A microscopic and spectroscopic study of rapid antimonite sequestration by a poorly crystalline phyllosmanganate: differences from passivated arsenite oxidation†

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During the reaction of arsenite (As(III)) with δ-MnO₂ (a typically poorly crystalline phyllosmanganate), a significant decrease in the oxidation rate is frequently observed, which is mainly attributed to the surface passivation of δ-MnO₂. However, whether surface passivation also occurs during the antimonite (Sb(III)) oxidation process is unclear. In this study, the behavior and mechanisms of Sb(III) oxidation were compared with those of As(III) during their reactions with δ-MnO₂. The experimental kinetics results indicated that the oxidation rate of Sb(III) was 6.14–44.71 times faster than that of As(III) with initial concentrations ranging from 100 to 1000 μM. The macroscopic and spectroscopic results suggested that surface passivation during the adsorption of Mn(II) and the formation of Mn(III) were the predominant causes for the decrease in the As(III) oxidation rate, whereas surface passivation may not have been the limiting factor during Sb(III) oxidation. Compared to As(III) oxidation, the rapid oxidation of Sb(III) by δ-MnO₂ led to significant changes in the structure and properties of δ-MnO₂, and contributed to the precipitation of Mn(II) antimonate (MnSb₂O₆). The results of this study facilitate a better understanding of the environmental behavior of Sb and As on metal-oxide surfaces in aquatic environments.

1. Introduction

Arsenic (As) and antimony (Sb) are two metalloids that belong to group VA of the periodic table. Elevated levels of As and Sb in soils and groundwater from geological and anthropogenic sources have attracted worldwide attention due to their high toxicity to humans, plants and microorganisms. The predominant forms of As and Sb in contaminated environments are inorganic species. These species are most commonly present in the pentavalent state in the forms of antimonates (Sb(OH)₆³⁻, pKₐ = 2.72) and arsenates (H₃AsO₄⁻, HAsO₄²⁻, and AsO₄³⁻, pKₐ ≈ 3 = 2.20, 6.97 and 11.53, respectively) in oxidizing and aerobic surroundings, while in anoxic environments, antimonites (Sb(OH)₃⁻, pKₐ = 11.9) and arsenites (H₃AsO₃⁻, HAsO₃²⁻, AsO₃³⁻, pKₐ ≈ 3 = 9.22, 12.13 and 13.4) are present in the trivalent state. As(III) is considered more mobile in soils and sediments than As(V) because of its weak binding to metal mineral surfaces, and it is also more toxic because it binds to sulphydryl (–SH) groups, affecting the function of many proteins. The toxicity of Sb is similar to that of As, i.e., Sb(V) < Sb(III) but its environmental behavior is not as well understood.

The oxidation of As(III) to As(V) is an important reaction because this process can decrease not only the mobility of As(III) by increasing its tendency to be absorbed onto mineral surfaces but also its toxicity. Manganese (Mn) oxides are powerful oxidizing and detoxifying agents, and they can play an important role in many elemental geochemical processes. The reactivity of Mn oxides varies with their mineralogy, and previous studies have suggested that layered Mn oxides (i.e., phyllosmanganates) are more reactive than Mn oxides with tunnel structures (e.g., pyrolusite and romanechite). Due to their high specific surface areas and structures with highly reactive vacancy sites, these phyllosmanganates can absorb metals, such as Zn(II), Cu(II), Pb(II) and Ni(II). However, these materials can also readily oxidize many reduced toxic metals and metalloids, such as As(III), Cr(III), and Co(II), as well as organic contaminants.
Many Mn oxides found in surface environments are poorly crystalline, of biogenic origin and highly reactive. Specifically, δ-MnO₂, an amorphous crystalline form of hexagonal birnessite, is quite reactive with respect to As(III) oxidation. However, during reactions with As(III), the δ-MnO₂ surface is usually passivated, i.e., the oxidation initially proceeds rapidly followed by a significant decrease in the oxidation rate. The passivation of δ-MnO₂ is primarily caused by the retention of the reaction products, including the sorption of Mn(II) and As(III) and the formation of Mn(III). The sorption of As(III) and Mn(II) at the edge sites, which are the location at which As(III) oxidation occurs, can cover the reactive Mn(II) sites, thus physically blocking them. In addition, the adsorption of Mn(II) onto the δ-MnO₂ surface may undergo a cascade of reactions that gradually lead to the formation of less reactive Mn(III) sites as a result of Mn(II)/Mn(IV) comproportionation. Another possible passivation pathway is the formation of Mn(II) arsenate precipitates on the δ-MnO₂ surface.

