The arsenate-ferrihydrite system from minutes to months: A macroscopic and IR spectroscopic study of an elusive equilibrium.

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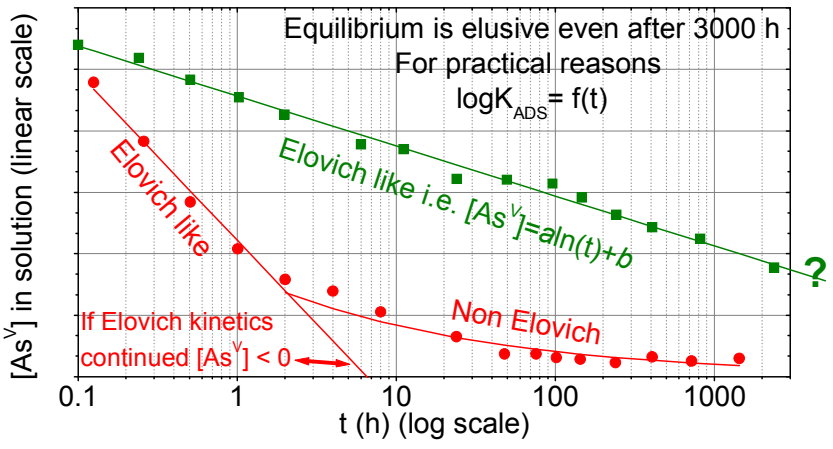
ABSTRACT: Sorption by ferrihydrite is an important control on As(V) concentrations in many oxic aquatic systems. There are significant discrepancies in reported sorption constants ($logK_{As}$) which presents a problem for quantifying and understanding this important system. A review of reported ferrihydrite-As(V) sorption studies indicated a positive correlation between reaction time used in the experiments and the $logK_{As}$ values derived from the data. In this paper we study the kinetics of As(V) sorption over ≈ 3000 h in nine systems with varying pH and As(V)/Fe. Ferrihydrite was stable in all systems containing As(V) and the [As(V)] in solution decreased linearly as a function of log(t) (termed Elovich kinetics) over the full 3000 h in most systems. A stable [As(V)] was only observed in systems with low As(V)/Fe and low pH. Apparent As(V) sorption constants were derived from the data at specific times intervals using the Diffuse Layer Model and equations describing $logK_{As}$ values as a function of time provide a way to describe this elusive equilibrium. IR spectra support the hypothesis that slow inter-particle diffusion is responsible for the slow approach to equilibrium. This work resolves previous discrepancies in previous studies of As(V)-ferrihydrite and provides equations to allow for system appropriate $logK_{As}$ values to be used.

TOC\Abstract Graphic



Introduction

Uncertainty remains in the geochemical controls of arsenic solubility despite the fact that arsenic in drinking water adversely impacts millions of people globally.[1] In oxic systems the principal mechanisms controlling solution AsO_4^{-3} concentrations, termed As_{sol}, are reactions on the surfaces of iron oxyhydroxides which under most circumstances have been shown to be sorption reactions.[2] Ferrihydrite is an important AsO_4^{-3} sorbent however there is considerable variation in reported equilibrium constants for AsO_4^{-3} sorption by ferrihydrite[3] This paper demonstrates how kinetic factors contribute to discrepancies in modelling the ferrihydrite-AsO_4^{-3} system and presents an explanation for this and an approach for modeling the system on a variable time scale.

Surface complexation models can be powerful tools to decipher and quantify the complex interactions affecting sorption. Using a small number of adjustable parameters the Diffuse Layer Model (DLM) is able to describe the macroscopic features of the ferrihydrite sorption of anions such as the effects of pH,[4] ionic strength (I),[5] surface coverage (Γ) and competing ions.[6] The DLM is used in this work for this reason and to allow comparison with the large number of previous studies using the DLM for AsO_4^{-3}-ferihydrite systems. The DLM derives its utility for macroscopic predictions by separating out chemical and electrostatic contributions to sorption reactions but the model does not provide information relating to surface complex structures and this dichotomy has been discussed.[7] Debate persists on surface complex structure and model approaches[8, 9] and all the data from this study are presented in the Supplementary Information section to support alternative model approaches.

In the DLM AsO_4^{-3} sorption is a ligand exchange reaction with a hydroxide group on a ferrihydrite surface site (≡FeOH) forming surface complexes of different degrees of protonation.

The equilibrium expressions are given in Table 1 with the means and ranges of DLM sorption constants (logK's) compiled from available literature data by Gustafsson and Bhattacharya.[3] These logK values have a high level of variability which creates significant uncertainty in predicted AsO_4^{-3} sorption and it is desirable to resolve this. In general anomalously large $logK_{As}$ values were derived from the data from Swedlund and Webster[6] that was obtained with an anomalously long reaction time of 200 h. Note that Gustafsson and Bhattacharya[3] mistakenly state the reaction time used for all Swedlund and Webster[6] data was 24 h. Regression analysis of the $logK_{As}$ values from Gustafsson and Bhattacharya[3] versus the log_{10} of the reaction time have positive slopes but these have a high uncertainty (Table 1) which is partly a reflection of the fact that the kinetics of sorption depends greatly on the AsO_4^{-3}/Fe ratio and this is discussed further in the modeling section.

In this work we quantify the significant contribution of kinetic factors to the variance in these reported ferrihydrite-AsO_4^{-3} logK's. Numerous studies have shown that the concept of equilibrium is not directly applicable to ion sorption on iron oxides. For example in ferrihydrite sorption experiments Scheinost et al[10] observed that Cu^{+2} and Pb^{+2} solution concentrations decreased linearly as a function of log(time) for 10^3 h, which was the duration of the experiment. Zhang and Stanforth[11] found that the adsorption kinetics of AsO_4^{-3} on goethite were generally well described by the Elovich Equation in which Γ has a linear dependence on log(t) and this has been variously attributed to inter- or intra-particle diffusion or site heterogeneity.[12, 13] Aquatic systems of interest to public health such as water treatment systems or aquifers involve time scales ranging from minutes to decades and a model with a single set of equilibrium constants cannot be applicable to AsO_4^{-3} distribution across all of these systems.

