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In situ Structural Study of Sb(V) Adsorption on Hematite (1 $\bar{1}$ 02) Using X-ray Surface Scattering

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Abstract

The binding mechanism of Sb(V) on a single crystal hematite (1 $\bar{1}$ 02) surface was studied using crystal truncation rod X-ray diffraction (CTR) under in situ conditions. The best fit CTR model indicates Sb(V) adsorbs at the surface as an inner-sphere complex forming a tridentate binding geometry with the nearest Sb-Fe distance of 3.09(4) Å and an average Sb-O bond length of 2.08(5) Å. In this binding geometry Sb is bound at both edge-sharing and corner-sharing sites of the surface Fe-O octahedral units. The chemical plausibility of the proposed structure was further verified by bond valence analysis, which also deduced a protonation scheme for surface O groups. The stoichiometry of the surface reaction predicts the release of one OH⁻ group at pH 5.5.

1. Introduction

Recent concerns over antimony (Sb) contamination and potential toxicity have resulted in increased attention to the chemistry of this element in aquatic and soil environments. Antimony is widely used in commercial products, including as a fire retardant, a catalyst in plastic manufacturing, a lubricant in automobile brake linings, and as a hardener in Pb-alloy used for the manufacture of lead-acid batteries and ammunition.^{1,2} Release of Sb into the environment,

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28 whether unintentional or intentional like in the case of spent ammunition at shooting ranges,^{3,4}
29 represents a potential risk to human health. Concerns associated with elevated Sb in the
30 environment are due to its toxicity and its potential to cause respiratory irritation,
31 pneumoconiosis, antimony spots on the skin and gastrointestinal symptoms.⁵ Furthermore,
32 antimony trioxide (Sb₂O₃) is classified as potentially carcinogenic (Group 2B) to humans by the
33 International Agency for Research on Cancer.⁶ Although Sb has some therapeutic uses for the
34 treatment of leishmaniasis and schistosomiasis,⁷ it has been found to cause serious side effects
35 such as cardiotoxicity and pancreatitis.^{8,9} The United States Environmental Protection Agency
36 has added Sb to the list of priority contaminants and set the maximum contamination level of Sb
37 in drinking water at 6 µg L⁻¹.¹⁰ The evaluation of environmental risks posed by Sb necessitates
38 the knowledge of its environmental behavior, such as its speciation and dispersion in soils and
39 ground water, which are mainly determined by the associated retention mechanisms and
40 interactions with different minerals in the environment.

41 Antimony is typically found in three oxidation states, including Sb(0), Sb(III), and Sb(V).
42 Elemental Sb is readily oxidized to Sb(III) (within minutes) under ambient environmental
43 conditions. Further oxidation of Sb(III) to Sb(V) is kinetically controlled with a time scale
44 of >10 hours depending on the aqueous composition.¹¹ Numerous studies of Sb(III) binding
45 mechanisms on the surfaces of natural sorbents, such as pyrite and goethite, suggest surface
46 adsorption can greatly facilitate Sb(III) oxidation.¹²⁻¹⁴ While Sb(III) is found to be prevalent
47 within some reducing aqueous systems,¹⁵ the facile oxidation of Sb(III) in the natural
48 environment results in Sb speciation being dominated by Sb(V).¹⁶

49 Adsorption of Sb(V) on natural substrates, such as Fe/Al-(oxyhydr)oxides, is among the
50 primary mechanisms controlling the environmental fate and dispersion of Sb in soil and aquatic
51 settings.^{17, 18} A number of recent studies have focused on elucidating Sb adsorption, including
52 batch adsorption experiments,^{12, 19, 20} X-ray spectroscopy (XAFS)^{4, 17, 21, 22} and theoretical
53 methods.^{23, 24} Batch adsorption experiments **coupled with surface complexation modeling**
54 **methods** suggest Sb(V) adsorption to Fe-(oxyhydr)oxides is mainly via an inner-sphere binding
55 mode with different binding geometries depending on the substrate types. For example, Sb(V)
56 sorption to goethite was explained via a mononuclear bidentate binding mode.^{12, 19} This was in
57 contrast to a different iron-oxide-rich soil sample, where Sb(V) was found to adsorb at the
58 substrate surface with a bidentate binding structure.²⁵ Interestingly, Sb(V) sorption to in-lab

59 synthesized iron-oxide-coated sands was found to occur with both inner-sphere and outer-sphere
60 binding modes.²⁰

61 Consistent with results from batch adsorption studies, XAFS studies also suggest inner-
62 sphere binding configurations with further structural details that identify two types of inner-
63 sphere species corresponding to Sb-Fe separations of $\sim 3.1 \text{ \AA}$ and $\sim 3.5 \text{ \AA}$, respectively.^{3, 4, 17, 22,}
64 ²⁶ The shorter of the two Sb-Fe was assigned to a bidentate edge-sharing binding mode, while
65 the longer Sb-Fe distance ($\sim 3.5 \text{ \AA}$) was attributed to a bidentate corner-sharing binding
66 configuration. Results from XAFS studies also suggest the substrate type plays a key role in
67 determining the binding structure. Synthetic iron (hydr)oxide samples, such as hydrous ferric
68 oxide,²² goethite,¹⁷ and ferrihydrite¹⁷ exhibit Sb(V) binding through an edge-sharing mode while
69 less ordered iron (hydr)oxide samples, such as ferrihydrite,¹⁷ also show affinity for Sb(V)
70 binding through a corner-sharing mode. A similar coexistence of two binding geometries was
71 reported for shooting range soils^{3, 4} and sediment samples close to a Sb mining site.²⁶ The
72 heterogeneity of Sb(V) adsorption modes on Fe-(oxyhydr)oxide surfaces was also implied in a
73 desorption test, where different desorption rates of Sb(V) from amorphous iron oxide samples
74 were observed.²⁷ These results all suggest an inner-sphere binding mode; however, they do not
75 provide a consensus on the binding geometry or identify any impact surface structure may have
76 on the binding configuration.