The surface passivation of δ-MnO₂ during the oxidation of Cr(III) and U(IV) has also been reported in the literature, but the related data for Sb(III) oxidation are rather limited. The decrease in δ-MnO₂ reactivity when it reacts with Cr(III) can be attributed to the surface precipitation of Cr(OH)₃, which coats the δ-MnO₂ surface, whereas U(IV) adsorption on the mineral surface can decrease the reactivity of δ-MnO₂ during U(IV) oxidation. Although surface passivation has been observed for many toxic metals, such as As(III) and Cr(III) (including metalloids), during the oxidation process, to the best of our knowledge, a study that focuses on the mechanisms that control Sb(III) oxidation by δ-MnO₂ has not been published.

This study aims to investigate the oxidation behavior and mechanisms of Sb(III) during its reaction with δ-MnO₂. The kinetics of the reaction of Sb(III) with δ-MnO₂ were examined and compared with those of As(III) using batch kinetic experiments. A combined microscopic and spectroscopic approach, including X-ray photoelectron spectroscopy (XPS), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and X-ray diffraction (XRD), was used to characterize the changes in the δ-MnO₂ mineral composition and the properties involved in the As(III) and Sb(III) oxidation process and to identify the newly formed secondary precipitates. In addition, the oxidative mechanism and passivation behavior of As(III) and Sb(III) during their respective reactions with δ-MnO₂ were discussed.

2. Materials and methods

2.1 Chemicals and materials

All chemicals used in this study were of analytical grade or guaranteed grade. Sodium arsenite (Na₃AsO₄·12H₂O) (>98.0%) and sodium arsenate (Na₂AsO₄·12H₂O) (>98.0%) were obtained from Xiya Reagent Co., Ltd., China. Potassium antimony(III)-tartrate hemihydrate (>99.0%), antimony pentoxide (>98.0%), and potassium pyroantimonate (K₂H₂Sb₂O₄·4H₂O) (>98.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. The stock solutions of As(III) and Sb(III) (10 mM) and working solutions of various concentrations were prepared using deionized water.

The δ-MnO₂ used in this study was prepared following the methods described in a previous study. The properties of δ-MnO₂ were analyzed using XRD, SEM-EDS, and a particle size analysis and the detailed results were published in our recent report. Batch kinetic experiments

Batch experiments to evaluate As(III) and Sb(III) oxidation by δ-MnO₂ were conducted in 500 mL Erlenmeyer flasks. A series of As(III) or Sb(III) stock solutions was added to 300 mL of the solution containing δ-MnO₂. The initial As(III) or Sb(III) concentrations ranged from 100 to 1000 μM (100, 200, 500 and 1000 μM), and the dosage of δ-MnO₂ was 100 mg L⁻¹. The background electrolyte was 0.01 M KCl and the pH of all test solutions during the kinetic experiments was maintained at 5.0 using a 0.1 M acetic acid and sodium acetate buffer system. All reaction flasks for the kinetic experiments were sealed and then shaken using a reciprocating shaker at 200 rpm and 25 °C. At different time intervals (0, 5, 10, 15, 20, 25, 30, 45 and 60 min), 2 mL samples of the suspension were collected and filtered through 0.22 μm hydrophilic polyvinylidene fluoride membrane filters (Durapore PVDF, Millipore) to quench the oxidation reaction. All filtered samples were stored at 4 °C in the dark prior to instrumental analysis. The kinetic experiments were performed in triplicate. All glassware used in this study was soaked overnight in 10% HNO₃ and washed thoroughly with deionized water before use.