In this paper we follow AsO_4^{-3} adsorption onto ferrihydrite over 3600 h in batch systems with a range of total AsO_4^{-3} concentrations (termed As_{tot}) and pH. Because ferrihydrite is metastable,

solid samples were freeze dried and analyzed with infrared and Raman spectroscopy to test the stability of the ferrihydrite phase. The data were used to derive new time-dependent $\log K_{As}$ which account for the change in As_{sol} with time. The system was also probed with *in situ* and *ex situ* attenuated total reflectance infrared (ATRIR) spectroscopy in separate experiments to shed light on the processes involved.

Method

All experiments were conducted at room temperature (21°C) using water with resistivity of 18.2 MΩ cm which was acidified (pH < 4) and sparged with N_2 for 1 hour to remove CO_2. All solutions were kept under N_2. The pH was adjusted with HNO_3 or with NaOH. To minimise the presence of carbonate NaOH solutions were prepared weekly from 1:1 (w/w) NaOH:H_2O. Ferrihydrite was synthesized 12-18 h before sorption experiments by rapidly raising the pH of a $Fe(NO_3)_3$ solution from 2 to 8 and the phase present was confirmed by XRD.[6]

Arsenate sorption by ≈ 1mM ferrihydrite (i.e. ≈ 0.089 g L^{-1}) was measured as a function of time in batch systems having As_{tot} of ≈ 50, 100, or 200 μM and 0.06 M $NaNO_3$. At each As_{tot} sorption was measured at pH 6, 8, and 10 so that in all 9 systems were studied. Polycarbonate containers were used and previous experiments have shown that at these concentrations of As_{tot} sorption to container walls is negligible compared to sorption by iron oxides.[6] Samples were taken at ≈ 0.13, 0.25, 0.5, and 1 h and then at increasing time intervals over 3,000 h (125 days). The suspensions were stirred rapidly during sampling so that there was no change in the solids concentration over time. Suspensions were kept on a magnetic stirrer for the first 8 h to allow for continuous pH

monitoring and manual correction but after 8 h the pH drift was small and samples were placed on an end-over-end mixer at a rate of ≈ 5 rpm and pH drifts (typically < 0.1 pH unit) were manually corrected daily at least one hour prior to sampling. Samples were centrifuged (4,000 rpm, 5 minutes), the supernatant was filtered (0.2 μm cellulose acetate membrane) and the solids collected, briefly rinsed once with ≈ 0.06 M KCl and freeze dried for IR and Raman analysis to test ferrihydrite phase stability. A 10 mL unfiltered aliquot of each suspension was digested with ≈ 1 drop of 35 % HCl to determine the total Fe and As concentrations.

Aqueous Analysis

The suspension pH was measured using a London Scientific Instruments annular ring electrode. The As_{sol} was determined using either the molybdenum blue method[14] or ICP-MS. The molybdenum blue method LOD was 0.45 μM and samples with lower As_{sol} were analysed by ICP-MS which had a LOD of 0.067 μM. Selected samples with $1 < As_{sol} < 200$ μM were analysed by both methods and a linear regression of this data had a slope of 1.0037 with R^2 0.993. All HCl digests of unfiltered suspensions were analysed by ICP-MS.

Vibrational spectroscopy

The freeze-dried solid samples collected during the batch sorption experiments were characterized by Raman and IR to check for development of crystalline phases. Raman spectra were measured using a 785 nm laser on a Renishaw Raman System 1000 spectrometer. The IR spectra were measured using a single bounce 45° diamond ATR crystal on a Nicolet® 8700 Spectrometer. Freeze dried reference samples of ferrihydrite, goethite, lepidocrocite and hematite were prepared following the method of Schwertmann and Cornell[15] and phases confirmed by X-ray diffraction. In addition two types of ATRIR experiments probed the interfacial AsO_4^{-3}. *In situ* ATRIR spectra were recorded over time as AsO_4^{-3} reacted with

ferrihydrite that had been deposited by drying on a single bounce 45° diamond ATR crystal as previously described.[16] In addition ATRIR spectra were measured of ferrihydrite pastes that were obtained by centrifuging (4,000 rpm) suspensions to which AsO_4^{-3} was added.

Modelling

The adsorption data were modeled using the DLM and ferrihydrite parameters of Dzombak and Morel.[17] This includes a single sorption site type with a site density of 0.2 mol (mol Fe)$^{-1}$, a surface area of 600 m^2g^{-1}, a ferrihydrite M_w of 89 g mol^{-1} and surface site pK_A's of 7.29 and 8.93. Adsorption constants were determined at each sampling time from 0.125 h to ≈ 3000 h using FITEQL4.[18] At each time interval a set of 9 data points are available to optimize the $logK_{As}$'s. Each data point consists of a solids concentration in gL^{-1} (i.e. 89 $gmol^{-1}$ x $[Fe^{+3}]$ in M), the number of surface sites (i.e. 0.2 x $[Fe^{+3}]$ in M), the As_{tot}, the As_{sol} and the -pH (i.e. $log(H^+)$). Equations describing the decrease in As_{sol} over time allow for any time interval to be chosen. All the values can simply be input as serial data although the solids concentration is usually input as a single value for a series of data. The solids concentration is combined with the surface area (m^2g^{-1}) to give the number of m^2 of surface present so that a surface charge can be calculated. In our case the solids concentration varied slightly between different systems and it was desirable to be able to use the appropriate value for each data point. Methods to use FITEQL with different [solids] have been reported[19] but a little known feature in FITEQL is that solids concentrations can be input as serial data using component number 160 which is formally the surface potential component.[20] The measured As_{sol} was input as a "dummy component".