77 To accurately determine the surface binding structure of compounds with XAFS
78 measurements, the surface structure of the substrate must be well characterized. This is typically
79 difficult when using powder samples. For example, while XAFS provides direct structural
80 information of metal(loid) binding there is potential for ambiguity in describing sorbate binding
81 sites when it is in the presence of multiple reactive surface sites on the substrate.^{28, 29} In the
82 context of multiple potential binding configurations as suggested in the aforementioned XAFS
83 studies,^{4, 17, 21, 22} the nature of Sb binding on mineral surfaces cannot be fully understood without
84 knowing the detailed structure of the surface. Therefore, studies of sorption to well-characterized
85 mineral surfaces can be used to reduce the ambiguity in identifying binding sites and geometries.

86 To better quantify Sb binding to hematite, we used crystal truncation rod X-ray diffraction
87 (CTR) to characterize Sb(V) adsorption on a single crystal hematite ($1\bar{1}02$) surface. CTR probes
88 long-range structural ordering at a single crystal surface with high sensitivity.³⁰ The method
89 allows the determination of preferred binding site(s) and the associated binding modes for

90 aqueous ions, which provides a detailed structural interpretation of sorption reactions. The
91 hydrated hematite ($1\bar{1}02$) surface has been extensively studied using both CTR diffraction and
92 theoretical methods³¹⁻³⁵ and thus serves as an ideal model substrate to examine structure-
93 reactivity relationships on Fe-oxides surfaces. **The surface binding structure proposed in this
94 work based on a single crystal system, adds to our understanding of the molecular interactions of
95 Sb(V) with minerals in the environment. This will be useful for developing remediation efforts,
96 and, if the species can be incorporated into thermodynamic models, for predicting Sb(V)'s fate in
97 the environment.**

98

99 **2. Methods and experiments**

100 2.1 Sample preparation

101 A natural single crystal hematite sample was first cut into a round shape with a diameter of ~
102 1 cm and a thickness of ~ 0.2 cm and was then oriented within 0.1° parallel to the ($1\bar{1}02$) plane
103 using a custom orientation and polishing jig. The oriented sample surface was ground and
104 polished using successively smaller sizes of diamond paste down to 0.25 μm . Single crystal
105 samples were further polished following chemical mechanical polishing (CMP) procedures
106 described elsewhere.³² Antimonate solutions (200 μM) were prepared inside a 4% $\text{H}_2/96\%$ N_2
107 filled glove box to avoid the influence of CO_2 . Potassium hexahydroxyantimonate ($\text{KSb}(\text{OH})_6$)
108 was dissolved in deionized water, which was degassed in advance by boiling and sparging with
109 N_2 (>99.999% pure) for 2 hours. The solution pH was carefully adjusted to pH 5.5(± 0.1) using
110 HCl and NaOH. **At pH 5.5, we ensure the dominant Sb(V) species existing as $\text{Sb}(\text{OH})_6^-$ in
111 solution (> 99%) and a positively charged hematite surface (p.z.c. at pH 8-9^{36,37}) to facilitate
112 Sb(V) surface binding reactions.** The Sb(V) solutions were stored inside the glove box prior to
113 CTR measurements. The CMP-prepared hematite surface was reacted with Sb(V) solutions *in*
114 *situ* using a liquid cell designed for surface diffraction measurements.³⁸ The sample cell used a
115 Kapton membrane to confine a liquid film with a thickness of several μm that was maintained
116 for the duration of the CTR measurement. To avoid dehydration of the liquid film due to
117 diffusion of water vapor through the Kapton film, the liquid cell was capped with an additional
118 Kapton dome with water-saturated He (relative humidity >90%) flowing through the dome
119 headspace.

120

121 2.2 CTR Measurements

122 CTR measurements were conducted at the GSECARS bending magnet beamline 13BMC at
123 the Advanced Photon Source (APS), Argonne National Laboratory, Argonne, Illinois. The
124 energy of the incoming X-ray beam was fixed at 13 keV and the beam was focused to $0.25 \times$
125 0.44 mm. A Kappa geometry Newport diffractometer (4S+2D) was used for sample and detector
126 orientation with angles and diffractometer coordinates defined according to You.³⁹ Intensity of
127 scattered X-rays was measured using a Dectris PILATUS 100K 2D pixel array detector with
128 195×487 pixels (vertical \times horizontal).⁴⁰ Nine CTRs (specular rod and eight non-specular rods)
129 were collected to probe electron density in lateral and vertical dimensions. Non-specular CTR
130 data were collected with the incident angle of the beam fixed at 2° relative to the sample surface.
131 And the specular rod was measured with the the sample surface normal being constrained to lie
132 in the lab-frame horizontal plane. We verified that there was no beam-induced change of the
133 sample surface by repeating the collection of a CTR segment several times during the
134 measurements. Repeat measurements over a defined region of $(2\ 0\ L)$ rod ($L = 0.6\text{--}2$) showed no
135 change in intensities within experimental errors throughout the course of data collection.