2.3 Solid phase analysis

After the kinetic experiments, the δ-MnO₂ suspensions that were exposed to various As(III) and Sb(III) concentrations were centrifuged at 10 000 rpm for 10 min. The residual samples were washed three times with deionized water and freeze dried at −60 °C for 12 h in a vacuum freeze dryer (FD-1B-50, Shanghai BiLang Instruments Co., Ltd. China). The freeze-dried samples were further analyzed using XPS, SEM-EDS, XRD, FTIR, and Raman spectroscopy.

SEM images of the original δ-MnO₂ and δ-MnO₂ after reacting with As(III) or Sb(III) were recorded using a Zeiss Super 55 VP SEM coupled with a Bruker XFlash 5010 EDS system. The samples were fixed onto the SEM stage prior to SEM-EDS analysis using double-sided adhesive carbon tape. A thin gold coating (<5 nm) was sputtered onto the carbon to prevent surface charging during the SEM analyses. The SEM images were acquired at magnifications ranging from 1000× to 100 000× with an accelerating voltage of 20 kV. The coated samples were also examined using the EDS system to obtain a rapid semi-quantitative elemental analysis. The EDS spectra were measured obtained at selected areas of the particles with a counting time of 60 s. The detection limit was approximately 0.1% (wt) for most elements and the relative percentage content of the elements was normalized. The amorphous state and any crystalline phases of δ-MnO₂ before and after reacting with As(III) or Sb(III) were determined using an X-ray diffractometer.
was vacuum-deposited on the Mn standards to charge reference
the binding energy with respect to the Au 4f7/2 peak position
(84.0 eV). After non-linear Shirley-type background subtraction,
the data were normalized by comparison with Mn(II), Mn(III) and
Mn(IV) reference standards. For each sample, a direction set
method was conducted to adjust every fitting parameter
(FWHM, the full width at half maximum; H, the peak height; E,
the peak position center) and minimize the value of residual
standard deviation (STD). The peak position and relevant
parameters from curve fitting of Mn 3s, Mn 3p and O 1s high
resolution spectra are listed in Tables S1–S3.†

The zeta potentials and particle sizes of the fresh δ-MnO2
were determined using a Malvern Zetasizer Nano analyzer
(Malvern, UK). The BET surface of δ-MnO2 was examined using
an ASAP 2010 specific surface area and porosity analyzer
(Micromeritics, USA).

2.4 Determination of As, Sb and Mn(II) in solution

The concentrations of As(III/V) and Sb(III/V) in solution were
determined using liquid chromatography combined with an
AFS 830 hydride generation atomic florescence spectroscope
(LC-HG-AFS) (Beijing Jitian, China). The inorganic As and Sb
species were separated using a Hamilton PRP-X100 anion
exchange column (250 mm × 4.1 mm, 10 μm) with a flow rate of
1 mL min⁻¹ and a 100 μL sample injection volume. The mobile
phases for the As(III)/As(V) and Sb(III)/Sb(V) separation were
15 mM (NH₄)₂HPO₄ (pH adjusted to 6.0 using 10% formic acid)
and 1 mM potassium hydroxide phosphate with 10 mM EDTA–
2Na, respectively. The retention times of the As(III) and As(V)
species were 2.54 min and 10.16 min, respectively, while those
of Sb(III) and Sb(V) were 4.03 min and 2.63 min, respectively. The
concentrations for the standard curves of As and Sb ranged
from 10 to 100 μg L⁻¹. The current-carrying and reducing agents
used were 5% HNO₃ (v/v) and 2% KBH₄ (m/v) (prepared in 0.5%
KOH), respectively. The recovery rates from the Sb(III), Sb(V),
As(III) and As(V) analyses using the LC-HG-AFS system were
97.5%, 99.1%, 102.4% and 99.5%, respectively. The amounts of
As or Sb in the solid during the oxidation process were deter-
mined by calculating the difference between the initial
concentrations of As(III) or Sb(III) and the residual concen-
trations of As or Sb in solution with the reaction time. The Mn(II)
concentration in solution was determined using manganese
formaldehyde oxime spectrophotometry.₃₅

