

SPECTROSCOPY STUDY OF ARSENITE [As(III)] OXIDATION ON Mn-SUBSTITUTED GOETHITE

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Abstract—Mn-substituted goethite was synthesized and the interaction between arsenite (As(III)) and Mn-substituted goethite was investigated by both solution chemistry and X-ray adsorption near edge structure (XANES) spectroscopy. Results indicate that the oxidation of As(III) is favored by Mn-substituted goethite. This reaction was more sensitive to temperature than to pH. Different reaction mechanisms may account for As(III) oxidation. Since As(III) is more mobile and toxic than As(V), the oxidation reaction of As(III) with Mn-substituted goethite may decrease arsenic toxicity under some conditions.

Key Words—Arsenate, Arsenite, Mn-Substituted Goethite, Oxidation, XANES.

INTRODUCTION

The toxicity and bioavailability of arsenic (As) is closely related to its oxidation states. There are two main inorganic species of As in terrestrial ecosystems. The reduced state, arsenite [As(III)], is much more toxic, soluble, and mobile than the oxidized form, arsenate [As(V)] (Duel and Swoboda, 1972; Ferguson and Gavis, 1972). The surfaces of Fe and Mn oxyhydroxides are the major sources and sinks of As and other trace elements (Sung and Morgan, 1981). Recent studies (Waychunas *et al.*, 1993, 1995; Manceau, 1995; Sun and Doner, 1996; Fendorf *et al.*, 1997) indicated that iron oxides can strongly adsorb As(V) by forming binuclear complexes. Mn oxides, on the other hand, are effective oxidants for the transformation of As(III) to As(V) (Oscarson *et al.*, 1981a; Moore *et al.*, 1990; Scott and Morgan, 1995). Thus, the combined influences of As(III) depletion by oxidation and adsorption in systems composed of Mn and Fe oxides present in terrestrial environments may have a major influence on the toxicity and bioavailability of As (Sun and Doner, 1998).

Mn and Fe are closely related in chemical properties and occur together in soils and sediments. Ferric iron in the octahedral positions of oxyhydroxides may be partially replaced by other trivalent metal cations such as Al³⁺, Cr³⁺, and Mn³⁺ (Schwertmann and Cornell, 1991). Mn-substituted goethite was first synthesized by Stiers and Schwertmann (1985). However, Mn-substituted goethite is not known to occur naturally and studies of Mn-bearing goethite indicate Mn is mainly in the tetravalent oxidation state (Manceau *et al.*, 1992). Manganese can replace <50 mol % of the Fe in the structure of synthetic goethite, α -FeOOH (Ebinger and Schulze, 1990).

Compared to other oxidation states of manganese, aqueous Mn(III) is not stable and is an oxidizing agent powerful enough to evolve oxygen from water.

However, Mn(III) can form stable mineral structures, *e.g.*, manganite (γ -MnOOH), hausmanite (Mn₃O₄, containing both Mn(II) and Mn(III)), and birnessite (phyllosmanganate) (McKenzie, 1989). Manceau *et al.* (1997) compared the stability of γ -MnOOH with β -MnO₂ and showed that at pH values <7 the Mn(III) form is a much stronger oxidant than the Mn(IV) form. Iron oxyhydroxides, such as goethite, can adsorb and increase the oxidation rate of adsorbed Mn(II) to Mn(III) by oxygen and stabilize Mn(III) on the goethite surface (Davies and Morgan, 1989). As indicated above, free forms of aqueous Mn(III) are unstable. Little information is available on the redox activities of the structural Mn(III) in goethite where the combined effects of adsorption and changes in oxidation state may be important factors controlling surface reactions.

