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Individual and competitive adsorption of phosphate and arsenate on goethite in artificial seawater

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Abstract

Phosphate and arsenate adsorption on goethite was studied in single batch experiments at 25 °C upon the addition of Ca^{2+}, Mg^{2+} and SO_4^{2-} to a 0.7 M NaCl solution at their respective seawater concentrations. Phosphate adsorption increases slightly in the presence of Mg^{2+} and Ca^{2+} and decreases at low pH upon the addition of SO_4^{2-}. The enhanced adsorption may result from the formation of ternary surface complexes. In contrast, arsenate adsorption is not affected by the addition of Mg^{2+} or Ca^{2+} to the 0.7 M NaCl solution. Similarly, phosphate adsorption in seawater is enhanced at neutral pH relative to 0.7 M NaCl, whereas arsenate adsorption is identical in both solutions except for a decrease at low pH in seawater.

An equilibrium model derived by combining interaction parameters obtained from the single adsorbate subsystems predicts the phosphate and arsenate adsorption behaviours in the PO_4–SO_4–goethite and AsO_4–Ca–goethite systems very well but fails to accurately reproduce the adsorption data in the PO_4–Ca–goethite, PO_4–Mg–goethite, PO_4–seawater–goethite, AsO_4–Mg–goethite and AsO_4–seawater–goethite systems. The inclusion of ternary surface complexes in the latter systems improves model fits significantly at high pH.

Experimental investigations of phosphate and arsenate competitive adsorption in seawater were also carried out. The fraction of phosphate adsorbed in the competitive experiments in seawater is identical to the results obtained in the 0.7 M NaCl solution, whereas arsenate adsorption is greater in seawater at pH>7. The difference in the extent of arsenate adsorption in both solutions is proportional to the initial amount of phosphate in solution. In competitive experiments in seawater, phosphate adsorption is underpredicted at pH < 6.5, whereas arsenate adsorption is reproduced well using the constant capacitance model (CCM) with the inclusion of ternary surface complexes.

Keywords: Adsorption; Goethite; Phosphate; Arsenate; Competitive; Seawater

1. Introduction

The geochemical behaviours of phosphate and arsenate have been the subject of numerous studies in various disciplines. The interest stems from the fact that phosphorus and arsenic are both Group V elements and thus have similar chemical properties, but their biogeochemical behaviours contrast in many respects. Phosphorus is an essential nutrient in aquatic environments, but excessive phosphorus input may lead to eutrophification. In contrast, arsenic is an important anthropogenic contaminant and is known for its acute toxicity. Because of its chemical similar-

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ity to phosphate, arsenic can be taken up by marine phytoplankton (Sanders and Windom, 1980) and lead to the inhibition of oxidative phosphorylation and growth (Planas and Healy, 1978; Stryer, 1981). Unlike phosphorus, the speciation of inorganic arsenic in aquatic environments depends on the redox conditions. Arsenate, As(V), is the dominant species in oxygenated waters, whereas arsenite, As(III), is predominant under reducing conditions.

The amount of phosphate and arsenate available to organisms in estuarine and marine environments is dependent on the strength of the source, biological uptake, speciation and scavenging by settling detrital and authigenic particulate matter. Adsorption of phosphorus and arsenic onto particulate matter is an important process and may significantly affect their mobility in natural environments. Laboratory experiments have demonstrated that iron oxides are strong sorbents for both phosphate and arsenate (e.g., Hingston, 1970; Pierce and Moore, 1982; Hawke et al., 1989; Nilsson et al., 1992; Gao and Mucci, 2001), and they appear to dominate the solution chemistry of Group V elements in natural waters (Millward et al., 1985). In estuarine and marine environments, the fate and diagenetic behaviour of both phosphate and arsenate are intimately linked to the chemistry of iron oxyhydroxides (Krom and Berner, 1981; Aggett and O'Brien, 1985; Froelich, 1988; Lucotte and d'Anglejan, 1988; Belzile and Tessier, 1990; Sundby et al., 1992; Slomp et al., 1996; Mucci et al., 2000).

Goethite (α-FeOOH) is one of the most common crystalline iron oxyhydroxides in natural environments. Consequently, its surface and adsorptive properties have been studied in detail, including the adsorption behaviour of phosphate and arsenate (e.g., Hingston, 1970; Sigg and Stumm, 1981; Goldberg, 1985, 1986; Hawke et al., 1989; Nilsson et al., 1992, 1996; Geelhoed et al., 1997; Rietra et al., 1999, 2001; Zhao and Stanforth, 2001) and results used to develop surface complexation models (SCM). These adsorption studies, however, were mostly conducted in single or dilute electrolyte solutions. Few adsorption studies (e.g., Balistrieri and Murray, 1981; Hawke et al., 1989; Rietra et al., 1999) have been carried out in concentrated or complex electrolyte solutions, and little is known of the mechanism(s) of phosphate and arsenate adsorption or their competitive adsorption behaviours on goethite in seawater.

The adsorption behaviour of goethite in seawater is expected to be different than in freshwater because its surface electrical properties will be modified by the high ionic strength and competition for surface sites by major and minor seawater constituents. The surface chemistry of goethite in seawater was first characterized by Balistrieri and Murray (1981). They reported that the equilibrium SCMs developed from single adsorbate systems are able to predict the competitive adsorption of Mg^{2+}, Ca^{2+} and SO_4^{2-} on the surface of goethite in diluted artificial seawater. Their model (i.e., triple layer model) could also reproduce the experimental titratable surface charge on goethite in solution but only at high pH. Phosphate adsorption on goethite in seawater was investigated by Hawke et al. (1989), and they reported that equilibrium constants derived from single adsorbate systems using the triple layer model (TLM) failed to reproduce phosphate adsorption data measured in major ion seawater. The same model also failed to reproduce phosphate adsorption on manganese dioxide in the presence of Ca^{2+} and Mg^{2+} (Yao and Millero, 1996). Gao and Mucci (2001) investigated phosphate and arsenate adsorption as well as their competitive adsorption on goethite in a 0.7 M NaCl solution. They found that a constant capacitance model (CCM), which includes three monodentate surface complexes, describes single adsorbate systems successfully but is unable to predict the behaviour of competitive adsorption systems. At present, little is known about the adsorption behaviour of arsenate and the competitive adsorption between phosphate and arsenate on goethite in seawater. Given the ubiquity of goethite and its role on the fate of both phosphorus and arsenic in marine and estuarine environments, models describing phosphate and arsenate adsorption as well as their competitive adsorption behaviour in seawater are greatly needed.

A prerequisite for good model description is the availability of relevant thermodynamic data. Gao and Mucci (2001) determined the surface acidity constants of goethite and surface complexation constants of phosphate and arsenate on goethite in a 0.7 M NaCl solution. These constants will be incorporated as a subset of the thermodynamic database used to model phosphate and arsenate adsorption on goethite in artificial seawater. The surface complexation constants for Mg^{2+}, Ca^{2+} and SO_4^{2-} on goethite were determined by Balistrieri and Murray (1981) using the TLM. These constants, however, are model-dependent and cannot be used in other SCMs. In the present work, a systematic adsorption study including the determination of the surface complexation constants for Mg^{2+}, Ca^{2+} and SO_4^{2-} using both the constant capacitance model (CCM) and the basic Stern model (BSM) is carried out before the modeling of phosphate and arsenate adsorption in seawater is undertaken.

In this paper, we report on our attempts to (1) determine the effect of Mg^{2+}, Ca^{2+} and SO_4^{2-} on phosphate and arsenate adsorption on goethite and (2) model phosphate and arsenate adsorption as well as their competitive adsorption behaviours on goethite in artificial seawater.

2. Materials and experimental methods

2.1. Goethite

Goethite was synthesized according to the method of Schwertmann and Cornell (1991). This and other methods of synthesis were tested in the laboratory (Shaw, 1996), and the former was found to yield the purest and best-crystallized phase. Briefly, a $Fe(NO_3)_3$ solution (100 ml at 1 M) was mixed with a KOH solution (180 ml at 5 M) and diluted to 2 l with Nanopure™ water. The suspension was then held in a closed polyethylene bottle at 70 °C for 60 h. X-ray diffraction analysis of the precipitate confirmed its mineralogy (Gao and Mucci, 2001). The precipitate was rinsed several times with Nanopure™ water following centrifugation and decantation. The goethite slurry was then stored in Nanopure™ water at 4 °C. The precipitate was allowed to age for at least 6 months to minimize changes in surface properties (Nilsson et al., 1992). The specific surface area of the synthetic goethite was determined by the single-point N_2-BET method (Brunauer et al., 1938) to be 33.5 $m^2\ g^{-1}$.

2.2. Solutions

Hydrochloric acid solutions were prepared from 32% HCl (pro-analysi, Merck) and standardized using a gravimetrically prepared Na_2CO_3 (alkalimetric standard) solution. NaOH solutions were made from NaOH pellets and standardized using a gravimetric solution of the acidimetric standard salt, potassium hydrogen phthalate. A solution of dihydrogen phosphate was prepared by dissolution of KH_2PO_4 which was oven-dried at 110 °C and kept in a dessicator. Arsenate stock solutions were made by dissolution of $As_2O_5{\cdot}XH_2O$ ($X \cong 3$), and 0.7 M NaCl solutions were made from pre-dried NaCl powder. Magnesium, calcium and sulfate solutions were prepared from $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}2H_2O$ and Na_2SO_4 salts, respectively. Three seawater buffers, Tris., Bis. and Amino-pyridine, were prepared as described in Millero et al. (1993). AnalaR-grade chemicals and doubly distilled deionized water (Nanopure™) were used to make all solutions.

