ABSTRACT

BI, YUQIANG. Production of Co-Siderophore Complexes by Ligand-Promoted Dissolution. (Under the direction of Owen Duckworth.)

Recent research indicates that siderophores, a class of biogenic ligands with known exceptional affinity for Fe(III), can also strongly complex Co(III), an element essential to normal metabolic function of microbes and animals. This study was conducted to examine the siderophore-promoted dissolution rates and mechanisms of Co from model synthetic Co-bearing minerals to elucidate the role of siderophores in biogeochemical processes of Co. Dissolution of heterogenite (CoOOH) and four Co-goethites (Co-FeOOH) with different levels of Co substitution were investigated in the presence of a trihydroxamate siderophore, desferrioxamine B (DFOB), using batch and flow-through experiments, respectively. By measuring the complex and total metal concentrations in dissolution products, dissolution rates via multiple pathways were measured as a function of pH. Results showed that DFOB promoted dissolution of Co from Co-bearing minerals via pH-dependent mechanisms. For heterogenite, ligand-promoted dissolution was the dominant pathway at neutral to alkaline pH, while reductive dissolution became dominant for pH < 6. Cobalt substitution in Co-goethite resulted in increased total dissolution rates of both Co and Fe, but ligand-promoted and reductive Co dissolution pathways were difficult to examine due to the slow dissolution rates. The fast dissolution rate of heterogenite, coupled with the high affinity of Co(III) for DFOB, suggests that siderophore-promoted dissolution of Co(III) oxides is a biogeochemically favorable process. Although the association of Co with Fe oxide mineral may limit the Co dissolution rate, siderophore-promoted Co dissolution may still be an effective enough way to increase Co bioavailability. The results also suggest possible
mobilization of radionuclide $^{60}$Co by siderophores from recalcitrant Fe oxide phases, which may be important to the fate and transport of $^{60}$Co in contaminated environments.
Production of Co-Siderophore Complexes by Ligand-Promoted Dissolution

by
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Yuqiang Bi was born and raised in Urumqi, China as the only child in the family. He spent most of his childhood living with his paternal grandparents, who gave endless love and support to him. After graduation in a local high school, he attended Nanjing University where he studied Environmental Sciences. It was the first time he left his family for education. In college, Yuqiang was an active organizer in many school activities and kept a passion of learning sciences and protecting the environment. He decided to pursue graduate study abroad after the completion of his BS degree. In August 2007, Yuqiang moved to the United States and started his study in Soil Science as a master’s student at NC State University. Here he experienced a different language and culture, and worked with an outstanding group of people contributing to the knowledge of Soil Science. With a continuous interest in environmental research, Yuqiang plans to pursue her Ph.D. in Environmental Engineering at University of Michigan.
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Chapter 1

Introduction
By altering the habitat wherein they live, soil organisms participate in the genesis and formation of soil along with other environmental factors (viz. parent material, climate, topography, and time). During the complicated physical and chemical processes induced by soil organisms, soil minerals consistently provide a major source of inorganic micronutrients to support metabolic activities. In environments with low nutrient availability, organisms synthesize and exude a myriad of compounds, such as low molecular mass organic acids and siderophores (multi-dentate iron specific biogenic chelators), to their local environment that facilitate mineral weathering [1]. The case of siderophore-promoted dissolution of Fe oxides is of particular interest from both chemical and evolutionary perspectives. It has been postulated that the biological system of siderophore synthesis, which is widespread in the bacteria, fungi, and plant kingdoms, evolved in response to the Earth’s increasingly oxic environment, resulting in the highly effective Fe acquisition strategy [2, 3]. Siderophores may, however, also promote the dissolution or desorption of metals other than Fe [4-6], and thus metal-siderophore complexes can enter into the environment. The consequent effects of the transport and transformation of metals in terrestrial environments may have broader implications for both natural processes and anthropogenic activities.

The work presented in this thesis examines the production of Co complexes through the dissolution of Co-bearing minerals by a siderophore to give new perspectives on biogeochemical role of siderophores and their interactions with transition metals.
1.1 Siderophores

Siderophores are biogenic low molecular weight organic chelating agents that are produced by a number of microorganisms and plants [7]. Because of their exceptional affinity and specificity for Fe(III), siderophores are utilized to acquire Fe in many Fe-limiting environments. Siderophores function as ligands to labilize Fe from the various Fe recalcitrant pools in soils and aquatic environments [7]. Based on the different biological sources, siderophores are generally categorized as microbial siderophores and phytosiderophores. Currently, approximately 500 different microbial siderophores have been identified among bacteria and fungi [8]. Most microbial siderophores contain hydroxamate, catecholate, or α-hydroxycarboxylate functional groups for Fe coordination in linear, cyclic, or tripodal configurations [8]. To satisfy the octahedral coordination preferred by Fe$^{3+}$, microbial siderophores usually act as hexadentate ligands to form 1:1 complexes. The known stability constants of such 1:1 Fe(III)-siderophore complexes range from $10^{30}$ to $10^{50}$ [7], which are many orders of magnitude higher than those of most Fe complexes formed by common organic ligands, such as EDTA and oxalate [9, 10].

Graminaceous plants, including barley, wheat, and rice, also produce siderophores (commonly called phytosiderophores) as a response of Fe deficiency [11]. The exudation pattern of the phytosiderophore release follows a diurnal rhythm with an estimated concentration of up to 1 mM in the rhizosphere [11, 12]. Classified as mugineic acid family containing carboxylate and hydroxyl groups, phytosiderophores usually behave in the same manner as microbial siderophores forming 1:1 complexes with Fe(III) [7, 11]. However, the stability constant of Fe(III)-phytosiderophore complexes are generally lower than microbial
siderophore iron complexes [11, 13]. Figure 1.1 shows the molecular structures of two siderophores: the microbial siderophore desferrioxamine B (DFOB) (a, b) and the phytosiderophore mugineic acid (c).

Siderophore concentrations in most natural systems are in the range of ca. $10^{-9}$ to $10^{-6}$ M, with the observed concentrations in the order: marine environment $<$ bulk soil $<$ fresh water $<$ rhizosphere [7, 14]. The importance of siderophores in the acquisition of Fe has been recognized for more than 50 years [15]. Several recent reviews have summarized progress in our understanding in siderophore-mediated Fe uptake in soil and marine systems [7, 16, 17]. Emerging research, however, has suggested additional biogeochemical roles of siderophores with metals beyond this well-characterized uptake system [5, 18-20].

1.1.1 Chemistry of Desferrioxamine B (DFOB)

Desferrioxamine B (DFOB), the most commonly studied siderophore, is a trihydroxamate microbial exudate produced by terrestrial and marine microbes with the structure depicted in Figure 1.1 (a). Its three hydroxamate functional groups form 1:1 solution complexes by satisfying the octahedral coordination sphere of Fe(III). Each hydroxamate group results in a five-membered ring between Fe(III) and the carbonyl and hydroxylamine (-NO) groups. The stability of the aqueous Fe(III)-DFOB complex arises in part from the efficacy of the hydroxamate functionality as a Lewis base, donating electron density to the central Fe(III). This chelation results in a stable complex with considerable delocalization of electron density in the complex core [21]. Figure 1.1 (b) shows the molecular structure of Fe(III)-DFOB complex [18, 21, 22].
In this study, DFOB was chosen as the model siderophore for its representation of the trihydroxamate class of siderophores, commercial availability, and its known interaction with Co(III) [18]. The DFOB sample utilized is the mesylate salt [(C\(_{25}\)H\(_{46}\)N\(_{5}\)O\(_{8}\)NH\(_{3}\))^+(CH\(_{3}\)SO\(_{3}\))^−] of molecular weight 656.8 g mol\(^{-1}\), having the addition of a coordinate CH\(_{3}\)SO\(_{3}\)^+ functional group as a synthesis adduct. The sample was purchased from Sigma-Aldrich. If the mass of the CH\(_{3}\)SO\(_{3}\)^+ moiety is subtracted, the remaining mass is 545.5 g mol\(^{-1}\); addition of Fe to the structure renders a molecular weight of 601.3 g mol\(^{-1}\).

Based on the thermodynamic formation constants for free DFOB and Fe(III)-DFOB complex species in Table 1.1, aqueous speciation distribution of DFOB [Figure 1.2 (a)] and Fe(III)-DFOB [Figure 1.2 (b)] can be calculated by MINEQL+ 4.6 as a function of pH. It is worth noting that over the majority of environmental pH, both free DFOB and trivalent Fe(III)-DFOB complexes are cations.

Recent research indicates that siderophores can strongly complex, in addition to Fe(III), other hard metal cations, such as Mn(III) and Co(III) (Table 1.1). Structurally, these 1:1 metal–DFOB complexes are analogous to Fe(III)HDFOB\(^+\) with octahedral or distorted octahedral geometries [23]. Duckworth et al. [18] reported the largest currently known stability constant for Co(III)HDFOB\(^+\) among the known 1:1 M\(^{x+}\)HDFOB\(^{x-2}\) complexes, which is five orders of magnitude larger than that for Fe(III)HDFOB\(^+\). It is now becoming apparent that siderophores may engage in a diverse chemistry with a variety of environmentally and biologically important metal cations [3, 5, 18, 24]. The high affinity of DFOB for Co(III) suggests that Co speciation and transport may be strongly affected by siderophores.

5
1.2 Hydrous Metal Oxides

Hydrous oxide minerals, including oxides, hydroxides, and oxyhydroxides of metals, are important secondary minerals that usually serve as the stable end products of weathering processes in oxic environments. Environmentally important oxides are those of Al, Fe, and Mn, which are abundant components of the Earth’s crust. Metal oxides usually occur in soils as small crystals or coatings with large reactive surfaces, especially for those poorly crystalline oxides, which are capable of forming strong surface complexes with a myriad of metal, ligand, and molecular species (both inorganic and organic). Therefore, these minerals may have significant influence over the chemical characteristics of a soil solution and greatly impact the fate and behavior of substances in the soil environment.

1.2.1 Iron Oxides

The oxides, hydroxides, and oxyhydroxides of Fe, collectively called Fe oxides, are important components of many natural and human-made systems. They are widespread in soils, sediments, and rocks, and act as a major pool of Fe in terrestrial and aquatic environments [25]. Goethite (α-FeOOH), hematite (α-Fe₂O₃), magnetite (Fe₃O₄) and ferrihydrite (~Fe₅HO₈·4H₂O) are the common Fe oxides in soils or other terrestrial environments. Of all Fe oxides, goethite is most common and ubiquitous [25-27].

Under oxic conditions, Fe oxides are very insoluble in aquatic systems with low thermodynamic solubility constants (K_{sp}). Generally, solubility of common Fe oxides decreases in the order: ferrihydrite > maghemite > hematite ≥ goethite [28]. The solubility of
Fe oxides can be strongly influenced by crystal size and solution pH, with observed minimum solubility in the neutral to alkaline pH range [7, 29]. Due to low solubility and slow dissolution kinetics of Fe oxides, biological Fe deficiency is a wide-spread problem in many natural aerobic systems.

In the environment, Fe oxides usually incorporate foreign metals in their structures by isomorphous substitution. The cations Al, Cr, Mn, Co and Ni have been reported to exist in naturally occurring and synthetic goethites [30, 31]. Natural magnetites may also host many cations, such as Zn, Cu, Mn, Co, Mg and Ti [32]. The degree to which Fe is replaced by a foreign cation depends on the similarity in size and valence of the substitute cation, and its tendency to form comparable structure. Isomorphous substitution of Fe$^{3+}$ by foreign metals can affect many physical and chemical properties of Fe oxides, such as particle size, surface area and lattice energy [33]. The consequent influence on solubility of Fe oxides raises interesting questions in understanding the geochemical fate of both Fe and various metals during weathering processes.

1.2.2 Cobalt and Metal Oxides

Cobalt is a transition metal that naturally exists in compound forms. Common oxidation states of Co include +2 and +3, although an oxidation state of +1 is also known in some biological systems. As a trace nutrient, Co is required by certain microorganisms for N$_2$ fixation, such as free-living bacteria and cyanobacteria [34]. Cobalt is also a constituent of vitamin B$_{12}$, which is required by all animals for red blood cell formation and by most microbes for a wide array of metabolic processes [35]. Despite being essential for most
multicellular organisms, Co in most natural systems is present at very low concentrations: 3-70 mg·kg⁻¹ in soils [36]; 4-20 pM in oceanic surface waters [37]. The bioavailability of Co to plants is of general concern, because plants are one of the major sources of Co for humans and animals [34, 35].

Cobalt is also a concern to public health due to the radioactive isotope cobalt ⁶⁰Co [38]. ⁶⁰Co is produced by neutron capture of ⁵⁹Co in steel components of nuclear reactors and particle accelerators [38]. Despite a trace amount globally, ⁶⁰Co may be present as a contaminant at certain locations, for example, Department of Energy (DOE) facilities such as the Hanford Site and Oak Ridge National Laboratory [38, 39]. The gamma rays that accompany the radioactive decay of ⁶⁰Co may be acutely hazardous in high doses or increase risk of developing cancer with chronic exposure.

In many cases, Co has been found to preferentially adhere to soil either by sorption to mineral surfaces or by isomorphous substitution in mineral crystal lattices [34, 40]. Various investigations found that Co accumulates in hydrous oxides of Fe and Mn in soils. Burns [41] indicated that Co was associated with Fe oxides; similarly, Mn oxides play a key role in the chemistry of soil Co [42, 43]. Taylor and McKenzie [44] have shown that Co associated with Mn minerals could account for almost all of the Co in soils in some cases, suggesting Mn minerals as an important sink for Co in soil.

Because of the intimate relationship between Co and metal oxides, weathering processes of oxides can also influence the geochemical fate of Co, posing risks of dispersion of ⁶⁰Co in the environment. At Oak Ridge, TN, ⁶⁰Co has been reported to have migrated several miles away from a disposal site in the presence of organic chelating agents such as
EDTA [39, 45]. Brooks et al. [46] further indicated that Fe oxides could be more important for the formation of the very stable and mobile $^{60}\text{Co(III)EDTA}^-$ complex by promoting Co(II) oxidation. Given the exceptionally high affinity of siderophores DFOB for Co(III), the fate and transport of Co in terrestrial environments may be strongly coupled to Fe oxides in the presence of siderophores.

1.3 Dissolution of Metal Oxides

1.3.1 Surface Chemistry of Oxides and Adsorption Reactions

Hydrous oxide minerals usually bear highly reactive surface sites that are responsible for the retention of many classes of substances [47]. The surfaces of oxides are therefore the location of many important chemical reactions. Under hydrated conditions, hydrous oxide surfaces contain surface hydroxyl functional groups that are subject to protonation and deprotonation, resulting in the pH-dependent charge of minerals. The combination of mineral surface, type and number of hydroxyl groups, and the environment in which the mineral resides, largely determine the reactivity of hydrous oxides. For example, there are three types of surface hydroxyl functional groups in the goethite structure [47]. The number of structural Fe atoms bound to hydroxyl groups poses differences in surface reactivity due to different extents of polarization of oxygen atoms [47]. For other oxide minerals, the valence and coordination of the structural metal atoms also influence the reactivity of surface hydroxyl groups.

