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Sherman, DM and Peacock, CL orcid.org/0000-0003-3754-9294 (2010) Surface complexation of Cu on birnessite (d-MnO₂): Controls on Cu in the deep ocean. *Geochimica et Cosmochimica Acta*, 74 (23). pp. 6721-6730. ISSN 0016-7037

<https://doi.org/10.1016/j.gca.2010.08.042>

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Accepted Manuscript

Surface Complexation of Cu on Birnessite (δ -MnO₂): Controls on Cu in the Deep Ocean

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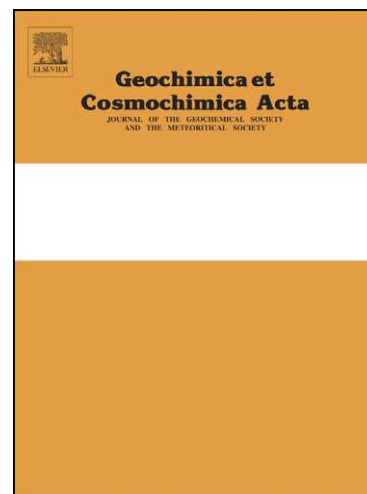
PII: S0016-7037(10)00505-3
DOI: [10.1016/j.gca.2010.08.042](https://doi.org/10.1016/j.gca.2010.08.042)
Reference: GCA 6914

To appear in: *Geochimica et Cosmochimica Acta*

Received Date: 26 October 2009
Accepted Date: 26 August 2010

Please cite this article as: Sherman, D.M., Peacock, C.L., Surface Complexation of Cu on Birnessite (δ -MnO₂): Controls on Cu in the Deep Ocean, *Geochimica et Cosmochimica Acta* (2010), doi: [10.1016/j.gca.2010.08.042](https://doi.org/10.1016/j.gca.2010.08.042)

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1 **Surface Complexation of Cu on Birnessite (δ -MnO₂):**
2 **Controls on Cu in the Deep Ocean**

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14 Revised 22 July 2010

15
16 *Submitted to Geochimica et Cosmochimica Acta*

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23 Index Terms: *copper, birnessite, marine ferromanganese crusts, manganese nodules,*
24 *seawater, EXAFS, surface complexation, density functional calculations*

25
26 Running Head: *Surface complexation of Cu on birnessite (δ -MnO₂)*

27 ABSTRACT

28

29 Hexagonal birnessite (γ - MnO_2) is a close analogue to the dominant phase in hydrogenetic
30 marine ferromanganese crusts and nodules. These deposits contain ~ 0.25 wt. % Cu which is
31 believed to be scavenged from the overlying water column where Cu concentrations are near
32 $0.1 \mu\text{g/L}$. Here, we measured the sorption of Cu on γ - MnO_2 as a function of pH and surface
33 loading. We characterized the nature of the Cu sorption complex at pH 4 and 8 using EXAFS
34 spectroscopy and find that, at pH 4, Cu sorbs to birnessite by inner-sphere complexation over
35 the vacancy site to give a 3- to 4-fold coordinated complex with 6 Mn neighbors at $\sim 3.4 \text{ \AA}$.
36 At pH 8, however, we find that some Cu has become structurally incorporated into the MnO_2
37 layer by occupying the vacancy sites to give 6 Mn neighbors at $\sim 2.91 \text{ \AA}$. Density functional
38 calculations on $\text{CuMn}_{18}\text{O}_{24}(\text{OH})_{30}(\text{H}_2\text{O})_3^{-4}$ and $\text{CuMn}_{18}\text{O}_{21}(\text{OH})_{33}(\text{H}_2\text{O})_3^{-1}$ clusters
39 predict a 3-fold coordinated surface complex and show that the change from surface
40 complexation to structural incorporation is a response to protonation of oxygens surrounding
41 the vacancy site. Consequently, we propose that the transformation between sorption via
42 surface complex and vacancy site occupancy should be reversible. By fitting the Cu sorption
43 as a function of surface loading and pH to the formation of the observed and predicted surface
44 complex, we developed a surface complexation model (in the basic Stern approximation) for
45 the sorption of Cu onto birnessite. Using this model, we demonstrate that the concentration of
46 inorganic Cu in the deep ocean should be several orders of magnitude lower than the observed
47 total dissolved Cu. We propose that the observed total dissolved Cu concentration in the
48 oceans reflects solubilization of Cu by microbially generated ligands.

49

50 1. INTRODUCTION

51 The depth-concentration profile of Cu in the oceans is intermediate between that
52 characteristic of scavenged and nutrient elements (Bruland & Lohan, 2004). Dissolved
53 copper is strongly scavenged by sorption to colloidal iron and manganese oxides; these
54 accumulate to form ferromanganese crusts and nodules with Cu concentrations enriched by
55 10^6 over average seawater concentration (Arrhenius, 1963). In addition to being scavenged,
56 dissolved Cu^{+2} is complexed by microbially generated ligands which may play a role in
57 detoxifying Cu (Coale and Bruland, 1988; Bruland and Lohan, 2004). There is recent
58 evidence that such ligands may be significant for Cu even in the deep ocean (Moffat and
59 Dupont, 2007).

60 Within ferromanganese crusts, Cu tends to be more strongly associated with the
61 manganese oxide phase (Cronan, 1969; Kumar et al., 1994). The nature of the manganese
62 oxide phases and the mechanism by which such minerals become highly enriched in trace
63 metals is still unclear. The dominant manganese oxide phase in marine ferromanganese
64 precipitates is birnessite (Burns and Burns, 1979). Birnessite is a phyllosulfate
65 consisting of sheets of edge-sharing MnO_6 octahedra; the sheets yield X-ray diffraction lines
66 at 2.4 Å and 1.4 Å. In well-crystalline birnessites, the sheets of edge-sharing MnO_6
67 octahedra are stacked in the c-direction to give additional diffraction lines at ~7 Å (001) and
68 ~3.6 Å (002). However, marine birnessites usually show only diffraction lines at 2.4 and 1.4
69 Å and are termed “vernadite” or $\delta\text{-MnO}_2$. The absence of the ~7 Å (001) and ~3.6 Å (002)
70 lines is due to a lack of coherent stacking order of the MnO_6 sheets in the c-direction.

71 In addition to the degree of stacking order, natural and synthetic birnessites show
72 variations in the oxidation state and fraction of vacancies within the MnO_6 sheet. Natural
73 marine birnessites have all Mn as Mn(IV) (Murray et al., 1984) and hexagonal symmetry
74 (Jones and Milne, 1956; McKenzie, 1989; Post, 1992). Drits et al. (1997) showed that this
75 symmetry results from ordered vacancies in the octahedral sites. Sorption of Ni on synthetic
76 hexagonal-birnessites occurs via complexation over vacancy sites (Peacock and Sherman,
77 2007a; Manceau et al., 2007), as does sorption of Cu (Manceau et al., 2002). With increasing
78 pH, however, surface-complexed Ni cations move into the vacancy site and become
79 structurally incorporated (Peacock and Sherman, 2007a; Peacock and Sherman, 2007b).
80 Significantly, this transition between surface complexation and structural incorporation has
81 been demonstrated to be reversible (Peacock, 2009). For $\delta\text{-MnO}_2$, Villalobos et al. (2006)

82 report 0.06 vacancies per Mn octahedron although a more recent study indicates the number
83 of vacancies per octahedron may be higher (Grangeon et al., 2008). This suggests that
84 hexagonal birnessites may sorb transition metals in excess of 6 mole % via complexation over
85 vacancy sites.

86 The sorption of Cu to birnessite is rapid (compared to its oceanic residence time) and
87 we hypothesize that dissolved Cu in the oceans is in chemical equilibrium with birnessite.
88 To develop this hypothesis further, we need a thermodynamic model for the uptake
89 (scavenging) of Cu by phases such as $\gamma\text{-MnO}_2$. This model would enable us to predict how
90 dissolved Cu concentrations might respond to anthropogenic perturbations and may help us
91 decipher how paleochemical records indicate past chemical perturbations (e.g., changes in pH
92 and inputs due to hydrothermal fluxes). In the work presented here, we report results of
93 sorption experiments of copper to synthetic birnessite as a function of pH and concentration.
94 We characterize the nature of the sorption complexes using EXAFS spectroscopy and *ab*
95 *initio* (density functional) predictions of the structures and energetics of model clusters that
96 correspond to possible sorption complexes. We then fit the sorption edges to a surface
97 complexation model based on the sorption complexes determined from EXAFS and *ab initio*
98 simulations. From this model, we attempt to predict the equilibrium distribution of Cu
99 between seawater and ferromanganese crusts.

101 2. EXPERIMENTAL AND COMPUTATIONAL METHODS

102 2.1. Mineral preparation and characterisation

103 As shown by Murray et al. (1984), the Mn oxides which occur in marine
104 ferromanganese nodules and crusts have Mn entirely as Mn(IV). Synthetic birnessites can
105 have variable oxidation states of Mn with charge compensation provided by H^+ or Na, K
106 cations. The $\gamma\text{-MnO}_2$ form of birnessite was prepared by following the synthesis procedure
107 outlined in Villalobos et al. (2003) based on the reaction:



110 to yield a product which Villalobos et al. (2003) demonstrated had all of the Mn as Mn(IV).
111 The Mn K-edge XANES of the $\gamma\text{-MnO}_2$ used here is identical to that of the $\gamma\text{-MnO}_2$ phase in
112 Villalobos et al. (2003). Iodometric titration of our product was unable to detect Mn^{+3} , this is

114 consistent with the synthesis product of Villalobos et al. (2003). However, Grangeon et al.
115 (2008) have reanalyzed the Villalobos et al. (2003) birnessite using a Mohrs salt titration
116 method and found an average oxidation state of 3.9. The significance of any trace Mn^{+3} to
117 the sorption of metals to birnessite is unclear. X-ray diffraction patterns of the dried product
118 show asymmetric peaks at $\sim 7 \text{ \AA}$, 2.4 \AA and 1.4 \AA in agreement with the product described in
119 Villalobos et al. (2003). The surface area (measured using the BET method), is $107 \text{ m}^2/\text{g}$.
120 As will be shown below, however, this surface area greatly underestimates the sorption
121 capacity of the birnessite.