The input uncertainties in measured values were based on the method of Dzombak and Morel[17]. Calculations were done at the average ionic strength of 0.064 M using activity coefficients for solution species calculated from the Davis equation and all reported logK's are reported at an ionic strength of 0 M. Initial guesses for the $logK_{Asx}$ were taken from

VMINTEQ.[21] The goodness of fit is judged by the weighted sum of squares divided by the degrees of freedom (WSOS/DF) with values between 0.1 and 20 are considered a good fit.[6, 17] To check the validity of the FITEQL4 input files speciation was compared with that predicted by VMINTEQ and was identical. An example of a text input and the screen shots from the FITEQL Preprocessor are shown in the Supplementary Information section.

Results and Discussion

Ferrihydrite phase stability

Before considering the kinetic data it is necessary to assess the stability of the ferrihydrite as changes in iron oxide phase will affect As_{sol}. The Raman and IR spectra of the freeze dried solids (Figures SI1 and SI2) collected over the course of the kinetic experiments had no discernible hematite, goethite or lepidocrocite bands. In addition the broad feature at ≈ 800 cm^{-1} shows the presence of AsO_4^{-3} on the ferrihydrite surface while the absence of IR bands at ≈1350 and 1470 cm^{-1} demonstrates the absence of carbonate on the ferrihydrite surface. Ferrihydrite is only a meta-stable phase and over time converts to more stable iron oxides, including goethite and hematite. In previous experiments with pure ferrihydrite kept in suspension at pH 10 we have observed large goethite IR bands after 10 days.[5] Goethite forms from ferrihydrite via Fe^{3+} dissolution and reprecipitation and Das *et al*[22] found that the adsorbed arsenate produces stable surface complexes that prevents Fe^{+3} dissolution and inhibits the transformation into goethite or hematite. The Raman and IR spectra from the current study show that the AsO_4^{-3} has stabilized the ferrihydrite against transformation to goethite and we can state that the data in this work represent the reaction of AsO_4^{-3} with ferrihydrite over time with no confounding effects due to ferrihydrite phase transformations.

Kinetics of arsenate adsorption

The decrease in As_{sol} over time in systems with $As_{tot} \approx 200$ μM is presented in Figure 1 and Table SI1. If data for the first 150 h are plotted with a linear time scale then AsO_4^{-3} sorption shows the typical "two-stage" kinetics described in many studies with a rapid sorption step after which sorption continues at a slower pace. With a logarithmic time scale data over the whole course of the experiment (≈3,000 h) show a linear decrease in As_{sol} as a function of log(t) at each pH. As the pH of the suspension is decreased from pH 10 to pH 6 there is a corresponding decrease in As_{sol} and an increase in slope of the As_{sol} vs log(t) line. This behavior is very similar to that previously reported for cation sorption by ferrihydrite such as Scheinost *et al*[10] who explained the slow adsorption stage as being due to diffusion toward surface sites buried in the interior of ferrihydrite aggregates. Fuller *et al*[23] also made a similar observation for AsO_4^{-3} and ferrihydrite over ≈ 200 h and reached a similar explanation for the phenomenon. Figure 1 also shows the predicted As_{sol} for each system using the sorption constants from both Gustafsson (derived from data with t = 1 to 200 h) and Swedlund and Webster which were derived from data with t = 24 to 200 h[6]. The Gustafsson model agrees with the data from this work at t ≈ 2 -10 h while the Swedlund and Webster model agrees with the data from this work at t ≈ 100 – 2000 h. The data from this work is evidently reasonably consistent with both these previous studies.

[Fig 1 about here]

For systems with As_{tot} of ≈100 μM (Figure 2 and Table SI2) the As_{sol} decreases linearly with log(t) over the ≈ 2,500 h course of the experiment at pH 10 and 8. However at pH 6 this is only true for the first 10 h after which time As_{sol} decreases asymptotically over log(t). This is a physical necessity because the As_{sol} would become negative beyond 18 h if the Elovich behavior

was extrapolated. In fact the As_{sol} would become negative at some time for any system if it continued to decrease linearly vs log(t) and in the system with pH 6 and 100 μM As_{tot} this occurs within the time frame of the experiment. After ≈ 10 hours the decrease is more appropriately described by a power function rather than a logarithmic function and the equations used to describe all As_{sol} vs time data are given in the figure. We do not attempt to infer some mechanistic model from the change in function but use these functions to interpolate the As_{sol} so that we may calculate $logK_{As}$ values at any time interval. The data at pH 6 and 8 agree with the Gustafsson model at t ≈ 6 h and with the Swedlund and Webster model at t ≈ 1000 h. In comparison the data for the system at pH 10 are all a bit below the Gustafsson model and agrees with the Swedlund and Webster model at t = 1 h.

[Fig 2]

For systems with As_{tot} of ≈50 μM (Figure 3 and Table SI3) the linear decrease in As_{sol} vs log(t) is only evident for the first 8 h at pH 10 and the first 2 h a pH 8. At pH 6 after just 7.5 minutes 99.4 % of the As_{tot} has been adsorbed and from 1 to 1000 h the As_{sol} decrease is minimal, from ≈ 0.1 to 0.08 μM. The decrease over the first hour is best described by a power function and the very slight decrease in As_{sol} after 1 h is described by a log function with a slope of just -0.013. The experiments with ≈50 μM As_{tot} and pH 6 and 8 were the only two systems where some sort of As_{sol} stability was achieved with no clear decrease in As_{sol} after 20 or 100 h at pH 6 or 8 respectively. It is also noteworthy that there is no increase in As_{sol} over time under any conditions. In experiments where ferrihydrite was aged for up to 144 h prior to AsO_4^{-3} addition the amount of AsO_4^{-3} sorption decreased the longer the ferrihydrite was aged and this was attributed to the number of surface sites decreasing due to either crystallite growth or ongoing coagulation as ferrihydrite aged.[23] In light of this result the absence of any increase in As_{sol} over

time in the current study suggests that the presence of AsO_4^{-3} stabilizes the ferrihydrite not only against phase transformation but also against processes which decrease surface site concentrations over time.