The surface hydroxyl groups can exhibit both Lewis acid and Lewis base character in aqueous environments [48]. For example, a ligand from solution phase can replace the
surface-bond water of the $\equiv\text{Fe-OH}_2^{+2}$ group on a goethite surface through ligand exchange. Conversely, hydroxyl groups can also behave as ligands so that protons and cations in solutions are bound to the structural surface oxygen. These properties of surface hydroxyl groups establish the significant role of solution pH in governing the extent of adsorption [48].

When surface hydroxyl groups react with ions or molecules dissolved in soil solution, adsorption of solute is observed. In a microscopic view, surface complexes are formed by exchange processes. Non-specific adsorption occurs when outer-sphere surface complexes are formed and maintained by electrostatic bonding [36]. This type of surface complex can be easily dissociated because there is no specific bond between the hydroxyl group and adsorbed species. Inner-sphere surface complexes are formed if aqueous species bind directly to the surface with no intervening water molecule [36]. This specific adsorption mechanism creates surface bonds of a relatively high degree of structural configuration and some covalent character, making surface complexes harder to dissociate. In the scenario of inner-sphere surface complexes, the type of surface configuration may control reactivity. For example, mononuclear multidentate complexation usually favors mineral dissolution reactions. To predict the interactions on metal oxide surfaces, aqueous ligand exchange rates have been correlated with the tendency for surface complexation [47].

In addition to many chemical models to interpret adsorption reactions, adsorption isotherms are often utilized to provide a quantitative measure of substance adsorption by soil minerals as a nonmechanistic approach [49]. The data are typically presented as a graph of the equilibrium surface excess or the amount of a solute adsorbed versus the equilibrium solution concentration of the solute. Four common types of isotherms can be derived from
adsorption experiments: L-type, H-type, S-type and C-type. Langmuir and Freundlich equations have been widely employed to mathematically describe L-type adsorption behavior, the most common pattern observed in isotherms [47]. Understanding sorption behavior is critical to the interpretation of dissolution data because dissolution rates are typically directly related to the surface concentration of active dissolution sites [50].

1.3.2 Dissolution Mechanisms

Surface complexes formed from adsorption reactions can affect metal-to-lattice bond strength by polarizing, and thus weakening the critical metal-oxygen bonds. The strength of surface complexes, and thus degrees to which the bonds between surface metal centers and crystal lattice are weakened can determine the dissolution rate of metal oxides. In particular, mononuclear multidentate complexation by strongly electron-donating moieties usually favors dissolution reactions [48].

The dissolution of metal oxides is typically the combination of several reactions, including ligand-promoted, reductive, and proton-promoted dissolutions. Dissolution kinetics are assumed to be controlled by these chemical processes in this thesis, because physical processes, such as transport of reactants to surface or dissolution products to bulk solution, are anticipated to be much faster than dissolution in our systems [50]. The overall dissolution rate is therefore assumed to be the sum of reaction rates for separate pathways that occur in parallel.
1.3.2.1 Non-Reductive Ligand-Promoted Dissolution

Natural and anthropogenic ligands can promote dissolution of metal oxide minerals. If surface complexes formed through adsorption reactions facilitate the dissolution of metals from the surface to the adjacent solution, the dissolution rates of oxides increase. The dissolution mechanism is usually expressed by the following three steps: (1) fast adsorption of ligands on oxide surface by ligand exchange of surface hydroxyl groups and formation of surface complexes, (2) detachment of surface metal species, usually facilitated by polarization of metal-oxygen bonds within the mineral structure, (3) regeneration of the surface site and transport of the detached metal into bulk solution [47]. Since the detachment of surface complexes is usually the rate-limiting step, rate laws of surface-controlled reactions can be derived in terms of the concentration of surface complexes (Eq. 1.1):

$$ R_L = \frac{d}{dt}[\text{Me} - L] $$


(1.1)

where $R_L$ is the dissolution rate, $k_L$ is the corresponding dissolution rate constant, and $[\text{Me} - L]$ is the concentration of active surface complexes. If the surface speciation is proportional to the surface excess of adsorbed ligands $[L]_{ads}$, the equation can be simplified to [48]:

$$ R_L = k_L[L]_{ads} $$

(1.2)

Any factors that influence the ligand surface concentration or coordination are also likely to influence dissolution rates. For example, bidentate ligands such as hydroxamates can form relatively strong bidentate surface complexes [51, 52] that have a significantly greater effect on oxide dissolution kinetics than monodentate surface complexes [48]. Even among bidentate surface complexes, five-membered chelate rings tend to have a higher effect
on dissolution rates than six- or seven-membered rings [7]. In addition, Ludwig et al. [53] suggested that the rate constant may be correlated with the stability constant of ligands with metal ions in solution.

1.3.2.2 Reductive Dissolution

Because transition metals may be prone to redox reactions, changes in oxidation state have a dramatic impact on both their solubility and speciation. Under anoxic conditions, oxides of Fe(III), Co(III), and Mn(III,IV) can be reduced to their divalent oxidation state, greatly increasing solubility. Additionally, in aerobic environments at neutral pH, adsorbed ligand can act as reductant to promote reductive dissolution of oxides [48].

Reductive dissolution involves electron transfer between ligands and surface metal, which is a surface-controlled process. Adsorption reactions produce inner-sphere and outer-sphere surface complexes that could increase the density of reductant molecules and facilitate electron transfer. Two mechanisms, inner-sphere and outer-sphere electron transfer, are therefore postulated to interpret dissolution reactions. Electron transfer via the inner-sphere mechanism is limited by ligand exchange rates of surface metal centers. In contrast, the outer-sphere mechanism generates reactions independent of ligand exchange rates. The electron transfer causes reduction of surface metal and the concomitant oxidation of the ligand. The bond between the surface metal and the lattice oxygen is weakened by reduction so that detachment of metals is observed. As with ligand-promoted dissolution, detachment of the metal ion is often the rate determining step in reductive dissolution [48].
1.3.2.3 Proton-Promoted Dissolution

Mineral dissolution may also occur via a proton-promoted pathway that is distinct from ligand-promoted and reductive dissolution reactions. The protonation of surface sites polarizes the critical bonds between metal centers and lattice, promoting the dissolution of metal oxides. Kinetically, the fast adsorption of protons onto the surface is followed by a slow detachment of the metal ion from crystal lattice, which is the rate-limiting step. The surface structure is then quickly restored by further surface protonation. Because the protonated surface sites are precursors of the rate-determining step, a rate law can be expressed as a function of surface excess of adsorbed protons ([H]$_{ads}$) (in excess of the protonation state at the zero point of charge) (Eq. 1.3):

$$ R_H = k_H [H]^{n}_{ads} $$

with $k_H$ as dissolution rate constant, and $n$ as reaction order. [H]$_{ads}$ can be related to the concentration of the protonated surface sites [54]. The exponent ($n$) is typically approximately equal to the charge on the dissolving metal [54].

Also controlled by solution pH, alkaline dissolution can be denoted as a special case of ligand-promoted dissolution. Under alkaline conditions, the deprotonated water or hydroxyl groups on oxides surface facilitate the detachment of a metal center and enhance dissolution rate. For the common cases of dissolution of metal oxides, proton- and alkaline-promoted dissolution mechanisms occur parallel to the ligand-promoted and reductive dissolution processes. However, at circumneutral pH where acidic- and alkaline-promoted
dissolution rates are negligible, the overall rate may be dominated only by ligand-promoted or reductive dissolution.

1.3.2.4 Siderophore-Promoted Dissolution

To increase the bioavailability of Fe in oxic environments, microbes and graminaceous plants may exude siderophores to promote the dissolution of Fe oxides. The dissolution of Fe oxides by siderophores arises from siderophore-surface interactions that lead to the specific adsorption of siderophore to the mineral surface. Siderophores with donor oxygen atoms can preferentially form surface complexes with the lattice Fe center. The resulting metal-siderophore bond at the surface destabilizes the interaction of the metal center with the bulk solid, facilitating the removal of the metal from the solid. The detachment of surface complexes is slow relative to adsorption and solution speciation, resulting in a surface-controlled dissolution process that follows the ligand-promoted dissolution mechanism.

The catecholate, hydroxamate, or $\alpha$-hydroxycarboxylate functional groups of siderophores can serve as effective Lewis bases that form surface complexes, while the extent of surface interactions will depend on siderophore structure, charge, and hydrophobicity [55]. DFOB has three hydroxamate groups that act as a hexadentate ligand. It is reasonable to hypothesize that hydroxamate groups should have significant covalent interaction with the surface metal centers. Based on geometry of DFOB, Holmén and Casey [56] have speculated that only one hydroxamate group in the siderophore coordinates a single Fe(III) surface site at the mineral surface, which is analogous to the behavior of
acetohydroxamic acid (aHA). This assumption is supported by the similarities of a compensation law, which relates the pre-exponential factor to the apparent activation energy in the Arrhenius equations, in the complexation of Fe(III) by DFOB and aHA in solution and at goethite surfaces [52]. The formation of mononuclear bidentate surface species is therefore expected to be important in facilitating dissolution reactions of Fe oxides in the presence of DFOB.

In addition to covalent interactions proposed above, pH-dependent charge of oxide surfaces and DFOB can make their interactions more complicated. For goethite, the point of zero charge (pH_pzc) is approximately at pH = 9 [7, 52]. Kraemer et al. [6] measured the effect of surface charge on siderophore sorption and found lower adsorption of DFOB at pH < 8 due to electrostatic repulsion between the cationic ligand and the positively charged goethite surface. Near pH = 9, the protonation state of the hydroxamate groups on the DFOB molecule changes, generating species with positive charge at the terminal amine and negative charge distributed over the hydroxamate functional groups. Furthermore, adsorption of charged species will result in changes in both surface charge and surface potential. Thus simple trends in DFOB surface interactions as a function of pH are not necessarily expected.

To make the situation more complicated, DFOB has been observed to serve as a reductant in reductive dissolution of Mn(III,IV) oxides at circumneutral to acidic pH [57]. Based on the similar electrode potential of Mn(III,IV) oxides and Co(III)OOH [58], it is reasonable to postulate that reductive dissolution of Co(III)-bearing minerals, such as heterogenite, can also occur in the presence of DFOB, resulting in the enhanced transport of Co. As a result, DFOB-promoted dissolution of Co(III)-bearing minerals studied in this work
will possibly undergo strongly pH-dependent dissolution pathways, including both ligand-promoted and reductive pathways. The rate law and mechanisms proposed earlier for ligand-promoted and reductive dissolutions will be thus utilized to explain observed dissolution behaviors. Additionally, the interactions will greatly depend on not only mineral structure but also chemical composition in terms of Co concentration of mineral. The production of Co-DFOB complexes is by no means a simple biogeochemical process, which necessarily needs to be addressed in this thesis.

1.4 Summary

Microbes and plants are known to produce siderophores, a class of biogenic ligands with high affinity and specificity for Fe(III) [7, 8, 59]. It has been reported that siderophores promote dissolution rates of Fe oxides mainly through surface-controlled ligand-promoted mechanism [6, 9, 55]. However, due to the complexities of molecular structure and mineral surface properties, the siderophore-surface interactions are difficult to characterize so as to fully understand the mechanisms of dissolution for this class of ligands. The determination of dissolution rates, on the other hand, can indirectly provide insights into the details of dissolution reactions. By applying rate laws to dissolution experiments, observed behaviors of the system can be related to proposed dissolution mechanism. Dissolution rates of metal oxides in the presence of siderophores thus can fundamentally help us better understand mineral weathering and metal cycling in the environment.

The fact that Co(III) can also form complexes with DFOB that have much greater stability constants than that of Fe(III)HDFOB\(^+\) raises interesting questions about the roles of
Co(III)-siderophore complexes in biogeochemical cycling of Co. The fate, transport, and bioavailability of Co in terrestrial environments may be strongly coupled to siderophores. This observation may be significant to organism nutrition because Co is essential to normal metabolic function of microbes and animals. Conversely, the risk of transport of radioactive $^{60}$Co is another reason that we need to determine the dissolution rates and mechanisms of Co-bearing minerals.

The experiments presented in this thesis assess the effect of DFOB, a model trihydroxamate siderophore, on the dissolution rate of environmentally relevant minerals, including synthetic heterogenite (CoOOH), goethite ($\alpha$-FeOOH), and Co-substituted goethite (Co-$\alpha$-FeOOH). We propose that siderophore-promoted dissolution in our systems is a surface-mediated process that is related to concentrations of surface species. System pH, ionic strength, temperature, and [DFOB] can all significantly influence the extent of interactions. By controlling these experimental parameters, we try to develop a quantitative understanding on dissolution rates to probe dissolution mechanisms as a function of pH.

The objectives of this study are to (1) determine the dissolution rates and identify dissolution mechanisms of synthetic Co-bearing minerals in the presence of desferrioxamine B as a function of pH, (2) quantify the effects of Co substitution for Fe in goethite on DFOB-mediated dissolution rates and mechanisms of goethite. This study as a whole will help to fill critical knowledge gaps about the Co(III)-DFOB system and help predict the behavior of Co in the presence of siderophores in the environment.
1.5 References


55. Lloyd, T. Dissolution of Fe(III) and Mn(III, IV) (hydr)oxides by desferrioxamine B. California Institute of Technology, 1999.


