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Photoinduced Oxidation of Arsenite to Arsenate in the Presence of Goethite

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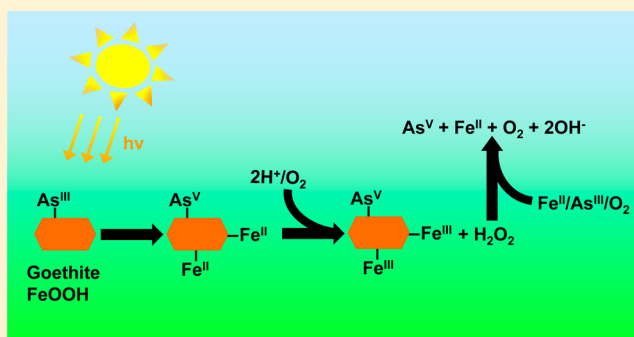
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S Supporting Information

ABSTRACT: The photochemistry of an aqueous suspension of goethite in the presence of arsenite (As(III)) was investigated with X-ray absorption near edge structure (XANES) spectroscopy and solution-phase analysis. Irradiation of the arsenite/goethite under conditions where dissolved oxygen was present in solution led to the presence of arsenate (As(V)) product adsorbed on goethite and in solution. Under anoxic conditions (absence of dissolved oxygen), As(III) oxidation occurred, but the As(V) product was largely restricted to the goethite surface. In this circumstance, however, there was a significant amount of ferrous iron release, in stark contrast to the As(III) oxidation reaction in the presence of dissolved oxygen. Results suggested that in the oxic environment ferrous iron, which formed via the photoinduced oxidation of As(III) in the presence of goethite, was heterogeneously oxidized to ferric iron by dissolved oxygen. It is likely that aqueous reactive oxygen species formed during this process led to the further oxidation of As(III) in solution. Results from the current study for As(III)/goethite also were compared to results from a prior study of the photochemistry of As(III) in the presence of another iron oxyhydroxide, ferrihydrite. The comparison showed that at pH 5 and 2 h of light exposure the instantaneous rate of aqueous-phase As(V) formation in the presence of goethite ($12.4 \times 10^{-5} \text{ M s}^{-1} \text{ m}^{-2}$) was significantly faster than in the presence of ferrihydrite ($6.73 \times 10^{-6} \text{ M s}^{-1} \text{ m}^{-2}$). It was proposed that this increased rate of ferrous iron oxidation in the presence of goethite and dissolved oxygen was the primary reason for the higher As(III) oxidation rate when compared to the As(III)/ferrihydrite system. The surface area-normalized pseudo-first-order rate constant, for example, associated with the heterogeneous oxidation of Fe(II) by dissolved oxygen in the presence of goethite ($1.9 \times 10^{-6} \text{ L s}^{-1} \text{ m}^{-2}$) was experimentally determined to be considerably higher than if ferrihydrite was present ($2.0 \times 10^{-7} \text{ L s}^{-1} \text{ m}^{-2}$) at a solution pH of 5.



1. INTRODUCTION

In the context of human health, arsenic (As) is one of the most toxic metals present in the Earth's crust. Arsenic exists in the form of various oxyanions in groundwater, is adsorbed on mineral/rock, and is present in combination with other metal ores such as gold, copper, and lead.¹ Elevated levels of As in aquatic environments are due to the result of both natural processes and anthropogenic activities.^{2,3} Even though As is a known carcinogen for human organs that include the skin, lungs, and kidney,⁴ there are still over 150 million people around the globe who are estimated to be exposed to elevated arsenic concentrations in drinking water.^{5,6}

In the natural environment, As exists in a variety of oxidation states and in numerous organic and inorganic forms. Inorganic arsenic species, such as arsenite (As(III)) and arsenate (As(V)), are predominant in most environmental settings. The speciation of the inorganic As species is pH dependent.⁷ In most aqueous environments, inorganic As(III) largely occurs as a neutral species (H_3AsO_3), while As(V) generally exists as an oxyanion (e.g., H_2AsO_4^-). While As in general is toxic in the

realm of human health in either oxidation state, As(III)-bearing species are considered to be more toxic and more difficult to immobilize than As(V)-bearing oxyanions.⁸ Therefore, processes that enhance the transformation of As(III) to As(V) are currently of considerable interest.

Among the many oxidation methods that have relevance to the conversion of As(III) to As(V), the photocatalytic oxidation (PCO) of As(III) has received considerable attention as a more advanced approach. Of the various PCO methods, TiO_2 -assisted As(III) oxidation has been extensively studied in the past decade⁹ (and references therein). However, the major drawback of the TiO_2 system is that a very small portion of solar radiation (3–5%) is able to activate the material and drive chemical reactions.¹⁰ Furthermore, the use of TiO_2 requires the use of coagulants for the complete removal of both aqueous

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As(V) and TiO_2 .¹¹ The photooxidation of As(III) in the presence of dissolved Fe(II), Fe(III), and citrate has also been suggested,^{8,12} although an optimal ratio of aqueous Fe and citrate needs to be maintained for effective removal.¹² Other photochemical conversion schemes relevant to the oxidation of As(III) include UV-ferrioxalate,¹³ UV-peroxydisulfate ions,¹ and vacuum-UV lamp radiation (185 and 254 nm).¹⁴ All these strategies show promise, but they all require a separate adsorbent for the complete removal of the relevant reactants and products and/or need a cumbersome technology to apply the strategy. Thus, the development of an inexpensive, environmentally relevant and efficient As(III) removal method is still of interest.