3. Results and discussion

3.1 Kinetics of As(III) and Sb(III) oxidation by δ-MnO₂

The kinetic experiments in this study were performed by
reacting 100, 200, 500 and 1000 μM As(III) or Sb(III) with 100 mg
L⁻¹ δ-MnO₂ at pH 5.0 (Fig. 1). The residual As(III) concentrations
in solution decreased as a function of the reaction time, and the
As(III) oxidation rate decreased with the increasing initial As(III)
concentrations. The reaction process for Sb(III) oxidation
showed a similar pattern. However, the oxidation rate of Sb(III)
was more rapid than that of As(III).
Sb(III) reacted with 100 mg L\(^{-1}\) Mn(II) in the solution by a first-order rate model, where \(k_{\text{obs}}\) is the rate constant of the first-order model, \(C_0\) is the concentration of As(III) or Sb(III) remaining in solution at time \(t\), \(C_0\) is the initial concentration of As(III) or Sb(III), and \(t_{1/2}\) represents the time required when the As(III) or Sb(III) concentration is decreased to half of its initial value.

The kinetics data were generally well fitted for As(III) (\(R^2 = 0.930\)–0.993) and Sb(III) (\(R^2 = 0.870\)–0.996) after oxidation by \(\delta\)-MnO\(_2\) (Table 1). The \(k_{\text{obs}}\) values for the Sb(III) concentrations from 100 to 1000 \(\mu\)M were 6.14–44.71 times higher than those for As(III). In contrast, the half-life values for Sb(III) oxidation were only 2.20–15.97% of those of As(III).

The disparities in the oxidation rates between Sb(III) and As(III) were possibly due to the significant surface passivation of \(\delta\)-MnO\(_2\) during As(III) oxidation. During the oxidation process of As(III), As(V) and Mn(II) were produced according to the following reaction (eqn (3)).

\[
\text{MnO}_2(\text{s}) + \text{H}_3\text{AsO}_3(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightarrow \text{Mn}(\text{aq})^{2+} + \text{H}_2\text{AsO}_4(\text{aq})^- + \text{H}_2\text{O}(\text{aq})
\]

As shown in Fig. 1, at a low As(III) concentration (100 \(\mu\)M), the release of As(V) into the solution increased with the reaction time, and the concentrations of As(V) were significantly higher than those of Mn(II) in solution. This observation was attributed to the Mn(II) adsorption at the reactive sites, leading to the inhibition of As(V) adsorption.\(^{24}\) With the increasing initial As(III) concentration, the difference between the As(V) and Mn(II) concentrations diminished and eventually disappeared at a high As(III) concentration (1000 \(\mu\)M). These results suggest that once the \(\delta\)-MnO\(_2\) reactive sites were completely occupied, freshly formed Mn(II) and As(V) tended to fully release into the solution at a mole ratio of 1:1. In addition, a slow oxidation rate was observed for \(\delta\)-MnO\(_2\) with a high concentration of As(III). This result is consistent with the study reported by Lafferty et al. (2010a); in their study, during the As(III) reaction process, the oxidation rate significantly decreased but still continued in the Mn(II)-saturated \(\delta\)-MnO\(_2\) system.\(^{26}\)

As(III) must adsorb onto mineral surfaces prior to oxidation, but a number of studies have indicated that only As(V) can be retained at the reactive sites of \(\delta\)-MnO\(_2\).\(^{20,21,26}\) In the high-resolution XPS spectra (Text S1–S9, Fig. 2 and S1 and Table S4), the peaks correlated with the binding energies at 45.4 ± 0.1 eV and 540.4 ± 0.2 eV were assigned to As 3d and Sb 3d\(_{3/2}\), respectively, which indicated that only As(V) and Sb(V) were present on the surface of \(\delta\)-MnO\(_2\).\(^{34,35}\)