Figure 1.1. Molecular structures of a bacterial and plant siderophores. Desferrioxamine B (DFOB) (a) is a trihydroxamate siderophores produced by bacteria including the soil bacterium *Streptomyces pilosum* and other organisms. The Fe(III)HDFOB\(^+\) complex (b). Mugineic acid (c) is a derivative of the structurally related phytosiderophores produced by graminaceous plants.
Figure 1.2. Percentage distribution of DFOB (a) and Fe(III)-DFOB (b) species as a function of pH predicted by MINEQL+ 4.6. Model conditions: 100 μM Fe$^{3+}$, 100 μM DFOB, I = 0. Constants are taken from Table 1.1.
Table 1.1 Thermodynamic formation constants for DFOB species and Fe(III), Co(II,III) and Mn(III) complexes with DFOB at 298.15 K. Stability constants were corrected to zero ionic strength with the Davies equation.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \text{Log} \ K_{298} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{DFOB}^{3+} + \text{H}^+ = \text{HDFOB}^{2+} )</td>
<td>11.45</td>
</tr>
<tr>
<td>( \text{DFOB}^{3+} + 2\text{H}^+ = \text{H}_2\text{DFOB}^{-} )</td>
<td>21.44</td>
</tr>
<tr>
<td>( \text{DFOB}^{3+} + 3\text{H}^+ = \text{H}_3\text{DFOB}^{a} )</td>
<td>30.62</td>
</tr>
<tr>
<td>( \text{DFOB}^{3+} + 4\text{H}^+ = \text{H}_4\text{DFOB}^{a} )</td>
<td>38.94</td>
</tr>
<tr>
<td>( \text{HDFOB}^{2+} + \text{Fe}^{3+} = \text{Fe(DFOB)}^{+} )</td>
<td>32.02</td>
</tr>
<tr>
<td>( \text{FeDFOB}^{b} + \text{H}^+ = \text{Fe(DFOB)}^{+} )</td>
<td>10.40</td>
</tr>
<tr>
<td>( \text{Fe(DFOB)}^{+} + \text{H}^+ = \text{FeH(DFOB)}^{2+} )</td>
<td>0.68</td>
</tr>
<tr>
<td>( \text{DFOB}^{3+} + \text{Co}^{2+} = \text{Co(II)DFOB}^{-} )</td>
<td>10.7 ± 0.5</td>
</tr>
<tr>
<td>( \text{HDFOB}^{2+} + \text{Co}^{2+} = \text{Co(II)HDFOB}^{a} )</td>
<td>10.1 ± 0.2</td>
</tr>
<tr>
<td>( \text{H}_2\text{DFOB}^{-} + \text{Co}^{2+} = \text{Co(II)H}_2\text{DFOB}^{a} )</td>
<td>7.6 ± 0.3</td>
</tr>
<tr>
<td>( \text{H}_3\text{DFOB}^{b} + \text{Co}^{2+} = \text{Co(II)H}_3\text{DFOB}^{a} )</td>
<td>4.1 ± 0.1</td>
</tr>
<tr>
<td>( \text{HDFOB}^{2+} + \text{Co}^{3+} = \text{Co(II)HDFOB}^{+} )</td>
<td>37.5 ± 0.4</td>
</tr>
<tr>
<td>( \text{HDFOB}^{2+} + \text{Mn}^{3+} = \text{Mn(III)HDFOB}^{+} )</td>
<td>29.9</td>
</tr>
</tbody>
</table>

\(^a\) Martell et al. (1998) [60]

\(^b\) Duckworth et al. (2009) [18]
Chapter 2

DFOB-Promoted Dissolution of Heterogenite
2.1 Introduction

Recent work indicates that siderophores may form very stable aqueous complexes with Co(III). Duckworth et al. [1] measured the stability constant for 1:1 Co(III)HDFOB\(^+\) complex of 10\(^{37}\) and suggested that Co-siderophore complexes may be important in the biogeochemical cycling of Co in marine environments. Given the exceptional stability of Co(III)HDFOB\(^+\), Co(III) solubility can be enhanced by the complexation with DFOB, potentially facilitating the transport of Co. Siderophores may thus enhance the bioavailability of Co, an important trace nutrient; however, Co also exists as a hazardous radionuclide, \(^{60}\)Co, and enhanced mobility may result in \(^{60}\)Co exposure to humans and other organisms. It is thus critical to determine whether siderophores increase the dissolution and potential mobility of Co-bearing minerals.

Heterogenite, a cobalt oxyhydroxide (CoOOH), has a brucite-like structure with layers of edge-sharing Co(III) oxohydroxo octahedra [2]. The dissolution of synthetic heterogenite via nonreductive ligand-promoted or reductive reactions has been studied using several organic chelating agents [2-4]. Previous reports have shown that CoOOH undergoes solely ligand-promoted dissolution by the aminocarboxylate ligand iminodiacetic acid (IDA), with the dissolution product following a stoichiometric ratio of Co:IDA of 1:2 [2]. Enhanced dissolution of heterogenite has been observed with hydroquinone (H\(_2\)Q) through only a reductive pathway, producing Co\(^{2+}\) and \(p\)-benzoquinone (Q) into aqueous solution. Penn et al. [2] further examined the morphological change of heterogenite during the dissolution by IDA and H\(_2\)Q using high-resolution transmission electron microscopy (HRTEM), and suggested preferential reactive sites at edge-type faces. McArdell et al. [3] demonstrated that
ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) promote dissolution of heterogenite via both ligand-promoted and reductive dissolution pathways from pH 4.3 to 7.6. The difference in dissolution mechanisms is attributed to the reactivity of Co(III) at differing surface sites as well as the chemical properties of ligands.

In biological-active systems, the weathering of heterogenite and other Co-bearing minerals by biogenic ligands is also of interest for the implications for biogeochemical cycling of Co; however, few studies have examined heterogenite dissolution in the presence of biogenic ligands. Because DFOB can form stable complex with Co(III) that has stability constant comparable with Co(III)EDTA\(^{-}\) (10\(^{37}\) versus 10\(^{12}\)) [5, 6], dissolution of heterogenite by DFOB through a ligand-promoted pathway is expected to occur at soil pH range. DFOB and other siderophores have been shown to promote non-reductive, ligand-promoted dissolution of Fe(III) and Mn(III) oxides (minerals that contain redox-active metals that form strong complexes with siderophores) at alkaline pH [7-10]. However, DFOB can also function as a reductant at mineral surfaces, promoting reductive dissolution of Mn oxides. Duckworth and Sposito [9] found pH-dependent reductive dissolution of manganite (\(\gamma\)-MnOOH) by DFOB, with Mn\(^{2+}\) as a dissolution product at pH < 6.5. The one-electron-transfer reaction on manganite surfaces can be partly explained by the large electrode potential of MnOOH/Mn\(^{2+}\) half-reaction (\(E_{\text{MnOOH/Mn}^{2+}}^{\circ} = 1.50\text{V}\) ) [11]. With a nearly equal electrode potential (\(E_{\text{CoOOH/Co}^{2+}}^{\circ} = 1.48\text{V}\) ) [12], heterogenite may have a similar surface chemistry in the presence of DFOB. This process may also provide a sink for siderophores by concomitant degradation that occurs in reductive dissolution. However, the rates and
mechanisms of siderophore-promoted dissolution of heterogenite have not been reported so far.

The present work investigates the reactions of DFOB with heterogenite by quantifying DFOB-promoted dissolution rates and identifying the dominant pH-dependent dissolution mechanisms. Utilizing synthetic heterogenite, experiments were conducted under chemical conditions that were designed to be representative of those found in environmental systems. A mechanistic approach based on the summation of elementary reactions was employed to evaluate the reaction pathways that occur during DFOB-promoted dissolution. This research seeks to elucidate the role of siderophores in biogeochemical cycling of Co by promoting dissolution of Co-bearing solid phases in the environment, a critical knowledge gap in understanding of trace metal biogeochemistry [1].

2.2 An Overview of Possible Dissolution Pathways

As indicated above, heterogenite’s surface chemistry, coupled with the redox activity of Co and DFOB, allows for many potential homogeneous and heterogeneous reactions. We thus discuss potential reactions that may occur in CoOOH/DFOB systems. Ligand-promoted dissolution is defined as the process of dissolving Co(III) from heterogenite (Eq. 2.1), which results in the Co(III)HDFOB⁺ complex that does not involve electron transfer.

\[
\text{Co(III)OOH}_{(S)} + \text{H}_4\text{DFOB}^+ \rightarrow \text{Co(III)HDFOB}^+ + 2\text{H}_2\text{O} \quad (2.1)
\]

The reaction is initiated by adsorption of free DFOB on CoOOH surfaces that leads to the formation of surface complexes through ligand exchange with surface hydroxyl groups [13].
In equation 2.1 and subsequent equations, $H_4DFOB^+$ is chosen to represent all DFOB species as reactant due to its high $pK_a$ value and dominance over large pH range [$pK_a = 8.32$].

When serving as a reductant toward the surface, DFOB can promote dissolution as expressed in equation 2.2 through a reduction of Co oxidation number from III to II and release of DFOB oxidation products.

$$\text{Co(III)OOH}_{(S)} + H_4DFOB^+ \rightarrow \text{Co}^{2+} + \text{DFOB}_{ox}$$  \hspace{1cm} (2.2)

Duckworth and Sposito [9] observed reduction of several $>\text{Mn(III)}$ sites in manganite by a single DFOB molecule. It is possible that multiple reactions may also occur between DFOB (or DFOB$_{ox}$) and heterogenite during reductive dissolution (Eq. 2.3). However, in this study, no effort was attempted to characterize the oxidation products of DFOB due to the anticipated diversity of species [9].

$$\text{Co(III)OOH}_{(S)} + \text{DFOB}_{ox} \rightarrow \text{Co}^{2+} + \text{DFOB}_{ox}'$$  \hspace{1cm} (2.3)

where DFOB$_{ox}'$ indicates an additional electron has been donated by the molecule.

In addition to electron transfer between CoOOH surface and DFOB, electron-transfer reactions between CoOOH and aqueous Co(II) complexes have been hypothesized to explain autocatalytic behavior [3]. The reaction shown in equation 2.4 is driven by the lower electrode potential for Co(III)HDFOB$^+$/Co(II)DFOB$^0$ half-reaction ( $E^0 = 0.215$ V ) in comparison to that of the CoOOH/Co$^{2+}$ half-reaction.

$$\text{Co(II)HDFOB}^0 + \text{CoOOH}_{(s)} \rightarrow \text{Co}^{2+} + \text{Co(III)HDFOB}^+$$  \hspace{1cm} (2.4)

Because autocatalytic dissolution must be fast relative to equation 2.1-2.3 in order to significantly contribute to total dissolution, it causes a lag in Co(II) concentration.
accompanied by a characteristic sigmoidal curve in batch dissolution kinetics [3]. This feature is considered diagnostic of autocatalytic dissolution pathway.

The Co species generated by the above reactions can also be involved in homogeneous complexation, exchange, and redox reactions:

\[
\begin{align*}
\text{Co}^{2+} + \text{DFOB} & \rightarrow \text{Co(II)-DFOB} \\
\text{Co(III)-DFOB}_{\text{ox}} + \text{DFOB} & \rightarrow \text{Co(III)-DFOB+DFOB}_{\text{ox}} \\
\text{Co(II)-DFOB}_{\text{ox}} + \text{DFOB} & \rightarrow \text{Co(II)-DFOB+DFOB}_{\text{ox}} \\
\text{Co(III)HDFOB}^- & \rightarrow \text{Co}^{2+} + \text{DFOB}_{\text{ox}}
\end{align*}
\]

Free DFOB is capable of complexing free Co\(^{2+}\) ions or displacing oxidation products via ligand exchange (Eq. 2.5-2.7). Equation 2.6 and 2.7 assume DFOB has a higher affinity for Co(II) and Co(III) than its degradation products. From the speciation distribution of Co(II)-DFOB predicted by MINEQL+ 4.6 (Figure 2.1), the speciation shown by equation 2.5 varies strongly with solution pH; the speciation of Co(II)-DFOB is thought to be largely pH-invariant. If internal electron transfer occurs in Co(III)HDFOB\(^+\) (Eq. 2.8), soluble Co(II) and oxidized DFOB are produced [3]. Mn(III)HDFOB\(^+\) has been demonstrated to degrade at pH < 7 [14], so it is possible that a similar reaction can occur for Co(III)HDFOB\(^+\). The kinetics of reaction 2.8 at pH < 8 remains unknown for Co(III)HDFOB\(^+\), although Co(III)EDTA\(^0\) was observed to degrade on the order of hours [3], and this reaction is assumed to happen more rapidly at lower pH.
2.3 Heterogenite Synthesis and Characterization

2.3.1 Materials and Methods

CoOOH (heterogenite) was prepared using the method described by McArdell et al. [3]. All solutions used in the synthesis were made with deionized (DI) water with a resistivity of 18.3 MΩ·cm. The 3 L of DI water was sparged with N₂ gas for 1 hour at 80 °C in a 4 L glass beaker before adding 250 mL of 0.71 M NaOH solution. After sparging with N₂ for another 1 h, 300 mL of 0.228 M CoCl₂ solution (sparged for 90 min) was added. A blue suspension was immediately formed with the color changing quickly from blue to pale pink. Under constant stirring, 200 mL of 0.74 M NaOCl solution was added to oxidize Co(II) oxide in the suspension 20 minutes after the addition of CoCl₂. For the next 6 hours, up to 500 mL of NaOCl were added to the suspension at 80 °C while stirring continuously. The suspension was then transferred to an oven and aged for 62 hours at 80-85 °C. A cold-wash process in DI water by centrifugation and sonication was repeated for four times after the aging process. Further wash/centrifuge cycles were impossible due to very fine particle size of heterogenite. To remove the rest of the salt in the suspension, the suspension was dialyzed until absence of Cl⁻ in the suspension was indicated by a silver nitrate (AgNO₃) test. The washed heterogenite was lyophilized until dry and stored in a freezer until use. The percentage yield of heterogenite was approximately 95%.

2.3.2 Particle Characterization

Dried heterogenite was characterized to determine its morphology, phase, and specific surface area. The powder X-ray diffraction (XRD) pattern of solid sample was
collected from 15-95° with Inel XRG-3000 Diffractometer equipped with a Co-Kα source (λ=1.789 Å). Results (Figure 2.2) showed relative sharp diffraction peaks with d spacings of 4.42, 2.42, 2.30, 1.78, 1.42 and 1.35 Å, which agree with d spacings of heterogenite standard on powder diffraction data card (26-1107) [15, 16]. The XRD pattern indicated a relatively crystalline heterogenite, which can commonly contain a lot of defects [2], and confirmed the dominant phase in the sample.

A sample for transmission electron microscopy (TEM) analysis was prepared by dispersing solid particles in methanol. A drop of suspension was placed onto the surface of 3 mm carbon filmed Cu grid. After allowing the suspension to dry for 2 minutes, TEM micrographs of synthesized solid were collected on a Hitachi HF-2000 Transmission Electron Microscope. Figure 2.3 showed uniform platelike thin hexagonal particles with an average width of approximately 80 -100 nm. The morphology description of the figure and lack of other particle morphologies also indicate that CoOOH is the only phase in the synthesized sample.

Surface area of heterogenite particles was determined by Brunauer–Emmett–Teller (BET) N₂ adsorption isotherm with an Autosorb-1-MP (Quantachrome Corp.). Prior to analysis, samples were outgassed for 24 hours at 150 °C. N₂ adsorption was measured at 9 different relative nitrogen pressures (P/P₀) between 0 and 0.3 using 0.1 g sample (Figure 2.4). The analysis yielded a surface area of 59.8 ± 0.9 m²·g⁻¹.

X-ray adsorption near-edge structure (XANES) (Beamline X-11B of the National Synchrotron Light Source (NSLS) at Brookhaven National Lab, New York) was utilized to confirm the average Co oxidation state. Aqueous Co(II) chloride and a well-characterized
Co(III)OOH (obtained from Dr. Owen Duckworth) were used as reference standards for
divalent and trivalent Co, respectively. The results confirmed the Co oxidation state of ca. +3
in our heterogenite sample, close to the stoichiometry of CoOOH.