X-ray adsorption near edge structure (XANES) spectroscopy provides a direct method of determining oxidation states of elements such as As and Mn. Different oxidation states of an element have different electron bonding energies. In an X-ray adsorption spectrum, the energies of the edge-peak increase with increasing oxidation state. The edge shift between As(III) and As(V) in XANES spectra is great enough for determining As(III) and As(V) semiquantitatively in a soil sample with unknown As oxidation states (Foster *et al.*, 1995). Also, the oxidation states of Mn in soils can be observed directly by XANES (Schulze *et al.*, 1995), although the accuracy of the method may be limited.

In this paper, Mn-substituted goethite was synthesized and the interaction between As(III) and Mn-substituted goethite was studied by XANES spectroscopy and solution chemical methods. In addition, the effects of environmental conditions such as pH and temperature were also investigated.

Table 1. Some properties of prepared goethite and Mn-substituted goethite samples.

Property	Pure goethite	1% Mn goethite	5% Mn goethite	10% Mn goethite
Surface area ¹ (m ² /g)	90.8 ± 1.2	83.3 ± 2.0	81.5 ± 3.8	94.5 ± 2.6
pH _{PZNPC} ²	8.31 ± 0.03	5.97 ± 0.03	5.74 ± 0.02	5.65 ± 0.15
Total Mn(%, Mn/(Mn + Fe))	0.00	1.10	5.39	10.9
0.01 M NaCl soluble Mn (% of total Mn)	0.00	0.00	0.01	0.02
0.05 M CuCl ₂ extractable Mn ³ (% of total Mn)	0.00	2.30	1.20	1.80
Color	2.5y 7/8	2.5y 5/8	5y 4/3	5y 3/2

¹ EGME method (Heilman *et al.*, 1965).

² Acid-base titration (Sposito, 1981).

³ Adapted from Traina and Doner (1985).

METHODS AND MATERIALS

Preparation and characteristics of Mn-substituted goethite

Mn-substituted goethite was synthesized by the method of Schwertmann and Cornell (1991) using analytical grade reagents, except those mentioned specifically. A quantity of 175 mL of 2.0 M NaOH was added to 50 mL of a mixed solution of Fe(NO₃)₃·9H₂O and Mn(NO₃)₂·4H₂O having a total Fe + Mn concentration of 0.53 M and Mn/(Mn + Fe) ratios to 0.00, 0.01, 0.05, and 0.10. The products were centrifuged, washed, and stored in polyethylene bottles in 250 mL of 0.3 M NaOH solution at 60°C for 15 d. The samples were washed and centrifuged again several times with deionized water, placed in molecular porous membrane tubing (VWR Scientific, Catalog No. 25225-281), and dialyzed in deionized water until the electric conductivity of the dialysis water equaled that of the deionized water. The samples were oven dried at 60°C, then ground with a mortar and pestle and passed through a 37 µm sieve. All solid products showed X-ray diffraction patterns identical to pure goethite. The total Mn in Mn-substituted goethite was determined by dissolving the solid products in 6.0 M HCl at 70°C and analyzing by inductively coupled plasma (ICP) spectroscopy. The NaCl and CuCl₂ extractable Mn from Mn-substituted goethite were determined by addition of 10 mL 0.01 M NaCl or 0.05 M CuCl₂ (modified from Traina and Doner, 1985) solution to 50 mL centrifuge tubes which contained 0.10 g solid samples. The tubes were shaken for 1 h, centrifuged, and filtered. The Mn in the supernatant was determined by ICP spectroscopy. Some properties of the products are listed in Table 1.

XANES study

The Mn oxidation state in Mn-substituted goethite was examined by using the sample with lowest Mn concentration (1% Mn) to minimize self-absorption effects (Schulze *et al.*, 1995). Mn(II) and Mn(IV) standards were prepared by mixing MnSO₄ (analytical

agent, ground) and MnO₂ (99.5% MnO₂, Matheson Coleman & Bell, ground) with boron nitride powder to give solid mixtures which contained the same amount of Mn as 1% Mn-substituted goethite. The powder samples were mounted in a 2 × 8 × 25 mm milled slot cut in a Teflon sheet, and sealed with thin Kapton polyimide film to minimize X-ray absorption.

