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3 Antimonate and Arsenate Speciation on Reactive Soil Minerals Studied

4 by Differential Pair Distribution Function Analysis

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Sb(V) adsorbed to ferrihydrite:
 ^1E and ^2C Geometries

As(V) adsorbed to ferrihydrite:
 ^2C Geometry

Graphical Abstract

Abstract

The pentavalent oxyanions antimonate (Sb(V)) and arsenate (As(V)) are toxic metalloids in environmental systems. In this study, we compare their sorption and surface speciation on 2-line ferrihydrite (Fh), δ -MnO₂ and Na-montmorillonite (Mont) at pH 5.5. The Sb(V) and As(V) sorption affinity and the highest measured surface excess (mmol:g) show that mineral reactivity towards Sb(V) or As(V) sorption increases in the order of Mont < δ -MnO₂ < Fh. In addition, Sb(V) showed greater uptake relative to As(V) by both Fh and δ -MnO₂. Using differential pair distribution function (d-PDF) analysis of high-energy X-ray scattering data, we found that the larger SbO₆ octahedron ($R_{\text{Sb-O}} = 1.95 \text{ \AA}$) can bind in both single edge- (¹E) and double corner-sharing (²C) geometries to Fh and δ -MnO₂, whereas the smaller AsO₄ tetrahedron ($R_{\text{As-O}} = 1.69 \text{ \AA}$) binds only in the ²C geometry. Thus, a greater number of surface sites support Sb(V) adsorption relative to As(V) adsorption on Fh and δ -MnO₂. Conversely, Mont supports only ²C adsorption geometries, which is consistent with the similar uptake behaviors of Sb(V) and As(V) on this mineral. Finally, we indexed atomic pairs from adsorbed Sb(V) and As(V) at $R > 6 \text{ \AA}$ in the d-PDFs. The analysis of the intermediate-ranged surface structure of our samples substantiated our interpretations of oxyanion adsorption geometries and provided information regarding changes in the underlying mineral surface upon ion adsorption. Our results show that the differences between Sb(V) and As(V) interactions with reactive soil minerals, including their sorption geometries, are linked to their distinct first-shell coordination environments.

1. Introduction

Antimony (Sb) and arsenic (As) are toxic metalloids in environmental systems. The release of As to the environment occurs via both anthropogenic sources, including mining and petroleum production (Han et al., 2003), and geogenic sources. Geogenic As contamination is a profound global public health and environmental concern (Argos et al., 2010; Smedley and Kinniburgh, 2002), which has provoked considerable interest in studying the environmental chemistry of As (Bissen and Frimmel, 2003; Melamed, 2005; Mudhoo et al., 2011). Conversely, Sb release derives primarily from anthropogenic activities, such as mining and a variety of industrial applications (e.g., brake lining, small arms ammunition, treatment for protozoan diseases and HIV) (Filella et al., 2002a, b; Wilson et al., 2010). Due to its widespread use, Sb extraction exceeded more than 160,000 tons in 2013 (USGS, 2014). In addition, antimony's anthropogenic mobilization factor (AMF, the mass ratio of Sb extracted by humans normalized by Sb released naturally) of nearly 250 is one of the highest of any element (Klee and Graedel, 2004; Sposito, 2008). Despite the potential for significant Sb contamination (1 – 100 g/kg) of soil and aquatic ecosystems via anthropogenic sources (Majzlan et al., 2011; Scheinost et al., 2006) studies informing the fate and mobility of Sb in natural systems are scarce.

In oxic environments, both Sb and As exist as pentavalent oxyanions, with the Sb(OH)_6^- and $\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$ species predominating at circumneutral pH (Filella et al., 2002a; Wilson et al., 2010). The aqueous concentrations of these oxyanions are largely controlled by surficial reactions with secondary oxides and clays in soils (Wilson et al., 2010). For example, iron (Fe) (oxyhydr)oxide minerals (Majzlan et al., 2011; Scheinost et al., 2006; Waychunas et al., 1993), manganese (Mn) oxides (Belzile et al., 2001; Foster et al., 2003; Villalobos et al., 2014), and clay minerals sorb Sb(V) and As(V) effectively (Arai, 2010; Beaulieu and Savage, 2005; Ilgen and Trainor, 2012; Xi et al., 2014). A rich

literature has documented the structure of As(V) surface complexes on these soil minerals, typically identifying inner-sphere complexes where AsO₄ tetrahedra join corners with adjacent FeO₆, MnO₆, or AlO₆ octahedra (Arai, 2010; Villalobos et al., 2014; Waychunas et al., 1993). By contrast, the structures of Sb(V) surface species have only been investigated in studies of Sb(V) sorption to kaolinite, nontronite, and hydrous aluminum oxide (Ilgen and Trainor, 2012) and Sb(V) incorporation into Fe(III) (oxyhydr)oxides during mineral phase transformation (Mitsunobu et al., 2013; Mitsunobu et al., 2010). The surface speciation of Sb(V) sorbed to Mn oxides or 2:1 clay minerals, which are both important natural scavengers, is not well documented (Filella et al., 2009).

Based on the chemical similarity of Sb(V) and As(V), we expect that the characterization techniques used previously to determine As(V) adsorption geometries on mineral adsorbents can be applied to study Sb(V) surface reactions and provide a useful baseline from which Sb(V) speciation can be interpreted. Differential pair distribution function (d-PDF) analysis is an innovative synchrotron-based total X-ray scattering approach that has been used successfully to probe As(V) surface structures (Harrington et al., 2010; Li et al., 2011). Due to their high atomic number, both Sb(V) and As(V) can provide high-quality d-PDF data extending beyond the spatial range (interatomic distance, R , $> 4 \text{ \AA}$) permitted by extended X-ray absorption fine structure (EXAFS) and Fourier-transform infrared (FTIR) spectroscopies. The detection of atomic pairs in higher-order coordination spheres can provide more reliable identification of Sb(V) and As(V) sorption mechanisms. Additionally, detailed information on the nature of reactive mineral surface sites and the effect of ion sorption on the adsorbent structure occurs at $R > 4 \text{ \AA}$ from the adsorbed ion, which can be probed experimentally with d-PDF analysis.

