SORPTION CHARACTERISTICS OF DISSOLVED PHOSPHORUS COMPOUNDS ONTO IRON (OXY)HYDROXIDES IN SEAWATER

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ABSTRACT

Sorption of phosphorus (P) compounds by iron (Fe) (oxy)hydroxides significantly influences dissolved P concentrations in marine environments. This research offers comparisons of the kinetics and extent of the sorption of phosphate (PO_4), adenosine monophosphate (AMP), adenosine triphosphate (ATP), and glucose 6-phosphate (G6P) onto the Fe phases ferrihydrite, goethite, and hematite. Isotherm experiments were conducted in which artificial seawater solutions containing various concentrations of a single P compound were mixed with a single Fe-phase and allowed to equilibrate for three days. Kinetics experiments in which several identical samples were shaken at a constant temperature and sacrificed in a time series were also carried out. For all P compounds, the extent and rate of uptake from solution was in the order ferrihydrite $\gg$ goethite $>$ hematite. The extent of uptake of P onto ferrihydrite and goethite was of the order PO_4 >G6P>ATP>AMP, while for hematite the order was ATP>PO_4 >AMP>G6P. While PO_4 and organic P compounds displayed similar sorption behavior, there exist differences in the sorption capacities and affinities of different P compound/Fe-phase combinations. The different sorption behavior for the various P compound/Fe-oxide combinations has important implications for the potential release of sorbed P compounds and the bioavailability of P in aquatic systems.

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CHAPTER 1

INTRODUCTION AND BACKGROUND

Phosphorus (P) is a key macronutrient that is necessary for all life. In aquatic environments P is taken up in the dissolved form, almost exclusively as free orthophosphate (PO_4), by primary producers and incorporated into compounds that make up tissues, carry and store genetic information, and store energy. Understanding the processes that control P bioavailability is essential to understanding biological production in aquatic ecosystems. Sorption onto solid particles is one process that can remove P from solution, redering it unavailable to organisms.

Phosphorus is a highly particle reactive element (e.g. Barrow, 1978; Bolan et al., 1985; Fox, 1990; Khare et al., 2004, and many others). Sorption and desorption processes involving P compounds and sediment particles exert significant influence on dissolved P concentrations. Iron (Fe) (oxy)hydroxides have a high capacity to sorb P (e.g. Strauss et al., 1997; Khare et al., 2004). Additionally, the Fe in these minerals is subject to reductive dissolution as it is used as an electron acceptor during organic matter respiration in anoxic sediments (e.g. Froelich et al., 1979). Upon dissolution any sorbed ions are liberated and may diffuse back into pore water or the water column.

There is a great deal of interest in the interactions between P and soils and sediments. Several studies have examined the sorption of PO_4 onto sediments (e.g.

Rodel et al., 1977; Slomp et al., 1996; Sundareshwar and Morris, 1999) and Fe (oxy)hydroxides (e.g. Bolan et al., 1985; Parfitt, 1989; Strauss et al., 1997). Far fewer studies have explored dissolved organic P (DOP) sorption, and these have focused on sorption onto terrertrial soils (Leytem et al., 2002; Berg and Joern, 2006). Currently no studies have been published regarding DOP sorption onto Fe (oxy)hydroxides in seawater.

1.1 The Importance of Phosphorus to Marine Organisms

Phosphorus is an essential nutrient to all forms of life on Earth. Marine primary production can be heavily dependent on the availability of P to primary producers, and P is the ultimate limiting nutrient for oceanic primary production over geological time scales (e.g. Redfield, 1958; Van Capellen and Ingall, 1996). Photosynthetic organisms in aquatic environments utilize dissolved nutrients, including P, and energy from the sun to build their tissues. These organisms form the base of a food web that supports many more organisms at higher trophic levels.

Phosphorus serves a variety of roles within the cells of living organisms. Organisms use P for structural support by incorporating it into membranes as phospholipids, and into bones and teeth as hydroxyapatite. Phosphorus is essential in the storage and transfer of genetic information as a component of both dioxyribonucleic acid (DNA) and ribonucleic acid (RNA). Chemical bonds between PO_4 groups in adenosine triphosphate (ATP) store the energy that organisms use to carry out life processes.

1.2 The Global Phosphorus Cycle

Chemical weathering of tectonically uplifted continental rocks is the ultimate source of P in terrestrial ecosystems (Guidry et al., 2000). Apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) is the most significant primary P mineral in crustal rocks (e.g Garrles and Mackenzie, 1971). Phosphorus within apatite is solubilized during weathering in a congruent reaction (Ruttenberg, 2003). Phosphate anions that are liberated to solution during weathering are often immediately removed by sorption onto soil minerals, rendering them potentially unavailable for uptake by biota.

The major soil reservoirs of P change over time as weathering and soil development continue. As weathering progresses, the apatite associated P reservoir diminishes. Organic matter and secondary minerals become more important reservoirs of P. Some sorbed PO_4 will undergo diffusion into the interior of minerals. This occluded PO_4 is generally unavailable to biota (Cross and Schlesinger, 2001). Non-occluded P is adsorbed onto the surfaces of soil minerals where certain plant roots or associated fungi can utilize it by releasing chelating compounds, acids, or enzymes that resolubilize PO_4 (Ruttenberg, 2003, and citations therein). Over the course of soil development, occluded and organic P become the primary reservoirs of P.

Erosion and weathering deliver P to rivers, which are the main conduits for transporting P from terrestrial to marine ecosystems (e.g. Froelich et al., 1982; Ruttenberg, 2003). Rivers deliver about 21 x 10^{12}g(P)yr^{-1} to the ocean. Phosphorus is highly particle reactive, and over 90% of the P in rivers is associated with particles (Ruttenberg, 2003). Inorganic particulate P forms include iron (Fe) and aluminum (Al) (oxy)hydroxide associated P, clay associated P, and apatite (e.g Lijklema, 1980; Benitez-Nelson, 2000). During riverine transport, any particular atom of P may cycle between organic and inorganic forms through the process of nutrient spiraling. This process can repeat itself several times as an atom of P makes its way to the ocean

(Webster and Patten, 1979).

Groundwater and atmospheric deposition are other avenues through which P can be delivered to the ocean. Atmospheric deposition is relatively unimportant, with a global flux of only about 1.40 x 10^{12}g(P)yr^{-1} (Graham and Duce, 1979). This flux includes soil dust, sea spray, and phosphine gas. The flux of P to the oceans from groundwater is not well documented, though it is potentially important. Valiela et al. (1990) suggested that even if the volume of groundwater flow into the ocean in an area is small, it could still be a significant contributor of nutrients due to its high nutrient concentrations. Valiela et al. (1990) observed PO_4 concentrations in groundwater on the west coast of Cape Cod to be two to three orders of magnitude higher than those in the receiving marine waters.

Once in the ocean, P can only be removed through burial within marine sediments. Certain factors enhance this process in coastal waters relative to the deep sea. At the continental margins there is a large flux of particulate P into the ocean, the majority of which settles to the bottom and is subsequently buried (Benitez-Nelson, 2000). The large input of nutrients from land stimulates high rates of primary production in coastal areas relative to the deep sea. This production causes P to cycle through different organic and inorganic forms, as it is used by organisms and subsequently remineralized during organic matter breakdown. Also, the water column over continental shelves is shallower than it is in the pelagic ocean, allowing less time for organic matter respiration to occur during sinking. Because of these factors, the rate of burial of P in shelf and slope sediments is higher than that in the pelagic ocean (Ruttenberg, 2003).

1.3 Phosphorus in the Marine Environment

1.3.1 Marine Phosphorus Pools

Phosphorus in the marine environment can be divided into four major pools. These pools are particulate inorganic P (PIP), particulate organic P (POP), dissolved inorganic P (DIP), and dissolved organic P (DOP). Phosphorus is constantly being exchanged between these pools by both biological and physical processes. Phosphorus bioavailability to marine organisms largely depends upon its form in the environment.

Particulate inorganic P (PIP) is the largest pool of P delivered to the oceans, accounting for a flux of 12 to 27.9 x 10^{12}g (P) yr^{-1} (e.g Meybeck, 1982; Compton et al., 2000). This pool consists of both detrital and sorbed PIP. Detrital PIP includes igneous, sedimentary, and metamorphic apatites as well as P present as a trace element in other minerals. Phosphorus within detrital PIP is covalently bonded within mineral structures rendering it unavailable for uptake by marine organisms unless it is released by chemical weathering. Sorbed P is attached to particles such as iron or manganese (oxy)hydroxides. Sorbed P has the potential to be liberated to the water column where it would be available for uptake by primary producers. Some of the particulate P that is delivered to the ocean may be desorbed from particles as they are delivered to waters with a higher ionic strength (Fox, 1990), but most is rapidly removed in the nearshore environment due to sedimentation (Benitez-Nelson, 2000). Therefore most of the P that actually enters the oceanic biogeochemical cycle is delivered in the dissolved form.

Dissolved P in the marine environment has both inorganic and organic forms. The inorganic forms include the phosphate ion (PO_4^{3-}), the hydrogen phosphate ion (HPO_4^{2-}), and the dihydrogen phosphate ion ($H_2PO_4^-$) (Compton et al., 2000, and citations therein), as well as linear (polyphosphate) and condensed cyclic (metaphosphate) phosphate polymers (Karl and Björkman, 2002). Collectively, these forms are referred to as dissolved inorganic phosphorus (DIP). Dissolved organic phosphorus (DOP) compounds originate in the cells of biota. Phosphorus is incorporated into many compounds during cell growth that have a variety of functions including structure, metabolism, and regulation (Karl and Björkman, 2002). These compounds can be excreted by living cells or liberated to the surrounding environment upon cell death.

The percentage of the total dissolved P (TDP) pool that is made up of DOP can vary significantly between different environments. In coastal waters, Björkman and Karl (1994) reported DOP being responsible for 37-43% of the TDP pool in the surface waters of Mamala Bay, USA, while DOP makes up 98% of the TDP in surface waters of Sandfjord, Norway (Thingstad et al., 1993). Within the upper 25 meters of continental shelf waters DOP has been reported to make up from 33% to 86% of the TDP pool (Ammerman and Azam, 1985; Orrett and Karl, 1987; Ridal and Moore, 1990; Furnas and Mitchell, 1999; Monaghan and Ruttenberg, 1999).

Kolowith et al. (2001) reported that the dominant forms of DOP in the ocean are P esters (containing C-O-P bonds) and phosphonates (containing direct C-P bonds). Phosphorus esters are made by all living organisms, forming such compounds as nucleic acids, membrane phospholipids, and phosphosugars. These include both phosphomonoesters and phosphodiesters. Phosphonates are found in membrane structures and may provide structural support or protection from enzymatic breakdown (Kolowith et al., 2001).

1.3.2 Phosphorus Bioavailability

Orthophosphate has long been considered to be the preferred substrate for microorganisms, and it is readily available for uptake. Dissolved organic P compounds are often overlooked by researchers, though they are also available to organisms.

Certain organisms are able to produce specific enzymes that enable them to obtain phosphorus from dissolved organic compounds. Through enzymatic cleavage, PO_4 is separated from the rest of the organic compound, and this PO_4 can then be taken up by organisms. Often the activity of these enzymes is induced by low concentrations of PO_4, so that the availability of P from DOP may change depending on PO_4 concentrations (Cembella et al., 1984; Karl and Björkman, 2002). Additionally, the form of DOP affects its bioavailability. Suzumura et al. (1998) isolated high molecular weight ($< 1\mu$m but $>$10kDa) DOP from Tokyo Bay surface waters. The isolated DOP compounds were not identified, but a major portion of them (43-67%) were resistant to hydrolysis by the phosphohydrolytic enzymes alkaline phosphatase and phosphodiestrase. Additionally, surface waters are enriched in phosphonates over phosphoesters relative to their respective concentrations in plankton (Clark et al., 1998). This suggests that phosphoesters are selectively removed from the environment over phosphonates.

1.4 Iron Minerals in the Marine Environment

Iron is a common constituent of soils and sediments, having an average crustal abundance of 5% by weight (Eckel, 1914). Iron oxides in sediments can exert control on the cycling of P and other elements in marine systems through the processes of sorption and microbially induced reductive dissolution. Both the form and abundance of Fe oxides will influence the extent to which they affect P cycling. The redox state of sediments containing Fe oxides also influences the cycling of both Fe and P.

