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Reply to Comment on “Molecular controls on Cu and Zn isotopic fractionation in Fe-Mn Crusts.”

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In our paper “Molecular controls on Cu and Zn isotopic fractionation in Fe-Mn Crusts”, we present an explanation for the observed isotopic fractionations of Cu and Zn in seawater. We hypothesise that the isotopic fractionation of Cu and Zn is driven by the scavenging of these metals by particulate Fe-Mn oxides as reflected in the isotopic composition of Zn and Cu in marine ferromanganese crusts. Zn sorbed to ferromanganese crusts is isotopically heavier than dissolved Zn in seawater by 0.5 ‰. EXAFS spectra show that Zn in ferromanganese crusts is sorbed to birnessite and in tetrahedral coordination. Dissolved inorganic Zn in seawater, however, is primarily octahedrally coordinated as  $\text{Zn}(\text{H}_2\text{O})_6^{+2}$ . The difference in the Zn coordination environment gives a qualitative explanation for the sorption (scavenging) of isotopically heavy Zn by ferromanganese crusts (predominantly birnessite).

In contrast to Zn, Cu in ferromanganese crusts is isotopically light relative to dissolved Cu in seawater. Cu scavenged by ferromanganese crusts is also associated with birnessite. This is evidenced by the correlation between Cu and Mn in ferromanganese crusts. Moreover, the EXAFS of Cu on ALV-539 (Little et al., 2014a) is, within the noise of the data, indistinguishable from that of Cu sorbed to synthetic  $\delta\text{-MnO}_2$  at pH 8 (Sherman and Peacock, 2010). Modelling the EXAFS of Cu sorbed to birnessite at pH 8 shows that Cu binds as both surface complexes (~65 %) and as a replacement for  $\text{Mn}^{+4}$  in the manganate layer (~35 %); we find that Cu is in fourfold-coordination on the surface complex. Dissolved inorganic Cu in seawater, however, is in five-fold coordination as  $\text{Cu}(\text{H}_2\text{O})_5^{+2}$ . Consequently, we would expect that Cu associated with ferromanganese crusts to be isotopically heavier than inorganic Cu in seawater if the lower coordination number favours the heavy isotope. We hypothesise (following Vance et al. (2008)) that the observed presence of isotopically heavy dissolved Cu in seawater (relative to Cu in ferromanganese crusts) reflects the nearly complete complexation of dissolved Cu by organic ligands and that this complexation favors the heavy isotope.

In the comment by Manceau and Nagy (2015), they first argue that Cu in the surface complex of birnessite should be in 6-fold coordination rather than the 4-fold coordination obtained from our EXAFS model fit. An increase in coordination number upon sorption might favour the light isotope of Cu.

Distinguishing 4-fold from 6-fold coordination using EXAFS for Zn is fairly easy as the Zn-O bond lengths are quite different in the two coordination environments. However, distinguishing 4- and 6-fold coordination of Cu using EXAFS ~~for Cu~~ is very difficult if the 6-fold complex is a structure with  $D_{4h}$  symmetry (as expected via the Jahn-Teller effect) with two long ( $\sim 2.2$  Å) axial distances and four short ( $\sim 2.0$  Å) equatorial distances. The Debye-Waller factors for the axial oxygens will be much greater than those of the equatorial oxygens and the scattering by the axial oxygens will be much weaker. The EXAFS of Cu on a ferromanganese crust is, within the noise of the data, indistinguishable from that of Cu sorbed to synthetic birnessite ( $\delta$ -MnO<sub>2</sub>) at pH 8 (Figure 1). The EXAFS of Cu sorbed to synthetic  $\delta$ -MnO<sub>2</sub> (Sherman and Peacock, 2010) gives a useful reference as the spectra do not suffer from noise due to low Cu concentrations and Fe-fluorescence. At pH 4, the EXAFS can be modelled using Cu in fourfold-coordination occupying a surface complex over a vacancy site; at pH 8, the EXAFS can be modelled with a mixture of the surface complex and a Cu occupying the vacancy site itself to have 6-fold coordination. The nature of the surface complex is well defined. Nevertheless, for reasons outlined above, it is inherently difficult to distinguish 4-fold  $T_d$  symmetry ~~with~~ 6-fold  $D_{4h}$  symmetry. Therefore, we have revisited our model of the surface complex of Cu on birnessite by further testing it against the structure predicted using density functional theory. Figure 2 shows an optimised structure for Cu coordinated over a vacancy site on a birnessite nanoparticle calculated using a triple-zeta basis set with the PBE exchange correlation functional. This calculation is an improvement over that presented by Sherman & Peacock (2010) in that a more extensive explicit solvation layer was included in addition to a long-range solvation using the COSMO formalism. In spite of the presence of additional waters, we find that only one H<sub>2</sub>O is bonded to the Cu in addition to the three oxygens from the MnO<sub>2</sub> surface; the Cu coordination is 4-fold. In terms of Pauling's second rule (bond-valence theory), the low coordination number of Cu on the surface complex might be expected given that the uncomplexed surface oxygens receive a "Pauling bond valence" of 1.33 from their two Mn neighbors. Accordingly, such oxygens would favor being bonded to fourfold-coordinated Cu rather than sixfold-coordinated copper as they would then each receive a total

