

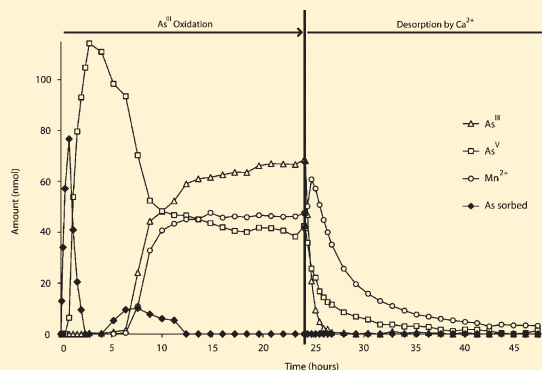
Arsenite Oxidation by a Poorly-Crystalline Manganese Oxide. 3. Arsenic and Manganese Desorption

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S Supporting Information

ABSTRACT: Arsenic (As) mobility in the environment is greatly affected by its oxidation state and the degree to which it is sorbed on metal oxide surfaces. Manganese oxides (Mn oxides) have the ability to decrease overall As mobility both by oxidizing toxic arsenite (As^{III}) to less toxic arsenate (As^{V}), and by sorbing As. However, the effect of competing ions on the mobility of As sorbed on Mn-oxide surfaces is not well understood. In this study, desorption of As^{V} and As^{III} from a poorly crystalline phyllosmanganate ($\delta\text{-MnO}_2$) by two environmentally significant ions is investigated using a stirred-flow technique and X-ray absorption spectroscopy (XAS). As^{III} is not observed in solution after desorption under any conditions used in this study, agreeing with previous studies showing As sorbed on Mn-oxides exists only as As^{V} . However, some As^{V} is desorbed from the $\delta\text{-MnO}_2$ surface under all conditions studied, while neither desorptive used in this study completely removes As^{V} from the $\delta\text{-MnO}_2$ surface.



INTRODUCTION

Arsenic (As) is an element with toxic properties, commonly found in the environment. Elevated As levels in soils result from both natural weathering processes and anthropogenic activities such as mining, agriculture, and manufacturing.¹ In several locations throughout the world, As contamination of soil and water occurs near human populations, posing a significant threat to human health. Therefore, understanding the chemical reactions controlling As mobility in the environment is critical.

Arsenic behavior in the environment is significantly determined by its chemical speciation. Usually, As occurs as one of two inorganic oxyanions: arsenite (As^{III}) or arsenate (As^{V}). Below pH 9, As^{III} appears predominately in its fully protonated form (H_3AsO_3), while at circumneutral pH values, As^{V} occurs as a mixture of H_2AsO_4^- and HASO_4^{2-} . Arsenic speciation also determines its toxicity because As^{III} is more toxic than As^{V} .³ Several Mn-oxides can readily oxidize As^{III} to As^{V} , most notably layered Mn-oxides (i.e., phyllosmanganates),^{4–14} thus Mn-oxide minerals can have a determining effect on As speciation in soils and sediments.

In terrestrial environments, As mobility is generally determined by the extent to which it is adsorbed by metal oxides.^{15–21} Phyllosmanganates represent one type of metal oxide that exhibit the ability to sorb As.^{6,11,12,22–25} However, sorption of As on Mn-oxide surfaces can be quite complex. Interestingly, a higher level of As sorption has been observed when As^{III} is reacted with phyllosmanganates (oxidation and sorption) compared to reaction of As^{V} with phyllosmanganates (sorption alone).^{4,6,11,23,25} Also, when As^{V} is sorbed on Mn-oxide surfaces, it forms a variety of surface complexes.^{14,22–24}

Since Mn-oxides have shown a propensity to oxidize and sorb As in nature, it is important to understand potential mobility of As adsorbed on Mn-oxide surfaces. Because As^{V} forms multiple surface complexes with Mn-oxides, it is possible that mobility of As sorbed on Mn-oxides varies depending on the surface complexes present. Also, in nature, As coexists with other ions which can compete for sorption sites on Mn-oxide surfaces. Therefore, understanding As mobility in the environment requires understanding the mobility of various As surface complexes, as well as the potential for competing ions to desorb As from Mn-oxide surfaces. To date, few studies have investigated the ability of common environmental ions to desorb As from the surface of Mn-oxides. The purpose of this study is to determine to what extent a cation (Ca^{2+}), and oxyanion ($\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$), both common in the environment, are able to desorb As from a poorly crystalline phyllosmanganate ($\delta\text{-MnO}_2$).