In this work, our objective is to compare the uptake and surface speciation of Sb(V) and As(V) on 2-line ferrihydrite, δ -MnO₂ and Na-montmorillonite. These minerals were selected due to their well-documented role in controlling contaminant and nutrient transport in natural settings (e.g. (Wilson et al., 2010)). We integrate batch sorption experiments at

pH 5.5 with detailed short- and intermediate-ranged surface structural data ($R < 10 \text{ \AA}$) provided by d-PDF analysis to generate molecular-scale information of Sb(V) and As(V) adsorption by important natural adsorbent phases. We link oxyanion coordination geometry to sorption behavior in order to assess the relative importance of these common solid phases in the attenuation of oxyanion concentrations. Finally, we demonstrate that the d-PDF approach can be used effectively as a surface characterization method to investigate the fate of contaminants with large atomic numbers.

2. Materials and Methods

2.1 Materials

Stock solutions of reagent grade KSb(OH)_6 (5 mM), Na_2HAsO_4 (10 mM), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1 M), KNO_3 (0.5 M) and NaNO_3 (0.5 M) were prepared using 18 M Ω -cm deionized (DI) water. The Schwertmann and Cornell (1991) recipe was used to synthesize 2-line ferrihydrite (Fh). The “redox method” described in Villalobos et al. (2003) was followed to synthesize δ - MnO_2 . Wyoming Na-montmorillonite (SWy-2) was obtained from the Source Clays Repository (Clay Minerals Society) and was used as received. The phase of each mineral was confirmed by X-ray scattering (Figure S1 in the Supplementary Data). Further information regarding the structure of the minerals used in our study is given in the Supplementary Data. Mineral stock suspensions of 0.1 M (10.7 g/L) Fh, 0.05 M (4.3 g/L) δ - MnO_2 and 10 g/L Na-montmorillonite (Mont) were stored at room temperature and were discarded if not used after 1-2 weeks of preparation.

2.2 Sorption Experiments

Sorption experiments were prepared by adding aliquots of 5 mM Sb(V) or 10 mM As(V) stock solutions, background electrolyte, mineral stock suspension, and DI water to achieve a final volume of 40 mL in 50 mL polypropylene tubes. Initial oxyanion concentrations ranged from 0.01 – 2.5 mM and were selected to include those found in contaminated environments (Majzlan et al., 2011) and to allow for oxyanion surface loadings (0.1 – 3.2 mmol:g) that encompass the d-PDF detection limit. Aliquots of the oxyanion stock solutions were added slowly to the suspension to avoid local supersaturation with respect to Sb(V) or As(V)-bearing minerals, the absence of which was confirmed for all samples by bulk X-ray scattering. The ionic strength was set to 10 mM with NaNO_3 for the As(V) experiments and KNO_3 for the Sb(V) experiments to

avoid the formation of the insoluble mineral, mopungite (NaSb(OH)_6) (Leuz et al., 2006). The total solids concentration was 0.42 g/L for Fh (4 mM Fe), 0.35 g/L for $\delta\text{-MnO}_2$ (4 mM Mn) and 0.5 g/L for Mont. After adding all components, the initial pH was adjusted to 5.5 ± 0.3 using KOH, NaOH or HNO_3 . Each tube was sealed immediately to the atmosphere and placed on an end-over-end shaker for 24 h. Suspensions were removed from the shaker periodically to measure pH and adjust, if needed, to 5.5 ± 0.3 . Drift in pH was less than 0.3 after the first 4 h of the reaction.

After the 24-h reaction, an aliquot of the suspension was filtered through 0.2 μm PTFE filters. Concentrations of Sb, As, Ca, Fe, Mn, Si, and Al in the initial suspension (c_{total}) and filtrate (c_{eq}) were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) on acidified samples (2% HNO_3 , 0.05 M oxalic acid). The surface excess (q_i) was calculated as the difference between the initial and final Sb(V) and As(V) concentrations, normalized by the amount of adsorbent added either on a mass or surface area basis. Sample names are derived from their corresponding oxyanion surface loading (Table 1).

Additional sorption experiments were prepared with 1 mM Ca in the initial mineral suspension. We found that Ca did not enhance As(V) sorption by any of the minerals and only slightly increased Sb(V) sorption at the largest initial Sb(V) concentration in the Fh and $\delta\text{-MnO}_2$ systems (data not shown). Additionally, the d-PDFs of these samples displayed identical features as the samples generated in the absence of Ca for each concentration series. Therefore, samples generated in the presence of Ca are included in the d-PDF analysis as replicates to augment the data set in each mineral series. These samples are identified by “+Ca” (Table 1).