At pH 10 the data agree with the Gustafsson model and the Swedlund and Webster model at ≈ 0.5 and 1 h respectively while at pH 8 this occurs at t ≈ 2 and 40 h. After 1 h at pH 6 the As_{sol} was ≈ 0.1 μM while the models were 2 nM (Gustafsson) and 0.4 nM (Swedlund and Webster). This is the most significant discrepancy between the data and the models (considering As_{sol} on a logarithmic scale) and may indicate that some other process is occurring in these systems with very low As_{sol}. If one considers sorbed As on any scale or considers As_{sol} on a linear scale the difference is not significant. This has an impact on how one configures the FITEQL file and is discussed below.

[Fig 3]

The Log K_{As}'s over time

Values for the $logK_{As1}$ to $logK_{As4}$ were optimized from the data at each time interval. Because the data at pH 6 with ≈50 μM As_{tot} were not well described by the model, these data were excluded in the parameter optimization process so at each time point there are eight data points. Also note that Ali and Dzombak[4] removed data points that corresponded to greater than or equal to 85% sorption with the justification that FITEQL weights these data points too heavily which produces biased log K values. All four $logK_{As}$'s values could be optimized from the data provided at each time interval and the optimized $logK_{As}$'s as a function of time are presented in Figure 4 and Table 2. The WSOS/DF all lay between 1.4 and 2.03 which demonstrates that the data are well described by the model system and that the data also reasonably constrain the $logK_{As}$ values.

There is a clear linear increase for $\log K_{As1}$ to $\log K_{As3}$ as a function of log(t) although $\log K_{As4}$ appears to start to plateau after ≈ 10 h. In general, the slope of the line increases as the charge on the surface species decreases and this was also observed in Table 1. This derives from the effect of surface coverage on the modeled surface speciation. For simple electrostatic reasons a higher AsO_4^{-3} surface coverage will in general favor the modeled species with a lower charge. For example with 1 mM ferrihydrite the $\equiv FeOHAsO_4^{-3}$ species pH between 4 and 12 accounts for 62 % or 15 % of the sorbed AsO_4^{-3} with 1 μM As_{tot} or 100 μM As_{tot} respectively (Figure SI4). From Figure SI4 it is clear that data with a lower As_{tot}/[ferrihydrite] more tightly constrain $\log K_{As4}$ while data with higher As_{tot}/[ferrihydrite] will more tightly constrain $\log K_{As1}$. Similarly σ_1 and σ_4 change systematically with Γ in Table 2. Data with lower As_{tot}/[ferrihydrite] approach equilibrium As_{sol} more rapidly thus the value of $\log K_{As4}$ changes less with time than $\log K_{As1}$.

IR Spectroscopy of AsO_4^{-3} on ferrihydrite

The As-O stretching region of the *in situ* ATR-IR spectra recorded over time as 200 μM AsO_4^{-3} at pH 8.0 in 0.06 M NaCl reacted on a ferrihydrite film deposited on a diamond ATR crystal are shown in Figure 5a. The area of this feature increased linearly as a function of log(time) but the spectra are shown with absorbance normalized to emphasize the fairly subtle change in their shape over time. All spectra have a broad maximum at ≈ 810 cm^{-1} with a shoulder at ≈ 870 cm^{-1}. Over time as Γ increases the shoulder becomes more prominent and shifts from 861 to 876 cm^{-1} as is particularly evident in the 2nd derivatives. Figure 5a also has the IR spectrum for scorodite and it is clear that formation of scorodite, as has been proposed in some studies,[24] does not explain the observed change in shape of the ATRIR spectra as Γ increases.

ATRIR spectra were also measured of ferrihydrite pastes obtained by centrifuging suspensions 5-15 minutes after AsO_4^{-3} had been added either a) prior to ferrihydrite precipitation (i.e.

coprecipitated), b) to ferrihydrite that had been freeze dried and then resuspended in electrolyte or c) to ferrihydrite that had been aged in the electrolyte for 24 h but had not been dried. The three spectra have a maximum at 790 cm^{-1} and a shoulder at ≈870 cm^{-1} (Figure 5b). In the coprecipitated system the shoulder is most pronounced and at 875 cm^{-1} in the 2nd derivative while for the freeze dried ferrihydrite the shoulder is less pronounced and at 864 cm^{-1} in the 2nd derivative. The pastes with AsO_4^{-3} sorbed for 5 minutes on a ferrihydrite that had not been dried are intermediate between the coprecipitated and sorbed on freeze dried.

The nanometer sized primary ferrihydrite particles are composed of between 20 and 60 domains[25] and in coprecipitation experiments AsO_4^{-3} can sorb onto domain surfaces prior to aggregation and as the coprecipitates age the process of iron oxide aggregation or crystal growth displaces AsO_4^{-3} causing desorption to occur over time.[23] This has been described as the reverse of "post synthesis" absorption of AsO_4^{-3} where the AsO_4^{-3} has been considered to start at the ferrihydrite particle surface and diffuse to sorption sites located within particles.[23] The spectra in Figure 5 support this model from Fuller et al[23] in which slow diffusion of AsO_4^{-3} from external sorption sites to internal sorption sites accounts for the slow approach to equilibrium. Initially the ATRIR spectra of AsO_4^{-3} in the *in situ* experiments are similar to the spectra where AsO_4^{-3} had just been added to freeze dried ferrihydrite, where AsO_4^{-3} species at the particle surface would dominate. Over time the ATRIR spectra of AsO_4^{-3} in the *in situ* experiments change to become similar to the spectra from the system where AsO_4^{-3}-ferrihydrite had just been coprecipitated, where AsO_4^{-3} species at sites located within particles would be more prevalent. It should be noted that in the case of the *in situ* experiments the ferrihydrite film had been dried onto the ATR crystal.

