A predictive model (ETLM) for arsenate adsorption and surface speciation on oxides consistent with spectroscopic and theoretical molecular evidence

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ABSTRACT

The nature and behavior of adsorbed arsenate species over a wide range of minerals and environmental conditions is fundamental to prediction of the migration and long-term fate of arsenate in natural environments. Spectroscopic experiments and theoretical calculations have demonstrated the potential importance of a variety of arsenate surface species on several iron and aluminum oxides. However, integration of the results of these studies with surface complexation models and extrapolation over wide ranges of conditions and for many oxides remains a challenge. In the present study, in-situ X-ray and infrared spectroscopic and theoretical molecular evidence of arsenate (and the analogous phosphate) surface speciation are integrated with an extended triple layer model (ETLM) of surface complexation, which takes into account the electrostatic work associated with the ions and the water dipoles involved in inner-sphere surface complexation by the ligand exchange mechanism.

Three reactions forming inner-sphere arsenate surface species

\[ 2 > SOH + H_3AsO_4^0 = (> SO)_2AsO_2^- + H^+ + 2H_2O \]

\[ 2 > SOH + H_3AsO_4^0 = (> SO)_2AsOOH + 2H_2O \]

and

\[ > SOH + H_3AsO_4^0 => SOAsO_3^{2-} + 2H^+ + H_2O \]

were found to be consistent with adsorption envelope, adsorption isotherm, proton surface titration and proton coadsorption of arsenate on hydrous ferric oxide (HFO), ferrihydrite, four goethites, amorphous aluminum oxide, \(\alpha\)-Al\(_2\)O\(_3\), \(\beta\)-Al(OH)\(_3\), and \(\alpha\)-Al(OH)\(_3\) up to surface coverages of about 2.5 \(\mu\)moles.m\(^{-2}\) (at higher surface coverages adsorption is not the predominant mode of arsenate sorption). The four goethites showed a spectrum of speciation behavior from
predominantly binuclear to mononuclear. The adsorption models for two goethites in the middle of this spectrum of behavior, together with the models for all the other oxides, predicted changes in arsenate surface speciation with changes in pH, ionic strength and surface coverage consistent with qualitative trends from most in-situ X-ray and infrared spectroscopy for arsenate and phosphate on goethite, HFO and α- and β-Al(OH)₃.

The equilibrium constants for arsenate adsorption expressed in terms of site-occupancy standard states show systematic differences for different solids. The differences can be explained with the aid of Born solvation theory, which enables the development of a set of predictive equations for arsenate adsorption equilibrium constants on all oxides. The predictive equations indicate that the Born solvation effect for mononuclear species is much stronger than for binuclear species. This favors the development of the mononuclear species on iron oxides such as HFO with high values of the dielectric constant relative to aluminum oxides such as gibbsite with much lower dielectric constants. However, on hematite and corundum, with more similar dielectric constants, the predicted surface speciations of arsenate are similar.
1. INTRODUCTION

Arsenic has received a great deal of public attention because of its links to certain types of cancers and its high levels in some drinking water supplies (Hopenhayn, 2006; Nordstrom, 2002). Arsenate is the predominant species of arsenic in oxidized aquatic systems (Myneni et al., 1998). The concentration of arsenate in natural waters is strongly influenced by adsorption on oxide surfaces (Fukushi et al., 2003; Fuller and Davis, 1989; Pichler et al., 1999). To predict the migration and long-term fate of arsenate in natural environments, the behavior and the nature of adsorbed arsenate species must be known for a wide variety of minerals and over the full range of environmental conditions.

The surface speciation of arsenate on oxide powders, and more recently, on single crystal surfaces, has been studied through X-ray spectroscopic and infrared investigations as well as theoretical molecular calculations. On powders, a variety of surface species have been inferred from extended X-ray absorption fine structure (EXAFS) studies. The majority of these studies have been concerned with iron oxides and a very limited range of ionic strengths. For arsenate on ferrihydrite and FeOOH polymorphs (goethite, akaganeite and lepidocrocite) at pH = 8 and I = 0.1, it was inferred that arsenate adsorbed mainly as an inner-sphere bidentate-binuclear complex (Waychunas et al., 1993). Monodentate-monomonuclear complexes were also inferred. The monodentate / bidentate ratio decreased with increasing arsenate surface coverage. In contrast, Manceau (1995) reinterpreted the EXAFS spectra as indicating bidentate-monomonuclear species. The possible existence of such a species, in addition to
the ones described by Waychunas et al. (1993) was described in Waychunas et al. (2005).

All three of the above species were subsequently inferred for arsenate adsorption on goethite from EXAFS results obtained at pH = 6 - 9 and I = 0.1 (Fendorf et al., 1997). The monodentate-mononuclear species was inferred to dominate at higher pH values and lower surface coverages, whereas the bidentate-binuclear species dominated at lower pH and higher surface coverages. The bidentate-mononuclear species was detected in only minor amounts at high surface coverage. For arsenate on goethite and lepidocrocite at pH = 6, a bidentate-binuclear species was inferred (Farquhar et al., 2002). The same species was inferred for arsenate on goethite, lepidocrocite, hematite and ferrihydrite at pH = 4 and 7 and I = 0.1 through EXAFS combined with molecular calculations (Sherman and Randall, 2003). For arsenate on hematite, as a function of pH = 4.5 - 8 and surface coverage, Arai et al. (2004) interpreted EXAFS data to infer a predominant bidentate-binuclear and a minor amount of a bidentate-mononuclear species. In the only powder studies of aluminum oxides, EXAFS and XANES of arsenate adsorption on β-Al(OH)₃ at pH = 4, 8, and 10 and I = 0.1 and 0.8 by Arai et al. (2001) showed that arsenate adsorbs to β-Al(OH)₃ as a bidentate-binuclear inner-sphere species (their XANES data did not indicate any outer-sphere species regardless of pH and ionic strength), and an EXAFS study of arsenate on α-Al(OH)₃ at pH = 5.5 (in dilute Na-arsenate solutions) also showed that arsenate forms an inner-sphere bidentate-binuclear species (Ladeira et al., 2001).
On single crystal surfaces of corundum and hematite, several arsenate surface species have been reported recently. For the (0001) and (10-12) planes of hematite, prepared at pH = 5 with 10^{-4} M sodium arsenate solutions, then studied with GIXAFS and surface diffraction in a humid atmosphere, 71 - 78% of the adsorbed arsenate was determined to be a bidentate-mononuclear species, with the remainder present as a bidentate-binuclear species (Waychunas et al., 2005). However, in bulk water at pH = 5, resonant anomalous X-ray reflectivity studies of the (01-12) planes of corundum and hematite, have established a bidentate-binuclear species, and the first reported occurrence of an outer-sphere or H-bonded arsenate species (Catalano et al., 2006a, b). In the present study, we wish to emphasize that distinguishing between an outer-sphere and H-bonded species is not possible in surface complexation models of reaction stoichiometry, although considerations of Born solvation theory may facilitate the distinction.

Overall, the X-ray studies on powders and single crystals provide strong indications of a variety of surface arsenate species, presumably present under different conditions of pH, ionic strength and surface coverage, as well as being present on different solids and crystallographically different surfaces. Even on a single crystal surface, a great variety of possible surface species coordination geometries can be proposed, e.g. monodentate, bidentate and tridentate possibilities (Waychunas et al., 2005). However, the most frequently reported inner-sphere arsenate species coordination geometries in X-ray studies remain the bidentate-binuclear, bidendate-mononuclear, and the monodentate-mononuclear types of species. In this regard, it should also be emphasized that
none of the protonation states of these coordination geometries are established by X-ray studies. A variety of possible protonation states adds even further potential complexity to the speciation of adsorbed arsenate. It is here that other spectroscopic techniques (e.g. infrared and Raman) and molecular calculations, as well as the reaction stoichiometries in surface complexation models can possibly help.

In-situ ATR-FTIR studies of arsenate on ferrihydrite and amorphous hydrous ferric hydroxide have inferred that adsorption of arsenate occurred as inner-sphere species (Roddick-Lanzilotta et al., 2002; Voegelin and Hug, 2003). However, only small shifts with changes of pH may occur (Goldberg and Johnston, 2001). The assignment of arsenate surface species from infrared and Raman spectra is sufficiently difficult (Myneni et al., 1998) that a definitive study has yet to be done. Consequently, in the present study we have made use of infrared results for an analogous anion phosphate.

Phosphate and arsenate are widely considered to have very similar adsorption characteristics (Arai et al., 2004; Goldberg and Johnston, 2001; Hiemstra and van Riemsdijk, 1999; Waychunas et al., 1993). Furthermore, infrared studies of phosphate adsorption indicate enough shifts of the spectra with experimental conditions to assign the phosphate surface species (Arai and Sparks, 2001; Loring et al., 2006; Nelson et al., 2006; Persson et al., 1996; Tejedor-Tejedor and Anderson, 1990). The phosphate surface species inferred by Tejedor-Tejedor and Anderson (1990) has already been used to develop a CD surface complexation model for arsenate on goethite (Hiemstra and van Riemsdijk, 1999). In the present study, we take a similar approach using the
studies by Tejedor-Tejedor and Anderson (1990) and Arai et al. (2001) which are the most definitive currently published studies of phosphate adsorption referring to *in situ* conditions. We investigate a surface complexation application of the species suggested by these authors to a wide range of oxides.

According to Tejedor-Tejedor and Anderson (1990), phosphate on goethite adopts three surface species: protonated bidentate-binuclear, deprotonated bidentate-binuclear and deprotonated monodentate species. The relative abundances of these species were shown to be strong functions of pH and surface coverage at an ionic strength of 0.01. The protonated bidentate-binuclear species predominated at pH values of about 3.6 to 5.5 - 6.0 (at surface coverages of 190 and 150 $\mu$moles/g). The deprotonated bidentate-binuclear species became predominant between pH values of about 6 to 8.3. The monodentate species was detectable at pH values as low as 6 at surface coverages of 190 $\mu$moles/g and increased in relative abundance as the surface coverage decreased towards 50 $\mu$moles/g. Consistent results have been obtained for phosphate on ferrihydrite (Arai and Sparks, 2001). The latter assigned protonated bidentate-binuclear species at pH values of 4 to 6 and surface coverages of 0.38 to 2.69 $\mu$moles/m$^2$ and a deprotonated bidentate-binuclear species at pH > 7.5, as well as a possible non-protonated Na-phosphate surface species at high pH values. Broadly speaking, the *in situ* infrared studies for phosphate adsorption on iron oxides are consistent with the results of the X-ray studies for arsenate discussed above. However, infrared studies of phosphate provide invaluable additional information on the state of protonation of the surface phosphate species, which we use as a first step in
developing a surface complexation model for arsenate adsorption below. It should be noted here that recent ATR-FTIR studies of phosphate on goethite suggest an increased emphasis on the importance of mononuclear adsorbed phosphate species (Loring et al., 2006).

The surface structure and protonation state of adsorbed arsenate have been addressed through theoretical density functional theory (DFT) and molecular orbital density functional theory (MO/DFT) calculations. DFT calculations for arsenate with aluminum oxide clusters indicated that a bidentate-binuclear species was more stable than bidentate-monomonuclear, monodentate-monomonuclear or monodentate-binuclear species (Ladeira et al., 2001). From predicted geometries of arsenate adsorbed on iron hydroxide clusters using DFT comparing EXAFS data, it was suggested that arsenate was adsorbed as a doubly protonated species (Sherman and Randall, 2003). Predicted energetics indicated that a bidentate-binuclear species was more stable than a bidentate-monomonuclear and monodentate species. In contrast to these DFT calculations, MO/DFT calculations by using different type of iron hydroxide clusters (containing solvated waters) showed that deprotonated arsenate surface species resulted in good agreement with spectroscopic data (Kubicki, 2005). The bidentate-binuclear configuration is most consistent with spectroscopic data, but the model Gibbs free energies of adsorption of clusters suggested that the monodentate configuration is energetically more stable as a cluster. The MO/DFT calculations also indicated a strong preference for arsenate to bind to iron clusters relative to aluminum hydroxide clusters.
Numerous studies have focused on surface complexation modeling of arsenate on oxides (Arai et al., 2004; Dixit and Hering, 2003; Dzombak and Morel, 1990; Gao and Mucci, 2001; Goldberg, 1986; Goldberg and Johnston, 2001; Grossl et al., 1997; Halter and Pfeifer, 2001; Hering and Dixit, 2005; Hiemstra and van Riemsdijk, 1999; Manning and Goldberg, 1996; Manning and Goldberg, 1997). Surface complexation modeling has the capability to predict the behavior and the nature of adsorbed arsenate species as functions of environmental parameters. However, the complexation reactions have not always been consistent with in-situ spectroscopic results. Instead, with the exception of the study by Hiemstra and Van Riemsdijk (1999), regression of macroscopic adsorption data has often been carried out merely to fit the data with the minimum number of surface species (Hering and Dixit, 2005). It is now widely recognized that the evidence of oxyanion speciation from spectroscopic studies should be integrated with models describing macroscopic adsorption data (Blesa et al., 2000; Goldberg and Johnston, 2001; Hiemstra and van Riemsdijk, 1999; Suarez et al., 1997).