2.4 Dissolution of Heterogenite (CoOOH) in the Presence of DFOB

2.4.1 Materials and Methods

All chemicals are reagent grade unless otherwise specified. All solutions were made
with type I deionized water with a resistivity of 18.3 MΩ-cm. The sample of desferrioxamine
B (DFOB) utilized in this study was the mesylate salt [(C_{25}H_{46}N_{5}O_{8}NH_{3}^+(CH_{3}SO_{3})^{-}]
purchased from Sigma-Aldrich.

Dissolution experiments were conducted in batch reactors to measure initial
dissolution rates of heterogenite. Dissolution was investigated as a function of pH (pH = 5–
9), both in the absence and presence of DFOB. Batch experiments were conducted in 500 mL
Erlenmeyer flasks wrapped with aluminum foil and capped with rubber stoppers.
Experiments were initiated by adding 0.100 g CoOOH to 450 mL 0.1 M NaCl (Fisher)
solution buffered to the desired pH without DFOB. Buffers, namely acetate (Ac) (Fisher), 3-
(N-morpholino) propanesulfonic acid (MOPS) (Fisher), 4-(2-hydroxyethyl)-1-
piperazineethanesulfonic acid (HEPES) (Acros Organic), or N-Cyclohexyl-2-
aminoethanesulfonic acid (CHES) (MP Biomedical), were utilized for pH 5 (Ac), 6 (MOPS),
7 (MOPS), 8 (HEPES), and 9 (CHES), respectively, at the concentration of 10 mM for all
experiments. After sonication for 10 min, the reactors were then placed in a recirculating
water bath set to 25 °C with magnetic stirrers at the bottom to ensure thorough mixing.
Experiments were initiated by adding 50 mL DFOB solution containing 0.1 M NaCl and 10 mM buffer to make the total volume in the reactor of 500 mL. The resulting solid concentration was 0.20 g·L\(^{-1}\) (or 2.2 mM) with final DFOB concentration of 100 μM. Similar procedures were conducted at each pH for control experiments by adding 0.100 g heterogenite solid into 500 mL solution containing 0.1 M NaCl and 10 mM buffer but no DFOB. In addition, control experiments were used to reflect proton-promoted dissolution of heterogenite. Each set of experiments was run in duplicate.

After the reaction started, samples were collected in 15 mL aliquots using a 25 mL syringe, and then filtered quickly through a 0.22 μm nylon syringe filter (Fisher, Millipore). Samples were usually collected ca. 15 times over 3 hours of a dissolution experiment. The UV-visible absorbance of samples was measured for Co(III)HDFOB\(^+\) at 390 nm on a Shimadzu UV-2101PC spectrometer immediately after filtration to minimize homogeneous degradation of Co(III)HDFOB\(^+\) complex (Eq. 2.8). [Co(III)HDFOB\(^+\)] was calculated using published molar extinction coefficient of \(\varepsilon_{390\text{nm}} = 450 \pm 20 \text{ M}^{-1}\text{cm}^{-1}\) [1]. The pH value of each sample was recorded by using Fisher XL20 pH meter after the absorbance measurement. All samples were then analyzed for total dissolved Co concentration ([Co]\(_T\)) using a Perkin–Elmer 3100 atomic absorption spectrometer (AAS) at 240.7 nm.

2.4.2 Analysis of Dissolution Data

The overall rate of heterogenite dissolution (mol·kg\(^{-1}\)·h\(^{-1}\)) can be expressed as the rate of change in the total number of moles of dissolved Co per unit mass of reacting solid; similarly, the dissolution rate of heterogenite by ligand-promoted mechanism can be
expressed as the change of moles of \( \text{Co(III)HDFOB}^+ \) per unit mass of solid. The dissolution rates can be mathematically written as (Eq. 2.9):

\[
R_{net} = \frac{1}{M} \frac{dN}{dt}
\]  

(2.9)

with \( N \) (mol) as the moles of total Co or Co(III)HDFOB\(^+\) released into solution, and \( M \) (kg) as the initial total mass of solid.

Because the concentration, rather than molar amount, of Co species, is conveniently measured in the experiments, the equation above can be transformed to (Eq. 2.10):

\[
R_{net} = \frac{1}{M} \frac{dN}{dt} = \frac{1}{M} \frac{dC}{dt} \cdot L = \frac{1}{m} \frac{dC}{dt}
\]  

(2.10)

where \( m \) (kg·L\(^{-1}\)) is the solid loading rate and \( C \) (M) is the concentration of the total Co or Co(III)HDFOB\(^+\). The term \( \frac{dC}{dt} \) (mol·L\(^{-1}\)·h\(^{-1}\)) reflects the slope of plot of Co concentration versus time. Typically, a plot of this type is initially linear and then plateaus as the batch system equilibrates. Only the linear portion is used to derive the slope which, once normalized by loading rate (kg·L\(^{-1}\)), represents the initial dissolution rate. For the linear regression analysis, 7-10 points were utilized with \( R^2 \) values greater than 0.97 for all least-square fit lines. Error bars (reflecting 95% confidence intervals) were also obtained from regression analysis. Both initial total and ligand-promoted dissolution rates were then calculated after normalization by surface area. Because uncomplexed Co(III) is unstable and sparingly soluble over the pH range of our experiments, we assume that all dissolved Co, except Co(III)HDFOB\(^+\) complex, is Co(II). The total initial dissolution is assumed to represent the sum of several parallel reactions (e.g. ligand-promoted, reductive, and proton-
promoted reactions). We also assume the lack of synergistic dissolution effects in our experiments [17]; we therefore can calculate reductive dissolution rate by subtracting ligand-promoted and proton-promoted rates from total dissolution rate.

2.5 Results and Discussion

2.5.1 Dissolution Rates and Mechanisms of Heterogenite

Kinetic data for duplicate batch experiments at pH 5, 6, 7, 8, and 9 are shown in Figure 2.5. For each pH, dissolution products of [Co(III)HDFOB\(^-\)] or [Co]\(_T\) are plotted against time. The [Co]\(_T\) represents background-adjusted Co concentration after AAS measurement. The background from control experiments reflects proton-promoted dissolution of heterogenite. For all pH except pH = 6, dissolution rates of control experiments are below the limit of detection (L.O.D. \(\approx 2\ \mu\text{M};\) data not shown). Even at pH 6, the dissolved Co concentration from the control experiment is less than 10 \(\mu\text{M}\) within 2 hours of reaction. Because dissolution does not occur at pH = 5 in control experiments, the dissolved Co at pH 6 may be attributed to the MOPS-promoted reductive dissolution instead of proton-promoted dissolution. However, no dissolution is observed at pH = 7 in control experiment using the same buffer, possibly due to the pH-dependent speciation change of MOPS. Because uncomplexed aqueous Co(III) should not be present at detectable quantities at pH = 6, and MOPS forms very weak or negligible complex with Co(III) [18], we assume that the small amount of aqueous of Co is Co(II).

It is evident in Figure 2.5 that [Co(III)HDFOB\(^-\)] eventually approaches a steady value; however, [Co]\(_T\) does not plateau within the time scale of batch experiment.
Additionally, no plot of experimental data yields a sigmoidal pattern, suggesting absence of the autocatalytic dissolution pathway (Eq. 2.4). For both ligand-promoted and total dissolution of heterogenite, a linear trend is observed at the beginning of experiments. The surface-area-normalized total and ligand-promoted dissolution rates derived from the initial portion of the data are plotted as a function of pH in Figure 2.6.

The non-reductive ligand-promoted dissolution rates of heterogenite exhibit pH dependence in the pH range studied, with greater rate at neutral pH and decreased rate at lower or higher pH. The plateau concentration of Co(III)HDFOB$^+$ follows a similar trend with ligand-promoted dissolution rates as a function of pH. The total dissolution rates, on the other hand, increase with decreasing pH, showing a strong correlation with pH change. Comparing the two dissolution rates at each pH, ligand-promoted dissolution is the dominant pathway at pH $> 6$.

Figure 2.7 shows the rates of reductive dissolution of heterogenite as a function of pH, with a rate near the limit of detection at pH $\geq 7$ and increasing greatly at pH $< 7$. For pH $< 6$, the reductive dissolution becomes the dominant dissolution pathway. This shift in mechanism may be attributed to the fundamental change in the thermodynamic driving force as pH moves to acidic range, as described for DFOB-promoted dissolution of manganite [9]. However, the decomposition of Co(III)HDFOB$^+$ following ligand-promoted dissolution through internal electron transfer reaction (Eq. 2.8) can not be ruled out from the data, because the contribution of each reaction to the overall dissolution is difficult to identify. In addition, the rates of degradation of Co(III)HDFOB$^+$ at pH $< 8$ are currently unknown.
At pH 5 and 6, despite eventual steady value of [Co(III)HDFOB\(^+\)] in the systems, total dissolved Co concentration is observed to continuously increase [Figure 2.8 (a, b)], indicating accumulation of Co(II) in aqueous solution. Assuming longer equilibration time for reductive dissolution in the batch experiments, ligand-promoted and reductive reaction may not occur on the same time scale. At pH = 5, [Co(II)] reaches about 0.2 mM after 3 hours of reaction. Except for the DFOB that is complexed with Co(III), the ratio of [Co(II)] to remaining [DFOB] is about 3.5. If all uncomplexed DFOB reacts to reduce and solublize Co(III), then each DFOB molecule and its oxidized fragments would have to react with the surface more than three times. Since the Co(II) is still increasing after 3 hours, the oxidized DFOB may continue to react with heterogenite. Similar reasoning suggests that DFOB or its oxidation products would react more than once at pH = 6. Because DFOB contains many possible sites for an oxidation reaction to occur [19], it is reasonable for DFOB or its oxidation products to react multiple times with heterogenite surface, yielding products of different levels of oxidation. Due to the possibility of multiple reaction pathways, it is very difficult to evaluate the reactivity of products with CoOOH surface or even to identify products in the system. Nonetheless, the nearly linear increase of Co(II) even after the equilibrium of ligand-promoted dissolution (Figure 2.8), may suggest the similar efficiency of oxidized DFOB in promoting reductive reaction of heterogenite. It is also possible that the rate of metal detachment, which is commonly the rate-determining step in reductive dissolution [13], does not depend on the identity of the reactant.
2.5.2 Comparison Between Mn(III), Fe(III) and Co(III) Oxides

Cobalt is usually strongly associated with various Fe and Mn oxides in soils and natural waters [20, 21]. Cobalt(II) can be retained by Fe and Mn oxides, especially at neutral to alkaline pH, and possibly precipitate on oxide surface as Co(III) oxide through heterogeneous redox reactions [22]. Because of their chemical similarity and association in the environment, the reactions of Mn(III) and Fe(III) oxides with DFOB provide not only a useful comparison of the chemical properties and reactivities of metal oxides, but also implication for interactions with Co in the presence of siderophores (Also see Chapter 3 for more information). Figure 2.9 shows nonreductive DFOB-promoted dissolution rates of Co(III), Fe(III), and Mn(III) oxides at similar conditions (100 μM DFOB). Fe(III) oxides dissolve solely via a ligand-promoted pathway that is pH-independent over a wide pH range. Dissolution rates of both goethite (α-FeOOH) and hematite (α-Fe₂O₃) are several orders of magnitude slower than those determined for heterogenite in this study [23]. The ligand-promoted manganite (γ-MnOOH) dissolution rates are generally independent of pH for 6 < pH < 9, and decrease for pH < 6 [9]. Heterogenite dissolution rates do not follow the trend of manganite for complex formation, with rates fastest at neutral pH and reducing at both alkaline and acidic pH. In addition, heterogenite dissolution rates are approximately 10-fold greater than those of manganite. The fast kinetics of heterogenite dissolution, coupled with the high affinity of Co(III) for DFOB, suggests that the uptake of Co by microbes and animals can be greatly facilitated in the presence of siderophores. Given the trace concentration of Co in soils (3-70 mg·kg⁻¹) [24], however, siderophore-promoted dissolution
of Co(III)-bearing minerals may not be a competitor with that of Fe or Mn oxides in common terrestrial environments.

The ligand-promoted dissolution rates of Co(III), Mn(III), and Fe(III) oxides do not follow the order predicted from the stability constants of corresponding aqueous DFOB complexes as proposed by Ludwig et al. [25] (Table 1.1). Many studies instead have utilized the ligand exchange and electron transfer rates of transition metal ions to explain the dissolution rates of metal oxides [3, 4, 26]. Ligand-promoted dissolution rates of heterogenite by many chelating agents (EDTA, IDA, H2Q, and NTA) were observed to be much lower than those of Fe(III) and Mn(III) oxides in previous studies [2-4]. They attributed the slow dissolution rate of heterogenite to low rates of Co(III)-O bond breaking within the mineral structure, a phenomenon that is known to correlate with aqueous ligand exchange rate. Predictions based on exchange rates of aqueous cations would project dissolution rates in the order of MnOOH > FeOOH > CoOOH [27]. The present work, however, shows a very reactive surface of heterogenite that does not follow the experimental or theoretical trends. Differences in mineral structure, surface charge, and DFOB speciation at oxide surfaces are likely to have more important influence on the dissolution rates. It is thus difficult to rationalize the disparity between predicted rates and our experimental results. In addition, different methods on dissolution experiments can also yield discrepancy in measuring rates. The initial dissolution rates from batch experiments (this study and goethite data) reflect structural defects which have high-energy sites [10, 28], while the same is not true for steady-state dissolution rates from flow-through experiments (manganite data). For example, under the similar conditions of aqueous solution, steady-state rates of Mn oxides were
observed to be lower than initial dissolution rates from batch experiments [10, 29]. However, this difference is fairly small and does not account for the increase in ligand-promoted rates of heterogenite as compared to Mn and Fe oxides.

Both manganite and heterogenite undergo reductive dissolution pathways that follow the same trend (Figure 2.10). The reductive dissolution rates of heterogenite are comparable to those of manganite. This can be partly explained by the electrode potentials of their half reactions in Table 2.1 [4]. The very close electrode potentials indicate heterogenite and manganite are equally strong oxidants, both capable of oxidizing DFOB. Compared to heterogenite and manganite, Fe(III) oxides are much weaker oxidants, thus the reduction of Fe(III) by DFOB is very likely thermodynamically unfavorable (absolute quantification is impossible because electrode potential of DFOB is unknown). In addition, mineral structure and the adsorption configuration of DFOB on surfaces can contribute to the resulting reductive dissolution rates of metal oxides. Nevertheless, it is unknown to what extent and at what rate the Co(III)HDFOB\(^+\) complex degrades to Co(II) species as a function of pH. Future work may be needed to examine internal electron transfer reactions within Co(III)HDFOB\(^+\) complex at circumneutral pH.