Recently, we demonstrated that simulated solar light can facilitate the oxidation of As(III) to As(V) on ferrihydrite, a nanocrystalline iron oxyhydroxide (2–3 nm diameter particles).¹⁵ We showed that As(III) oxidation primarily occurred on ferrihydrite in the presence of simulated solar radiation until the mineral surface became saturated with surface-bound As(V) product and that the details of the As(III) oxidation process were similar under anoxic and oxic solution conditions.

In the present study, we extend our investigations of photoinduced As(III) oxidation on iron oxyhydroxides to the environmentally relevant mineral goethite. Prior studies that have investigated As(III) adsorption and oxidation on goethite under dark conditions showed that a small amount of oxidation occurred at extended reaction times (~ 20 days),¹⁶ but no evidence of As(III) oxidation was observed within a few days.¹⁷ To our knowledge there are no prior studies that have investigated the photochemical reactions of As(III) on goethite. A goal of the current study is to compare the photochemical behaviors of goethite and ferrihydrite with regard to As(III) oxidation under a range of experimental conditions. Specifically, we compare the oxidation of As(III) on goethite to As(III) on ferrihydrite in the presence of light at different solution pH values, and in both anoxic and oxic solutions. We will show that under specific reaction conditions the details of As(III) oxidation on goethite in the presence of simulated solar light are different than those for As(III) oxidation chemistry on ferrihydrite. We believe that the results bring forward important mechanistic details that help to explain how the redox chemistry underlying As(III) oxidation can vary on two different iron oxyhydroxides.

2. EXPERIMENTAL SECTION

Synthesis and Characterization of Goethite. Nanosized goethite particles were synthesized according to the method developed by Anschutz and Penn.¹⁸ BET surface area measurements of synthesized goethite yielded average values of $146 \pm 10 \text{ m}^2/\text{g}$. Transmission electron microscopy (TEM), infrared spectroscopy (IR), and X-ray diffraction (XRD) data showed (see Supporting Information, Figures S1–S3) that the size and crystallinity of the synthesized dry solids were consistent with what was expected for goethite nanorods.¹⁸

Batch Studies. Geochemical batch photoirradiation and dark control experiments were conducted in a way similar to that for our previous contributions.^{15,19} Briefly, 50 mg of dry goethite was suspended in 199 mL of 2.5 mM NaCl solution and sonicated for 5–10 min to obtain well-suspended particles. One milliliter of As(III) solution (from a 50 mM NaAsO_2 stock solution) was added to the suspension, and the solution pH was maintained at 4, 5, or 7 until the completion of experimentation by using an autotitrator (718 STAT Titrino, Metrohm

Switzerland) and 0.1 M NaOH or HCl. The suspension was allowed to equilibrate for a period of 24 h in the absence of light, and then the suspension was exposed to light emitted from a 900 W high-pressure xenon lamp (Schoeffel Instruments, Westwood, NJ).²⁰ A pyrex filter was used during all photochemical experiments (transmits ultraviolet A, 315–400 nm and visible light),²¹ and the reaction temperature was maintained at $25 \pm 2^\circ\text{C}$. The average intensity of light (UVA + visible) impinging on the reaction vessel was measured under our experimental configuration to be $\sim 1450 \text{ W m}^{-2}$, slightly higher than the maximum global irradiance of natural sunlight ($\sim 1050 \text{ W m}^{-2}$).²² Other details regarding the spectral output of light sources were discussed in prior work from our laboratory.^{15,19} One of the purposes of this study was to compare the As photochemistry between ferrihydrite and goethite. To account for the smaller specific surface area of goethite, a smaller initial As(III) concentration was used (approximately half of what was used for ferrihydrite) for this mineral. Hence, the concentration of solution-phase As(III) was similar after goethite and ferrihydrite were individually equilibrated with As(III) for 24 h, prior to irradiation. In addition, we note that these different initial As(III) concentrations led to a maximum As loading on the respective iron oxyhydroxides based on adsorption isotherm experiments (see Supporting Information, Figure S4).

Anoxic batch studies were conducted by bubbling N_2 gas (high purity, Airgas) though the solution of interest for 1 h prior to irradiation, and a constant N_2 environment was maintained in the reactor headspace throughout the experiment. All other experiments were performed in solutions that were exposed to the ambient atmosphere and hence contained dissolved oxygen and dissolved CO_2 .

Analyses. Samples for the determination of dissolved Fe(II) and aqueous As species were taken from the suspensions, centrifuged, and filtered through a Millipore filter ($0.2 \mu\text{m}$). Dissolved Fe(II) was determined by using a ferrozine assay.^{19,23} Aqueous-phase arsenic species were analyzed using an ion chromatograph (IC, Dionex ICS-1000), with a detection limit of $\sim 5 \mu\text{M}$. The IC was equipped with a Dionex IonPacAS22 ($4 \text{ mm} \times 250 \text{ mm}$) analytical column and a conductivity detector. Details regarding the analytical methodology for As species are described in a prior contribution.¹⁵ All the chemicals that were used in this study that included sodium arsenite, sodium arsenate, ferric chloride, ferric nitrate, ferrous ammonium sulfate, sodium hydroxide, hydrochloric acid, and hydrogen peroxide were obtained from Sigma Aldrich (analytical grade). All the batch studies were conducted in triplicate, and calculated standard errors of estimation were within 3–6%. For the sake of clarity, error bars are not shown.