MATERIALS AND METHODS

Stirred Flow Method. Stirred flow experiments were conducted using the same 30 mL reactor and experimental procedures described previously.⁶ All stirred flow reactions were conducted in a background electrolyte (10 mM NaCl), buffered at pH 7.2 (5 mM 3-(N-morpholino)propanesulfonic acid (MOPS)),

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and had a constant flow rate of 1 mL/min. Also, all experiments were mixed via a magnetic stir bar with a constant rate of stirring (100 rpm).

In all desorption reactions, 1 g/L δ -MnO₂ was reacted with 100 μ M As^{III} (i.e., As is oxidized and sorbed) to ensure maximum As sorption on the solid phase, followed immediately by reaction with a desorptive. Oxidation of As^{III} (and As sorption) prior to desorption was carried out for 4, 10, or 24 h. The desorptives used were 100 μ M calcium chloride (CaCl₂, abbreviated Ca²⁺) in the presence of background electrolyte (10 mM NaCl and 5 mM MOPS), 100 μ M sodium phosphate (NaH₂PO₄, abbreviated PO₄) in the presence of background electrolyte, or background electrolyte alone. All solutions were adjusted to pH 7.2 with HCl and NaOH prior to experiments, and background electrolyte was introduced into the stirred flow reactor (containing δ -MnO₂) for at least 2 h at a rate of 1 mL/min prior to each experiment. In each reaction, As^{III} oxidation was stopped (after 4, 10, or 24 h) by introducing desorbing solution into the reactor, thus beginning the desorption phase of the reaction. Changing influent solution from As^{III} solution to desorption solution took less than 5 s, and thus flow of solution into the reactor was effectively constant throughout each experiment (oxidation followed by desorption). A plot showing the full data (As^{III} oxidation followed by desorption) from one experiment is presented in the Supporting Information (Figure S1).

As, Mn, Ca, and P Analysis. Inorganic arsenic in the stirred flow effluent was analyzed via liquid chromatography inductively coupled plasma mass spectrometry (LC-ICP-MS), and aqueous Mn was analyzed by ICP-MS as described in Lafferty et al.⁶ Total P and Ca in the reactor effluent were analyzed by ICP-OES to verify the concentration of desorptive present in the stirred-flow reactor (data not shown).

EXAFS Analysis. Extended X-ray absorption fine structure (EXAFS) spectroscopic analysis was performed at the National Synchrotron Light Source (Brookhaven National Laboratory) on reacted δ -MnO₂ after 24 h of desorption (following reaction with 100 μ M As^{III} for 4, 10, and 24 h). Detailed descriptions of sample collection, data collection and data processing for samples analyzed using these techniques can be found in the Supporting Information.

Sorption and Desorption Calculations. To quantify the total amount of sorbed and desorbed As^V, As^{III}, and Mn²⁺ data were integrated using the “area below curves” tool in SigmaPlot 8 (Systat Software Inc., San Jose, California).

RESULTS AND DISCUSSION

δ -MnO₂ Structure. Mineral structure must be taken into consideration in order to accurately interpret adsorption and desorption data. The δ -MnO₂ used in this study is a poorly ordered form of hexagonal birnessite.²⁴ Hexagonal birnessite (and thus δ -MnO₂) has two types of reactive sites: at vacancies within Mn^{IV} octahedral sheets (vacancy sites) and at the edges of Mn^{IV} octahedral sheets (edge sites).^{26,27} It has been shown that As reacts primarily with edge sites, rather than vacancy sites of birnessite;^{14,23,24} therefore, in this study, As desorption is expected to occur at δ -MnO₂ edge sites. However, heavy metals tend to sorb strongly at phyllosmanganate vacancy sites,^{26–33} as well as react with edge sites of phyllosmanganates.^{31,34} Because of the high affinity of vacancy sites for Mn²⁺, vacancy sites are likely the primary location of Mn²⁺ sorption on δ -MnO₂, however, once δ -MnO₂ vacancy sites begin to fill, Mn²⁺ is expected to react