### 2.6 Conclusion

Dissolution of heterogenite (CoOOH) in the presence of DFOB occurred via multiple pathways. By assuming parallel reactions of the pathways, the total dissolution rate of heterogenite can be interpreted as the sum of the individual pathways: non-reductive ligand-promoted, reductive, and proton-promoted dissolution. Ligand-promoted dissolution was the
dominant pathway at neutral to alkaline pH, with the greatest rate at neutral pH. Reductive
dissolution was negligible for pH ≥ 7, but it became the dominant dissolution pathway for pH < 6, resulting in Co$^{2+}$ and several possible DFOB oxidation products. At all studied pH values in this work, proton-promoted dissolution rates were below the limit of detection (dissolved Co at pH 6 is attributed to MOPS-promoted reductive dissolution). Overall, the total dissolution rate of heterogenite increased with decreasing pH, exhibiting a linear trend ($R^2 = 0.98$). The dissolution rates from batch experiment were straightforward, but the detailed dissolution mechanisms were difficult to interpret. The observed dissolution rates were a result of interactions of heterogenite surfaces with aqueous DFOB species that depend on combined effects of surface charge, DFOB molecule configuration, and solution pH.

The dissolution of heterogenite occurred faster than the dissolution of Mn(III) and Fe(III) oxides at similar conditions (Table 2.2). The fast dissolution rate, coupled with the high affinity of Co(III) for DFOB, suggest that siderophore-promoted dissolution of Co(III) oxides is a biogeochemically favorable process. Given that Co concentration is less than 0.1% of Fe in most terrestrial environments [24], siderophore-promoted dissolution of Co(III)-bearing minerals may not affect siderophore-induced solubilization of Fe. However, the results in this study imply that siderophores may preferentially dissolve Co from solids despite the fact that Fe or Mn oxides are much more abundant in soils. The fast kinetics of Co(III) dissolution may thus be significant for increasing the bioavailability of Co that occurs in trace concentrations in soils.

In the environment where radioactive waste $^{60}$Co accumulates, siderophores could be effective chelating agents to mobilize $^{60}$Co in a manner similar to EDTA, which has been
demonstrated to move $^{60}$Co away from the original disposal site at Oak Ridge, TN [30, 31]. Currently, siderophore-enhanced mobility of $^{60}$Co has not been evaluated, although it has been suggested as an important mechanism for natural Pu and U dispersion [32, 33]. Additional dissolution data for metal oxides may further help with more complicated situations when many of transition metals exist in the same system. The work described in the following chapter on the dissolution of Co-substituted goethite by DFOB will probe a model system that is more representative of Co-bearing minerals in natural environments.
2.7 References


23. Lloyd, T. Dissolution of Fe(III) and Mn(III, IV) (hydr)oxides by desferrioxamine B. California Institute of Technology, 1999.


Figure 2.1. Percentage distribution of Co(II)-DFOB species as a function of pH predicted by MINEQL+ 4.6. Only important species that contribute to the total concentration are presented. Model conditions: 100 μM Co$^{2+}$, 100 μM DFOB, I=0. Constants are taken from Table 1.1.
Figure 2.2. XRD pattern of heterogenite (CoOOH) using Co-K$_\alpha$ radiation ($\lambda=1.789$ Å)
Figure 2.3. Transmission electron micrograph (TEM) of heterogenite at the magnification of 30000X. Heterogenite particles are hexagonal plates with average width of about 80 nm.
Figure 2.4. Multiple-point BET plot for heterogenite using N₂ gas. The specific surface area is determined to be 59.83 m²·g⁻¹.
Figure 2.5. Heterogenite dissolution kinetics for experiments conducted in batch reactors initially at pH 5 (a), pH 6 (b), pH 7 (c), pH 8 (d), and pH 9 (e) in the presence of DFOB as measured in [CoHDFOB$^+$] ($\bullet$) and [Co]$^T$ (▲). Replicates are presented in filled markers or empty markers.
Figure 2.6. Total (■) and ligand-promoted (□) initial dissolution rates of heterogenite as a function of pH (mol·m⁻²·s⁻¹). Error bars represent 95% confidence intervals. Experimental conditions: 0.2 g·L⁻¹ heterogenite, 100 μM DFOB, 0.1 M NaCl, and 10 mM buffer.
Figure 2.7. Reductive dissolution rates (mol·m$^{-2}$·s$^{-1}$) of heterogenite as a function of pH. Error bars represent 95% confidence intervals. Experimental conditions: 0.2 g·L$^{-1}$ heterogenite, 100 μM DFOB, 0.1 M NaCl, and 10 mM buffer.
Figure 2.8. Heterogenite dissolution kinetics for experiments conducted in batch reactors initially at pH 5 (a), pH 6 (b) in the presence of DFOB as measured in [CoHDFOB⁺] (♦) and [Co(II)] (●). Replicates are presented in filled markers or empty markers.
Figure 2.9. Log_{10} of nonreductive DFOB-promoted dissolution rates of Co(III), Mn(III), and Fe(III) (hydr)oxides (mol·m⁻²·s⁻¹) as a function of pH in the presence of 100 μM DFOB. Heterogenite (CoOOH) (●) (this study); manganite (γ-MnOOH) (△) [9]; hematite (α-Fe₂O₃) (◇) [23]; and goethite (α-FeOOH) (□) [23].
Figure 2.10. Reductive DFOB-promoted dissolution rates (mol·m⁻²·s⁻¹) of heterogenite (CoOOH) (■) (this study) and manganite (γ-MnOOH) (△) [9] as a function of pH in the presence of 100 μM DFOB.
Table 2.1. Standard electrode potential of selected transition metal oxides. ([i]=1.0 M)

<table>
<thead>
<tr>
<th>Half-reaction</th>
<th>$E^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoOOH(s)+3H$^+$+$e^-$ = Co$^{2+}$+2H$_2$O $^a$</td>
<td>+1.48</td>
</tr>
<tr>
<td>Mn$^{III}$OOH(s)+3H$^+$+$e^-$ = Mn$^{2+}$+2H$_2$O $^a$</td>
<td>+1.50</td>
</tr>
<tr>
<td>FeOOH(s)+3H$^+$+$e^-$ = Fe$^{2+}$+2H$_2$O $^a$</td>
<td>+0.67</td>
</tr>
<tr>
<td>$\frac{1}{2}$Fe$_2$O$_3$(s)+3H$^+$+$e^-$ = Fe$^{2+}$+$\frac{2}{3}$H$_2$O $^a$</td>
<td>+0.66</td>
</tr>
</tbody>
</table>

Table 2.2. Ligand-promoted and reductive dissolution rates of Mn(III) and Fe(III) oxides in the presence of 100 μM DFOB.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>RL $\times 10^{-12}$ (mol·m$^{-2}$·s$^{-1}$)</th>
<th>RR $\times 10^{-13}$ (mol·m$^{-2}$·s$^{-1}$)</th>
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</thead>
<tbody>
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<td>1600</td>
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<tr>
<td>Manganite</td>
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<td>145</td>
<td>1200</td>
</tr>
<tr>
<td>Manganite</td>
<td>5.6</td>
<td>122</td>
<td>1260</td>
</tr>
<tr>
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<td>5.8</td>
<td>135</td>
<td>1190</td>
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<tr>
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<td>286</td>
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<td>Manganite</td>
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<td>90.9</td>
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<tr>
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<td>242</td>
<td>64.9</td>
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<tr>
<td>Goethite</td>
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<td>1.02</td>
<td>N/A</td>
</tr>
<tr>
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<td>2.42</td>
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<tr>
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<td>1.57</td>
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</tr>
<tr>
<td>Hematite</td>
<td>9.0</td>
<td>2.05</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*a* Duckworth and Sposito [9].  
*b* Lloyd [23].
Chapter 3

DFOB-Promoted Dissolution of Co-Substituted Goethite
3.1 Introduction

As important components of soil minerals, Fe oxides are widespread in most terrestrial systems [1]. In many mineral soils which have pH values of 5 or higher, goethite is the major Fe oxide [2, 3]. Naturally occurring goethite usually incorporates foreign metal cations, such as Al, Cr, Mn, and Ni [4]. In addition, Co, Cd, Pb, and Cu have been reported to structurally exist in synthetic goethite [5-7]. The existence of these cations and the level of substitution in goethite may lead to alterations in crystal size, surface area, and structural properties, which influence the rates and mechanisms of goethite dissolution [8-10]. Proton-promoted dissolution of goethite has been demonstrated to be affected by metal substitution, either decreasing (Al, Cr) or increasing (Mn, Co) Fe dissolution rates [10]. The nature of substituted elements may also play a major role in bacterial and chemical reductive dissolution of goethite by decreasing dissolution rates, a phenomenon that has been attributed to the blocking of active sites for reduction by foreign metals on goethite surface [6, 11].

Generally, the solubility of goethite in aquatic systems is extremely low under oxic conditions [12]. To overcome the low bioavailability of Fe in such environment, microbes and graminaceous plants produce siderophores, which have high affinity for Fe(III). The dissolution kinetics of goethite in the presence of the siderophore DFOB have been investigated by many studies [13-15], and DFOB-promoted dissolution of goethite is believed to occur via a surface-controlled process that follows a ligand-promoted dissolution mechanism. However, the effects of metal substitution on goethite dissolution in the presence of siderophores are rarely examined. Cervini-Silva and Sposito [11] reported on DFOB-promoted dissolution of Al-substituted goethite (2.6-10 mol% Al), and found increasing
steady-state dissolution rates with increasing level of Al substitution. Although the stability constant for Al(III)HDFOB$^+$ complex is much smaller than that for Fe(III)HDFOB$^+$, approximately congruent dissolution of Al-goethites was observed [11].

Cobalt has been shown to be incorporated into goethite as low-spin Co$^{3+}$ ion after synthesis [8, 16]. The maximum degree of Co(III) substitution reported for these Co-goethites was about 10 mol\% [7, 8], which is much lower than that observed for Al (up to 33\%) [9, 11]. The smaller ionic radius of Co$^{3+}$ compared to that of Fe$^{3+}$ (0.545 Å versus 0.645 Å) may cause distortion of the crystal lattice, and thus changes in physical and chemical properties of goethite [17]. In addition, given the fast dissolution of heterogenite in the presence of DFOB (Chapter 2), Co substitution in goethite may significantly influence its siderophore-promoted dissolution rates and mechanisms. However, dissolution of Co-substituted goethite in the presence of siderophores remains unexplored. In light of the exceptionally large binding constant for Co(III)HDFOB$^+$ (log K = 37.5), this knowledge gap raises interesting questions about the siderophore-induced dissolution and weathering of Co-bearing Fe oxides in natural systems, which are important processes in the biogeochemical cycling of both Co and Fe.

The present work investigates the reactions of DFOB with Co-goethite by conducting flow-through dissolution experiments. Using this approach, DFOB-promoted dissolution rates are quantified, and the dominant pH-dependent dissolution mechanisms are identified. This study extends efforts to understand the interactions between pure mineral phase and DFOB (Chapter 2), but the dissolution reactions and products may be more complicated.
It has been reported that dissolution of goethite in the presence of DFOB occurs only via a ligand-promoted pathway, which results in the formation of Fe(III)HDFOB\(^{+}\) complex [12, 13, 15]. The lack of electron transfer reaction is attributed to the low electrode potential of half-reaction FeOOH/Fe\(^{2+}\) (\(E^0 = 0.67\) V), which is unlikely to oxidize DFOB [18]. The dissolution rate of goethite was also observed to be generally independent of solution pH [19]. It is thus reasonable to expect that DFOB enhances Fe release from Co-goethite only via ligand-promoted pathway (Eq. 3.1). However, it is also reasonable, based on the results of DFOB-promoted CoOOH dissolution presented in Chapter 2, to surmise that Co may be dissolved from Co-goethite by both ligand-promoted and reductive pathways as a function of pH. The possible dissolution reactions that are hypothesized to occur between DFOB and Co-goethite are expressed in equation 3.1-3.3:

\[
\text{Co-FeOOH}_{(S)} + H_4\text{DFOB}^- \rightarrow \text{Fe(III)HDFOB}^+ \quad \text{(Unbalanced equation)} \quad (3.1)
\]

\[
\text{Co-FeOOH}_{(S)} + H_4\text{DFOB}^- \rightarrow \text{Co(III)HDFOB}^+ \quad \text{(Unbalanced equation)} \quad (3.2)
\]

\[
\text{Co-FeOOH}_{(S)} + H_4\text{DFOB}^- \rightarrow \text{Co}^{2+} + \text{DFOB}_{\text{ox}} \quad \text{(Unbalanced equation)} \quad (3.3)
\]

In addition to the reactions proposed above, aqueous ligand exchange and redox reactions are also possible. When reductive dissolution of Co takes place in the system, products of dissolution can be involved in a number of homogeneous phase reactions, which include not only all reactions in equation 2.5-2.8 (Chapter 2), but also ligand exchange reactions with Fe(III) species. The complicated interactions between aqueous species and Co-goethite surfaces make it impossible to identify and measure separately every individual reaction from the determination of dissolution rates.
3.2 Co-Goethite Synthesis and Characterization

3.2.1 Materials and Methods

Four samples of Co-substituted goethites were synthesized by co-precipitation and hydroxylation of Fe(III) and Co(II) solutions similar to procedures described in Gasser et al. [8]. All solutions were made with type I deionized (DI) water with a resistivity of 18.3 MΩ·cm. All chemicals are reagent grade unless otherwise specified. Aliquots of 1 M Co(NO₃)₂ solution (0, 11.2, 22.3, and 33.5 mL) were added to 223 mL 1M Fe(NO₃)₃ to make initial Co/(Fe+Co) mole ratio equal 0%, 4.7%, 9.1% and 13.1%, respectively. (Attempts to make a sample with 16.7% mole ratio were unsuccessful due to the formation of multiple phases.) The solutions were then mixed with 5M KOH to adjust pH to 12.5 in polypropylene bottles. The resulting suspensions were transferred to 500 mL HDPE bottles and shaken for 10 min before placed in an oven at 63 ± 1 °C for 15 days. The bottles were opened for 2 min, recapped and shaken once a day. After aging process was complete, the samples were centrifuged, and the products were washed once with 200 mL of 3M H₂SO₄ at 50°C for 2 hours to remove amorphous materials. Samples were then washed four times with deionized water prior to oven drying at 55°C for 3 days. After drying, the samples were gently crushed in an agate mortar, and stored in centrifuge bottles in freezer. These four samples will be referred to as S1-S4. The percentage yield of Co-goethites decreases with increasing Co substitution, ranging from approximately 92% to 40%.
3.2.2 Particle Characterization

Dried Co-goethite samples were characterized to determine Co concentration, morphology, phase, surface area, and Co oxidation state.