Quick-Scanning X-ray Absorption Spectroscopy (Q-XAS). The oxidation state of the arsenic was determined using As K-edge X-ray absorption near-edge structure (XANES) spectroscopy. Initial XANES analyses of the As-reacted goethite samples were performed at a synchrotron beamline using focusing optics and revealed that As(III) underwent partial oxidation to As(V) upon exposure to the synchrotron beam over the time scale of the several minutes needed to collect a spectrum. Beam-induced oxidation of As(III) has been reported in previous studies.²⁴ To avoid this experimental artifact we used quick-scanning X-ray absorption spectroscopy (Q-XAS) as implemented at beamline X18B at the National Synchrotron Light Source (Brookhaven National Laboratory). The Q-XAS technique developed at X18B has been described previously in

detail.^{25,26} Continuous, cam-driven scanning of the channel-cut Si(111) monochromator allowed collection of a full XAS spectrum in as little as 100 ms. We used a slower scanning rate in our work to achieve a better signal from the dilute samples. Individual XANES scans were obtained in approximately 1 s, and we collected scans continuously for 30-s intervals. This allowed comparison of successive XANES spectra immediately upon opening the X-ray photon shutter to the sample. Comparison of individual scans from As(III)-reacted goethite control samples revealed no evidence of any oxidation for these experimental conditions. This test was repeated several times for As(III) and As(V) control samples and aqueous As(III) and As(V) reference samples, revealing no changes in any of the spectra over the duration of the brief scan sequence. Thus, we can rule out beam-induced oxidation in these Q-XAS measurements. The monochromator was calibrated by assigning the first peak in the derivative of the aqueous As(III) reference sample spectrum an energy value of 11867 eV.

The photoirradiated As(III)–goethite suspension and the As(III)- and As(V)-sorbed goethite control samples (prepared in the dark) were individually centrifuged, washed once with pH 5 deionized water, dried, and loaded into Lucite sample holders and sealed with Kapton tape. Arsenic K-edge Q-XAS data were collected as described above. After confirmation that individual scans within the 30 s sequence were identical, eight to nine scans were averaged to reduce noise. Spectra for reference samples were collected before and after the sorption samples to confirm no change in monochromator calibration. A linear pre-edge background was subtracted, and the XANES spectra were normalized using a single postedge point (11915 eV) as described in a previous study from our laboratory.¹⁵

3. RESULTS AND DISCUSSION

As(III) Oxidation in Goethite Suspensions Containing Dissolved Oxygen. Geochemical batch reactions were carried out to quantify the amount of As(III) oxidation as well as the nature of the aqueous and surface-bound products formed on goethite during irradiation. Figure 1a plots the amount of total As adsorbed on goethite as a function of irradiation time after the 24 h period in which goethite was exposed to As(III) in the dark. Time-zero on this plot is associated with the amount of As(III) (triangles) that adsorbs on goethite after this 24 h equilibration period (i.e., no irradiation). The experimental data show that the total amount of As adsorbed to goethite is enhanced noticeably in the presence of light. In addition we also experimentally observed aqueous Fe(II) and As(V) product. Figure 1b plots the concentration of aqueous Fe(II) and As(V) as a function of time during the irradiation of an As(III)/goethite suspension. We presume that the aqueous ferrous iron product is due to the reduction of ferric iron associated with the goethite during the oxidation of As(III) to As(V) because no measurable amount of Fe(II) was observed when a goethite suspension was exposed to light in the absence of aqueous As(III).

Evidence for the presence of As(V) product adsorbed on the goethite surface after irradiation is obtained from XANES. Figure 2 exhibits As K-edge XANES spectra for goethite that was exposed to As(III) in the dark for 24 h and then exposed to light for 2, 5, and 12 h. Also included are reference data for goethite that was exposed to As(III) and As(V) for 24 h in dark conditions. The XANES spectra of the goethite samples that were individually exposed to As(III) and As(V), but not exposed to the light source, exhibit well-resolved edge

