 1.0 mM dissolved Fe(II); reactor B: 4 g/L goethite, no initial dissolved Fe(II); reactor C: 1.8 g/L ferrihydrite, 1.0 mM dissolved Fe(II); reactor D: 1.8 g/L ferrihydrite, no initial dissolved Fe(II).
Figure 2. Bulk solution $\delta^{18}$O (in unit of permil) in batch reactors A (red), B (blue), C (green) and D (yellow) with shared experiment conditions: 15 ml liquid volume, 25 mM MOPS buffer, 25 mM KBr, initial pH 7.5; reactor A: 4 g/L goethite, 1.0 mM dissolved Fe(II); reactor B: 4 g/L goethite, no initial dissolved Fe(II); reactor C: 1.8 g/L ferrihydrite, 1.0 mM dissolved Fe(II); reactor D: 1.8 g/L ferrihydrite, no initial dissolved Fe(II).
Figure 3. Release of structural $^{18}$O into the reactor solutions in goethite reactors A (red), B (blue) during Fe(II)-catalyzed electron transfer and atom exchange process; the experiment conditions are: solids loading 4 g/l $^{18}$O-enriched goethite, reactor liquid volume 15ml, 25 mM MOPS buffer, 25 mM KBr, pH 7.5, reactor A has 1 mM initial dissolved Fe(II), reactor B has no initial dissolved Fe(II).
Figure 4. release of structural $^{18}$O into the reactor solutions in ferrihydrite reactors C (green), D(yellow) during Fe(II)-catalyzed electron transfer and atom exchange process; the experiment conditions are: solids loading 1.8 g/l $^{18}$O-enriched ferrihydrite, reactor liquid volume 15ml, 25 mM MOPS buffer, 25 mM KBr, pH 7.5, reactor C has 1 mM initial dissolved Fe(II), reactor D has no initial dissolved Fe(II).
Figure 5. The aqueous Fe(II) and water O exchange for regular sorption reactors (1 to 8) in the second experiment. The shared conditions are: 7 ml liquid, pH 7.2±0.05, 25mM MOPS, 25mM NaCl. Each reactor group has a different ratio of goethite mass loading to initial Fe(II) concentration. A) 2.4 g/l goethite, 1.5 mM Fe(II)\textsubscript{aq}; B) 2.4 g/l goethite, 0.4 mM Fe(II)\textsubscript{aq}; C) 1.6 g/l goethite, 1.5 mM Fe(II)\textsubscript{aq}; and D) 0.8 g/l goethite, 1.5 mM Fe(II)\textsubscript{aq}. The % O exchange calculation was based on the initial $\delta^{18}$O values of both the stock solution and the goethite samples. The mass balance for this calculation is described in Section 2.4.2.
Figure 6. Sorbed Fe concentration expressed as µmoles of Fe(II) removed from aqueous solution normalized to the mass (grams) of goethite in the reactor. The unit is µmoles Fe / gram goethite. The data shown in the above plot are calculated for regular sorption reactors (1 to 8 in group A to D). For detailed reactor setup, refer to Table 3.
Figure 7. Experiment group aqueous iron (II) concentration 24 hours after the start of the sorption reactors, bars on the horizontal axis from left to right are reactor A, B, C and D respectively, with shared conditions: suspended goethite 1.1 g/L, pH 7.1±0.1; and different concentrations of selenite [Se(IV)] or selenate [Se(VI)], A) 125 µM selenate, B) 12.5 µM selenate, C) 125 µM selenite, and D) 12.5 µM selenite.
Figure 8. Control group aqueous iron (II) concentration 24 hours after the start of the sorption reactors, bars on the horizontal axis from left to right are reactor E, F, G and H respectively, with shared conditions: suspended goethite 1.1 g/L, pH 7.1±0.1; and different concentrations of selenite [Se(IV)] or selenate [Se(VI)], E) 125 µM selenate, F) 12.5 µM selenate, G) 125 µM selenite, and H) 12.5 µM selenite.
Figure 9. Bulk solution phase selenate and/or selenite concentrations at t=0 and t=24 h after sorption onto goethite with or without aqueous Fe(II) for reactors A ~ H; selenate is indicated using green bars, and selenite indicated in blue bars. The lighter and darker colored bars corresponds to initial (t = 0) and end of reaction (t=24 h) concentrations respectively. The experimental conditions are: suspended goethite solids with mass loading of 1.1 g/L, pH 7.1±0.1. The selenium species analyses were performed with ICP-MS. Table 5 has experimental details. Greater removal of selenate or selenite from solution was observed when Fe(II) was present compared to when Fe(II) was absent.
Table 1. Reactor design and sample time organization for batch reactors containing either $^{18}\text{O}$-enriched goethite or $^{18}\text{O}$-enriched ferrihydrite. Batch reactors contained 4 g/L goethite or 1.8 g/L ferrihydrite, 25 mM MOPS buffer, 25 mM KBr, 1.0 mM dissolved Fe(II) at pH 7.5.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Initial Reactor Configuration</th>
<th>Solid</th>
<th>$^{18}\text{O}$ Sample Times</th>
<th>Aqueous Fe(II) Sample Times</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>25 mM MOPS buffer + 25 mM KBr +Fe(II)</td>
<td>Goethite 60.210 mg</td>
<td>4</td>
<td>10min, 30min, 1h, 3h, 1d, 7d, 14d</td>
</tr>
<tr>
<td>B</td>
<td>25 mM MOPS buffer + 25 mM KBr</td>
<td>Goethite 60.257 mg</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>25 mM MOPS buffer + 25 mM KBr +Fe(II)</td>
<td>Ferrihydrite 27.067</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>25 mM MOPS buffer + 25 mM KBr</td>
<td>Ferrihydrite 26.997</td>
<td>1.8</td>
<td></td>
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</tbody>
</table>
Table 2. Percent of bulk oxide structural $^{18}$O that has been mixed with the reactor solutions during Fe(II)-catalyzed electron transfer and atom exchange processes; the experiment conditions are: solids loading 4 g/l goethite or 1.8 g/l ferrihydrite, both $^{18}$O-enriched, reactor liquid volume 15ml, 25 mM MOPS buffer, 25 mM KBr, pH 7.5, the initial dissolved ferrous iron was 1 mM.