2.3 High-energy X-ray scattering

Samples for high-energy X-ray scattering (HEXS) experiments were prepared as described above and collected on 0.2 μm filters. A mineral blank sample for each sorption series was also prepared as described above without the addition of Sb(V) or As(V). Solids were air-dried, loaded into 1 mm Kapton capillaries, and sealed with epoxy. HEXS data of samples and reference materials were collected at beam line 11 ID-B of the Advanced Photon Source at Argonne National Laboratory (ANL; Argonne, IL). Scattering data were collected to a momentum transfer, Q , value of 29 $\text{\AA}^{-1}$ at room temperature using 58.6 keV X-rays ($\lambda = 0.2114 \text{ \AA}$). An amorphous Si image-plate detector (General Electric) was used for data collection, which allows for rapid acquisition of X-ray scattering patterns (Chupas et al., 2003). Scattering patterns were integrated radially and converted to 1D plots of the scattering intensity versus scattering angle using Fit2D (Hammersley et al., 1996). The program PDFgetX2 (Farrow et al., 2007) was used to obtain the total structure function, $S(Q)$, and the pair distribution function (PDF), $G(r)$, from the scattering data using standard correction and normalization procedures, including those to correct for image-plate geometry (Chupas et al., 2003; Farrow et al., 2007). To ensure that the experimental PDFs were free of artifacts due to the background subtraction and normalization steps, we examined the effect of varying i) the chemical formula used to correct for Compton scattering and ii) the Fourier-transform range on the PDF peak positions and relative intensities. This sensitivity analysis (Figure S3 in the Supplementary Data) revealed that relative peak intensities and positions are robust from $R = 1.5 \text{ \AA}$ out to $R > 25 \text{ \AA}$.

2.4 Differential pair distribution function analysis

Differential PDFs (d-PDFs) were generated by subtracting the PDF of the mineral blank (host) from the PDF of the oxyanion-loaded sorption sample (host+guest). Following standard procedures (Harrington et al., 2010; Li et al., 2011; Zhu et al., 2014), the mineral blank PDFs were multiplied by a factor of 1 – 2.5 (typically < 1.3) to minimize the amplitude of peaks in the d-PDF at $R > 5 \text{ \AA}$ due to the adsorbent. Gaussian functions were fit to the short-ranged ($< 4 \text{ \AA}$) peaks of the d-PDFs using IGOR Pro (WaveMetrics, Lake Oswego, OR) to determine peak position, which corresponds to interatomic distance, and peak amplitude, which reflects the total number of atomic pairs, the scattering power of these atoms, and their bonding disorder (Egami and Billinge, 2003). To facilitate comparisons between samples, the values of fit-derived peak amplitudes were normalized by the intensity of the first shell correlation (Table 1). However, the d-PDFs are plotted without any normalization to show the increase in d-PDF peak magnitudes as surface loading increases.

Experimental d-PDFs were also compared to calculated d-PDFs derived from model nanoparticles consisting of 250-800 atoms with surface bound Sb(V) or As(V). The model particles were used to generate atomic coordinates fed to the program PDFgui (Farrow et al., 2007) to calculate theoretical d-PDFs and partial component d-PDFs over the R-range of 1-10 $\text{\AA}$. All input parameters used in the d-PDF calculations are described in the Supplementary Data. The 2-line ferrihydrite model nanoparticle was based on the crystal structure proposed by Michel et al. (2007) and consisted of a spherical particle with a 2.0 nm diameter. The δ -MnO₂ model was constructed from the crystal structure of Na-rich birnessite (Lanson et al., 2002) and consisted of a single sheet of edge-sharing MnO₆ octahedra with an approximately 3.0 nm diameter in the *ab* plane and 9% Mn vacancy content. The stacking of MnO₂ sheets, which contributes to the PDF at $R > 8 \text{ \AA}$,

was not accounted for in our model. The montmorillonite model particle was derived from the crystal structure of Viani et al. (2002) and consisted of two layers of 2:1 SiO₄ and AlO₆ polyhedra sheets, each with a diameter of 2.5 nm.

To each model particle supercell, SbO₆ or AsO₄ polyhedra were added with their first-shell coordination spheres derived from the structures of tripuhyite (FeSbO₄) (Berlepsch et al., 2003) or scorodite (FeAsO₄·2H₂O) (Xu et al., 2007), respectively. The oxyanions were affixed to the nanoparticle surface in different coordination geometries, including single edge- (¹E) and corner-sharing (¹C) complexes, double corner-sharing (²C) complexes, and in the case of δ-MnO₂, triple corner-sharing (³C) complexes to layer cation vacancies. These adsorption geometries are based on spectroscopic studies (Ilgen and Trainor, 2012; McComb et al., 2007; Mitsunobu et al., 2010; Waychunas et al., 1993), quantum mechanical calculations (Mason et al., 2012; Sherman and Randall, 2003), and surface complexation models (Stachowicz et al., 2008; Vithanage et al., 2013).

3. Results and Discussion

3.1 Macroscopic Sb(V) and As(V) sorption behavior

Figure 1 shows the Sb(V) and As(V) sorption isotherms for each mineral normalized by the mass of adsorbent (Figure 1A – 1C) and by the adsorbent surface area (Figure 1D – 1F). In the Fh system, the steep initial slopes of the Sb(V) and As(V) isotherms follow H-curve isotherm behavior (Sposito, 2008). Because the initial slope of the sorption isotherms is related to sorption affinity (Hinz, 2001), we conclude that Sb(V) and As(V) have similarly high affinities for Fh surfaces. However, Fh shows a moderately higher sorption capacity for Sb(V) compared to As(V). Arsenate sorption to Fh plateaus at a solids ratio near 1.8 mmol As:g Fh, which is consistent with previously reported As(V) sorption capacities (Raven et al., 1998), whereas Sb(V) sorption reaches a loading above 2.2 mmol Sb:g Fh.