*Acid digestion and acid dissolution kinetics*

Cobalt substitution concentrations were determined by complete dissolution of Co-goethite samples in concentrated HCl as described by Schwertmann [10]. A 100 mg sample of Co-goethite was loaded in a 100 mL beaker with 10 mL 12 M HCl at 80 °C until total dissolution was achieved. The solutions after proper dilution were analyzed for Fe and Co concentration using a PerkinElmer 1100 atomic absorption (AA) spectrometer. The Co content in Co-goethites was lower than initial concentration in synthesis (Table 3.1), probably due to incomplete incorporation of Co during synthesis or release of amorphous phases during the washing procedures.

Kinetic studies of acid dissolution of Co-goethites were conducted to ensure homogeneous distribution of Co in goethite structure. After dispersion of particles by sonication, 150 mg of Co-goethite sample was added to 225 mL of 8 M HCl at 25 °C. The suspension was stirred constantly with magnetic stirring bar throughout the experiment. Samples (8 mL aliquots) were collected every 10 minutes for 3 hours. Samples were filtered quickly by a 0.22 μm PTFE syringe filter (Fisher, Millipore). Dissolved Fe and Co concentrations in samples were then analyzed using a PerkinElmer 1100 atomic absorption spectrometer (AAS) at excitation wavelengths of 240.7 nm and 248.3 nm, respectively.

The concentrations of dissolved Fe were plotted as a function of dissolution time for each of the samples. All plots followed a S-shaped dissolution curve (plotted in the appendix...
Figure A3.1), which was similar to previous acid dissolution experiments on Fe oxides [9]. Cobalt substitution increased the initial dissolution rates of goethite, which agreed with the observation of Schwertmann [10]. The concentrations of dissolved Fe were also plotted against the concentration of dissolved Co for each time, showing a linear relationship between dissolved Fe and Co (in the appendix Figure A3.2). Cobalt thus dissolved congruently with respect to Fe throughout the entire time course of the experiment, indicating even distribution of Co within goethite [20].

**X-ray diffraction (XRD)**

Powder X-ray diffraction (XRD) pattern of solid Co-goethite samples was collected from 15-80° 2θ with Inel XRG-3000 diffractometer equipped with a Co-Kα source (λ=1.789 Å). No internal reference standard was used in the identification. About eight diffraction peaks corresponding to Miller indices (hkl) were used to indentify goethite phase: 020, 110, 130, 021, 111, 140, 221, and 151. Results (Figure 3.1) agreed with d spacings of goethite standard on powder diffraction data card (29-713) [21, 22], indicating single goethite phase in all samples. In addition, no significant unidentified peaks were present in the diffractogram. No effort was attempted to investigate unit-cell parameters from XRD patterns, although they previously were observed to decrease with increasing Co concentrations [8].

**Transmission electron microscopy (TEM)**

Samples for transmission electron microscopy (TEM) analysis were prepared by dispersing solid Co-goethite particles in methanol. A drop of suspension was placed onto the surface of 3 mm carbon filmed Cu grid. After allowing the suspension to dry for 2 minutes,
TEM micrographs of synthetic solids were collected on a Hitachi HF-2000 Transmission Electron Microscope. Figure 3.2 showed uniform needle-like particles with an average length of approximate 700 nm. The morphology of the particles is consistent with literature reports of goethite and Co-goethite [8]. In addition, the lack of other particle morphologies confirms that a single phase is present in the synthetic samples.

Surface area (BET)

Specific surface area of Co-goethite samples was determined by Brunauer–Emmett–Teller (BET) N₂ adsorption isotherm with an Autosorb-1-MP (Quantachrome Corp.). Prior to analysis, samples were outgassed for 24 hours at 150 °C. N₂ adsorption was measured at 18 different relative nitrogen pressures (P/P₀) between 0 and 0.3 using 0.1 g sample (Figure 3.3). Surface areas of Co-goethite samples, which do not systematically vary with Co substitution, are listed in Table 3.1.

X-ray absorption near edge structure (XANES)

Co-goethites were analyzed by using X-ray adsorption near-edge spectroscopy (XANES) (Beamline X-11B of National Synchrotron Light Source (NSLS) at Brookhaven National Lab, New York) to determine the fraction of Co(III) in samples S2-S4. Samples for XANES analysis were prepared by dilution of solid Co-goethite with boron nitride (BN), yielding an estimated adsorption (based on the known elemental composition of the sample) edge step of 1.0 με. A transparent rectangular plastic holder with opening window of 0.75 cm² was used to mount solid sample. Both sides of the window were then sealed with Kapton tape.
Aqueous Co(II) chloride and solid-phase Co(III) oxyhydroxide (CoOOH) were used as reference standards for divalent and trivalent oxidation states of Co, respectively. The $K_{\alpha}$-edge XANES spectra of Co-goethite samples (Figure 3.4) were fit to a linear combination of the spectra of Co standards using Athena [23], which makes use of the Ifeffit code [24]. In agreement with previous works [8, 16], Co cations are incorporated in the goethite particles mainly as Co(III). Results showed increasing Co(III) fraction with increasing Co substitution in goethite, with the highest percentage of 91 mol% Co(III) for S4 (Table 3.1).

3.3 Steady-State Dissolution of Co-Goethite in the Presence of DFOB

3.3.1 Materials and Methods

All chemicals are reagent grade unless otherwise specified. All solutions were made with type I deionized water with a resistivity of 18.3 MΩ·cm. The sample of desferrioxamine B (DFOB) utilized in this study was the mesylate salt $[(C_{25}H_{46}N_{5}O_{8}NH_{3})^+(CH_{3}SO_{3})^{-}]$ purchased from Sigma-Aldrich.

Absorption spectra and Beer-Lambert law extinction coefficients were first examined for Fe(II)HDFOB$^+$ and Co(III)HDFOB$^+$. Complexes of DFOB with Fe(III) were synthesized by adding 100 ppm Fe reference standard to 2 mM DFOB solution in 50 mL volumetric flasks. Five 1:1 Fe(III)HDFOB$^+$ standard solutions were prepared in concentrations of 43, 86, 129, 172, and 215 µM, and the absorption spectra were obtained from 280 nm to 800 nm on a Shimadzu UV-2101PC spectrophotometer. As reported previously [25], a red-orange Fe(III)HDFOB$^+$ complex was formed in solution. Due to the difficulty of quantitatively synthesizing Co(III)HDFOB$^+$, absorption spectra of the complex was obtained directly from
Dr. Duckworth (unpublished data). Two wavelengths, 425 nm and 310 nm, were chosen from the overlapping spectra of the two complexes (Figure 3.5) for determining complexes concentration of their mixed solution. The extinction coefficients of Fe(III)HDFOB$^+$ were then measured by standard solutions as $\varepsilon_{425\text{nm}} = 2700 \pm 100 \, \text{M}^{-1} \cdot \text{cm}^{-1}$ and $\varepsilon_{310\text{nm}} = 700 \pm 60 \, \text{M}^{-1} \cdot \text{cm}^{-1}$. The extinction coefficients of Co(III)HDFOB$^+$ are $\varepsilon_{425\text{nm}} = 330 \pm 30 \, \text{M}^{-1} \cdot \text{cm}^{-1}$ and $\varepsilon_{310\text{nm}} = 510 \pm 50 \, \text{M}^{-1} \cdot \text{cm}^{-1}$.

To test for the effects of buffers on determination of extinction coefficients, Fe(III)HDFOB$^+$ standard solutions were prepared in the same concentrations as above, but 10 mM buffers [Ac (Fisher), MOPS (Fisher), or CHES (MP Biomedical)] were also added with pH adjusted to 5, 7, or 9, respectively. The results (not shown) of these experiments agreed within error, suggesting no interference between Fe(III)HDFOB$^+$ and buffers. This result also suggests a lack of interference with Co(III)HDFOB$^+$, which was assumed in all measurements.

Continuous-flow stirred tank reactors (UHP-43, Advantec MFS, Inc.) were utilized to study flow-through dissolution of Co-substituted goethites in the presence of DFOB. Different from batch experiment, dissolution reactions in flow-through systems are kept far from equilibrium by constantly refreshing reactant solution. The reactors were made from polycarbonate for body with polyacetal cap and base. The volume of each reactor was determined to be 80 mL by measuring the difference of weight before and after adding DI water to the reactor. A 0.22 µm Millipore® nitrocellulose filter membrane was placed at the bottom of each reactor. The reactors were filled with 0.1 M NaCl without DFOB prior to the loading of ca. 0.40 g Co-goethite; this resulted in a suspension concentration of 5 g·L$^{-1}$. The
reactors were then capped, sonicated for 10 min, and connected with influent and effluent solution container using laboratory grade Tygon® tubing. The influent solution was pumped at a rate of 4 to 9 mL·h⁻¹ through reactors with a Watson-Marlow® Bredel 403U/VM4 peristaltic pump equipped with Marprene® long-life process tubing. Influent solutions contained 100 μM DFOB, 0.1 M NaCl, and 10 mM buffer with the pH set using 1 M NaOH (Fisher) or HCl (Fisher). Ac, MOPS, and CHES were chosen as buffers for pH 5, 7, and 9, respectively. To control temperature at 25 °C, the reactors were immersed in circulating water bath. The entire system, including influent and effluent solution containers, was covered with aluminum foil to exclude light. Each set of experiment was run in duplicate.

Samples of effluent solution from each reactor were collected once a day into 15 mL disposable polyethylene tubes. Absorbance of samples was immediately measured photometrically at 425 nm and 310 nm to determine [Fe(III)HDFOB⁺] and [Co(III)HDFOB⁺] prior to the measurement of sample pH. Flow rate was also determined by dividing the sample mass by collecting time. All samples were then analyzed for total dissolved Fe and Co concentrations with a 3100 Perkin−Elmer atomic absorption spectrometer (AAS) or a 2000DV Perkin−Elmer inductively coupled plasma optical emission spectrometer (ICP-OES).

3.3.2 Analysis of Dissolution Data

Based on Beer-Lambert law, UV-visible spectroscopic measurement at two wavelengths yields two equations which can be utilized to calculate the concentrations of
complexes Fe(III)HDFOB\textsuperscript+ and Co(III)HDFOB\textsuperscript+. An example of an equation for a specific wavelength follows (Eq. 3.4):

$$A_{\text{total}} = A_{\text{Co}} + A_{\text{Fe}} = - \left[ \log\left( \frac{I_{\text{Fe}}}{I_{0}} \right) + \log\left( \frac{I_{\text{Co}}}{I_{0}} \right) \right] = \varepsilon_l C_{\text{Fe}} + \varepsilon_l C_{\text{Co}} \tag{3.4}$$

where $A$ as the absorbance, $I_0$ as the intensity of incident light, $I_1$ as the intensity of light after the samples, $\varepsilon$ as molar extinction coefficient (L·mol\textsuperscript{-1}·cm\textsuperscript{-1}), $l$ as path length of light (cm), and $C$ as the concentration of sample (mol·L\textsuperscript{-1}).

After quantification of complex concentrations, the non-reductive ligand-promoted dissolution rates of Co-goethite ($R_L$) (mol·kg\textsuperscript{-1}·h\textsuperscript{-1}) with respect to Fe and Co, can be calculated as follows (Eq. 3.5):

$$R_L = \frac{[\text{Me(III)}\text{HDFOB}^+]}{m} \times q \tag{3.5}$$

where $m$ (g) is the mass of Co-goethite in the reactor, $q$ (L·h\textsuperscript{-1}) is the flow rate, and $[\text{Me(III)}\text{HDFOB}^+]$ (M) is the concentration of Fe(III)HDFOB\textsuperscript+ or Co(III)HDFOB\textsuperscript+ in effluent solution. Ligand-promoted Fe and Co dissolution rates from Co-goethites were then calculated for each collected sample until a steady-state dissolution rate was achieved, which were typically confirmed by 4-6 samples (for 96-144 hrs) after reaching stable values.

Similarly, total dissolution rates ($R_T$) (mol·kg\textsuperscript{-1}·h\textsuperscript{-1}) of Co-goethite can be mathematically expressed as (Eq. 3.6):

$$R_T = \frac{[\text{Me}]}{m} \times q \tag{3.6}$$

where $[\text{Me}]$ is the concentration of total dissolved Fe or Co in effluent solution. Total dissolution rates usually follow the same trend as ligand-promoted dissolution rates in this
study, so steady-state total dissolution rates were calculated using the same numbers of samples as above. On the basis of total aqueous Fe flux, the mass of Co-goethite in the reactor changes by less than 2% in all experiments.

Because free aqueous Co(III) or its hydrolysis species, do not typically occur over the pH range of this study, we assume that all dissolved Co, except that complexed by DFOB, is Co(II). Reductive Co dissolution rate \( (R_R) \) (mol·kg\(^{-1}\)·h\(^{-1}\)) is thus (Eq. 3.7):

\[
R_R = \frac{[\text{Co(II)}] \times q}{m} \tag{3.7}
\]

Where Co(II) represents reduced free Co(II) ions \( ([\text{Co(II)}] = [\text{Co}]_T - [\text{Co(III)HDOB}^-]) \). Steady state reductive dissolution rates were obtained when steady values of [Co(II)] were observed.

A point of steady-state dissolution rate suspected as an outlier was discarded when it differed by more than twice the standard deviation from the average rate based on all of the remaining values determined in an experiment. These anomalies usually corresponded to known events, such as temperature fluctuations or interruptions in stirring. Dissolution rates of Co-goethite were usually determined from the average of last 4-6 samples of experiments after reaching steady-state values (corresponding to 96-144 hrs of sampling). Error bars on ligand-promoted and total dissolution rates are presented as two standard deviation of the rate calculated from the reactor output at steady state, reflecting ca. 95% confidence interval. Error bars of reductive dissolution rates were then obtained by propagating errors from ligand-promoted and total dissolution rates.
3.4 Results and Discussion

The Fe dissolution rates via a ligand-promoted pathway were measured from [Fe(III)HDFOB⁺] and compared with total Fe dissolution rates. Results (Table 3.2) consistently show that ligand-promoted dissolution rates agree with total dissolution rates within experimental error, indicating the ligand-promoted is the dominant mechanism for Fe dissolution from Co-goethite at all pH and Co substitution levels studied. Figure 3.6 displays the surface-area-normalized total Fe dissolution rates from Co-goethite as a function of pH, exhibiting generally pH-independent rates for the less substituted samples (S1 – S3) but not for S4. The DFOB-promoted Fe dissolution rate increases with level of Co substitution (Figure 3.7). The results for S1 agree with previous work that found pH-independent dissolution rates of unsubstituted goethite in the presence of DFOB over a wide pH range [19]. For the highest possible Co substitution in goethite (mol% Co = 10.4), Fe dissolves in a pH-dependent manner, with faster dissolution at acidic pH; however, the Fe dissolution rate from S4 does not considerably change for pH ≥ 7. The pH-dependent Fe dissolution rate for S4 cannot be solely explained by the change of goethite surface charge and DFOB speciation at different pH, because these properties do not significantly change from pH = 5 to 7 [13]. It is possible that higher Co substitution causes greater alteration in goethite structure, or that dissolution of Co from goethite affects Fe dissolution rates (discussed below).