136

137 2.3 CTR modeling

138 2.3.1 Data analysis

139 The full CTR dataset consisted of 1227 unique data points. The structure factor (magnitude)
140 of each data point was extracted from each PILATUS image using the TDL software package
141 (<http://github.com/xraypy/tld>). Each data point was subject to background subtraction followed
142 by corrections for active area, polarization, and Lorentz factors to account for the variance of the
143 intercept between Ewald-sphere and the CTR as a function of Q using a method according to
144 Schlepütz et al.⁴¹

145

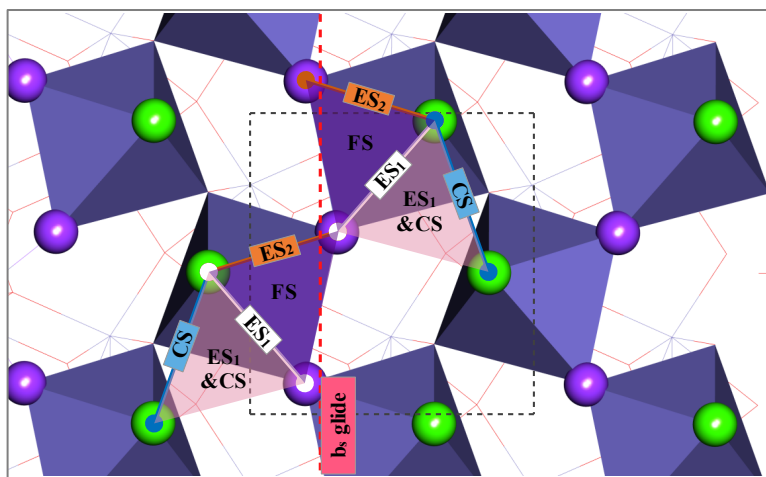
146 2.3.2 Hematite ($1\bar{1}02$) structure and terminations

147 The crystal structure of hematite ($\alpha\text{-Fe}_2\text{O}_3$) belongs to the $R\bar{3}c$ space group and can be
148 defined in terms of a hexagonal close packing of oxygen with iron occupying two-thirds of the
149 octahedral holes. The lattice parameters of $\alpha\text{-Fe}_2\text{O}_3$ (5.035 \AA , 13.747 \AA , 90° , 90° , 120°) as well as
150 the bulk isotropic Debye-Waller factors have been previously reported.⁴² For convenience, the
151 hematite ($1\bar{1}02$) surface was re-indexed by defining a pseudo unit cell (5.035 \AA , 5.427 \AA , 7.364

152 Å, 90°, 90°, 90°) that contains the new c-axis (c_s) normal to the surface and the a- (a_s) and b- (b_s)
 153 axes in-plane following the method defined by Trainor et al.³⁸ The re-indexed unit cell contains
 154 ten atom layers with a stoichiometric sequence of ($O_2-Fe_2-O_2-Fe_2-O_2-O_2-Fe_2-O_2-Fe_2-O_2-R$)
 155 along the c_s axis, where R is the stoichiometric repeating sequence (Fe_2O_3) in the bulk structure.

156 Both experimental and theoretical approaches have provided a consensus on the surface
 157 terminations of hematite ($1\bar{1}02$).³²⁻³⁵ It was found that the stoichiometric sequence would
 158 dominate when the crystal sample is prepared under thermal annealing conditions.³⁴ However,
 159 when hydroxylated this surface, termed here the full layer termination (FLT), would bear singly
 160 coordinated oxygen $^I O$ and triply coordinated oxygen $^{III} O$.³⁴ It has been observed in several
 161 studies that CMP sample preparation results in a mixed surface termination that is typically
 162 dominated (~80%) by the so-called half layer termination (HLT).^{32, 43} The HLT displays a
 163 sequence ($O_2-X-O_2-Fe_2-O_2-O_2-Fe_2-O_2-Fe_2-O_2-R$) that has a missing near surface Fe-layer (X).
 164 As displayed in Fig. S2, due to the vacancy of the near-surface Fe layer, the HLT of
 165 hydroxylated hematite ($1\bar{1}02$) surface bears doubly coordinated oxygen $^{II} O$ in addition to singly
 166 coordinated oxygen $^I O$ and triply coordinated oxygen $^{III} O$, which are also present in the FLT
 167 surface.

168



169
 170 Figure 1. Potential surface binding sites on the half layer termination (HLT) of hematite ($1\bar{1}02$)
 171 including bidentate corner-sharing sites (CS), bidentate edge-sharing sites (ES_1 and ES_2),
 172 tridentate face-sharing sites (FS), and tridentate corner-sharing/edge-sharing sites (ES_1 &CS).
 173 One surface unit cell is outlined by black dashed lines. Each type of site has a symmetry copy
 174 based on b_s glide plane symmetry highlighted as red dashed line. Terminal $^I O$ groups are

175 displayed as green spheres, ^{16}O atoms are displayed as purple spheres, near-surface Fe atoms are
176 displayed as octahedra, and all the other atoms are shown as solid lines for better visual clarity.

177

178 2.3.3 Potential binding sites

179 With the surface functional groups identified potential surface sites for Sb adsorption on the
180 HLT surface could be deduced (Fig. 1). When considering possible binding sites on the HLT we
181 ignored the monodentate binding mode since it would result in a large Fe-Sb distance ($>3.8 \text{ \AA}$),
182 that was not observed in previous XAFS studies.^{4, 17, 22} In addition, Sb(V) adsorption in an
183 octahedral coordination shell at the available bidentate edge-sharing sites (ES_1 and ES_2 in Fig. 1)
184 were ignored, since it would lead to sterically unfavorable configuration with abnormally small
185 O-O separations ($<2.0 \text{ \AA}$) between the ‘distal’ oxygens (bonding only to Sb) and the surface
186 oxygens. As a result, the Sb binding configuration on the HLT surface was examined by
187 comparing three trial models; bidentate corner-sharing (Model CS), tridentate corner-
188 sharing/edge-sharing (Model CS&ES) and tridentate face-sharing (Model FS) configurations
189 (Fig. 1). Besides the HLT, the FLT represents another type of surface domain on a CMP-
190 prepared surface that occupies only $\sim 20\%$ of the substrate surface.³² The FLT domain
191 contribution to the overall structure factors is minor, and incorporation of sorbates within this
192 domain are poorly constrained due to the small contribution. Therefore, we ignore surface Sb
193 species on the FLT, and account for the presence of this surface using an average structure
194 model, which displays as a HLT-like structure but with the top three atomic layers bearing partial
195 occupancy to account for the coexistence of the FLT.