Similar to oxyanion sorption behavior in the Fh system, δ -MnO₂ shows a larger sorption capacity for Sb(V) compared to As(V). The initial slope of the Sb(V) sorption isotherm for δ -MnO₂ is steeper than that of As(V), but both are significantly less steep than those for Fh. This result indicates that Sb(V) and As(V) have a lower affinity for δ -MnO₂ surfaces than for Fh, which is consistent with the net negative charge of δ -MnO₂ (PZC < 3.0) at pH 5.5, whereas Fh is positively charged (PZC $\approx$ 7) (Kosmulski, 2009). The maximum As(V) surface excess measured is less than 0.6 mmol As:g δ -MnO₂, which is consistent with values reported previously (Villalobos et al., 2014), whereas the Sb:Mn loading achieves nearly 1.1 mmol Sb:g δ -MnO₂.

In the Mont system, the Sb(V) and As(V) sorption isotherms show similar initial slopes and maximum measured surface loadings. However, compared to Fh and δ -MnO₂,

the initial slopes of both sorption isotherms are significantly lower. The low initial slope of the Mont isotherms suggest that the affinity of Mont surfaces for Sb(V) and As(V) sorption is lower than that of Fh and δ -MnO₂ (Sposito, 2008). The roughly linear shapes of both Sb(V) and As(V) sorption isotherms on Mont is consistent with Sb(V) and As(V) sorption by other clay minerals (Ilgen and Trainor, 2012; Xi et al., 2010; Xi et al., 2014).

When surface excess was calculated on a mass basis, the Sb(V) and As(V) sorption capacity increased in the order of Mont < δ -MnO₂ < Fh. However, normalizing oxyanion uptake by specific surface area results in maximum oxyanion loadings increasing in the order δ -MnO₂ < Fh < Mont, which reflects the considerably larger specific surface area of Fh ($\approx 300 \text{ m}^2/\text{g}$) and δ -MnO₂ ($\approx 250 \text{ m}^2/\text{g}$) compared to that of Mont ($\approx 30 \text{ m}^2/\text{g}$). In addition, normalizing oxyanion uptake by specific surface area emphasizes the differences in oxyanion sorption affinity among the three minerals. That Mont displays a significantly lower sorption affinity than Fh and δ -MnO₂, as inferred from the initial slopes of the isotherms, but a larger sorption capacity when normalized by surface area, suggests that Mont surfaces are dominated by low affinity oxyanion sorption sites, whereas the surfaces of Fh and δ -MnO₂ contain a larger fraction of high affinity sites.

3.2 Differential PDFs in the Fh system

3.2.1 Experimental d-PDFs. The experimental d-PDFs of As(V) and Sb(V) sorbed to Fh are given in Figure 2. For As(V)-sorbed Fh (Figure 2A), the experimental d-PDF with surface loading of 1.5 mmol/g shows two symmetric peaks of similar amplitude at $R < 4 \text{ \AA}$, which are centered at 1.70 ± 0.01 and $3.29 \pm 0.01 \text{ \AA}$ (Table 1).

These peak positions and relative amplitudes are consistent with As-O and As-Fe scattering due to As(V) bound to Fh in the ^2C geometry (Harrington et al., 2010; Sherman and Randall, 2003). However, the As-Fe distance obtained from the d-PDF fit ($3.29 \pm 0.01 \text{ \AA}$) is larger by 0.04-0.05 $\text{\AA}$ than the As-Fe distance of the ^2C geometry derived from EXAFS analyses (Waychunas et al., 1993). Apart from the ^2C geometry, the d-PDF data showed no evidence for additional As(V) coordination geometries, such as the ^1E complex ($R_{\text{As-Fe}} = 2.9 \text{ \AA}$) (Fendorf et al., 1997). The absence of other prominent peaks at $R < 4 \text{ \AA}$ is consistent with a previous d-PDF study at similar As(V) surface loading (Harrington et al., 2010). At $R > 4 \text{ \AA}$ in the d-PDF, a broad peak appears at 4.6 $\text{\AA}$, which has not been indexed previously.

Figure 2B compares the experimental d-PDFs of Sb(V) adsorbed to Fh with surface loadings ranging from 1.0 – 3.2 mmol:g. Although the positions of the d-PDF peaks do not change significantly with increasing Sb surface loading, the absolute magnitudes of the peaks increase due to the increasing fraction of Sb atoms in the solid phase. In contrast to the two major peaks at $R < 4 \text{ \AA}$ in the As(V) d-PDF, all Sb(V) d-PDFs display three symmetric peaks centered at 1.98, 3.05-3.10, and 3.60-3.61 $\text{\AA}$ (Table 1), which indicates the presence of at least two Sb(V) adsorption geometries. These peak positions are in excellent agreement with Sb-O and Sb-Fe interatomic distances previously attributed to the ^1E ($R_{\text{Sb-Fe}} \approx 3.1 \text{ \AA}$) and ^2C ($R_{\text{Sb-Fe}} \approx 3.6 \text{ \AA}$) sorption geometries to Fe(III) (oxyhydr)oxides (Mitsunobu et al., 2013). At $R > 4 \text{ \AA}$, the Sb(V) d-PDFs exhibit broad, but well-resolved next-nearest-neighbor peaks near 4.8, 5.6, and 6.4 $\text{\AA}$ with larger amplitude than the corresponding peaks in the As(V) d-PDF data.

3.2.2 Model d-PDFs. The calculated d-PDFs of As(V) and Sb(V) sorbed to Fh are shown in Figure 2. Partial component d-PDFs, which show the contribution of As/Sb-O

and As/Sb-Fe pairs to the calculated d-PDF, are also included in Figure 2. The calculated d-PDF based on the model of As(V) bound to Fh in the ^2C geometry reproduces well the positions of the As-O and As-Fe peaks near 1.7 and 3.3 Å, respectively. Although recent DFT studies (Loring et al., 2009; Otte et al., 2013) suggest that the interatomic distance of ^1C complexes can match those of the ^2C complex, the good agreement in relative intensities of the As-O and As-Fe peaks between our model and data argues against this ^1C geometry, which would display an As-Fe peak with roughly half the amplitude.