Ferrihydrite is an amorphous Fe (oxy)hydroxide that is often the first precipitate to form as Fe^{2+} ions in aqueous solution diffuse from an anoxic to an oxic environment (Thamdrup, 2000). This process occurs regularly in marine sediments. Ferric iron (Fe(III)) is used by specific microbial communities as an electron acceptor for the mineralization of organic compounds. As Fe(III) is reduced, Fe^{2+} is liberated to solution within pore water. These Fe^{2+} ions diffuse upwards to areas of lower concentration. When reduced Fe^{2+} reaches an oxidized area within sediments, ferric (oxy)hydroxides precipitate. Ferrihydrite then can age and form the crystalline Fe (oxy)hydroxide goethite. These two Fe phases, along with hematite, which forms in arid environments, are among the most common Fe (oxy)hydroxides in natural surfical environments (van der Zee et al., 2003).

The form of Fe(III) present in sediments influences the extent to which it is used as an electron acceptor for organic matter breakdown. Ferric iron in an amorphous form is used preferentially over crystalline Fe(III) (Lovley and Phillips, 1986). This has significant implications for P cycling, as amorphous Fe oxides have the potential to sorb much more P than crystalline Fe oxides, as was observed in this study.

1.5 Sorption and Sorption Isotherms

1.5.1 Phosphorus Sorption onto Iron Oxides

Dissolved P compounds are generally highly particle reactive. Sorption of these compounds on Fe (oxy)hydroxides exerts control over the concentrations of P in both solid and liquid phases (Pomeroy et al., 1965; Chitrakar et al., 2006). It has been proposed that sorption and desorption processes act to buffer PO_4 concentrations in rivers (Mayer and Gloss, 1980; Froelich, 1988) and estuaries (Pomeroy et al., 1965; Fox et al., 1985). Thus, sorption processes are important controllers of bioavailable P concentrations in natural waters and exert significant control on biological productivity.

Sorption of P compounds onto Fe (oxy)hydroxides consists of a fast initial uptake onto mineral surfaces, taking place over the course of minutes, and a slow reaction, lasting for days or even weeks (Barrow, 1978; Strauss et al., 1997; Luengo et al., 2006). The fast reaction is dominated by ligand exchange in which hydroxyl groups or water molecules on (oxy)hydroxide surfaces are replaced by PO_4^{3-} anions (Parfitt, 1978). This first reaction may be reversible, allowing for the release of sorbed P to solution if environmental conditions favor desorption (McGechan and Lewis, 2002). The slower reaction represents diffusion of PO_4 into the interior of Fe phases (Barrow, 1983). This second reaction is largely irreversible. The amount of sorbed P available for desorption is therefore influenced by the amount of time that P compounds and Fe (oxy)hydroxides spend in an environment in which sorption is favorable prior to being exposed to conditions that favor desorption (Munns and Fox, 1976).

1.5.2 Sorption Isotherms

Several models are used to describe sorption onto mineral surfaces. Here, three commonly used models will be discussed: the Langmuir and Fruendlich isotherms, and the metastable-equilibrium adsorption (MEA) theory. These models are useful for summarizing and comparing systems, and may be able to predict sorption behavior outside of experimental conditions. Unfortunately, these models are generally unable to provide a specific mechanism for sorption reactions.

The Langmuir equation was first used to describe the adsorption of gas onto solid surfaces, but has since been adapted to describe solid-solution interactions (Barrow, 1983). This equation can be written as:

$$\Gamma = \frac{a\Gamma_m C_{eq}}{1 + aC_{eq}} \tag{1}$$

where Γ is the amount of sorbate sorbed per unit sorbent, C_{eq} is the concentration of sorbate in solution at equilibrium, a is an affinity term, and Γ_m is the maximum sorption density (Barrow, 1983). The Langmuir equation makes use of several assumptions: (1) a solid has a finite number of surface sites, and each site can accommodate one molecule of sorbant; (2) the adsorption energy for each surface site is the same, regardless of surface coverage; and (3) sorption is a reversible process (Hinz, 2001). This equation may describe sorption data with some accuracy, although its assumptions clearly do not reflect reality. Sorbed compounds diffuse into particles (Barrow, 1983), so that a single layer adsorption model is inaccurate. Also, particle surfaces become more electronegative as more anions are adsorbed, which decreases sorption affinity. Still, the Langmuir equation can be useful in describing sorption reactions, and it has the advantage of being able to predict a maximum sorption capacity.

The Fruendlich equation has also commonly been used to describe anion sorption onto mineral surfaces. This equation can be written as:

$$\Gamma = k_{sp} C_{eq}^{\beta} \tag{2}$$

where k_{sp} and β are coefficients, the values of which are determined by best fits to experimental data, and Γ and C_{eq} have the same meanings as in equation 1. This equation was developed as an empirical model, and has been noted to provide good fits to sorption data for nearly all soils (McGechan and Lewis, 2002). Despite being developed as an empirical model, it has been noted that the Fruendlich equation corresponds to a model of adsorption in which the affinity of the sorbate for the sorbant decreases exponentially as sorption increases (Barrow, 1978).

The metastable-equilibrium adsorption (MEA) theory (Pan and Liss, 1998b) offers another way to describe and compare adsorption data. Unlike the above models, MEA theory does not assume that sorption density (Γ in the above equations) is a state variable. When treated as a state variable, it is assumed that the sorption density should be unique for any given adsorption reaction under constant temperature, pressure, and solution concentration, and that it should be independent of the particle concentration and kinetic history of the process. Pan and Liss (1998b) present a Fruendlich type isotherm equation that accounts for the particle concentration used in the reaction. The equation is written as:

$$\Gamma = k_{sp} C_p^{-n} C_{eq}^{\beta} \tag{3}$$

where C_p is the amount of solid in solution, n is a constant determined by best fits to experimental data, and all other variables are as defined above. This equation has the advantage of including the effects of particle concentration when describing sorption data. This is important because particles in systems with lower particle concentrations may reach higher equilibrium sorption densities than those in systems with higher particle concentrations (Pan and Liss, 1998b).

Chapter 2

Materials and Methods

Experiments were carried out to explore sorption interactions between Fe (oxy)hydroxides and dissolved P compounds. Sorption isotherms were created to explore differences in the capacities of the different Fe (oxy)hydroxides to sorb P compounds, and to compare the affinities of each mineral for different P compounds. Kinetics experiments were conducted in order to examine differences in rates of uptake of P from solutions for different combinations of Fe (oxy)hydroxide and P compound.

All chemicals used were reagent grade. All glasswear and plastic wear used were washed with phosphate-free soap, rinsed with deionized water (DI-H_2O), soaked in 10% hydrochloic acid (HCl) for a minimum of three days, and again rinsed a minimum of three times with DI-H_2O. All non-volumetric glasswear was then muffled at 500°C for two hours.

2.1 Phosphorus Compounds and Artificial Seawater

2.1.1 Phosphorus Compounds

In addition to PO_4, three different organic P compounds were selected for experiments. Care was taken to select various DOP compounds representing a variety of molecular sizes and P bonds. Adenosine triphosphate (ATP) (498 g mol^{-1}) and adenosine monophosphate (AMP) (347 g mol^{-1}) were chosen as mid-level molecular weight compounds. Adenosine triphosphate and AMP have the same nucleoside (adenosine), but differ in that the P in ATP is part of a polyphosphate chain, whereas the P in AMP is a single P monoester. Comparison of these two compounds will thus reveal the relative sorption affinity of mid-level molecular weight polyphosphate versus monoester P. Glucose 6-phosphate (G6P) (260 g mol^{-1}) was chosen to evaluate a low molecular weight P-monoester. Phosphate (95 g mol^{-1}) was also evaluated in order to provide a comparison between PO_4 and the different DOP compounds.

2.1.2 Artificial Seawater

All solutions were made in artificial seawater (ASW) with a salinity of 30 parts per thousand. Sigma sea salts were added to DI H_2O (30 g Sigma sea salts for every 970 ml H_2O), and the solution was stirred until all salt dissolved. The solution was then filtered through 0.20 μm polyethylene filters. The ASW had a pH of 8.5. Ionic composition of the ASW is given in table 2.1.

Table 2.1: Artificial seawater composition

Ion	Concentration (mgL^{-1})
Chloride	17,070
Sodium	9,541
Sulfate	2,359
Magnesium	1,169
Potassium	356
Calcium	353
Carbonate/Bicarbonate	171
Bromide	57.6
Strontium	7.63
Boron	4.97
Fluoride	0.89
Iodide	0.19
Lithium	0.16

2.2 Iron (Oxy)hydroxides

Ferrihydrite, goethite, and hematite were the chosen Fe minerals to use in sorption experiments. Ferrihydrite and goethite were synthesized using modifications of methods presented by Schewtmann and Cornell (1991). The methods of synthesis are summarized in table 2.2. Hematite was obtained as an analytical reagent. All minerals were analyzed by powder X-ray diffraction (XRD) to examine purity and mineralogy.

Table 2.2: Iron (oxy)hydroxide synthesis

	Total $FeCl_3$ (g)	Total NaOH (moles)	Total Volume of Solution (L)	Final pH of Reaction	Mineral Yield (g)
Ferrihydrite	33.073	0.62	1.62	7.88	18.76
Goethite	32.396	1.35	3.00	14	14.05

2.2.1 Ferrihydrite Synthesis

Anhydrous ferrous chloride ($FeCl_3$) was weighed on an analytical balance and transferred to a large beaker. Deionized water (DI H_2O) was added, and the mixture was stirred until all $FeCl_3$ dissolved. One molar sodium hydroxide (NaOH) was added to raise the pH (see table 2.2 for details), and a red precipitate formed. The mixture was centrifuged, and the supernatant was decanted. In order to remove excess salt, the precipitate was re-suspended in DI H_2O. The mixture was again centrifuged, and the supernatant was decanted. This washing process was repeated twice, and the pH of the supernatant after the second washing was 6.26. The ferrihydrite was then frozen and subsequently freeze dried.

2.2.2 Goethite Synthesis

Goethite was synthesized in a manner similar to ferrihydrite with certain changes. After dissolving $FeCl_3$, five molar NaOH was added in place of one molar NaOH to raise the pH (see table 2.2), and a dark red precipitate (ferrihydrite) formed. Deionized H_2O was then added and the solution was transferred to three one liter polypropylene bottles. The bottles were capped, shaken, and placed in an oven at 70°C. The bottles were checked and stirred periodically over the following three days. During the three days the red precipitate changed to a yellow orange color. The mixture was centrifuged and the supernatant was decanted. The precipitate was washed twice with DI H_2O as above. After the second washing, the pH remained high at 11.18. A greater number of washings were not done because the low ionic strength of the DI H_2O caused flocculation of the precipitate, and precipitate was being lost with supernatant. The goethite was then dried in an oven at 55°C for four days.

2.2.3 Preparation of Fe Phases for Experiments

In order to optimize comparison of experimental results, efforts were made to ensure that all Fe-phases had equivalent grain sizes. After freeze drying, the ferrihydrite appeared as large aggregates of particles with a vitreous luster. The ferrihydrite particles would not pass through a sieve with a mesh size of 125μm without being ground. Both goethite and hematite easily passed through a sieve with a mesh size of 75μm, and both had very dull luster. Ferrihydrite was therefore ground with mortar and pestle to a size that could easily pass through a 75μm sieve prior to use in sorption experiments. After grinding, the ferrihydrite had a dull luster similar to the other minerals.

2.2.4 X-Ray Diffraction

Powder XRD was used to confirm the purity and structure of the three Fe-phases. Bulk powder samples with random orientation were analyzed on a Scintag PAD V using copper (Cu) K_α radiation and a solid state Ge detector. Samples of each powdered Fe phase were scanned from 10° to 65° at a rate of 0.03° per minute.

2.3 Sorption Experiments and Isotherms

Sorption isotherms were created for each mineral and P compound combination. Three different particle concentrations (C_P) were used (C_{P1} = 1.5 g L^{-1}, C_{P2} = 2.0 g L^{-1}, C_{P3} = 3.0 g L^{-1}). Minerals were weighed on an analytical balance and transferred to 50 mL polypropylene centrifuge tubes (30.00 ± 0.20 mg for C_{P1}, 40.00 ± 0.20 mg for C_{P2}, and 60.00 ± 0.20 mg for C_{P3}). Twenty milliliters of ASW containing a range of concentrations (Table 2.3) of the P compound being tested were then added by pipette. Samples were shaken in a water bath at 25°C at a speed such that all particles remained suspended in solution. Samples were allowed to equilibrate for three days.

After equilibration, samples were removed from the water bath and filtered through 0.45 μm polypropylene syringe filters into 20 mL borosilicate vials. The filtrates were acidified to a pH of one by the addition of 0.200 mL concentrated HCl. Samples were stored refrigerated until analyzed.

Careful consideration was given to the running of replicate samples. The experiments allowed the creation of isotherms that could be described by different models. Any data point that was outside of the realm of reasonable values would have been easily identified by adjacent points of the isotherm, and replicate samples could have been run at that time. Therefore, in the interest of maximizing the number of unique data points to describe the isotherms, samples were not replicated during experiments.