Table 1 Rate constants \(k_{\text{obs}}\) and \(t_{1/2}\) for As(III) and Sb(III) by \(\delta\)-MnO\(_2\)

| Items  | Con. (\(\mu\)M) | \(k_{\text{obs}}\) | \(t_{1/2}\) (min) | \(R^2\) |
|--------|----------------|------------------|-----------------|--------|
| As(III)| 100            | 0.188            | 3.68            | 0.930  |
|        | 200            | 0.034            | 20.32           | 0.993  |
|        | 500            | 0.009            | 80.58           | 0.932  |
|        | 1000           | 0.007            | 100.43          | 0.987  |
| Sb(III)| 100            | 2.923            | 0.23            | 0.996  |
|        | 200            | 1.520            | 0.45            | 0.870  |
|        | 500            | 0.145            | 4.79            | 0.982  |
|        | 1000           | 0.043            | 16.04           | 0.962  |

As(V) and Sb(V) tended to adsorb strongly at both the vacant and edge sites of \(\delta\)-MnO\(_2\).\(^{27,28}\) The surface passivation of \(\delta\)-MnO\(_2\) was primarily caused by the...
In addition, as shown in Fig. 1(a), at low As(m) concentrations, the adsorption of As(v) onto the solid quickly increased within 10 min, followed by a continuous decrease in As(v) adsorption until the end of the experiments. The decrease in the As(v) adsorption on the solid was attributed to the competition between As(v) and Mn(II) for the reactive sites. In Sb(v) in the solid also exhibited a similar tendency with the Sb(m) concentrations in solution (Fig. 1(b) and (d)). At high As(m) or Sb(m) concentrations (Fig. 1(e)–(h)), As(v) or Sb(v) in the solid slightly increased with the reaction time. The Sb(v) content in the solid increased more significantly than the As content (Fig. 2).

### 3.2 Mn oxidation state analysis

To better understand the mechanisms of the Sb(m) and As(m) reactions with δ-MnO₂, the changes in the Mn oxidation states were investigated. The magnitude of the Mn 3s XPS multiplet splitting was used to determine changes in the δ-MnO₂ oxidation state during the As(m) and Sb(m) reactions (Fig. S2 and S3 and Table S5†). The pristine δ-MnO₂ sample showed multiplet splitting at 4.86 eV. According to the linear correlation between the Mn 3s multiplet splitting and the average oxidation state of Mn (Fig. S3†), the Mn in δ-MnO₂ exhibited an average oxidation state at 3.56 eV, indicating the presence of Mn(III) and Mn(II) impurities. After reacting with As(m), the values for the Mn 3s multiplet splitting increased slightly with the increasing initial As(m) concentrations. The average Mn oxidation states ranged from 3.36 to 3.13, which coincided with the decrease in the Mn oxidation state from Mn(IV) to Mn(III/IV). The oxidation of 1000 μM Sb(m) by δ-MnO₂ led to a more significant increase in the multiplet splitting from 4.86 to 5.82 than that observed in the As(m) reaction, indicating the rapid reduction of Mn(IV) to Mn(II).

The changes in the relative content of Mn(IV), Mn(III) and Mn(II) in the pristine and reacted δ-MnO₂ were quantified by conducting a high-resolution XPS spectral analysis of the Mn 3p level (Fig. S4† and Table 2). The percent contents of Mn(IV), Mn(III) and Mn(II) in the pristine δ-MnO₂ were 57.6%, 28.43% and 13.97%, respectively. After reacting with As(m) or Sb(m), the Mn 3p high-resolution spectra shifted toward a lower binding energy, indicating a decrease in the percentage of Mn(IV) on the δ-MnO₂ surface. During the reaction of δ-MnO₂ with various...
As(III) and Sb(III) oxidation were investigated using FTIR, Raman than those obtained a slightly during the reactions with Sb(III) and As(III), indicating to lattice oxygen (Olatt), surface-absorbed oxygen (Oads) and peaks located at 530.0, 531.4 and 532.4 eV, which corresponded to controlling Sb(III) oxidation. Additional O 1s high-resolution spectra were divided into three peaks located at 530.0, 531.4 and 532.4 eV, which corresponded to lattice oxygen (O_{latt}), surface-absorbed oxygen (O_{ads}) and chemisorbed oxygen species (O_{chem}), respectively. The predominant source of O_{latt} originated from the δ-MnO_2 itself, and it changed during the oxidation process. O_{ads} was primarily derived from As(III) and Sb(III) and thus existed as an experimental condition. After the reactions with Sb(III) and As(III), the percentage of O_{ads} significantly decreased along with the increasing percentage of O_{latt}, indicating that the reactions of Sb(III) and As(III) with δ-MnO_2 led to changes in the δ-MnO_2 structure. The higher values of O_{ads}/O_{latt} after Sb(III) oxidation than those obtained after As(III) oxidation were primarily attributed to the fact that more Sb(V) was retained on the δ-MnO_2 surface. The percentage of O_{ads} in the δ-MnO_2 changed slightly during the reactions with Sb(III) and As(III), indicating that the adsorbed H_2O did not participate in the reaction between δ-MnO_2 and Sb(III) or As(III).