The shift in the ATRIR spectra over time in the *in situ* experiments and the contrast in the spectra for the coprecipitation vs. freeze dried systems described above suggest that the

coordination environment of AsO_4^{-3} on an external sorption site is different from AsO_4^{-3} on an internal surface site. It has been proposed that H_4SiO_4 co-precipitated with ferrihydrite may bridge domains[25, 26] and in the case of AsO_4^{-3} there could also be bridging between particles or domains which could be electrostatic or covalent. It is also noteworthy that when AsO_4^{-3} was exposed for just 5 minutes to ferrihydrite that had not been dried the ATRIR spectrum was intermediate between the spectra for the coprecipitated and sorbed on freeze dried ferrihydrite systems. Comparing this to the shoulder position in the *in situ* spectra on the dried ferrihydrite film suggests that some development of AsO_4^{-3} complexes on internal sorption sites (by diffusion or by bridging particles) is fairly rapid with a ferrihydrite that has not been dried.

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Table 1 Equilibrium expressions and constants for arsenate surface complexation reactions.

Equilibrium Expression[a]	$logK_{As}$[b]	*Range*	*Slope*[c]
$(\equiv FeH_2AsO_4) = (\equiv FeOH)(AsO_4^{-3})(H^+)^3 K_{As1}$	31.0 (*30.5, 31.5*)	30.2-32.5[d]	0.54 (-0.03, 1.1)
$(\equiv FeHAsO_4^{-1}) = (\equiv FeOH)(AsO_4^{-3})(H^+)^2 e^{\frac{F\Psi}{RT}} K_{As2}$	25.8 (*25.6, 26.1*)	25.0-27.0 [d]	0.47 (0.06, 0.87)
$(\equiv FeAsO_4^{-2}) = (\equiv FeOH)(AsO_4^{-3})(H^+) e^{\frac{2F\Psi}{RT}} K_{As3}$	19.5 (*19.4, 19.6*)	19.8-20.3 [d]	0.18 (-0.3,0.6)
$(\equiv FeOHAsO_4^{-3}) = (\equiv FeOH)(AsO_4^{-3}) e^{\frac{3F\Psi}{RT}} K_{As4}$	11.9 (*11.9, 12.0*)	10.9-12.8[e]	0.0 (-0.4, 0.4)

[a] F,Ψ, R, T have their usual meaning, (X)=activity of species X
[b] Weighted average with 95 % confidence interval in brackets (data from [3])
[c] Slope and 95 % confidence interval for $logK_{Asn}$=m(log(t))+c where t is reaction time (data from [3])
[d] Highest value derived from Swedlund and Webster data [6]
[e] Swedlund and Webster $logK_{As4}$ values were 11.40-11.73 [6]

Table 2 The log equilibrium constants (log K_{Asn}) values and associated standard deviations for arsenate adsorption to ferrihydrite calculated FITEQL4 which take into account adsorption time. The $As_T \approx 50$ μM pH 6 values were excluded from the FITEQL4 input file.

Hours	log K_{As4}	σ_4	log K_{As3}	σ_3	log K_{As2}	σ_2	log K_{As1}	σ_1	WSOS/DF
0.5	12.135	0.069	19.202	0.105	25.569	0.103	30.049	0.309	2.026
1	12.205	0.075	19.381	0.098	25.724	0.096	30.405	0.168	1.683
2	12.293	0.055	19.498	0.485	25.891	0.096	30.660	0.111	1.416
4	12.404	0.079	19.565	0.107	26.064	0.075	30.889	0.093	1.292
8	12.540	0.080	19.576	0.138	26.236	0.065	31.120	0.080	1.607
12	12.597	0.077	19.646	0.124	26.315	0.062	31.238	0.074	1.779
24	12.650	0.081	19.745	0.119	26.432	0.058	31.418	0.068	1.748
48	12.699	0.086	19.838	0.114	26.548	0.055	31.589	0.064	1.700
96	12.743	0.090	19.927	0.109	26.663	0.054	31.758	0.062	1.627
150	12.769	0.094	19.983	0.107	26.736	0.053	31.866	0.062	1.555
300	12.808	0.100	20.062	0.103	26.851	0.052	32.035	0.062	1.473
600	12.844	0.107	20.137	0.101	26.967	0.051	32.206	0.062	1.392
1000	12.869	0.107	20.186	0.101	27.054	0.051	32.334	0.062	1.400
1300	12.883	0.114	20.209	0.100	27.100	0.052	32.400	0.064	1.442