Mixtures of As(III) and As(V) treated pure goethite were prepared for XANES spectral analysis. This was done by adding 300 µL solution of various concentrations of arsenate (Na₂HAsO₄) and arsenite (NaAsO₂) at pH 6.5 to 50 mg of pure goethite to give a total adsorption density of 150 µmol As g⁻¹ goethite. After 2 h the paste samples were mounted in the milled Teflon slots as described above. The sample cells were sealed with thin Kapton polyimide film to prevent moisture loss and to minimize X-ray absorption during scans. Preliminary experiments showed that the adsorption maximums of different Mn-substituted goethite for As(V) and As(III) were all above 180 µmol As g⁻¹ goethite at pH 6.5. This was estimated by fitting the Langmuir equation to the data and extrapolation to an adsorption maximum. Thus, all treatments were undersaturated with respect to the adsorption maximum.

Mn-substituted goethite suspensions for kinetic study were prepared as follows: 0.05 g of Mn-substituted goethite was added to 5.0 mL of 0.01 M NaCl solution, followed by the addition of 0.1 mL of 75 µmol/mL As(III) producing 150 µmol As(III) g⁻¹ solid. The pH was adjusted to 6.5 with 0.1 M HCl. Samples were then mixed continuously to 10 d in capped centrifuge tubes on a shaker. Following the different aging periods, the mixtures were centrifuged and sediment-pastes were collected. The paste samples for XANES spectral analysis were prepared at different time intervals ranging from 2 h to 5 d before scanning.

To examine the effects of dry conditions on As(III) stability, samples were prepared as follows: 0.1 mL of 75 µmol mL⁻¹ As(III) was added to 1.0 mL of a 5% (w/w, 5 g solid in 100 g solution) Mn-substituted goethite suspension in a 0.01 M NaCl solution producing 150 µmol As(III) g⁻¹ solid. The pH was adjusted to

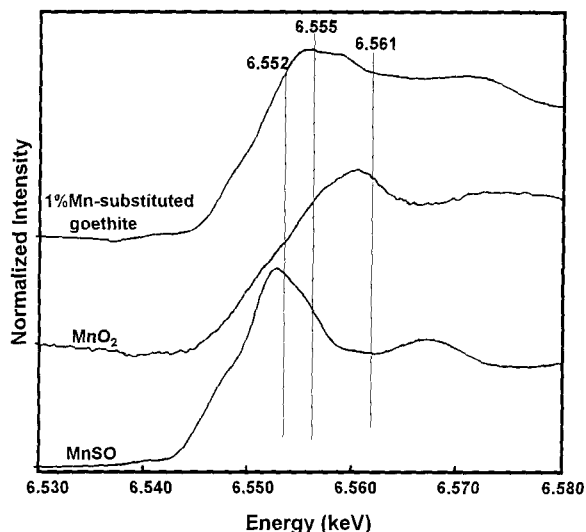


Figure 1. Normalized K XANES spectra of Mn in 1% Mn-substituted goethite, MnO_2 , and MnSO_4 .

6.5 with 0.1 M HCl, mixed and aged in air-dry condition to 10 d. The air-dried samples for XANES spectral analysis were prepared by using the same procedure as above.

pH and temperature effects on As(III) oxidation by Mn-substituted goethite were studied by adding 0.05 g of Mn-substituted goethite to 5.0 mL of 0.01 M NaCl solution. To this suspension, 0.1 mL of $75 \mu\text{mol mL}^{-1}$ As(III) was added to produce $150 \mu\text{mol As(III) g}^{-1}$ solid. The pH was adjusted to 5.0, 6.5, and 8.0 with 0.1 M HCl or NaOH. Samples were then mixed continuously to 10 d in capped centrifuge tubes on a shaker. The treatments at pH 6.5 were aged at 25, 45, and 65°C to 10 h in capped centrifuge tubes. Following the different aging periods, the mixtures were centrifuged. Sediment-paste samples were collected for XANES spectral study. Replicates of the above treatments were used to determine extractable Mn(II) produced from the reaction with As(III). The samples were centrifuged and the supernatant was taken for Mn analysis. Then 10.00 mL of 0.05 M CuCl_2 was added to the mineral residue, shaken for 1 h and centrifuged again. The supernatant was taken, combined with the previous collection and all Mn released to the solution phase was determined by ICP.