3.3 δ-MnO_2 property analysis

The changes in the properties of δ-MnO_2 before and after the As(III) and Sb(III) oxidation were investigated using FTIR, Raman spectroscopy, SEM-EDS and XRD. The results are shown in Fig. 4 and 5. FTIR and Raman spectra analyses were used to identify the functional groups of δ-MnO_2 involved in the reactions with As(III) and Sb(III). As shown in Fig. 4a, several of the typical absorption bands for pristine δ-MnO_2 that were observed in the absorption band at 1624 cm^{-1} were ascribed to the hydroxyl (–OH) groups of the physically adsorbed water molecules, and two broad features at 520 and 460 cm^{-1} were assigned to the Mn–O lattice vibration of the Mn oxides. The changes in the bond positions of δ-MnO_2 in the FTIR spectra were insignificant during its reaction with various concentrations of As(III) (Fig. 4a). After the reactions between δ-MnO_2 and Sb(III), significant changes in the FTIR spectra were observed (Fig. 4b). The Mn–O located in the “fingerprint zone” disappeared in the presence of high concentrations of Sb(III) (500 and 1000 μM). A new peak near 1060 cm^{-1} appeared, and the relative adsorption intensity increased with the Sb(III) concentration, which was ascribed to the formation of the Sb–O bond (Fig. 4b and S5†). The spectral results indicate that remarkable changes to δ-MnO_2 occurred during the reaction with Sb(III), whereas the δ-MnO_2 structure was not significantly affected during the As(III) oxidation process.

Fig. 4c and d shows the Raman spectra of δ-MnO_2 before and after reacting with As(III) and Sb(III). For the pristine δ-MnO_2, the sharp peak near 640 cm^{-1} was assigned to the characteristic peak of the Mn oxides. Significant changes were not observed in δ-MnO_2 during its reaction with 1000 μM As(III) (Fig. 4c), whereas the Raman spectra clearly changed after Sb(III) reacted with δ-MnO_2 (Fig. 4d). The characteristic peak of the Mn oxides widened and became more intense, and a new peak located near 470 cm^{-1} appeared.
SEM coupled with EDS is a useful technique for identifying mineral structures, wherein major elements on the surface of the tested sample can be determined simultaneously. The high-magnification SEM image (Fig. 5a) reveals that the pristine δ-MnO₂ particles were approximately 30–50 nm in diameter and poorly crystalline. The EDS spectrum showed that pristine δ-MnO₂ was predominantly composed of O (48.72%, wt) and Mn (47.28%, wt) (data not shown). During the reaction of As(III) with δ-MnO₂, the δ-MnO₂ surface structure did not significantly change (Fig. 5b). A similar study also confirmed the particle morphology did not change after δ-MnO₂ reacted with As(III), as shown in the transmission electron microscopy images.

In addition, negligible amounts of As on the δ-MnO₂ surface were detected using EDS (data not shown), similar to the results of the XPS survey analysis. A further XRD analysis showed that the newly formed mineral was Mn(II) antimonate (MnSb₂O₆, PDF#39-0980). The results showed a similar crystal structure as Sb₂O₅, but low and broad peaks located at 27.5° (2θ) and 54° (2θ) were observed. The crystal structure of Mn(II) antimonate could be related to the ratio of Mn/Sb. A similar study reported by Zhang et al. (2016) also confirmed that the formation of Mn(II) antimonate during reaction of Sb(III) with KMnO₄.