Pauling bond valence of 1.83 rather than 1.67. Furthermore, we would not expect the coordination number of Cu to increase over the five-fold coordination it has in aqueous solution when it binds to the more reactive oxygens on the MnO<sub>2</sub> surface. However, it is arguable whether qualitative arguments using bond-valence theory are reliable as they are not based on quantum mechanics. The *ab initio* simulations give a clear result. Moreover, the predicted Cu-O and Cu-Mn distances are in good agreement with those obtained from the EXAFS presented in Sherman & Peacock (2010) (and better than that found in the earlier calculation from Sherman and Peacock, 2010). In particular, the predicted Cu-Mn distance is near 3.4 Å in agreement with that found for the Cu surface complex via EXAFS. Manceau and Nagy (2015) argued that this Cu-Mn distance was not consistent with the tetrahedral Cu complex; however, the *ab initio* structure shows that the Cu-Mn distance is consistent with the tetrahedral complex. Unfortunately, the EXAFS of Cu in the ferromanganese crust presented in Little et al. (2014) is much noisier than that of Cu sorbed to δ-MnO<sub>2</sub>; consequently, the Cu-Mn distances obtained in Little et al., (2014) are not as well constrained. Our fit to the Cu-Mn scattering in Little et al. (2014) required 3 paths but these are of low statistical significance (fitting the noise). Nevertheless, when combined with the results of the *ab initio* predicted structure, we see no reason to revise our original assertion that the surface complex of Cu on birnessite has Cu in four-fold coordination.

The second objection of Manceau and Nagy (2015) was that our choice of possible ligands (Cu hydroxamate and Cu malonate) as examples of siderophore and humic acid coordination environments are inappropriate. They argue that Cu histidine and Cu malate complexes would be better choices. It should be clarified that Manceau and Nagy's comments do not detract from our overall hypothesis that the isotopic fractionation of Cu between particulate and dissolved fractions (Vance et al., 2008) reflects isotopic fractionation between ferromanganese oxides (in the particulate phase) and organic complexes (in the dissolved phase). We can predict the isotopic fractionation associated with the organic complexes proposed by Manceau and Nagy (2015). Here, *ab initio* calculations of the geometries and vibrational modes of these complexes were done as in (Sherman, 2013). The resulting reduced partition function ratios for

the Cu(histadine)<sub>2</sub> and Cu(malate)<sub>2</sub> complexes are shown in Figure 3 and compared with those of Cu(H<sub>2</sub>O)<sub>5</sub><sup>+2</sup> and Cu(hydroxamate)<sub>2</sub> from Sherman (2013). The isotopic fractionation between species A and B is

$$\Delta_{A-B} = 1000\ln(^{65-63}\beta_A) - 1000\ln(^{65-63}\beta_B)$$

We find that the Cu(histadine)<sub>2</sub> and Cu(malate)<sub>2</sub> complexes favour the heavy Cu isotope relative to Cu(H<sub>2</sub>O)<sub>5</sub> ( $\Delta = 0.7$  ‰) but to a lesser degree than does the Cu(hydroxamate)<sub>2</sub> complex ( $\Delta = 1.4$  ‰). The complexes proposed by Manceau and Nagy (2015) do not seem to offer a strong enough isotopic fractionation to explain the observed isotopic fractionation of dissolved Cu in seawater relative to that scavenged by ferromanganese crusts if birnessite takes up the heavy isotope relative to Cu(H<sub>2</sub>O)<sub>5</sub><sup>+2</sup>. The results of this work suggest that the isotopic fractionation of Cu in the oceans might help provide insight on the nature of the Cu-organic complexes once we have a strong constraint on the isotopic fractionation between Cu sorbed to birnessite and dissolved inorganic Cu. Work is in progress to address this issue.

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## Figure Captions

Figure 1: EXAFS of Cu on ALV 539 ferromanganese crust (Little et al., 2014) compared to EXAFS of Cu on synthetic  $\delta$ -MnO<sub>2</sub> (Sherman and Peacock, 2010).

Figure 2: Optimised structure (from density functional calculation) of Cu complexed over a vacancy site on birnessite.

Figure 3: Predicted reduced isotopic partition function ratios for complexes proposed by Manceau and Nagy (2015) compared to those for Cu(H<sub>2</sub>O)<sub>5</sub><sup>+2</sup> and Cu hydroxamate (Sherman, 2013).