2.3. Artificial seawater

Artificial seawater was prepared in a 20-kg batch according to the method of Kester et al. (1967). In order to minimize the effect of HCO_3^- on phosphate and arsenate adsorption (Van Geen et al., 1994), $NaHCO_3$ was excluded from the recipe (Table 1). The anhydrous salts (NaCl, Na_2SO_4, KCl, KBr, $B(OH)_3$ and NaF) were dried, whereas stock solutions of the hydrated salts ($MgCl_2$, $CaCl_2$ and $SrCl_2$) were titrated with a standardized $AgNO_3$ solution before being weighed and added to the preparation. The salinity (S) of the artificial seawater was determined by titration with a $AgNO_3$ solution standardized using International Association for the Physical Sciences of the Ocean (IAPSO) standard seawater. The salinity of the artificial seawater prepared for this study was 34.9 ± 0.1 p.s.u. (practical salinity units).

Table 1
Composition of artificial seawater used for phosphate and arsenate adsorption experiments

Electrolytes	Concentration (mol/kg)
NaCl	0.4104
Na_2SO_4	0.02824
KCl	0.00937
$MgCl_2$	0.05282
$CaCl_2$	0.01028
$SrCl_2$	0.00009
KBr	0.00084
$B(OH)_3$	0.00041
NaF	0.00007

2.4. Instrumentation and methods

A GK2401C combination glass electrode and Radiometer PHM 84 Research pH-meter were used for the pH measurements. The glass electrode was calibrated at 25 °C using NIST-traceable buffers at pH of 4.01, 7.00 and 10.00 and seawater buffers at pH of 6.770, 8.074 and 8.810.

A Bausch & Lomb Spectronic 21 spectrophotometer was used for the analysis of phosphate according to the phosphomolybdate method of Koroleff (1976). The detection limit of this method is reported as 0.01 μmol/l and the linear range is 0.01–28 μmol/l. The analytical uncertainty of this method was estimated to be better than 5%, based on multiple measurements of a single standard on the same day. Arsenate concentrations were determined by the method of Aggett and Aspell (1976). Arsenate was reduced to arsine by a Na–borohydride solution and analyzed by flameless Atomic Absorption Spectrophotometry (AAS). The analysis was conducted on a Perkin-Elmer 5100 AAS equipped with a FIAS 200 flow injection system and an AS 90 autosampler. The detection limit for this procedure is 1.4 nmol/l, and the relative standard deviation (RSD) of three replicate analyses was generally below 5%. Magnesium and calcium were analyzed by flame AAS on a Perkin-Elmer 3100 Atomic Absorption Spectrometer. The detection limits for Mg^{2+} and Ca^{2+} using this method are 0.5 and 2.0 μmol/l, respectively, and the RSD of both analyses on three replicate measurements was generally below 3%. Sulfate concentration was determined on a Dionex 4500i Ion Chromatograph with an anion micromembrane suppressor and a conductivity detector. NaOH, 5 mM, and 0.5 mM Na_2CO_3 solutions were used as eluants at a flow rate of 1.5 ml/min. A 25 mN H_2SO_4 solution was used as regenerant at a flow rate of 4 ml/min. Two columns were used in the system: a cation guard and a cation separation analytical column (IonPac CG5 and CS5). Sample solutions were diluted before analysis. The detection limit for SO_4^{2-} using this method is 0.2 μmol/l, and the RSD on three replicate measurements was below 1%. The X-ray diffraction analysis of the synthetic goethite was conducted using a RIGAKU D/Max 2400 Automated X-ray Powder Diffractometer. A copper X-ray source was used and the analysis was conducted at 40 kV and 160 mA.

2.5. Batch adsorption experiments

Batch adsorption experiments of phosphate and arsenate on goethite were carried out in a 0.7 M NaCl solution, in the presence of either Ca^{2+}, Mg^{2+} or SO_4^{2-} at their respective seawater ($S=35$ p.s.u.) concentrations. The ionic strengths of the final $NaCl+Ca^{2+}$, $NaCl+Mg^{2+}$ and $NaCl+SO_4^{2-}$ solutions were 0.73, 0.82 and 0.78 M, respectively. The solutions were transferred to 50-ml Pyrex glass tubes, and 1 ml of the goethite slurry (10 g/l) was added. The glass tubes were then covered with Parafilm and swirled by hand several times (two to three times) a day during the reaction period. Each solution pH was adjusted by dropwise addition of a dilute HCl or NaOH solution before the addition of the goethite slurry. The duration of each experiment was 80 h, and the temperature was controlled by immersion of the sealed sample tubes in a water bath maintained at 25 °C. At the end of each experiment, reaction tubes were centrifuged and the supernatant solutions were withdrawn with a syringe and filtered through 0.45-μM Millipore filters (type HA). The pH of each solution was measured immediately after sampling. The same experimental protocol was adopted for the individual phosphate and arsenate adsorption experiments as well as the competitive adsorption experiments in artificial seawater except that the equilibration period in seawater was extended to 1 week.

The adsorption of Mg^{2+}, Ca^{2+} and SO_4^{2-} on goethite was determined at 25 °C in similar batch experiments. Preliminary experiments showed little or no detectable adsorption of these ions at their respective seawater concentration at a goethite slurry concentration of 0.24 g/l. To obtain a measurable adsorption edge, a goethite concentration of 2.4 g/l (10 ml of 10 g/l was added to 31 ml of solution) was used at $[Mg]_{init} \cong [Ca]_{init} \cong [SO_4]_{init} \cong 10$ μmol/l. In this particular case, the ionic strength of the final solutions remained close to 0.7 M since very small amounts of Mg^{2+}, Ca^{2+} and SO_4^{2-} were added.

2.6. Phosphate analysis in competitive adsorption experiments

The presence of arsenate interferes with the phosphomolybdate method. In fact, Johnson and Pilson

(1972) recommended that phosphate measurements should be conducted in the absence of arsenate because of the formation of arseno-molybdenum blue complexes. Nevertheless, phosphate measurements in the presence of arsenate can be corrected. A nearly 1:1 linear relationship was found between the excess phosphate concentration ($\Delta[PO_4]=[PO_4]_{measured}-[PO_4]_{STD}$) and the amount of arsenate in solution, i.e., $\Delta[PO_4]\cong[AsO_4]$ as determined by AAS (Gao and Mucci, 2001).

3. Experimental results

3.1. Magnesium, calcium and sulfate complexation at the surface of goethite

The fractions of Mg^{2+}, Ca^{2+} and SO_4^{2-} adsorbed on the goethite surface in the 0.7 M NaCl solution as a function of pH are shown in Fig. 1. The amount of adsorbed Mg^{2+}, Ca^{2+} and SO_4^{2-} was calculated from the difference between the equilibrated final and initial solution concentrations. Mg^{2+} and Ca^{2+} show typical cation adsorption patterns on the goethite surface, whereas SO_4^{2-} displays its anion adsorption character. The fraction of Ca^{2+} adsorbed is below our detection limit up to pH = 7.5 and increases to about 50% at pH = 10. Mg^{2+} shows a stronger affinity than Ca^{2+} for the goethite surface. The fraction of Mg^{2+} adsorbed is 25% at pH = 7.5 and increases to 100% at pH = 9. The Mg^{2+}/goethite adsorption experiment was repeated on two different occasions and the results are highly reproducible. The fraction of SO_4^{2-} adsorbed is 60% at pH = 3 and decreases to 0% at pH = 6. The adsorption affinities of Mg^{2+}, Ca^{2+} and SO_4^{2-} for the goethite surface are much weaker than phosphate and arsenate (Gao and Mucci, 2001). The maximum adsorption densities of phosphate and arsenate ($[PO_4]_{init}\cong[AsO_4]_{init}\cong 23$ μmol/l) in the pH range investigated (3–10) are 1.71 and 1.90 μmol/m^2, respectively, whereas the adsorption densities of Mg^{2+},

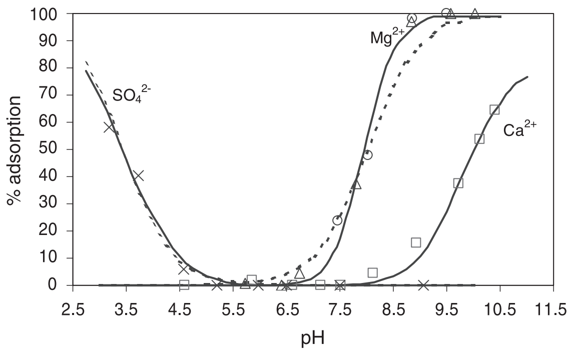

Fig. 1. Percent adsorption of Ca^{2+}, Mg^{2+} and SO_4^{2-} on goethite (2.4 g/l) as a function of pH in a 0.7 M NaCl solution. ×: SO_4^{2-}, ○: Mg^{2+} (04/16), Δ: Mg^{2+} (04/07), □: Ca^{2+}. The model fits using the CCM (solid lines) and the BSM (dashed lines) are presented.