122 We measured the experimental pH_{PZC} of our $\gamma\text{-MnO}_2$ by potentiometric titration at two
123 salt concentrations (0.01 and 0.1 M NaNO_3). Freshly prepared, air-dried $\gamma\text{-MnO}_2$ (0.83 g/L)
124 was suspended in pre-boiled, nitrogen purged ($<1 \text{ ppm CO}_2 \text{ (g)}$) $18.2 \text{ m}\Omega$ MilliQ water, and
125 nitrogen purged ($<1 \text{ ppm CO}_2 \text{ (g)}$) for several hours. Titrations were performed at $25 \text{ }^\circ\text{C}$ in an
126 air-tight vessel with constant stirring to avoid settling. Base (NaOH , free from carbonate),
127 acid (HNO_3) and salt solutions (NaNO_3) were added via an automated titrator. A nitrogen
128 atmosphere ($<1 \text{ ppm CO}_2 \text{ (g)}$) was maintained throughout the experiment. Electrolyte was
129 added to bring the ionic strength to 0.01 M and then acid added gradually to lower the pH to
130 ~ 1.5 . Incremental addition of base then produced a titration from acid pH to pH ~ 9 . After
131 each incremental addition of base, up to 5 mins were allowed for pH equilibration. The
132 suspension was returned to acid pH by reverse acid titration, electrolyte added to adjust the
133 ionic strength to the next level and the titration repeated following the same method. No
134 significant hysteresis was observed between the base and acid legs. We find $pH_{PZC} = 2.3 \pm$
135 0.2 and this is in good agreement with previous acid-base titrations of $\gamma\text{-MnO}_2$ (e.g., Catts and
136 Langmuir, 1986).

137

138 2.2. *Cu vs. pH adsorption edge experiments*

139 Batch sorption edge experiments were prepared with Cu(II) aqueous solution using
140 AR grade reagents and $18.2 \text{ m}\Omega$ Milli-Q water. All solutions and resulting suspensions were
141 purged with $\text{N}_2 \text{ (g)}$ ($<1 \text{ ppm CO}_2 \text{ (g)}$) and all adsorption experiments were conducted at $25 \text{ }^\circ\text{C}$.
142 pH measurements were calibrated to ± 0.05 pH units using Whatman NBS grade buffers.

143 Copper(II) stock solution was prepared at 1000 ppm from $\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 0.1 M
144 HNO_3 . NaNO_3 stock solution was prepared at 0.1 M for use as background electrolyte.
145 Adsorption experiments at 143, 77 and 32 ppm $[\text{Cu}]_{\text{total}}$ were prepared by adding 5, 2.5, and 1

146 ml of 1000 ppm Cu stock solution to 0.100 g solid δ -MnO₂ to 30 mL of 0.1 M NaNO₃,
147 respectively. Adsorbent concentration was therefore 3.3 g/L, with the adsorbent containing ~
148 5, 2.5 and 1 wt.% Cu at 100% adsorption, respectively. Stock solution was added
149 incrementally after ~pH 5.5 to avoid the possible precipitation of solid Cu (hydr)oxide phases
150 (Cu speciation in our experimental solutions was calculated using PHREEQC (Parkhurst and
151 Appelo, 1999) and the MINTEQA4 database (Charlton and Parkhurst, 2002)). The resulting
152 suspensions were immediately shaken. Suspension pH was varied between pH 1-7 by the
153 dropwise addition (<1 mL) of either HNO₃ or NaOH and recorded after stabilization to two
154 decimal places. Adsorption edge experiments were then shaken continuously for 1 week
155 during which pH values were adjusted using NaOH or HNO₃. Final pH measurements were
156 obtained for the experimental suspensions before centrifugation or filtering.

157 All adsorption suspensions were separated by centrifugation (~3000 g for 10 min) into
158 an adsorption sample (thick paste) and a clear supernate for determination of total Cu
159 concentration. Thick paste adsorption samples at pH 4 and 8 and with 5 wt.% Cu were
160 subject to EXAFS after storing at 1 – 4 °C for a maximum of 48 hours before scanning.
161 Supernates were filtered using 0.2 μ m cellulose nitrate membrane filters, acidified with 1%
162 HNO₃ and analyzed for Cu by inductively-coupled plasma atomic emission spectroscopy
163 (ICP-AES). Supernates from the experiments used for EXAFS (at pH 4 and 8 and with 5
164 wt.% Cu) were analysed for Cu and Mn by ICP-MS. Cu and Mn analytical detection limits
165 were better than 10 ppb. Aqueous Mn was <100 ppb for both EXAFS sample supernates.
166

167 2.3. EXAFS spectra of Cu sorption complexes

168 EXAFS data were collected at the CCLRC Synchrotron Radiation Source at
169 Daresbury Laboratory, U.K. Spectra of the Cu K-edge (8979 eV) were collected on station
170 16.5, which was designed for measurements on ultra-dilute systems. During data collection,
171 storage ring energy was 2.0 GeV and the beam current varied between 130 and 240 mA.
172 Adsorption samples were presented to the X-ray beam as a wet paste held in a 2 mm-thick
173 Teflon slide with a 4 x 10 mm sample slot. Small sheets of 250 μ m-thick Mylar were placed
174 on either side of the Teflon slide and sealed with a small amount of vacuum grease to hold the
175 wet pastes in place and prevent drying of the samples. EXAFS data were collected from up to
176 20 fluorescence mode scans using an Ortec 30-element solid-state detector.

177 EXAFS data reduction was performed using Daresbury Laboratory software
178 (EXCALIB and EXBACK, Dent and Mosselmans, 1992). EXCALIB was used to calibrate

179 from monochromator position (millidegrees) to energy (eV) and to average multiple spectra
180 from individual samples. EXBACK was used to define the start of the EXAFS oscillations
181 (determined from the inflection point on the K-edge) and perform background subtraction.
182 The pre-edge was fit to a linear function and the post-edge background to two 2nd-order
183 polynomial segments. The phase-shifts and potentials were calculated in the small atom
184 (plane-wave) approximation and we allowed for multiple scattering as coded in EXCURV98
185 (Binsted, 1998). The phase-shift functions used in the curve fitting were derived by *ab initio*
186 methods in EXCURV98 using Hedin-Lundqvist potentials (Hedin and Lundqvist, 1969) and
187 von Barth ground states. No Fourier filtering was performed during the data analysis.
188 Typical errors associated with EXAFS modelling over the k-range used here are 15 % and 25
189 % for first and second shell coordination numbers, respectively, ± 0.02 and 0.05 \AA for first
190 and second shell distances, respectively, and 15 % and 25 % for first and second shell Debye-
191 Waller factors, respectively (Binsted, 1998).

192

193 *2.4. Density functional theory calculations*

194 Quantum mechanical calculations on $\text{CuMn}_{18}\text{O}_{24}(\text{OH})_{30}(\text{H}_2\text{O})^{-4}$ and
195 $\text{CuMn}_{18}\text{O}_{21}(\text{OH})_{33}(\text{H}_2\text{O})^{-1}$ clusters were used to predict bond lengths and energies of
196 proposed Cu sorption complexes. Calculations were done using the ADF code of te Velde et
197 al. (2001). ADF implements density functional theory for finite clusters and molecules using
198 the linear combination of atomic orbital formalism. For all atoms except hydrogen, we used
199 frozen core orbitals (i.e., 1s, 2s, 2p, 3s and 3p for Mn and Cu; 1s for O). Molecular orbitals in
200 the ADF code are constructed from Slater type atomic orbitals which consist of a cartesian
201 part $r^{kr}x^{kx}y^{ky}z^{kz}$ with $k_x+k_y+k_z = l$ (l = angular momentum quantum number) and an
202 exponential part $e^{-\zeta r}$. For all atoms, we used an uncontracted, triple-zeta basis set with
203 polarization functions (Van Lenthe and Baerends, 2003). No optimization of the basis set
204 was done. With this basis set, counterpoise corrections for basis set superposition energy,
205 evaluated by replacing a Cu with a ghost atom in a simple $\text{Cu}(\text{H}_2\text{O})_6^{+2}$ cluster, are found to
206 be negligible ($< 1 \text{ kJ/mole}$).

207 The calculations were done using the PBE version (Perdew et al., 1996) of the
208 generalized gradient approximation (GGA) of the exchange-correlation functional (Perdew et
209 al., 1992). All calculations were done using the spin-unrestricted formalism to account for the

210 three unpaired 3d-electrons of Mn and the 1 unpaired 3d-electron of Cu; in each cluster, the
211 Mn and Cu atoms were set up in a ferromagnetic configuration. The geometries of the
212 clusters were optimized using a Newton-Raphson method and Broydon-Fletcher update of the
213 Hessian matrix as coded in ADF. The total energies of each complex during geometry
214 optimizations were converged to ± 0.3 kJ/mole.

215

216 *2.5. Surface complexation modelling*

217 Surface complexation modelling was done using a FORTRAN90 program EQLFOR
218 (Sherman et al., 2008; Sherman, 2009) based on the original “tableau” speciation algorithm
219 described by Morel and Morgan (1972). Modifications to the mass balance, Jacobian and
220 convergence routines were made to include the surface and diffuse layer charges of the basic
221 (2 layer) Stern model (Sherman, 2009). Equilibrium constants for surface complexes were
222 derived by fitting all sorption edges simultaneously. The speciation routines are called by a
223 gradient search fitting algorithm (Bevington and Robinson, 2002) to optimize the equilibrium
224 constants. The fitting was obtained by minimizing χ^2 , which is calculated assuming a relative
225 error of 2 % in concentrations/pH.