All filtrates from sorption experiments were analyzed spectrophotometrically. Inorganic phosphate was analyzed using the procedure of Koroleff (1976). All organic P compound samples were analyzed using the procedure of Monaghan and Ruttenberg (1999). Sorbed P was assumed to be the difference between the initial solution P concentration (C_0) and the solution P concentration after completion of the experiment, which was at or near equilibrium (C_{eq}). Control samples containing solutions without minerals were run alongside actual samples to rule out P-uptake by container walls.

In order to obtain Langmuir isotherm constants, the Langmuir equation:

$$\Gamma = \frac{a\Gamma_m C_{eq}}{(1 + aC_{eq})} \tag{1}$$

was rearranged to give:

$$\frac{C_{eq}}{\Gamma} = \frac{1}{\Gamma_m} C_{eq} + \frac{1}{a\Gamma_m} \tag{4}$$

which is the linear form of the Langmuir isotherm. C_{eq} is then plotted against $\frac{C_{eq}}{\Gamma}$, and a straight line was fit to the data. It can be seen that the slope of such a line is equal to $\frac{1}{\Gamma_m}$, and the intercept is equal to $\frac{1}{a\Gamma_m}$.

To obtain Fruendlich isotherm constants, the natural logarithm was taken of both sides of the Fruendlich equation:

$$\Gamma = k_{sp} C_{eq}^{\beta} \tag{2}$$

resulting in:

$$\ln \Gamma = \ln k_{sp} + \beta \ln C_{eq} \tag{5}$$

which is the linear form of the Fruendlich isotherm. Plots of $\ln C_{eq}$ vs. $\ln \Gamma$ were then made, and a straight line was fit to the data. The slope of such a line is equal to β, and the intercept is equal to $\ln k_{sp}$.

2.4 Sorption Kinetics

Sorption kinetics experiments were conducted for each mineral P compound combination. A particle concentration of 2.0 g L^{-1} was used for all kinetics experiments. An initial P concentration of 200 μM was used for all compounds. All solutions were made in 0.2 μm-filtered ASW with a salinity of 30 parts per thousand. For each sample, 40.00 ± 0.20 mg of mineral was weighed on an analytical balance and transferred to a 50 mL polypropylene centrifuge tube. Twenty milliliters of ASW containing 200 μM P were then added to each centrifuge tube via pipette. The samples were placed in a water bath at 25°C and shaken at a speed such that all particles remained suspended in solution. Twelve replicates for each P compound-Fe (oxy)hydroxide combination were added to the water bath at time t=0. Samples were sacrificed in series. Within the first 24 hours, the sampling intervals progressed from minutes at the beginning of the experiment to hours at the end of this initial period. Final samples were allowed to react for a period of four days. After removal from the shaker table, each sample was filtered, acidified to a pH of one with concentrated HCl, and the filtrate was analyzed for P as in isotherm experiments (see section 2.3). The difference between amount of P present in solution at the time of sampling and C_0 equates to the amount of P that was sorbed onto the particles. Control samples containing solution without minerals were run for periods of three days in order to determine the extent of hydrolysis of each organic P compound over the duration of the experiments.

Table 2.3: Isotherm experimental conditions

Iron Phase	P Compound	[a]C_P (g L^{-1})	[b]C_0 (μM (P))
Ferrihydrite	Phosphate	1.5	195-485
		2.0	250-500
		3.0	435-680
	G6P	1.5	75-83.33
		2.0	83.33-95.83
		3.0	95.83-116.67
	AMP	1.5	52-150
		2.0	64-180
		3.0	79-200
	ATP	1.5	100-180
		2.0	125-220
		3.0	200-340
Goethite	Phosphate	1.5	50-105
		2.0	70-135
		3.0	130-220
	G6P	1.5	2.67-23.33
		2.0	3.17-30.50
		3.0	4.83-50
	AMP	1.5	20-90
		2.0	16-110
		3.0	13-150
	ATP	1.5	40-90
		2.0	50-100
		3.0	60-110
Hematite	Phosphate	1.5	10-45
		2.0	20-60
		3.0	30-110
	G6P	1.5	4.17-11
		2.0	5.83-14.33
		3.0	5.67-31.67
	AMP	1.5	6-28
		2.0	10-35
		3.0	15-60
	ATP	1.5	20-60
		2.0	25-75
		3.0	40-100

[a] Particle concentration

[b] Initial solution P concentration

CHAPTER 3

RESULTS

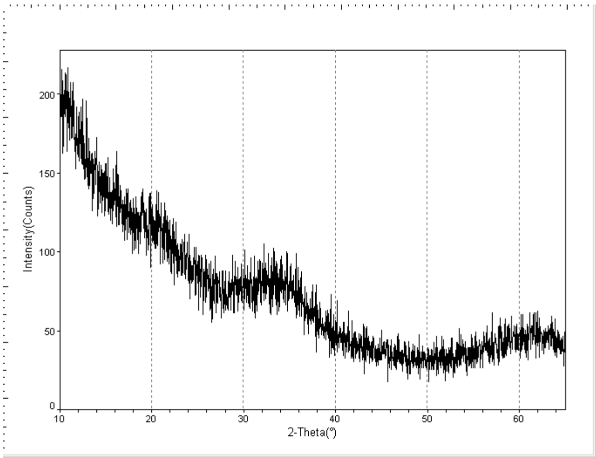
3.1 X-ray Diffraction

X-ray diffraction analysis confirmed the purity and composition of all Fe phases. The ferrihydrite XRD trace had no sharp peaks as was expected due its amorphous nature (Figure 3.1(a)). All peaks that are consistant with XRD patterns for both goethite and hematite (Figures 3.1(b) and 3.1(c), respectively) were present (Berry, 1974), confirming the mineralogy of these phases. Absence of any exteraneous peaks confirmed the purity of all phases.

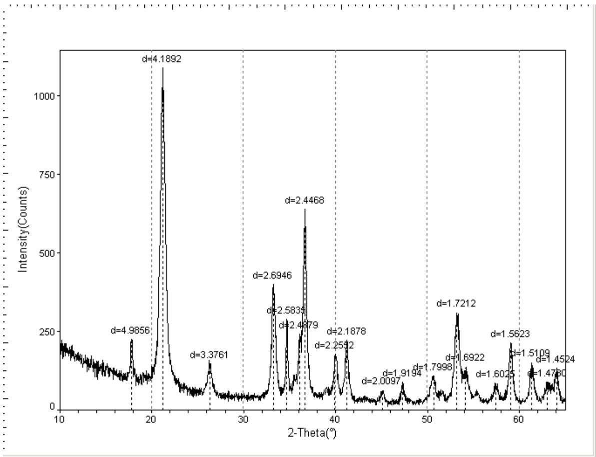
3.2 Isotherms

Sorption trends were similar for all Fe phases and all P compounds (Figures 3.2 - 3.6, note different scales on figures). Generally, the sorption behavior can be split into two regions. In the first region a small increase in equilibrium dissolved P concentration (C_{eq}) results in a large increase in sorption density (Γ). The opposite behavior is observed in the second section, where a large increase in C_{eq} results in only a minor increase in Γ.

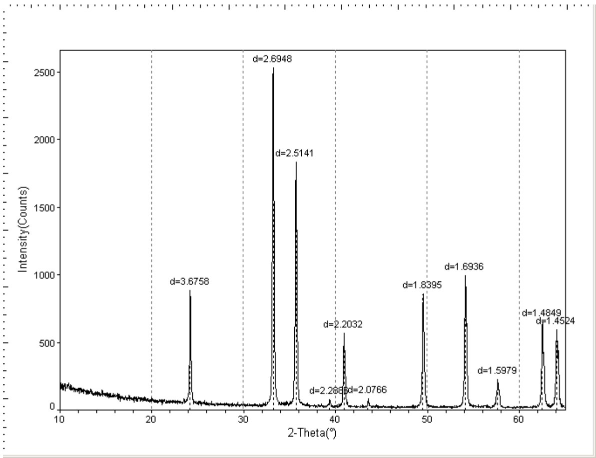
The total amount of P compound sorbed onto both ferrihydrite and goethite



(a) Ferrihydrite



(b) Goethite



(c) Hematite

Figure 3.1: X-ray Diffraction Traces

followed the order:

$$\mathrm{PO_4} > \mathrm{ATP} > \mathrm{AMP} > \mathrm{G6P}$$

The sorption capacity of the P compounds on hematite followed the order

$$\mathrm{ATP} \geq \mathrm{PO_4} > \mathrm{AMP} > \mathrm{G6P}$$

For all compounds, ferrihydrite had the highest sorption capacity, goethite was intermediate, and hematite sorbed the least (on a per gram dry weight basis).

All data were fit using both the Langmuir and Fruendlich equations (Figures 3.2-3.6). Constants for each isotherm fit are presented in table 3.2. For the Langmuir isotherms, R^2 values were above 0.93 for all experiments. Fruendlich isotherms had similarly good fits with R^2 values above 0.91 for all experiments, except hematite-AMP with particle concentrations of 1.5 and 2.0 gL^{-1} (R^2 of 0.845 and 0.693, respectively), and hematite-G6P with particle concentrations of 1.5 and 2.0 gL^{-1} (R^2 of 0.551 and 0.226, respectively).

Control samples were analyzed in order to ensure that there was no sorption of P compounds onto centrifuge tubes, and to determine the amount of each DOP compound that hydrolyzed to PO_4 over the course of sorption experiments. Total dissolved P (TDP) analysis of control samples confirmed that all P removed from solution was sorbed onto Fe particles. Soluble reactive P analysis confrimed that rates of hydrolysis of organic compounds were lower than 1% (Table 3.2). Higher rates of hydrolysis in samples containing minerals cannot be ruled out.

3.3 Kinetics

The kinetics of sorption onto ferrihydrite was similar for all P compounds (Figure 3.7). An initial rapid uptake of P from solution occurred for approximately the

Table 3.1: Langmuir and Fruendlich Isotherm Constants*

			Langmuir			Fruendlich		
Fe Phase	P Compound	C_p (gL^{-1})	Γ_m	a	R^2	β	k_{sp}	R^2
Ferrihydrite	PO_4	1.5	660	0.186	1.00	0.223	173	0.972
		2.0	683	0.243	1.00	0.214	179	0.983
		3.0	614	0.272	1.00	0.234	186	0.967
	ATP	1.5	119	0.508	0.999	0.172	63.0	0.967
		2.0	107	0.788	0.998	0.160	61.2	0.970
		3.0	113	0.693	1.00	0.176	62.3	0.966
	AMP	1.5	82.4	0.350	0.995	0.242	32.2	0.977
		2.0	78.4	0.353	1.00	0.282	28.6	0.915
		3.0	83.1	0.318	0.994	0.331	27.0	0.952
	G6P	1.5	72.3	0.120	0.991	0.507	10.5	0.987
		2.0	88.2	0.0971	0.996	0.504	11.7	0.968
		3.0	102	0.0897	0.963	0.536	12.0	0.999
Goethite	PO_4	1.5	71.0	1.77	0.997	0.0846	52.7	0.959
		2.0	73.9	2.51	0.999	0.0900	53.0	0.980
		3.0	79.4	0.944	0.997	0.0973	52.8	0.987
	ATP	1.5	76.0	0.162	0.989	0.314	20.8	0.996
		2.0	77.0	0.139	0.996	0.342	18.2	0.992
		3.0	84.5	0.104	0.999	0.365	15.3	0.979
	AMP	1.5	28.4	0.487	0.979	0.145	14.8	0.921
		2.0	30.7	0.297	0.960	0.215	11.7	0.961
		3.0	27.7	0.208	0.951	0.330	7.22	0.992
	G6P	1.5	10.8	0.370	0.929	0.479	2.87	0.965
		2.0	11.7	0.272	0.981	0.524	2.42	0.977
		3.0	12.9	0.197	0.946	0.507	2.35	0.995
Hematite	PO_4	1.5	21.0	1.35	0.996	0.207	11.5	0.926
		2.0	20.7	1.53	0.998	0.130	13.2	0.988
		3.0	22.5	0.561	0.998	0.147	12.2	0.995
	ATP	1.5	21.4	0.488	0.994	0.189	10.9	0.998
		2.0	22.3	0.344	0.998	0.215	9.95	0.996
		3.0	23.3	0.244	0.996	0.225	9.51	0.993
	AMP	1.5	16.4	0.942	0.981	0.217	8.17	0.845
		2.0	15.9	0.670	0.993	0.210	7.60	0.693
		3.0	11.7	0.759	0.975	0.176	6.31	0.953
	G6P	1.5	4.25	1.98	0.974	0.168	2.93	0.551
		2.0	3.28	4.36	0.973	0.126	2.59	0.226
		3.0	4.90	0.446	0.938	0.479	1.61	0.926

* Γ_m, a, β, and k_{sp} are as defined in Section 1.5.2

Table 3.2: Hydrolysis of Organic P Compounds

		Immediately after making solution		After 3 days shaking at 25°C	
Compound	Total Dissolved P(μM)	[a]SRP (μM) Measured	[b]Percent Hydrolyzed	[c]SRP (μM) Measured	[d]Percent Hydrolyzed
adenosine 5'-triphosphate disodium salt trihydrate	200	6.10	3.1	1.00	0.5
adenosine 5'-monophosphate	200	5.40	2.7	0	0
α-D-glucose-6-phosphate monosodium salt	200	3.19	1.6	0.33	0.16

[a] Compounds analyzed for SRP immediately after being brought into solution.