The recently developed dipole modification of the triple-layer model (ETLM, Sverjensky and Fukushi 2006a) is capable of independently predicting surface speciation as functions of pH, ionic strength and surface coverage consistent with spectroscopic results for wide ranges of experimental conditions and different types of oxides. This is possible because the ETLM takes into account a previously neglected phenomenon integral to inner-sphere surface complexation reactions: the electrostatic work associated with desorption of the water dipoles displaced from a charged surface by the ligand exchange mechanism. It has
been shown that the magnitude of the electrostatic work associated with this dipole modification to the TLM is substantial and depends only on the stoichiometry of the surface reaction. No new fitting parameters are involved. As a result, the sensitivity of the ETLM to predicting alternate speciation schemes is enhanced. When the structures of adsorbed anions established in spectroscopic studies and theoretical molecular calculations are used to calibrate models of bulk adsorption data, the models then independently predict the proportions of surface species as function of pH, ionic strength and surface coverage. The predicted surface speciation with changes in environmental parameters compares very favorably with the results of in situ spectroscopic studies. The applicability of this model to a range of oxyanion adsorption including sulfate, selenate, oxalate and arsenite on a wide variety of oxides is being investigated (Fukushi and Sverjensky, 2006; Sverjensky and Fukushi, 2006; Sverjensky and Fukushi, 2006).

In the present study, we use the results of the in situ X-ray and infrared studies to guide the choice of surface species in our application of the ETLM to a wide variety of surface chemical measurements for arsenate. These include adsorption envelope, adsorption isotherms, proton surface titration in the presence of arsenate, and proton coadsorption with arsenate on a wide range of oxides including goethite, hydrous ferric oxide (HFO), ferrihydrite, hematite, amorphous aluminum oxide, β-Al(OH)$_3$, α-Al(OH)$_3$ and α-Al$_2$O$_3$ (Arai et al., 2001; Arai et al., 2004; Dixit and Hering, 2003; Gao and Mucci, 2001; Goldberg and Johnston, 2001; Halter and Pfeifer, 2001; Jain and Loeppert, 2000; Jain et al., 1999; Manning and Goldberg, 1996). The main purpose of the study is to
determine the effects of pH, ionic strength, surface coverage and type of solid on the surface speciation of arsenate. The results are then compared with independent trends established in X-ray and infrared spectroscopic studies for arsenate and phosphate. The calculations summarized below show the surface species selected in this way can be applied to all the available arsenate surface chemical measurements. A second goal of the present study is to provide a predictive basis for arsenate surface speciation on oxides. Systematic differences in the equilibrium constants for the surface arsenate species from one oxide to another can be established and explained with the aid of Born solvation theory. This makes it possible to predict arsenate adsorption and surface speciation on all oxides in simple electrolyte systems.

2. ETLM TREATMENT OF ARSENATE ADSORPTION

2.1 Aqueous speciation, surface protonation and electrolyte adsorption

Aqueous speciation calculations were carried out taking into account aqueous ionic activity coefficients appropriate to single electrolytes up to high ionic strengths calculated with the extended Debye-Hückel equation (Criscenti and Sverjensky, 1999; Helgeson et al., 1981). Electrolyte ion pairs used were consistent with previous studies (Criscenti and Sverjensky, 1999; Criscenti and Sverjensky, 2002). Aqueous arsenate protonation equilibria were taken from a recent study (Nordstrom and Archer, 2003).

\[
\begin{align*}
\text{H}^+ + \text{H}_2\text{AsO}_4^- &= \text{H}_3\text{AsO}_4^6; \quad \log K = 2.30 \\
\text{H}^+ + \text{HAsO}_4^{2-} &= \text{H}_2\text{AsO}_4^-; \quad \log K = 6.99
\end{align*}
\]
\[
\text{H}^+ + \text{AsO}_4^{3-} = \text{HAsO}_4^{2-}; \quad \log K = 11.8 \quad (3)
\]

The sample characteristics and surface protonation and electrolyte adsorption equilibrium constants used in the present study are summarized in Table 1. Although HFO and ferrihydrite might be thought to have extremely similar surface chemical properties, we distinguish between them when there is a significant difference in pH_{ZPC} (7.9 and 8.5, respectively), as discussed in our previous paper (Sverjensky and Fukushi, 2006). Taking account of the difference in pH_{ZPC} in terms of different effective dielectric constants has enabled explanation of the difference in arsenite adsorption characteristics of these two solids. HFO, with the higher effective dielectric constant, has a negligible Born solvation energy opposing adsorption. Consequently, the arsenite adsorption equilibrium constants on HFO are stronger than on ferrhydrite (or other ferric oxides and oxyhydroxides), It will be shown below that the same approach works for differences in arsenate adsorption. Surface protonation constants referring to the site-occupancy standard states (denoted by the superscript “θ”), i.e. \( \log K_1^θ \) and \( \log K_2^θ \), were calculated from values of \( pH_{ZPC} \) and \( \Delta pK_θ^θ \) (Sverjensky, 2005) using
\[
\log K_1^θ = pH_{ZPC} - \frac{\Delta pK_θ^θ}{2} \quad (4)
\]
\[
\text{and} \quad \log K_2^θ = pH_{ZPC} + \frac{\Delta pK_θ^θ}{2} \quad (5)
\]
Values of \( pH_{ZPC} \) were taken from measured low ionic strength isoelectric points or point-of-zero-salt effects corrected for electrolyte adsorption (Sverjensky, 2005). For goethite and HFO examined by Dixit and Hering (2003), neither isoelectric points nor surface titration data were reported. The value of \( pH_{ZPC} \) for
the goethite was predicted for the present study using Born solvation and crystal chemical theory (Sverjensky, 2005). For HFO, the $pH_{ZPC}$ was assumed to be the same as in Davis and Leckie (1978), consistent with our previous analysis for arsenite adsorption on the same sample of HFO (Sverjensky and Fukushi, 2006). Values of $\Delta pK_a$ were predicted theoretically (Sverjensky, 2005).

For convenience, protonation constants referring to the hypothetical 1.0 molar standard state (denoted by the superscript "0") are also given in Table 1. The relationship between the two standard states is given by (Sverjensky, 2003)

$$\log K_1^0 = \log K_1^0 - \log \left( \frac{N_S A_S}{N_A^1 A_F^1} \right)$$  \hspace{1cm} (6)

$$\log K_2^0 = \log K_2^0 + \log \left( \frac{N_S A_S}{N_A^1 A_F^1} \right)$$  \hspace{1cm} (7)

where,

$N_S$ represents the surface site density on the $s$th solid sorbent (sites.m$^{-2}$)

$N_F^1$ represents the standard state sorbate species site density (sites.m$^{-2}$)

$A_S$ represents the BET surface area of the $s$th solid sorbent (m$^2$.g$^{-1}$)

$A_F^1$ represents a standard state BET surface area (m$^2$.g$^{-1}$)

In the present study, values of $N_F^1 = 10 \times 10^{18}$ sites.m$^{-2}$ and $A_F^1 = 10 m^2.g^{-1}$ are selected for all solids.

Electrolyte adsorption equilibrium constants referring to site-occupancy standard states, $\log K_M^\phi$, and $\log K_L^\phi$, and capacitances, $C_1$, were obtained from regression of proton surface charge data when such data were available. Otherwise, these parameters were obtained from theoretical predictions (Sverjensky, 2005). For convenience, Table 1 also contains values of the
electrolyte adsorption equilibrium constants relative to the \( > \text{SOH} \) species (denoted by the superscript “*”) and with respect to the hypothetical 1.0 molar standard state, i.e. \( \log^* K^0_M \) and \( \log^* K^0_L \). The relationships of \( \log^* K^0_M \) and \( \log^* K^0_L \) to \( \log K^\theta_M \) and \( \log K^\theta_L \) are given by (Sverjensky, 2003, 2005)

\[
\log^* K^0_M = \log K^\theta_M - pH_{ZPC} - \Delta pK^\theta_n - \log \left( \frac{N_S A_S}{N^* A^*} \right) \tag{8}
\]

\[
\log^* K^0_L = \log K^\theta_L + pH_{ZPC} - \Delta pK^\theta_n - \log \left( \frac{N_S A_S}{N^* A^*} \right) \tag{9}
\]

Surface areas \( (A_S) \) were taken from experimental measurements (BET) for goethite, \( \alpha\text{-Al(OH)}_3 \), \( \beta\text{-Al(OH)}_3 \) and \( \alpha\text{-Al}_2O_3 \). However, for samples of HFO, ferrihydrite and am. AlO, it was assumed that the surface areas are 600 m\(^2\)g\(^{-1}\) consistent with our previous analyses of arsenite and sulfate adsorption on these oxides.

Site densities \( (N_S) \) together with arsenate adsorption equilibrium constants were derived from regression of adsorption data, where these data referred to a wide enough range of surface coverage. This procedure was adopted because oxyanions probably form inner-sphere complexes on only a subset of the total sites available, most likely the singly coordinated oxygens at the surface (Catalano et al., 2006a-d; Hiemstra and Van Riemsdijk, 1996, 1999). Theoretical estimation of these site densities is impossible for powdered samples when the proportions of the crystal faces are unknown, as is the case for all the experimental studies analyzed below. Furthermore, for goethites, surface chemical characteristics vary widely, even for those synthesized in the absence of CO\(_2\) (Sverjensky, 2005). Together with site densities for goethites already
published (Sverjensky and Fukushi, 2006a, b), the goethite site densities obtained by regression in the present study, with one exception, support an empirical correlation between site density and surface area of goethite (Fukushi and Sverjensky, 2006). This correlation should enable estimation of site densities for those goethites for which oxyanion adsorption data over a wide range of surface coverage are not available. In the cases of arsenate adsorption on HFO, ferrihydrite, goethite from Dixit and Hering (2003), and β-Al(OH)₃ and am.AlO, the site densities were taken from our previous regression of arsenite adsorption data (Sverjensky and Fukushi, 2006b).

For simplicity, we used a single site density for each sample applied to all the surface equilibria: oxyanion, surface protonation and electrolyte equilibria. This is possible because the predicted surface protonation and electrolyte adsorption equilibrium constants summarized above (e.g. from Sverjensky, 2005) refer to site-occupancy standard states independent of the site densities and surface areas of actual samples. They can be transformed to equilibrium constants referring to individual sample characteristics (e.g. the hypothetical 1.0 M standard states) using relationships such as Eqns. (6) - (9) above. All the calculations reported here were carried out with the aid of the computer code GEOSURF (Sahai and Sverjensky, 1998). However, any code that treats a triple-layer model could also be used for the ETLM calculations reported in the present paper because the water dipole correction described below only affects how the electrostatic factor for inner-sphere arsenate complexes is formulated.
2.2 Arsenate adsorption reaction stoichiometries

We constructed our ETLM for arsenate adsorption on oxides by choosing surface species based on the *in situ* X-ray and infrared spectroscopic studies of phosphate and arsenate and the molecular calculations for arsenate interaction with metal oxide clusters. We used three reaction stoichiometries expressed as the formation of inner-sphere surface species as illustrated in Fig. 1. These three reactions produce surface species that are identical to the ones proposed to account for the *in situ* ATR-FTIR study of phosphate adsorption on goethite (Tejedor-Tejedor and Anderson, 1990), but are also consistent with the X-ray studies cited above.