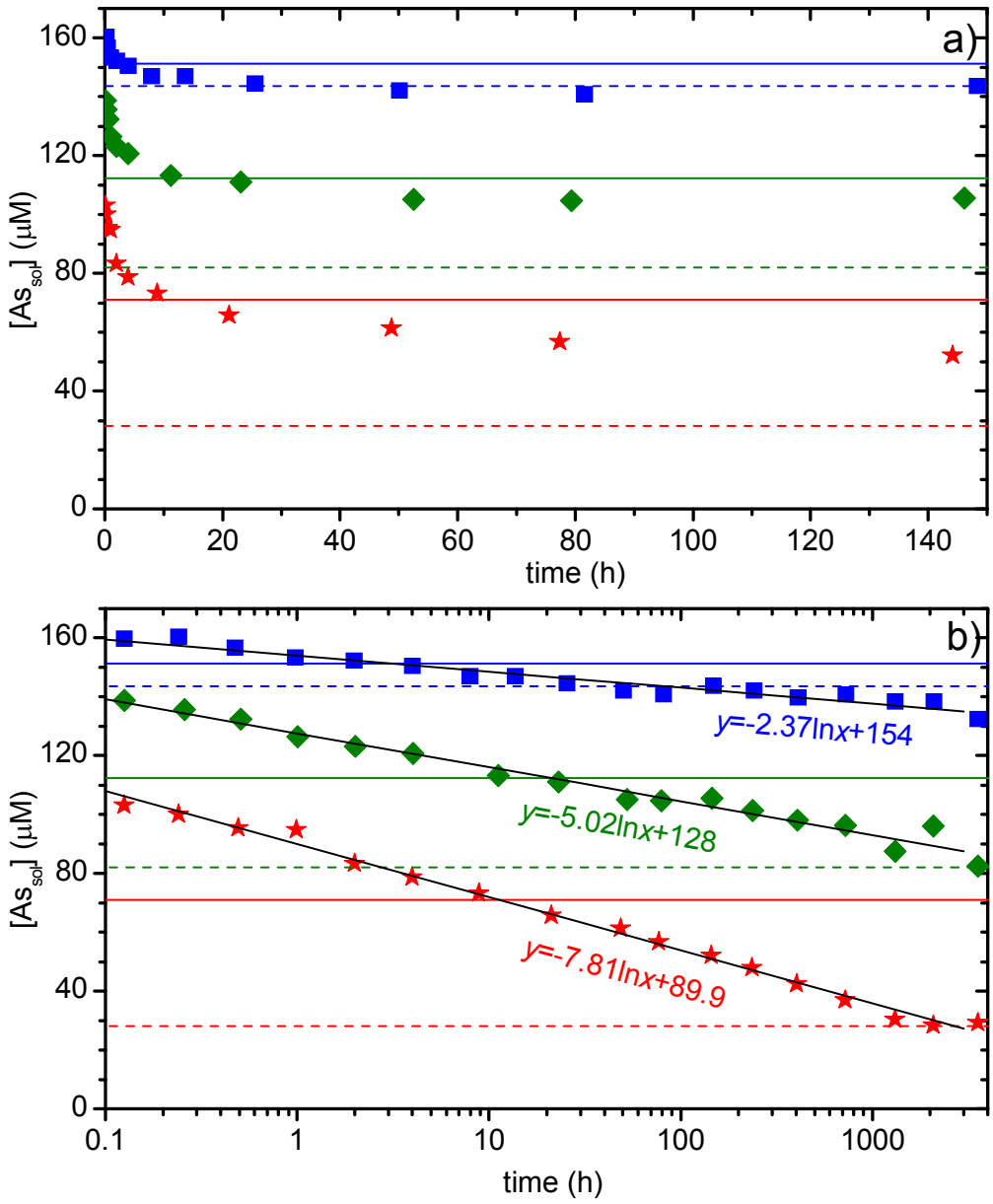

Figure 1 Solution arsenate concentrations over time in systems with ≈ 1 mM Fe, 200 μM total [AsO_4^{-3}] and 0.06 M $NaNO_3$. Blue, green and red are pH 10, 8 and 6 respectively. Horizontal lines are the model predictions using the values from Gustafsson [21] (solid lines) and Swedlund and Webster [6] (dashed lines).

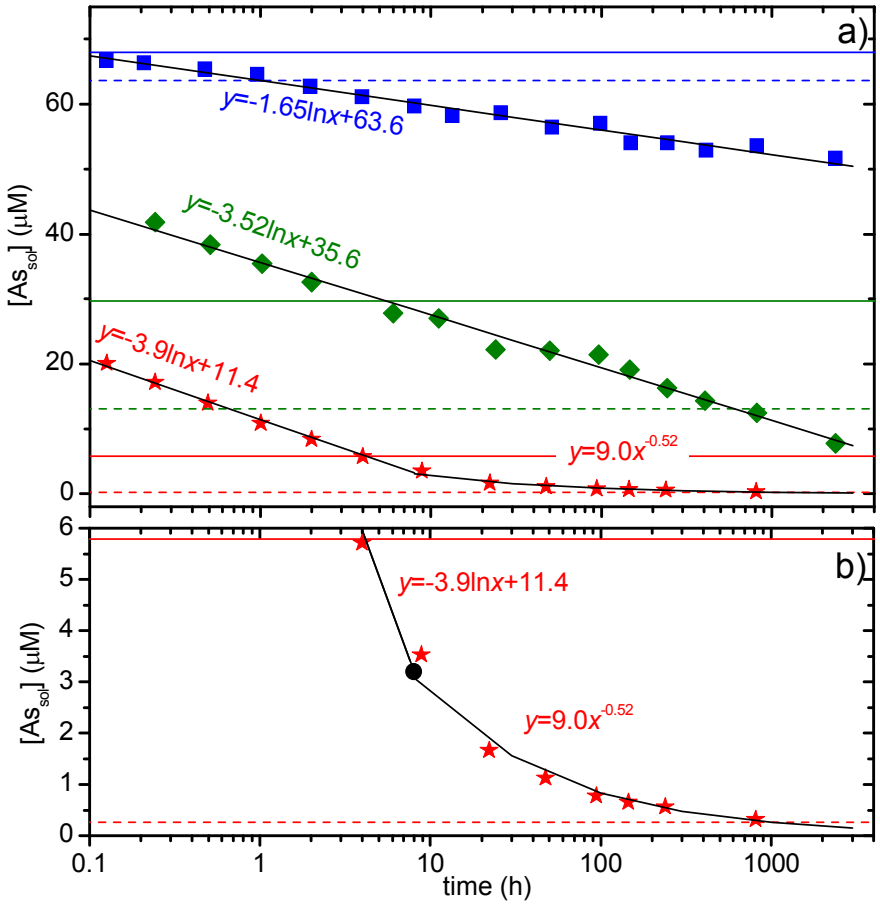

Figure 2 Solution arsenate concentrations over time in systems with ≈ 1 mM Fe, 100 μM total [AsO_4^{-3}] and 0.06 M $NaNO_3$. Blue, green and red are pH 10, 8 and 6 respectively. Horizontal lines are the model predictions using the values from Gustafsson [21] (solid lines) and Swedlund and Webster [6] (dashed lines).