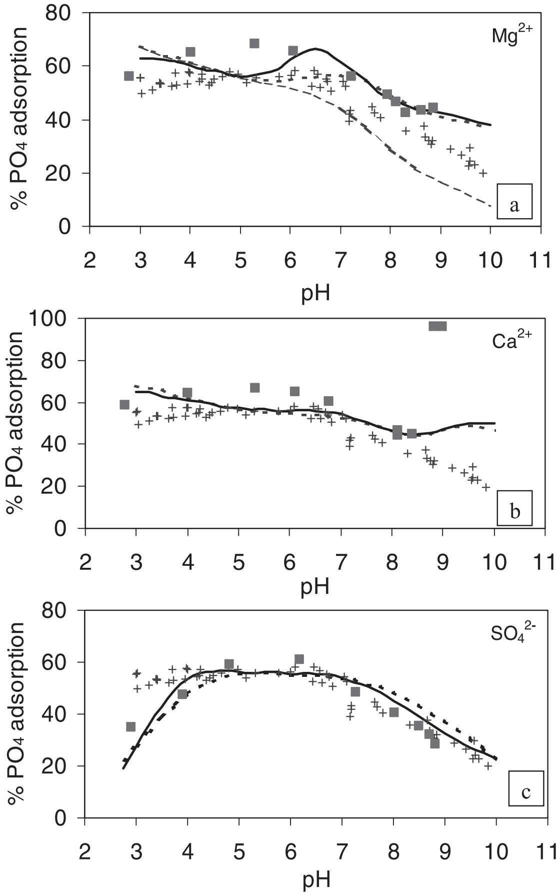

Fig. 2. Effect of Mg^{2+}, Ca^{2+} and SO_4^{2-} on the percent adsorption of phosphate on goethite (234 mg/l) as a function of pH. (a) ■: 0.7 M NaCl + 52.82 mmol/kg Mg^{2+} and $[PO_4]_{init}$ = 24.9 μM; (b) ■: 0.7 M NaCl + 10.28 mmol/kg Ca^{2+} and $[PO_4]_{init}$ = 24.5 μM; (c) ■: 0.7 M NaCl + 28.24 mmol/kg SO_4^{2-} and $[PO_4]_{init}$ = 24.7 μM. The adsorption data measured in 0.7 M NaCl (+, Gao and Mucci, 2001) are presented for comparison. In (a) and (b), the CCM (solid line) and the BSM (dashed line) fits with the inclusion of ternary complexes are presented. The long-dashed line in (a) represents the BSM fit without the inclusion of ternary complexes. In (c), the solid and the dashed lines represent the CCM and the BSM fits, respectively.

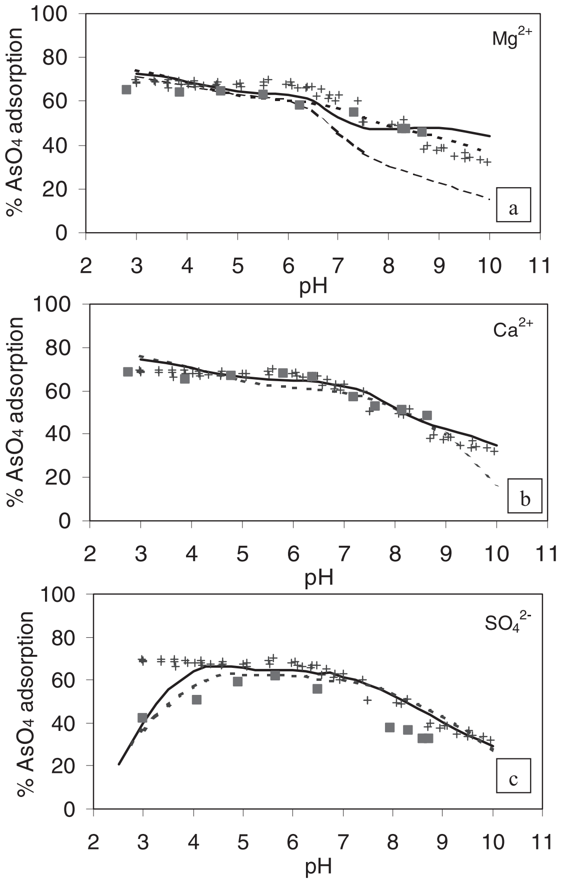

Fig. 3. Effect of Mg^{2+}, Ca^{2+} and SO_4^{2-} on the percent adsorption of arsenate on goethite (234 mg/l) as a function of pH. (a) ■: 0.7 M NaCl + 52.82 mmol/kg Mg^{2+} and $[AsO_4]_{init} = 22.9$ μM; (b) ■: 0.7 M NaCl + 10.28 mmol/kg Ca^{2+} and $[AsO_4]_{init} = 22.4$ μM; (c) ■: 0.7 M NaCl + 28.24 mmol/kg SO_4^{2-} and $[AsO_4]_{init} = 22.8$ μM. The adsorption data measured in 0.7 M NaCl (+, Gao and Mucci, 2001) are presented for comparison. In (a), the CCM (solid line) and the BSM (dashed line) fits with the inclusion of ternary complexes are presented. The long-dashed line represents the CCM fit without the inclusion of ternary complexes. In (b) and (c), the solid and the dashed lines represent the CCM and the BSM fits, respectively.

Ca^{2+} and SO_4^{2-} ($[Mg]_{init} \cong [Ca]_{init} \cong [SO_4]_{init} \cong 10$ μmol/l) are 0.13, 0.074 and 0.072 μmol/m^2, respectively.

3.2. Effect of major seawater ions on phosphate and arsenate adsorption on goethite

The individual effect of Mg^{2+}, Ca^{2+} and SO_4^{2-} on phosphate and arsenate adsorption on the goethite surface was studied in the presence and absence of these ions at their respective seawater concentrations. The fractions of phosphate adsorbed on goethite in the presence of Mg^{2+}, Ca^{2+} and SO_4^{2-} are presented in Fig. 2. The presence of Mg^{2+} enhances phosphate adsorption at all pHs but most strikingly between 4 and 6. These observations contrast with those of Hawke et al. (1989) who reported that the addition of Mg^{2+} at its seawater concentration to a 0.422 M NaCl solution decreased phosphate adsorption at pH 3–6 but did not significantly affect its adsorption at pH>6.

The addition of Ca^{2+}, at its seawater concentration to a 0.7 M NaCl solution, increases phosphate adsorption on the goethite surface, slightly at pH < 8.5 and extensively at pH>9 (Fig. 2b). The presence of SO_4^{2-} decreases phosphate adsorption at pH < 4.5, whereas the amount of phosphate adsorbed at pH>4.5 is identical to the results obtained in its absence in the

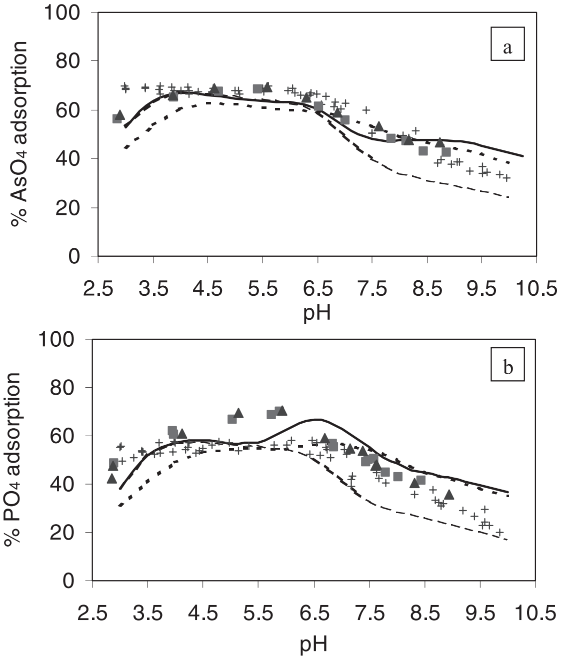

Fig. 4. Percent adsorption of phosphate and arsenate on goethite (234 mg/l) as a function of pH in artificial seawater. (a) Arsenate, ■ and ▲ are two distinct replicate studies at $[AsO_4]_{init} \cong 23$ μM. (b) Phosphate, ■ and ▲ are two distinct replicate studies at $[PO_4]_{init} \cong 25$ μM. The adsorption data measured in 0.7 M NaCl (+, Gao and Mucci, 2001) are presented for comparison. The CCM (solid line) and the BSM (dashed line) fits with the inclusion of ternary complexes are presented. The long-dashed line represents the CCM fit without the inclusion of ternary complexes.

0.7 M NaCl solution (Fig. 2c). Similar observations were reported by both Hawke et al. (1989) and Rietra et al. (2001).

The fractions of arsenate adsorbed on goethite in the presence of Mg^{2+}, Ca^{2+} and SO_4^{2-} as a function of pH are shown in Fig. 3. The addition of Mg^{2+} at either $[Mg]_{init} = 500$ μmol/l or 5.28×10^{-2} mol/kg (seawater concentration) does not affect the arsenate adsorption behaviour on the goethite surface. The amount of arsenate adsorbed is also unaffected by the presence of Ca^{2+} throughout the whole pH range investigated. The presence of SO_4^{2-} decreases arsenate adsorption at all pH investigated but most significantly at $pH < 5$.