The three reactions produce a deprotonated bidentate-binuclear species according to

\[
2 > \text{SOH} + H_3\text{AsO}_4^0 = (\text{SO})_2\text{AsO}_2^- + H^+ + 2H_2O
\]  

(10)

\[
^*K_{(\text{SO})_2\text{AsO}_2^-}^\theta = \frac{a_{\text{SOH}} a_{H^+}^2}{a_{H_3\text{AsO}_4^0}} \frac{F(\Delta\Psi,r)_{\text{SOH}}}{2.303RT}
\]  

(11)

a protonated bidentate-binuclear species according to

\[
2 > \text{SOH} + H_3\text{AsO}_4^0 = (\text{SO})_2\text{AsOOH} + 2H_2O
\]  

(12)

\[
^*K_{(\text{SO})_2\text{AsOOH}}^\theta = \frac{a_{\text{SOH}} a_{H^+}^2}{a_{H_3\text{AsO}_4^0}} \frac{F(\Delta\Psi,r)_{\text{SOH}}}{2.303RT}
\]  

(13)

and a deprotonated monodentate species according to

\[
> \text{SOH} + H_3\text{AsO}_4^0 => \text{SOAsO}_3^{2^-} + 2H^+ + H_2O
\]  

(14)

\[
^*K_{\text{SOAsO}_3^{2^-}}^\theta = \frac{a_{\text{SOAsO}_3^{2^-}} a_{H^+}^2}{a_{\text{SOH}} a_{H_3\text{AsO}_4^0}} \frac{F(\Delta\Psi,r)_{\text{SOH}}}{2.303RT}
\]  

(15)
Here the superscript \(^{\theta}\) again represents site-occupancy standard states (Sverjensky, 2003, 2005). The exponential terms contain an electrostatic factor, \(\Delta \Psi\), which is a reaction property arising from the work done in an electric field when species in the reaction move on or off the charged surface. With the ETLM, \(\Delta \Psi\) is evaluated taking into account the adsorbing ions and the water dipoles released in Eqns. (10), (12) and (14) (Sverjensky and Fukushi, 2006). The ions experience changes in potential relative to the bulk solution depending on which plane they are placed. Similarly, the water molecule(s) released in the above reactions must also experience a change in potential because they are dipoles leaving a charged surface. Electrostatic work is done in both instances and is reflected in the formulation of \(\Delta \Psi\).

We place the charge of the adsorbing protons on the 0-plane and the charge of the oxyanion on the \(\beta\)-plane. This is a departure from the practice of placing the oxyanion charge on the 0-plane for inner-sphere complexes in the TLM (Hayes et al., 1988). In our calculations, with the dipole modification and the arsenate or protonated arsenate charge on the \(\beta\)-plane, the ETLM is able to describe arsenate adsorption data of all kinds. As noted below, the same location for the charge has recently been used for arsenate adsorption on hematite (Arai et al., 2004). For the sake of completeness, we have also included in the present paper some model calculations in which the arsenate or protonated arsenate are placed on the 0-plane (as originally advocated by Hayes et al.) in conjunction with our dipole correction. This approach results in very poor fits to adsorption and surface proton titration data (see below).
In the ETLM, the water dipole(s) leaving the charged surface experience a change in potential equal to \(-n(\psi_0 - \psi_{\beta})\) where \(n\) is the number of desorbed waters per reaction. For the reactions in Eqns. (11), (13) and (15), this results in

\[
\Delta\psi_{r,11} = 2\psi_0 - 3\psi_{\beta} - 2(\psi_0 - \psi_{\beta}) = -\psi_{\beta}
\]

\[
\Delta\psi_{r,13} = 2\psi_0 - 2\psi_{\beta} - 2(\psi_0 - \psi_{\beta}) = 0
\]

\[
\Delta\psi_{r,15} = \psi_0 - 3\psi_{\beta} - (\psi_0 - \psi_{\beta}) = -2\psi_{\beta}
\]

Interestingly, Eqn. (16) is the same overall result for \(\Delta\psi_r\) as found in a recent study using the CD-TLM approach for arsenate on hematite (Arai et al., 2004). In the latter study, it was found by regression of adsorption data that \(\Delta\psi_{10} = -\psi_{\beta}\) fitted the data better than alternate fractional distributions of charge. We have the same preferred form for \(\Delta\psi_{r,10} = -\psi_{\beta}\), but we explain it in terms of the dipole correction to the TLM without the need for a CD approach.

We wish to emphasize here that alternate states of arsenate reaction stoichiometry could not fit the bulk arsenate adsorption data. Having said this, it is still true that surface species in addition to those given in Fig. 1 may be present in the real systems, but difficult to detect using surface complexation models. This possibility arises when two different surface species have extremely similar, if not identical, reaction stoichiometries. For example, a bidentate-mononuclear arsenate species (suggested by some X-ray studies, see above) is clearly not included in Fig. 1. However, such a species could have a reaction stoichiometry such as

\[
> \text{S(OH)}_2 + \text{H}_3\text{AsO}_4^+ = > \text{SO}_2\text{AsO}_4^- + \text{H}^+ + 2\text{H}_2\text{O}
\]
which is so similar to that in Eqn. (10) that it would be difficult to detect the difference in a surface complexation model without examining data referring to a very wide range of surface coverages. Another possible reaction stoichiometry for a bidentate-mononuclear species would be

$$\text{SOH} + \text{H}_2\text{AsO}_4^\delta + 2\text{H}^+ + \text{H}_2\text{O}$$

(20)

which has the same reaction stoichiometry as that in Eqn. (14). However, the reaction in Eqn. (20) involves a coordination increase for the surface metal, which may be detectable through the comparison of theoretical molecular calculations with infrared data (e.g. Yoon et al., 2004).

Another interesting possibility involves outer-sphere or H-bonded surface species. All the above arsenate surface reactions involve inner-sphere species. Until recently, no outer-sphere or H-bonded surface species for arsenate had been detected in experimental spectroscopic studies. The recent reports of such a species (Catalano et al., 2006a and b) are of great interest because they bring arsenate surface speciation in line with almost all other oxyanions for which both inner- and outer-sphere (or H-bonded) species have been reported. In our study, we have examined many possible speciation schemes involving different inner- and outer-sphere (or H-bonded) species for consistency with the bulk adsorption data, and have only come up with one possible reaction stoichiometry for an outer-sphere or H-bonded species given by

$$2 \text{SOH} + \text{H}_2\text{AsO}_4^\delta = (\text{SOH})_2\text{AsO}_2(OH)_2 + \text{H}^+$$

(21)

$$K^0_{(\text{SOH})_2\text{AsO}_2(OH)_2} = \frac{a_{\text{SOH}} a_{\text{H}_2\text{AsO}_4^\delta} a_{\text{H}^+}}{a_{(\text{SOH})_2\text{AsO}_2(OH)_2} a_{\text{H}_2\text{AsO}_4^\delta} 10^{\frac{1.14}{2.303RT}}}$$

(22)
It can be seen that Eqn. (21) differs from Eqn. (10) only by the release of two waters in the latter reaction. For example, subtracting Eqn. (21) from (10) gives

\[ (>\text{SOH})_2\text{AsO}_4\text{(OH)}_2^- = (>\text{SO})_2\text{AsO}_4^- + 2\text{H}_2\text{O} \]  

(24)

\[ K^o = \frac{a_{(>\text{SO})_2\text{AsO}_4^-}}{a_{(>\text{SOH})_2\text{AsO}_4^-}a_{\text{H}_2\text{O}}} \]  

(25)

Based on Eqns. (24) and (25), it can be expected that the relative activities of the two arsenate surface species will be a function of the activity of water only. The ratio should be independent of pH and surface loading. It is interesting to note that preliminary experimental studies indicate that the ratio of the inner- and outer-sphere arsenate surface species is experimentally insensitive to the arsenate concentration in solution (Catalano et al., 2006b), which is consistent with Eqns. (24) and (25). Large variations in ionic strength might affect the activity of water, and hence the relative activities of the arsenate species, but would still be difficult to detect by surface complexation modeling. Overall, we wish to emphasize that it is the relative importance of the three reaction stoichiometries in Fig. 1 that we can establish in our analysis of bulk experimental data. Additional surface species such as those described above may also be present in experimental systems, but would require additional experimental results to establish their relative importance.

The relationships of the site-occupancy standard states to the hypothetical 1.0 M standard state for the arsenic surface species are given by

\[ \log^* K^o_{(>\text{SO})_2\text{AsO}_4^-} = \log^* K^o_{(>\text{SO})_2\text{AsO}_4^-} + \log \left( \frac{(N_{\text{As}})^2}{N^2A^2} \cdot C_b \right) \]  

(26)
\[
\log^r K^\theta_{(\text{SO}_2\text{AsOOH})} = \log^r K^\theta_{(\text{SO}_2\text{AsOOH})} + \log\left(\frac{(N_8A_8)^2}{N^rA^r}\right) C_S \tag{27}
\]

\[
\log^r K^\theta_{\text{SO}_2\text{AsOOH}^2} = \log^r K^\theta_{\text{SO}_2\text{AsOOH}^2} + \log\left(\frac{N_8A_8}{N^rA^r}\right) \tag{28}
\]

where \(C_S\) denotes solid concentration (\(g/L\)).

The equilibrium constants represented relative to the species \(\text{SO}_2\text{H}^+\), expressed by the superscript \(**\) in Eqns. (11), (13) and (15), depend on the 
\(pH_{ZPC}\) and \(\Delta pK^\theta_n\) of solid samples. It is convenient to correct for differences in the 
\(pH_{ZPC}\) and \(\Delta pK^\theta_n\) with the following equations (Sverjensky, 2005):

\[
\log K^\theta_{(\text{SO}_2\text{AsOOH})} = -\log^r K^\theta_{(\text{SO}_2\text{AsOOH})} - 2pH_{ZPC} + \Delta pK^\theta_n \tag{29}
\]

\[
\log K^\theta_{(\text{SO}_2\text{AsOOH}^2)} = -\log^r K^\theta_{(\text{SO}_2\text{AsOOH}^2)} - 2pH_{ZPC} + \Delta pK^\theta_n \tag{30}
\]

\[
\log K^\theta_{\text{SO}_2\text{AsOOH}^2} = -\log^r K^\theta_{\text{SO}_2\text{AsOOH}^2} - pH_{ZPC} + \frac{\Delta pK^\theta_n}{2} \tag{31}
\]

The resultant values of \(K^\theta_{(\text{SO}_2\text{AsOOH})}\), \(K^\theta_{(\text{SO}_2\text{AsOOH}^2)}\) and \(K^\theta_{\text{SO}_2\text{AsOOH}^2}\) are independent of the 
site density, surface area or solid concentration of the specific samples, as well as the 
\(pH_{ZPC}\) and \(\Delta pK^\theta_n\) used in the experiments. Values of the logarithms of the 
above equilibrium constants are summarized in Table 2.

### 3. APPLICATION TO ARSENATE ADSORPTION

#### 3.1 Adsorption of arsenate on goethite from Dixit and Hering (2003), Gao and Mucci (2003), Antelo et al. (2005) and Manning and Goldberg (1996)

The adsorption data depicted in Figs. 2a and b refer to arsenate adsorption envelopes over a range of surface coverages and an adsorption isotherm on goethite at a single ionic strength (Dixit and Hering, 2003). The solid
curves in Figs. 2a and b represent regression calculations using the three reactions given in Fig. 1. It should be emphasized that the site density used in the present calculations was not a regression parameter. Only the three equilibrium constants were regression parameters. The site density was taken from independent ETLM analysis of arsenite adsorption on the same goethite (Sverjensky and Fukushi, 2006a, b). It can be seen in Fig. 2a that the solid curves provide a close description of the arsenate adsorption data over a wide range of pH and surface coverage (error bars are not reported in the study by Dixit and Hering, 2003).