The XRD patterns of the pristine δ-MnO₂ exhibited only two main peaks at 37° and 66° (2θ) (Fig. 5c), which are characteristic of poorly crystalline phyllomanganates. The XRD patterns were slightly different for δ-MnO₂ before and after reacting with As(III). However, changes in the XRD patterns were apparent after Sb(III) reacted with δ-MnO₂. The two typical peaks for δ-MnO₂ disappeared, and two broad peaks at approximately 27° (2θ) and 54° (2θ) and a sharp peak at 36.3° (2θ) appeared, indicating that δ-MnO₂ structures were altered after reacting with Sb(III). A further XRD analysis showed that the newly formed mineral was Mn(II) antimonate (MnSb₂O₆, PDF#39-0980). The results showed a similar crystal structure as Sb₂O₅, but low and broad peaks located at 27.5° and 54° (2θ) were observed. The crystal structure of Mn(II) antimonate could be related to the ratio of Mn/Sb. A similar study reported by Zhang et al. (2016) also confirmed that the formation of Mn(II) antimonate during reaction of Sb(III) with KMnO₄. The high ratio of Mn/Sb contributes to a poorly crystallized structure with low and broad diffraction peaks. In addition, a cubic morphology Mn(II) antimonate with a particle size of 50–150 nm was observed by TEM analysis, which is in accordance with the SEM observations in Fig. 5c. These results suggesting that the δ-MnO₂ properties changed more significantly during the reaction with Sb(III) than with As(III).
3.4 Mechanisms of the As(III) and Sb(III) reactions with δ-MnO₂

The mechanisms of the As(III) oxidation by δ-MnO₂ were well revealed. Namely, one mole of As(III) molecules reacted with one mole of Mn(IV) reactive sites to generate one mole of As(V) anions and one mole of Mn(II) ions (eqn (3)). In this study, the oxidation rate for Sb(III) by δ-MnO₂ was faster than that for As(III). A decreasing As(III) oxidation rate was observed after the reaction of 100–1000 mM As(III); the decreased rate was mainly caused by the surface passivation of δ-MnO₂ by secondary products. During the reactions with low concentrations of As(III) (100 and 200 μM), the releases ratio of As(V) and Mn(II) from the solution was not equal to the theoretical value of 1 (Fig. S6†). The ratio Mn(II)/As(V) was less than 1, which was primarily attributed to the adsorption of Mn(II) onto the δ-MnO₂ surface. Mn(II) could compete with As(III) for the reactive sites, and when the reactive sites were occupied completely by Mn(II), freshly formed Mn(II) and As(V) tended to completely release into the solution at a mole ratio of 1 : 1. Increasing values of Mn(II)/As(V) approaching 1 were observed when using high concentrations of As(III) (500 and 1000 μM). Previous studies have indicated that the adsorption of Mn(II) onto the δ-MnO₂ surface is one of the major causes of early δ-MnO₂ passivation. Meanwhile, less reactive Mn(III) sites could be formed via comproportionation between the adsorbed Mn(II) and Mn(III) at the δ-MnO₂ surface, passivating the δ-MnO₂. The results from the Mn 3s and 3p XPS analyses agreed with the increase in the Mn(II) and Mn(III) content on the δ-MnO₂ surface. In addition, the macroscopic and spectroscopic analyses conducted using the SEM-EDS,
XRD, FTIR and Raman spectra indicated that surface passivation did not significantly change the surface structure of δ-MnO₂ during the reaction with As(III).

In contrast to the As(III) oxidation, surface passivation might be not have been a key factor in controlling the oxidation rate of Sb(III). The surface passivation of δ-MnO₂ by the adsorption of Mn(II) did not contribute to the remarkable depletion of Mn(II) rather than the complete release of Sb(III) in the δ-MnO₂ structure, but the Mn(II) percentage decreased from 57.6% to 8.60% after reacting with 1000 μM Sb(III). Moreover, the increasing Mn(II) content on the δ-MnO₂ surface could also induce surface passivation during the As(III) oxidation process, but the Mn(II) content decreased with the increasing initial Sb(III) concentration. This observation suggests that Mn(II) may have had the same ability as Mn(IV) to oxidize Sb(III). These results indicated that the surface passivation of δ-MnO₂ might not have occurred during the oxidation of Sb(III).