3.3. Phosphate and arsenate adsorption on goethite in artificial seawater

The fraction of arsenate adsorbed on goethite in artificial seawater as a function of pH is shown in Fig. 4a and is compared to the results obtained in a 0.7 M NaCl solution (Gao and Mucci, 2001). The percent of arsenate adsorbed increases with pH under strongly acidic conditions; it levels off and remains nearly constant between pH 4 and 7, and then decreases as the solution becomes more alkaline. The arsenate adsorption patterns in artificial seawater and the 0.7 M NaCl solution are almost identical except for a slight difference at $pH < 4$.

The fraction of phosphate adsorbed onto goethite in artificial seawater as a function of pH is shown in Fig. 4b. The amount of phosphate adsorbed on goethite in seawater increases with pH until circumneutral values and then decreases as the solution becomes more alkaline. Clearly, the pH dependence of phosphate adsorption in seawater is different from that in the 0.7 M NaCl solution. Most noteworthy is an enhanced adsorption at pH = 4.5–6.5. These observations are consistent with the combined influence of Mg^{2+}, Ca^{2+} and SO_4^{2-} on phosphate adsorption except that we did not observe an increase of phosphate adsorption at high pH. Hawke et al. (1989) reported a similar pattern for phosphate adsorption on goethite from seawater but observed less adsorption than in the 0.7 M NaCl solution at $pH < 8$. In contrast

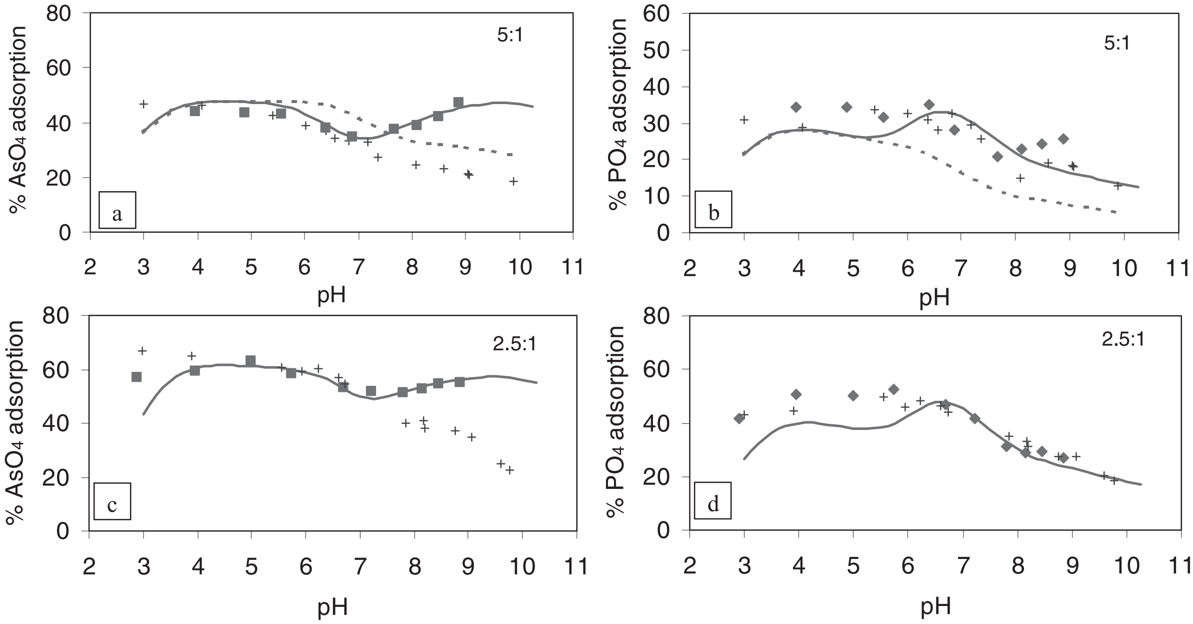

Fig. 5. Percent adsorption of phosphate (◆) and arsenate (■) on goethite (234 mg/l) as a function of pH in competitive adsorption experiments in seawater. (a) and (b) are arsenate and phosphate adsorption at $[PO_4]_{init} = 47$ μM and $[AsO_4]_{init} = 8.8$ μM (5:1), respectively. (c) and (d) are arsenate and phosphate adsorption at $[PO_4]_{init} = 24.9$ μM and $[AsO_4]_{init} = 9.6$ μM (2.5:1), respectively. The adsorption data measured in 0.7 M NaCl (+, Gao and Mucci, 2001) are presented for comparison. The model predictions using the CCM with and without the inclusion of ternary complexes are represented by the solid and dashed lines (a and b), respectively.

to the 0.7 M NaCl solution, phosphate and arsenate display comparable affinities for the goethite surface in seawater at pH = 4–9.

3.4. Competitive adsorption of phosphate and arsenate on goethite in artificial seawater

Results of phosphate and arsenate competitive adsorption experiments on goethite in artificial seawater at $[PO_4]/[AsO_4]$ ratios of 5:1 and 2.5:1 are shown in Fig. 5. They are compared to those obtained in the 0.7 M NaCl solution (Gao and Mucci, 2001). The fractions of arsenate uptake from artificial seawater and from the 0.7 M NaCl solution are similar at pH < 7 but diverge at pH>7 (Fig. 5a and c). The difference increases with increasing $[PO_4]/[AsO_4]$ ratio. With the exception of a slight increase of phosphate adsorption at high pH and $[PO_4]/[AsO_4] = 5:1$ (Fig. 5b), the fractions of phosphate adsorbed from seawater at both $[PO_4]/[AsO_4]$ ratios are identical to those measured in the 0.7 M NaCl solution.

4. Thermodynamic modeling and discussion

4.1. Data treatment

4.1.1. Equilibria at the surface of goethite

In this study, we characterized the acid-base properties of the goethite surface using the classical two surface acidity constant SCM. The acid-base properties of the surface are described by the following two reactions and corresponding mass action laws:

$$>FeOH + H^+ => FeOH_2^+$$
$$K^s_{1\,int.} = \{[>FeOH_2^+]/([>FeOH]*[H^+])\}*\exp(F\psi_0/RT) \quad (1)$$

$$>FeOH => FeO^- + H^+$$
$$K^s_{2\,int.} = \{[>FeO^-]*[H^+]/[>FeOH]\}*\exp(-F\psi_0/RT) \quad (2)$$

where > represents surface species, ψ_0 is the surface potential, F is the Faraday constant, R is the gas constant and T is the absolute temperature. This 2-pK model is based on the assumption that the goethite surface is homogeneous with only one type of active surface functional group.

Cation adsorption is analogous to metal hydrolysis in solution (Stumm and Morgan, 1981). Metal ions form either monodentate surface complexes (Eq. (3)) or bidentate surface complexes (Eq. (4)) resulting in the release of H^+ from the surface.

$$>FeOH + M^{Z+} => FeOM^{(Z-1)+} + H^+ \quad (3)$$

$$2 >FeOH + M^{Z+} = (>FeO)_2M^{(Z-2)+} + 2H^+ \quad (4)$$

Anion adsorption is usually described as ligand exchange reactions leading to the release of OH^- from the surface. The formation of inner-sphere complexes is illustrated in reactions (5) and (6), whereas an outer-sphere complex is usually formed through reactions (7) and (8).

$$>FeOH + A^{Z-} => FeA^{(Z-1)-} + OH^- \quad (5)$$

$$2 >FeOH + A^{Z-} = (>Fe)_2A^{(Z-2)-} + 2OH^- \quad (6)$$

$$>FeOH + A^{Z-} + H^+ => FeOH_2^+ - A^{Z-} \quad (7)$$

$$>FeOH + A^{Z-} + 2H^+ => FeOH_2^+ - HA^{(Z-1)-} \quad (8)$$

Several electrostatic models (e.g., constant capacitance, diffuse layer, triple layer and basic Stern models) have been developed to describe the spatial distribution of charges at the surface of a solid (Stern, 1924; Stumm et al., 1970; Stumm and Morgan, 1981, 1996; Westall, 1986). These models all adopt the classic 2-pK concept but differ from each other on the basis of the distribution and relation between surface charge and electrical potential. Among them, the triple layer model (TLM) was used to model ion adsorption in seawater, but the results were unsatisfactory (Balistrieri and Murray, 1981; Hawke et al., 1989; Yao and Millero, 1996). In the present study, phosphate and arsenate adsorption in seawater was described using both the constant capacitance model (CCM) and the basic Stern model (BSM). The CCM is the simplest surface complexation model and has been used widely (e.g., Goldberg, 1985; Lovgren et al., 1990; Nilsson et al., 1992; Lu and Smith, 1996; Boily and Fein, 1996; Manning and Goldberg, 1996;

Daughney, 1997). This model is an appropriate choice for solutions of high ionic strength in which the diffuse portion of the double layer is compressed to the mineral surface. The CCM divides the charged surface into two sheets, one is at the solid surface and the other is in the solution. A specific capacitance (C) is used to relate the surface charge (σ_0) to the surface potential (ψ_0).