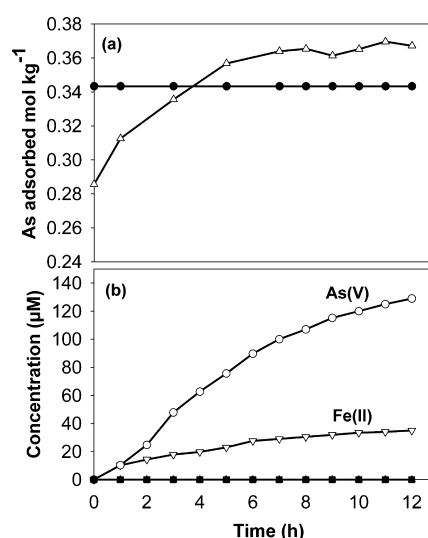


Figure 1. (a) Amount of As adsorbed on goethite as a function of time in the presence of light (open triangles) in a 0.25 g L⁻¹ goethite suspension at pH 5 with an initial 0.250 mM As(III) concentration. The amount of arsenic adsorption at time-zero on this plot is representative of the amount of adsorbed As(III) after aqueous As(III) was equilibrated with goethite in the dark for 24 h. No As(V) product forms during this equilibration in the dark. Filled circles represent the amount of As(V) adsorbed in a similar time frame with an initial As(V) concentration of 0.250 mM under dark conditions. (b) Concentration of aqueous-phase Fe(II) (open triangles) and As(V) (open circles) in solution during the photoirradiation process used for plot a. Control studies (in absence of light) showed no Fe(II) (filled triangles) or As(V) (filled squares) in solution. All of the experiments utilized reaction solutions that contained dissolved O₂.

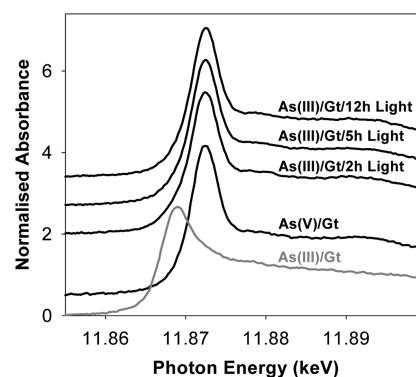


Figure 2. Normalized As K-edge Q-XAS (XANES) spectra recorded for As(III) and As(V) adsorbed on goethite (Gt) in the dark, and for photoirradiated As(III)/goethite for the given light exposure time as indicated in the figure. The results show that the predominant species on the goethite surface after irradiation is As(V).

structures characteristic of the As(III) and As(V) oxidation states, respectively. Specifically, the energy difference between the absorption maxima associated with the two surface species is ~3.7 eV, which is consistent with edge positions for As(III) and As(V) coordinated to oxygen, respectively.^{15,27} We point out that by using the Q-XAS method, which permits individual XANES spectra to be collected in ~1 s, we were able to avoid any beam-induced oxidation state changes of the As, as demonstrated by testing reference samples. Importantly, the similarity of the As(V)/goethite reference and light-exposed As(III)/goethite XANES data lead to the conclusion that As(V)

Table 1. Summary of the Amount of Surface Bound and Aqueous As Species for Various Experiments That Used Goethite and Ferrihydrite under Dark and Light Conditions

experiments ^a	aqueous phase		solid phase				
	As(III) %	As(V) %	As(III) %	As(V) %	As(III) mol/kg (μ mol/m ²)	As(V) mol/kg (μ mol/m ²)	Fe(II)/As(V) ratio
Gt+As(V) dark	<i>b</i>	66	<i>b</i>	34	<i>b</i>	0.34 (2.32)	—
Gt+As(III) dark	72	<i>b</i>	28	<i>b</i>	0.28 (1.91)	<i>b</i>	—
Gt+As(III) light	18	45	<i>b</i>	37	<i>b</i>	0.37 (2.53)	0.21
Gt+As(III) light (anoxic)	55	7	<i>b</i>	38	<i>b</i>	0.37 (2.53)	1.73 ^c
Fh+As(V) dark	<i>b</i>	31	<i>b</i>	69	<i>b</i>	1.12 (3.39)	—
Fh+As(III) dark	53	<i>b</i>	47	<i>b</i>	0.77 (2.33)	<i>b</i>	—
Fh+As(III) light	23	2	19	56	0.25 (0.75)	0.98 (3.09)	1.90 ± 0.1
Fh+As(III) light (anoxic)	24	1	20	55	0.25 (0.75)	0.97 (3.12)	1.93 ^d

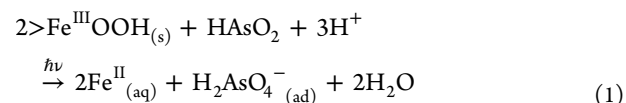
^aGt and Fh indicate goethite and ferrihydrite, respectively. All experiments were conducted under ambient (oxic) condition at pH 5 unless otherwise mentioned. The initial concentrations of As in Gt and Fh experiments were 250 and 410 μ M, respectively, and all light experiment data were at 8 h of light exposure in either case. Data associated with ferrihydrite were obtained from ref 15. ^bConcentration below detection limit. ^cSee text for the details. ^dAssuming \sim 80% of total As species are As(V) on the surface.

is the predominant As-bearing species adsorbed on the goethite surface when a As(III)-equilibrated goethite suspension is exposed to light. In the absence of light, no oxidation of As(III) to As(V) is observed to occur in the presence of goethite.