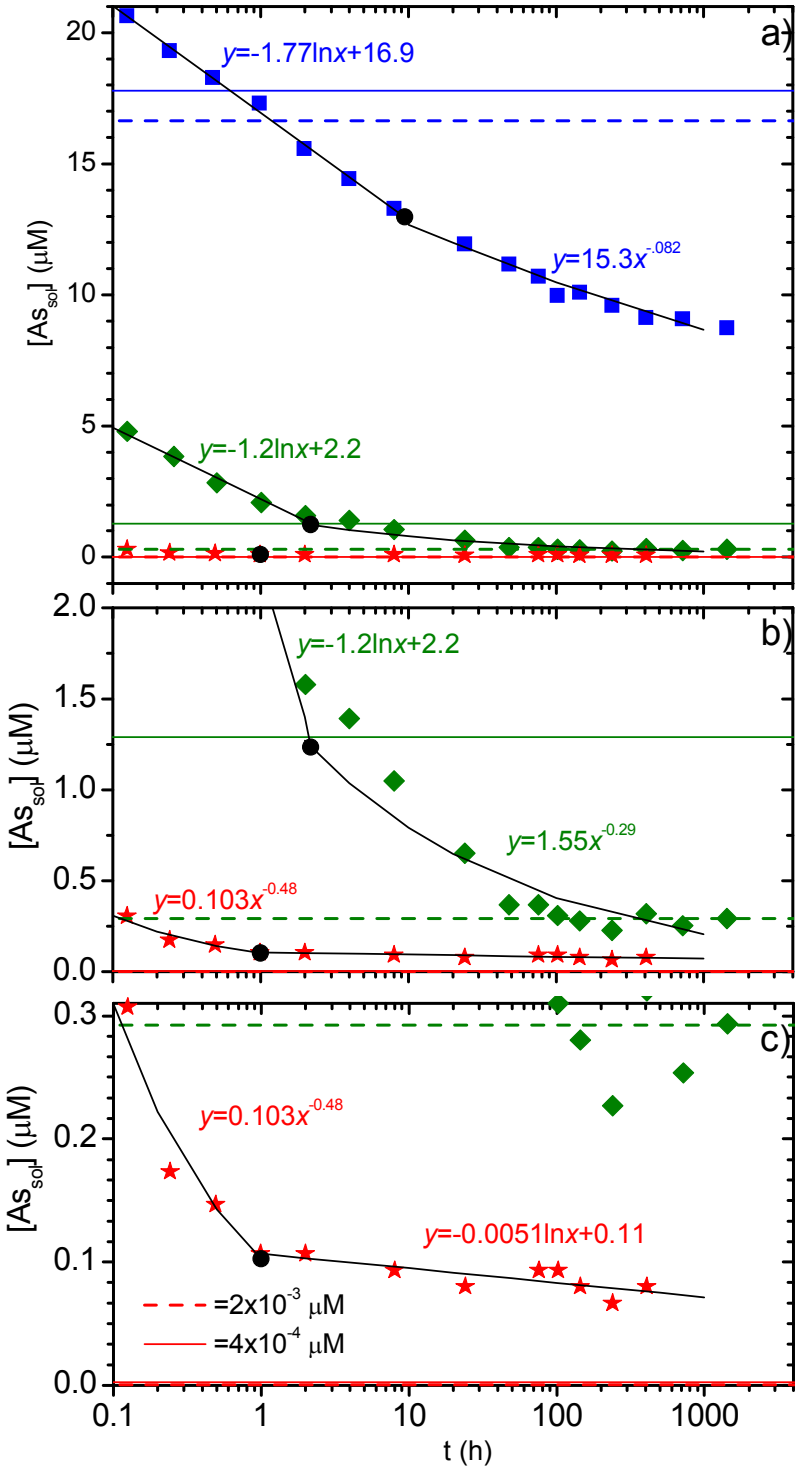

Figure 3 Solution arsenate concentrations over time in systems with ≈ 1 mM Fe, 50 μM total [AsO_4^{-3}] and 0.06 M $NaNO_3$. Blue, green and red are pH 10, 8 and 6 respectively. Horizontal lines are the model predictions using the values from Gustafsson [21] (solid lines) and Swedlund and Webster [6] (dashed lines).