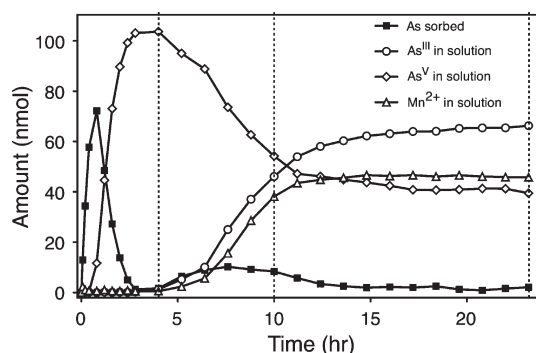
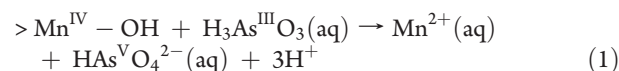


Figure 1. The amount (nmol) of As^{III}, As^V, and Mn²⁺ in stirred flow reactor effluent as well as the amount (nmol) of As sorbed during As^{III} oxidation by δ -MnO₂, prior to desorption by Ca²⁺, PO₄, or background electrolyte. Vertical dashed lines indicate times for which desorption was initiated.

more with δ -MnO₂ edge sites.^{6,24} Therefore, in these experiments, desorption of Mn²⁺ is expected to occur at both edge and vacancy sites of δ -MnO₂ depending on the extent to which δ -MnO₂ vacancy sites are filled with Mn²⁺. A graphic representation of As and Mn sorption on the δ -MnO₂ surface can be found in Figure 4 of Lafferty et al.²⁴

As^{III} Oxidation and Sorption. All desorption experiments in this study are preceded by reaction of As^{III} with δ -MnO₂ for 4, 10, or 24 h. This initial reaction between As^{III} and δ -MnO₂ results in As^{III} oxidation and produces As^V and Mn²⁺ (eq 1). Subsequently, As^V and Mn²⁺ produced during As^{III} oxidation are sorbed on the δ -MnO₂ surface.



To briefly summarize Lafferty et al.,^{6,24} the reaction between As^{III} and δ -MnO₂ in a stirred-flow reactor, under the conditions used in this study, proceeds in two distinct phases. First, an initial reaction phase occurs from 0 to 6.4 h, which includes the period of fastest As^{III} oxidation, highest As^V sorption, and no Mn²⁺ release into solution (Figure 1). A second reaction phase characterized by lower δ -MnO₂ reactivity occurs beyond 6.4 h, which includes a second period of (decreased) As sorption, a decrease in As^{III} oxidation rate, and the presence of Mn²⁺ in solution (Figure 1). Decreased δ -MnO₂ reactivity in the second phase of this reaction has been attributed to Mn²⁺ sorption on the δ -MnO₂ surface and the subsequent production of Mn^{III} via Mn(II)/(IV) conproportionation at the δ -MnO₂ surface.²⁴

In this study, desorption experiments are conducted by stopping the initial reaction between As^{III} and δ -MnO₂ after 4, 10, or 24 h (Figure 1), and simultaneously beginning desorption by PO₄, Ca²⁺, or background electrolyte alone. The first time point for beginning desorption is after 4 h of reaction between As^{III} and δ -MnO₂, which coincides with maximum As^V concentration in the stirred-flow reactor effluent, and the end of an initial period of As^V sorption (Figure 1). Between 0 and 4 h of As^{III} oxidation, Mn²⁺ is expected to react primarily with vacancy sites and not edge sites. The second time point for beginning desorption is after 10 h of As^{III} oxidation by δ -MnO₂, which is near the end of a second period of lesser As sorption, and occurs early in the second, less reactive phase of As^{III} oxidation (Figure 1). Between 4 and 10 h, Mn²⁺ is expected to begin reacting with edge sites, resulting in formation of some Mn^{III}.²⁴ A change in the sorption