The solid points in Fig. 2b represent the two highest surface coverages at pH = 4 in Fig. 2a (50μM and 100μM of arsenate). The two lowest coverage data are not included in Fig. 2b because of high uncertainties of the aqueous arsenate concentrations near 100% adsorption. It can be seen in Fig. 2b that although the model calculation provides a close description of much of the isotherm data, it systematically underestimates the amount of adsorbed arsenate at surface coverages above approximately $10^{-5.6}$ moles.m$^{-2}$ (2.5 μmoles.m$^{-2}$). Under these conditions, arsenate apparently accumulates at the surface through processes other than adsorption alone, for example surface precipitation, surface polymerization, or diffusion into the structure (Jain et al., 1999; Jia et al., 2006; Raven et al., 1998; Stanforth, 1999; Zhang and Stanforth, 2005).

The predicted surface speciation as a function of pH and surface coverage at the highest and lowest arsenate concentrations in Fig. 2a can be seen in Figs. 2c and d. These predictions serve as a test of the model which can be compared with qualitative trends in speciation with pH and surface coverage defined
spectroscopically which were not used in the regression calculations. In Fig. 2c, which refers to a relatively high surface coverage, 2.2 μmoles.m⁻² at 60% adsorption, the protonated bidentate-binuclear species is predicted to predominate at the lowest pH values of 3 to 5, and the deprotonated bidentate-binuclear species at pH values of 5 to 8. This agrees remarkably well with the trends from an early in situ FTIR study of phosphate on goethite at surface coverages of about 1.9 to 2.3 μmoles.m⁻² (Tejedor-Tejedor and Anderson, 1990). These authors inferred a protonated bidentate-binuclear species at pH = 3.6 to 5.5 - 6.0 and a deprotonated bidentate-binuclear species between pH values of about 6 to 8.3. 

It can also be seen in Fig. 2c that the relative importance of the mononuclear species increases with pH and it predominates at pH values of 9 to 10. At the lower surface coverage of Fig. 2d, 0.37μmoles.m⁻² at 100% adsorption, it can be seen that the mononuclear species is predicted to dominate from pH values of about 4.5 to 10. Both trends are consistent with inferences about the relative importance of the mononuclear species from EXAFS and IR spectroscopy as a function of oxyanion loading and pH (Fendorf et al., 1997; Tejedor-Tejedor and Anderson, 1990; Waychunas et al., 1993). It is also interesting that Farquhar et al (2002) and Sherman and Randall (2003) did not find the mononuclear species in their EXAFS spectra. However, Farquhar et al. obtained their spectra for adsorption conditions of pH = 5.5 - 6.5 and coverage of 6 μmoles.m⁻², and Sherman and Randall used adsorption conditions of pH = 3.9 and 1 μmoles.m⁻². Under these conditions, the present calculations indicate
that the mononuclear species should not be important compared to the bidentate-binuclear species.

Overall, the predictions depicted in Figs. 2c and d agree very well with the speciation trends indicated by the above in situ FTIR and X-ray studies of phosphate and arsenate on goethite, which provides strong support for the model reactions proposed in Fig. 1. Similar predicted trends of surface speciation were found using the CD model approach for phosphate surface complexation on goethite (Hiemstra and Van Riemsdijk, 1999).

The data in Fig. 2a also permit a test of an alternate approach to the surface complexation modeling described above. If instead of placing the charge of the arsenate or biarsenate ion on the β-plane, it is placed on the 0-plane, in conjunction with the same water dipole correction described above, the values of \( \Delta \Psi_i \) in Eqns. (11), (13) and (15) become equal to \(-3\Psi_o - 2\Psi_\beta\), \(-2\Psi_o - 2\Psi_\beta\), and \(-3\Psi_o + \Psi_\beta\), respectively (footnote in Table 2). The results of applying this approach to the adsorption data are depicted in Fig. 2e. The calculated model curves in Fig. 2e do not have the correct shape to fit the data adequately (another example of the poor model behavior associated with the 0-plane assumption is given below). The predicted surface speciation for the highest surface coverage in Fig. 2e is shown in Fig. 2f. It can be seen that the predominant species is the mononuclear species, in contrast to the corresponding ETLM calculation shown in Fig. 2c.

Figures 3a and b show the proton surface titration and arsenate adsorption data on goethite at much higher ionic strength from Gao and Mucci
(2001). The solid curves in Fig. 3b represent regression calculations with the ETLM again using the surface species from Fig. 1. In these calculations, the site density was retrieved together with the three equilibrium constants for arsenate adsorption. Predicted surface speciation plots are shown in Figs. 3c and d for the highest and lowest surface coverages from Fig. 3b. It can be seen in Figs. 3c and d that the deprotonated bidentate species is dominant except at the highest and lowest pH conditions. As in Figs. 2c and d, the protonated bidentate-binuclear species becomes important at low pH conditions whereas the importance of the monodentate species increases with pH and decreases with surface coverage. However, in contrast to the goethite in Figs. 2c and d, the mononuclear species in Figs. 3c and d is dominant only at pH values above 9. A direct comparison between the Dixit and Hering goethite and the Gao and Mucci goethite can be made using Figs. 2d and 3e, which are constructed for the same ionic strength and surface coverage. It can clearly be seen that the predicted surface speciations for the two goethites differ significantly (see below).

Experimental surface titration and arsenate adsorption isotherm data for a third goethite from Antelo et al. (2005) are depicted in Figs. 4a - c. Experimental uncertainties are not cited by the authors for these data, nevertheless it can be seen in Figs. 4b and c that the solid regression curves generated in the present study provide a representation of the data within about 10%. In these calculations again, the site density and the equilibrium constants for arsenate adsorption were all obtained. The predicted speciation plots in Figs. 4d - f. show a marked predominance of the monodenate-mononuclear species at high pH values. In particular, Fig. 4f was constructed to represent the same conditions as in Figs. 2d
and 3e in order to directly compare the three goethites. It can be seen in Fig. 4f that the Antelo et al. goethite shows an extremely high predominance of the mononuclear species. In this regard, it forms an end-member for the goethites analyzed in the present study. It is interesting to note that such behavior has been reported recently in ATR-FTIR spectroscopic studies of phosphate and arsenate on goethite (Loring et al., 2006; Nelson et al., 2006).

Experimental arsenate adsorption data for a fourth goethite (Manning and Goldberg, 1996) are depicted in Fig. 5a. The solid curves in Fig. 5a again represent regression calculations using the reactions in Fig. 1. In these calculations, a predicted site density was used based on the linear correlation between site density and BET surface area for goethites developed previously and shown in Fig. 6 (Fukushi and Sverjensky, 2006). It can be seen in Fig. 5a that the calculated curve for the higher arsenate concentration results in a significant underestimation of the amount adsorbed at pH values less than 4.5, which may indicate the need for an additional surface species of arsenate. In contrast, the calculated curve for the lower arsenate concentration slightly overestimates the amount adsorbed at pH values above 9.

Predicted speciation plots for the goethite studied by Manning and Goldberg (1996) are shown in Figs. 5b - d. It can be seen in Figs. 5b. and c. that the surface speciation for this goethite is similar to that shown above for the Dixit and Hering goethite. A more accurate comparison can be made with the aid of Fig. 5d, where the surface coverage and ionic strength are the same as in Fig. 2d. The speciation in Fig. 5d is actually intermediate between the speciation for
that shown in Fig. 2d and the Antelo et al. goethite in Fig. 4f, although it is closer to the speciation in Fig. 2d.

In summary, our model speciation results for the behavior of arsenate adsorption on the four goethites studied here vary quite markedly. A spectrum of speciation behavior is apparent. Two out of the four goethites (from Dixit and Hering, and Manning and Goldberg) have similar calculated surface speciation in that both the binuclear and mononuclear arsenate species play important roles, depending on the conditions under consideration. Furthermore, for these two goethites, the calculated trends in speciation with pH and surface coverage agree well (qualitatively) with the trends inferred from the in situ study of a goethite by Tejedor-Tejedor and Anderson (1990) and are consistent with the trends and specific conditions associated with EXAFS results for goethites studied by Waychunas et al. (1993), Farquhar et al. (2002), and Sherman and Randall (2003). However, on the Gao and Mucci goethite the model surface speciation indicates a much greater importance of the binuclear surface species than for the other goethites. In contrast, on the Antelo et al. goethite, the mononuclear species is predicted to be dominant. Consequently, the spectrum of speciation runs from dominantly binuclear to dominantly mononuclear. If we consider the goethites of Dixit and Hering, Manning and Goldberg, Tejedor-Tejedor and Anderson, Waychunas et al., Farquhar et al., and Sherman and Randall as a compatible group, it would appear that many goethites are clustered in the middle of the overall spectrum of behavior, where either binuclear or mononuclear species can predominate depending on the conditions under consideration.
Further comparisons of the different goethites can be made in terms of site densities derived for arsenate adsorption in the present study. It can be seen in Fig. 6 that the Dixit and Hering, Manning and Goldberg, Gao and Mucci and Antelo goethites have site densities close to or on the correlation with surface area depicted by the solid line. The site density used in the present study for the Dixit and Hering goethite is identical to that for the arsenite calculations for this goethite (Table 2). The site density used for the Manning and Goldberg goethite was predicted from the correlation line in Fig. 6. However, the site densities for the Gao and Mucci and the Antelo et al. goethites were retrieved by regression calculations in the present study. All four are therefore in reasonable agreement with the additional data shown on the plot derived from regression of sulfate and arsenite adsorption data. The negative slope of the line in Fig. 6 is qualitatively consistent with results for another oxyanion, carbonate, on goethites with different surface areas (Villalobos et al., 2003).

The differences of site densities and/or equilibrium constants for the goethites may result from fundamental differences in sample characteristics for each goethite. For example, if arsenate only adsorbs on singly coordinated oxygen groups, e.g. \( > O_4FeO(H) \) or \( > O_5FeO(H) \) groups (Catalano et al., 2006a-d), the availability of these groups will depend on the proportions of different faces making up the surface area of the goethite samples. Unfortunately, the proportions of different crystal faces for the goethite samples in Fig. 6 are not known. However, significant differences have been demonstrated for two goethites with different surface areas (Gaboriaud and Ehrhardt, 2003). On the lower surface area goethite (49 m²g⁻¹), the (001) face was much more abundant.
than the (101) face (Pnma space group). On the higher surface area goethite (95 m²g⁻¹), the reverse distribution was found. The (001) face of goethite has a site density for singly-coordinated oxygens of 3.3 sites.nm⁻² (Koretsky et al., 1998). However, if we assume that the (001) face is faceted with (210) faces (Weidler et al., 1996), which have a site density of 7.4 sites.nm⁻², then the overall site density for the faceted (001) surface may approach 6 to 7 sites.nm⁻², depending on the degree of faceting. In contrast, the (101) face has a much lower site density (e.g. 3.0 sites.nm⁻², Hiemstra and Van Riemsdijk, 1996). As a consequence, a goethite with a high proportion of faceted (001) surfaces relative to (101) surfaces should have a relatively high site density of singly-coordinated oxygens, i.e. the 49 m²g⁻¹ sample referred to above should have a higher site density than the 95 m²g⁻¹ sample. Qualitatively, this could explain the negative slope of the line in Fig. 6. Further work in characterizing all the faces on goethite samples with different surface areas is clearly needed.

Our previous ETLM analyses for sulfate and selenate adsorption on goethite showed that there were also significant differences in site density and \( \log K^\theta \) values for different goethites (Fukushi and Sverjensky, 2006). Some of these differences were attributed to contamination by atmospheric carbonate and/or amorphous hydrous ferric oxides during the synthesis of the specimen which could change the fundamental surface characteristics of the goethites.