226 In the Morel and Morgan (1972) method, the speciation is calculated using mass
227 balance constraints to give the molal concentrations of surface species. The correct
228 thermodynamic formulation (i.e., one that gives the correct ideal configurational entropy of a
229 species) of the activity of a surface species is in terms of the mole fraction of surface sites
230 occupied by the species. The resulting stability constants are obtained from the apparent
231 (fitting to mass balance) stability constants by converting the concentration of each surface
232 species to its mole fraction. Activity corrections to the stability constants for aqueous species
233 were made using the Davies equation.

234

235 3. RESULTS AND DISCUSSION

236 *3.1. Sorption of Cu on birnessite*

237 The sorption of Cu to birnessite at several different surface loadings is shown in
238 Figure 1. The results obtained here are very different from those obtained by Catts and
239 Langmuir (1986) and Fu et al. (1991). In those experiments, the Cu sorption edge occurs at
240 ~ 2 pH units higher for similar degrees of loading (Figure 1). Both of those studies used a
241 birnessite or δ -MnO₂ phase synthesized by reacting solutions of Mn⁺² and KMnO₄. X-ray

242 diffraction of the phases used by these authors are reported to have the same diffraction lines
243 as those obtained here; however, the intensities of the (001) and (002) reflections are
244 unknown. A highly crystalline birnessite in which the phyllosmanganate sheets are stacked in
245 the c-direction will have a smaller fraction of vacancy sites relative to edge-sites available for
246 surface complexation. The discrepancies between the results obtained here and those reported
247 by previous authors may reflect differences in the crystallinity of the birnessite. Marine
248 birnessites typically show no (001) reflection and, consequently, surface complexation should
249 be dominated by vacancy rather than edge-site sorption.

250

251 3.2 EXAFS of Cu sorbed to birnessite

252 EXAFS spectra of Cu sorbed to birnessite (5.0 wt. %) at pH 4 and 8 are shown in
253 Figure 2. The Fourier transform of the EXAFS of Cu-birnessite at pH 4 indicates a first
254 coordination shell containing ~4 oxygen atoms near 1.95 Å and a further coordination shell
255 corresponding to ~6 Mn near 3.4 Å. We interpret this as indicating a Cu surface complex
256 formed over a vacancy site; consequently, we forward-modelled the EXAFS spectrum using
257 the cluster shown in Figure 3a. During the fit, we refined a total of 9 parameters (the
258 correction to the Fermi energy (EF), 2 Cu-O distances, 2 Cu-Mn distances and 4 Debye-
259 Waller factors (DWF's). These are given in Table 1. Stern's rule (Stern, 1993) limits the
260 number of independent data parameters N_{ind} as $2\Delta k\Delta R/\pi + 2$ (Booth and Hu, 2009) where Δk
261 and ΔR are the range in k - and R -space actually fitted. For our experiment, $N_{\text{ind}} = 15$; hence
262 our model should not be over-fitting the data. Note that the apparent resolution of the two Mn
263 shells at 3.39 and 3.43 Å is not statistically significant since such small differences in Cu-Mn
264 distances cannot be resolved with the k -range used. The two distances simply reflect the
265 symmetry of the cluster used.

266 Our model for Cu-birnessite at pH 4 differs somewhat from the interpretation of
267 Manceau et al. (2002); they fit their EXAFS of Cu-birnessite at pH 4 (described in Lanson et
268 al., 2002) to 4 O at 1.96 Å and two O at 2.23 Å, with a much larger DWF, as expected for Cu
269 in a Jahn-Teller distorted environment. However, we cannot resolve the second oxygen shell
270 in our fit. Moreover, we do not expect Cu to be in 6-fold coordination when complexed to a
271 surface vacancy. First, our predicted geometries from density functional calculations on a Cu
272 surface complex cluster (discussed below) do not predict 6-fold coordination of Cu.

273 Secondly, it is now realized that the coordination number of Cu^{+2} in aqueous solution is
274 actually 5 (Pasquarello et al., 2001; Amira et al., 2005). On the other hand, we are in good

275 agreement with the interpretation of Manceau et al. (2002) regarding the outer shell of 6 Mn
276 atoms near 3.43 Å and we also find no evidence for Cu sorption at edge sites or for Cu
277 surface precipitation.

278 The EXAFS of Cu sorbed at pH 8 is similar to that at pH 4 except that there is an
279 additional scattering due to Mn atoms near 2.9 Å. This indicates a second coordination
280 environment of Cu; we interpret this as Cu occupying a vacancy site. To forward-model the
281 EXAFS of Cu sorbed at pH 8, we used two clusters simultaneously: a surface complex
282 cluster (Figure 3a) and a cluster corresponding to Cu occupying the vacancy site (Figure 3b).
283 From the fit, we estimate that ~20 % of the Cu has occupied the vacancy site. The calculated
284 fit parameters are given in Table 1. The Cu EXAFS at pH 8 was refined with total of 12
285 parameters (EF, 2 Cu-O distances, 3 Cu-Mn distances, 5 DWF's and the fraction of Cu
286 occupying a vacancy (see Table 1)). Since this is less than N_{ind} for the k- and r-ranges used,
287 we have not over-fit the data. However, as with the surface complex cluster, the apparent
288 resolution between the two Mn shells at 2.81-2.91 Å in cluster 2 is not statistically significant
289 since such small differences in Cu-Mn distances cannot be resolved with the k-range used.

290 By analogy with Ni (Peacock and Sherman, 2007a), a surface complex formed on the
291 edge-sites of birnessite (as opposed to a complex formed over a vacancy), would have a Cu-
292 Mn distance intermediate between that found for the vacancy complex and solid solution.
293 Including such an edge complex is not necessary to fit the EXAFS; consequently, although
294 edge-complexes may be present they cannot be resolved.

295

296 *3.3 DFT Optimized geometries and energetics of surface complexes*

297 The optimized structures and energies of clusters corresponding to Cu sorbed as a
298 surface complex and Cu occupying a vacancy sites are shown in Figures 4 and 5. The
299 geometry of the surface complex predicts the Cu will be in 3-fold coordination in an
300 approximately trigonal arrangement with an average Cu-O bond length of 1.93 Å and an
301 average Cu-Mn distance of 3.29 Å. Note that the water molecules in Figure 5 are > 3 Å away
302 from the Cu atom and not part of its coordination shell. The predicted average Cu-O distance
303 is in good agreement with that observed (1.95 Å) using EXAFS, although the EXAFS were fit
304 to four nearest neighbor oxygens. However, in the EXAFS fit, the DWF of the fourth oxygen
305 is quite large (0.02). The difference in coordination number between that predicted and that
306 derived from the EXAFS may simply reflect the uncertainty in the DWF's and coordination
307 numbers derived from EXAFS. The predicted average Cu-Mn distance (3.29 Å) is 4 %

308 smaller than that observed using EXAFS. The origin of this discrepancy is unclear but might,
309 for example, reflect longer range structural relaxation associated with next nearest-neighbor
310 vacancies. The discrepancy might also reflect a dependence of the Cu-Mn distance on the
311 protonation state of the vacancy oxygen as discussed below.

312 If Cu occupies the vacancy site (solid solution) instead of forming a surface complex,
313 the expected Jahn-Teller distortion gives Cu-O distances of 2.0 (x2), 2.1 (x 2) and 2.2 (x2) to
314 give an average distance of 2.1 Å which is about 8 % higher than those observed with
315 EXAFS; however, the experimental Cu-O distance is poorly constrained due to overlap with
316 the Cu-O scattering in the surface complex. The predicted average Cu-Mn distance of 2.92 Å
317 is in good agreement with the EXAFS result of ~2.9 Å where this peak is well resolved.

318 The cluster calculations, moreover, provide insight on sorption via surface
319 complexation vs. sorption via solid solution. When the oxygen atoms surrounding the
320 vacancy site are not protonated, the surface complex cluster is calculated to be 40 kJ/mole
321 less stable than the cluster with Cu occupying the vacancy site. However, if the opposite
322 three oxygens surrounding the vacancy site are protonated as in Figure 4, the surface complex
323 is 40 kJ/mole more stable than the complex having Cu occupy the vacancy site. This could
324 explain why Cu forms only a surface complex at low pH but occupies a vacancy site at high
325 pH. A more quantitative understanding of the relative proton affinities of the surface oxygen
326 sites on birnessite is needed before we can predict the protonation of the surface oxygens as a
327 function of pH. Unfortunately, we still have an incomplete understanding of the surface
328 protonation of goethite (-FeOOH) even though the goethite surface has received far more
329 attention than that of birnessite (e.g., Sherman, 2009 and references therein).

330

331 *3.4. Surface complexation modelling*

332 The batch sorption experiments show that the Cu sorption edge occurs below pH 4.
333 EXAFS results indicate that sorbed Cu forms a surface complex at this pH but starts to
334 occupy vacancy sites at high pH. The optimized structures and energies of clusters
335 corresponding to Cu sorption complexes suggest that the transformation between surface
336 complex and incorporation into the vacancy sites is a response to changes in the protonation
337 state of the vacancy site oxygens. Given this molecular understanding of Cu sorption, we can
338 now fit the sorption edges to a surface-complexation model. To this end, we need to know
339 the surface site densities and the protonation of the birnessite surface oxygens.