Table 1. Structural Parameters Derived from Least-Square Fits to Raw k^3 -Weighted As-EXAFS Spectra for δ -MnO₂ after 24 h Desorption by Background Electrolyte (Elec), Calcium Solution (Ca), and Phosphate Solution (PO₄)^a

sample	As–O			As–Mn			As–Mn		
	CN ^b	r ^b	σ^{2b}	CN ^b	r ^b	σ^{2b}	CN ^b	r ^b	σ^{2b}
10 h-elec	4.1(2)	1.70(1)	0.003(0)	1.1(3)	3.12(2)	0.005(1)	0.6(4)	3.50(5)	0.005(3)
10 h-Ca	4.1(2)	1.70(1)	0.003(0)	0.7(4)	3.14(3)	0.005(2)	0.3(5)	3.51(9)	0.004(7)
10 h-PO ₄	4.2(2)	1.70(1)	0.003(0)	0.8(3)	3.16(3)	0.005(2)			
24 h-elec	4.1(1)	1.70(1)	0.003(0)	0.8(3)	3.15(2)	0.005(2)			
24 h-Ca	4.1(1)	1.69(0)	0.003(0)	0.9(3)	3.14(2)	0.005(2)			
24 h-PO ₄	4.3(2)	1.69(0)	0.003(0)	0.7(3)	3.16(3)	0.006(3)			

^a Desorption data shown here followed 10 or 24 h of As^{III} oxidation. ^b Coordination number (CN), interatomic distance (r), and Debye–Waller factor (σ^2) were obtained by fitting data with theoretical phase and amplitude functions. Estimated errors at 95% confidence interval from the least-squares fit are given in parentheses.

complexes formed between As^V and δ -MnO₂ also occurs between 4 and 10 h of As^{III} oxidation.²⁴ The last time point for desorption is after 24 h of reaction, when the system is stable within the less reactive phase of the reaction (Figure 1).

As^{III} Desorption. No As^{III} is desorbed from the δ -MnO₂ surface in any desorption experiments discussed here. Also, As EXAFS analysis indicates that all As associated with δ -MnO₂ after desorption is present as As^V (Table 1 and Figures 2 and 3), which agrees with previous results indicating that As present on phyllo-manganate surfaces only occurs as As^V.^{14,23,24,35} However, it should be noted that there is not a sufficient amount of As remaining on the surface of δ -MnO₂ after 4 h of As^{III} oxidation followed by 24 h of desorption to measure As using EXAFS analysis.

As^V Desorption. Previous studies have shown that As reacts primarily with edge sites of phyllo-manganates rather than vacancy sites,^{14,23,24} therefore As^V desorption in this study is expected to occur at δ -MnO₂ edge sites. Of the desorptives used in this study, PO₄ is expected to desorb As^V most readily because it is chemically similar to As^V and is known to compete with As^V for sorption sites on metal oxide minerals.^{12,36–38} However, Ca²⁺ has the potential to react with δ -MnO₂ vacancy sites as well as edge sites, therefore, Ca²⁺ also has the potential to desorb As^V. The background electrolyte (MOPS and NaCl) used in these studies is expected to react weakly with δ -MnO₂ edge sites, and thus should not desorb As^V to a large extent.

When As^V is desorbed (for 24 h) after 4 h of As^{III} oxidation, roughly 67% of As^V sorbed during the 4 h of As^{III} oxidation is mobilized from the δ -MnO₂ surface by all three desorptives (Figure 2). Because of this, one can infer that the majority of As^V sorbed on the δ -MnO₂ surface during the initial phase of high δ -MnO₂ reactivity is fairly labile. Conversely, there is a portion of As^V sorbed during the first 4 h of As^{III} oxidation that remains immobile on the δ -MnO₂ surface, even in the presence of PO₄. Previous EXAFS analysis of δ -MnO₂ reacted with As^{III} under identical experimental conditions revealed that As^V is bound in mononuclear-monodentate as well as binuclear-bidentate complexes on the δ -MnO₂ surface during the first 4 h of As^{III} oxidation by δ -MnO₂.²⁴ Unfortunately, there is not a sufficient amount of As remaining on the surface of δ -MnO₂ after 4 h of As^{III} oxidation followed by 24 h of desorption to determine the stability of these two complexes by EXAFS analysis.