According to the XRD results in this study and a previous study, the reaction of Sb(III) with δ-MnO₂ can be expressed as shown in eqn (4).

\[
\text{MnO}_2(s) + \text{Sb(OH)}_3(aq) + \text{H}^+(aq) \rightarrow 0.5\text{Mn}^{2+} + 0.5\text{MnSb}_2\text{O}_6(s) + 2\text{H}_2\text{O}(aq)
\]

(4)

During the δ-MnO₂ reaction with Sb(III), the transfer of two electrons was responsible for the Sb(III) oxidation, i.e., one mole of As(III) reacted with one mole of Mn(II) to produce one mole of Sb(IV) and one mole of Mn(II). As shown in Fig. S6, the Mn(II)/As(III) ratios in solution during the Sb(III) oxidation were higher than those during the As(III) oxidation. According to the two-electron transfer reaction, the oxidation of one mole of Sb(III) produces one mole of Sb(IV) and Mn(II), but the formation of one mole of precipitated Mn(II) antimonate requires one mole of Sb(IV) and 0.5 mole of Mn(II) (eqn (4)). The unprecipitated Mn(II) could be adsorbed onto the δ-MnO₂ surface or released into the solution. At low Sb(III) concentrations, the low values of Mn(II)/Sb(IV) were attributed to the adsorption of Mn(II) onto the δ-MnO₂ surface. Due to the decrease in the number of Mn(II) reactive sites, the adsorption of Mn(II) could be inhibited when reacting with high concentrations of Sb(III) (from 200 to 1000 μM). Interestingly, during the reaction, the maximum Mn(II)/Sb(IV) ratios were observed in the presence of 500 μM Sb(III). This result was ascribed to the adsorption of Mn(II) onto the newly formed Mn(II) antimonate precipitates; this phenomenon reduced the concentration of Mn(II) in the solution. Previous studies have suggested that Mn(II) antimonate can effectively adsorb a series of divalent metals including Sr(II), Co(II), Ca(II) and Ba(II).51-54

In addition, Sb(IV) was also released into the solution. This release was attributed to two causes. First, during the Sb(III) oxidation process, Sb(IV) could adsorb onto the surface of δ-MnO₂. A similar study reported by Wang et al. (2012) suggested that the oxidation of Sb(III) by manganite (γ-MnOOH) occurred within 10 min, and Sb(IV) was absorbed by forming inner-sphere complexes at the manganite surface.55 Second, the dissolution of the Mn(II) antimonate precipitates might have contributed to the release of Sb(IV) into the solution.

4. Conclusions

In geochemical processes, the migration and transformation of Sb and As are critically determined by minerals present in the environments. Poorly crystalline phyllosilicates such as δ-MnO₂ can act as powerful oxidizers and scavengers for Sb(III) and As(III) in these environments. Therefore, understanding the retention mechanism between δ-MnO₂ and Sb(III) or As(III) has important environmental implications. In this study, As(III) and Sb(III) were both oxidized by δ-MnO₂, but the oxidation rate of Sb(III) was more rapid than that of As(III). The decreasing As(III) oxidation rate was primarily attributed to the surface passivation of δ-MnO₂ by the adsorption of Mn(II) and the formation of Mn(II). In contrast, the surface of δ-MnO₂ was not significantly passivated during the Sb(III) oxidation. The rapid oxidation of Sb(III) by δ-MnO₂ favors the precipitation of Mn(II) antimonate rather than the complete release of Sb(IV) into the solution. Thus, the difference between the Sb(III) and As(III) oxidation mechanisms in this study facilitated a better understanding of the environmental behavior of Sb and As on Mn oxide surfaces in aquatic environments.

Acknowledgements

This work was financially supported by the Shandong Province Natural Science Foundation (Grant ZR2016DQ008), the CPSF-CAS Joint Foundation for Excellent Postdoctoral Fellows (Grant 2016LH0048), the China Postdoctoral Science Foundation funded project (Grant 2016M600829), and the National Natural Science Foundation of China (Grant 51678315).

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