[b] % hydrolyzed = ([SRP]measured/total P concentration) x 100%. Note that the measured SRP may include SRP that was present in the original chemical used to make solution, and this amount may thus not derive from hydrolysis during the colorimetric procedure.

[c] [SRP]measured after three days shaking - [SRP]measured immediately after being brought into solution.

[d] (([SRP]measured after three days shaking - [SRP]measured immediately after being brought into solution)/total P concentration) x 100%.

first 0.5 hour. Uptake then continued at a much slower rate for the duration of the experiment. The initial rate of uptake onto ferrihydrite followed the order:

$$\mathrm{PO_4} > \mathrm{ATP} > \mathrm{AMP} > \mathrm{G6P}.$$

The kinetics of sorption of PO_4, AMP, and G6P onto goethite were also characterized by an initial rapid uptake from solution which lasted for approximately 30 minutes giving way to a continuous slow uptake for the remaider of the experiment (see Figure 3.8, note different scale on verticle axis relative to Figure 3.7). Adenosine triphosphate sorption displayed a different behavior, with an initial uptake leading to a maximum sorption density at time $t = 1$ hour. Sorption density then decreased until time $t = 48$ hours, and increased slightly between times $t = 72$ hours and $t = 96$ hours. The initial rate of uptake of P onto goethite was in the order

$$\mathrm{ATP} > \mathrm{PO_4} > \mathrm{AMP} > \mathrm{G6P}.$$

The apparent desorption of ATP between one and 48 hours while PO_4 continued to be sorbed led to a crossover in the sorption densities of these two compounds between 12 and 24 hours (Figure 3.8).

An initial rapid uptake of all P compounds onto hematite was also observed (Figure 3.9, note different scale on the verticle axis relative to Figures 3.8 and 3.7). The initial rate and final sorption densities of the P compounds onto hematite followed the order:

$$\mathrm{ATP} > \mathrm{PO_4} > \mathrm{AMP} > \mathrm{G6P}.$$

Following the initial rapid uptake, a stage of slower uptake of P from solution was observed for both G6P and AMP. The amount of PO_4 sorbed remained constant between 24 and 96 hours. A decrease in sorption density between 0.5 and 48 hours was observed for ATP, after which time the amount of P sorbed appeared to remain constant. The decrease in the soption density of ATP was not enough to cause a crossover of ATP and PO_4 sorption densities; this type of crossover was unique for goethite.

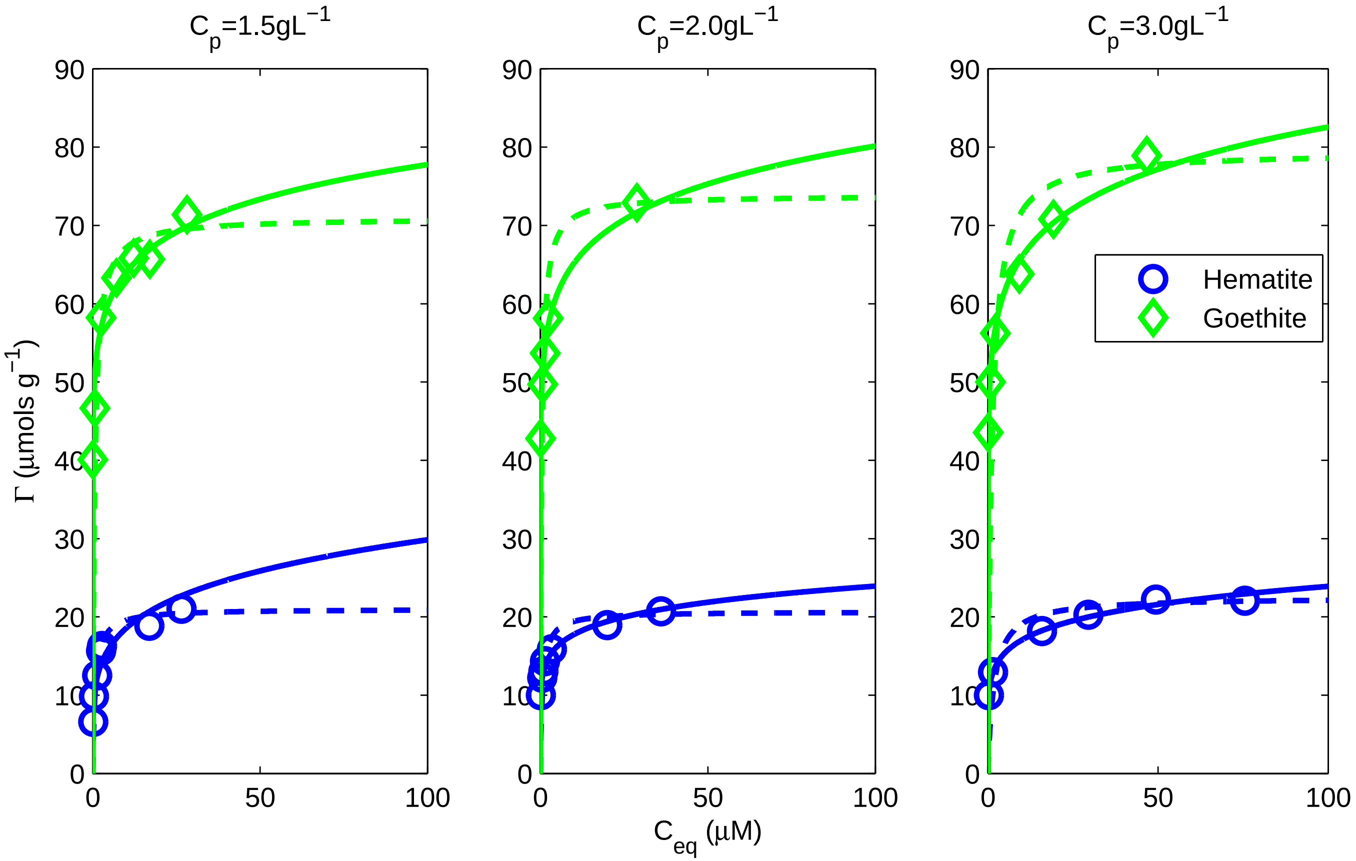


Figure 3.2: Phosphate Isotherms for Goethite and Hematite: Symbols are data points, solid lines are Fruendlich isotherms, and dashed lines are Langmuir isotherms.

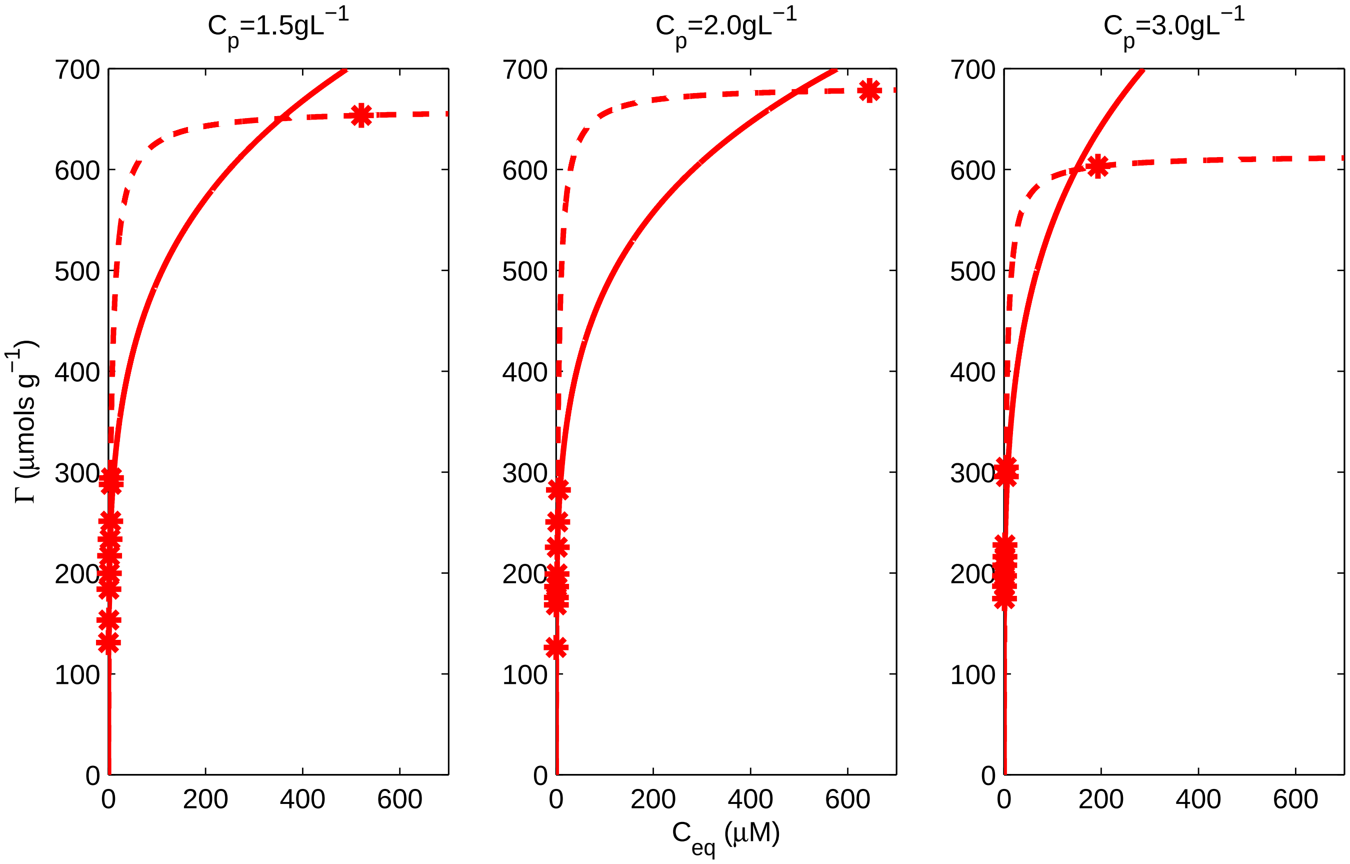


Figure 3.3: Phosphate Isotherms for Ferrihydrite: Symbols are data points, solid lines are Fruendlich isotherms, and dashed lines are Langmuir isotherms. Ferrihydrite was separated from other minerals because of the large difference in the maximum sorption density.