At $R > 4$ Å, the calculated As(V) d-PDF reproduces the position of the peak near 4.6 Å, which is shown in the partial d-PDFs to arise from As-O atomic pairs. However, the calculated d-PDF overpredicts the amplitude of this peak and the amplitude of the two As-Fe peaks near 5.5 and 6.2 Å. This overprediction can be explained by differences in bonding disorder between the model and experimental data. The calculated d-PDF was generated using disorder terms derived from the average Fh structure (Michel et al., 2007; van Genuchten et al., 2014). Thus, the overpredicted amplitudes of the As-Fe peaks at 5.5 and 6.2 Å indicate that intermediate-ranged Fe(III) polyhedra (i.e. next-nearest-neighbor Fe atoms) located near adsorbed As(V) are more disordered than in the average Fh structure. The bonding of tetrahedral oxyanions (TO_4) to adjacent FeO_6 octahedra in the ^2C geometry has been shown to induce FeO_6 octahedral distortions to accommodate the shorter and more rigid T-O and O-O bond lengths (Kwon and Kubicki, 2004). As a consequence, the distortion of surface Fe(III) polyhedra upon As(V) adsorption likely propagates through the particle and leads to increased structural disorder at R values greater than 4 Å.

The calculated Sb(V) d-PDFs derived from the ^1E and ^2C models reproduce closely the positions of the nearest-neighbor Sb-O and Sb-Fe peaks at $R < 4$ Å. The ^2C model

provides a better fit than the ^1E model to the next-nearest-neighbor peaks at 4.8, 5.6, and 6.4 Å, which are shown in the partial component d-PDFs to arise from Sb-O, Sb-Fe, and Sb-Fe atomic pairs, respectively. Better agreement between the model and experimental Sb(V) d-PDFs at $R > 4$ Å is observed relative to the As(V) d-PDFs. This closer agreement between the experimental and model Sb(V) d-PDFs, which were derived using the same bulk Fh disorder parameters as the model As(V) d-PDF, suggests that Sb(V) adsorption introduces less disorder to Fh than As(V) adsorption. This result is consistent with the similar size and shape of SbO_6 ($R_{\text{Sb-O}} = 1.98$ Å) and FeO_6 ($R_{\text{Fe-O}} = 2.00$ Å) octahedra and the ability of Sb(V) to become incorporated into Fe(III) (oxyhydr)oxide minerals (Mitsunobu et al., 2013; Mitsunobu et al., 2010).

3.3 Differential PDFs in the $\delta\text{-MnO}_2$ system

3.3.1 Experimental d-PDFs. Figure 3 shows the experimental and model d-PDFs in the $\delta\text{-MnO}_2$ system. In contrast to the As(V) d-PDF in the Fh system, the d-PDF of As(V) adsorbed to $\delta\text{-MnO}_2$ (Figure 3A) lacks prominent peaks, which prevented reliable Gaussian peak fits and additional analysis by comparison with calculated d-PDFs. The poor signal from As(V) likely arises from the insufficient As(V) surface loading of this sample (0.5 mmol:g $\delta\text{-MnO}_2$ compared to 1.5 mmol:g for Fh). However, based on previous spectroscopic investigations (Foster et al., 2003; Villalobos et al., 2014), we can attribute the small peaks near 1.7 and 3.2 Å in the d-PDF to As-O and As-Mn atomic pairs, respectively, from As(V) adsorbed to $\delta\text{-MnO}_2$ in the ^2C geometry.

The d-PDFs of Sb(V) adsorbed to $\delta\text{-MnO}_2$, which have surface loadings from 0.6 to 1.0 mmol:g, each display three well-resolved peaks at $R < 4$ Å. These short-ranged peaks located at 1.97-1.98, 3.09, and 3.59-3.62 Å (Table 1) are analogous to those in the

d-PDFs of Sb(V) adsorbed to Fh and are consistent with Sb(V) adsorbed in the ^1E and ^2C geometries. The presence of well-resolved peaks in the d-PDF of the sample with the lowest loading in this series (0.6 mmol Sb:g), which is only slightly larger than the loading of the As(V)- $\delta\text{-MnO}_2$ d-PDF (0.5 mmol As:g), can be explained by the larger atomic number of Sb ($Z = 51$) relative to As ($Z = 33$). Beyond 4 Å, the d-PDFs of Sb(V) adsorbed to $\delta\text{-MnO}_2$ display well-defined intermediate-ranged peaks at 4.6, 5.2 and 6.2 Å, which reflects an ordered bonding environment that extends beyond the Sb-Mn second-shell.

3.3.2 Model d-PDFs. The calculated d-PDFs of Sb(V) adsorbed to $\delta\text{-MnO}_2$ particle edges in the ^1E and ^2C geometries are shown in Figure 3B. The ^1E and ^2C models reproduce well the positions of the Sb-O and Sb-Mn nearest-neighbor peaks at 2.0, 3.1 and 3.6 Å. Good agreement in peak position and amplitude between the experimental and model d-PDFs at $R > 4$ Å suggests that the disorder parameters taken from bulk $\delta\text{-MnO}_2$ (Manceau et al., 2013; Zhu et al., 2012) can be used to describe adequately the atomic environment of Sb(V) adsorption sites on $\delta\text{-MnO}_2$ particle edges. However, at $R > 7$ Å, the calculated d-PDF reproduces the peak positions in the experimental data less accurately, which may be rationalized by the contribution of inter-sheet atomic pairs not accounted for in our single-sheet model.