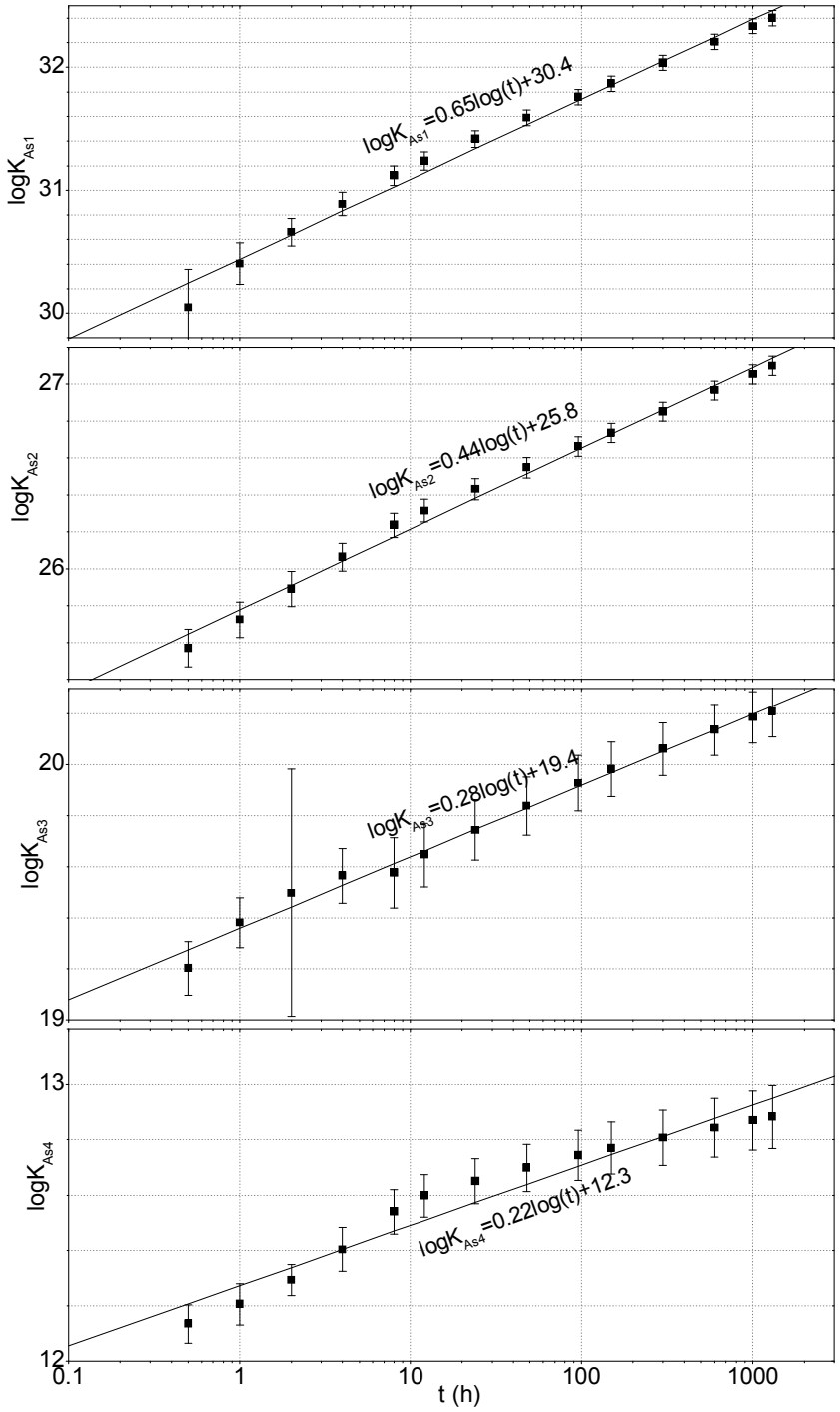

Figure 4 Optimized logK values from the data in Figures 1-3. Error bars are the reported standard deviations in logK.

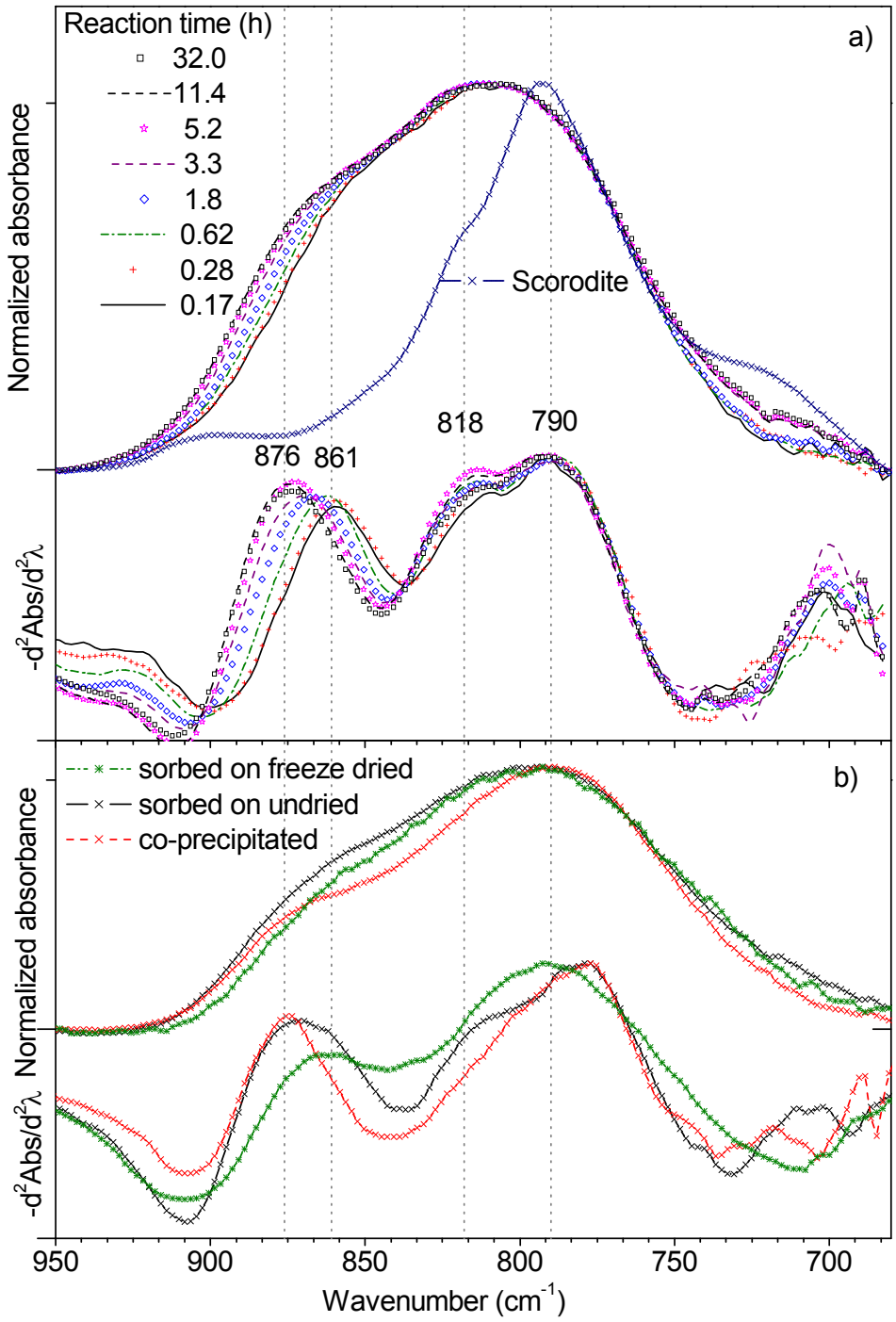

Figure 5 Absorbance normalized ATR-IR spectra and the negative 2nd derivatives of AsO_4^{-3} on ferrihydrite in systems with 200 μM total AsO_4^{-3} at pH 8 and 0.06 M NaCl a) *in situ* spectra recorded over time as AsO_4^{-3} reacted with a ferrihydrite film dried onto an ATRIR crystal b) spectra of pastes obtained by centrifugation 5-10 minutes after AsO_4^{-3} was added to ferrihydrite or was coprecipitated with ferrihydrite. The IR spectrum of scorodite is also shown.