$$\sigma_0/\psi_0 = C \tag{9}$$

The basic Stern model is a combination of the CCM and the diffuse layer model. In this model, charges are distributed among a surface plane (o-plane), a β-plane and a diffuse layer. It is a simpler model than the TLM since the surface potential distribution is represented by a single specific capacitance. Furthermore, at high ionic strengths, as in this study, the BSM is similar to an extended CCM since the two compact planes of adsorption are terminated by an extremely thin diffusive layer. The BSM is used to separate the charges involved in inner-sphere complexes (in the o-plane) from those in outer-sphere complexes (in the β-plane). In the BSM, the relationships between charge and potential are:

$$\sigma_0 = C(\psi_0 - \psi_\beta) \tag{10}$$

$$\sigma_\beta = -\sigma_0 - \sigma_d = C(\psi_\beta - \psi_0) - \sigma_d \tag{11}$$

$$\sigma_d = -0.1174 I^{1/2} \sinh(ZF\psi_d/2RT) \tag{12}$$

In the present study, results of phosphate and arsenate adsorption in seawater were treated using the CCM and the BSM with the aid of the computer program FITEQL, version 4.0 (Herbelin and Westfall, 1999). FITEQL is a computer program used extensively for the determination of chemical equilibrium constants in adsorption studies (Goldberg, 1985; Lovgren et al., 1990; Hayes et al., 1991; Nilsson et al., 1992; Lu and Smith, 1996; Boily and Fein, 1996; Manning and Goldberg, 1996; Daughney, 1997). The value of $V(Y)$ is an indicator of the goodness of the fit.

$$V(Y) = \Sigma(Y/S_Y)^2/(n_p n_{II} - n_u) \tag{13}$$

where Y is the actual error in the mass balance equation, S_Y is the estimated experimental error given by FITEQL, and the reciprocal of the variance S_Y is the weighting factor. n_p is the number of data points, n_{II} is the number of chemical components with known total and free concentrations and n_u is the number of adjusting parameters.

A model describing the acid-base properties of the goethite surface as well as phosphate and arsenate complexation at the surface of goethite in a 0.7 M NaCl solution was obtained previously (Gao and Mucci, 2001) using the CCM and BSM. The surface acidity constants, the phosphate and arsenate complexation constants and the corresponding model parameters are listed in Table 2. These constants are used as the thermodynamic foundation in the following modeling exercise.

4.1.2. Equilibria in solution

The stoichiometric aqueous association constants used for modeling phosphate and arsenate adsorption in artificial seawater are presented in Table 3. All these constants were taken either from Millero (1982) or Millero and Schreiber (1982) for $I = 0.7$ M and 25 °C.

Table 2
Summary of surface complexation reactions and constants describing the phosphate and arsenate adsorption at the surface of goethite in a 0.7 M NaCl solution (25 °C)

Reactions	log K^a (CCM)	log K^a (BSM)
	$C = 1.86$ F m^{-2}	$C = 3.44$ F m^{-2}
$>FeOH + H^+ => FeOH_2^+$	7.45 ± 0.06	7.90 ± 0.14
$>FeOH => FeO^- + H^+$	− 9.60 ± 0.13	− 9.11 ± 0.23
$>FeOH + H_2PO_4^- = >FePO_4^{2-} + H^+ + H_2O$	0.70 ± 0.46	0.96 ± 0.50
$>FeOH + H_2PO_4^- = >FePO_4H^- + H_2O$	7.83 ± 0.06	8.29 ± 0.24
$>FeOH + H_2PO_4^- + H^+ = >FePO_4H_2^0 + H_2O$	12.47 ± 0.20	12.93 ± 0.25
$>FeOH + H_2AsO_4^- = >FeAsO_4^{2-} + H^+ + H_2O$	1.40 ± 0.24	1.56 ± 0.29
$>FeOH + H_2AsO_4^- = >FeAsO_4H^- + H_2O$	8.41 ± 0.10	8.80 ± 0.18
$>FeOH + H_2AsO_4^- + H^+ => FeAsO_4H_2^0 + H_2O$	12.85 ± 0.12	13.26 ± 0.23

C: the specific capacitance.

[a] Values were taken from Gao and Mucci (2001). The error interval corresponds to the 95% confidence level.

Table 3
Stoichiometric aqueous complexation constants used to model phosphate and arsenate adsorption on goethite in seawater (25 °C)

Reactions	log K
$H_2O = H^+ + OH^-$	– 13.16[a]
$Na^+ + H_2O = NaOH^0 + H^+$	– 13.39[b]
$Mg^{2+} + H_2O = MgOH^+ + H^+$	– 11.46[b]
$Ca^{2+} + H_2O = CaOH^+ + H^+$	– 12.42[b]
$SO_4^{2-} + H^+ = HSO_4^-$	1.49[b]
$SO_4^{2-} + Na^+ = NaSO_4^-$	0.30[b]
$SO_4^{2-} + Mg^{2+} = MgSO_4^0$	1.01[b]
$SO_4^{2-} + Ca^{2+} = CaSO_4^0$	1.03[b]
$Cl^- + Mg^{2+} = MgCl^+$	– 1.10[b]
$H^+ + F^- = HF^0$	2.92[b]
$Mg^{2+} + F^- = MgF^+$	1.29[b]
$Ca^{2+} + F^- = CaF^+$	0.65[b]
$Na^+ + F^- = NaF^0$	– 1.0[b]
$Na^+ + H_2PO_4^- = NaH_2PO_4^0$	– 0.54[b]
$Na^+ + H_2PO_4^- = NaHPO_4^- + H^+$	– 6.51[b]
$Na^+ + H_2PO_4^- = NaPO_4^{2-} + 2H^+$	– 17.43[b]
$Na^+ + H_2AsO_4^- = NaH_2AsO_4^0$	– 0.54[b]
$Na^+ + H_2AsO_4^- = NaHAsO_4^- + H^+$	– 6.51[b]
$Na^+ + H_2AsO_4^- = NaAsO_4^{2-} + 2H^+$	– 17.43[b]
$H_2PO_4^- + H^+ = H_3PO_4$	1.73[a]
$H_2PO_4^- = H^+ + HPO_4^{2-}$	– 6.55[a]
$H_2PO_4^- = 2H^+ + PO_4^{3-}$	– 18.03[a]
$H_2AsO_4^- + H^+ = H_3AsO_4$	1.97[a]
$H_2AsO_4^- = H^+ + HAsO_4^{2-}$	– 6.30[a]
$H_2AsO_4^- = 2H^+ + AsO_4^{3-}$	– 16.94[a]
$Mg^{2+} + H_2PO_4^- = MgH_2PO_4^+$	0.37[b]
$Mg^{2+} + H_2PO_4^- = MgHPO_4^0 + H^+$	– 5.05[b]
$Mg^{2+} + H_2PO_4^- = MgPO_4^- + 2H^+$	– 14.11[b]
$Ca^{2+} + H_2PO_4^- = CaH_2PO_4^+$	0.24[b]
$Ca^{2+} + H_2PO_4^- = CaHPO_4^0 + H^+$	– 5.28[b]
$Ca^{2+} + H_2PO_4^- = CaPO_4^- + 2H^+$	– 13.45[b]
$B(OH)_4^- + H^+ = H_3BO_3^0 + H_2O$	8.83[a]
$B(OH)_4^- + Na^+ = NaB(OH)_4^0 + H_2O$	– 0.24[b]
$B(OH)_4^- + Mg^{2+} = MgB(OH)_4^+ + H_2O$	0.93[b]
$B(OH)_4^- + Ca^{2+} = CaB(OH)_4^+ + H_2O$	1.11[b]
$Mg^{2+} + H_2AsO_4^- = MgH_2AsO_4^+$	0.37[b]
$Mg^{2+} + H_2AsO_4^- = MgHAsO_4^0 + H^+$	– 5.05[b]
$Mg^{2+} + H_2AsO_4^- = MgAsO_4^- + 2H^+$	– 14.11[b]
$Ca^{2+} + H_2AsO_4^- = CaH_2AsO_4^+$	0.24[b]
$Ca^{2+} + H_2AsO_4^- = CaHAsO_4^0 + H^+$	– 5.28[b]
$Ca^{2+} + H_2AsO_4^- = CaAsO_4^- + 2H^+$	– 13.45[b]

[a] Values were taken from Millero (1982).

[b] Values were taken from Millero and Schreiber (1982).

Ion pairs between Na^+, Ca^{2+}, Mg^{2+}, phosphate and sulfate as well as other possible reactions between major seawater ionic constituents were considered during the modeling of phosphate adsorption in seawater. Based on the speciation calculation, in the PO_4–NaCl–Mg system, $MgHPO_4^0$, HPO_4^{2-} and $NaHPO_4^-$ are the dominant species at pH < 8 and $MgPO_4^-$ becomes predominant at pH>8.5; in the PO_4–NaCl–Ca system, HPO_4^{2-}, $NaHPO_4^-$ and $CaHPO_4^0$ are the most important aqueous species at pH < 8 and $CaPO_4^-$ is predominant at pH>8.5. The distribution of phosphate species in seawater as a function of pH is shown in Fig. 6. At pH = 8, 63% of the phosphate forms ion pairs with the major seawater cations. By analogy, arsenate should also be ion-paired with major seawater cations. We know of only one set of metal–arsenate complexation constants (Whiting, 1992 in Langmuir et al., 1999). An attempt to extrapolate these constants to $I = 0.7$ M using both the Davies equation (Davies, 1938) and PHREEQC (Parkhurst, 1995) yielded values which indicate that the arsenate ion pairs are more stable than those that form with phosphate, a result that is incompatible with estimates of the activity coefficients of both oxyanions in 0.7 M NaCl and seawater (Millero, 1982; Millero and Schreiber, 1982; Millero and Pierrot, 1998). Alternatively, we assumed that the metal–arsenate ion pair association constants are identical to those with phosphate.

