Isotopic disequilibrium of Cu in marine ferromanganese crusts: Evidence from ab initio predictions of Cu isotope fractionation on sorption to birnessite

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A B S T R A C T

In the oceans, Cu is strongly scavenged by ferromanganese (Fe-Mn) crusts. The isotopic fractionation of Cu between seawater and crusts provides insight into the mechanisms of trace metal cycling in the oceans. Dissolved Cu in seawater is isotopically heavy ($+0.66 \pm 0.19$‰) relative to Cu in crusts ($+0.31 \pm 0.24$‰). The primary mineral phase sorbing divalent trace metals in Fe-Mn crusts is birnessite. Recent laboratory measurements show that isotopically light Cu is preferentially sorbed on birnessite, with a fractionation factor of 0.45 ± 0.18‰. Here, we use first-principles (quantum mechanical) calculations to predict the isotopic fractionation between aqueous Cu^{2+} complexes and Cu as a surface complex on birnessite. We find that isotopic fractionation between the $Cu(H_2O)_5^+$ complex and sorbed Cu should be 0.49‰ (at 25°C), in close agreement with experiments, confirming that these experimental results reflects equilibrium fractionation. We then predict the isotopic fractionation between dissolved inorganic Cu in seawater and birnessite given the thermodynamic speciation of dissolved Cu at pH 8. We find dissolved inorganic Cu should be 0.94‰ (at 5°C) heavier than Cu sorbed to birnessite. This value is substantially greater than the observed fractionation between seawater and Fe-Mn crusts ($\Delta_{sw\text{-}fmc} \approx +0.35$‰). Moreover, it is well established that dissolved Cu in seawater is strongly complexed by organic ligands. Based on model Cu complexes and published experimental data, we estimate that fractionation of Cu by organic ligands should increase the equilibrium fractionation between seawater and Fe-Mn crusts by 0.2 to 1.5‰ to yield $\Delta_{sw\text{-}fmc} = +1.1$ to 2.4‰. We conclude that Cu in marine Fe-Mn crusts in not in isotopic equilibrium with dissolved Cu in seawater, and consider the possible explanations of this surprising finding.

1. Introduction

Copper is both an essential micronutrient and a toxicant in aquatic ecosystems (e.g., Bruland et al., 2013). In oxic environments it is strongly scavenged (sorbed), particularly by manganese (IV) (hydr)oxides (e.g., Koschinsky and Hein, 2003). In aquatic environments, dissolved Cu will complex with a range of organic (and inorganic) ligands (e.g., Coale and Bruland, 1988; Moffett and Dupont, 2007). Each of these processes (biological uptake, sorption, organic complexation) is associated with Cu isotope fractionation (e.g., Bigalke et al., 2010; Navarrete et al., 2011; Pokrovsky et al., 2008; Ryan et al., 2014; Sherman, 2013). Therefore, Cu isotopes

offer a potential tool to investigate the relative importance of different processes in the biogeochemical cycling of Cu.

Here, we determine the Cu isotope fractionation during sorption to birnessite, a phyllomanganate (layer-type MnO_2) phase which is the dominant phase in marine ferromanganese crusts and nodules. Birnessite is a key scavenger of divalent cations like Cu (Koschinsky and Hein, 2003; Sherman and Peacock, 2010; Post, 1999). It is common both in the terrestrial environments, in soils and rivers, and in the marine environment, for which sorption to Mn oxides represents one of the major oceanic Cu removal fluxes (e.g., Little et al., 2014a, 2014b; Sherman and Peacock, 2010).

Little et al. (2014a) investigated the phase association and co-ordination chemistry of Cu in hydrogenetic Fe-Mn crusts, using micro-focus XRF and EXAFS spectroscopy. Ferromanganese crusts consist of micro-scale intergrowths of birnessite and goethite (α-FeOOH). Copper, as expected, is associated with the birnessite phase. Analysis of EXAFS spectra indicated that it is predomi-

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nantly sorbed as III-IV fold surface complexes over the vacancy sites, with up to 35% incorporation in the mineral structure (Little et al., 2014a). In a mixed hydrogenetic-diagenetic Fe-Mn nodule, Manceau et al. (2014) reported that all Cu^{2+} was incorporated into the mineral structure.

Models of hydrogenetic Fe-Mn crust formation have emphasized the importance of inorganic sorption processes (Koschinsky and Hein, 2003). However, the formation of Mn(III,IV) oxide minerals can be catalysed by microorganisms (Tebo et al., 2004), with rates of biological Mn(II) oxidation that are up to five orders of magnitude faster than those of abiotic oxidation. As a result, biological Mn oxidation is thought to dominate in terrestrial and shallow water aquatic environments and, though the relative roles of biotic and abiotic Mn oxidation in deep sea settings remains uncertain, there is increasing evidence for diverse communities of microbial life living in and on marine Fe-Mn coatings and nodules (e.g., Shiraishi et al., 2016; Tully and Heidelberg, 2013). Study of Mn biooxides produced by *P. putida* strain Mn-B1 find that they are structurally similar to synthetic δ-MnO_2, i.e. poorly crystalline Mn(IV) minerals with hexagonal sheet symmetry, of the type common in the natural environment (e.g., Villalobos et al., 2003).