After 10 and 24 h of As^{III} oxidation, PO₄ is a more efficient desorptive of As^V than Ca²⁺ or the background electrolyte (Figure 2). Also, the proportion of As^V desorbed by PO₄

increases in the 10 and 24 h experiments (Figure 2). It should be noted that after 10 and 24 h of As^{III} oxidation by δ -MnO₂, two significant changes occur in the speciation of Mn associated with δ -MnO₂. First, Mn²⁺ begins sorbing at edge sites after δ -MnO₂ vacancy sites are occupied by sorbed Mn²⁺ (at \sim 6.4 h).^{6,24} Also, Mn^{III} begins to appear in Mn octahedral layers of δ -MnO₂ between 4 and 10 h of As^{III} oxidation, and increases between 10 and 24 h.²⁴ An increase in the proportion of As^V desorbed by all desorptives after 10 and 24 h (compared to 4 h) happens concurrently with increased competition from Mn²⁺ for edge sites, and an increase in Mn^{III} content within the δ -MnO₂ structure. Thus, increased As^V desorption in the 10 and 24 h experiments could be the result of direct competition between As^V and Mn²⁺ for sorption sites or the formation of weaker bonds between As^V and Mn^{III}.³⁹ It is difficult to distinguish between the effects of increased Mn²⁺ sorption and increased Mn^{III} content at δ -MnO₂ edge sites as they occur simultaneously.

EXAFS analysis of δ -MnO₂ after As^{III} oxidation for 10 h and subsequent desorption by Ca²⁺ and background electrolyte revealed As–Mn distances of \sim 3.13 Å and \sim 3.50 Å (Table 1). These distances correspond to As^V bound to the δ -MnO₂ surface in bidentate-binuclear and monodentate-mononuclear complexes, respectively.^{22–24} However, for all other desorption experiments after 10 (PO₄) and 24 (Ca²⁺, PO₄, and background electrolyte) hours of As^{III} oxidation by δ -MnO₂ the only As–Mn distances present in EXAFS spectra was \sim 3.15 Å (Table 1 and Figure 3), corresponding to a bidentate-binuclear complex between As^V and the δ -MnO₂ surface. While, it is tenuous to attribute a specific desorption event with a single adsorption complex, EXAFS data of As sorption complexes before and after desorption seem to indicate that bidentate-mononuclear and monodentate-mononuclear complexes between As^V and the δ -MnO₂ surface are less stable than As^V- δ -MnO₂ bidentate-binuclear complexes.

Mn Desorption. During As^{III} oxidation by δ -MnO₂, Mn²⁺ is produced and subsequently sorbed by δ -MnO₂ (eq 1 and Figure 1).^{6,24} Mn²⁺ tends to initially sorb at δ -MnO₂ layer vacancy sites under the conditions used in this study, followed by sorption at δ -MnO₂ edge sites as vacancy sites become more occupied.²⁴ Previous studies have indicated that some As sorbed on phyllo-manganate surfaces could be bound through a bridging complex through sorbed Mn.^{12,25} Although As/ δ -MnO₂ bridging complexes were not seen in previous studies conducted under the experimental conditions used in the reactions described here, it is possible that Mn²⁺ on δ -MnO₂ could facilitate As sorption.