The calculated d-PDF of Sb(V) bound in a triple corner-sharing configuration (^3C model) to layer vacancies (Figure S4 in the Supplementary Data) contains Sb-Mn peaks at similar positions to the ^2C model, but with considerably more amplitude. Although the ^3C model reproduces the peak positions of the experimental d-PDFs, we argue against the formation of the Sb(V) ^3C complex for several reasons. First, although ions with octahedral coordination can sorb to vacancy sites, the negative charges of vacancy sites and

Sb(V) oxyanions should promote strong electrostatic repulsion. Second, the low initial slope of the Sb(V) adsorption isotherm on δ -MnO₂ is consistent with a low extent of ion sorption to vacancies (Villalobos et al., 2014). Last, similar 2:1 and 3:1 peak amplitude ratios (Table 1) are observed in the d-PDFs of Sb(V) adsorbed to δ -MnO₂ and Fh, where Fh has no vacancies and thus adsorbs Sb(V) in ¹E and ²C geometries.

3.4 Differential PDFs in the Mont system

3.4.1 Experimental d-PDFs. Due to electrostatic repulsion between Mont particles and capillary tubes, we were unable to load sufficient material for high-quality HEXS data suitable for d-PDF analysis for the As(V)-sorbed Mont sample. However, As(V) has been shown to bind to adjacent AlO₆ octahedra on mineral edges in the ²C adsorption complex for kaolinite and chlinochlore (Arai, 2010; Beaulieu and Savage, 2005). This As(V) adsorption geometry will be used in the discussion of the Sb(V)-Mont data.

The d-PDFs of Sb(V) adsorbed to Mont are given in Figure 4 and display two intense peaks at 1.94-1.95 and 3.64 Å (Table 1). Two peaks at identical positions are also observed in the d-PDF of a Mont sample with roughly half the Sb(V) loading (Figure S5 in the Supplementary Data), suggesting similar sorption geometries independent of surface loading. Although the formation of Sb(V) polynuclear complexes on the surface of kaolinite has been reported, the short-ranged atomic pair correlations in all experimental d-PDFs are significantly different than the characteristic Sb-Sb distances of Sb(V) oligomers (3.24 ± 0.05 and 4.00 ± 0.01 Å) (Ilgen and Trainor, 2012), or Sb oxide phases, such as KSb(OH)₆ or Sb₂O₅ (3.07, 3.32, 3.90, and 4.91 Å) (Scheinost et al., 2006). Thus, the major peaks in the Mont d-PDFs are consistent with oxyanion adsorption. The positions of the major peaks at $R < 4$ Å in the experimental d-PDFs are in excellent

agreement with Sb-O and Sb-Al interatomic distances derived from Sb K-edge EXAFS analysis of Sb(V) adsorbed to kaolinite (Ilgen and Trainor, 2012). Consistent with the d-PDFs of Sb(V) adsorbed to δ -MnO₂, the d-PDFs of Sb(V) adsorbed to Mont display resolved peaks extending to $R > 8 \text{ \AA}$, indicating an ordered bonding environment beyond the first few coordination shells.

3.4.2 Model d-PDFs. The calculated d-PDF based on the model of Sb(V) adsorbed in the ²C geometry to edge-sharing surface AlO₆ octahedra reproduces well the positions of the peaks in the experimental d-PDF near 2.0 and 3.6 $\text{\AA}$. The model also reproduces the peaks at 6.2, 7.1, and 8.2 $\text{\AA}$, which are shown in the partial d-PDFs to arise primarily from combinations of Sb-Al and Sb-Si atomic pairs. However, the calculated d-PDF contains peaks in the region from 4 – 6 $\text{\AA}$ that are not present in the experimental d-PDFs. This poor agreement from 4 – 6 $\text{\AA}$ suggests that the edge sites of Mont include more complexity, particularly with respect to the configuration of next-nearest-neighbor Si and Al atoms, than is accounted for by the perfectly-cleaved aluminosilicate edges in the d-PDF model (Viani et al., 2002).

To better constrain the nature of Sb(V) sorption sites on Mont edges, additional d-PDFs were calculated based on models of Sb(V) bound to surface sites with different AlO₆/SiO₄ configurations. Model d-PDFs based on Sb(V) bound directly to the SiO₄ tetrahedra of Mont basal surfaces or to AlO₆ octahedra that do not share edges (Figure S6 in the Supplementary Data) poorly reproduced the data at all R values. The best fit to the data (Figure 4B) was obtained for a model in which Sb(V) was bound in the ²C geometry to edge-sharing AlO₆ octahedra that are surrounded by fewer or more disordered SiO₄ tetrahedra than are present on the model particle edge. This calculation suggests that

oxyanion sorption by Mont may be favored at particle edges that terminate in a corrugated or stepwise manner, with the AlO_6 layer exposed to the bulk solution more than the SiO_4 layer.

3.5 Differences between Sb(V) and As(V) surface interactions linked to distinct coordination environments

Antimonate and As(V) have identical valence electron configurations, but take on different first-shell coordination geometries. This latter property, together with the underlying mineral structure, drives the difference in Sb(V) and As(V) interactions with the adsorbents in our study. The larger first-shell distance of SbO_6 octahedra ($R_{\text{Sb-O}} = 1.94\text{--}1.98 \text{ \AA}$) relative to that of AsO_4 tetrahedra ($R_{\text{As-O}} = 1.69 \text{ \AA}$) permits both ^1E ($R_{\text{Sb-Fe/Mn}} = 3.05\text{--}3.11 \text{ \AA}$) and ^2C ($R_{\text{Sb-Fe/Mn}} = 3.59\text{--}3.64 \text{ \AA}$) adsorption geometries to the underlying FhO_6 and MnO_6 octahedra in Fh and $\delta\text{-MnO}_2$ (Figure 5). By contrast, As(V) adsorbs only in the ^2C geometry, which is consistent with previous work reporting that the ^1E As(V) surface complex on metal (oxyhydr)oxides is energetically unfavorable (Sherman and Randall, 2003). The flexibility of Sb(V) to bind in multiple adsorption geometries, which arises from its more compatible size and first-shell coordination leads to more surface sites on Fh and $\delta\text{-MnO}_2$ that can support Sb(V) adsorption and thus increased Sb(V) uptake relative to As(V). In the Mont system, Sb(V) adsorbed only in the ^2C geometry, thus explaining the similar uptake of Sb(V) and As(V) by this mineral.