The surface-area-normalized total Co dissolution rates in the flow-through experiments are listed in Table 3.3. The Co dissolution rates from Co-goethite (Figure 3.8) follow a similar trend as total Fe dissolution, which does not exhibit pH dependence for less-substituted Co-goethite (S2 and S3) over the pH range studied. For S4, Co dissolution rate is
invariant with pH for pH ≥ 7, but is greater at pH = 5. The total Co dissolution rate increases with Co substitution in goethite structure. Enhanced Co dissolution rates are observed for S4, which are 6-fold greater than those for S2 and S3. The ratio of total Co:Fe dissolution rates are listed as $R^Co_{TR} / R^Fe_{TR}$, along with Co solid concentration (mol% Co/ mol% Fe) in Co-goethite (Table 3.4). If dissolution were congruent, then the two ratios would scale with each other. Results show approximately congruent dissolution for samples S2 and S3, whereas total Co dissolution rate for S4 is much greater than what is expected from congruent dissolution.

A number of physical and chemical factors may lead to the incongruent dissolution observed for S4. Uneven distribution of Co in mineral phases (e.g., an enhancement of surficial Co) may occur at high Co substitution. As suggested by Bousserrhine et al. [26], not all the foreign metals in metal-substituted goethite may be in solid solution with Fe. The possibility of uneven distribution has been investigated for Al-goethite, which is likely the case if mol% Al > 4 [11, 27]. If Co could exist as minor inclusions or coatings on goethite surfaces, incongruent dissolution of Co-goethite would occur in the presence of siderophores. Because less than 2% of Co-goethite samples are dissolved in all flow-through experiments based on mass balance, Co and Fe released into effluent solution are likely to be limited to the near surface regions. For S4, which has about the highest Co substitution (mol% Co = 10.4), it is possible that small amount of Co is coated on the surface, which results in preferential Co dissolution. However, this hypothesis is refuted for S4 because particle characterizations (viz. acid dissolution trend and TEM images) of Co-goethite do not lend
any evidence for the existence of Co coatings on goethite surfaces. For the same reason, the possibility of uneven Co distribution in goethite structure is excluded.

If Co is indeed in homogeneous solid solution with Fe, substitution of Co may still facilitate incongruent dissolution. It is possible that the greater intrinsic lability of Co may overcome a limited number of surface sites. If this were the case, we could expect a direct relationship between dissolution rate and level of Co substitution, a trend not observed in our dissolution data.

Another possibility is that, upon reaching a critical concentration, substitution of Fe by Co may destabilize the goethite lattice. Indeed, Co(III) is significantly smaller than Fe(III) (0.545 Å versus 0.645 Å), suggesting that Co(III) may be a poor fit in goethite lattice. This supposition is supported by the fact that heterogenite has an analogous chemical formula but a distinct crystallographic structure from goethite (layer-type versus network solid). In addition, the lack of solid solution in the sample prepared with initial Co/(Fe+Co) mole ratio of 16.7% indicates a significant mismatch. The distortion of the crystal structure may result in increased lattice strain, factors that may contribute to increased dissolution rate of Co (and Fe) [28].

Determination of the dissolution rates of Co(III)HDFOB$^+$ via a ligand-promoted pathway were attempted by multi-wavelength UV-visible measurements as described in section 3.3.2. However, steady-state [Co(III)HDFOB$^+$] in effluent solution were below the limit of detection of UV-visible spectrophotometer (L.O.D > 4 µM) for lower-substituted Co-goethite (S2 and S3). It is thus impossible to determine ligand-promoted Co dissolution rates for S2 and S3. Although [Co(III)HDFOB$^+$] may be above L.O.D for S4, results for S4 (not
shown) exhibit extremely high ligand-promoted Co dissolution rate at pH = 9 (faster than total Co dissolution rate), and near zero dissolution rates at pH = 5 and 7; concentrations based on calculation of Beer-Lambert law yield very high systematic errors due to the errors of extinction coefficients, essentially making the measurement meaningless. Based on patterns of DFOB-promoted heterogenite dissolution, it may be reasonable to expect the ligand-promoted dissolution rate to be similar to the total Co dissolution rate at pH = 9, or at least the production of some Co(III)HDFOB⁺ complexes, with reductive dissolution becoming more important at lower pH.

This unexpected difficulty in determining ligand-promoted Co dissolution rates is mainly attributed to the very low dissolution rate of Co-goethite. In addition, because Co substitution in Co-goethite is relatively low for all samples (mol% Co ≤ 10.4), the resulting low complex concentrations cause great difficulty in choosing appropriate analytical techniques. Although liquid chromatography (LC) and capillary electrophoresis (CE) have the capability of separating and measuring Co(III)HDFOB⁺, the nature of these two techniques will make it hard to prove their competence: Co(III)HDFOB⁺ would likely be unstable during elution, and L.O.D of CE would be too high to quantitate complexes.

Due to the difficulty in measuring [Co(III)HDFOB⁺], Co dissolution rates via a reductive pathway were also not feasible to determine. Nevertheless, the heterogenite dissolution (Chapter 2) suggests that Co dissolution from Co-goethite could be dominated by the reductive pathway at acidic pH with an enhanced rate. It is thus probable that preferential dissolution of Co could be enhanced by reductive pathway at acidic pH. For S4 (mol% Co = 10.4), the enhanced Co dissolution rate at pH = 5, compared to pH = 7 and 9, is consistent
with more rapid dissolution rate by a reductive pathway at acid pH. Enhanced reductive
dissolution of significant amount of Co should result in great defects on goethite surfaces,
also facilitating the concomitant release of Fe. This assertion corresponds to the earlier
thought that high concentrations of Co in S4 may significantly change the dissolution
reactivity of goethite. We thus speculate that Co may be reductively dissolved from Co-
goethites at acidic pH; however, this assertion is tentative and can not be directly
demonstrated from the results of our Co-goethite dissolution experiments.

In comparison to metal-substituted goethite, siderophore-promoted dissolution of
unsubstituted goethite has been extensively studied. Many studies investigated dissolution
kinetics at similar conditions with a pH range of 5-9. Those and our results (Table 3.5) show
comparable dissolution rates between unsubstituted goethite samples. Dissolution rates in the
presence of DFOB reported in the literature range from $0.81 - 10.9 \times 10^{-13}$ mol·m$^{-2}$·s$^{-1}$ [14,
15, 19, 29, 30], depending on the experimental conditions. Our data on DFOB-promoted
dissolution rate of unsubstituted goethite ($1.2 - 1.5 \times 10^{-13}$ mol·m$^{-2}$·s$^{-1}$ ) are within this range.
The disparity in literature dissolution rates can be attributed to the difference in goethite
properties from synthesis and different methods on dissolution experiments (e.g. batch versus
flow-through experiment, changes in ionic strength, etc).

Because the DFOB-promoted dissolution kinetics of Co-substituted goethite have not
been previously reported, it is important to compare the results with similar experiments.
Cervini-Silva and Sposito [11] investigated dissolution of Al-goethite in 100 μM DFOB
solution at pH = 5. Consistent with what we observed for Co-goethite, DFOB-promoted Fe
dissolution increased with Al substitution in Al-goethite [11], with dissolution rates
approximately the same as those of Co-goethite samples at corresponding conditions (Table 3.5). The results suggest that common incorporation of foreign metals (Al and Co) in the goethite structure increase the rate of Fe dissolution, possibly by destabilizing the goethite lattice, however, this assumption cannot be necessarily extended to other metal-substituted goethites.

3.5 Conclusion

This chapter presents data that illustrate the influence of siderophore DFOB on the dissolution of Co-goethite samples with different levels of Co substitutions. By measuring the complex and total metal concentrations in the effluent solution from a flow-through experiment, it is possible to examine both Fe and Co dissolution rates. Ligand-promoted dissolution was the dominant pathway for Fe dissolution from all Co-goethite samples over the pH range of 5-9. Co substitution resulted in increasing Fe dissolution rate, while the rate did not exhibit pH dependence at Co substitution < 7.2 mol%. Enhanced Fe dissolution rates at pH = 5 relative to pH ≥ 7 for a sample with 10.4% mol Co substitution (S4) may indicate alteration of goethite structure at this highest Co substitution that facilitates DFOB-promoted Fe dissolution, or perhaps concomitant dissolution of Fe promoted by the loss of Co from the lattice.

Because of the relatively slow dissolution rate of Co-goethite, ligand-promoted and reductive Co dissolution rates were difficult to measure. This difficulty was unexpected and was not easy to resolve due to the limitations of the photometrical analyses used. Alternative experimental designs or analytical methods are needed to improve the analysis of dissolution.
mechanisms. Total Co dissolution rate, nevertheless, increased with Co substitution, and the rate showed pH-independence for Co-goethite samples with 4.4% and 7.2% mol Co substitutions. Only sample S4 (mol% Co = 10.4) exhibited pH-dependent Co dissolution rate, accompanied by preferential dissolution of Co, indicating incongruent dissolution of Co-goethite. Based on the DFOB-promoted dissolution of heterogenite, it may be reasonable to suggest that Co(III)HDFOB⁺ and Co(II) preferentially form at alkaline and acidic pH, respectively. The preferential dissolution of Co from Co-goethite may be enhanced by reductive dissolution at acidic pH. These mechanisms, however, were not confirmed by experimental data in this study. After all, the observed dissolution rates were a result of complicated interactions of mineral surface with aqueous DFOB species that depend on combined effects of surface charge, DFOB molecule configuration, and solution pH.

Co-goethite in this work serves as a model mineral for the Co in association with Fe oxides, which has been found to occur in many environments [31]. A caveat of this approximation is that Co concentration is less than 0.1% of Fe in most soils [32], and thus naturally Co in Fe oxides may be unlikely to be found in the concentrations used in this study. The results from this work show that the behavior of Co-goethite in DFOB-promoted dissolution is much more analogous to goethite than to heterogenite (Figure 3.9), with Fe dissolution rates comparable to both unsubstituted goethite and Al-goethite. The association of Co with Fe oxide minerals may limit the DFOB-promoted Co dissolution rate, when compared to the very fast dissolution of CoOOH. Given that the requirement of nutrient Co is much lower than Fe in most organisms [33], siderophore-promoted Co dissolution may be an effective enough way to increase Co bioavailability.
Siderophore may affect cycling of radionuclide $^{60}\text{Co}$ through mineral weathering and dissolution processes. $^{60}\text{Co}$ at Oak Ridge National Lab, TN, has been shown to specifically associate with Fe and Mn Oxides. The work here suggests that siderophores can indeed solubilize Co from recalcitrant Fe oxide phases. Given the reactivity of siderophores with Mn oxides [34, 35], it is entirely possible that they may solubilize Co from those phases as well. The implications of this work are limited by our inability to identify the products of dissolution. Presumably, Co(III) complexes are more persistent and mobile than Co(II) under oxic conditions, however, only indirect evidence supports their formation from dissolution reactions at circumneutral to alkaline pH.
3.6 References


19. Lloyd, T. Dissolution of Fe(III) and Mn(III, IV) (hydr)oxides by desferrioxamine B. California Institute of Technology, 1999.


Figure 3.1. XRD pattern of Co-substituted goethite samples using Co-K$_\alpha$ radiation ($\lambda=1.789$ Å)
Figure 3.2. Transmission electron micrograph (TEM) of Co-goethite samples at the magnification of 10000X.
(Figure 3.3 Continued)
Figure 3.3. Multiple-point BET plot for Co-goethite samples using N$_2$ gas.

$y = 6.987 \times 10^{-2}x + 4.643 \times 10^{-4}$

$R^2 = 0.999$
Figure 3.4. Co Kα-edge XANES spectra of Co-goethite samples and standards. (Standards were obtained from Dr. Duckworth) Spectra were energy corrected and normalized using Ifeffit code. Co-goethite samples are in solid lines, fits are in dotted lines.
Figure 3.5. UV-visible spectra of 0.25 mM Fe(III)HDFOB$^+$ (solid line) and 6.5 mM Co(III)HDFOB$^+$ (dotted line) from 280 nm to 800 nm.
Figure 3.6. Total steady-state Fe dissolution rates (mol·m$^{-2}$·s$^{-1}$) of Co-goethites as a function of pH: S1 (△); S2 (○); S3 (□); S4 (◇). Error bars represent standard deviation of the rates. Experimental conditions: 5 g·L$^{-1}$ sample, 100 μM DFOB, 0.1 M NaCl, and 10 mM buffer.
Figure 3.7. Total steady-state Fe dissolution rates of Co-goethites as a function of Co substitution in the presence of 100 μM DFOB. Conditions: pH = 5 (◇); pH = 7 (□); pH = 9 (△).
Figure 3.8. Total steady-state Co dissolution rates of Co-goethites as a function of pH (mol·m⁻²·s⁻¹): S2 (○); S3 (□); S4 (◇). Error bars represent standard deviation of the rates. Experimental conditions: 5 g·L⁻¹ sample, 100 μM DFOB, 0.1 M NaCl, and 10 mM buffer.
Figure 3.9. Log$_{10}$ of total steady-state Co dissolution rates of Co-goethites and heterogenite as a function of Co substitution in the presence of 100 μM DFOB. Conditions: pH = 5 (◇); pH = 7 (□); pH = 9 (△).
Table 3.1. Properties of the Co-goethite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Co concentration (mol. % Co)</th>
<th>Solid Co concentration (mol. % Co)</th>
<th>Surface area (m$^2$/g)</th>
<th>Co(III) percentage (mol. % Co(III)/Co)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0</td>
<td>0</td>
<td>52.2 ± 0.4</td>
<td>0</td>
</tr>
<tr>
<td>S2</td>
<td>4.8</td>
<td>4.4</td>
<td>87.5 ± 0.5</td>
<td>72</td>
</tr>
<tr>
<td>S3</td>
<td>9.1</td>
<td>7.2</td>
<td>57.7 ± 0.4</td>
<td>78</td>
</tr>
<tr>
<td>S4</td>
<td>13.1</td>
<td>10.4</td>
<td>61.9 ± 0.5</td>
<td>91</td>
</tr>
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</table>
Table 3.2. Ligand-promoted and total Fe release rates from Co-goethite in the presence of DFOB.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH, buffer</th>
<th>$R_L \times 10^{-13}$ (mol·m$^{-2}$·s$^{-1}$)</th>
<th>$R_T \times 10^{-13}$ (mol·m$^{-2}$·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 (unsubstituted)</td>
<td>5.0, Ac</td>
<td>$1.4 \pm 0.2$</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>5.0, Ac</td>
<td>$1.5 \pm 0.2$</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>$1.5 \pm 0.2$</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>8.8, CHES</td>
<td>$1.2 \pm 0.2$</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>8.8, CHES</td>
<td>$1.4 \pm 0.2$</td>
<td>N/A</td>
</tr>
<tr>
<td>S2</td>
<td>5.0, Ac</td>
<td>$2.3 \pm 0.1$</td>
<td>$2.5 \pm 0.2$</td>
</tr>
<tr>
<td></td>
<td>5.0, Ac</td>
<td>$2.2 \pm 0.2$</td>
<td>$2.7 \pm 0.4$</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>$1.7 \pm 0.5$</td>
<td>$2.1 \pm 0.4$</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>$1.4 \pm 0.1$</td>
<td>$1.5 \pm 0.2$</td>
</tr>
<tr>
<td></td>
<td>8.7, CHES</td>
<td>$1.8 \pm 0.2$</td>
<td>$2.0 \pm 0.1$</td>
</tr>
<tr>
<td></td>
<td>8.7, CHES</td>
<td>$2.3 \pm 0.2$</td>
<td>$2.7 \pm 0.3$</td>
</tr>
<tr>
<td>S3</td>
<td>5.0, Ac</td>
<td>$3.8 \pm 0.2$</td>
<td>$4.1 \pm 0.3$</td>
</tr>
<tr>
<td></td>
<td>5.0, Ac</td>
<td>$4.8 \pm 0.4$</td>
<td>$5.0 \pm 0.6$</td>
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<tr>
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<td>7.0, MOPS</td>
<td>$4.0 \pm 1.1$</td>
<td>$4.7 \pm 1.2$</td>
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<tr>
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<td>$4.1 \pm 0.8$</td>
<td>$4.9 \pm 0.9$</td>
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<tr>
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<td>8.9, CHES</td>
<td>$3.2 \pm 0.3$</td>
<td>$3.7 \pm 0.2$</td>
</tr>
<tr>
<td></td>
<td>8.7, CHES</td>
<td>$3.1 \pm 0.4$</td>
<td>$3.9 \pm 0.3$</td>
</tr>
<tr>
<td>S4</td>
<td>5.0, Ac</td>
<td>$10 \pm 0.5$</td>
<td>$9.3 \pm 0.9$</td>
</tr>
<tr>
<td></td>
<td>5.0, Ac</td>
<td>$9.8 \pm 0.6$</td>
<td>$9.3 \pm 0.8$</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>$6.4 \pm 1.0$</td>
<td>$6.1 \pm 0.9$</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>$7.2 \pm 1.0$</td>
<td>$6.9 \pm 1.0$</td>
</tr>
<tr>
<td></td>
<td>8.9, CHES</td>
<td>$5.7 \pm 0.2$</td>
<td>$5.8 \pm 0.5$</td>
</tr>
<tr>
<td></td>
<td>8.9, CHES</td>
<td>$6.3 \pm 0.4$</td>
<td>$6.4 \pm 0.4$</td>
</tr>
</tbody>
</table>