### 3.2 Adsorption of arsenate on HFO from Dixit and Hering (2003)

The adsorption data depicted in Figs. 7a and b refer to arsenate adsorption edges and an isotherm on HFO, respectively (Dixit and Hering, 2003).
The solid curves in Figs. 7a and b represent regression calculations using the three reactions in Fig. 1 and a site density taken from regression calculations for arsenite on the same HFO sample. It can be seen that the calculated curves provide a close description of the arsenate adsorption data over a range of pH and surface coverage except at the conditions of the lowest pH and highest surface coverages (Figs. 7a and b). At pH = 4 and surface coverages greater than 2.8 μmoles.m⁻² the calculated curves underestimate the amount of arsenic at the surface. This could indicate the need for an additional surface species. However, the isotherm result is very similar to the goethite case discussed above, which was attributed to surface precipitation, polymerization or diffusion in the bulk structure. Jia et al. (2006) have documented surface precipitation of arsenate on ferrihydrite by means of X-ray diffraction and Raman spectroscopy. They showed that surface precipitation of ferric arsenate occurred at pH values of 3 to 5 and surface surface coverages of 2.4 - 9.3 μmoles.m⁻², which is in excellent agreement with our estimate of the limit of adsorption based on the ETLM calculations in Figs. 7a and b.

The predicted model speciation of arsenate on HFO surfaces is given in Figs. 7c and d for the highest and lowest surface coverages of Fig 7a, respectively. For both surface coverages, it can be seen that the bidentate-binuclear species dominate at pH values less than about 8 to 9. Comparing Fig. 7c with d, it can be seen that the importance of the mononuclear species increases with decrease of surface coverage, which is consistent with the trend indicated by EXAFS spectroscopy of arsenate adsorption on poorly crystalline iron oxide as a function of arsenate coverage (Waychunas et al., 1993). The
protonated bidentate-binuclear species becomes important at low pH values, consistent with IR spectroscopy of phosphate adsorption on poorly crystalline iron oxide (Arai and Sparks, 2001).

3.3 Adsorption of arsenate on ferrihydrite from Jain et al (1999) and Jain and Loeppert (2000)

A much greater variety of experimental data types are depicted in Figs. 8a-c. These include proton surface charge in the absence and presence of arsenic (Fig. 8a), proton coadsorption with arsenic at two fixed pH values (Fig. 8b), and percent arsenic adsorption (Fig. 8c). Although the uniqueness of surface species for surface complexation modeling has been questioned when only macroscopic percent adsorption data are modeled (Hering and Dixit, 2005), the great variety of types of data in Figs. 8a - c provide strong constraints on the reaction stoichiometries of the arsenate surface species. The solid curves in Figs. 8a - c represent regression calculations again using the three reactions in Fig. 1 and the same site density used previously for arsenite calculations for this sample (Table 1). It can be seen that the solid curves represent a reasonable fit to the data in Fig. 8a - c. Only data represented by the solid symbols were regressed in Fig. 8b. Data at higher surface coverages presumably represent processes in addition to adsorption.

The dashed curves in Figs. 8a and c represent the alternative approach of placing the arsenate on the 0-plane, as described above for Fig. 2e (see the footnotes to Table 3). This approach is clearly inconsistent with the trends represented by the data.
The predicted surface speciation of arsenate on the surface of ferrihydrite is given in Fig. 8d for the higher surface coverage of Fig 8c. It is predicted that the deprotonated bidentate-binuclear species is dominant for most pH conditions. However, the importance of the mononuclear species is again predicted to increase with pH similar to HFO and consistent with EXAFS and IR spectroscopic results for HFO (Arai et al., 2001; Waychunas et al., 1993).

3.4 Adsorption of arsenate on amorphous aluminum oxide (am.AIO) from Goldberg and Johnston (2001)

The data depicted in Fig. 9a show arsenate adsorption envelopes on am.AIO as functions of pH, ionic strength and surface coverage. The solid curves in Fig. 9a represent regression calculations using the three reactions in Fig. 1 and the same site density used previously for arsenite calculations for this sample (Table 1). The calculated curves provide a close description of the arsenate adsorption data. In addition to the adsorption data, Goldberg and Johnston (2001) measured electrophoretic mobilities of am.AIO with and without arsenic to obtain the effect of arsenic on the isoelectric point. The experimental isoelectric points are 9.4 (no arsenic), 9.4 (0.01 mM As) and 6.5 (1mM As). Using the extended triple-layer model, the isoelectric point is predicted to shift strongly from 9.4 to 6.5 and 2.3. Although too large, these shifts are in qualitative agreement with the direction of the experimental shifts with As loading.

The predicted model speciation of arsenate on the surface of am.AIO is given in Figs. 9b – d for I = 0.01 and I = 1.0 for 4g.L\(^{-1}\) as well as I = 1.0 for 0.5 g.L\(^{-1}\) from Fig. 9a. It can be seen in Figs. 9b –d that the bidentate-binuclear
species dominates for all pH values less than about 10. It is noteworthy that the monodentate species appears to be much less important compared with iron oxides.

3.5 Adsorption of arsenate on $\beta$-Al(OH)$_3$ from Arai et al. (2001)

The adsorption data depicted in Fig. 10a refer to arsenate adsorption envelopes on $\beta$-Al(OH)$_3$ (Arai et al., 2001). The limited amount of data in Fig. 10a can be fit using only the deprotonated bidentate-binuclear species in Fig. 1. The other species were included in the model solely to place upper limits on their importance under the experimental conditions studied by Arai et al. (2001). Consequently, the values of $\log K_{(\gamma SO_4, \delta OH)}^\theta$ and $\log K_{(\delta SO_4, \gamma OH)}^\theta$ in Table 2 merely represent upper limits. Arai et al. (2001) also measured a decrease of the isoelectric point with increasing arsenate concentrations from electrophoretic mobility studies. The ETLM prediction again agrees with the direction of the shift, although the overall predicted shift is too large.

The predicted model speciation for arsenate on the surface of $\beta$-Al(OH)$_3$ is given in Figs. 10b-c for the lowest and highest ionic strength of Fig. 10a as well as a prediction of the surface speciation at a lower arsenate loading (0.07 mM of arsenate) in Fig. 10d. It can be seen that the bidentate-binuclear species is predicted to dominate in any of these conditions regardless of the pH and ionic strength. These predictions of surface speciation are consistent with the EXAFS and XANES spectroscopic results on the same sample from Arai et al. (2001) which showed no other species except the bidentate-binuclear species regardless of pH and ionic strength. Our predictions in Fig. 10d for even lower
surface coverages than those investigated by Arai et al. (2001) indicate that the mononuclear species would become important only at very high pH values (e.g. > 10), even when the surface coverages are very low. This is again a significant difference to the results discussed above for the iron oxides.

3.6 Adsorption of arsenate on \(\alpha\)-Al(OH)\(_3\) from Manning and Goldberg (1996)

The data depicted in Fig. 11a show two arsenate adsorption envelopes on \(\alpha\)-Al(OH)\(_3\) as a function of pH. The solid curves in Fig. 11a represent regression calculations using the three species in Fig. 1 and a site density of 3.0 sites.nm\(^{-2}\) derived from work on arsenite adsorption on gibbsite (Sverjensky and Fukushi, 2006b). With the exception of data at the highest pH values, the calculated curves provide a close description of the arsenate adsorption over a wide range of conditions shown in Fig. 11a.

The predicted model speciation of arsenate on the surface of \(\alpha\)-Al(OH)\(_3\) is given in Figs. 11b - d. The surface coverages from Fig. 11a are shown in Figs. 11b and c, and a prediction of the surface speciation in lower ionic strength solutions (0.01 M NaCl) is shown in Fig. 11d. It can be seen in Figs. 11b - d that the bidentate-binuclear species predominates at pH values up to about 10. The predicted surface speciation at low pH is consistent with an EXAFS study of arsenate on \(\alpha\)-Al(OH)\(_3\) at pH 5.5, which inferred an inner-sphere bidentate-binuclear species (Ladeira et al., 2001). As in Figs. 9 and 10, the mononuclear species is predicted to occur only at the highest pH values, and is little influenced by ionic strength (c.f. Figs. 11c and d).
3.7 Adsorption of arsenate on $\alpha$-Al$_2$O$_3$ from Halter and Pfeifer (2001)

The data depicted in Fig. 12a and b show proton surface titration without arsenate as well as arsenate adsorption envelopes on $\alpha$-Al$_2$O$_3$ as functions of pH and surface coverage. The solid curves in Fig. 12a represent regression of the data shown in order to generate values of the electrolyte adsorption equilibrium constants (Table 1). The solid curves in Fig. 12b represent regression calculations using the three reactions in Fig. 1 and a site density of 3.0 sites.nm$^{-2}$ derived from work in progress on oxalate adsorption on corundum which refers to a very wide range of surface coverages. This site density is reasonable for singly-coordinated oxygens on corundum. For example, the abundance of such oxygens that can participate in bidentate-binuclear surface complexes varies from 0 to 3.3 to 8.2 sites.nm$^{-2}$ on the (0001), (10-10) and (01-12) faces, respectively. The calculated curves show excellent agreement with the experimental data over a wide range of pH values and the surface coverages shown in Fig. 12b.

The predicted model speciation of arsenate on the surface of $\alpha$-Al$_2$O$_3$ is given in Figs. 12c - e for the high and low surface coverage of Fig. 12b, as well as a prediction of the surface speciation in solutions with higher arsenate (0.133 mM) to give the same surface coverage as in Fig. 11c for gibbsite. It can be seen in Figs. 12c - e that the bidentate-binuclear species dominates at pH values less than about 8 to 9 and that the mononuclear species contributes substantially to adsorption above these pH values. In this regard, the relative importance of the mononuclear species appears to be greater on corundum than on the other aluminas discussed above. However, when comparing the same surface
coverage on corundum (Fig. 12e) with that for gibbsite (Fig. 11c), it can be seen that the arsenate surface speciation on the two aluminas is quite similar.

The predicted dominance of the bidentate-binuclear species at low pH values in Figs. 12c - e is consistent with resonant anomalous X-ray reflectivity (RAXR) studies of arsenate adsorption at pH = 5 on the (012) surface of corundum which also established a bidentate-binuclear type of species (Catalano et al., 2006a, b). If the current calculations can be extrapolated to single crystal surfaces, the results of the present study suggest that at high pH values the (012) surface of corundum should show a transition from predominantly binuclear to mononuclear arsenate surface species (see below).

4. PREDICTION OF EQUILIBRIUM CONSTANTS FOR ARSENATE ADSORPTION

4.1 Prediction of arsenate adsorption on all oxides

The ETLM calculations summarized above have shown that the three reactions producing the species \( (> FeO)_2 AsO_2^- \), \( (> FeO)_2 AsOOH \) and \( > FeO_2 AsO_2^- \) (Fig. 1), can describe a variety of arsenate adsorption data including adsorption envelopes, proton coadsorption, and proton titration with arsenic for a very wide range of pH, ionic strength, surface coverage and types of oxides. The equilibrium constants of the arsenate surface species for each oxide retrieved from the regression calculations are summarized in Table 2. In order to compare the equilibrium constants for adsorption on different solids, it is essential to use equilibrium constants referring to site-occupancy standard states (i.e. \( \log K_j^0 \)). On
this basis, it can be seen in Table 2 that the strength of adsorption of arsenate on oxide surfaces depends strongly on the nature of the solid. An understanding of the systematic differences in the equilibrium constants from one solid to another permits prediction of the adsorption equilibrium constants on all oxides (Sverjensky, 2005; Sverjensky, 2006; Sverjensky and Fukushi, 2006).

According to theoretical studies of proton, electrolyte cation and anion, divalent metal ion, and arsenite adsorption (James and Healy, 1972; Sahai and Sverjensky, 1997; Sverjensky, 2005; Sverjensky, 2006; Sverjensky and Fukushi, 2006; Sverjensky and Sahai, 1996), the solvation free energy associated with an adsorbing ion can be a major determinant of the differences in the overall equilibrium constants for different solids. The solvation free energy associated with the removal of water molecules from an adsorbing ion opposes the adsorption process. Born solvation theory predicts that the magnitude of the opposition varies from one solid to another, thereby enabling explanation of the differences in equilibrium constants for adsorption of a given ion on a variety of solids. It should be noted that ligand exchange processes during arsenate adsorption also result in release of water as shown in Fig. 1. However, it is assumed that the release of this water is distinct from the release of waters of solvation associated with the adsorbing ions (Sverjensky and Fukushi, 2006).