4.2. Effect of magnesium, calcium and sulfate on phosphate and arsenate adsorption on goethite

In simulating the effect of Mg^{2+}, Ca^{2+} and SO_4^{2-} on phosphate and arsenate adsorption on goethite, all the surface complexation constants and surface acidity constants as well as other related parameters were fixed at the values derived from the

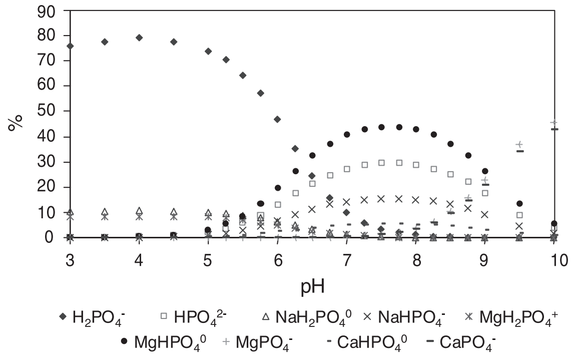

Fig. 6. The distribution of phosphate species in seawater as a function of pH.

Table 4
Surface complexation reactions and constants used to describe magnesium, calcium and sulfate adsorption at the surface of goethite in a 0.7 M NaCl solution (25 °C)

Reactions	CCM, $C=1.86$ F m^{-2}		BSM, $C=3.44$ F m^{-2}	
	log K	$V(Y)$	log K	$V(Y)$
$>FeOH+Mg^{2+}= >FeOMg^{+}+H^{+}$	− 3.90	0.22	− 3.96	0.20
$>FeOH+Ca^{2+}= >FeOCa^{+}+H^{+}$	− 6.93	0.48	− 9.58	2.60
$>FeOH+SO_4^{2-}+H^{+}= >FeSO_4^{-}(>FeOH_2SO_4^{-})$	6.26	0.07	7.75	0.12
$>FeOH+SO_4^{2-}+2H^{+}= >FeHSO_4^{0}(>FeOH_2HSO_4^{0})$	12.47	0.07	13.91	0.12

C: the specific capacitance.

single adsorbate subsystems. FITEQL was used to determine chemical speciation as a function of pH without any adjustable parameter. The Mg^{2+}, Ca^{2+} and SO_4^{2-} surface complexation reactions and constants used in the model were determined in this study. The modeling results are summarized in Table 4 and the model fits are displayed in Fig. 1. As shown in Fig. 1, the fractions of Mg^{2+} and SO_4^{2-} adsorbed on the goethite surface can be reproduced well using both the BSM and the CCM, whereas a reasonable fit to the Ca^{2+} adsorption data was obtained only by the CCM. In the case of the BSM, Mg^{2+} and SO_4^{2-} adsorption on goethite is treated as outer-sphere complexation or adsorption on the β-plane.

The modeling results of phosphate and arsenate adsorption on goethite in the presence of Mg^{2+}, Ca^{2+} and SO_4^{2-} are illustrated in Figs. 2 and 3. For comparison, phosphate and arsenate adsorption data in the 0.7 M NaCl solution are plotted as crosses. The addition of other sea salts to the 0.7 M NaCl solution increased the solution ionic strength, particularly in the Mg–NaCl system (from 0.7 to 0.82 M). Fortunately, the surface acidity constants, the specific capacitance as well as phosphate and arsenate complexation constants are not affected significantly by changing the solution ionic strength from 0.7 to 0.82 M (Gao and Mucci, 2001). Therefore, the constants and parameters previously determined in the 0.7 M NaCl solutions were used in the present modeling exercise.

As shown in Figs. 2a and 3a, phosphate and arsenate adsorption in the presence of Mg^{2+} was underpredicted by both the BSM and the CCM. The models, derived by combining the single adsorbate subsystems, not only underestimate the adsorption data of PO_4/AsO_4 on goethite with Mg^{2+}, but also predict less adsorption in the presence of Mg^{2+} than its absence at pH>6 due to site blockage by Mg^{2+}. Similarly, Hawke et al. (1989) reported that phosphate adsorption on goethite in the presence of Mg^{2+} was slightly underpredicted at pH>5 by the TLM. Clearly, the addition of Ca^{2+} and Mg^{2+} to the 0.7 M NaCl solution increased the adsorption of phosphate on the goethite surface. Since Ca^{2+} and Mg^{2+} generally form outer-sphere complexes at the goethite surface, the effect of these ions on phosphate adsorption results from the change in the electrical properties of the interface rather than the competition for surface sites. At high pH, the adsorption of Ca^{2+} and Mg^{2+} make the goethite surface more positively charged and therefore more attractive to phosphate adsorption. Similarly, Balistrieri and Murray (1982) observed that the adsorption of Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} on goethite was enhanced by the presence of SO_4^{2-} and suppressed by the addition of Mg^{2+}. They suggested that the effect of Mg^{2+} and SO_4^{2-} on the adsorption of metals could be explained by the change in electrostatic conditions at the goethite–water interface. A similar explanation was proposed by Kawashima et al. (1986) to account for the dramatic increase of phosphate adsorption on hydrous manganese oxide (HMO) in the presence of alkaline earth cations and transition metal ions at pH = 6–9. The formation and adsorption of ion pairs may also modify the electrostatic environment at the surface of the adsorbent. In concentrated and complex electrolyte solutions like seawater, phosphate forms strong ion pairs with Ca^{2+} and Mg^{2+}. The formation of these ion pairs increases phosphate adsorption because the electrostatic repulsion between the negatively charged goethite surface and phosphate ion pairs in solution is reduced under alkaline conditions. A similar mechanism was proposed by Helyar et al. (1976) to explain the increased phosphate adsorption by gibbsite at pH = 5.5 in the presence of Ca^{2+}. At high pH, both the

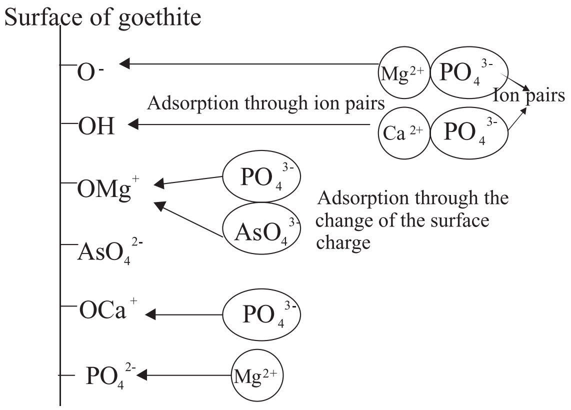

Fig. 7. A simplified, schematic representation of the adsorption of phosphate and arsenate ion pairs and the formation of ternary surface complexes on goethite at high pH.

adsorption of divalent cations on goethite and the formation of ion pairs in solution may favor the formation of ternary surface complexes and ultimately increase anion adsorption. A simplified, schematic representation of the adsorption of phosphate and arsenate ion pairs and the formation of ternary surface complexes is shown in Fig. 7.

The modeling results that include the formation of ternary surface complexes are represented in Figs. 2a, b and 3a. Different combinations of various ternary complexes were tested, and the best fit to the experimental data (the minimum *V*(*Y*) value) was obtained with a model consisting of two ternary surface complexes described by Eqs. (14)–(19). Models including one ternary complex gave a worse fit to the adsorption data, and FITEQL never converged when three ternary complexes were considered. The surface complexation constants of the ternary surface complexes determined using both the BSM and the CCM are listed in Table 5.

$Mg{-}PO_4$ system,

$$>FeOH + Mg^{2+} + H_2PO_4^- => FeOMgHPO_4^- + 2H^+ \tag{14}$$

$$>FeOH + Mg^{2+} + H_2PO_4^- => FeOMgH_2PO_4^0 + H^+ \tag{15}$$

$Ca{-}PO_4$ system,

$$>FeOH + Ca^{2+} + H_2PO_4^- => FeOCaHPO_4^- + 2H^+ \tag{16}$$

$$>FeOH + Ca^{2+} + H_2PO_4^- => FeOCaH_2PO_4^0 + H^+ \tag{17}$$

$Mg{-}AsO_4$ system,

$$>FeOH + Mg^{2+} + H_2AsO_4^- => FeOMgHAsO_4^- + 2H^+ \tag{18}$$

$$>FeOH + Mg^{2+} + H_2AsO_4^- => FeOMgH_2AsO_4^0 + H^+ \tag{19}$$

These ternary surface complexes were treated as inner-sphere complexes in the CCM but as outer-sphere complexes in the BSM. It is important to note that, although Eqs. (14)–(19) illustrate ternary surface complexes as Type A (i.e., metal-in-the-middle) complexes, our model cannot distinguish between the coordination mode of the ternary surface complexes. In fact, we assumed that Mg^{2+} and Ca^{2+} form ion pairs with phosphate/arsenate first; these ion pairs are then adsorbed on either the o-plane (CCM) or the β-plane (BSM) as point charges.