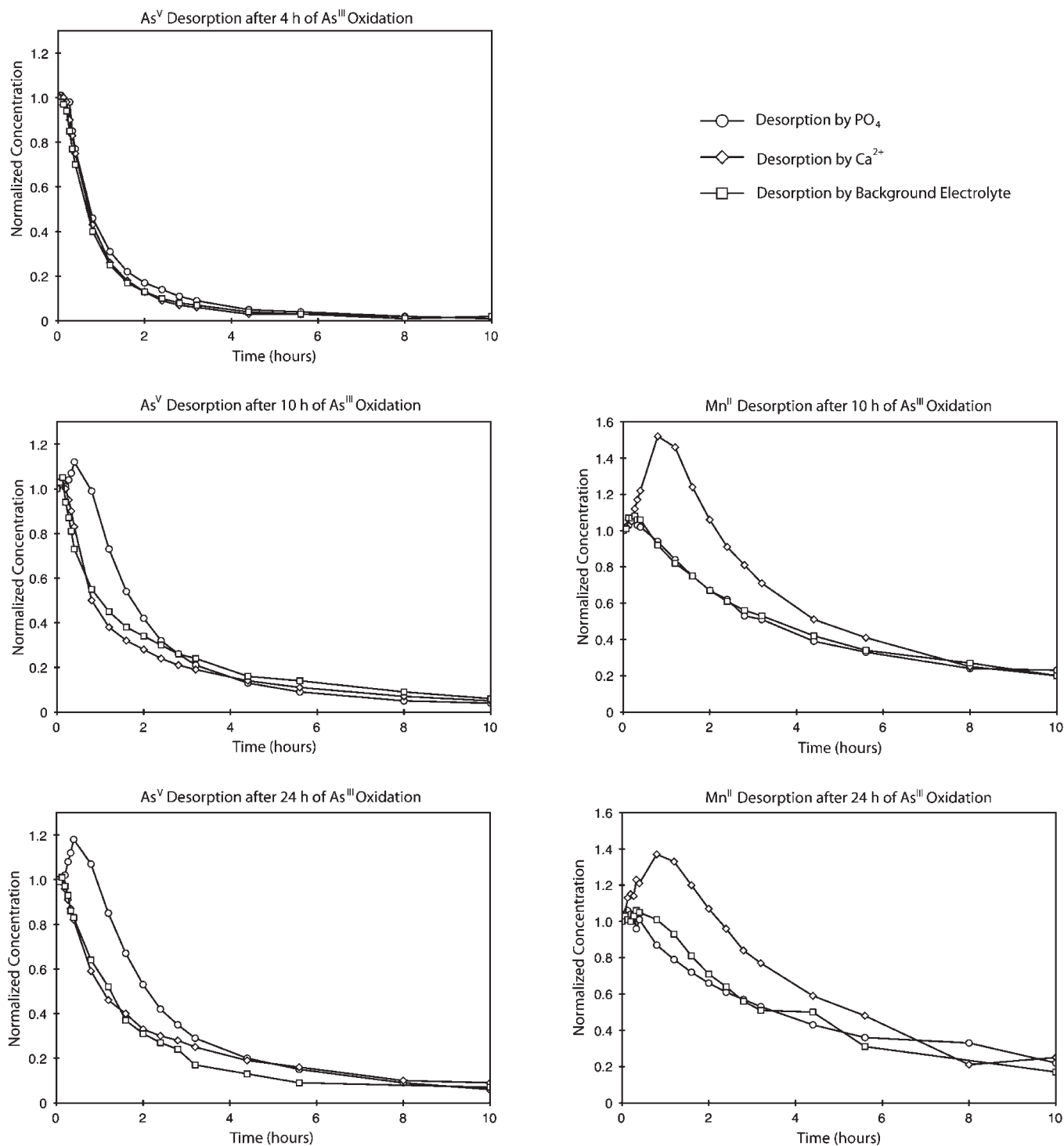


Figure 2. As^V (left) and Mn²⁺ (right) desorbed by Ca²⁺, PO₄, and background electrolyte (10 mM NaCl, 5 mM MOPS) after As^{III} oxidation by δ -MnO₂. The initial data points on each graph (time = 0 h) correspond to the beginning of desorption (initial As^{III} oxidation data not shown). Data shown are first 10 h of 24 h desorption experiments.

Of the desorptives used in this study, Ca²⁺ is expected to react with δ -MnO₂ sorption sites most similarly to Mn²⁺.⁴⁰ Some cations could potentially desorb Mn²⁺ more readily than Ca²⁺,^{32,41,42} however Ca²⁺ is ubiquitous in nature, and thus has a high probability of interacting with Mn²⁺ sorbed on Mn-oxide surfaces. Desorption of Mn²⁺ by Na⁺ (in background electrolyte) is predicted to be negligible because Na⁺ reacts with δ -MnO₂

interlayers differently than Ca²⁺ or Mn²⁺, in that Na⁺ is not expected to bind in triple corner sharing complexes at vacancy sites as is the case with Mn²⁺ and Ca²⁺.⁴⁰

When As^{III} is reacted with δ -MnO₂ for only 4 h, no Mn²⁺ is desorbed under the conditions used in this study (data not shown). It is important to note that no Mn²⁺ appears in the stirred-flow reactor effluent during the first 4 h of As^{III} oxidation, and all Mn²⁺