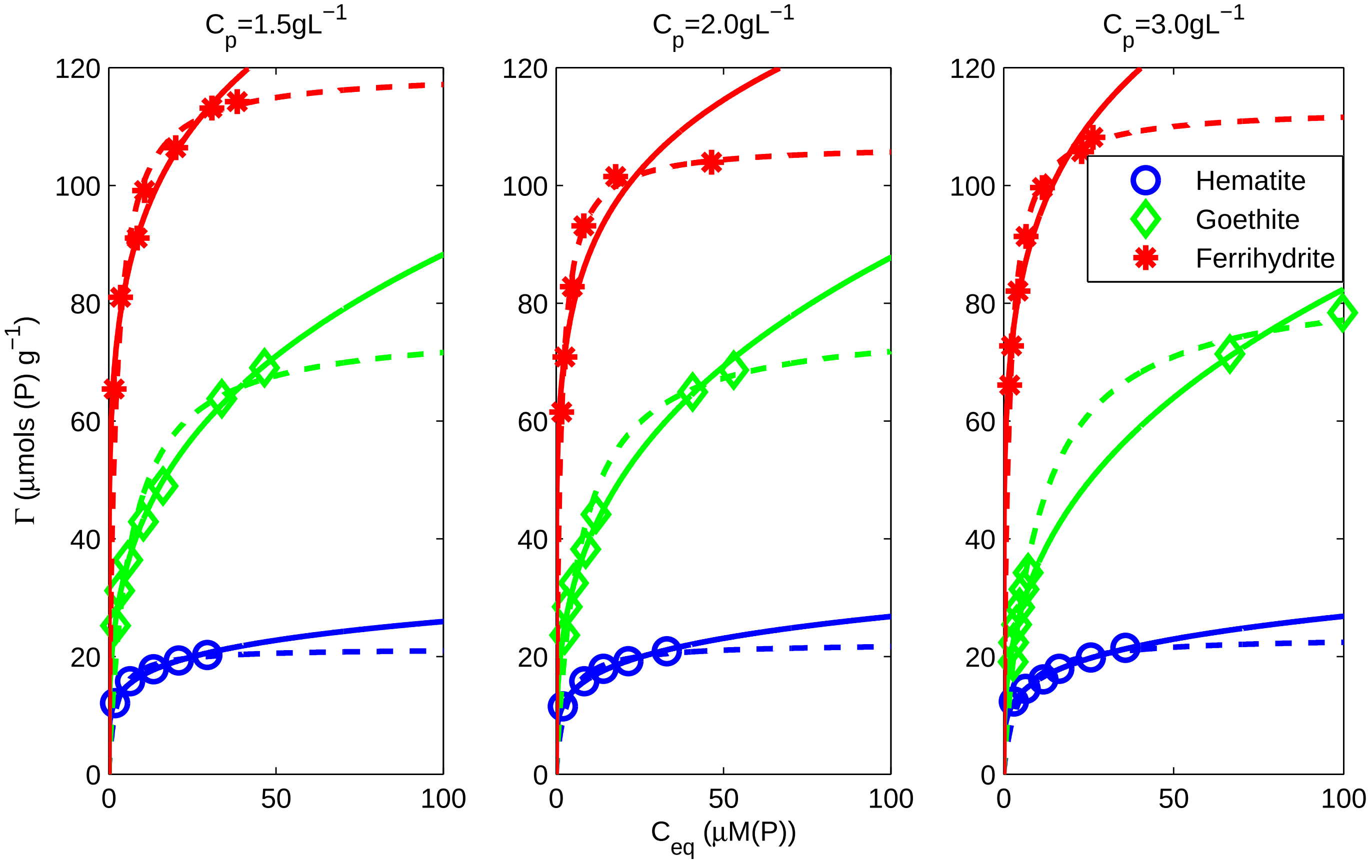


Figure 3.4: ATP Isotherms: Symbols are data points, solid lines are Fruendlich isotherms, and dashed lines are Langmuir isotherms.

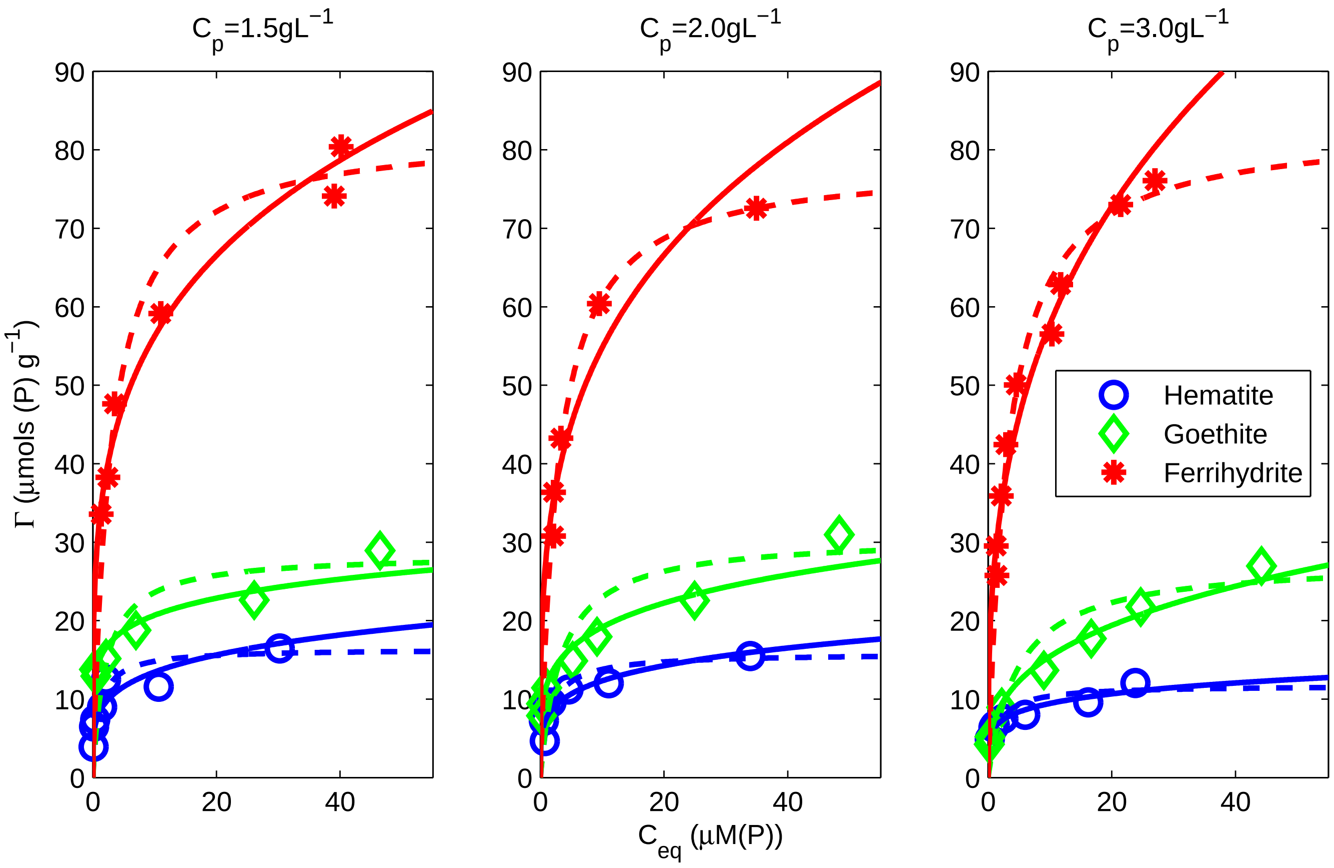


Figure 3.5: AMP Isotherms: Symbols are data points, solid lines are Fruendlich isotherms, and dashed lines are Langmuir isotherms.

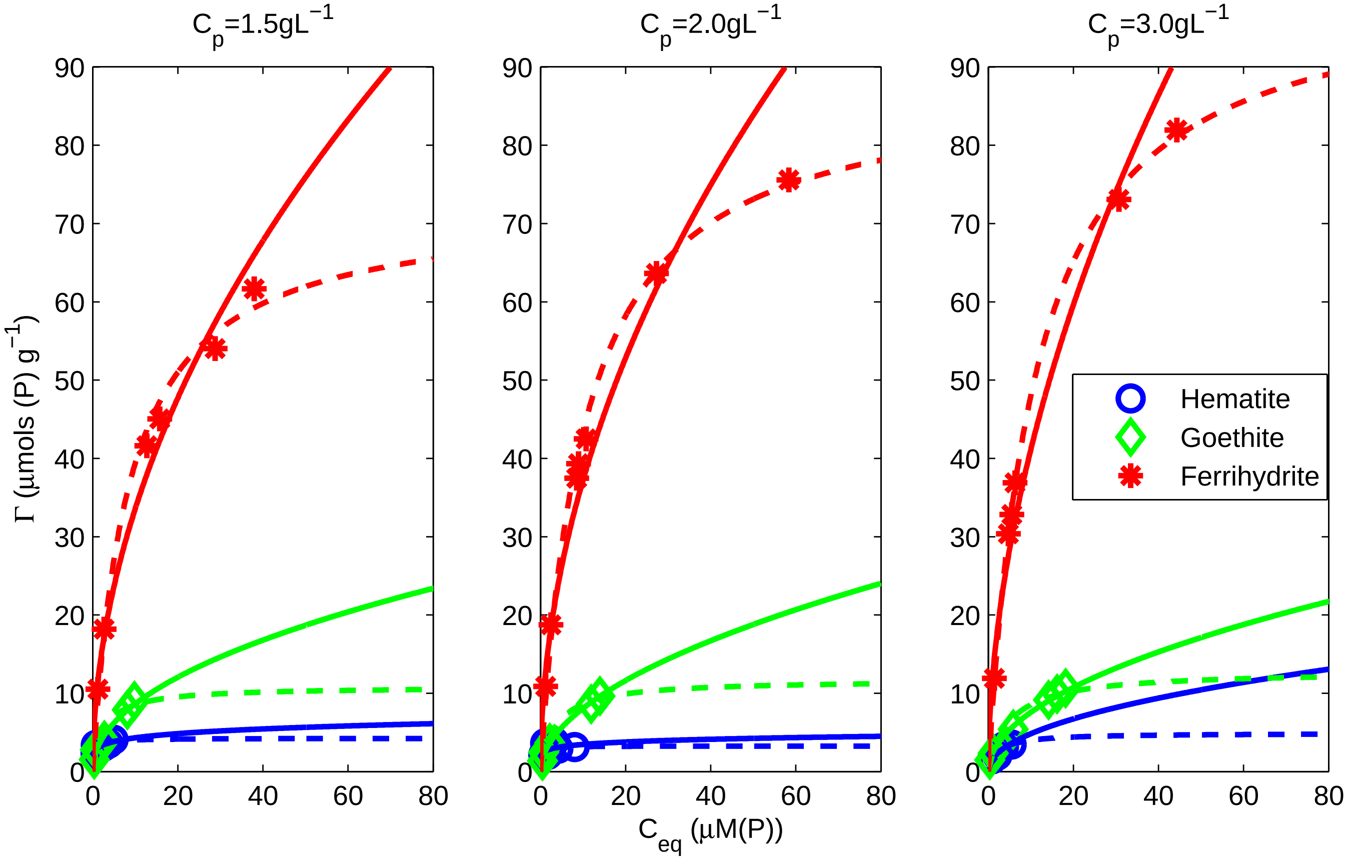


Figure 3.6: G6P Isotherms: Symbols are data points, solid lines are Fruendlich isotherms, and dashed lines are Langmuir isotherms.