<table>
<thead>
<tr>
<th>Days</th>
<th>$\delta^{18}$O value of water ($‰$)</th>
<th>Change in $\delta^{18}$O value of water ($‰$)</th>
<th>% of goethite O mixed with all water</th>
<th>Days</th>
<th>$\delta^{18}$O value of water ($‰$)</th>
<th>Change in $\delta^{18}$O value of water ($‰$)</th>
<th>% of goethite O mixed with all water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-5.55 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-5.55 0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>-4.68 0.870</td>
<td>1.26</td>
<td>1</td>
<td>1</td>
<td>-1.07 4.480</td>
<td>10.53</td>
<td>10.53</td>
</tr>
<tr>
<td>7</td>
<td>-3.37 2.180</td>
<td>3.15</td>
<td>7</td>
<td>7</td>
<td>-0.75 4.800</td>
<td>11.29</td>
<td>11.29</td>
</tr>
<tr>
<td>14</td>
<td>-2.79 2.760</td>
<td>3.99</td>
<td>14</td>
<td>14</td>
<td>-0.43 5.120</td>
<td>12.04</td>
<td>12.04</td>
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<tr>
<td>0</td>
<td>-6.40</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>-6.47 -0.070</td>
<td>0.10</td>
<td>1</td>
<td>1</td>
<td>-6.06 0.340</td>
<td>0.80</td>
<td>0.80</td>
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<tr>
<td>7</td>
<td>-6.44 -0.040</td>
<td>0.06</td>
<td>7</td>
<td>7</td>
<td>-5.53 0.870</td>
<td>2.05</td>
<td>2.05</td>
</tr>
<tr>
<td>14</td>
<td>-6.37 0.030</td>
<td>0.04</td>
<td>14</td>
<td>14</td>
<td>-5.39 1.010</td>
<td>2.37</td>
<td>2.37</td>
</tr>
</tbody>
</table>
Table 3. The reactor setup for the second experiment in Chapter 2. The regular sorption reactors are numbered 1 to 8 in all four groups (A, B, C and D), reactors numbered 9, 10 and 11 in those four groups are goethite controls with no initial Fe(II) spiked. D1, D2 and E1, E2 are Fe(II) controls. The conditions specified in the header row are shared among the reactors in the same column and the running time for those reactors are shown in the bracket. For example, C7 has solution conditions of 25 mM MOPS, 25 mM NaCl, around 1.5 mM of aqueous Fe(II) and the solid loading is 1.6 g/ml, and the reactor ran a total of 30 days. All reactors contained 7 ml liquid and the pH of the stock solutions were maintained at 7.2±0.05.

<table>
<thead>
<tr>
<th>GROUP (shared conditions)</th>
<th># (shared conditions)</th>
<th>1 to 8</th>
<th>9 to 11</th>
<th>1 to 2</th>
</tr>
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<tbody>
<tr>
<td><strong>GROUP</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>2.4g/l goethite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.4g/l goethite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1.6g/l goethite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.8g/l goethite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Aqueous Fe(II) present</strong>; 25 mM MOPS &amp; 25 mM NaCl (15min, 12hr, 1.5d, 3d, 6d, 15d, 30d, 40d)</td>
<td><strong>Aqueous Fe(II) absent</strong>; 25mM MOPS &amp; 25mM NaCl (0, 15d, 30d)</td>
<td><strong>Aqueous Fe(II) present</strong>; 25 mM MOPS &amp; 25 mM NaCl (0, 15d, 30d)</td>
</tr>
<tr>
<td>Sorption reactors</td>
<td>1.5mM Fe(II)</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>0.4mM Fe(II)</td>
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</tr>
<tr>
<td></td>
<td>1.5mM Fe(II)</td>
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</tr>
<tr>
<td></td>
<td>1.5mM Fe(II)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Goethite control reactors</td>
<td>no Fe(II)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>no Fe(II)</td>
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<tr>
<td></td>
<td>no Fe(II)</td>
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<tr>
<td></td>
<td>no Fe(II)</td>
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<td></td>
</tr>
<tr>
<td>Fe(II) control reactors</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Two identical reactors each filled with 7ml reactor stock</td>
<td></td>
<td>Two identical reactors each filled with 7ml reactor stock</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Two identical reactors each filled with 7ml reactor stock</td>
<td></td>
<td>Two identical reactors each filled with 7ml reactor stock</td>
<td></td>
</tr>
</tbody>
</table>