Data presented in Figure 1a, taken together with results from XANES, indicate that the total amount of As(V) adsorbed on goethite during a 12 h light exposure (in the presence of As(III)) is 0.37 mol kg⁻¹ (see Table 1). This loading is \sim 30% higher than the amount of As (0.28 mol kg⁻¹) that adsorbed immediately after the goethite was equilibrated with As(III) for 24 h under dark conditions. Furthermore, the amount of As(V) adsorbed on goethite in the presence of light is higher than the amount of As (filled circle) that adsorbs on goethite when the mineral is exposed to 0.25 mM As(V) in the dark (i.e., 0.34 mol kg⁻¹). Taking into account the surface area of the goethite, the surface coverage of As(III) was 1.91 μ mol/m² before light exposure and the coverage of the As(V) product after irradiation was 2.53 μ mol/m². These values are reasonably consistent with prior studies at similar solution conditions that investigated As(III)/As(V) adsorption on goethite.²⁸ We mention that a similar increase in As(V) loading in the presence of light was also experimentally observed previously for ferrihydrite that was exposed to arsenite in the presence of light.¹⁵ In the prior study, the increase in arsenate coverage was attributed at least in part to the creation of adsorption sites for As(V) due to the removal of surface carbonate contamination during irradiation from the oxyhydroxide surface.¹⁵ Prior studies have often suggested that iron oxyhydroxide nanoparticles prepared in/exposed to the ambient atmosphere leads to the formation of surface carbonate^{15,19,29} (and references therein), and hence some carbonate is expected to be present on the goethite used in this study. Another possibility is that in the presence of aqueous Fe(II) an As-bearing ternary surface complex forms on the mineral surface,^{15,30,31} or new structural phases form during the irradiation of the goethite surface in the presence of As(III). While we cannot rule out such scenarios, TEM images and XRD data obtained (see Supporting Information, Figures S1 and S3) before and after irradiation do not show any evidence of large-scale structural changes. The absence of significant structural changes, however, is consistent with prior research that has shown no evidence for goethite phase changes when the mineral was exposed to Fe(II)^{32,33} and/or secondary Fe mineral formation under the simultaneous presence of As(III) and Fe(II) in the dark.³⁰

Reaction Stoichiometry and Effect of Solution pH. We

believe that it is useful at this point to address the relative amounts of aqueous Fe(II) and As(V) products that were formed during the irradiation of goethite in the presence of As(III). The amount of aqueous Fe(II) for a given irradiation time can be determined from data in Figure 1b while the total amount of As(V) product is equal to the sum of adsorbed and aqueous As(V), which can be determined from the data in Figure 1, parts a and b, respectively. Using the data associated with a 12 h irradiation time, we determined the ratio of aqueous Fe(II) to As(V) product (including both aqueous and surface bound) at pH 5 to be \sim 0.2. We believe this is an interesting result when viewed alongside results from our prior study that found that the aqueous Fe(II) to As(V) concentration ratio during the irradiation of a ferrihydrite suspension in the presence of As(III) was \sim 2:1, a stoichiometry consistent with the following redox reaction:



where > denotes a surface site. In the prior study, Fe(II) primarily partitioned into the aqueous phase and the vast majority of the As(V) product remained adsorbed on the ferrihydrite surface.¹⁵ In contrast with goethite as the reacting surface, we experimentally observe less aqueous Fe(II) and a higher fraction of the As(V) product (\sim 60% of total As(V) product) in solution. One possibility for the lower aqueous Fe(II) to As(V) product ratio observed in the goethite experiments is that ferrous iron is rapidly oxidized to ferric iron after partitioning into solution via a homogeneous oxidation reaction with dissolved oxygen. This possibility is deemed unlikely, however, because as already mentioned the irradiation of the As(III)/ferrihydrite system does give a \sim 2:1 ratio, suggesting that the homogeneous oxidation of aqueous Fe(II) by dissolved oxygen is relatively slow under our experimental conditions, consistent with prior research.³⁴

The reduced relative amount of aqueous Fe(II) (compared to As(V) product) in the goethite circumstance at least in part results from a surface-mediated process that couples the electron transfer from adsorbed As(III) to dioxygen in the presence of light. Indeed, the role of the semiconducting properties of iron (oxyhydr)oxides in coupling redox reactions at the mineral/water interface have been highlighted in recent

research.³⁵ The details of the process, however, should be consistent with our experimental observation that at pH 5, the amount of aqueous Fe(II) generated during the photochemical oxidation of As(III) in the presence ferrihydrite is relatively insensitive to the presence of dissolved oxygen. Both experimental and theoretical studies have shown that Fe(II) oxidation on an iron oxide surface (at circumneutral pH) occurs more rapidly than the homogeneous oxidation of aqueous Fe(II).^{27,34,36–38} Prior research on iron (oxyhydr)-oxides also has shown that under aerated solution conditions the amount of aqueous Fe(II) product that forms during the light-induced dissolution of lepidocrocite in the presence of oxalate (pH 3) is greater than during the light-induced dissolution of goethite and hematite.³⁹ It was proposed in this prior study that in the goethite and hematite cases the rate of surface Fe(II) oxidation was greater than the rate associated with Fe(II) detachment from the solid, whereas in the lepidocrocite case the rate of Fe(II) detachment was faster.³⁹ On the basis, in part, of this prior research, we believe that the difference in the aqueous Fe(II) yield for the goethite and ferrihydrite systems is likely due to differences in the kinetics of surface Fe(II) oxidation by dioxygen on the two surfaces. To test such a possibility, we individually exposed goethite and ferrihydrite to 0.16 mM Fe(II) in the presence of dissolved oxygen at pH 5 and measured the concentration of aqueous Fe(II) over a 3 h period. Our experimental results (see Supporting Information, Figure S5a) showed that after 3 h, the ratio of the aqueous Fe(II) concentration to the initial concentration of Fe(II) (i.e., $[\text{Fe(II)}]/[\text{Fe(II)}]_0$) was ~ 0.5 and 0.8 , for goethite and ferrihydrite, respectively. We attribute the greater loss of Fe(II) from solution in the case of goethite primarily to faster heterogeneous Fe(II) oxidation kinetics (homogeneous Fe(II) oxidation was relatively slower under these conditions).