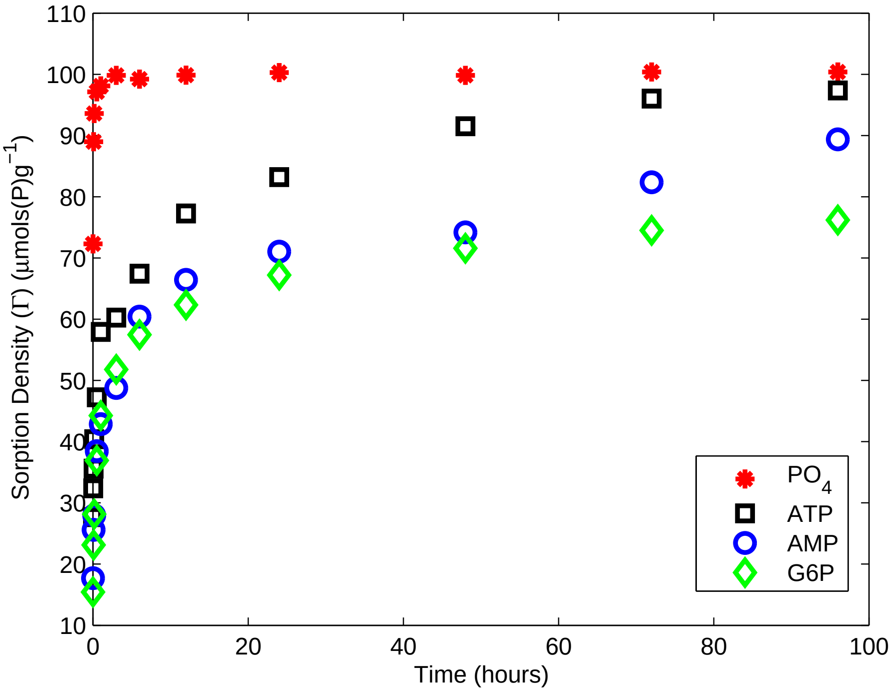


Figure 3.7: Ferrihydrite Sorption Kinetics

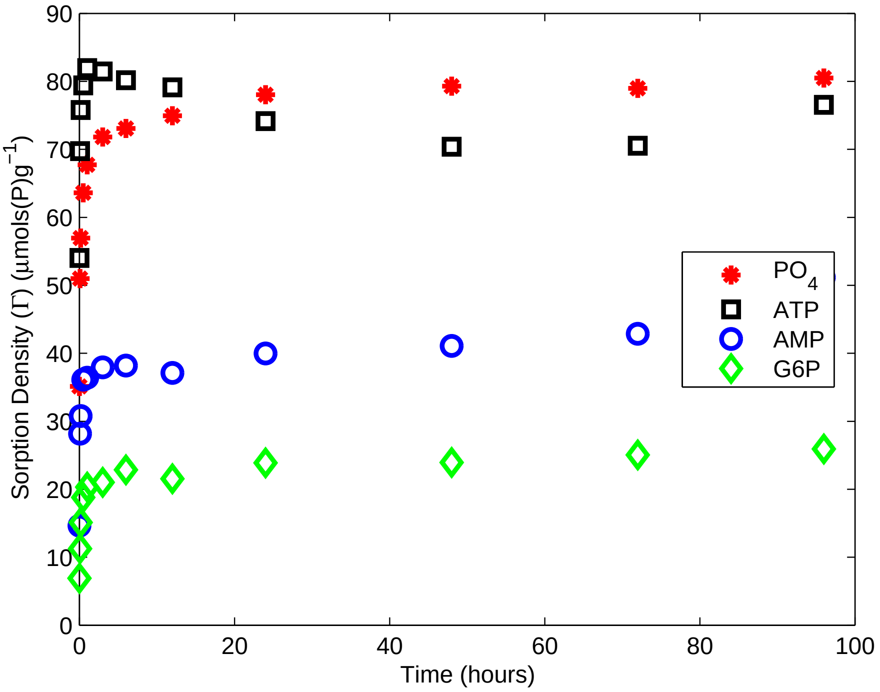


Figure 3.8: Goethite Sorption Kinetics

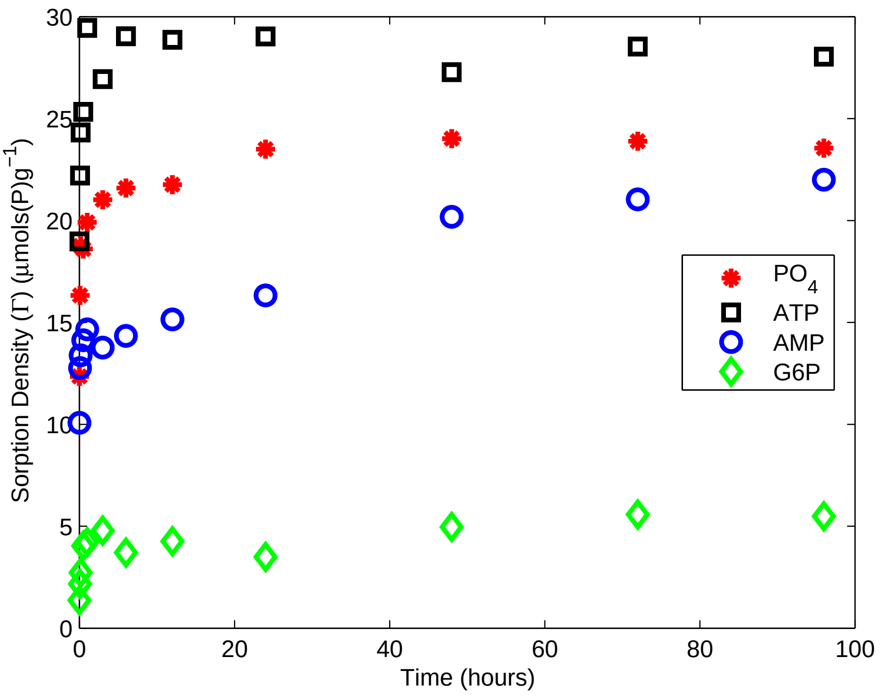


Figure 3.9: Hematite Sorption Kinetics

CHAPTER 4

DISCUSSION

4.1 Isotherms: Sorption Equilibria Conditions

Both the Langmuir and the Fruendlich equations provided good fits for all Fe-phase/P compound combinations while the metastable equilibrium adsorption (MEA) theory failed to describe sorption data. The Langmuir equation generally provided a fit with a higher R^2 value (Table 3.2) than did the Fruendlich. When more carefully inspected, however, it becomes clear that a higher R^2 value is not always indicative of a greater ability to describe the actual behavior of the sorption curve. The Langmuir equation was better able to describe the sorption reactions of ferrihydrite with all P compounds and the reaction of goethite with ATP. However, the Fruendlich equation resulted in a better fit to the data describing sorption of PO_4 onto goethite, ATP onto hematite, and AMP onto both goethite and hematite. The remainder of the isotherms were described equally well by both equations.

The Langmuir isotherm (Equation 1) can provide useful information about the nature of the sorption reactions. The Γ_m term corresponds to a predicted maximum sorption density. The a term corresponds to the affinity of a solid for the solute. The affinity term increases exponentially as the energy required to remove a sorbed particle from the surface increases, and is inversely proportional to Γ_m (Giles et al., 1973).

Because of the inverse relationship ($a \propto \frac{1}{\Gamma_m}$) a increases as the number of sorption sites decreases, and this leads to situations in which a low maximum sorption density is reached for a particular P compound/Fe-phase combination despite the fact that the Fe-phase may have a high affinity for the P compound. For example, hematite has a relatively high affinity for G6P (a in Table 3.2), yet the maximum observed sorption density for this combination was 4.08 μmols(P) g(hematite)$^{-1}$. Reactions with a high affinity are characterized by Langmuir adsorption curves with initial steep slopes, such as those for goethite and PO_4 (Figure 3.2, $0.94 < a < 1.77$), as contrasted with the those for the reactions of goethite with ATP (Figure 3.4, $0.10 < a < 0.17$). The slopes of the Langmuir isotherms should be constant as C_{eq} approaches zero, whereas the slopes of the Fruendlich isotherms approach infinity at this end of the plots (Hinz, 2001).

Sorption affinities of each Fe-phase for the different P compounds do not follow the same order as the maximum sorption densities onto the phases. According to the Langmuir isotherm results, sorption affinities (a in Table 3.2) follow the order:

$$\mathrm{ATP} > \mathrm{AMP} > \mathrm{PO_4} > \mathrm{G6P}$$

for ferrihydrite,

$$\mathrm{PO_4} > \mathrm{AMP} > \mathrm{G6P} > \mathrm{ATP}$$

for goethite and,

$$\mathrm{G6P} > \mathrm{PO_4} > \mathrm{AMP} > \mathrm{ATP}$$

for hematite when the particle concentration is 1.5 and 2.0 g L^{-1}, and

$$\mathrm{AMP} > \mathrm{PO_4} > \mathrm{G6P} > \mathrm{ATP}$$

for hematite when the particle concentration is equal to 3.0 g L^{-1}.

Differences between the order of sorption affinities of hematite with higher and lower particle concentrations may not be significant when errors that result from the low sorption capacities of hematite for both AMP and G6P are considered. The Langmuir isotherm equation predicts maximum sorption capacities on hematite of 16.4 and 4.90 μmols(P) g^{-1} for AMP and G6P, respectively (Table 3.2). These low capacities lead to greater error and a greater degree of randomness in the data for these reactions, which is seen in Figure 3.9 and indicated by lower R^2 values relative to other reactions for Fruendlich isotherms fits (Table 3.2).

The isotherms that are better described by the Fruendlich Equation (2) may involve reactions in which sorption affinity decreases with increased surface coverage. Hinz (2001) showed that the Fruendlich equation corresponds to a model in which sorption affinity goes to infinity as C_{eq} goes to zero. Though this aspect of the Fruendlich equation does not make sense thermodynamically (Hinz, 2001, and citations therein) the equation can still be useful for describing and comparing data such as those of PO_4 sorption onto goethite, ATP onto hematite, and AMP onto goethite and hematite. It should be noted that the Langmuir isotherm better described the data for ferrihydrite with all compounds. The high surface area and high number of surface sites characteristic of ferrihydrite may prevent the surface coverage from having any noticeable effect on the sorption affinity.

At the outset of this project, it was expected that the MEA theory (Equation 3) (Pan and Liss, 1998b,a; Pan et al., 2002) would provide superior fits to both the Langmuir and Fruendlich isotherms because its mathematical formula takes into account the effect of the concentration of particles in solution. However, the MEA theory did not accurately describe the data sets obtained in these experiments. The MEA theory predicts that sorption density (Γ) will vary in a predictable way under conditions where C_{eq} is equivalent for the same solid/solution mixture with different C_P values. Pan and Liss (1998b) introduce an extra term into the Fruendlich equation to account for the effect of particle concentration (C_P) on the sorption reaction (a more in depth review of this theory is presented in Section 1.5.2). If the predictions of the MEA theory were borne out, Γ_m would either continually increase, continually decrease, or remain constant as C_P were varied in one direction. The data obtained in these experiments did not conform to the above predictions. For several P compound/Fe-phase combinations Γ_m was either highest or lowest when C_P was intermediate (Table 3.2). Additionally, fitting data to the MEA theory requires that the β parameter in the Fruendlich equation be constant for any solid/solution mixture, and this also was not the case (Table 3.2).

4.2 Sorption Capacities

4.2.1 Influence of Fe-Phase on Sorption Behavior

Differences in the ability of the various Fe phases to sorb P may be attributed to the different characteristic surface areas and number of active surface sites of the three phases. The surface area of ferrihydrite typically ranges between 150 and 720 m^2g^{-1} depending on the method of measurement (Dzombak and Morel, 1990). The range of measured values is due in part to crystallization of the amorphous phase that can occur during the measurement process, causing underestimation of actual values. A value of 600 m^2g^{-1} has been suggested as a reasonable estimate of true ferrihydrite surface area (Dzombak and Morel, 1990). Common values reported for the surface area of goethite prepared in a similar manner to the goethite used in these experiments are an order of magnitude less than that for ferrihydrite, at around 50-60 m^2g^{-1} (e.g. Grossl et al., 1997; Luengo et al., 2006). Other measurements of goethite surface area range from 27.7 m^2g^{-1} (Gao and Mucci, 2001) to as much as 98.6 m^2g^{-1} (Rahnemaie et al., 2006). Hematite has an even lower surface area with measured values ranging from as low as 9 m^2g^{-1} (e.g. Jeon et al., 2001; Skulan et al., 2002) to up to 28 m^2g^{-1} (Christl and Kretzschmar, 1999). Observed sorption capacities were consistant with trends in surface areas of Fe-phases for all P compounds. That is, the higher the surface area for a phase, the higher was the observed sorption capacity for all compounds. A higher surface area does not necessarily correspond to a higher affinity, however, and a particular phase may sorb more of a certain P compound than a second phase despite the fact that the second phase may have a higher sorption affinity for that P compound.

4.2.2 Influence of P Compound on Sorption Behavior

At the outset of these experiments is was hypothesized that the size of P compounds would exert the greatest control on their ability to be sorbed onto the Fe-phases due to steric effects. It was also hypothesized that a greater amount of P may be apparently sorbed for the experiments involving ATP due to the fact that each ATP molecule contains three phosphate groups, and sorption of any one of the three phosphate groups would remove a total of three atoms of P from solution (note that all experimental results were reported as micromoles of P, not micromoles of compound, and that these were equivalent for all compounds except ATP). Had these hypotheses been confirmed the order of sorption for all compounds would have been:

$$\mathrm{PO_4} > \mathrm{G6P} > \mathrm{AMP},$$

with ATP sorption being greater than that of AMP, but it's placement relative to both PO_4 and G6P unknown. These were not the observed results. In all cases G6P sorbed the least despite is small size. Phosphate did display the greatest sorption onto ferrihydrite and goethite, but its sorption onto hematite was nearly the same as that of ATP.

4.3 Kinetics: Time Series of Phosphorus Uptake

Similar trends of P uptake were observed for several P compounds and Fe phases. In all cases, a rapid initial uptake was responsible for the majority of P uptake. A slower process of longer duration continued to remove P from solution for the full extent of several of the experiments. This two-step sorption behavior is consistant with that described by a model presented by Froelich (1988), after the work of Barrow (1983). In this model the initial uptake can be attributed to sorption of P compounds onto the surface of Fe particles. The second process occurs as P sorbed onto the surface diffuses inward, freeing surface sites which are then occupied by P from solution (Figure 4.1).

The setup of these experiments may not allow for a meaningful comparison of the ATP sorption data to other P compounds. All solutions used in kinetics experiments were made up to 200 μM with respect to P. Results were then calculated and presented as micromoles of P sorbed on the solid phase, or remaining dissolved in solution. The apparent sorption of ATP therefore may not reflect the actual capacity of the minerals to remove ATP from solution. In order to better compare the results of kinetics experiments, a solution of 200 μM ATP would need to be made and kinetics experiments repeated using this solution. Results reported in terms of micromoles of ATP could then be compared to results from other kinetic experiments.

Phosphate, AMP, and G6P all displayed similar sorption behavior with an initial rapid increase in sorption density giving way to a slower reaction in which sorption density continued to increase at a lower rate. Although the reaction of ATP with goethite and hematite exhibited a similar initial rapid uptake of P from solution, this initial drawdown was followed by a re-release of P to solution. The observed increase of P in solution could be due either to desorption of the entire ATP molecule from the surface of the solid phase, or hydrolysis of the ATP molecule.