Table 5
Surface complexation reactions and constants used to describe the ternary surface complexes at the surface of goethite using the constant capacitance (CCM) and basic Stern (BSM) models (25 °C)

Reactions	log *K* (CCM), $C = 1.86$ F m^{-2}	log *K* (BSM), $C = 3.44$ F m^{-2}
$>FeOH + Mg^{2+} + H_2PO_4^- = >FeOMgHPO_4^- + 2H^+$	− 5.22	− 5.44
$>FeOH + Mg^{2+} + H_2PO_4^- = >FeOMgH_2PO_4^0 + H^+$	2.48	2.57
$>FeOH + Ca^{2+} + H_2PO_4^- = >FeOCaHPO_4^- + 2H^+$	− 6.91	− 6.68
$>FeOH + Ca^{2+} + H_2PO_4^- = >FeOCaH_2PO_4^0 + H^+$	− 0.44	0.09
$>FeOH + Mg^{2+} + H_2AsO_4^- = >FeOMgHAsO_4^- + 2H^+$	− 4.74	− 5.28
$>FeOH + Mg^{2+} + H_2AsO_4^- = >FeOMgH_2AsO_4^0 + H^+$	1.79	2.42

In the AsO_4–Mg–goethite system, a reasonable fit of the arsenate adsorption data was obtained with the inclusion of ternary complexes, whereas they were underpredicted at pH>6 when modeled without ternary complexes. Clearly, the inclusion of ternary surface complexes significantly improves the model predictions for arsenate adsorption in the presence of Mg^{2+} (Fig. 3a). Nevertheless, the phosphate adsorption data in the presence of Mg^{2+} and Ca^{2+} are still slightly underestimated at pH = 4–6 (Fig. 2a and b). Yao and Millero (1996) reported that the inclusion of $Ca–PO_4$ and $Mg–PO_4$ ternary surface complexes to the TLM did predict higher phosphate adsorption on δMnO_2, but the model could not reproduce the pH dependence of the experimental data. The modeling results were not shown in their paper.

Fig. 2b shows that both the CCM and BSM underestimate phosphate adsorption in the presence of Ca^{2+} at pH = 4–6 and completely fail to reproduce the enhanced phosphate adsorption at pH>8.5. The enhanced phosphate adsorption at high pH may be an experimental artifact and may result from the precipitation of a calcium phosphate phase. The thermodynamic solubility product of apatite ($Ca_3(PO_4)_2$) at 25 °C is $10^{-28.7}$ (Krauskopf and Bird, 1995). Our speciation calculations show that all initial experimental solutions at pH < 8.3 were undersaturated with respect to $Ca_3(PO_4)_2$, but supersaturated (i.e., IAP> 10^{-27}) for the last two points at pH 8.8 and 9.0, results that are consistent with our observations and interpretation. Similarly, Hawke et al. (1989) suggested that the precipitation of a calcium phosphate phase was responsible for the apparent, enhanced phosphate adsorption at high pH in their experimental solutions. In contrast, Rietra et al. (2001) reported that the addition of Ca^{2+} increased phosphate adsorption on goethite significantly at high pH (pH = 10) in apatite undersaturated solutions and suggested that phosphate adsorption in a $Ca–PO_4$ system could be predicted by the CD-MUSIC model with model parameters derived from the single-ion subsystems and without invoking the formation of ternary complexes. However, the Ca^{2+} concentrations used in their experiments are much lower than those investigated in our study (i.e., up to 0.1 vs. 10 mmol/l), and experimental results of the two studies are not readily comparable. Unlike phosphate, arsenate adsorption on the goethite surface is almost unaffected by the presence of Ca^{2+} at its seawater concentration. The fraction of arsenate adsorbed is fairly well predicted by the CCM and the BSM (Fig. 3b).

Fig. 2c presents the modeling result of phosphate adsorption on goethite in the presence of SO_4^{2-}. Clearly, both the BSM and the CCM reproduce the phosphate adsorption behaviour in the presence of SO_4^{2-} using the surface complexation constants for phosphate and SO_4^{2-} derived from single adsorbate subsystems. The models predict a decrease in phosphate adsorption at pH < 4.5. This reflects the competition between $H_2PO_4^-$ and SO_4^{2-} for the limited surface sites and the change in the electrical properties of the interface upon the adsorption of SO_4^{2-}. At pH>4.5, model results are identical to those in the 0.7 M NaCl solution indicating that phosphate adsorption at high pH is not affected by the presence of sulfate. Similarly, Geelhoed et al. (1997) reported that phosphate and sulfate competitive adsorption on goethite in dilute solutions was predicted well by the CD-MUSIC model using parameters derived for single anion systems. In contrast, the CCM and BSM are less successful at predicting arsenate adsorption in the presence of SO_4^{2-}, but the BSM gives a better fit than the CCM at low pH (Fig. 3c). Our models predict the adsorption pattern but overestimate arsenate adsorption over the whole pH range, particularly at high pH. Xu et al. (1988) observed that the presence of sulfate decreased arsenate adsorption on alumina up to pH = 7.

4.3. Phosphate and arsenate adsorption on goethite in artificial seawater

At this stage, we attempt to model phosphate and arsenate adsorption in seawater using all the surface complexation constants previously determined from single or double adsorbate subsystems. The surface acidity constants, the surface complexation constants and other corresponding model parameters were taken directly from subsystem results and were not adjusted for the solution composition. A simple chemical speciation as a function of pH was performed with the aid of FITEQL. Surface complexation of other major seawater constituents such as Sr^{2+} and Br^{-} was not considered in the model because the complexation constants of these ions are not readily available.

The modeling results of phosphate and arsenate adsorption in seawater using the CCM and the BSM are presented in Fig. 4. As shown in Fig. 4a, arsenate adsorption in seawater is better described by the CCM than the BSM. The fraction of arsenate adsorbed on the goethite surface in seawater can be accurately reproduced by the CCM using surface complexation constants derived from either single or double adsorbate subsystems. The model including ternary surface complexes improves the model fit significantly emphasizing their role in arsenate adsorption in seawater.

In contrast, both the CCM and BSM fail to predict phosphate adsorption accurately in seawater (Fig. 4b), although the adsorption pattern was reproduced well. The inclusion of the ternary surface complexes did improve the model fit substantially at pH>7. Nevertheless, the pH dependence of the model prediction does not match the experimental data and is shifted by a few tenths to alkaline pH. Modeling phosphate adsorption in seawater appears to be a particularly difficult endeavor (e.g., Hawke et al., 1989). In a complex electrolyte solution like seawater, phosphate forms strong ion pairs and ternary surface complexes with seawater cations which enhance its adsorption (see Section 4.4 for a detailed discussion). Despite the inclusion of Ca^{2+} and Mg^{2+} ternary surface complexes, the models could not reproduce the enhanced adsorption at pH = 4–6.

4.4. Competitive adsorption of phosphate and arsenate on goethite in artificial seawater

To simulate phosphate and arsenate competitive adsorption on goethite in seawater, a modeling procedure similar to the one used in Section 4.3 was applied. Briefly, a simple surface speciation at varying pH involving phosphate and arsenate was performed with surface complexation constants determined previously from single or double adsorbate subsystems. Only the CCM prediction is reported in Fig. 5 since it gives a better fit to the experimental data than the BSM. As shown in Fig. 5a and c, arsenate adsorption in competitive experiments was reproduced fairly well using the CCM with the inclusion of the ternary surface complexes, whereas phosphate adsorption was underpredicted at pH < 6.5 (Fig. 5b and d).

In competitive experiments in seawater, the adsorption pattern of phosphate and arsenate as well as the model predictions, in general, resemble those obtained in the 0.7 M NaCl solution at pH < 6.5 (Fig. 5), but at pH>7, the fraction of arsenate adsorbed from seawater increases rather than decreases. Our model reproduces this interesting phenomenon successfully and thus further emphasizes the potential role of ion pairs and ternary surface complexes in the adsorption of both phosphate and arsenate from seawater. The amounts of phosphate and arsenate adsorbed in competitive experiments reflect the relative stability of their bimolecular surface complexes, ternary surface complexes and ion pairs in solution. Our model fits in the competitive systems require that the ternary complexes of arsenate be stronger than those that form with phosphate.

Phosphate adsorption was still underpredicted at pH < 6.5. The inability of the model to predict its competitive adsorption behaviour in seawater at low pH is in great part due to the fact that subsystems remain poorly understood. Gao and Mucci (2001) reported that, in competitive adsorption on goethite in a 0.7 M NaCl solution, phosphate adsorption is also underpredicted by the models used in their paper and proposed that their poor performance may be explained by site heterogeneity and adsorption kinetics. In contrast, Zhao and Stanforth (2001) indicated that the competitive adsorption behaviour of phosphate and arsenate on goethite is more complicated than the reactions assumed in a surface complexation model and suggested that surface precipitation may be occurring. Clearly, at this point, our understanding of phosphate and arsenate competitive adsorption on goethite and our ability to model such a complex system are still limited. Recently, a relatively new model (i.e., CD-MUSIC) was reported to be quite successful at reproducing anion adsorption (e.g., SO_4^{2-}, PO_4^{3-}, AsO_4^{3-} and F^{-}) on the goethite surface in dilute and 0.1 M NaCl solutions (Hiemstra and Van Riemsdijk, 1996, 1999, 2000; Geelhoed et al., 1997; Rietra et al., 1999, 2001). To our knowledge, the CD-MUSIC model has never been applied to high ionic strength solutions, and its performance in such solutions has not been tested.