196 2.3.4 CTR model refinement

197 The CTR structure factor calculation has been described in detail elsewhere.^{30, 44, 45} Briefly, the
198 total structure factor F is computed through a coherent addition of the bulk and surface
199 contributions. The bulk structure is left unchanged while the surface structure is subject to
200 change due to interfacial physiochemical processes including surface atom relaxation, foreign
201 ion binding, and the adsorption of interfacial water. The displacement (dx , dy , dz) of each
202 surface atom within an atomic layer was grouped according to the \mathbf{b}_s glide plane symmetry
203 mentioned above. Debye-Waller factors of surface atoms had negligible influence on the model
204 fit (FOM), and thus they were fixed to bulk values. The refinement of surface atom occupancies
205 is limited to the top three atom layers (Layer-1 O, Layer-2 O and Layer-3 Fe, Fig. S2), and the

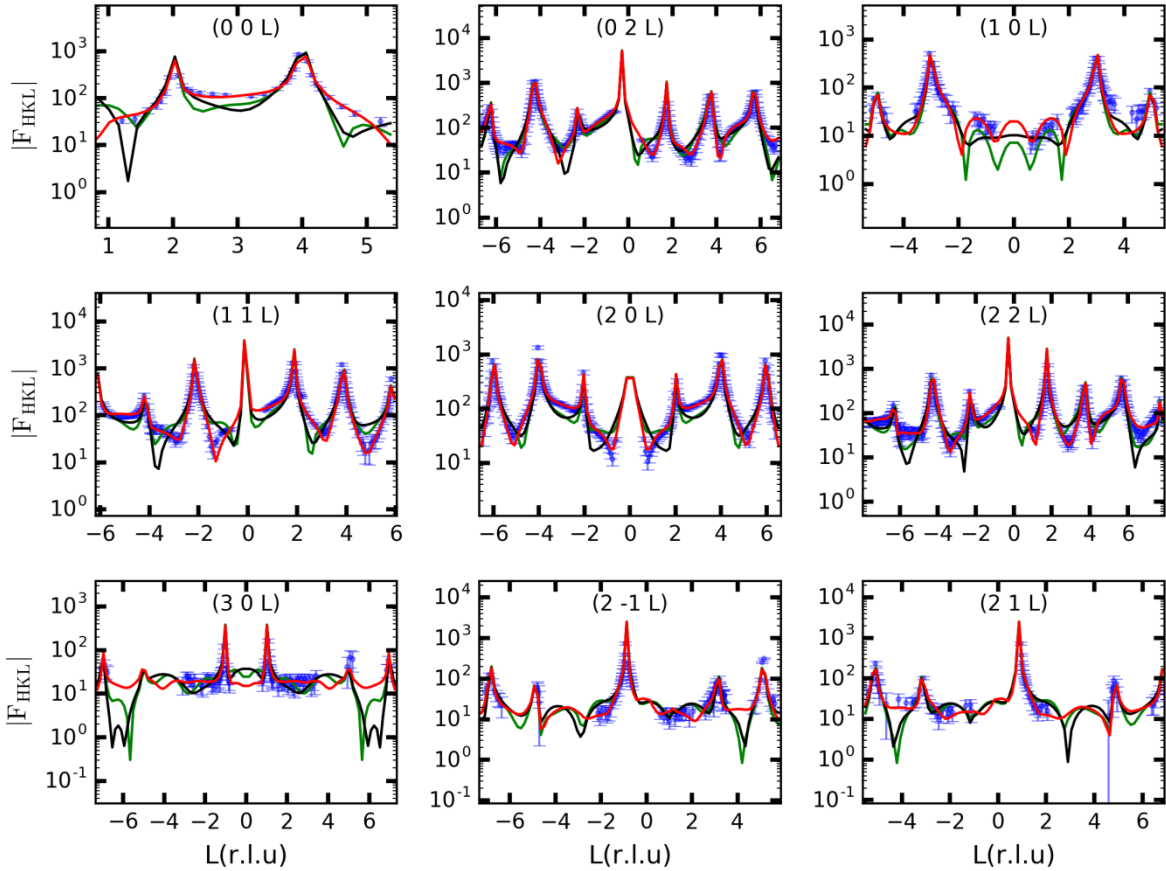
206 partial occupancy of top three atom layers are constrained to be equivalent to account for the
 207 presence of FLT surface. Sorbate atoms (Sb atom and distal O atoms coordinating to Sb only)
 208 parameters include occupancy, Debye-Waller factor as well as positions. To reduce the number
 209 of free model parameters we applied geometrical constraints to maintain a near octahedral
 210 coordination shell of oxygen surrounding the Sb atom (details in the Supplementary
 211 Information), consistent with previous XAFS studies.^{4, 17, 22} The occupancy of Sb and its
 212 coordinated distal O atoms are linked to be equivalent during model refinement. The distal O
 213 atoms are also constrained to have equivalent Debye-Waller factors. Interfacial water layers are
 214 included in the model by adding two pairs of O atoms above the substrate surface. The O atoms
 215 within each layer are grouped to have equivalent heights (z), occupancies, and Debye-Waller
 216 factors during model refinement. In addition, we applied \mathbf{b}_s glide plane symmetry to constrain
 217 the in-plane positions of each O atom within the same water layer.