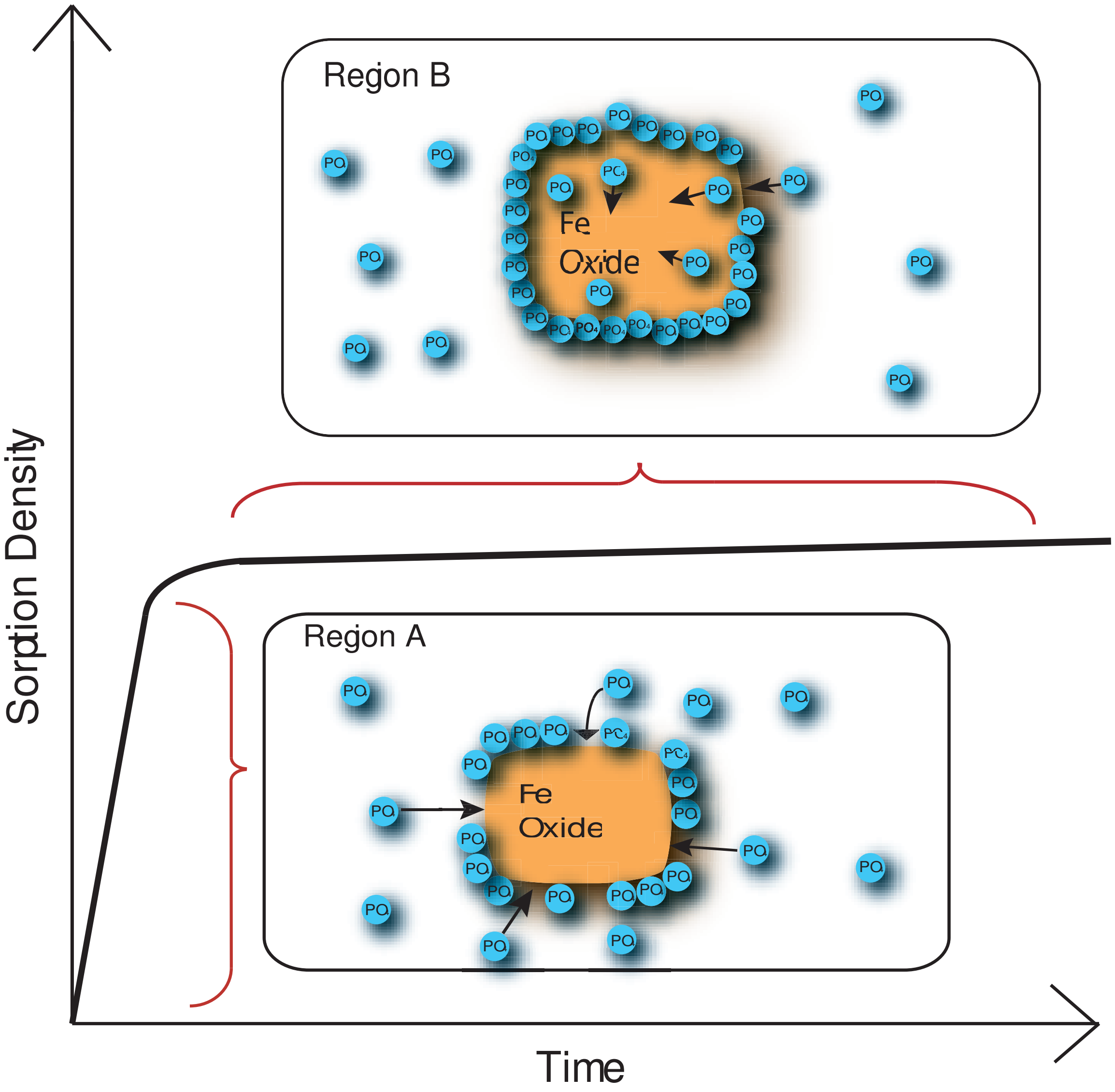


Figure 4.1: The relative timing of the two sorption processes

The polyphosphate structure of ATP may serve to explain the different kinetic sorption behavior of this compound relative to the other compounds tested. One possible hypothesis is that the high initial rate of uptake of P from ATP onto both goethite and hematite (Figures 3.8 and 3.9) is due to the sorption of the terminal phosphate group of the ATP molecule onto surface sites of these Fe phases. For each one ATP molecule that sorbs in this manner three P atoms are effectively removed from solution. As the sorption reaction procedes, a breakdown of the sorbed ATP molecules may leave this terminal phosphate group sorbed onto the solid phase while releasing one or two of the remaining phosphate groups with the adenosine nucleotide back into solution resulting in an apparent desorption of ATP.

The reaction between ferrihydrite and ATP does not exhibit the same behavior (Figure 3.7). The much greater surface area of ferrihydrite results in a greater density of reactive surface sites. The high density of surface sites may result in the participation of more than one of the phosphate groups of ATP in the initial sorption reaction. This being the case, a breakdown of ATP would not result in a release of P back into solution.

4.4 Implications for P-Uptake and Release in Natural Aquatic Systems

The results of this study illuminate several important processes that are important to understanding the uptake and release of dissolved P and ultimately its bioavailability in aquatic systems. The potential release of sorbed P into solution will depend upon the amount of time P compounds have spent sorbed onto Fe-phases. Different P compounds may be removed from or enriched in solution depending upon the types of Fe-phases that are present. Additionally, this research suggests ways that reservoirs of P in aquatic systems may change due to disturbances such as sedimentary re-suspension events.

The ability of a sorbed compound to be desorbed may depend upon the kinetic history of the sorption reaction. Particles that have spent only a short time in an environment in which the sorption of P compounds was favorable (region A in Figure 4.1) will primarily have compounds sorbed onto their surfaces. These compounds may be more easily desorbed back to solution than those associated with particles that have entered into the B region of Figure 4.1 where they are incorporated into particle interiors.

Different affinities of the various Fe-phases for the P compounds may also affect their desorbability. For example, if a particle of ferrihydrite is transported from an environment that favors sorption to one that favors desorption, it would tend to release G6P and PO_4 while retaining the adenosine compounds due to the higher affinity of ferrihydrite for the adenosine compounds. Enrichment of certain compounds in aquatic systems also may be a result of the difference in affinities. Goethite, for example, has the highest affinity for PO_4, and may preferentially remove this compound from aquatic systems, allowing other P compounds to remain dissolved.

The greater ability of ferrihydrite to remove dissolved P compounds from solution relative to either goethite or hematite may have important implications for the the uptake of dissolved P during re-suspension events. Aqueous Fe^{2+} is formed by the microbially mediated reduction of Fe(III) in solid Fe (oxy)hydroxides in anoxic sediments. When Fe(III) is reduced, the particle that it is associated with is dissolved, and any sorbed P is liberated to solution. If the associated particle was goethite or hematite, a relatively small amount of P may be liberated. During a re-suspension event, the dissolved ferrous iron in pore waters may be oxidized in an environment that favors the formation of ferrihydrite. With its much greater ability to sorb P compounds the newly formed ferrihydrite could act to draw down dissolved P concentrations.

4.5 Areas of Future Research

There are several areas of future research to pursue in order to evaluate the extent of the implications discussed in section 4.4. Questions remain concerning competitive sorption behavior, desorbability, sorption of P compounds onto other constituents of sediments, and sorption behavior under different environmental conditions. Additionally, two major classes of DOP compounds, phosphodiesters and phosphonates, were not examined in this study, and their sorption behavior calls for investigation.

Given the results of this study, it would be reasonable to expect that competition for sorption sites on Fe-phases would exist between different P compounds that were dissolved in the same solution. The competitive sorption of two or more P compounds in solution should be investigated in order to assess whether the presence of multiple P compounds affects the immediate bioavailability of P. If organic compounds outcompete PO_4 for sorption sites, it would be expected that PO_4, which is immediately available to all primary producers, may be enriched in aquatic systems. In contrast, greater relative sorption of PO_4 could lead to an enrichment in DOP in aquatic systems. Not all primary producers are able to synthesize the enzymes that are necessary to utilize DOP, and enrichment of DOP in natural waters could result in a shift in community structure to those organisms that are able to utilize DOP compounds.

The ability of Fe-phases to desorb P compounds is a topic of much interest that should be investigated in order to fully understand the biogeochemical cycling of P. There is currently no definitive evidence to suggest that P sorbed onto Fe-phases is released to solution, making it available to organisms, when it is transported from terrestrial to aquatic systems or between different aquatic environments. It is possible that once sorbed these compounds are unable to be desorbed from Fe-phases, and are thus unavailable to biota. The only avenue through which sorbed P compounds are released into solution may be via dissolution of the sorbing phase. Possible causes of desorption that should be examined in future studies include particle transport to environments of low dissolved P concentration, changes in ionic strength of the surrounding solution, and changes in pH, redox state, and temperature.

In order to better understand the cycling of marine DOP, studies of DOP sorption onto natural sediment samples would be useful. Carrying out these studies would require first quantifying the P already associated with the solid phase. The SEDEX (Ruttenberg, 1992) scheme would be useful for this purpose. Comparison of the results presented here with experiments carried out on natural sediments would give insight into the control of P sorption by Fe-(oxy)hydroxides. Additionally, the preferential sorption of PO_4 over DOP by ferrihydrite and goethite (the most reactive phases tested) suggests a necessity to quantify DOP concentrations in ecosystems in which P is suspected of limiting primary production. It is possible that systems with low PO_4 concentrations still have adequate bioavailable P in the form of DOP.

CHAPTER 5

CONCLUSIONS

Phosphorus (P) is an essential nutrient for all forms of life, and its bioavailability in aquatic ecosystems is significantly influenced by sorption reactions with sedimentary particles. Previous to this work, there have been extensive studies conducted exploring the interactions of inorganic orthophosphate (PO_4) with soil and sediment particles. Of the components of sediments, solid iron (Fe) phases are among the most reactive toward PO_4. Whether dissolved organic P (DOP) compounds, a potentially important source of P to marine organisms, react in similar ways to PO_4 with Fe-phases has not previously been explored. This research contrasted the interactions of the Fe-phases ferrihydrite, goethite, and hematite with PO_4 to those of the DOP compounds glucose 6-phosphate (G6P), adenosine monophosphate (AMP), and adenosine triphosphate (ATP).

Langmuir and Fruendlich equations were successfully applied to describe P sorption isotherms. Both can be used to describe and compare experimental results, and the equations may be useful in predicting sorption behavior outside of experimental conditions. The Langmuir equation is preferred due to the fact that the constants that are derived from the isotherm have physical meaning, in contrast to the constants derived from the Fruendlich equation, which are simply curve fitting parameters. The Langmuir isotherm constant Γ_m predicts a maximum sorption capacity for a sorption reaction, and the affinity term (a) provides insight into the amount of energy that is required to remove a sorbed compound from the substrate to which it is sorbed. Both of these parameters convey useful information about physical systems.

Kinetics experiments were carried out for several Fe-phase/P compound combinations. Reactions of G6P, AMP, PO_4, and ATP with ferrihydrite displayed a two stage behavior, whereas the reaction of ATP with goethite and hematite over time did not. The unique behavior of ATP can be attributed either to its desorption from Fe-phases or hydrolysis of this compound releasing P back into solution. The polyphosphate moiety of ATP may be responsible for its unique behavior.

The applicability of the results to natural systems was discussed, and several areas in need of future research were identified. Dissolved organic P compounds and dissolved PO_4 interact in similar ways with Fe (oxy)hydroxides in seawater. Organic P compounds will have the potential to be liberated into pore water upon the reductive dissolution of Fe (oxy)hydroxides in anoxic marine sediments. Additionally it is possible that sorbed organic P compounds could be released when Fe particles are transported between different environments, such as when riverine sediments are delivered to estuarine or coastal marine environments.

This research serves to fill part of the gap in knowledge concerning the biogeochemical cycling of DOP. The results presented contribute to our understanding of the cycling of DOP in marine ecosystems, and may serve to identify P compounds that will be preferentially sorbed onto Fe phases. Future research is needed to clarify and address issues that stem from the results of these studies.

WORKS CITED

Ammerman, J. W., and F. Azam (1985), Bacterial 5-nucliotidase in aquatic ecosystems: A novel mechanism of phosphorus regeneration, *Science*, *227*(4692), 1338–1340.

Barrow, N. J. (1978), The desciption of phosphate adsorption curves, *J. Soil Sci.*, *29*, 447–462.

Barrow, N. J. (1983), A mechanistic model for describing the sorption and desorption of phosphate by soil, *J. Soil Sci.*, *34*, 733–750.