340

341 3.4.1 Surface site densities

342 As discussed above, at the loading used here, Cu sorbs to birnessite by forming an
 343 inner-sphere complex above (and in) the vacancy sites. An idealized birnessite consisting of
 344 randomly stacked $\text{H}_4\text{Mn}_5\text{O}_{24}$ layers with a vacancy structure, as described in the model for
 345 the 1H phase of hexagonal birnessite (Lanson et al., 2000), would have 2.22 vacancy sites per
 346 nm^2 . However, the structural model of Villalobos et al. (2006) for $\delta\text{-MnO}_2$ has only 0.8
 347 vacancies per nm^2 . Assuming a maximum reactive surface area of $611 \text{ m}^2/\text{g}$ (i.e., only half
 348 of the surface area of a single phyllosmanganate sheet is counted assuming only 1 Cu atom can
 349 complex on each vacancy), we find the maximum sorption capacity for Cu would be 5.15 wt.
 350 %. However, given the measured BET surface area of $107 \text{ m}^2/\text{g}$ for the birnessite used here,
 351 the sorption capacity should be only 0.9 wt% Cu. This is well below that observed in the
 352 batch absorption experiments; the EXAFS at 5 wt. % loading do not show evidence for any
 353 $\text{Cu}(\text{OH})_2$ phase or resolvable evidence for complexes on particle edges. Consequently, we
 354 conclude that the BET surface greatly underestimates the reactive surface area of birnessite.
 355 This has been shown to be the case for ferrihydrite (Dzombak and Morel, 1990). Because of
 356 our uncertainty in the reactive surface area and in the number of available vacancy sites on the
 357 $\{001\}$ surfaces, the surface complexation modelling discussed below was done by using the
 358 number of reactive sites as an adjustable parameter. Since sorption edges at three different
 359 loadings were measured, it was possible to optimize the fit to the number of reactive sites.

361 3.4.2 Surface protonation

362 We modeled the protonation of $\{001\}$ surface oxygens on $\delta\text{-MnO}_2$ using the
 363 equilibrium



$$365 K_a = \frac{\{\text{>Mn}_2\text{OH}^{+1/3}\}}{\{\text{>Mn}_2\text{O}^{-2/3}\}[\text{H}^+]} \exp\left(-\frac{\Psi_0 F}{RT}\right) \quad (2b)$$

367 where Ψ_0 is the electrostatic potential at the 0-

368 plane, R is the gas constant, F is the Faraday constant and T is temperature. We use the log
 369 $K_a = 2.3$ for reaction (2a) from the potentiometric titration done described above. Here, and
 370 in what follows, we define the (ideal) activity of a surface complex as the mole fraction of the
 371 surface sites that it occupies (this is relative to a standard state of complete coverage). This

372 definition gives the correct treatment of the configurational entropy and for multidentate
 373 complexes this approach is essential (e.g., Tadanier and Eick, 2002). The surface
 374 electrostatic potential ψ_0 is defined from the surface charge distribution using the basic Stern
 375 model (Westall and Hohl, 1980). In the basic Stern model, the Stern layer (i.e., that between
 376 the 0-plane and 1-plane) has a capacitance of $C_{stern} = \epsilon_0 \epsilon_s / d$ where ϵ_0 is the permittivity of a
 377 vacuum (8.854×10^{-12}), ϵ_s is the Stern layer dielectric constant and d is the distance of charge
 378 separation in meters (assumed to be the average distance of approach of hydrated counter
 379 ions). Assuming d is $\sim 4 \text{ \AA}$ and that the dielectric constant is intermediate between that of
 380 pure water (78) and water at dielectric saturation (6), we estimate a Stern layer capacitance of
 381 1 F/m^2 . This is comparable to that used by Boily et al. (2001) for goethite. However,
 382 changing the capacitance by $\pm 0.5 \text{ F/m}^2$ had a negligible effect on the goodness of fit or the
 383 equilibrium constants for the sorption edges measured here.

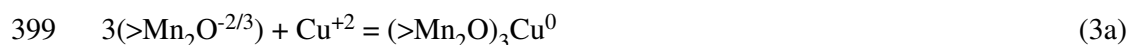
384 For the surface protonation reactions, the change in charge is assigned to the 0-plane.
 385 Following the approach used by previous workers (e.g., Hiemstra and Van Riemsdijk, 1996)
 386 for iron oxides, we assign a formal reference charge $-2/3$ to oxygens in the Mn_2O surface
 387 groups based on Pauling's second rule. (Note that it is only the change in surface charge that
 388 contributes to the free energy of sorption; the assignment of a formal charge to surface sites is
 389 simply to enable charge conservation in the mass-balance equations used when fitting the
 390 sorption data to a surface complexation model).

391

392 3.4.3 Cu surface complexation model

393 Based on the results from EXAFS spectroscopy, we will neglect any complexes
 394 forming at the particle edges and assume that Cu^{+2} only forms complexes with the three
 395 $>\text{Mn}_2\text{O}^{-2/3}$ oxygens associated with vacancy sites on the $\{001\}$ surface. We assume that the
 396 $>\text{Mn}_3\text{O}^0$ surface sites on $\{001\}$ do not protonate or form complexes with Cu^{+2} . The
 397 formation of the surface complex is then:

398



400

401 with conditional ($I = 0.1 \text{ M}$) equilibrium constant:

402

$$K_s = \frac{\{(>Mn_2O)_3Cu^0\}}{\{>Mn_2O^{-2/3}\}^3 [Cu^{+2}]} \exp\left(-\frac{2\psi_0 F}{RT}\right) \quad (3b)$$

404

405 where $\{(>Mn_2O)_3Cu^0\}$ is the mole fraction of $\{001\}$ surface $>Mn_2O$ sites occupied by the
 406 $(>Mn_2O)_3Cu^0$ complex. We assign all of the change in surface charge due Cu^{+2} adsorption
 407 $(+2)$ to the change in charge of the 0-plane. The optimized value of $\log K_s = 5.63$. The one-
 408 site surface complexation model fits to the Cu-birnessite adsorption data are shown on Figure
 409 1. The sorption edges ($pH < 5$) are fit to only the $(>Mn_2O)_3Cu^0$ surface complex. The
 410 transformation of the surface complex to the occupied vacancy site at high pH is not included
 411 in the sorption equilibria. This means that we are not completely describing the surface
 412 electrostatic contribution to the surface sorption at high pH. If Cu atoms occupying the
 413 vacancy sites can disorder to form a complete solid solution with Mn, then we are not
 414 correctly including the entropy of mixing. Neglect of these effects suggests that our model
 415 will underestimate the sorption of Cu to birnessite at high pH (e.g., as in seawater).

416

417 3.5 Application to the Deep Ocean

418 Using our surface complexation model, we can estimate an upper limit for the
 419 dissolved concentration of inorganic Cu^{+2} (e.g., Cu^{+2} , $CuOH^+$ and $CuCO_3$) that would be in
 420 chemical equilibrium with a ferromanganese crust with 0.25 wt. % Cu. For a marine
 421 birnessite with 1.1×10^{-3} moles of vacancy sites/g, as estimated for the birnessite used in this
 422 study (Table 2), this corresponds to a mole fraction of ~ 0.035 surface sites complexed to Cu.
 423 To estimate the concentration of dissolved Cu in seawater, we implemented our surface
 424 complexation model in PHREEQC (Parkhurst and Appello, 1999) together with the
 425 MINTEQ.V4 database (Charlton and Parkhurst, 2002) and a solution with the major ion
 426 composition of seawater. We find that, at pH 7-8, a birnessite with 0.25 wt. % Cu would be
 427 in equilibrium with a dissolved inorganic Cu^{+2} concentration $< 10^{-6}$ $nmol\ kg^{-1}$. This is
 428 many orders of magnitude below that observed (~ 4 $nmol\ kg^{-1}$); we conclude that essentially
 429 all dissolved Cu in deep ocean seawater must be present in chelated form. This is consistent
 430 with the observed deep-water complexation of Cu observed by Moffet and Dupont (2007).

431

432 *Acknowledgements* - We are grateful to Ewa Bednarz for help with the sorption experiments
433 and to Chung Choi (University of Bristol) for ICP-AES measurements. We are especially
434 grateful to Bob Bilsborrow, station manager of 16.5 at the Daresbury Synchrotron radiation
435 source, for his help in optimising the experimental conditions. We are also grateful for the
436 helpful comments of four anonymous reviewers and the Associate Editor. Synchrotron
437 beamtime was provided by direct access awards from CCLRC. This work was supported by
438 NERC Grant NER/B/S/2003/00293.

439

440

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441 REFERENCES

- 442 Amira S., Spangberg D., Hermansson K. (2005) Distorted five-fold coordination of Cu²⁺
443 (aq) from a Car-Parrinello molecular dynamics simulation, *Phys. Chem. Chem. Phys.*,
444 **7**, 2874-2880.
- 445 Arrhenius G. (1963) Pelagic sediments. In: M. N. Hill (ed.) *The sea: ideas and observations*
446 *on progress in the study of the seas*, vol. 33, 655-718. Interscience, New York.
- 447 Bevington, P. and Robinson, D.K. (2002) *Data Reduction and Error Analysis for the physical*
448 *sciences*. McGraw-Hill, New York 326 pp.
- 449 Binsted, N. (1998) *SERC Daresbury Laboratory EXCURV98 program*. Daresbury
450 Laboratory, Warrington, U.K.
- 451 Boily J-F., Lützenkirchen J., Balmés O., Beattle J., and Sjöberg S. (2001) Modelling proton
452 binding at the goethite (α-FeOOH)-water interface. *Colloids and Surfaces A:*
453 *Physicochemical and Engineering Aspects*, **179**, 11-27.
- 454 Booth C. H., Hu Y-J. (2009) Confirmation of standard error analysis techniques applied to
455 EXAFS using simulations. *Journal of Physics: Conference series* **190**, 1-6.
- 456 Bruland K.W., and Lohan M.C. (2004) The control of trace metals in seawater. Chpt 2 in
457 *The Oceans and Marine Geochemistry*, Vol. 6 (Ed. Harry Elderfield) in *Treatise on*
458 *Geochemistry* (Eds. H.D. Holland and K.K. Turekian), 6, 34-47.
- 459 Burns R.G., and V.M. Burns (1979) Manganese oxides, in *Marine Minerals* (R.G. Burns,
460 Ed.). *Reviews in Mineralogy*, 6, 1-46. Mineralogical Society of America, Washington,
461 D.C.
- 462 Catts J. G., and Langmuir D. (1986) Adsorption of Cu, Pb and Zn by δ-MnO₂: applicability
463 of the site binding-surface complexation model. *App. Geochem.* **1**, 255-264.
- 464 Charlton S.R., and D.L. Parkhurst D.L. (2002) *PhreeqcI—A graphical user interface to the*
465 *geochemical model PHREEQC*. U.S. Geological Survey Fact Sheet FS- 031-02.
- 466 Coale K.H., and Bruland K.W. (1988) Copper complexation in the northeast Pacific. *Limnol.*
467 *Ocean.*, **33**, 1084-1011.
- 468 Cronan D.S. (1969) Inter-element associations in some pelagic deposits. *Chem. Geol.*, **5**, 99-
469 106.
- 470 Dent, A. J., and Mosselmans, J. F. W. (1992) *A guide to EXBACK, EXCALIB, and*
471 *EXCURV92*. Daresbury Laboratory, Warrington, U.K.
- 472 Drits V.A., Silvester, E., Gorshkov A.I., and Manceau A. (1997) Structure of synthetic