218 An additional constraint to the modeling included the use of bond-valence rules directly in the
 219 model refinement (detailed description in SI). In the process of model refinement, the bond
 220 valence saturation status of each surface atom is computed and used as a penalty factor P . Each
 221 structure model is fit against the CTR data to obtain the best fit model parameters including
 222 positions, Debye-Waller factors, and occupancies of surface and sorbate atoms, where the figure
 223 of merit (FOM) of the refinement includes both the comparison between experimental and
 224 calculated structure factors and the bond-valence penalty factor P . We applied a global
 225 optimization algorithm to minimize the figure of merit (FOM) during model refinement.^{46, 47} The
 226 FOM is computed from the modified χ^2 value according to:

$$227 \quad \text{FOM} = P \sum_{i=1}^N \frac{\left[\frac{|F_i - F_{i,c}|}{e_i} \right]^2}{N-p}. \quad (1)$$

228 In the equation (1), P is the bond valence penalty factor mentioned above, F_i represents the
 229 experimental value for the structure factor, $F_{i,c}$ is the calculated structure factor, e_i is the error of
 230 the i^{th} data point, N is the number of data points, and p is the number of fitting parameters.

231



232

233 **Figure 2.** Experimental (blue circles) and model-based structure factors (F_{HKL}) as a function of
 234 perpendicular momentum transfer (L , in reciprocal lattice units) for the hematite ($1\bar{1}02$) surface
 235 reacted with $200\ \mu\text{M}$ Sb(V) at pH 5.5. The green lines represent the calculated CTR profiles
 236 based on the optimized corner-sharing model (CS), black lines represent the calculated CTR
 237 profiles based on the optimized face-sharing model (FS), and red lines represent the calculated
 238 CTR profiles based on the optimized corner-sharing/edge-sharing model (CS&ES).

239

240 3. Results

241 3.1 Sb-bonded HLT

242 Optimized CTR profiles are compared to the experimental data in Fig. 2. Calculated CTRs
 243 based on Model CS (green lines in Fig. 2) and Model FS (black lines) could not reproduce the
 244 experimental data at numerous positions producing large FOM values (6.64 and 8.46 with bond-
 245 valence penalty factor P equaling 1, respectively). For example, sharp dips were observed near
 246 $(1\ 1\ -4)$, $(1\ 1\ 2.5)$, and $(2\ 2\ -5.5)$ in the calculated profiles (Fig. 2). In addition, the valley features

247 observed at anti-Bragg peak regions near ($2\ 0\ L = \pm 1$) could not be reproduced with those
248 models. On the contrary, Model CS&ES yielded a significantly better fit to the experimental data
249 with a FOM = 1.27 (bond-valence penalty factor $P=1$).

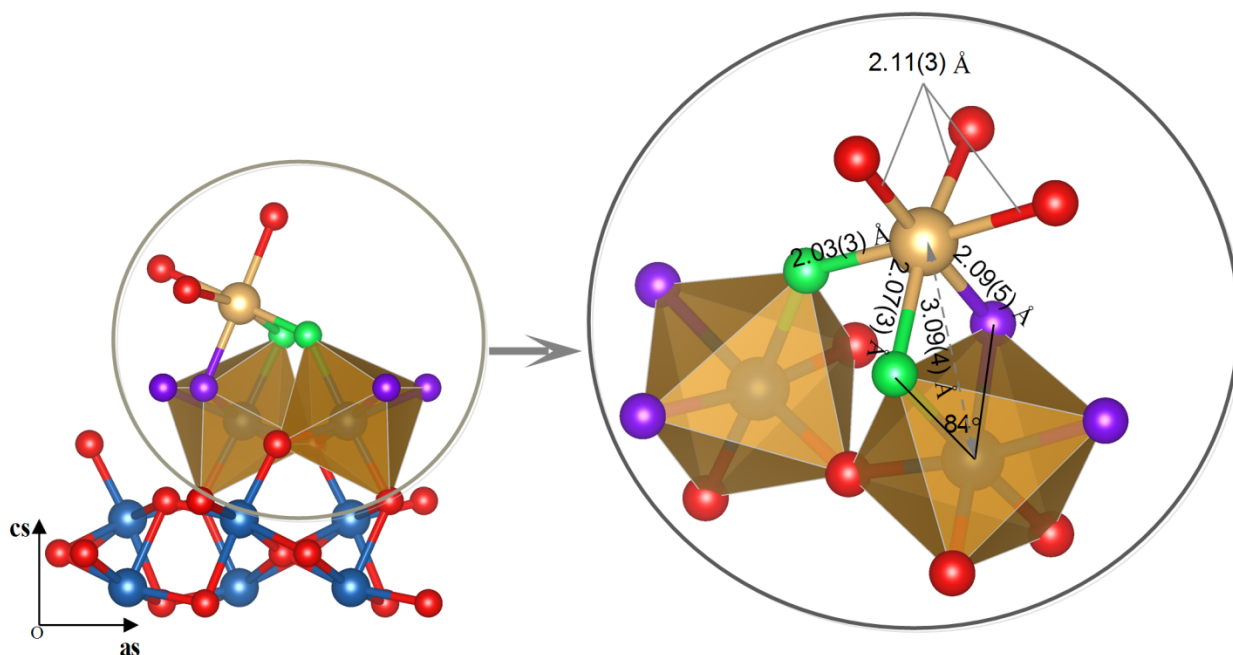
250 The best fit modeling results are compiled in Table S1. The best fit model gave rise to an
251 average surface structure containing top three atom layers with partial occupancy of 0.79(3),
252 which is equivalent to a 21(± 3)% clean FLT surface and a 79(± 3)% HLT surface. The HLT
253 surface was partially occupied by Sb, where the occupancy of 0.37(2) corresponds to a coverage
254 of 0.74(4) Sb/ A_{UC} (A_{UC} = area of the unit cell, 27.4 Å²). The proportion of FLT to HLT was in
255 good agreement with the ratio (72/28) previously reported on a clean surface³² and a Pb(II)-
256 reacted surface⁴⁸ using a similar preparation procedure. As shown in Fig. 3, the best fit structural
257 model generated an Sb surface complex binding at the HLT surface in a tridentate mode with a
258 corner-sharing/edge-sharing binding configuration. The Sb surface complex was slightly
259 distorted from a regular octahedron with similar Sb-O bond lengths ($3 \times 2.11(3)$ Å, 2.03(3) Å,
260 2.07(3) Å and 2.09(5) Å) and a nearest Sb-Fe separation of 3.09(4) Å. **It is worth noting the**
261 **relatively large error of Debye-Waller factor parameter found for distal oxygen ligands**
262 **($B = 2 (\pm 4)$ Å²). The large error bar is probably caused by the weak X-ray scattering for a distal**
263 **oxygen ligand that undergoes fast exchange with free hydroxyl ions in solution. Additional**
264 **model trials were performed to test the possible influence of this parameter on the surface**
265 **binding structure. After a series of model refinements with the Debye-Waller factor for the distal**
266 **oxygens fixed at three different values, i.e. 2, 4, and 6 Å², it was found that the results are**
267 **comparable to the best-fit model within errors, suggesting negligible influence of these**
268 **parameters.**