In the present study, we assume that the overall equilibrium constant for adsorption forming the jth arsenate surface species ($\log K_j$) can be expressed in terms of a solvation contribution and an intrinsic binding contribution (Sverjensky and Fukushi, 2006) according to
\[
\log K_j^\theta = -\frac{\Delta \Omega_{r,j}}{2.303RT} \left( \frac{1}{\varepsilon_s} \right) + \log K_{\theta,j}^s
\]  
(32)

In Eqn. (32), the first term on the right-hand side is derived from Born solvation theory. It contains \( \Delta \Omega_{r,j} \), which represents a Born solvation coefficient for the reaction forming the \( j \)th species, and \( \varepsilon_s \), which represents the dielectric constant of the \( s \)th solid. The second term, \( \log K_{\theta,j}^s \), represents an intrinsic binding of arsenate independent of the type of oxide, but also includes terms derived from solvation theory dependent on the dielectric constant of the interfacial water. It is assumed here that \( \log K_{\theta,j}^s \) is a constant for a given reaction. The values of \( \varepsilon_s \) used in the present study are summarized in Table 2.

Regression of the values of \( \log K_{(@SO_2,AsO_4)^2}^\theta \), \( \log K_{(@SO_2,AsOOH)}^\theta \), and \( \log K_{(>SO_4AsO_2)}^\theta \) with Eqn. (32) using dielectric constants from Table 2 resulted in the lines of best fit shown in Figs. 13a - c consistent with the equations

\[
\log K_{(@SO_2,AsO_4)^2}^\theta = -68.3\left( \frac{1}{\varepsilon} \right) + 5.60
\]  
(33)

\[
\log K_{(@SO_2,AsOOH)}^\theta = -73.3\left( \frac{1}{\varepsilon} \right) + 7.49
\]  
(34)

\[
\log K_{(>SO_4AsO_2)}^\theta = -87.9\left( \frac{1}{\varepsilon} \right) + 1.41
\]  
(35)

It should be noted that the values of \( \log K^\theta \) for arsenate adsorption in Fig. 13 can be directly compared because they refer to site-occupancy standard states and have been corrected for differences in the \( pH_{ZPC} \) as well as site-density and surface area. It is difficult to assess the overall uncertainties in the equilibrium constants because they include uncertainties from regression of the experimental
data (about ± 0.2 in the log $K$ values) as well as those from the parameters in Eqns. (29)-(31), for example the $pH_{ZPC}$. Overall, it is estimated that the uncertainties in the log $K^\theta$ values may be ± 0.5 units. It can be seen in Fig. 13 that many of the data points are within plus or minus 0.5 of the regression lines. Overall, the correlations in Fig. 13 provide a reasonable first order description of the major differences in arsenate adsorption equilibrium constants for a wide range of oxide types. Because Eqns. (33) - (35) have a theoretical basis, they can be used to predict the values of log $K^\theta_{\text{AsOSO}}$, log $K^\theta_{\text{AsOOH}}$ and log $K^\theta_{\text{AsOOH}^{-}}$ for other oxides (Table 3).

The four goethites analysed in the present study show a substantial range of values for each equilibrium constant type (Fig. 13 and Table 2). For the mononuclear species, three out of the four agree very well and only the value for the Antelo et al. goethite is anomalous (consistent with the discussion above). It was not included in the regression analysis. However, the equilibrium constants for each binuclear species shows a spread of values substantially greater than the estimated uncertainties. This is an interesting result given the spectrum of model speciation behavior for goethite discussed above. The range of goethite behavior is puzzling. Whether or not it is related to the effect of different crystal faces on different samples, remains to be established. Perhaps detailed electron microscopy studies of these goethites would help establish possible causes for the range of behavior. Nevertheless, it is interesting that the equilibrium constants for the Dixit and Hering and Manning and Goldberg goethites (goethite points a. and d. in Fig. 13) are consistently close to the regression lines and thus
are consistent with the equilibrium constants for arsenate adsorption on the other types of oxide. As noted above, the predicted surface speciation on these oxides is also the most closely consistent with in situ FTIR spectroscopic and X-ray results from the majority of experimental studies of arsenate and phosphate adsorption on a number of other goethites.

In comparison with the equilibrium constants for the Dixit and Hering (2003) and Manning and Goldberg (1996) goethites, those for the Gao and Mucci (2001) goethite are consistently higher (for the binuclear species). It should be noted that the adsorption data from Gao and Mucci all refer to high ionic strength conditions \((I = 0.7)\) under which additional ternary species may become important. Neglect of such species could cause the equilibrium constants for the Gao and Mucci goethite to be anomalously large.

It can also be seen in Fig. 13 that the differences in the equilibrium constants for HFO, ferrihydrite, and goethite (represented by the Dixit and Hering and Manning and Goldberg samples) are well accounted for by the simple solvation theory expressed by Eqn. (32). Even though the dielectric constants of HFO and ferrihydrite should only be regarded as tentative estimates, because they are based on the different \(\text{pH}_{\text{ZPC}}\) values of these solids, they do provide an adequate explanation through Born solvation theory of the substantial differences in the \(\log K^o\) values for arsenate adsorption. Higher dielectric constant solids are associated with less work opposing adsorption. A similar result for arsenite adsorption on HFO and ferrihydrite was previously obtained (Sverjensky and Fukushi, 2006). The results in Fig. 13 also indicate that Born solvation theory can
explain the stronger adsorption on most iron oxides relative to most aluminum oxides that has been noted in a number of studies (e.g. Kubicki, 2005).

It is also noteworthy that the slope of the line for the monodentate-monomonuclear complexes in Fig. 13 is significantly greater than for the two binuclear complexes (c.f. Eqns. 33 - 35 above). Clearly the Born solvation effect for mononuclear species is much stronger than for binuclear species. This favors the development of mononuclear species on solids with the highest dielectric constants, such as hydrous ferric oxide, relative to solids with the lowest dielectric constant considered here, such as gibbsite. However, other factors, particularly high pH values and low surface coverages, also strongly favor the mononuclear over the binuclear species as discussed above.

4.2 Comparison of arsenate surface speciation on corundum and hematite

A number of studies in the literature have compared ion adsorption on single crystal surfaces of corundum and hematite (Bargar et al., 2004; Bargar et al., 1997; Catalano et al., 2006a; Catalano et al., 2006b; Catalano et al., 2006c; Catalano et al., 2006d; Trainor et al., 2004; Trainor et al., 2001; Waychunas et al., 2005). Furthermore, MO/DFT calculations (Kubicki, 2005) have indicated a strong preference for arsenate to bind to iron clusters relative to aluminum hydroxide clusters. The general preference of binding of arsenate more strongly to iron oxides relative to aluminum oxides is certainly supported by the calculations and theoretical predictions discussed above. For example, comparison of the speciation and total adsorption of arsenate on HFO relative to goethite in Figs. 7d and 11d, respectively, indicate very different surface
speciation, and, at pH values above about 8, a different total amount of adsorption. However, depending on the specific iron and aluminum oxide, the dielectric constants of the two may be sufficiently close that the surface speciation on the two oxides are not as different as in Figs. 7d and 11d.

Even though our study at present does not specifically address single-crystal surfaces, it is interesting to compare the predicted surface speciation for arsenate on corundum and hematite powders, based on the equilibrium constant correlations discussed above. Predicted surface speciation plots for two different surface coverages are shown for corundum and hematite powders in Figs. 14 a. - d. Clearly, the predicted amounts of adsorption and the surface speciations for the two solids are very similar. For both solids, the binuclear species are predicted to predominate at pH < 9 at the higher surface coverage (Figs. 14a and c), and at pH < 5.5 - 6.5 at the lower surface coverage (Figs. 14b and d). However, at pH values higher than these, the mononuclear species is predicted to predominate. This result is a consequence of the stoichiometries of the reactions used for the binuclear versus the mononuclear species. Consequently, on a single crystal surface that has the appropriate spacing of sites such that either binuclear or mononuclear arsenate can adsorb, the results of the present study suggest that the binuclear and the mononuclear will adsorb at different pH values and surface coverages.

The speciation results in Fig. 14 agree qualitatively with the recent RAXR results at pH = 5 for corundum and hematite (012) surfaces (Catalano et al., 2006a, b), which indicate a bidentate-binuclear surface species. EXAFS results for a hematite powder at pH values of 4.5 to 8.0 and surface coverages of 0.45 to
3.10 μmoles.m⁻² (Arai et al., 2004) also reported a predominant bidentate-binuclear species. In addition, the latter authors noted a minor amount of a possible bidentate-mononuclear species. It seems possible that this mononuclear species is consistent with the mononuclear species in our speciation calculations for hematite (e.g. Eqn. 20, which has the same reaction stoichiometry as Eqn. 14). However, the possible pH and surface coverage dependence of this species was not addressed in the EXAFS study.

5. CONCLUSIONS

In the present study, we applied the ETLM to a wide variety of surface chemical measurements for arsenate on oxide surfaces. The main goal of the study was to use evidence from X-ray and infrared spectroscopic and theoretical molecular studies to guide the choice of arsenate surface species and to determine the effects of pH, ionic strength, surface coverage and type of oxide on the surface speciation. A second goal was to place arsenate surface equilibria on a predictive basis. The findings of the present study are as follows:

(1) Three reaction stoichiometries forming inner-sphere arsenate surface species

\[2 > SOH + H_3AsO_4^0 = (> SO)_2 AsO_2^- + H^+ + 2H_2O\]

\[2 > SOH + H_3AsO_4^0 = (> SO)_2 AsOOH + 2H_2O\]

and

\[> SOH + H_3AsO_4^0 => SOAsO_3^{2-} + 2H^+ + H_2O\]

were derived from in-situ X-ray and infrared spectroscopic evidence for arsenate and phosphate adsorption on goethite. These three reaction stoichiometries were found to be consistent with experimental studies of adsorption envelope, proton
titration and proton coadsorption with arsenate referring to wide ranges of pH, ionic strength and surface coverage for a variety of solids including goethite, HFO, ferrihydrite, amorphous aluminum oxide, β-Al(OH)₃, α-Al(OH)₃ and α-Al₂O₃. Surface coverage limits for adsorption (on goethite) were found to be about 2.5 μmoles.m⁻². At higher coverages, sorption processes in addition to adsorption (e.g. precipitation) must be important.

(2) On four different samples of goethite, the predicted surface speciations show a spectrum of results. Two goethite samples (from Dixit and Hering, 2003, and Manning and Goldberg, 1996) show behavior in which binuclear species predominate at higher surface coverages and lower pH values compared to mononuclear species. The specific conditions and speciation for these two goethites compare very favorably to in situ FTIR spectroscopic results for phosphate adsorption on a goethite studied by Tejedor-Tejedor and Anderson (1990) and EXAFS results for goethites studied by Waychunas et al. (1993), Farquhar et al. (2002), and Sherman and Randall (2003). Two other goethites show predicted surface speciations ranging from predominantly binuclear for one sample (from Gao and Mucci, 2001) to predominantly mononuclear on another sample (from Antelo et al., 2005). It is interesting that the latter result is consistent with recent in situ ATR-FTIR results for phosphate and arsenate on a goethite studied by Loring et al. (2006) and Nelson et al. (2006).

(3) The predicted surface speciation of arsenate on HFO, ferrihydrite, hematite, corundum and β-Al(OH)₃ showed that bidentate-binuclear species were
predominant under conditions consistent with EXAFS results (Arai et al., 2001; 
Arai et al., 2004; Waychunas et al., 1993) and recent RAXR studies of single 
crystal surfaces (Catalano et al., 2006a, b).