While the retention of Fe(II) on the sample surfaces is expected to contribute to Fe(II) removal from solution, it is not believed to be a primary contributor. We base this assertion on results from additional experiments carried out in our laboratory that individually exposed each mineral to aqueous Fe(II) under anoxic conditions and determined the relative amount of Fe(II) on the mineral surface to that in the aqueous phase as a function of pH (see Supporting Information, Figure S6). Our results show that, in contrast to goethite, ferrihydrite only shows a considerable amount of net Fe(II) sorption at pH values > 6.5 (good agreement with prior studies for Fe(II) sorption on goethite^{32,40,41} and ferrihydrite⁴¹). It is important to bring forward that the current understanding of the interaction of Fe(II) with ferric-bearing minerals involves an oxidative adsorption step with spontaneous electron transfer to lattice Fe(III),^{33,35,42–44} that leads to the formation of Fe(II) spatially removed from the adsorption step, and a pH-dependent desorption step⁴² of this reduced species. Hence, while we experimentally observe little change in the aqueous Fe(II) concentration in the presence of ferrihydrite ($\sim 2\%$ loss from solution) there may exist a rapid equilibrium between aqueous Fe(II) and the ferric-bearing mineral so that in essence there is oxidative adsorption of Fe(II) and subsequent desorption of Fe(II) from a spatially removed region of the lattice. In such a reaction sequence there is no net adsorption or redox chemistry, and this reaction sequence would not play a direct role in As(III) oxidation in the absence of dissolved oxygen.²⁷

In the presence of dissolved oxygen, electron transfer to dioxygen might be expected to compete with Fe(II) desorption. Such a competition would also be expected to be occurring on the goethite surface during the heterogeneous oxidation of Fe(II) by dissolved oxygen. With regard to the reduction of dioxygen, prior work has suggested that the heterogeneous reduction of Fe(II) on ferric iron hydroxide is a function of the sorbed Fe(II) concentration and likely proceeds via spatially removed sites that accommodate Fe(II) oxidative adsorption and dioxygen reduction³⁶ and which are electrically connected by the semiconductor material. It is likely that the higher rate of heterogeneous oxidation of Fe(II) on goethite than on ferrihydrite is due to a higher concentration of sorbed Fe(II) (supported by data in Figure S6 (Supporting Information) for anoxic conditions) at a given aqueous Fe(II) concentration that can undergo redox chemistry with dioxygen.

While the details of the surface process are not entirely understood, we can state that based on data in Figure S5b (Supporting Information) ($\ln[\text{Fe(II)}]/[\text{Fe(II)}]_0$ vs time plot) that the surface area normalized pseudo-first-order rate constant³⁶ associated with heterogeneous Fe(II) oxidation by dissolved oxygen in the presence of goethite and ferrihydrite is $1.9 \times 10^{-6} \text{ L s}^{-1} \text{ m}^{-2}$ and $2.02 \times 10^{-7} \text{ L s}^{-1} \text{ m}^{-2}$, respectively. We again infer from this result that in large part the reduced amount of aqueous Fe(II) during the photoinduced oxidation of As(III) in the presence of goethite is due to a more rapid heterogeneous oxidation rate of Fe(II) (relative to ferrihydrite).

Because the Fe(II) sorption/retention onto iron oxyhydroxides is a pH dependent process, we investigated the amount of aqueous Fe(II) and aqueous As(V) product during the irradiation of As(III)/goethite as a function of pH. Figure 3a and 3b plots the aqueous Fe(II) and As(V), respectively, as a function of irradiation time at a solution pH of 4, 5, and 7. These data show that the amount of Fe(II) released during the photochemical oxidation of As(III) on goethite is highest at pH 4 and lowest at pH 7, although at the latter pH the homogeneous oxidation of any aqueous Fe(II) by dissolved

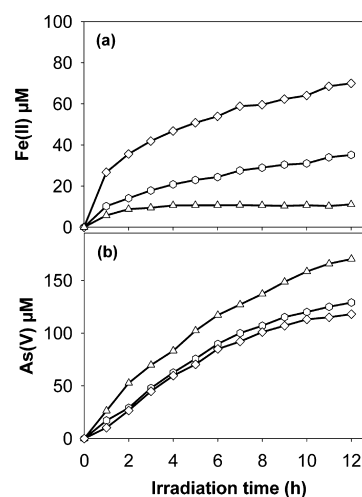


Figure 3. Concentration of aqueous (a) Fe(II) and (b) aqueous As(V) during the photoirradiation of a 0.25 g L^{-1} goethite suspension with an initial 0.250 mM As(III) concentration at pH 4 (open diamonds), pH 5 (open hexagons), and pH 7 (open triangles) in the presence of dissolved O_2 . Control studies (in absence of light) at these pHs showed no measurable amounts of aqueous Fe(II) or As(V). For comparison, data associated with pH 5 are replotted from Figure 1.