Benitez-Nelson, C. R. (2000), The biogeochemical cycling of phosphorus in marine systems, *Earth Science Reviews*, *51*, 109–135.

Berg, A. S., and B. C. Joern (2006), Sorption dynamics of organic and inorganic phosphorus compounds in soil, *J. Environ. Qual.*, *35*, 1855–1862.

Berry, L. G. (Ed.) (1974), *Selected Powder Diffraction Data for Minerals*, Joint Committee on Powder Diffraction Standards, Swarthmore, PA.

Björkman, K., and D. M. Karl (1994), Bioavailability of inorganic and organic phosphorus compounds to natural assemblages of microorganisms in hawaiian coastal waters, *Marine Ecology Progress Series*, *111*, 265–273.

Bolan, N. S., N. J. Barrow, and A. M. Posner (1985), Describing the effect of time on sorption of phosphate by iron and aluminum hydroxides, *Eur. J. Soil Sci.*, *36*(2), 187–197.

Cembella, A. D., N. J. Anita, and P. J. Harrison (1984), The utilization of inorganic and organic phosphorus compounds as nutrients by eukaryotic microalgae: A multidisciplinary perspective: Part i, *Critical Rev. Microb.*, *10*, 317–391.

Chitrakar, R., S. Tezuka, A. Sonoda, K. Sakane, K. Ooi, and T. Hirotsu (2006), Phosphate adsorption on synthetic goethite and akaganeite, *J. Colloid Interf. Sci.*, *298*, 602–608.

Christl, I., and R. Kretzschmar (1999), Competitive sorption of copper and lead at the oxide-water interface: Implications for surface site density, *Geochim. Cosmochim. Ac.*, *63*(19/20), 2929–2938.

Clark, L. L., E. D. Ingall, and R. Benner (1998), Marine phosphorus is selectively remineralized, *Nature*, *393*, 426.

Compton, J., D. Mallinson, C. R. Glenn, G. Filippelli, K. Föllmi, G. Shields, and Y. Zanin (2000), in Variations in the global phosporus cycle, *SEPM Special Publication*, *Marine Authigenesis: From Global to Microbial*vol.66, edited by C. R. Glenn, L. Prévôt-Lucas, and J. Lucaspp.35–52, SEPM, Tulsa.

Cross, A. F., and W. H. Schlesinger (2001), Biological and geochemical controls on phosphorus fractions in semiarid soils, *Biogeochemistry*, *52*, 155–172.

Dzombak, D. A., and F. F. M. Morel (1990), *Surface Complexation Modeling: Hydrous ferric oxide*, John Wiley & Sons, New York.

Eckel, E. C. (1914), *Iron Ores: Their Occurence, Valuation and Control*, McGraw-Hill Book Co., Madison.

Fox, L. E. (1990), Geochemistry of dissolved phosphate in the sepik river and estuary, papua, new guinea, *Geochim. Chosmochim. Ac.*, *54*, 1019–1024.

Fox, L. E., S. L. Sager, and S. C. Wofsy (1985), Factors controlling the concentrations of soluble phosphorus in the mississippi estuary, *Limnol. Oceanogr.*, *30*(4), 826–832.

Froelich, P. N. (1988), Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism, *Limnol. Oceanogr.*, *33*(4), 649–668.

Froelich, P. N., M. L. Bender, N. A. Luedtke, G. R. Heath, and T. DeVries (1982), The marine phosphorus cycle, *Am. J. Sci.*, *282*, 474–511.

Froelich, P. N., et al. (1979), Early oxidation of organic matter in pelagic sediments of the eastern equitorial atlantic: Suboxic diagenesis, *Geochim. Chosmochim. Ac.*, *43*(7), 1075–1090.

Furnas, M. J., and A. W. Mitchell (1999), Wintertime carbon and nitrogen fluxes on australia's northwest shelf, *Estuar. Coast. Shelf S.*, *49*(2), 165–175.

Gao, Y., and A. Mucci (2001), Acid base reactions, phosphate and arsenate complexation, and their competitive adsorption at the surface of goethite in 0.7 m nacl solution, *Geochim. Cosmochim. Ac.*, *65*(14), 2361–2378.

Garrles, R. M., and F. T. Mackenzie (1971), *Evolution of Sedimentary Rocks*, W. W. Norton, New York.

Giles, C. H., D. Smith, and A. Huitson (1973), A general treatment and classification of the solute adsorption isotherm, *J. Colloid Interf. Sci.*, *47*(3), 755–765.

Graham, W. F., and R. A. Duce (1979), Atmospheric pathways of the phosphorus cycle, *Geochim. Cosmochim. Ac.*, *43*(8), 1195–1208.

Grossl, P. R., M. Eick, D. L. Sparks, S. Goldberg, and C. C. Ainsworth (1997), Arsenate and chromate retention mechanisms on goethite. 2. kinetic evaluation using a pressure-jump relaxation technique, *Environ. Sci. Technol.*, *31*, 321–326.

Guidry, M. W., F. T. Mackenzie, and R. S. Arvidson (2000), in Role of techtonics in phosphorus distributions and cycling, *SEPM Special Publication*, *Marine Authigenesis: From Global to Microbial*vol.66, edited by C. R. Glenn, L. Prévôt-Lucas, and J. Lucaspp.35–52, SEPM, Tulsa.

Hinz, C. (2001), Description of sorption data with isotherm equations, *Geoderma*, *99*, 225–243.

Jeon, B.-H., B. A. Dempsey, W. D. Burgos, and R. A. Royer (2001), Reactions of ferrous iron with hematite, *Colloid Suface A*, *191*(1-2), 41–55.

Karl, D. M., and K. M. Björkman (2002), *Dynamics of DOP*, Elsevier Science.

Khare, N., D. Hesterberg, S. Beauchemin, and S. L. Wang (2004), Xanes determination of adsorbed phosphate distribution between ferrihydrite and boehmite in mixtures, *Soil Sci. Soc. Am. J.*, *68*, 460–469.

Kolowith, L. C., E. D. Ingall, and R. Benner (2001), Composition and cycling of marine organic phosphorus, *Limnol. Oceanogr.*, *46*(2), 309–320.

Koroleff, F. (1976), *Determination of nutrients*pp.117–156, Verlag-Chimie, Weinheim, NY.

Leytem, A. B., R. L. Mikkelsen, and J. W. Gilliam (2002), Sorption of organic phosphorus compounds in atlantic coastal plain soils, *Soil Sci.*, *167*(10), 652–658.

Lijklema, L. (1980), Interaction of orthophosphate with iron(iii) and aluminum hydroxides, *Environ. Sci. Technol.*, *14*, 537–541.

Lovley, D. R., and E. J. P. Phillips (1986), Organic matter mineralization with reduction of ferric iron in anaerobic sediments, *Appl. Environ. Microb.*, *51*(4), 683–689.

Luengo, C., M. Brigante, J. Antelo, and M. Avena (2006), Kinetics of phosphate adsorption on goethite: Comparing batch adsorption and atr-ir measurements, *J. Colloid Interf. Sci.*, *300*, 511–518.

Mayer, L. M., and S. P. Gloss (1980), Buffering of silica and phosphate in a turbid river, *Limnol. Oceanogr.*, *25*(1), 12–22.

McGechan, M. B., and D. R. Lewis (2002), Soil and water: Sorption of phosphorus by soil, part i: Principles, equations and models, *Biosyst. Eng.*, *82*(1), 1–24.

Meybeck, M. (1982), Carbon, nitrogen, and phosphorus transport by world rivers, *Am. J. Sci.*, *282*(4), 401–450.

Monaghan, E. J., and K. C. Ruttenberg (1999), Dissolved organic phosphorus in the coastal ocean: Reassessment of available methods and seasonal phosphorus profiles from the eel river shelf, *Limnol. Oceanogr.*, *44*(7), 1702–1714.

Munns, D. N., and R. L. Fox (1976), The slow reaction which continues after phosphate adsorption: Kinetics and equilibrium in some tropical soils, *Soil Sci. Soc. Am. J.*, *40*(1), 46–51.

Orrett, K., and D. M. Karl (1987), Dissolved organic phosphorus production in surface seawaters, *Limnol. Oceanogr.*, *32*(2), 383–395.

Pan, G., and P. S. Liss (1998a), Metastable-equilibrium adsorption theory ii. experimental, *J. Colloid Interf. Sci.*, *201*, 77–85.

Pan, G., and P. S. Liss (1998b), Metastable-equilibrium adsorption theory i. theoretical, *J. Colloid Interf. Sci.*, *201*, 71–76.

Pan, G., M. D. Krom, and B. Herut (2002), Adsorption-desorption of phosphate on airborne dust and riverborne particulates in ease mediterranean seawater, *Environ. Sci. Technol.*, *36*, 3519–3524.

Parfitt, R. L. (1978), Anion adsorption by soils and soil materials, *Adv. Agron.*, *30*, 1–50.

Parfitt, R. L. (1989), Phosphate reactions with natural allophane, ferrihydrite and goethite, *J. Soil Sci.*, *40*, 359–369.

Pomeroy, L. R., E. E. Smith, and C. M. Grant (1965), The exchange of phosphate between estuarine water and sediments, *Limnol. Oceanogr.*, *10*(2), 167–172.

Rahnemaie, R., T. Hiemstra, and W. H. van Reimsdijk (2006), Inner- and outer-sphere complexation of ions at the goethite solution interface, *J. Colloid Interf. Sci.*, *297*, 379–388.

Redfield, A. C. (1958), The biological control of chemical factors in the environment, *Am. Sci.*, *46*, 205–222.

Ridal, J. J., and R. M. Moore (1990), A re-examination of the measurement of dissolved organic phosphorus in seawater, *Mar. Chem.*, *29*, 19–31.

Rodel, M. G., D. E. Armstrong, and R. F. Harris (1977), Sorption and hydrolysis of added organic phosphorus compounds in lake sediments, *Limnol. Oceanogr.*, *22*(3), 415–422.

Ruttenberg, K. C. (1992), Development of a sequential extraction method for different forms of phosphorus in marine sediments, *Limnol. Oceanogr.*, *37*(7), 1460–1482.

Ruttenberg, K. C. (2003), in The global phosphorus cycle, *Treatise on Geochemistry, Biogeochemistry*vol.8, edited by W. H. Schlesinger, H. D. Holland, and K. K. Turekianpp.585–643, Elsevier-Pergamon, Oxford.

Skulan, J. L., B. L. Beard, and C. M. Johnson (2002), Kinetic and equilibrium fe isotope fractionation between aqueous fe(iii) and hematite, *Geochim. Cosmochim. Ac.*, *66*(17), 2995–3015.

Slomp, C. P., S. J. V. der Gaast, and W. V. Raaphorst (1996), Phosphorus binding by poorly crystalline iron oxides in north sea sediments, *Mar. Chem.*, *52*(1), 55–73.

Strauss, R., G. W. Brümmer, and N. J. Barrow (1997), Effects of crystallinity of goethite ii: Rates of sorption and desorption of phosphate, *Eur. J. Soil Sci.*, *48*, 87–99.

Sundareshwar, P. V., and J. T. Morris (1999), Phosphorus sorption characteristics of intertidal marsh sediments along an estuarine salinity gradient, *Limnol. Oceanogr.*, *44*(7), 1693–1701.

Suzumura, M., K. Ishikawa, and H. Ogawa (1998), Characterization of dissolved organic phosphorus in coastal seawater using ultrafiltration and phosphohydrolytic enzymes, *Limnol. Oceanogr.*, *43*(7), 1553–1564.

Thamdrup, B. (2000), Bacterial manganese and iron reduction in aquatic sediments, *Adv. Microb. Ecol.*, *16*, 41–84.

Thingstad, T. F., E. F. Skjoldal, and R. A. Bohne (1993), Phosphorus cycling and algal-bacterial competition in sandsfjord, western norway, *Marine Ecology Progress Series*, *99*, 239–259.

Valiela, I., J. Costa, K. Foreman, J. M. Teal, B. Howes, and D. Aubrey (1990), Transport of groundwater-borne nutrients from watersheds and their effects on coastal waters, *Biogeochemistry*, *10*(3), 177–197.

Van Capellen, P., and E. D. Ingall (1996), Redox stabilization of the atmosphere by phosphorus-limited marine productivity, *Science*, *271*, 493–496.

van der Zee, C., D. R. Roberts, D. G. Rancourt, and C. P. Slomp (2003), Nanogoethite is the dominant reactive oxyhydroxide phase in lake and marine sediments, *Geology*, *31*(11), 993–996.

Webster, J. R., and B. C. Patten (1979), Effects of watershed perturbations on stream potassium and calcium dynamics, *Ecol. Monogr.*, *49*(1), 51–72.