(4) After expressing the equilibrium constants for arsenate adsorption in terms of 
site-occupancy standard states, and correcting for differences in sample 
characteristics, systematic differences in the equilibrium constants $\log K^\theta_{\text{SO}_4\text{AsO}_4^{-1}}$, 
$\log K^\theta_{\text{SO}_4\text{AsOOH}^{-}}$ and $\log K^\theta_{\text{SO}_4\text{AsO}_4^{-2}}$ on different solids are apparent. The differences 
were explained with the aid of Born salvation theory which enabled the 
development of a set of predictive equations for arsenate adsorption equilibrium 
constants on all oxides.

(4) The predictive equations indicate that the Born solvation effect for 
mononuclear species is much stronger than for binuclear species. This favors the 
development of the mononuclear species on iron oxides with the highest 
dielectric constant, such as hydrous ferric oxide, relative to aluminum oxides with 
the lowest dielectric constant, such as gibbsite. On hematite and corundum, 
which have much closer dielectric constants, the surface speciation of arsenate 
is predicted to be rather similar, depending on the specific characteristics of the 
samples. The binuclear species are predicted to predominate at lower pH values 
and higher surface coverages than the mononuclear species.
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FIGURE CAPTIONS

**Figure 1** Diagrammatic representations and model reactions forming arsenate surface species derived from *in situ* spectroscopic evidence and molecular calculations. The species formed by ligand exchange reactions release one or two water dipole depending on the denticity of the surface species. This effect is taken into account in the electrostatic term for the reaction $\Delta \psi^*$, which includes contributions from the ions and the water dipoles released in the reactions.

**Figure 2** The data represent experimental results for arsenate adsorption on goethite from Dixit and Hering (2003). The curves in a. and b. represent regression calculations, but those in c. and d. represent predictions made with the ETLM using the arsenate surface species and parameters in Table 1 and 2.

a. Arsenate adsorption as a function of pH and surface coverage.

b. Arsenate adsorption as a function of arsenate loading.

c.- d. Predicted model arsenate surface and aqueous speciation. The proportion of monodentate species increases with pH, but decreases with surface coverage consistent with *in-situ* X-ray and infrared results.

e. - f. Regression of adsorption data and predicted surface speciation obtained with an alternate approach to the ETLM in which the arsenate charge is placed on the 0-plane and the water dipole correction is used as in the ETLM. Parameters used are given in Table 2 footnotes.
**Figure 3** The data points represent experimental results for proton surface titration and arsenate adsorption on goethite from Gao and Mucci (2001). The solid curves in a. and b. represent regression calculations with the ETLM using the arsenate surface species and parameters in Table 1 and 2.

a. Proton surface charge as a function of pH and ionic strength in NaCl solutions.
b. Arsenate adsorption as a function of pH and surface coverage.
c.-d. Predicted model arsenate surface and aqueous speciation.
e. Predicted arsenate speciation for the same conditions as in Fig. 2d. Note the greatly increased predominance of the bidentate-binuclear arsenate species.

**Figure 4** The data represent experimental results for arsenate adsorption on HFO from Antelo et al. (2005). The curves in a. - c. represent regression calculations but those in d. - f. represent predictions made with the ETLM using the arsenate surface species and parameters in Table 1 and 2.

a. Proton surface charge as a function of pH and ionic strength without arsenic.
b.-c. Arsenate adsorption as a function of arsenate loading.
d.-e. Predicted model arsenate surface and aqueous speciation as a function of arsenate loading.
f. Predicted arsenate speciation for the same conditions as in Figs. 2d and 3e. Note the overwhelming predominance of the mononuclear arsenate species.

**Figure 5** The data points represent experimental results for arsenate adsorption on goethite from Manning and Goldberg (1996). The solid curves in a. represent
regression calculations with the ETLM using the arsenate surface species and parameters in Table 1 and 2.

a. Arsenate adsorption as a function of pH and surface coverage.

b.- c. Predicted model arsenate surface and aqueous speciation.

d. The predicted arsenate speciation referring to the same conditions as in Figs. 2d, 3e, and 4f. Note that the speciation here is very similar to that in Fig. 2d for the Dixit and Hering goethite.

**Figure 6**

Empirical correlation of goethite site densities generated with the ETLM by regression of adsorption data referring to a wide range of surface coverages for a several different oxyanions. Site densities used in the present study are represented by the open triangles. Those close to but off the line were generated by regression of arsenate adsorption data. The open triangle lying on the line represents a prediction using the equation for the line from Fukushi and Sverjensky (2006). The negative slope of the line is consistent with likely abundances of singly-coordinated oxygens on different crystal planes (see text). It is also consistent with results obtained for carbonate on goethites with different surface areas by Villalobos et al. (2003).

**Figure 7** The data represent experimental results for arsenate adsorption on HFO from Dixit and Hering (2003). The curves in a. and b. represent regression calculations but those in c. and d. represent predictions made with the ETLM using the arsenate surface species and parameters in Table 1 and 2.
a. Arsenate adsorption as a function of pH and surface coverage.
b. Arsenate adsorption as a function of arsenate loading.
c.- d. Predicted model arsenate surface and aqueous speciation. The proportion of monodentate species increases with pH, but decreases with surface coverage consistent with in-situ X-ray results (Waychunas et al., 1993).

Figure 8 The data points represent experimental results for arsenate adsorption on ferrihydrite from Jain et al (1999) and Jain and Loeppert (2000). The solid curves in a.-c. represent regression calculations with the ETLM using the arsenate surface species and parameters in Table 1 and 2. The dashed curves in a. and c. were obtained by regression with an alternate approach to the ETLM in which the arsenate charge is placed on the 0-plane and the water dipole correction is used as in the ETLM (the parameters used are given in Table 2 footnotes).

a. Proton surface charge as a function of pH with and without arsenate.
b. Proton coadsorption with arsenate.
c. Arsenate adsorption as a function of pH and surface coverage.
d. Predicted model arsenate surface and aqueous speciation.

Figure 9 The data points represent experimental results for arsenate adsorption on am.AIO from Goldberg and Johnston (2001). The solid curves in a. represent regression calculations with the ETLM using the arsenate surface species and parameters in Table 1 and 2.

a. Arsenate adsorption as a function of pH, ionic strength and surface coverage.
b.- d. Predicted model arsenate surface and aqueous speciation.

**Figure 10.** The data points represent experimental results for arsenate adsorption on β-Al(OH)$_3$ from Arai et al. (2001). The solid curves in a. represent regression calculations with the ETLM using the arsenate surface species and parameters in Table 1 and 2.

a. Arsenate adsorption as a function of pH and ionic strength.

b.- d. Predicted model arsenate surface and aqueous speciation. The bidentate-binuclear species dominates in any experimental conditions regardless of pH and ionic strength consistent with *in-situ* X-ray results (Arai et al., 2001).

**Figure 11.** The data points represent experimental results for arsenate adsorption on α-Al(OH)$_3$ from Manning and Goldberg (1996). The solid curves in a. represent regression calculations with the ETLM using the arsenate surface species and parameters in Table 1 and 2.

a. Arsenate adsorption as a function of pH and surface coverage.

b.- d. Predicted model arsenate surface and aqueous speciation.

**Figure 12.** The data points represent experimental results for proton surface titration and arsenate adsorption on α-Al$_2$O$_3$ from Halter and Pfeifer (2001). The solid curves in a. and b. represent regression calculations with the ETLM using the arsenate surface species and parameters in Tables 1 and 2.

a. Proton surface charge on α-Al$_2$O$_3$ in the absence of arsenate.

b. Arsenate adsorption as a function of pH and surface coverage.
c.- d. Predicted model arsenate surface and aqueous speciation for the surface coverages in b.

e. Predicted arsenate surface and aqueous speciation on $\alpha$-Al$_2$O$_3$ to be compared with $\alpha$-Al(OH)$_3$ at the same surface coverage and ionic strength shown in Fig. 11c.

**Figure 13.** Correlation of the logarithms of the equilibrium constants for arsenate adsorption on oxides with the inverse of the dielectric constant of the oxide (Table 2). The lines were generated by regression with Eqns. (33) – (35). The equilibrium constants represent analysis of the data in Figs. 2 - 12 consistent with site-occupancy standard states and corrected for differences in the $pH_{ZPC}$ and $\Delta pK_{\mu}^o$ of the oxides. The error bars represent uncertainties of $\pm$ 0.5. The arrows for $\beta$-Al(OH)$_3$ in Fig. 11b and c indicate that upper limits. The four different goethites plotted are denoted by a. (Dixit and Hering, 2003), b. (Gao and Mucci, 2001), c. (Antelo et al., 2005), and d. (Manning and Goldberg, 1996).

**Figure 14.** Predicted arsenate surface speciation on corundum and hematite powders at two different surface coverages. The curves were calculated with the ETLM using the arsenate surface species and predicted equilibrium constants in Table 3 assuming values of the $pH_{ZPC} = 9.4$ and 9.5 for corundum and hematite, respectively.

a. Corundum, 2.0 $\mu$moles/m$^2$ of arsenate if 100% adsorbed.

b. Corundum, 0.2 $\mu$moles/m$^2$ of arsenate if 100% adsorbed.
c. Hematite, 2.0 μmoles/m² of arsenate if 100% adsorbed.

d. Hematite, 0.2 μmoles/m² of arsenate if 100% adsorbed.
ETLM treatment for arsenate adsorption on oxides

**Deprotonated bidentate-binuclear arsenate**

\[
2 > SOH + H_3AsO_4^0 = (> SO)_2 AsO_2^- + H^+ + 2H_2O
\]

\[
K_{ (>SO)_2 AsO_2^-} = \frac{a_{ (>SO)_2 AsO_2^-} \cdot a_{H^+} \cdot a_{H_2O}^2}{a_{SOH} \cdot a_{H_3AsO_4^0}} \frac{F(\Delta\Psi_r)}{2.303RT}
\]

ETLM \(\Delta\Psi_r = 2\Psi_0 - 3\Psi_\beta - 2(\Psi_0 - \Psi_\beta) = -\Psi_\beta\)

**Protonated bidentate-binuclear arsenate**

\[
2 > SOH + H_3AsO_4^0 = (> SO)_2 AsOOH + 2H_2O
\]

\[
K_{ (>SO)_2 AsOOH} = \frac{a_{ (>SO)_2 AsOOH} \cdot a_{H_2O}^2}{a_{SOH} \cdot a_{H_3AsO_4^0}} \frac{F(\Delta\Psi_r)}{2.303RT}
\]

ETLM \(\Delta\Psi_r = 2\Psi_0 - 2\Psi_\beta - 2(\Psi_0 - \Psi_\beta) = 0\)

**Monodentate-mononuclear arsenate**

\(> SOH + H_3AsO_4^0 \Rightarrow SOAsO_3^{2-} + 2H^+ + H_2O\)

\[
K_{SOAsO_3^{2-}} = \frac{a_{SOAsO_3^{2-}} \cdot a_{H^+} \cdot a_{H_2O}^2}{a_{SOH} \cdot a_{H_3AsO_4^0}} \frac{F(\Delta\Psi_r)}{2.303RT}
\]

ETLM \(\Delta\Psi_r = \Psi_0 - 3\Psi_\beta - (\Psi_0 - \Psi_\beta) = -2\Psi_\beta\)
Arsenate on goethite in 0.01 M NaClO₄ solutions
0.5 g L⁻¹; 54 m² g⁻¹

Dixit and Hering (2003)
- 10 μM arsenate
- 25 μM arsenate
- 50 μM arsenate
- 100 μM arsenate

Predicted arsenate species in 0.01 M NaClO₄ arsenate 100 μM

% arsenate species

Arsenate on goethite in 0.01 M NaClO₄ solutions
0.5 g L⁻¹; 54 m² g⁻¹

Predicted arsenate species in 0.01 M NaClO₄ arsenate 10 μM

H₃AsO₄
H₂AsO₄⁻
HAsO₄²⁻
(>FeO)₂AsOOH
(>FeO)₂AsO₂⁻
(>FeO)₃AsO₃²⁻

Figure 2
Predicted arsenate species in 0.7 M NaCl

**c.**

Predicted arsenate species in 0.7 M NaCl solutions
arsenate 34.2 μM

**d.**

Arsenate on goethite in 0.7 M NaCl solutions
0.235 g.L⁻¹, 27.7 m².g⁻¹

Gao and Mucci (2001)
8.8 μM arsenate
22.9 μM arsenate
34.2 μM arsenate

**e.**

Predicted arsenate species in 0.01 M NaCl
arsenate 2.5 μM

Figure 3
Predicted arsenate species in 0.01 M KNO₃; pH = 4.5

\( >\text{FeOAsO}_3^{-2} \)
\( (>\text{FeO})_2\text{AsO}_2^- \)
\( (>\text{FeO})_2\text{AsOOH} \)