- 473 monoclinic Na-rich birnessite and hexagonal birnessite: I. Results from X-ray
474 diffraction and selected-area electron diffraction, *Am. Mineral.* **82**, 946–961.
- 475 Dzombak D. A., and Morel F.M. (1990) *Surface Complexation Modelling: Hydrous ferric*
476 *oxide*. Wiley-Interscience, New York.
- 477 Fu G.M., Allen H.E., and Cowan C.E. (1991) Adsorption of cadmium and copper by
478 manganese oxide. *Soil Sci.*, **152**, 72-81.
- 479 Grangeon S., Lanson B., Lanson M., and Manceau A. (2008) Crystal structure of Ni sorbed
480 synthetic vernadite: a powder x-ray diffraction study. *Min. Mag.* **72**, 1279-1291.
- 481 Hedin L., and Lundqvist S. (1969) Effects of electron-electron and electron-phonon
482 interactions on the one-electron states of solids. *Solid State Phys.* **23**, 1-181.
- 483 Hiemstra T., and Van Riemsdijk W.H. (1996). A surface structural approach to ion
484 adsorption: the charge distribution (CD) model. *J. Colloid Interface Sci.* **179**, 488–
485 508.
- 486 Jones L.H.P., and Milne A.A. (1956) Birnessite, a new manganese oxide mineral from
487 Aberdeenshire, Scotland. *Mineral. Mag.* **31**, 283-288.
- 488 Kumar R., Das S.K., Ray R.K., and Biswas A.K. (1994) A SEM backscattered electron
489 mode study of microstructural features of ferromanganese nodules from central indian
490 ocean basin. *Trans. Indian Institute of Metals* **47**, 273-285.
- 491 Lanson B., Drits V.A., Silvester E., and Manceau A. (2000) Structure of H-exchanged
492 hexagonal birnessite and its mechanism of formation from Na-rich monoclinic
493 busserite at low pH, *Am. Mineral.* **85**, 826–838.
- 494 Lanson B., Drits V.A., Gaillot A.C., Silvester E., Plancon A., and Manceau A. (2002)
495 Structure of heavy-metal sorbed birnessite: Part I. Results from X-ray diffraction. *Am.*
496 *Min.* **87**, 1631-1645.
- 497 Manceau A., Lanson B., and Drits V. A. (2002) Structure of heavy metal sorbed
498 birnessite. Part III: Results from powder and polarized extended X-ray absorption fine
499 structure spectroscopy. *Geochim. Cosmochim. Acta* **66**, 2639-2663.
- 500 Manceau A., Lanson M., and Geoffroy N. (2007) Natural speciation of Ni, Zn, Ba, and As in
501 ferromanganese coatings on quartz using X-ray fluorescence, absorption, and
502 diffraction. *Geochim. Cosmochim. Acta* **71**, 95-128.
- 503 McKenzie, R.M. (1989) Manganese oxides and hydroxides. In: Dixon J. B. and Weed S. B.
504 (Eds.). *Minerals in soil environments*. Soil Science Society of America, Madison,
505 Wisconsin. pp. 493-502.

- 506 Morel F., and Morgan J. (1972) Numerical method for computing equilibria in aqueous
507 chemical systems. *Environ. Sci. Technol.* **6**, 58-67.
- 508 Moffett J.W., and Dupont C. (2007) Cu complexation by organic ligands in the sub- arctic
509 NW Pacific and Bering Sea. *Deep Sea Res. Part I*, **54**, 586-595.
- 510 Murray J.W., Balistrieri L.S., and Paul B. (1984) The oxidation state of manganese in marine
511 sediments and ferromanganese nodules, *Geochim. Cosmochim. Acta* **48**, 1237–1247.
- 512 Parkhurst D.L., and Appelo, C.A.J. (1999) *User's guide to PHREEQC (version 2)--A computer*
513 *program for speciation, batch-reaction, one-dimensional transport, and inverse*
514 *geochemical calculations: U.S. Geological Survey Water-Resources Investigations*
515 *Report 99-4259*, 312 p.
- 516 Pasquarello A., Petri I., Salmon P.S., Parisel O., Car R., Toth E., Powell D.H., Fischer H.E.,
517 Helm L., and Merbach A.E. (2001) First solvation shell of the Cu(II) aqua ion:
518 evidence for fivefold coordination. *Science* **291**, 856–9.
- 519 Peacock C.L. (2009) Physiochemical controls on the crystal chemistry of Ni in birnessite:
520 genetic implications for ferromanganese precipitates. *Geochim. Cosmochim. Acta*,
521 **73**, 3568-3578.
- 522 Peacock C.L., and Sherman D.M. (2007a) Sorption of Ni by birnessite: equilibrium controls
523 of Ni in seawater. *Chem. Geol.*, **238**, 94-106
- 524 Peacock C.L., and Sherman D.M. (2007b) Crystal chemistry of Ni in marine ferromanganese
525 crusts and nodules. *Am. Mineral.* **92**, 1087-1092.
- 526 Perdew J.P., Chevary J.A., Vosko S.H., Jackson K.A., Pederson M.R., Singh D.J.,
527 and Fiolhais C. (1992) Atoms, molecules, solids, and surfaces – applications of the
528 generalised gradient approximation for exchange and correlation. *Phys. Rev. B* **46**,
529 6671-6687.
- 530 Perdew J.P., Burke K., and Ernzerhof M. (1996) Generalized gradient approximation made
531 simple. *Phys. Rev. Lett.* **77**, 3865-3868.
- 532 Post, J.E., 1992. Crystal structures of manganese oxide minerals. In: Skinner H. C. W. and
533 Fitzpatrick R. W. (Eds.). *Biom mineralization Processes: Iron, Manganese*. Catena
534 Supplement 21, Catena, Cremlingen-Destedt, Germany. pp. 51-73.
- 535 Sherman D.M., Peacock C.L., and Hubbard C.G. (2008) Surface complexation of U(VI) on
536 goethite (α -FeOOH). *Geochim. Cosmochim. Acta* **72**, 298-310.
- 537 Sherman D.M. (2009) Surface complexation modelling: mineral-fluid equilibria at the

- 538 molecular scale. *Rev. Mineral Geochem.*, **70**, 181-205.
- 539 Silvester E., Manceau A., and Drits V.A. (1997) Structure of synthetic monoclinic Na-rich
540 birnessite and hexagonal birnessite: II. Results from chemical studies and EXAFS
541 spectroscopy, *Am. Mineral.* **82**, 962–978.
- 542 Stern E. A. (1993) Number of relevant independent points in X-ray absorption fine-structure
543 spectra. *Phys. Rev. B* **48**, 9825-9827.
- 544 te Velde, G., Bickelhaupt F.M., Baerends E.J., Fonseca Guerra C., van Gisbergen S.J. A.,
545 Snijders J.G., and Ziegler T. (2001) Chemistry with ADF. *J. Computational. Chem.*
546 **22**, 931-967.
- 547 Tadanier C.J., and Eick M.J. (2002) Formulating the charge-distribution multisite surface
548 complexation model with FITEQL. *Soil Sci Soc Am J* **66**:1505-1517.
- 549
- 550 Villalobos M., Toner B., Bargar J., and Sposito G. (2003) Characterization of the manganese
551 oxide produced by *Pseudomonas putida* strain MnB1. *Geochim. Cosmochim. Acta*
552 **67**, 2649-2662.
- 553 Villalobos M., Lanson B., Manceau A., Toner B., and Sposito G. (2006) Structural model for
554 the biogenic Mn oxide produced by *Pseudomonas putida*. *Am. Mineral.* **91**, 489–502.
- 555 Westall J., and Hohl H. (1980) A comparison of electrostatic models for the oxide/solution
556 interface, *Adv. Colloid Interface Sci.* **12**, 265–294.
- 557 Van Lenthe E., and Baerends E.J. (2003) Optimized Slater-type basis sets for the elements 1-
558 118. *J. Computational Chem.*, **24**, 1142-1156.
- 559

560 **Figure Captions**

561

562 FIGURE 1: Sorption of Cu to birnessite ($\delta\text{-MnO}_2$) as a function of surface loading (1 wt. %,
563 2.5 wt. % and 5 wt. % Cu maximum adsorbed) and pH. Solid lines are fits from the surface
564 complexation model obtained in this work. Also shown (hollow symbols) are results from
565 previous experiments (Catts and Langmuir, 1986; Fu et al., 1992).

566

567 FIGURE 2: EXAFS spectra (a) and their Fourier transforms (b) of Cu on birnessite at pH 4
568 and pH 8. Spectra were modeled using the clusters shown in Figure 3 with the parameters
569 given in Table 1. Note that the Fourier transforms calculated using EXCURV98 (Binsted,
570 1998) are corrected by Cu-O scattering phase shifts to give approximate actual distances.