*Error is estimated from the standard deviation of the rate calculated from the reactor output at steady-state. Conditions: 5 g L$^{-1}$ sample, 100 μM DFOB, 0.1 M NaCl, and 10 mM buffer. N/A: not available data
Table 3.3. Steady-state total Co release rates from Co-goethite in the presence of DFOB.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH, buffer</th>
<th>$R_T \times 10^{-13}$ (mol·m⁻²·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2</td>
<td>5.0, Ac</td>
<td>0.10 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>5.0, Ac</td>
<td>0.09 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>0.08 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>0.06 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>8.7, CHES</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>8.7, CHES</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td>S3</td>
<td>5.0, Ac</td>
<td>0.26 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>5.0, Ac</td>
<td>0.25 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>0.16 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>0.17 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>8.9, CHES</td>
<td>0.24 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>8.7, CHES</td>
<td>0.22 ± 0.04</td>
</tr>
<tr>
<td>S4</td>
<td>5.0, Ac</td>
<td>3.0 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>5.0, Ac</td>
<td>3.0 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>8.9, CHES</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>8.9, CHES</td>
<td>1.5 ± 0.1</td>
</tr>
</tbody>
</table>

*Error is estimated from the standard deviation of the rate calculated from the reactor output at steady-state. Conditions: 5 g·L⁻¹ sample, 100 μM DFOB, 0.1 M NaCl, and 10 mM buffer.
Table 3.4. Comparisons of Co solid concentration and total Co release rate relative to Fe in goethite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH, buffer</th>
<th>Solid concentration $^a$ (mol% Co/ mol% Fe)</th>
<th>$R_T^{\text{Co}} / R_T^{\text{Fe}}$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2</td>
<td>5.0, Ac</td>
<td>0.046</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>5.0, Ac</td>
<td>0.046</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>0.046</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>0.046</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>8.7, CHES</td>
<td>0.046</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>8.7, CHES</td>
<td>0.046</td>
<td>0.04</td>
</tr>
<tr>
<td>S3</td>
<td>5.0, Ac</td>
<td>0.077</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>5.0, Ac</td>
<td>0.077</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>0.077</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>0.077</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>8.9, CHES</td>
<td>0.077</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>8.7, CHES</td>
<td>0.077</td>
<td>0.06</td>
</tr>
<tr>
<td>S4</td>
<td>5.0, Ac</td>
<td>0.12</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>5.0, Ac</td>
<td>0.12</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>0.12</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>7.0, MOPS</td>
<td>0.12</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>8.9, CHES</td>
<td>0.12</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>8.9, CHES</td>
<td>0.12</td>
<td>0.23</td>
</tr>
</tbody>
</table>

$^a$ Average error = 5% for solid Co/Fe ratio.

$^b$ Average error = 10% for rate ratio.
Table 3.5. Fe release rates from different goethite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[DFOB] (µM)</th>
<th>pH, buffer</th>
<th>$R_T \times 10^{13}$ (mol·m⁻²·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted S1ᵃ</td>
<td>100</td>
<td>5.0, Ac</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>Unsubstituted S1ᵃ</td>
<td>100</td>
<td>5.0, Ac</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>Unsubstituted S1ᵃ</td>
<td>100</td>
<td>7.0, MOPS</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>Unsubstituted S1ᵃ</td>
<td>100</td>
<td>8.8, CHES</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>Unsubstituted S1ᵃ</td>
<td>100</td>
<td>8.8, CHES</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>Goethiteᵇ</td>
<td>100</td>
<td>6.0, none</td>
<td>7.32</td>
</tr>
<tr>
<td>Goethiteᵇ</td>
<td>100</td>
<td>7.0, none</td>
<td>9.85</td>
</tr>
<tr>
<td>Goethiteᵇ</td>
<td>100</td>
<td>8.0, none</td>
<td>10.90</td>
</tr>
<tr>
<td>Goethiteᵇ</td>
<td>100</td>
<td>9.0, none</td>
<td>10.23</td>
</tr>
<tr>
<td>3.6% Al-goethiteᶜ</td>
<td>100</td>
<td>5.0, MES</td>
<td>2.10</td>
</tr>
<tr>
<td>4.5% Al-goethiteᶜ</td>
<td>100</td>
<td>5.0, MES</td>
<td>2.67</td>
</tr>
<tr>
<td>10% Al-goethiteᶜ</td>
<td>100</td>
<td>5.0, MES</td>
<td>14.30</td>
</tr>
<tr>
<td>Goethiteᵈ</td>
<td>80</td>
<td>5.0, MOPS</td>
<td>3.9</td>
</tr>
<tr>
<td>Goethiteᵉ</td>
<td>80</td>
<td>6.0, none</td>
<td>6.1</td>
</tr>
<tr>
<td>Goethiteᶠ</td>
<td>240</td>
<td>6.5, MOPS</td>
<td>10.7</td>
</tr>
<tr>
<td>Goethiteᵍ</td>
<td>50</td>
<td>6.0, MOPS</td>
<td>0.81</td>
</tr>
</tbody>
</table>

ᵃ This study.ᵇ Lloyd [19].ᶜ Cervini-Silva and Sposito [11].
ᵈ Cheah et al. [15].ᵉ Carrasco et al. [30].ᶠ Cocozza et al. [14].ᵍ Reichard et al. [29]
Chapter 4
Summary and Conclusions
4.1 Summary of Major Findings

In this thesis, the dissolution rates and mechanisms of heterogenite and Co-goethite samples in the presence of siderophore DFOB were investigated using batch and flow-through experiments, respectively. By measuring the complex and total metal concentrations in dissolution products, these approaches provided ways to examine mineral dissolution rates via multiple pathways as a function of pH.

One major conclusion of this work is that siderophores may promote dissolution of Co from Co-bearing minerals via pH-dependent mechanisms. For heterogenite, ligand-promoted dissolution is the dominant pathway at neutral to alkaline pH, with decreasing rate at acidic pH; reductive dissolution rate increases with decreasing pH and only becomes dominant for pH < 6. Due to the relatively slow dissolution rates of Co-goethite, however, ligand-promoted and reductive Co dissolution rates from Co-goethite samples are difficult to measure. Given the behavior of heterogenite in DFOB-promoted dissolution, it may be reasonable to suggest that Co(III)HDFOB$^+$ and Co(II) preferentially form at alkaline and acidic pH, respectively; reductive dissolution may explain enhanced Co dissolution at pH = 5 for goethite containing high concentration of Co. These mechanisms, however, are not confirmed by experimental data for Co-goethite samples.

A second finding is that siderophores may facilitate Co transport and increase Co bioavailability in the environment. The dissolution of heterogenite occurs faster than the dissolution of Mn(III) and Fe(III) oxides at similar conditions. This fast dissolution rate, coupled with the high affinity of Co(III) for DFOB, suggests that siderophore-promoted dissolution of Co(III) oxides is a biogeochemically favorable process. Although the
association of Co with Fe oxide mineral may limit the Co dissolution rate (in the case of Co-goethite), siderophore-promoted Co dissolution may still be an effective enough way to increase Co bioavailability. This enhancement may be nutritionally sufficient for most organisms, given the low requirement of nutrient Co compared to Fe in most organisms. The results also suggest possible mobilization of radionuclide $^{60}\text{Co}$ by siderophores from recalcitrant Fe oxide phases. Because Co has been found to associate with Fe and Mn oxides, it is possible that siderophore-promoted dissolution of $^{60}\text{Co}$ from mixed mineral phases may be important to the fate and transport of radioactive $^{60}\text{Co}$ in contaminated environments.

4.2 Broader Implications of Major Findings

4.2.1 Role of Siderophores in Natural Waters

The work presented in this thesis has suggested a high efficacy of siderophores in promoting dissolution of Co and scavenging Co from complicated mineral phases, such as Co-goethite. Although production of siderophores and Co concentration are low in natural waters, especially in the marine environment, the ability of siderophores to access Co pools may still indicate a possible role of siderophores in the biogeochemical cycling of Co in natural waters, which was not previously evaluated. Cobalt, or the Co-bearing cofactor $\text{B}_{12}$, has been identified as a nutrient which may limit or co-limit growth of marine photosynthetic organisms. Because of the importance of these organisms to the global carbon cycle, the interactions of Co with siderophores may be critical, yet still poorly understood, marine biogeochemical processes.
4.2.2 Remediation of $^{60}$Co Contaminated Sites

Transport of $^{60}$Co in the environment is strongly influenced by its chemical form. Normally Co(II), the dominant form in the environment, is more mobile than Co(III). However, given the exceptionally large binding constant for Co(III)HDFOB$^+$, $^{60}$Co(III)-siderophore complexes, the products of dissolution of $^{60}$Co-bearing mineral phases by siderophores, may be more persistent and mobile than $^{60}$Co(II) in the environment [akin to the behavior of Co(III)EDTA complexes]. In addition, because Co dissolution by siderophores may occur via pH-dependent multiple pathways, it may be necessary to consider both dissolution rates and dissolution products when developing remediation strategies on $^{60}$Co contaminated sites. This study may provide useful information in fully understanding behaviors of accumulated $^{60}$Co in the environment where siderophores exist in fairly high concentrations.

4.3 Final Thoughts

4.3.1 Improvement for Present Work

Considering the problems confronted in this study, the improvements of present study may involve changing design of dissolution experiments and employing analytical methods of increased sensitivity to differentiate dissolution products. It is also unknown to what extent and at what rate the Co(III)HDFOB$^+$ complex degrades at pH < 8. Based on the similarity of the electrode potential of the complexes and the instability of Mn(III)HDFOB$^+$ at low pH, Co(III)HDFOB$^+$ may also be unstable at circumneutral pH. This information is important in examining dissolution mechanisms because determination of ligand-promoted dissolution
rate is based on direct measurement of [Co(III)HDFOB$^+$]. Future work may be needed to study internal electron transfer reaction within Co(III)HDFOB$^+$ complex at circumneutral pH.

Due to the lack of adsorption data for DFOB on minerals, direct interpretation of dissolution data is complicated. Experiments of adsorption isotherms of DFOB on heterogenite and Co-goethite would be necessary to understand surface concentration of active dissolution sites. These measurements, however, can be difficult due to the high rate of dissolution and the redox chemistry on the surface.

4.3.2 Suggestions for Future Work

The results presented in this thesis improve our understanding of interactions of siderophores with Co-bearing minerals at the macroscale. However, the complete interpretation of dissolution mechanisms depends on a detailed understanding of the surface chemistry of siderophores with mineral phases. We will need combined macroscopic/microscopic studies to provide advanced knowledge for elucidating the mechanism of interfacial biogeochemical reactions. By direct observation on changes in surface morphologies during dissolution, high-resolution transmission electron microscopy (HRTEM) may lend information by probing reactive sites on mineral surfaces.

Furthermore, DFOB utilized in this thesis is only an example of a diverse set of compounds that make up the pool of siderophores, so it is difficult to estimate to what extent DFOB represents the full spectrum of siderophore structures. It would be of great interest to examine the effect of other siderophores types, such as catecholate siderophore, on the
dissolution process. However, challenge for this work includes the time consuming exercise of isolating siderophores from iron-limited microbial cultures or plant exudates to make enough material for a complete study.

In natural terrestrial and aquatic systems, Co is in more complicated interactions with minerals and microorganisms. For example, given the reactivity of siderophores with Mn oxides and the association of Co with Mn oxides, it is entirely possible that siderophores may also solubilize Co from those phases. Thus extending the range of minerals examined would improve our current understanding of the significance of siderophores in biogeochemical cycling of Co. However, the greatest challenge in fully understanding the processes lays in the intrinsic complexity of natural environments, which often involve the influences of microorganisms, soil organic matter, and other biogenic low molecular weight organic acids.
4.4 References


Figure A 3.1 Dissolution-time curves of synthetic Co-substituted goethites in 8 M HCl at 25°C. Numbers in ( ) indicate Co substitution (mol%)
(Figure A 3.2 to be continued)
Figure A 3.2. Dissolved [Fe] as a function of dissolved [Co] from Co-goethites samples S2 (a), S3 (b), and S4 (c). The linear lines indicate even distribution of Co within goethite structure.