D, E, D1, D2, E1, E2 are Fe(II) controls.
Table 4. Initial reactor goethite mass to aqueous Fe(II) concentration (g/l goethite per mM) and the sorbed Fe concentration (in mmoles of sorbed Fe per gram of goethite in reactor). Reactors A, B, C, D are from the second sorption experiment in Chapter 2 and see Table 3 for reactor conditions; sorbed Fe data for this experiment collected from 15d. Reactor P is the goethite + dissolved Fe$^{2+}$ reactor in the first sorption experiment in Chapter 2, and the condition of the reactor is 25 mM MOPS, 25 mM KBr, pH 7.5, goethite mass loading and initial Fe(II)$_{aq}$ shown in above table.

<table>
<thead>
<tr>
<th>Measure</th>
<th>Goethite mass loading</th>
<th>Initial aqueous Fe(II)</th>
<th>Initial solid to aqueous Fe(II) ratio</th>
<th>Sorbed Fe concentration at day 14/15</th>
<th>14/15 day O exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Group</td>
<td>g/l</td>
<td>mM</td>
<td>g/l goethite per mM Fe(II)$_{aq}$</td>
<td>mmoles Fe sorbed per g goethite</td>
<td>%</td>
</tr>
<tr>
<td>B</td>
<td>2.4</td>
<td>0.4</td>
<td>6</td>
<td>121</td>
<td>Invalid</td>
</tr>
<tr>
<td>P</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>88.4</td>
<td>3.99</td>
</tr>
<tr>
<td>A</td>
<td>2.4</td>
<td>1.5</td>
<td>1.6</td>
<td>154</td>
<td>12.96</td>
</tr>
<tr>
<td>C</td>
<td>1.6</td>
<td>1.5</td>
<td>1.067</td>
<td>Invalid</td>
<td>23.35</td>
</tr>
<tr>
<td>D</td>
<td>0.8</td>
<td>1.5</td>
<td>0.53</td>
<td>Invalid</td>
<td>65.8</td>
</tr>
</tbody>
</table>
Table 5. Organization of sorption reactors in experimental and control groups with goethite loading, initial dissolved Fe(II) conditions and the spiked selenium species information. Other reactor conditions are: pH 7.1±0.1, constantly rotated on an end-over-end rotator.

<table>
<thead>
<tr>
<th>Experimental Group Reactors</th>
<th>Control Group Reactors</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong> [1.1 g/L Goethite + 1423 µM Fe(II)]</td>
<td>125 µM Se(VI)</td>
</tr>
<tr>
<td><strong>B</strong> [1.1 g/L Goethite + 1423 µM Fe(II)]</td>
<td>12.5 µM Se(VI)</td>
</tr>
<tr>
<td><strong>C</strong> [1.1 g/L Goethite + 1423 µM Fe(II)]</td>
<td>125 µM Se(IV)</td>
</tr>
<tr>
<td><strong>D</strong> [1.1 g/L Goethite + 1423 µM Fe(II)]</td>
<td>12.5 µM Se(IV)</td>
</tr>
</tbody>
</table>
Table 6. Percentage loss of dissolved Fe(II) from bulk solution within 24 hours of sorption in reactors A to D, with shared conditions: suspended goethite 1.1 g/L, pH 7.1±0.1; and different concentrations of selenite [Se(IV)] or selenate [Se(VI)], A) 125 µM selenite, B) 12.5 µM selenate, C) 125 µM selenite, and D) 12.5 µM selenite.

<table>
<thead>
<tr>
<th>Reactor Label</th>
<th>Reactor Configuration</th>
<th>Fe(II)\textsubscript{aq} after 24 hours [µM]</th>
<th>Aqueous phase Fe(II) loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>expt + 125 µM Se(VI)</td>
<td>1090.538</td>
<td>23.4</td>
</tr>
<tr>
<td>B</td>
<td>expt + 12.5 µM Se(VI)</td>
<td>1223.203</td>
<td>14.0</td>
</tr>
<tr>
<td>C</td>
<td>expt + 125 µM Se(IV)</td>
<td>1077.983</td>
<td>24.2</td>
</tr>
<tr>
<td>D</td>
<td>expt + 12.5 µM Se(IV)</td>
<td>1234.502</td>
<td>13.2</td>
</tr>
</tbody>
</table>
REFERENCES


4. Latta, D. E. A geochemical investigation of heterogeneous redox reactions between Fe(II), Fe(III), and uranium. *Dissertation, University of Iowa* 2010,