571

572 FIGURE 3: Clusters used to model the EXAFS of Cu on birnessite a) cluster with pseudo- C_{3v}
573 symmetry to model Cu as a surface complex over the vacancy b) cluster with pseudo- C_{2v}
574 symmetry to model Cu occupying a vacancy site. The distances were obtained by fitting to
575 the EXAFS spectra.

576

577 FIGURE 4: Optimized geometry of Cu surface complex over a vacancy site on birnessite
578 calculated using density functional theory a) view down z-axis b) view down x-axis c) close-
579 up viewed down the, z-axis showing Cu-O and Cu-Mn distances. Note that oxygens
580 surrounding the vacancy site are protonated unless bonded to Cu.

581

582 FIGURE 5: Optimized geometry of cluster corresponding to Cu occupying a vacancy site.
583 This is the minimum energy structure if all of the the oxygens surrounding the vacancy are
584 deprotonated .

585

Table 1: Cu coordination environment from fits to Cu K-edge EXAFS spectra.*Cluster 1: Surface Complex at pH 4 and 8*

	1 O	3 O	3 Mn**	3 Mn**
R	1.95	1.95	3.39	3.43
φ	<i>0</i>	<i>120</i>	<i>141</i>	<i>123</i>
θ	<i>0</i>	<i>0, ± 120</i>	± 90	± 30
$2\sigma^2$	0.024	0.011	0.02	0.02

Cluster 2: Occupied vacancy complex at pH 8

	3 O	3 O	2 Mn**	2 Mn**	2 Mn**
R	1.87	1.96	2.81	2.94	2.91
φ	<i>120</i>	<i>60</i>	<i>90</i>	<i>90</i>	<i>90</i>
θ	<i>0, ± 120</i>	<i>180, ± 60</i>	± 90	± 30	± 150
$2\sigma^2$	0.019	0.019	0.012	0.012	0.012

*Values in italics are constrained. φ and θ are the spherical coordinates defined as the angles from the z and x axes in Figure 3. **Note that, with the k-range used, distance differences $< 0.15 \text{ \AA}$ between shells are not statistically significant.

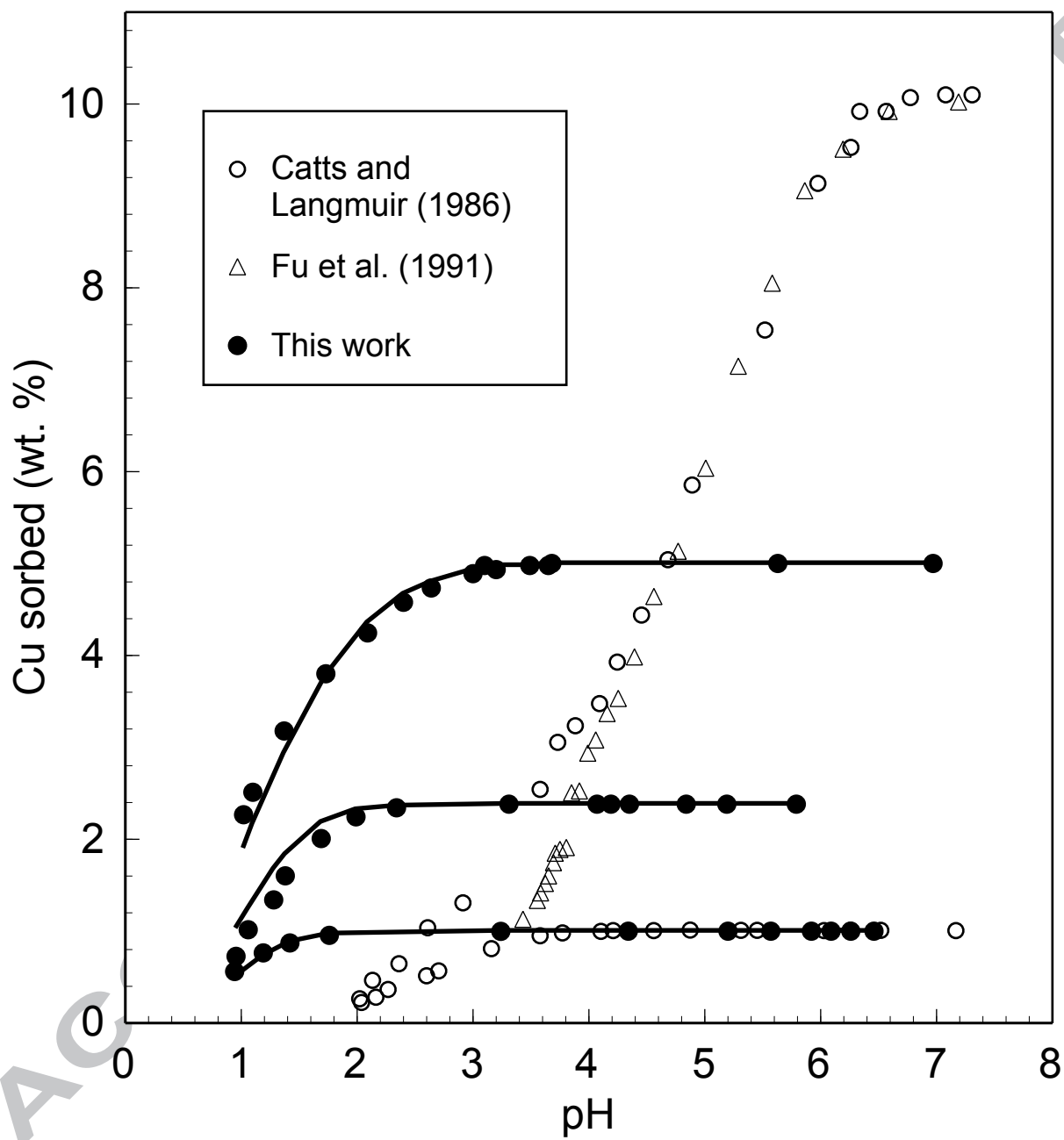
Table 2: Surface complexation modelling parameters

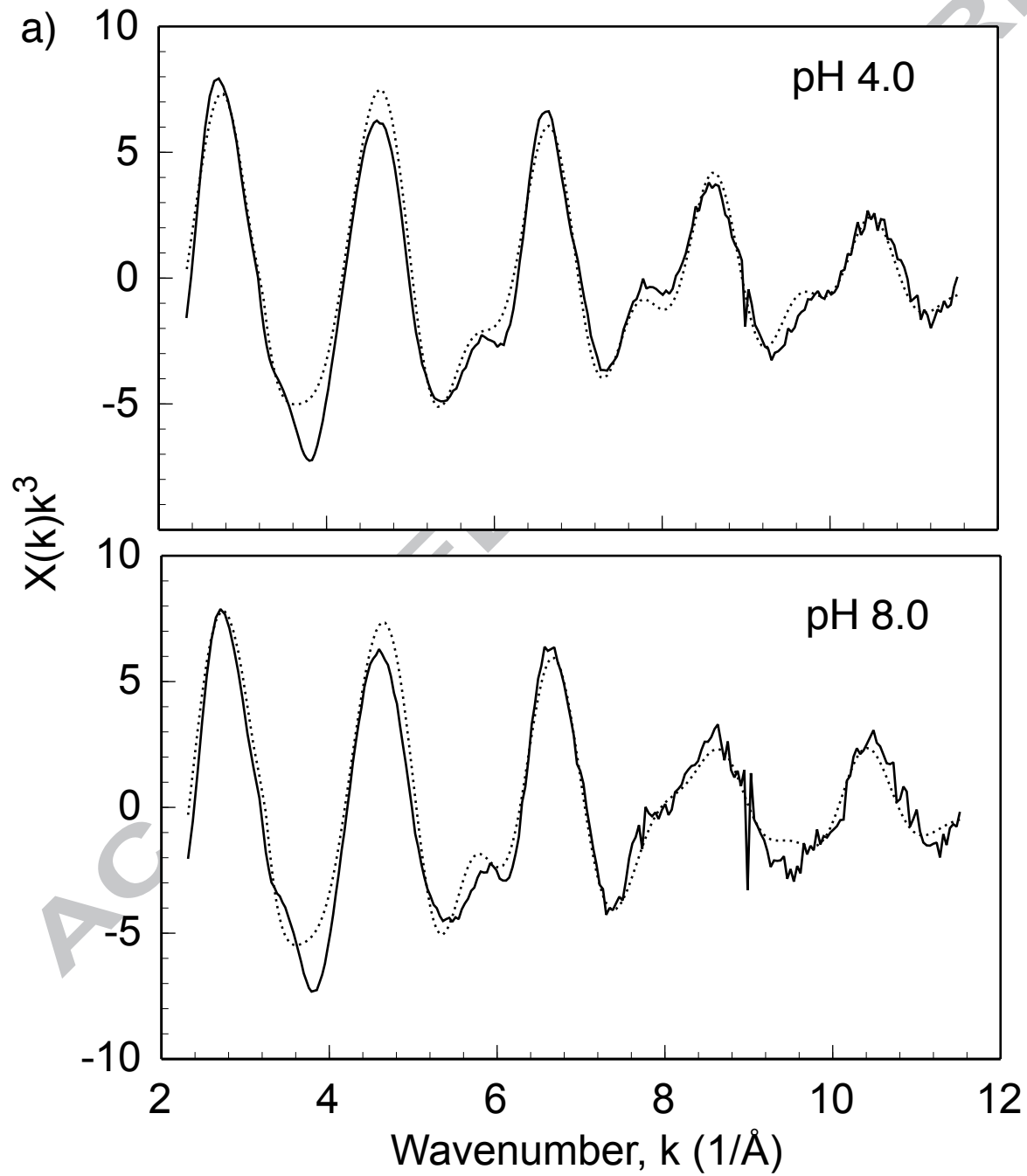
Surface area (m ² /g) ^a	107
C _{stern} (F/m ²) ^b	1.0
[Mn ₂ O ^{-2/3}] (mol/g) ^c	3.30 x10 ⁻³
Mineral surface reaction	Equilibrium constant log K
>Mn ₂ O ^{-2/3} + H ⁺ = >Mn ₂ OH ^{+1/3}	2.3 ^d
3>Mn ₂ O ^{-2/3} + Cu ⁺² = (>Mn ₂ O) ₃ Cu ⁰	5.6 ^c
Solution Speciation	
Cu ⁺² + H ₂ O = CuOH ⁺ + H ⁺	-7.497 ^e
Cu ⁺² + 2H ₂ O = Cu(OH) ₂ + 2H ⁺	-16.196 ^e
2Cu ⁺² + 2H ₂ O = Cu ₂ (OH) ₂ ⁺² + 2H ⁺	-10.594 ^e