The formation of both ^1E and ^2C Sb(V) coordination geometries in the Fh and $\delta\text{-MnO}_2$ systems suggests that the sorbents present surface sites of varying affinity for Sb(V). Relating the Sb(V) surface loading derived from wet chemistry to the fit-derived amplitude ratios of the 2nd:1st peaks and 3rd:1st peaks (Table 1) reveals a trend in the Fh and $\delta\text{-MnO}_2$ systems. An increase in the Sb:Fe or Sb:Mn surface loading is generally accompanied by

a decrease in the 2:1 peak ratio (fraction of ^1E geometries) and increase in the 3:1 peak ratio (fraction of ^2C geometries). This result is consistent with the preferential formation of the ^1E Sb(V) sorption geometry at high affinity Sb(V) sorption sites (Leuz et al., 2006; Scheinost et al., 2006; Vithanage et al., 2013) followed by the ^2C geometry as loading increases. This conclusion is also reflected in the Mont system, which exhibits a low Sb(V) sorption affinity and the absence of the ^1E Sb(V) geometry.

3.6 Advantages and limitations of d-PDF analysis

Differential PDF analysis is a novel approach to determine surface speciation that offers a number of advantages relative to established molecular-scale characterization techniques, such as EXAFS spectroscopy. For example, the intensities of d-PDF peaks decay with R significantly less than those of Fourier-transformed EXAFS spectra. This property of the d-PDF permitted indexing next-nearest-neighboring atoms beyond the adjacent coordination shells of sorbed Sb(V) and As(V), which substantiated our interpretation of oxyanion coordination geometry and allowed us to infer the impact of ion sorption on the adsorbent structure. Due to the larger accessible Q -range of HEXS data, the spatial resolution of the d-PDF approach is also 2 – 3 fold higher than EXAFS spectroscopy. Combined with this benefit, the d-PDF yields direct interatomic distances that do not require phase shift corrections, which permits straight-forward determination of bond lengths. Finally, only single scattering between atomic pairs contribute to the d-PDF, thus eliminating the influence of multiple scattering (MS) paths, which can complicate the interpretation of second-shell atomic pairs. As a result of these advantages, we consider the As-Fe distance (3.29 Å) obtained from our d-PDF analysis of As(V) sorption by Fh to be more reliable than the 3.24 – 3.26 Å value derived from previous EXAFS studies of As(V) adsorbed to nanocrystalline Fe(III) oxides (van Genuchten et al., 2012). Based on the

benefits enumerated above, the d-PDF approach can readily determine surface structures and should be particularly useful in model systems with heavy elements that scatter effectively.

Despite these advantages, the d-PDF approach suffers from some limitations. Although data collection is rapid (≈ 5 min/sample), data reduction procedures for wet samples are complicated (Egami and Billinge, 2003), which often requires samples to be analyzed as dry powders. Additionally, the d-PDF is constrained by a relatively high detection limit. For example, at surface loadings < 0.2 mmol:g, the signal from sorbed Sb(V) or As(V) was difficult to determine in the experimental d-PDFs. For this reason, we were unable to resolve d-PDF peaks of samples of Sb(V) and As(V) adsorbed to the crystalline Fe(III) oxyhydroxide, goethite (α -FeOOH), which showed a low oxyanion sorption maxima of < 0.2 mmol:g. Furthermore, poor signal from dilute species can lead to spurious peaks in the d-PDF, which highlights the importance of collecting d-PDF data on concentration series. Because d-PDF analysis cannot probe low concentrations, moderate to high surface loadings are required, complicating detection of high affinity sorption sites that constitute a minor fraction of the total reactive surface. When detection of dilute species is required, element specific techniques like EXAFS spectroscopy are especially useful in such cases and can complement d-PDF analysis to permit descriptions of sorption reactions across a wide range of surface loading.

4. Conclusions

In this study, we combine sorption isotherms and d-PDF analysis to show that mineral reactivity in terms of sorption affinity towards Sb(V) or As(V) increases in the order of Mont < δ -MnO₂ < Fh. Due to the high oxyanion sorption affinity of Fh and δ -MnO₂, these two minerals are expected to be major Sb(V) and As(V) sorbents in soils at low oxyanion concentrations. Although our results imply that Mont lacks a large proportion of high affinity sites relative to Fh, its impact on oxyanion speciation cannot be ignored at large oxyanion concentrations, such as those observed in mining-impacted waters (Majzlan et al., 2011; Ritchie et al., 2013). Differential PDF analysis indicates that Sb(V) forms both single edge-sharing (¹E) and double corner-sharing (²C) complexes on Fh surfaces and δ -MnO₂ particle edges and only the ²C geometry on Mont edges, whereas no evidence for As(V) sorption in ¹E complexes was found. We attribute the formation of multiple Sb(V) sorption geometries to the larger and more compatible shape of SbO₆ octahedron ($R_{\text{Sb-O}} = 1.95 \text{ \AA}$) relative to AsO₄ tetrahedron ($R_{\text{As-O}} = 1.69 \text{ \AA}$), which also explains the larger uptake of Sb(V) relative to As(V) by Fh and δ -MnO₂. For the first time, we indexed atomic pairs involving sorbed ions at $R > 6 \text{ \AA}$ using d-PDF analysis. This intermediate-ranged structural information revealed that the different sizes and shapes of SbO₆ and AsO₄ polyhedra impact structural properties of the adsorbent beyond the nearest coordinating metal shell. In the Fh system, our results show that adsorption of SbO₆ introduces less disorder to bulk Fe(III) polyhedra at $R > 4 \text{ \AA}$ than AsO₄ adsorption. These different surface and bulk structural modifications upon Sb(V) or As(V) adsorption likely alter the stability of the mineral towards chemical or biologically-mediated dissolution and mineral reactivity with respect to further ion sorption. Our study gives molecular scale perspectives on Sb(V) and As(V) interactions with reactive soil minerals, and shows that