oxygen is expected to be significant. A comparison of results for pH 4 and 5 shows a higher amount of aqueous Fe(II) but a somewhat lower amount of aqueous As(V). The increased amount of aqueous Fe(II) at pH 4 is likely due to the lesser sorption onto the mineral surface at this lower pH. Furthermore, the lower yield of As(V) at the lower pH may be suggesting that at least some fraction of the As(V) product is coupled with the heterogeneous oxidation of Fe(II) at the goethite surface. We associate this lower yield of solution As(V) to a decrease in the total As(V) product and not to a change in As-surface loading, because an analysis of all our data shows that As surface loading does not change significantly with pH: 0.38, 0.37, and 0.32 mol As/kg at pH 4, 5, and 7, respectively. Also, after 12 h of reaction, we determined based on the surface loading and data presented in Figure 3 that the ratios of aqueous Fe(II) to As(V) product (total of aqueous and surface bound) at pH 4, 5, and 7 were ~ 0.5 , 0.2, and 0.05, respectively.

The Role of Oxygen. To better understand the role of dissolved oxygen, we carried out As(III) oxidation reactions in goethite suspensions in the absence of dissolved oxygen. Figure 4a and 4b displays the solution concentration of aqueous Fe(II)

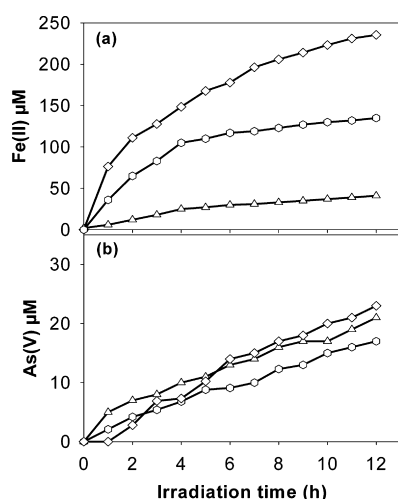


Figure 4. Aqueous-phase concentration of (a) Fe(II) and (b) As(V) as a function of irradiation time for a 0.25 g L⁻¹ goethite suspension with an initial 0.250 mM As(III) addition under anoxic conditions at pH 4 (open diamonds), at pH 5 (open hexagons), and at pH 7 (open triangles). For oxic conditions, see Figure 3. The irradiation of the As(III)/goethite suspension under oxic conditions at pH 4, 5, and 7 led to a more significant amount of As(III) oxidation.

and aqueous As(V) as a function of time during the As(III) oxidation process in the absence of dissolved oxygen at pH 4, 5, and 7. Inspection of the data shows not unexpectedly that under anoxic conditions, the amount of aqueous Fe(II) at any pH is greater than the amount present in solution under oxic conditions at the same pH (Figure 3) at a given reaction time. Inspection of the anoxic reaction data also shows that after 12 h of irradiation the amount of aqueous Fe(II) associated with the pH 4 reaction is 1.8 times higher than the amount present at pH 5, and 6.3 times higher than the amount of aqueous Fe(II) when the reaction occurs at pH 7. The amount of solution-phase As(V) product at these pH values, however, is similar over the course of the irradiation. It is believed that this particular observation suggests that the rate of As(V) product formation is fairly similar at each pH. Also, the As-surface loadings (primarily As(V), Supporting Information, Figure S7

for pH 5) under anoxic conditions were similar to the values obtained under oxic conditions (0.38, 0.37, and 0.32 As/kg for pH 4, 5, and 7, respectively). Therefore, the reduced amount of aqueous Fe(II) at higher pH conditions (i.e., pH 5 and 7) compared to the amount at pH 4 under anoxic conditions is likely due to the increased retention of iron product on the goethite surface at the higher pH (see Supporting Information, Figure S6).

It is interesting now to determine the aqueous Fe(II) to As(V) concentration ratio at pH 5 under anoxic conditions. On the basis of our data (see Supporting Information, Figure S6), we estimate that 20% of the ferrous iron generated during the photochemical As(III) oxidation reaction at pH 5 remains on the goethite surface. If all the Fe(II) was released into solution, then the solution concentration of ferrous iron would be $\sim 175 \mu\text{M}$. The total As(V) product concentration under anoxic conditions (taking into account both surface adsorbed and solution-phase As(V)) after 12 h of light exposure would be $\sim 105 \mu\text{M}$ (if all As(V) partitioned into solution). Under anoxic conditions, we therefore estimate the Fe(II)/As(V) ratio to be ~ 1.7 at pH 5. This value is much closer to the stoichiometric ratio of 2 and significantly higher than the ratio of 0.2 associated with oxic conditions at pH 5 where the heterogeneous oxidation of Fe(II) by dioxygen is likely occurring. Similarly, we estimate that the ratio of Fe(II)/As(V) at pH 4 to be 1.93 (under anoxic condition and considering no Fe(II) sorption), which is even closer to the expected stoichiometric ratio of 2. Therefore, these results strongly suggest that under anoxic conditions there is a significant amount of Fe(II) retention at elevated pH (such as at pH 5 and above) which is ultimately affecting the measured Fe(II)/As(V) ratios.