269

270 3.2 Interfacial water structure

271 The best fit model also yielded an interfacial water structure that contained a near-surface
272 water layer of an occupancy equivalent to $\sim 1.0(2)$ O/ A_{UC} at 3.2(1) Å above the surface and a
273 second water layer with similar layer height (3.4(3) Å) and a smaller occupancy (0.4(2) O/ A_{UC}).
274 The heights of interfacial water layers observed in this work are much larger than those (1.19(7)
275 Å and 1.91(4) Å) previously reported for a clean hydrated hematite surface (1 $\bar{1}$ 02).³² It appears
276 that interfacial water molecules, pre-bound on the hematite surface, have been displaced by the
277 Sb surface complex species. The interfacial waters observed here appear to be in positions

278 consistent with hydrogen bonding with the distal oxygen groups of the Sb surface complex rather
279 than with surface oxygen groups, as shown in Fig. S3. The best fit model results suggest that the
280 model fit quality (FOM) is insensitive to the Debye Waller factors of interfacial water layers.
281 The variations of best fit Debye Waller factors within a relatively large value (5.4 and 20.0 Å²
282 for the first and second water layer, respectively) only produce an increase of FOM smaller than
283 2%, which may hint at the weak lateral ordering of interfacial water layers above bound-Sb
284 species on the hematite surface. We also found that model refinement using the structure model
285 without interfacial water gave rise to a FOM = 1.52, a fit statistically worse, according to a
286 Hamilton significance test on the **R** factor, ⁴⁹ than the best fit using a structure model containing
287 water layers (FOM = 1.27). Therefore, we conclude that interfacial water layers are probably
288 displaced by the Sb surface complex that may form hydrogen-bonds with distal O ligands
289 coordinating to Sb. **The perturbation of the interfacial water structure induced by specific**
290 **sorption of cations on a charged plate has been previously described in a molecular dynamics**
291 **simulation study.⁵⁰ In that study, it was found that a localized point charge at a charged plate**
292 **surface would compel and displace the interfacial water layer to larger distances from the**
293 **substrate surface corresponding to so called ‘translational ordering’, similar to our findings here.**
294 **Nonetheless, the interfacial water structure resolved in this work could not provide any insight**
295 **into lateral structural ordering, likely due to a fast dynamic exchange between interfacial water**
296 **molecules. Some water coverage closer to the surface, i.e. where no Sb occupies the surface,**
297 **could also occur, but the low coverage and electron density (relative to the Sb surface**
298 **complexes) means these water molecules do not contribute significantly to the scattering signal.**



299

300 **Figure 3.** Left: A side view of molecular structure of the Sb(V) surface complex at the HLT of
 301 hematite ($1\bar{1}02$) surface based on the best fit Model CS&ES. Right: A detailed view of the Sb
 302 binding structure with proper orientation from the side view. The bond Sb-O lengths and the Sb-
 303 Fe separation are highlighted. The $^{\text{I}}\text{O}-\text{Fe}-^{\text{II}}\text{O}$ angle is also highlighted. Red spheres are O atoms,
 304 green spheres are singly coordinated surface O groups ($^{\text{I}}\text{O}$), purple spheres are doubly
 305 coordinated O groups ($^{\text{II}}\text{O}$), golden spheres are Sb atoms and blue spheres are Fe atoms. Near-
 306 surface Fe atoms are displayed as octahedra.