The XANES spectra of both As and Mn were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) beam line 4-3 equipped with a wiggler. The monochromator used Si(220) crystals and was detuned $\sim 50\%$. Arsenic XANES spectra were collected from 11.650 to 11.950 keV by using a Lytle-type fluorescence detector with a 6 mm Ge-filter. Energy was calibrated by the XANES spectrum of As(0) with the ion chamber positioned along the beam path and behind the primary sample. The half-height edge energy

of As(0) was taken to be 11.876 keV in transmission. The Mn XANES spectra were collected from 6.000 to 7.000 keV by using Mn metal foil to calibrate energy (half-height edge energy of Mn metal was taken as 6.539 keV). The Ge-fluorescence detector was used to collect spectral data. All spectral data are presented without smoothing.

RESULTS AND DISCUSSION

Manganese substituted goethite has a structure nearly identical to pure goethite according to X-ray diffraction data (data not shown). A previous study (Cornell and Giovanoli, 1987) indicated that, in alkali condition (pH = 11–13) and with Mn additions of as much as 15 mole %, Mn-substituted goethite was the sole reaction product. With an increase in Mn substitutions (Table 1), the color of goethite samples became darker and the point of zero net proton charge (PZNPC) decreased. Unsubstituted goethite was yellow, but as little as 1 mole % Mn produced an olive color, and highly substituted goethite was gray or black. Figure 1 shows Mn K XANES spectra of MnO_2 , MnSO_4 , and Mn-substituted goethite and these spectra are consistent with Schulze *et al.* (1995). Schulze *et al.* did not examine Mn-substituted goethite. Mn(II) (MnSO_4) K XANES spectrum was characterized by an edge-peak at 6.552 keV. For Mn(IV) (MnO_2), the edge-peak was at 6.561 keV whereas for Mn-substituted goethite the edge peak was ~ 6.555 keV. The position of the Mn edge-peak for Mn-substituted goethite was between that of Mn(II) and Mn(IV), suggesting the main oxidation state of Mn in Mn-substituted goethite was Mn(III). This is compatible with the suggestion of Schwertmann and Cornell (1991). They proposed that although Mn(II) is used in preparing of Mn-substituted goethite, it is oxidized to Mn(III) by atmosphere oxygen under alkaline conditions and incorporated into the goethite structure as Mn(III).

Arsenic K XANES spectra of pure goethite treated with $150 \mu\text{mol g}^{-1}$ arsenic at different As(V)/As(III) ratios are shown in Figure 2. This figure shows that the 100% As(III)-treated goethite has an edge-peak at 11.873 keV whereas the 100% As(V)-treated goethite has an edge absorption peak at 11.876 keV. As the mole fraction of As(III) increased, the intensity of the 11.873 keV peak increased whereas the 11.876 keV peak decreased gradually. These differences were used in a comparative way to identify the oxidation transformation from As(III) to As(V) on goethite surfaces.

Figure 3 shows the reaction of As(III) on Mn-substituted goethite at pH 5.0 and 8.0. At room temperature, no apparent oxidation occurred on pure goethite after 10 h. The oxidation of As(III) to As(V) by Fe(III) is a thermodynamically favorable reaction at low pH conditions (Oscarson *et al.*, 1980). However, they found that the conversion of As(III) to As(V) by synthetic Fe(III) oxyhydroxide did not occur within 72 h