Arsenate on goethite in 0.01 M KNO₃ solutions
70.8 m².g⁻¹

Dissolved arsenate (mM)
Adsorbed arsenate (µmol.m⁻²)

Antelo et al. (2005)

pH 4.5
pH 7.0
pH 8.0
pH 10.0

Figure 4

Predicted arsenate species in 0.01 M KNO₃; pH = 10.0

\( >\text{FeOAsO}_3^{-2} \)
\( (>\text{FeO})_2\text{AsO}_2^- \)
\( (>\text{FeO})_2\text{AsOOH} \)

Arsenate on goethite in 0.1 M KNO₃ solutions
70.8 m².g⁻¹
Arsenate on goethite in 0.1 M NaCl solutions
2.5 g.L⁻¹; 43.7 m².g⁻¹

Manning and Goldberg (1996)

● 133 μM arsenate
△ 266 μM arsenate

Predicted arsenate species in 0.1 M NaCl

arsenate 266 μM

HAsO₄²⁻
(>FeO)₂AsO₂⁻
(>FeO)₂AsOOH
>FeOAsO₃²⁻
H₂AsO₄⁻
AsO₄³⁻

Predicted arsenate species in 0.01 M NaCl

arsenate 41 μM

H₃AsO₄
(>FeO)₃AsOOH
>FeOAsO₃²⁻
(>FeO)₃AsO₂⁻

Figure 5
Goethite site densities from ETLM regression

\[ y = -0.0312x + 5.30 \quad r^2 = 0.906 \]

Figure 6
Predicted arsenate species in 0.01 M NaClO₄

- Arsenate 100 μM
- pH
- % arsenate species

H₄AsO₄⁻
(>FeO)₂AsO₂⁻
(>FeO)₂AsOOH
>FeOAsO₃²⁻

Figure 7
Ferrihydrite in I = 0.1M NaCl solutions with arsenate
600 m^2.g\(^{-1}\); 2g.L\(^{-1}\)

Jain et al. (1999)
- 1.6 mM arsenate
- 0.534 mM arsenate
- 0 M arsenate

pH

Arsenate on ferrihydrite in I = 0.1M NaNO\(_3\) solutions
2 g.L\(^{-1}\); 600 m^2.g\(^{-1}\)

Jain and Loeppert (2000)
- 1.00 mM arsenate
- 2.08 mM arsenate

Figure 8
Goldberg and Johnston (2001)

\[ \text{HAsO}_4^{2-} \] (\( >\text{AlO} \)) \[ \text{AsO}_2^{\,2-} \]

\[ \text{HAsO}_4^{2-} \] (\( >\text{AlO} \)) \[ \text{AsO}_2^{\,2-} \]

\[ \text{H}_2\text{AsO}_4^{-} \]

\[ \text{H}_2\text{AsO}_4^{-} \] (\( >\text{AlOAsO}_3^{\,2-} \))

\[ \text{H}_2\text{AsO}_4^{-} \] (\( >\text{AlOAsO}_3^{\,2-} \))

Figure 9
Arsene on β-Al(OH)₃ in NaNO₃ solutions
5 g·L⁻¹; 90.1 m²·g⁻¹ arsene 0.7 mM

Arai et al. (2001)
0.01 M NaNO₃
0.8 M NaNO₃

Figure 10
Arsenate on α-Al(OH)₃ in 0.1 M NaCl solutions
2.5 g.L⁻¹; 43.7 m².g⁻¹

Manning and Goldberg (1996)
• 133 μM arsenate
△ 266 μM arsenate

% arsenate species

Predicted arsenate species in 0.1 M NaCl
arsenate 266 μM

Figure 11: Predicted arsenate species in 0.1 M NaCl
arsenate 266 μM
**Figure 12**

**a.** Graph showing the surface charge density ($\sigma_H$) as a function of pH for $\alpha$-Al$_2$O$_3$ in NaNO$_3$ solutions with $10.9 \, \text{m}^2\cdot\text{g}^{-1}$.

**b.** Graph depicting arsenate adsorption on $\alpha$-Al$_2$O$_3$ in 0.1 M NaNO$_3$ solutions with 10 g.L$^{-1}$ and 10.9 m$^2$.g$^{-1}$.

**c.** Predicted arsenate species in 0.1 M NaNO$_3$ with 66.7 $\mu$M arsenate.

**d.** Predicted arsenate species in 0.1 M NaNO$_3$ with 13.3 $\mu$M arsenate.

**e.** Predicted arsenate species in 0.1 M NaNO$_3$ with 133 $\mu$M arsenate.
Figure 13

\[ 2 > SOH_{2}^{+} + H_{3}AsO_{4} = (SO)_{2}AsO_{5}^{-} + 3H^{+} + 2H_{2}O \]

\[ y = -68.3x + 5.60 \quad R^2 = 0.820 \]

\[ 2 > SOH_{2}^{+} + H_{3}AsO_{4} = (SO)_{2}AsOOH + 2H^{+} + 2H_{2}O \]

\[ y = -73.3x + 7.49 \quad R^2 = 0.739 \]

\[ > SOH_{2}^{+} + H_{3}AsO_{4} \rightarrow SO_{3}^{2-} + 3H^{+} + H_{2}O \]

\[ y = -87.9x + 1.40 \quad R^2 = 0.925 \]
Predicted arsenate species in 0.01 M NaNO₃
5 g L⁻¹; 20 m²·g⁻¹ arsenate 0.2 mM

Predicted arsenate species in 0.01 M NaNO₃
5 g L⁻¹; 20 m²·g⁻¹ arsenate 0.02 mM
Table 1. Sample characteristics, surface protonation and electrolyte adsorption equilibrium constants, and capacitances used in present study. Values of $\log K^\alpha$, $\log K^\beta^\omega$, and $\log K^\alpha_m^\omega$ refer to site-occupancy standard states for the reactions listed below. Values of $\log K^\alpha$ and $\log K^\beta$, were predicted using the given values of $pH_{ZPC}$ and $\Delta pK^\omega_n$. Values of $\log K^\alpha_m$, $\log K^\omega$, and $\log K^\omega_m^*$ refer to the hypothetical 1.0 M standard state and the reactions listed below. They were calculated from the values of $\log K^\alpha$, $\log K^\alpha_m^\omega$, $\log K^\beta$, and $\log K^\beta_m^\omega$ with the aid of Eqs. (6), (7), (8) and (9) using the tabulated values of $N_s$, $A_s$, $pH_{ZPC}$ and $\Delta pK^\omega_n$.

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<th>$\log K^\beta$</th>
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a. $\log K^\alpha$: $\text{SOH} + H^+ \rightarrow \text{SOH}^\omega$; $\log K^\alpha_m^\omega$: $\text{SO}^\omega + H^\omega \rightarrow \text{SOH}^\omega$.

b. $\log K^\alpha_m^\omega$: $\text{SO}^\omega + M^\omega \rightarrow \text{SO}^\omega^- M^\omega^-; \log K^\omega$: $\text{SOH}_2^\omega^+ L^- \rightarrow \text{SOH}_2^\omega^- L^-$.  

c. Values generated by regression of arsenate adsorption as a function of surface coverage, with the following exceptions: Values for HFO, ferrihydrite, β-Al(OH)$_3$, FeOOH (Dixit and Hering, 2003) and am.AIO were taken from previous regression calculations of arsenite adsorption data on the same samples (Sverjensky and Fukushi 2006b); the value for the Manning and Goldber and goethite was generated with the equation for the line in Fig. 6 based on arsenite and sulfate regressions (Fukushi and Sverjensky, 2006).  

d. Surface areas from BET measurements by the authors with the exception of HFO (Dixit and Hering 2003), ferrihydrite (Jain et al. 2001) and am.AIO (Goldberg and Johnston 2001) for which the surface area was taken from the study of hydrous ferric hydroxide by Davis and Leckie (1978).  

e. Zero points of charge taken from measured low ionic strength isoelectric points for FeOOH (Manning and Goldberg 1996), β-Al(OH)$_3$ (Arai et al. 2001), am.AIO (Goldberg and Johnston 2001) and α-Al(OH)$_3$ (Manning and Goldberg 1996). Value for FeOOH (Dixit and Hering 2003) is predicted theoretically (Sverjensky 2006). Value for hematite (Arai et al. 2003) is taken from low zpc hematite (Sverjensky 2005).  

f. Predicted theoretically (Sverjensky 2005)
Table 2. Equilibrium constants for As(V) adsorption from regression of the data in Figs. 2-10. Values of $\log K_{SOA}^0$ and $\log K_{SO}^0$ refer to the hypothetical 1.0 M standard state and reactions formed from $SOH$. Values of $\log K_{SOA}^0$, $\log K_{SO}^0$ and $\log K_{SO}^0$ refer to site-occupancy standard states for As(V) adsorption reactions calculated from the values of $\log K_{SOA}^0$, $\log K_{SO}^0$ and $\log K_{SO}^0$ with aid of Eqns. (16), (17), (18), (22), (23) and (24) using values of $N_S$, $A_S$, $pH_{ZPC}$ and $\Delta \psi_{a}$ from Table 1 and $C_\epsilon$ from Table 2.

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a. $\log K_{SOA}^0$: $\Delta \psi_a = -3 \Psi_a + \psi_r$, $\Delta \psi_a = -3 \Psi_a + \psi_r$, $\Delta \psi_a = -2 \Psi_a - 2 \psi_r$ for $SOH + H_3AsO_4 \rightarrow SOAsO_3^{-} + H^+ + H_2O$.

b. $\log K_{SO}^0$: $\Delta \psi_a = -3 \Psi_a + \psi_r$, $\Delta \psi_a = -3 \Psi_a + \psi_r$, $\Delta \psi_a = -2 \Psi_a - 2 \psi_r$ for $SOH + H_3AsO_4 \rightarrow SOAsO_3^{-} + H^+ + H_2O$.

c. Solid dielectric constant after Sverjensky and Fukushi (2006b).

d. The dashed curves is computed with $\Delta \psi_a = -3 \Psi_a + \psi_r$, $\Delta \psi_a = -3 \Psi_a + \psi_r$, $\Delta \psi_a = -2 \Psi_a - 2 \psi_r$ for $SOH + H_3AsO_4 \rightarrow SOAsO_3^{-} + H^+ + H_2O$.

e. The dashed curves is computed with $\Delta \psi_a = -3 \Psi_a + \psi_r$, $\Delta \psi_a = -3 \Psi_a + \psi_r$, $\Delta \psi_a = -2 \Psi_a - 2 \psi_r$ for $SOH + H_3AsO_4 \rightarrow SOAsO_3^{-} + H^+ + H_2O$.
Table 3. Predicted equilibrium constants for arsenate adsorption on oxides consistent with the extended triple-layer model:

\[
\log K_{(SOH,AsO)}^{\theta} : \quad > SOH_{3}^{+} + H_{3}AsO_{4} \rightleftharpoons SOH_{2}^{+} + 3H^{+} + H_{2}O
\]

\[
\log K_{(SOH,AsO)}^{\theta} : \quad 2 > SOH_{2}^{+} + H_{3}AsO_{4} = (> SOH)_{2}AsO_{2}^{+} + 3H^{+} + 2H_{2}O
\]

\[
\log K_{(SOH,AsOOH)}^{\theta} : \quad 2 > SOH_{2}^{+} + H_{3}AsO_{4} = (> SOH)_{2}AsOOH + 2H^{+} + 2H_{2}O
\]

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a. Calculated with Eqns. (29) - (31) and the dielectric constants tabulated.

b. Dielectric constant of the solid from Sverjensky and Fukushi (2006b).