Comparison of the data in Figures 3 and 4 shows that in general the rate of aqueous As(V) formation is significantly greater for oxic conditions than for anoxic conditions at any given pH. Analysis of the data for pH 5, for example, shows that the rate of aqueous As(V) formation at a 2 h irradiation time under oxic and anoxic conditions is $12.4 \times 10^{-5} \text{ M s}^{-1} \text{ m}^{-2}$ and $1.4 \times 10^{-5} \text{ M s}^{-1} \text{ m}^{-2}$, respectively. We suspect that under oxic conditions the oxidation of Fe(II) on goethite and reduction of O₂ to form reactive oxygen species (e.g., H₂O₂ and ultimately $\cdot\text{OH}$) facilitates As(III) oxidation by Fe(II)-mediated Fenton-like reactions^{27,34,45} during the photoinduced As(III) oxidation process and is the reason for the higher yield of solution-phase As(V) product. Whether in our study the oxidation of As(III) to As(V) occurs on the goethite surface cannot be discerned from our experimental data, although under anoxic conditions one might expect As(III) oxidation to be primarily a surface process. The photoinduced oxidation of As(III) on ferrihydrite under anoxic or oxic conditions does not result in a significant amount of aqueous arsenate product in the presence or absence of dissolved oxygen (see Table 1).¹⁵ For example, in the As(III)/ferrihydrite circumstance the rate of aqueous As(V) product formation at 2 h of irradiation is $6.73 \times 10^{-6} \text{ M s}^{-1} \text{ m}^{-2}$, compared to an aqueous As(V) product formation rate of $12.4 \times 10^{-5} \text{ M s}^{-1} \text{ m}^{-2}$ in the case of As(III)/goethite at an irradiation time of 2 h (determined from data in Supporting Information, Figure S8) under oxic conditions. This might suggest that the relatively high yield of aqueous-phase As(V) in the goethite circumstance is due to the oxidation of As(III) in the aqueous phase. It is conceivable that aqueous or adsorbed ferric iron formed from Fe(II)-mediated Fenton-like reactions in the goethite circumstance could also contribute to As(III)

oxidation. We conducted an experiment where we irradiated a solution containing only aqueous Fe(III) and As(III) and experimentally observed As(V) product (see Supporting Information, Figure S9).

The increased amount of heterogeneous Fe(II) oxidation on goethite that occurs under oxic conditions enhances the amount of As(III) oxidation by reactive oxygen species in the solution phase when compared to ferrihydrite. In addition, as shown in Figure S9, the photochemical reduction of thus-produced Fe(III) and the concurrent oxidation of As(III) are also expected to contribute to the formation of aqueous-phase As(V) in comparison to the ferrihydrite system. It is interesting to consider the relative insensitivity of the photoinduced As(III) in the presence of ferrihydrite at pH 5. A prior study has recently shown that As(III) oxidation (nonphotochemical) does not occur in the presence of aqueous Fe(II) and ferrihydrite at neutral pH under anoxic conditions but happens rapidly when the system is exposed to dissolved oxygen.²⁷ We speculate that at neutral pH the Fe(II) sorption on ferrihydrite is relatively high (compared to pH 5: Supporting Information, Figure S6) and the oxidation of Fe(II) plays a more significant role in the redox chemistry of As(III) oxidation than at pH 5.

General Remarks. The surface area-normalized As adsorption and oxidation on goethite and ferrihydrite are presented in the Supporting Information (Figure S10) for an 8 h exposure to light at a solution pH of 5 (in the presence of dissolved oxygen). The comparison shows that while the goethite surface is more efficient for As(III) oxidation ($5.3 \mu\text{mol}/\text{m}^2$ compared to $2.6 \mu\text{mol}/\text{m}^2$), ferrihydrite shows a higher surface concentration of adsorbed As(V) after the 8 h exposure to light (3.84 compared to $2.51 \mu\text{mol}/\text{m}^2$). We speculate that the use of iron (oxy)hydroxide surfaces in the presence of light might complement current technologies that require the use of UV light and also need to separate adsorbent and coagulant. Finally, we note that the arsenic concentrations used in this study are higher than typically encountered in contaminated water sources. However, there are many areas where populations are exposed to concentration several orders of magnitude greater than the World Health Organization (WHO) maximum level of $10 \mu\text{g}/\text{L}$.^{5,6}

■ ASSOCIATED CONTENT

■ Supporting Information

TEM images of goethite before and after reaction, IR spectra of goethite, XRD patterns, As(III)/As(V) adsorption isotherms, Fe(II) oxidation in the presence/absence of goethite and ferrihydrite, Fe(II) adsorption edges for goethite and ferrihydrite, X-ray photoelectron spectroscopy results of As speciation under anoxic conditions on goethite, concentration of aqueous-phase As(V) formation during photoirradiation of As(III)–ferrihydrite suspension under oxic conditions at pH 5, Fe(III)–As(III) oxidation and comparative bar diagram of As adsorption/oxidation profile on goethite and ferrihydrite. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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