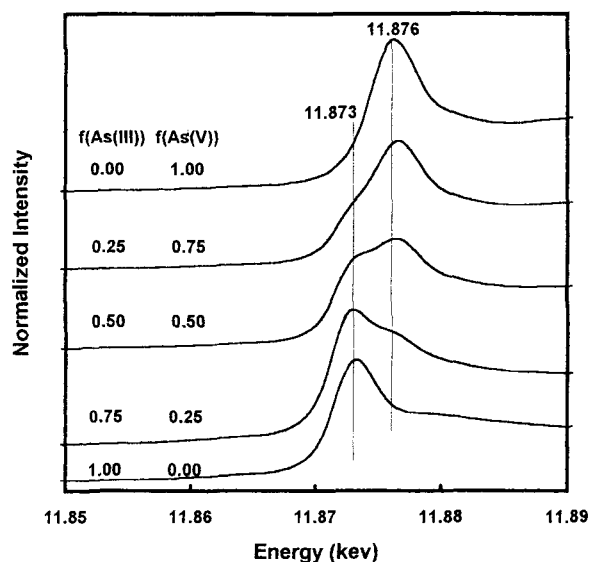


Figure 2. Normalized As K XANES spectra of As(III) and As(V) mixtures at different As(III)/As(V) ratios on goethite.

at neutral pH values, suggesting the reaction is kinetically controlled. Oxidation of As(III) increased with increased Mn substitution in goethite. This indicates that Mn-substituted goethite is a stronger oxidant for the oxidation of As(III) than pure goethite. There were no apparent significant differences between the amount of As(III) oxidized at pH 5.0 and 8.0. The absence of a strong pH influence is predicated from the acid-base chemistry of H_3AsO_3 ($\text{pK}_a = 9.3$) (Scott and Morgan, 1995). In the pH range studied here, the concentration of the H_3AsO_3^0 species remains nearly constant.

At room temperature, the oxidation of As(III) on Mn-substituted goethite was slow. Figure 4 shows the reaction of As(III) on 5% Mn-substituted goethite as a function of time. No apparent oxidation was observed within 3 d in either suspension or air-dry conditions. By day 5, comparing results in Figure 2 with those in Figure 4, we estimate 20% or less of As(III) was oxidized to As(V). An extended reaction period along with a more detailed spectral analysis may reveal differences in oxidation rates between suspension and air-dry samples.

Figure 5 shows that the oxidation of As(III) on Mn-substituted goethite was greatly enhanced at elevated temperatures. At 65°C, nearly all As(III) was oxidized to As(V) on 10% Mn-substituted goethite after 10 h. On 5% Mn-substituted goethite, the As(III) peak was dominant at 45°C whereas the As(V) peak dominated at 65°C. Even on pure goethite, As(III) oxidation occurred at 65°C after 10 h. Increasing temperature may favor an increase in As(III) oxidation in several ways. For example, the desorption and transfer rate of As(III) to sites near Mn may increase, thus increasing the