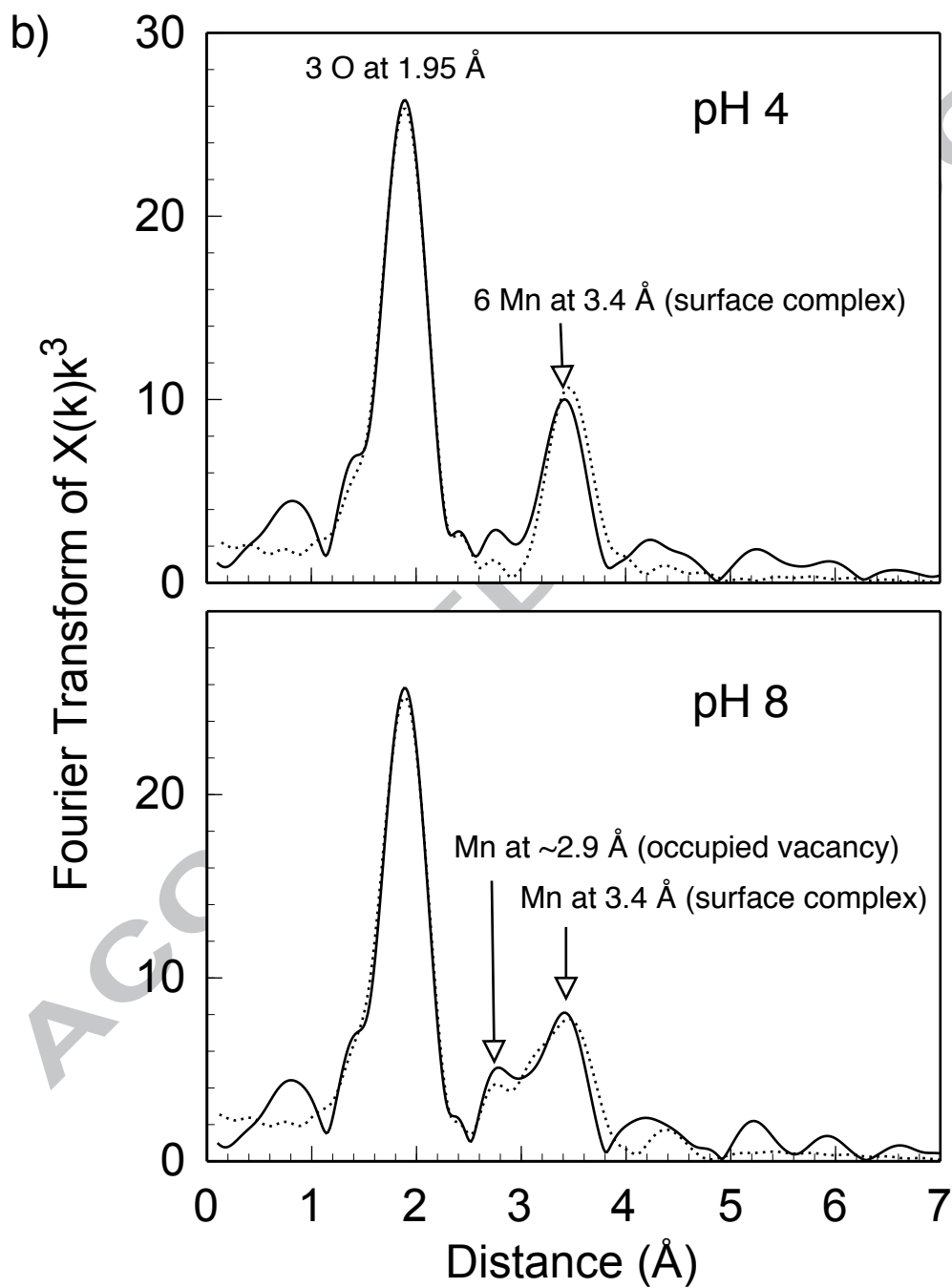
^aDetermined from BET analysis (this study). ^bFixed (this study). ^cDetermined from fitting Cu sorption data (this study) ^dDetermined from potentiometric titration (this study). ^e From MINTEQ.V4 database (Charlton and Parkhurst, 2002).

Sherman and Peacock. Figure 1

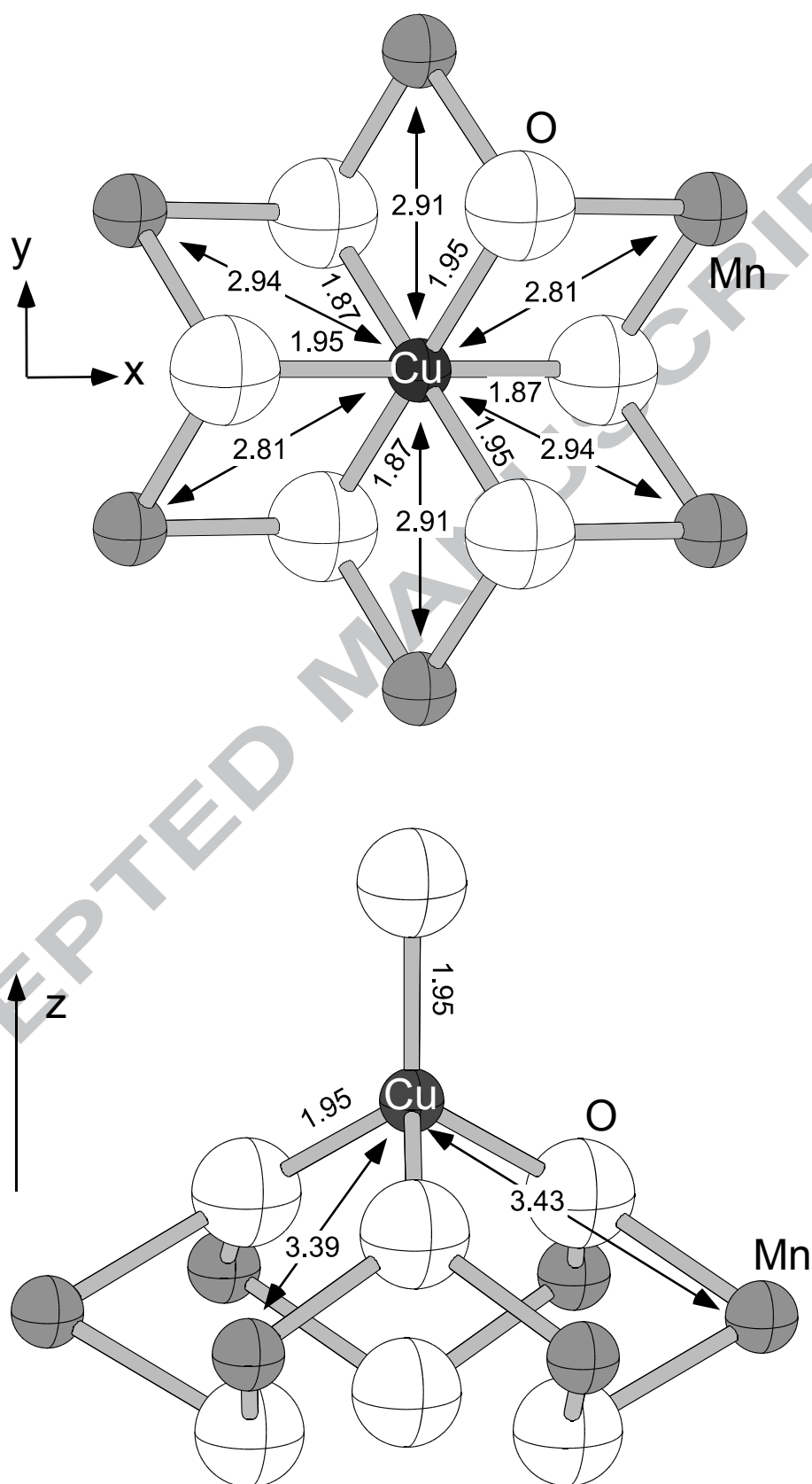
(one column wide)



Sherman et al. Figure 2a
(one column wide)