307

308 4. Discussion

309 4.1 Comparison of CTR-derived surface complexation structure with XAFS studies

310 The Sb surface complex species identified in this work has an nearest Sb-Fe separation
311 (3.09(4) Å) as well as an average Sb-O bond length (2.14(5) Å) comparable to those reported in
312 previous XAFS studies (3.00 to 3.19 Å for Sb-Fe distance, and 1.98(2) Å for Sb-O bond length)
313 using differently synthesized substrates, including goethite,¹⁷ ferrihydrite,¹⁷ hydrous ferric
314 oxide,²² and environmental samples.^{4, 26} In those XAFS studies, the Sb-Fe separations of 3.00-
315 3.19 Å were assigned to Sb(V) adsorption in an edge-sharing mode. Besides the short Sb-Fe
316 separation, a larger Sb-Fe separation (3.56 Å) is also found in shooting range soil samples,⁴ and
317 it was interpreted as corner-sharing surface complex species being simultaneously bound on the
318 ferrihydrite surface. Our results suggest that the relatively short Sb-Fe distance is also consistent
319 with the tridentate binding geometry, where the Sb complex shares both an edge and a corner of
320 the Fe octahedra (Fig. 3). In addition, the best fit structure proposed in this work gives rise to a
321 second nearest Sb-Fe distance (3.78 Å) that is much longer than the characteristic Sb-Fe distance
322 (3.56 Å) found for a corner-sharing complexation structure.⁴

323

324 4.2 Implications of the mechanism controlling the surface binding mode

325 The binding mechanism of a specific ion on a mineral surface is determined by a variety of
326 different factors. In the Sb-Fe (hydr)oxide systems the electrostatic repulsion between Sb(V) and
327 Fe(III) was found to be an important factor that may regulate Sb uptake according to a DFT
328 study.²³ This study suggests a general site preference trend with the larger Sb-Fe separation
329 corresponding to the energetically more favorable binding structure due to weaker repulsion
330 between the adsorbed Sb⁵⁺ cation and the nearest structural Fe³⁺ cation. The best fit model
331 structure in this work suggests surface O atoms were displaced by up to 0.22 Å (Table S1). As a
332 result, the ^{II}O-Fe-^IO bond angle (84(2)°, Fig. 3) shrinks significantly from the unrelaxed structure
333 (^{II}O-Fe-^IO = 91°), while increasing the Fe-Sb distance. In the context of the electrostatic effects
334 mentioned above, the reduction in the ^{II}O-Fe-^IO bond angle may be related to the necessity of
335 maintaining a larger Sb-Fe separation to weaken the electrostatic repulsion. Further
336 computational work could be helpful to disentangle the relationship between electrostatic
337 repulsion and strain caused by structural distortion. The influence of electrostatic repulsion
338 between the adsorbed and the structural cations was also highlighted in a study investigating the

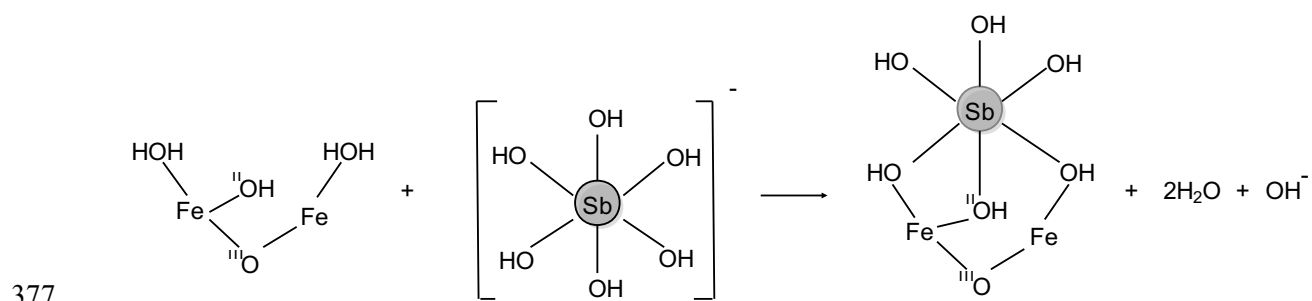
339 effect of Sb(V) on the transformation of 2-line ferrihydrite to hematite, goethite and
340 feroxyhyte.⁵¹ In that study, it was found that the presence of Sb(V) favored the transformation of
341 ferrihydrite to goethite and feroxyhyte while decreasing the yield of hematite. This phenomenon
342 was interpreted as the consequence of the presence of face-sharing octahedral units in hematite
343 structure, which inhibited the isomorphic substitution of Sb for Fe due to the strong Sb-Fe
344 electrostatic repulsion.

345 However, electrostatic effects cannot be used to explain the binding preference of Sb at the
346 tridentate ES₁&CS site compared to the bidentate CS site (Fig. 1) since Sb binding at the CS site
347 would produce an even larger Sb-Fe separation (with weaker electrostatic repulsion) as described
348 in previous XAFS studies.^{3, 4, 22, 26} We propose the tridentate species described here is likely
349 stabilized through a trade-off between the Sb-Fe repulsion and the energetic gains associated
350 with the higher denticity, and relaxation of the surface. **Such a tridentate binding configuration**
351 **was not observed in the adsorption of another pentavalent ion As(V) on the same substrate**
352 **surface.⁴³ Using X-ray reflectivity and Resonant Anomalous X-ray Reflectivity (RAXR),**
353 **Catalano et al. find a binding structure of As(V), which consists of simultaneous inner-sphere**
354 **and outer-sphere modes on hematite (1 $\bar{1}$ 02) surface.⁴³ The inner-sphere complex assumes a**
355 **bidentate corner-sharing structure, which is similar to the CS site, one potential surface site we**
356 **considered for Sb(V) binding as illustrated in Fig.1. The difference in binding configurations for**
357 **these two pentavalent ions is probably driven by the size of the molecular ions. As shown above,**
358 **the hematite surface needs to strain to accommodate Sb(OH)₆⁻; the corresponding H₂AsO₄⁻ unit**
359 **has yet larger bond angles, which likely makes the trifold bonding to the surface**
360 **thermodynamically unfavorable. In addition, the outer-sphere surface binding, deduced for**
361 **As(V), is not observed for Sb(V) in this study. The simultaneous inner-sphere and outer-sphere**
362 **binding modes was also reported for Pb(II) on hematite (1 $\bar{1}$ 02) surface in another RAXR study,**
363 **⁵² which was, however, not observed in our recent CTR work. ⁵³ While the driving force of this**
364 **simultaneous binding behavior remains unclear, the comparison of the binding structures**
365 **between Sb(V) and As(V) on hematite (1 $\bar{1}$ 02) emphasize the importance of surface structure –**
366 **reactivity relationship. Such a relationship should be addressed in a broader scope to take into**
367 **considerations not only the substrate surface structure itself but also the coordination structure of**
368 **sorbate ions.**