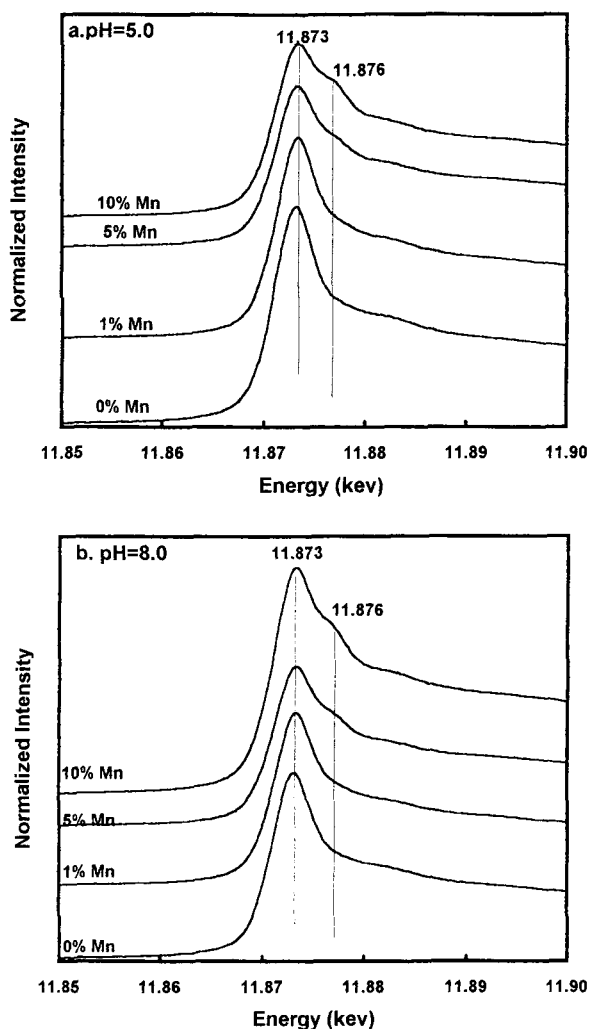


Figure 3. Normalized As K XANES spectra of As(III) adsorbed on Mn-substituted goethite 10 h after As treatment. a) pH = 5.0, b) pH = 8.0.

electron transfer rate. However, it may not be necessary for As(III) to come in close contact with Mn, but the oxidation potential of the entire solid phase may be more favorable for As(V) formation. Also, with increasing temperature, the activation energy of the As(III) oxidation reaction may decrease thereby making the reaction faster, such as the case with pure goethite.

Figure 6 shows the total extracted Mn(II) by CuCl_2 from Mn-substituted goethite after reacting with As(III) at 65°C. Note in Figure 5, nearly all of the As(III) ($150 \mu\text{mol g}^{-1}$ solid) was apparently oxidized to As(V) on 10% Mn-substituted goethite after 10 h. If we assume the reaction:



then $300 \mu\text{mol Mn(II) g}^{-1}$ solid will be produced.