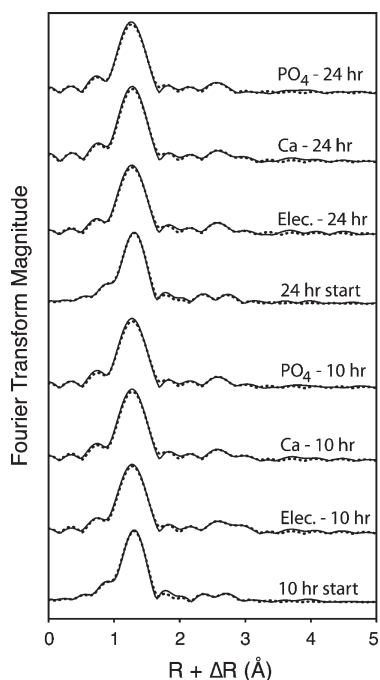


Figure 3. Fourier transformed As K-edge EXAFS of δ -MnO₂ reacted with As^{III} (100 μ M) in a stirred-flow reactor for 10 and 24 h (10 h start and 24 h start) and desorbed by Ca²⁺, PO₄, and background electrolyte for 24 h following As^{III} reaction. XAS data are presented as solid lines and fits are presented as dashed lines (fit data provided in Table 1).

produced during this time is expected to sorb strongly at δ -MnO₂ vacancy sites.²⁴ However, after 10 and 24 h of As^{III} oxidation, Mn²⁺ is desorbed by all desorptives studied (Figure 2), indicating that Mn²⁺ sorbed at δ -MnO₂ edge sites is more labile than Mn²⁺ sorbed at δ -MnO₂ vacancy sites. Mn EXAFS analysis of δ -MnO₂ revealed no detectable changes in Mn speciation of the solid material after desorption which would appear as a broadening and decrease in the peak height of the 9.25 \AA^{-1} peak in the EXAFS spectra²⁴ (Figures S2A and S2B and Table S1 of the Supporting Information, SI). As predicted, Ca²⁺ is the most efficient Mn²⁺ desorptive of those studied. The proportion of Mn²⁺ desorbed by Ca²⁺ is greatest after 10 h of As^{III} oxidation and decreases slightly after 24 h of As^{III} oxidation (Figure 2). This decrease in Mn²⁺ mobility with increased As^{III} oxidation time could potentially be due to increased formation of less mobile Mn^{III} after 10 h of reaction.^{6,24} Also, desorption by PO₄ (with background electrolyte present) is nearly identical to desorption by background electrolyte alone in the 10 and 24 h samples (Figure 2), which suggests that PO₄ does not desorb Mn²⁺ appreciably. Interestingly, increased Mn²⁺ desorption by Ca²⁺ compared to other desorptives does not result in an increase in As^V desorption, which provides some evidence that As^V is not bound to the δ -MnO₂ surface via a bridging complex through Mn²⁺.

Implications for As Mobility. Phyllosulfates are capable of sorbing As^V, especially during As^{III} oxidation. However, in this study, As^V can be desorbed from the δ -MnO₂ surface, to some extent, under all conditions studied. Even Na⁺ (present in background electrolyte) is able to desorb As^V, to some extent, under all conditions studied here, indicating that a portion of As sorbed by Mn-oxides is potentially quite mobile in the environment. Although some sorbed As^V can be desorbed from δ -MnO₂, there

is a certain amount of As that is not desorbed under any of the conditions studied here. Thus, if As comes in contact with Mn-oxides in nature, these minerals could potentially decrease As availability and mobility both by oxidation of As^{III} and sorption of As^V. It appears that As^V and Mn²⁺ desorption potential is intricately linked to the type of reaction site on the δ -MnO₂ surface to which each is bound, as well as Mn speciation within the δ -MnO₂ structure. This study emphasizes the importance of understanding mineral structures and temporal variability when predicting As mobility in the environment.

■ ASSOCIATED CONTENT

S Supporting Information. Supporting Information is provided which includes detailed information about EXAFS analysis, Mn EXAFS fitting results, further Mn desorption discussion, and an example of aqueous data from a full experiment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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