5. Summary and conclusions

Phosphate adsorption in the 0.7 M NaCl solution was increased slightly at pH = 4–6 by the presence of Mg^{2+} and Ca^{2+} at their seawater concentrations and decreased at $pH < 4$ in the presence of SO_4^{2-}. Similarly, arsenate adsorption in the 0.7 M NaCl solution was reduced at low pH by the addition of SO_4^{2-}. Unlike phosphate, the fraction of arsenate adsorbed was not affected by the addition of Mg^{2+} and Ca^{2+}. In the PO_4–SO_4–goethite and AsO_4–Ca–goethite subsystems, the competitive adsorption data in 0.7 M NaCl solution were reproduced successfully by both the CCM and the BSM with model parameters derived from the single adsorbate systems. The experimental data were underpredicted at high pH in the PO_4–Ca–goethite, PO_4–Mg–goethite and AsO_4–Mg–goethite systems, but the inclusion of ternary surface complexes improved model fits substantially. Nevertheless, phosphate adsorption data in the presence of Mg^{2+} and Ca^{2+} remain slightly underestimated at pH = 4–6.

In artificial seawater, the pH dependence of phosphate adsorption on goethite was modified by the presence of major seawater ions. The adsorption of phosphate was promoted by Ca^{2+} and Mg^{2+} at circum-neutral pH. In contrast, arsenate adsorption in seawater was almost identical to that in the 0.7 M NaCl solution except for a decrease at low pH, presumably as a result of SO_4^{2-} competition. In seawater, arsenate shows a similar adsorption pattern and affinity as phosphate for the goethite surface. The fraction of arsenate adsorbed can be predicted well using the CCM with the inclusion of ternary surface complexes and ion pairs. A similar model successfully predicted the phosphate adsorption pattern in seawater but failed to accurately reproduce the pH dependence of experimental data, particularly at circum-neutral pH.

The fraction of phosphate adsorbed in the competitive experiments with arsenate in seawater is identical to that in the 0.7 M NaCl solution. On the other hand, the amount of arsenate adsorption in competitive experiments in seawater is greater than in the 0.7 M NaCl solution at pH>7 and the difference is proportional to the initial concentration of phosphate. In competitive experiments in seawater, phosphate adsorption is underpredicted at $pH < 6.5$, whereas arsenate adsorption is reproduced well over the whole pH range, including some very unusual patterns, using the CCM and the inclusion of ternary surface complexes and ion pairs. These findings emphasize the important role of ion pairs and ternary surface complexes in the adsorption of both phosphate and arsenate from seawater.

Phosphate and arsenate adsorption as well as their competitive adsorption on goethite in seawater are better described by the CCM. Similarly, a previous study (Gao and Mucci, 2001) revealed that phosphate and arsenate adsorption on goethite in a 0.7 M NaCl solution is also better described by the CCM than the BSM or TLM. Although more sophisticated models may provide better fits to the data, it is not true to assume that they are inherently better than a simpler model given that they carry a larger number of undefined parameters. For a fixed high ionic strength solution like seawater, the CCM could be a more appropriate choice. Further studies should include investigations of adsorbate–electrolyte interactions, adsorption kinetics and the influence of site heterogeneity.

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Appendix A

(a) Experimental data of phosphate and arsenate adsorption on goethite (234 mg/l) in a 0.7 M NaCl solution in the presence of SO_4^{2-}, Ca^{2+} and Mg^{2+} at their respective seawater concentrations.

Sample no.	$[SO_4^{2-}]=28.24$ mmol/kg, $[PO_4]_{init}=24.7$ μM			$[Mg^{2+}]=52.82$ mmol/kg, $[PO_4]_{init}=24.9$ μM			$[Ca^{2+}]=10.28$ mmol/kg, $[PO_4]_{init}=24.5$ μM		
	pH	$[PO_4]_{fin}$	% ads	pH	$[PO_4]_{fin}$	% ads	pH	$[PO_4]_{fin}$	% ads
1	2.92	16.0	35	2.78	10.9	56	2.78	10.1	59
2	3.90	13.0	47	4.02	8.7	65	4.00	8.7	65
3	4.82	10.1	59	5.29	7.9	68	5.34	8.2	67
4	6.18	9.6	61	6.07	8.6	65	6.11	8.6	65
5	7.26	12.8	48	7.22	11.0	56	6.78	9.8	60
6	8.02	14.7	41	7.93	12.6	49	8.12	13.2	46
7	8.49	15.9	36	8.11	13.3	47	8.13	13.7	44
8	8.70	16.7	32	8.32	14.3	43	8.39	13.5	45
9	8.82	17.6	29	8.61	14.1	43	8.82	1.0	96
10				8.86	13.8	44	8.99	1.0	96

Sample no.	$[SO_4^{2-}]=28.24$ mmol/kg, $[AsO_4]_{init}=22.8$ μM			$[Mg^{2+}]=52.82$ mmol/kg, $[AsO_4]_{init}=22.9$ μM			$[Ca^{2+}]=10.28$ mmol/kg, $[AsO_4]_{init}=22.4$ μM		
	pH	$[AsO_4]_{fin}$	% ads	pH	$[AsO_4]_{fin}$	% ads	pH	$[AsO_4]_{fin}$	% ads
1	2.99	13.2	42	2.81	8.0	65	2.76	7.1	68
2	4.08	11.3	50	3.86	8.3	64	3.87	7.8	65
3	4.89	9.4	59	4.68	8.1	65	4.79	7.4	67
4	5.65	8.7	62	5.53	8.5	63	5.80	7.2	68
5	6.49	10.1	56	6.24	9.6	58	6.39	7.6	66
6	7.95	14.3	37	7.30	10.3	55	7.19	9.6	57
7	8.31	14.5	36	8.27	12.1	47	7.62	10.6	53
8	8.60	15.4	32	8.34	12.1	47	8.13	10.9	51
9	8.73	15.4	32	8.67	12.4	46	8.65	11.6	48

(b) Experimental data of phosphate (three replicates) and arsenate (two replicates) adsorption on goethite (234 mg/l) in seawater.

Sample no.	$[PO_4]_{init}=24.9$ μM (total 11 samples)			$[PO_4]_{init}=24.5$ μM (total 11 samples)			$[PO_4]_{init}=24.4$ μM (total 4 samples)		
	pH	$[PO_4]_{fin}$	% ads	pH	$[PO_4]_{fin}$	% ads	pH	$[PO_4]_{fin}$	% ads
1	2.86	14.4	42	2.88	12.8	48	2.90	12.5	49
2	3.95	9.5	62	4.11	9.5	61	3.97	9.7	60
3	5.03	8.3	67	5.14	7.5	69	5.89	7.4	70
4	5.75	7.8	69	5.92	7.2	71	6.83	10.5	57
5	6.87	11.1	55	6.69	10.1	59			
6	7.44	12.7	49	7.16	11.1	55			
7	7.48	12.5	50	7.37	11.3	54			
8	7.60	12.4	50	7.64	12.7	48			
9	7.79	13.7	45	7.61	12.9	47			
10	8.04	14.3	43	8.32	14.5	41			
11	8.45	14.6	41	8.93	15.8	36			

Sample no.	$[AsO_4]_{init} = 23.2$ μM (total 10 samples)			$[AsO_4]_{init} = 22.5$ μM (total 9 samples)		
	pH	$[AsO_4]_{fin}$	% ads	pH	$[AsO_4]_{fin}$	% ads
1	2.85	10.2	56	2.91	9.4	58
2	3.88	8.1	65	3.86	7.6	66
3	4.70	7.5	68	4.61	7.0	69
4	5.42	7.4	68	5.59	6.9	69
5	6.52	9.0	61	6.30	7.9	65
6	7.02	10.3	55	6.87	9.2	59
7	7.85	10.1	48	7.62	10.5	53
8	8.12	12.3	47	8.16	11.8	48
9	8.45	13.3	43	8.73	12.0	47
10	8.86	13.4	42			

(c) Experimental data of phosphate and arsenate competitive adsorption on goethite (234 mg/l) in seawater.

Sample no.	$[AsO_4]_{init} = 9.6$ μM, $[PO_4]_{init} = 24.9$ μM				
	pH	$[AsO_4]_{fin}$	% AsO_4 ads	$[PO_4]_{fin}$	% PO_4 ads
1	2.90	4.1	57	14.5	42
2	3.96	3.9	59	12.2	51
3	5.00	3.5	63	12.3	50
4	5.73	4.0	58	11.7	53
5	6.70	4.5	53	13.2	47
6	7.22	4.6	52	14.5	42
7	7.80	4.7	51	17.1	31
8	8.15	4.5	53	17.7	29
9	8.46	4.4	54	17.5	30
10	8.85	4.3	55	18.1	27

Sample no.	$[AsO_4]_{init} = 8.8$ μM, $[PO_4]_{init} = 47$ μM				
	pH	$[AsO_4]_{fin}$	% AsO_4 ads	$[PO_4]_{fin}$	% PO_4 ads
1	3.95	5.0	43	31	34
2	4.89	5.0	43	31	34
3	5.56	5.0	43	32	32
4	6.40	5.5	38	30	36
5	6.88	5.8	35	34	28
6	7.66	5.5	37	37	21
7	8.10	5.4	39	36	23
8	8.49	5.1	42	35	26
9	8.87	4.7	47	35	26

$[PO_4]_{init}$ and $[PO_4]_{fin}$ are the initial and final solution concentrations of phosphate.
$[AsO_4]_{init}$ and $[AsO_4]_{fin}$ are the initial and final solution concentrations of arsenate.
Blank cells: no data available.

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