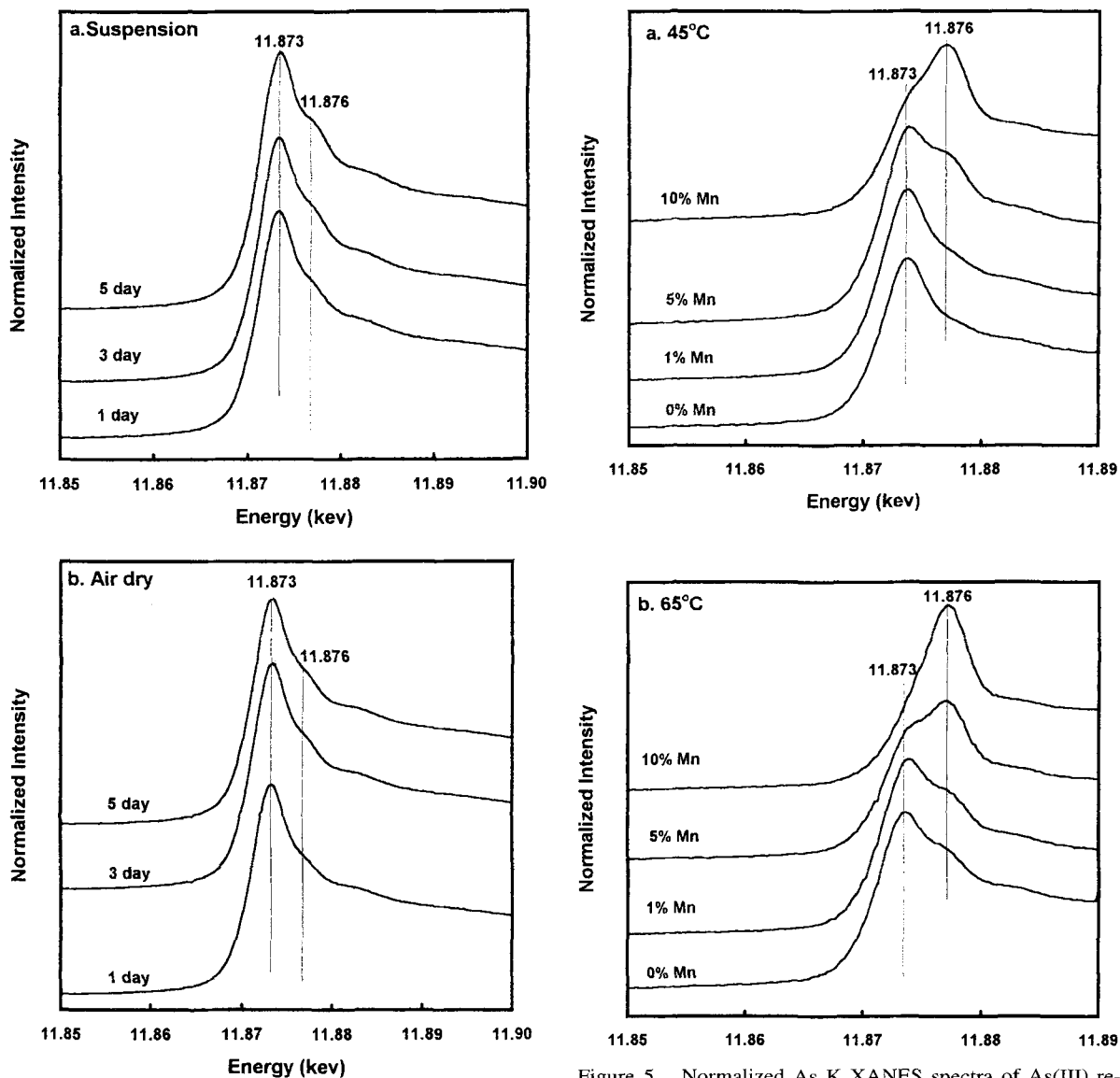


Figure 4. Normalized As K XANES spectra of As(III) adsorbed on 5% Mn-substituted goethite as a function of time. a) Suspension, b) Air-dry.

Figure 5. Normalized As K XANES spectra of As(III) reacted with different Mn-substituted goethite as a function of temperature. a) 45°C, b) 65°C.

However, the extracted Mn(II) from 10% Mn-goethite was only $\sim 30 \mu\text{mol g}^{-1}$, much less than calculated from reaction (1). For 1% Mn-goethite $\sim 30\%$ of As(III) was oxidized to As(V) as estimated by comparing Figures 5 and 2. The Mn(II) produced from reaction (1) will be $90 \mu\text{mol g}^{-1}$ solid, which is $\sim 80\%$ of the total Mn in 1% Mn-goethite. If this amount of Mn(II) is not extractable and remains in the solid phase, it will change the Mn XANES spectrum. However, there is no apparent difference in Mn oxidation states in 1% Mn-goethite before and after reaction with As(III) (Figure 7).

The results suggest that the oxidation of As(III) to As(V) was favored by Mn-substituted goethite. Previous research indicated that in a natural, open system (Oscarson *et al.*, 1981b) as well as in controlled environments (Scott and Morgan, 1995), Mn in Mn oxides is able to increase the rate of As(III) oxidation. Davis and Morgan (1989) found that the oxidation of Mn(II) to Mn(III) is very slow at pH values < 8.5 , but the rate increases through surface interactions with goethite. They found that oxidation is strongly temperature dependent. Molecular oxygen is assumed to be the terminal electron acceptor. Because of our experimental conditions, Mn(II) formation and re-oxidation to Mn(III) could not be detected.