369

370 4.3 Protonation schemes of interfacial oxygen groups

371 We predict the protonation schemes of surface functional groups in the best fit surface
372 complex structure through a bond valence analysis, which was detailed in our group's recent
373 publication.⁴⁸ With the protonation schemes of surface oxygen groups derived for this work
374 (compiled in Table 1) and the associated protonation schemes for a clean hydroxylated surface
375 reported previously,³² we propose the surface reaction stoichiometry for Sb(V) adsorption as
376 follows:



379 The stoichiometry outlined above indicates that surface complexation of Sb(V) on the HLT can
380 be described as a ligand exchange between hydroxyl groups (-OH) coordinating to Sb and
381 terminal hydro groups on the surface leading to the release of two water molecules and a
382 hydroxide ion. In addition, Sb binding does not change the protonation state of the ¹¹O group but
383 weakens the covalent hydrogen bond as suggested by a smaller bond valence of the H atom (0.68
384 v.u.) compared to that coordinating the unbound ¹¹O group (0.88 v.u.; Table 1). The release of
385 one hydroxyl ion in the stoichiometry above implies that a lower solution pH will favor the
386 uptake of Sb(V). This is consistent with the pH dependent sorption edge results reported
387 previously using different types of Fe-(oxy)hydroxide samples,^{12, 19, 25} which showed a maximum
388 uptake at **pH<7**. It should be noted that the surface oxygen groups at a clean surface will
389 protonate differently as a function of pH. For example, ¹O groups would deprotonate at a higher
390 pH, which will change the reaction stoichiometry accordingly to produce two OH⁻ groups.
391 Considering the relatively high pH (8-9) at the point of zero charge for hematite substrates,^{36, 37} it
392 is reasonable for the surface functional groups on the HLT to be fully protonated at pH 5.5
393 corresponding to one hydroxyl release in Sb surface complexation.

394 In light of the growing attention to the environmental risks associated with Sb contamination,
especially at sites with potentially high Sb concentrations in soils and soil pore waters (e.g.

395 shooting ranges), the fundamental structural details presented in this study help to identify the
 396 potential species that would immobilize Sb(V) through surface complexation reactions with iron-
 397 (hydr)oxides. The surface complexation reaction proposed in this work also predicts that Sb(V)
 398 uptake will be more effective under acidic conditions.

399

400 **5. Environmental impact**

401 Our results improve the molecular level understanding of the retention of Sb(V), an emerging
 402 contaminant in the environment, by Fe-bearing mineral phases. The proposed three-fold
 403 coordinated IS binding mode suggests a strong interaction with the mineral phase, which may
 404 indicate low mobility of Sb(V) under the experimental conditions of our work, and the
 405 possibility for remediation processes based on this molecular process. One aspect of this is the
 406 absence of a co-existing OS species, which had been previously observed for the adsorption of
 407 As(V) on the same hematite (1 $\bar{1}$ 02) surface.

408 The molecular scale binding structure derived in this CTR work has its limitation in a single
 409 set of reaction conditions, but it will nonetheless serve as a molecular reference in future research
 410 for example with respect to thermodynamic surface complexation modelling, chemically-guided
 411 reactive transport simulations, or quantum chemical studies to elucidate energetic barriers in the
 412 adsorption processes of molecular anion contaminants.

413

414 **Table 1.** Bond valence analysis of surface species based on the best fit structure model.

Surface Species	Original bond valence sum (v.u)	Protonation scheme and hydrogen bonding		Final bond valence sum (v.u)
		Number of H	Number of H bond	
Fe≡O—Sb	1.24	1 (0.76)	0	2.00
Fe≡O—Sb	1.13	1 (0.87)	0	2.00
Fe ₂ ≡O—Sb	1.44	1 (0.68)	0	2.12
Fe ₂ ≡O	0.70	1 (0.88)	1 (0.25)	1.83
Fe ₃ ≡O	1.87	0	1 (0.13)	2.00
O _{dist} —Sb	0.68	1(0.88)	2 (0.22)	2.00

415 The numbers inside the parentheses are bond valence sums assigned to a covalent hydrogen (H)
416 or a hydrogen bond (H bond), so that a bond valence sum is closest to the saturation state. The
417 ranges of the valence for an H and an H bond are 0.68-0.88 v.u and 0.13-0.25 v.u, respectively as
418 suggested by Bargar et al.⁵⁴

419

420 **Supporting information:** CTR model refinement strategy, bond valence constraint, geometrical
421 solution in model refinement (Figure S1), structure comparison between two surface
422 terminations of hematite ($1\bar{1}02$) (Figure S2), interfacial water structure (Figure S3), table of best
423 fit CTR model (Table S1)

424

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440

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