526 the d-PDF approach is a reliable alternative to standard surface characterization
527 techniques.

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Table 1: Surface loading and summary of Gaussian fits to d-PDF peaks at $R < 4 \text{ \AA}$

	Sb/As Surface Loading (mmol:g)	R_1 ($\text{\AA}$)	R_2 ($\text{\AA}$)	2:1 Peak Amp Ratio ($\text{\AA}^{-2}:\text{\AA}^{-2}$)	R_3 ($\text{\AA}$)	3:1 Peak Amp Ratio ($\text{\AA}^{-2}:\text{\AA}^{-2}$)
1.5 As_Fh	1.5	1.70	3.29	1.24	-	-
1.7 Sb_Fh	1.7	1.98	3.10	0.18	3.61	0.73
2.2 Sb_Fh	2.2	1.98	3.10	0.23	3.60	0.73
1.0 Sb+Ca_Fh	1.0	1.98	3.11	0.21	3.60	0.63
3.2 Sb+Ca_Fh	3.2	1.98	3.05	0.11	3.61	0.92
0.7 Sb_MnO ₂	0.7	1.98	3.09	1.18	3.60	0.58
1.0 Sb_MnO ₂	1.0	1.98	3.09	0.66	3.59	0.78
0.6 Sb+Ca_MnO ₂	0.6	1.97	3.09	0.42	3.61	0.52
0.8 Sb+Ca_MnO ₂	0.9	1.97	3.09	0.23	3.62	0.83
0.3 Sb_Mont	0.3	1.94	3.64	1.62	-	-
0.3 Sb+Ca_Mont	0.3	1.95	3.64	1.67	-	-

549 The fit-derived standard deviation in the reported values was less than 5% for the
550 amplitude and less than 1% for the interatomic distance. Insufficient signal from As(V)
551 in the d-PDF of As(V) adsorbed to δ -MnO₂ prohibited peaks fits. Sample names are
552 derived from the oxyanion surface loading in the presence or absence of Ca.

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Figure 1: Adsorption isotherms for Sb(V) (filled squares) and As(V) (empty squares) on Fh (A, D), δ -MnO₂ (B, E) and Mont (C, F). The top three isotherms are normalized by the mass of adsorbent, whereas the bottom three are normalized by specific surface area of the adsorbent. Data are plotted as the average of replicate measurements, with error bars indicating the standard deviation of replicates. The (*) symbols indicate samples for which characterization data are reported.

Figure 2: Differential PDFs of A) As(V) and B) Sb(V) adsorbed to Fh. In each panel, the experimental d-PDFs, calculated d-PDFs, and partial d-PDFs are given from top to bottom. Experimental d-PDFs are labeled with their corresponding oxyanion surface loading (mmol:g). Differential PDFs of samples with larger surface loading have higher first- and second-shell peak intensity. The ^1E and ^2C geometries correspond to single edge- and double corner-sharing adsorption modes.

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577 Figure 3: Differential PDFs of A) As(V) and B) Sb(V) adsorbed to δ -MnO₂.
578 Experimental d-PDFs are labeled with their corresponding oxyanion surface loading
579 (mmol:g). In A), only the experimental d-PDF is given, whereas in B) the experimental
580 d-PDFs, calculated d-PDFs, and partial d-PDFs are given from top to bottom. The ¹E and
581 ²C geometries correspond to single edge- and double corner-sharing adsorption modes.
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Figure 4: Differential PDFs of Sb(V) adsorbed to Mont. The experimental d-PDFs, calculated d-PDFs, and partial d-PDFs are given from top to bottom. Experimental d-PDFs are labeled with their corresponding oxyanion surface loading (mmol:g). The ${}^2\text{C}$ Geometry (Ideal edge) corresponds to Sb(V) bound to edge-sharing AlO_6 octahedra of a perfectly-cleaved Mont particle edge, whereas the ${}^2\text{C}$ Geometry (Diminished Si) model corresponds to Sb(V) bound to adjacent AlO_6 octahedra that are coordinated to fewer Si tetrahedral than in an ideal particle edge.

Figure 5: Adsorption models of Sb(V) and As(V) derived from d-PDF analysis. A) As(V) bound to Fh, B) Sb(V) bound to Fh, C) Sb(V) bound to δ -MnO₂, and D) Sb(V) bound Mont. An enlarged image of the atomic arrangements of the dominant adsorption mode determined in the d-PDFs are also given in each panel. SbO₆ octahedra and AsO₄ tetrahedra are shown in red and violet, respectively. The blue, green, and yellow polyhedra indicate the nearest, next-nearest, and next-next-nearest neighboring Fe, Mn, Al, or Si polyhedra.

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