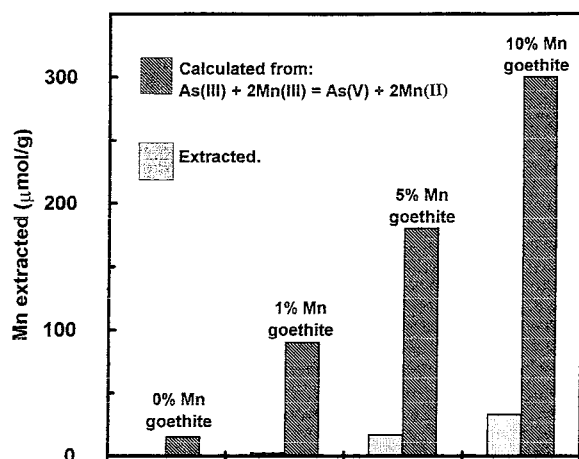


Figure 6. Mn released from Mn-substituted goethite after reaction with As(III) at 65°C.

Based on the above results, mechanism for electron transfer cannot be uniquely identified. Since Mn(III) ([Ar]3d⁴) has one electron less than Fe(III) ([Ar]3d⁵), Mn-substituted goethite may act as a p-type semiconductor (Bockris and Reddy, 1973). Thus, electrons accepted from As(III) oxidation by Mn-substituted goethite may be de-localized over the solid instead of associated with a specific surface atom. Only those electrons of Mn(II) on the surface may be desorbed and released to the solution. This may account for the relatively small amount of Mn(II) extracted from the Mn-substituted goethite shown in Figure 6. In terms of charge and size, Mn(II) atoms may not be stable in the goethite structure and thus re-oxidize to Mn(III), with O₂ acting as the electron acceptor. This re-oxidation may be a fast reaction because no change of oxidation state of Mn was observed. Other possible mechanisms may also explain our results. For example, it was observed for V that the oxidation rate of vanadyl(IV) by O₂ is increased by its adsorption on δ-Al₂O₃ and TiO₂ (anatase) (Wehrli and Stumm, 1988, 1989). This was attributed to a more favorable electron environment as a result of an inner-sphere complex formation (Wehrli *et al.*, 1989). Their results did consider isomorphous substitution in the mineral. More experimental data are needed to identify the process. Regardless of the mechanism for As(III) oxidation, Mn substitution in goethite and temperature are important in controlling the process.

CONCLUSIONS

Arsenite [As(III)] can be oxidized by Mn-substituted goethite. This reaction was more sensitive to temperature than to pH. An increase in Mn substitution in goethite results in an increase oxidation rate of As(III) to As(V). Different mechanisms may explain this observation. The surface of Mn-substituted goethite possibly acts like a semi-conductor in which electrons are

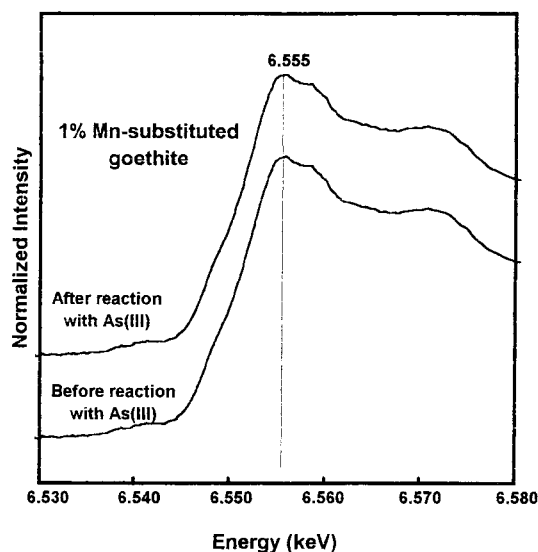


Figure 7. Normalized K XANES spectra of Mn in 1% Mn-substituted goethite before and after reaction with As(III) at 65°C.

de-localized in the entire mineral instead of only associated with surface atoms. Also, changes in the local environment of As(III) possibly produces the formation of an inner-sphere complex with Mn-substituted goethite enhanced oxidation. Oxygen may be the electron acceptor in either case. Since Mn-substituted goethite can both convert As(III) to As(V) and strongly adsorb As(V), under certain conditions the reactions may be useful in decreasing As toxicity in environments contaminated by As(III).

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