Figure 1

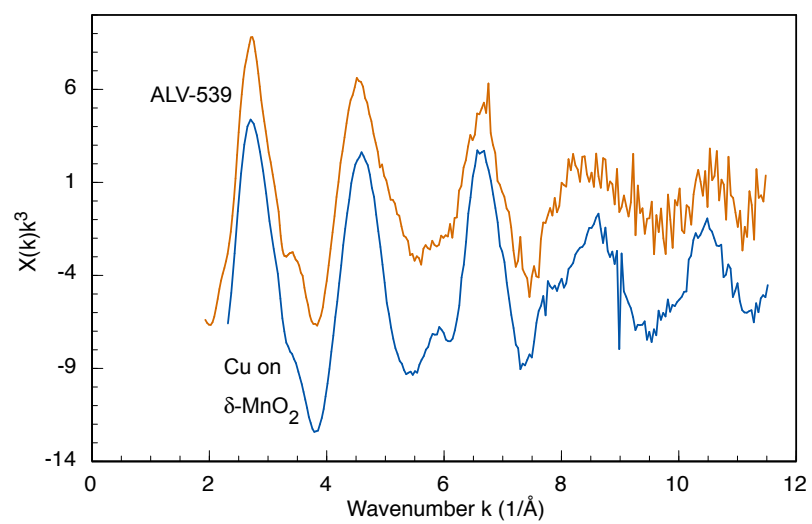




Figure 2

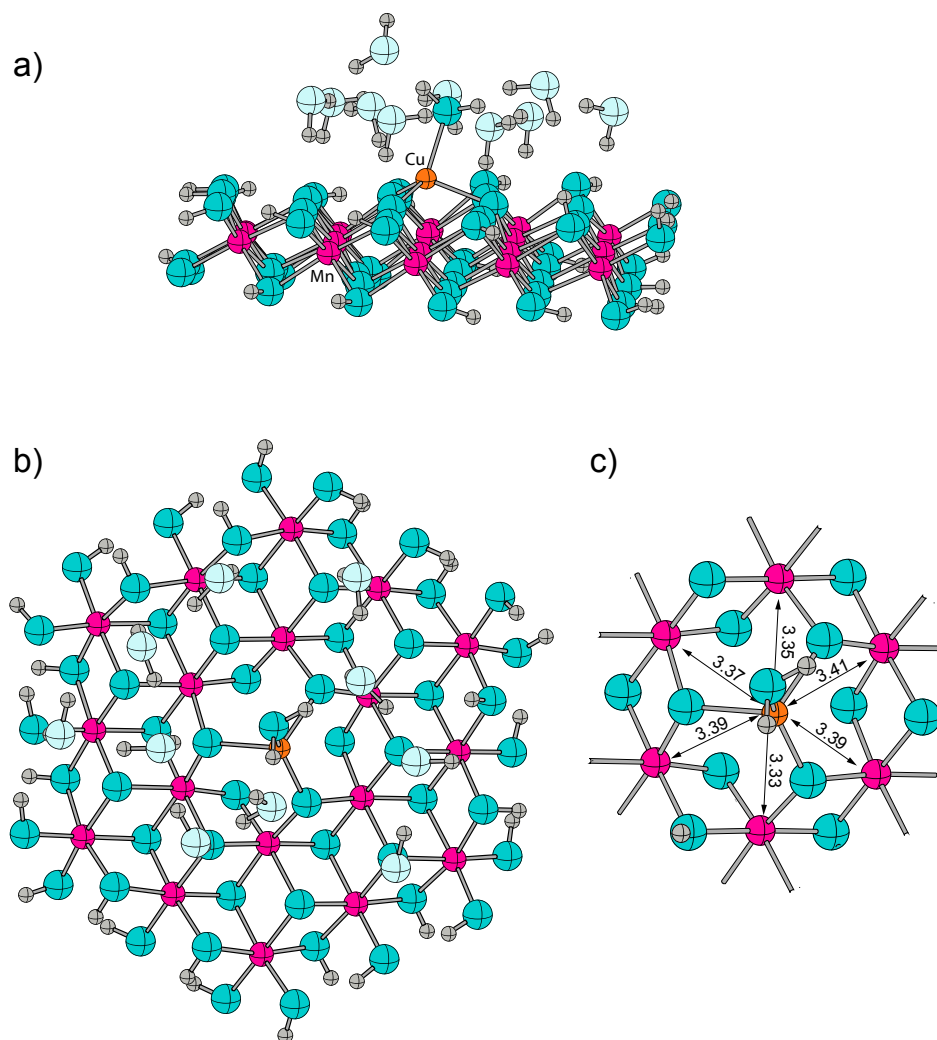


Figure 3