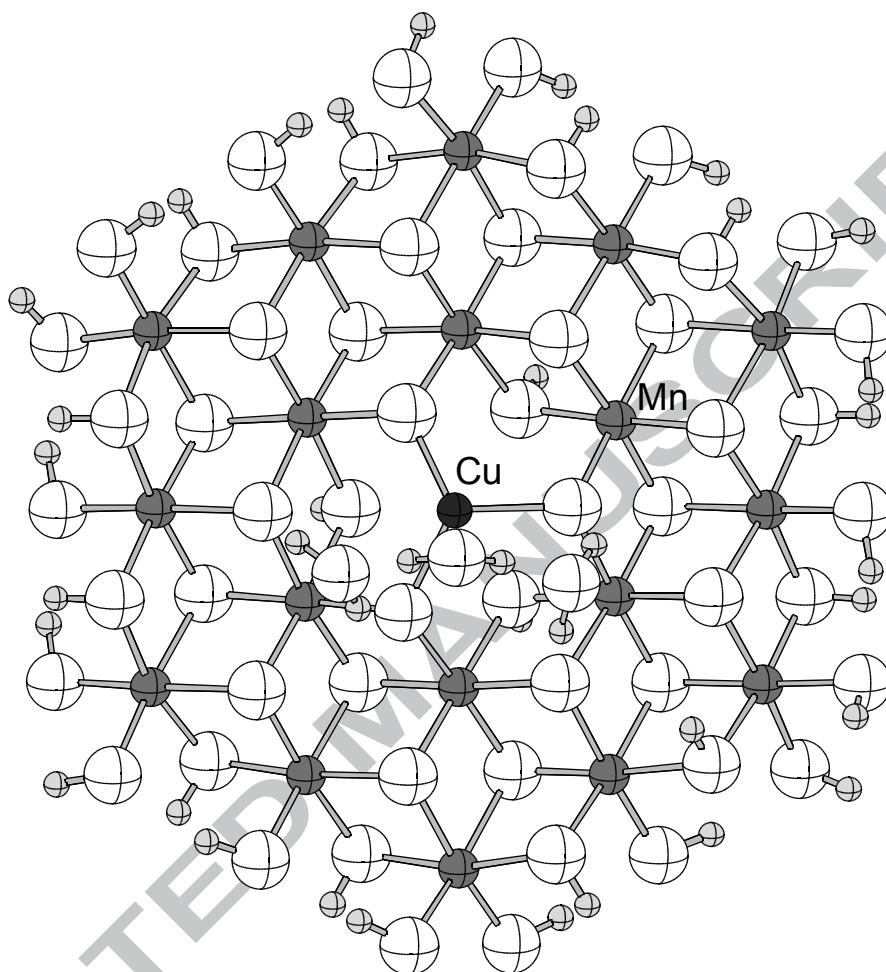
Sherman et al. Figure 2b
(one column wide)

Sherman and Peacock Figure 3 (one column wide)



Sherman Figure 4
(one column wide)

a)



b)

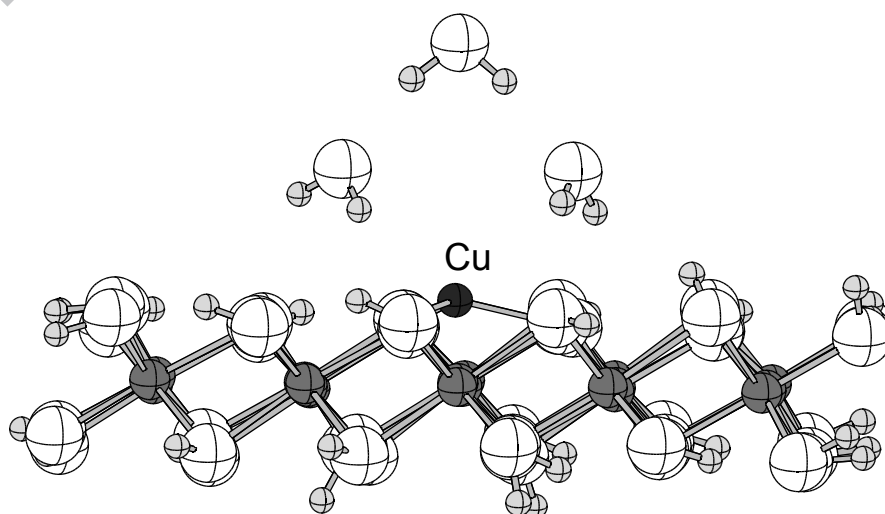
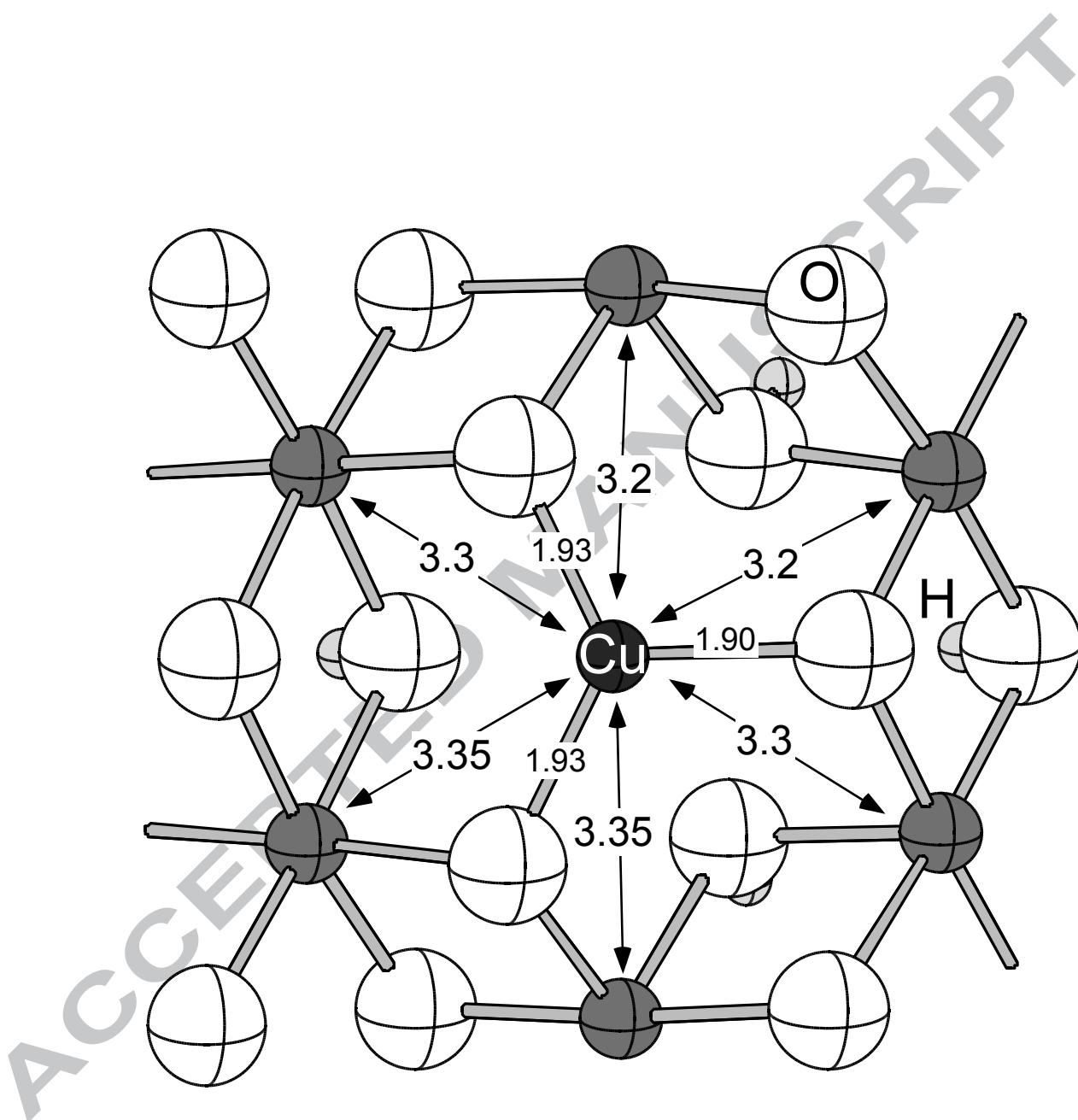
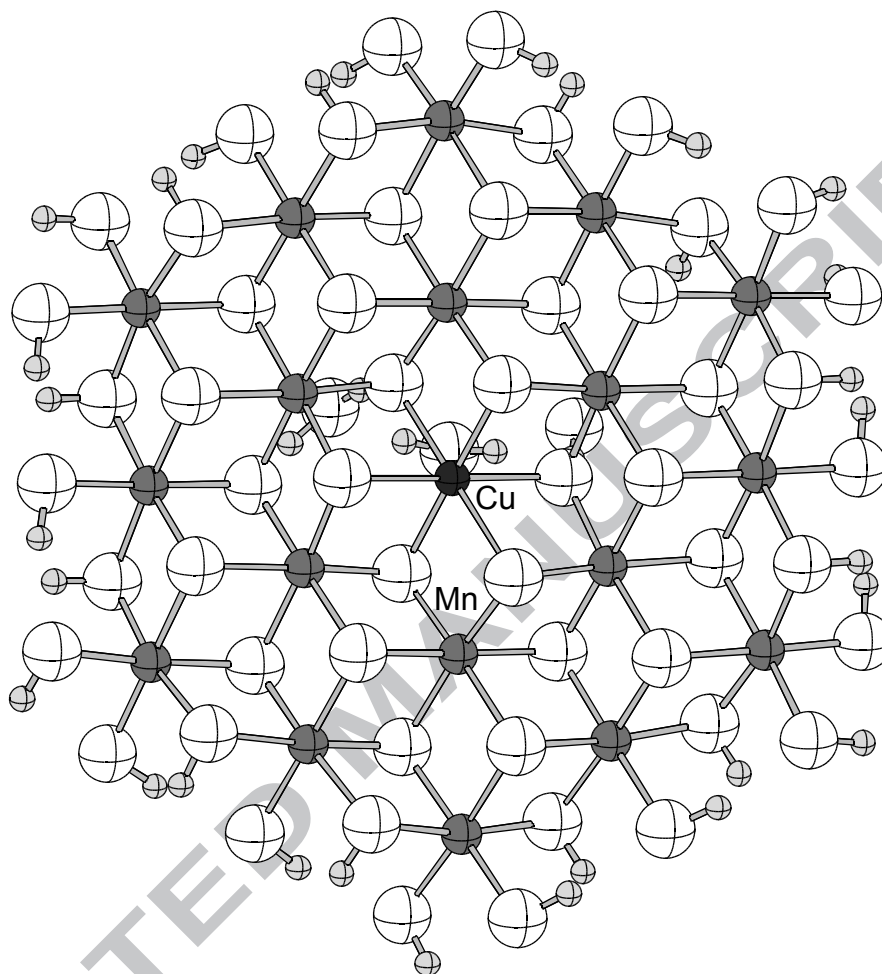


Figure 4c



Sherman and Peacock. Figure 5
(one column wide)

a)



b)