Several experimental and theoretical studies have investigated the mechanism of Cu adsorption on synthetic δ-MnO_2 (Kwon et al., 2013; Peña et al., 2015; Qin et al., 2017; Sherman and Peacock, 2010). Adsorption occurs primarily via the formation of triple-corner-sharing (TCS) surface complexes over the vacancy sites, with the local coordination environment of the Cu^{2+} ion reported to be either III-IV fold (Sherman et al., 2015; Sherman and Peacock, 2010) or V-VI fold (Kwon et al., 2013; Manceau and Nagy, 2015) coordinated. At high pH (pH ≈ 8), analysis of extended X-ray adsorption spectra (EXAFS) indicated that up to 20% of Cu is incorporated as a VI-fold solid solution inside the vacancy site (Sherman and Peacock, 2010). However, static subsequent density functional theory (DFT) calculations suggested that the formation of this incorporated Cu species should be energetically unfavourable (Kwon et al., 2013). At high Cu loading, recent work has argued for additional sorption of Cu as multinuclear complexes, particularly on edge sites (Peña et al., 2015; Qin et al., 2017).

All else being equal, mass-dependent isotopic fractionation tends to partition the heavy isotope into complexes with lower coordination numbers and shorter, stronger bonds. In inorganic aqueous solution, Cu^{2+} occurs as the $Cu(H_2O)_5^{2+}$ (V-fold coordinated) complex (Amira et al., 2005; Pasquarello et al., 2001). Consequently, sorption by complexation over the vacancy sites of birnessite (assuming III-IV fold coordination) was expected to favour the heavy isotope (Little et al., 2014a). However, in laboratory-based sorption and desorption experiments, Ijichi et al. (2018) observed sorption of isotopically light Cu on birnessite, with $\Delta^{65/63}Cu_{dissolved-sorbed} = 0.45 \pm 0.18‰$ (2 SD, n = 12). Fe-Mn crusts are also isotopically light ($\delta^{65}Cu = +0.31 \pm 0.24‰$, 2 SD, n = 34; Albarède, 2004; Little et al., 2014b) compared to deep seawater ($\delta^{65}Cu = +0.66 \pm 0.19‰$, 2 SD, n = 185; Baconnais et al., 2019; Boyle et al., 2012; Little et al., 2018; Takano et al., 2014; Thompson and Ellwood, 2014), which has been hypothesised to reflect organic complexation of isotopically heavy Cu in the aqueous phase (Little et al., 2014a).

Experimental measurements of isotopic fractionation between minerals and aqueous solutions are needed before we can interpret observed fractionations in natural systems. However, it is often difficult to unequivocally establish equilibrium isotope fractionation under experimental conditions. Isotopic fractionation in experiments is influenced by the kinetics of mineral precipitation, by nucleation and crystallisation pathways, and by solution speciation. In addition, analytical constraints mean that experiments are typically carried out at sorbent concentrations many orders of magnitude higher than usually occur in the natural environment

(e.g., in the ocean). Calculations from first-principles circumvent many of these complications, providing independent estimates of equilibrium isotope fractionation factors that can be compared to experimental data.

In this study, we predict the equilibrium isotopic fractionation of birnessite-sorbed Cu via the statistical mechanical partition function from the relevant vibrational modes of finite clusters used to approximate the surface complexes using first-principles (ab initio) simulations. Comparison of the theoretical equilibrium fractionation with experimental values and that observed in the oceans will be used to understand fractionation process in the marine environment.

2. *Ab initio* calculations

Ab initio MD simulations were done using the open source molecular dynamics code CP2K/QUICKSTEP package (VandeVondele et al., 2005) based on density functional theory using a local orbital basis set and pseudopotentials for the core electrons. We used the DZVP-MOLOPT-SR-GTH basis set (VandeVondele and Hutter, 2007) and the PBE exchange correlation functional (Perdew et al., 1996)). Plane-wave cutoffs of 400 eV and REL_CUTOFF at 60 Ry were used in the calculation. All calculations were done using spin-unrestricted calculations with Mn and Cu in a ferromagnetic configuration. The molecular dynamics are run in the NVT ensemble with the temperature controlled at 323 K using a Nose thermostat to avoid the glassy behaviour of liquid water found at lower temperature. The simulation of Cu on sorbed to birnessite was based on a model structure consisting of a single birnessite slab with unit cell composition $Mn_{16}O_{36}H_4$ with 62 H_2O molecules. This slab contains two vacancy sites. Addition of 2 Cu atoms yielded a system with 0 charge with copper in +2 oxidation state upon convergence of the wavefunction. The resulting unit cell was orthorhombic with cell parameters 15.173 Å, 18.0 Å and 8.76 Å. As discussed in the results section, the nature of the Cu surface complex depends on the starting protonation of the vacancy sites, so we started with simulation with one vacancy site protonated and the other non-protonated. The starting atomic coordinates are given in the supplemental data.

Calculations of the local structures and vibrational models of finite clusters used to model the local coordination environment of Cu in aqueous complexes and the birnessite surface was done using the Amsterdam Density Functional (ADF) program (te Velde et al., 2001). Molecular orbitals in the ADF code are constructed from Slater type atomic orbitals. For all atoms, an uncontracted, triple-zeta basis set with polarization functions (Van Lenthe and Baerends, 2003) was used. No optimization of the basis set was done. With this basis set, counterpoise corrections for basis set superposition energy, evaluated by replacing a Cu with a ghost atom in a simple cluster, are found to be negligible (<1 kJ/mole). All calculations were done using a spin unrestricted formalism.

The calculations for aqueous complexes were done using the B3LYP hybrid exchange-correlation functional and were described in (Sherman, 2013) and (Sherman et al., 2015). The geometry of each complex was optimized before the harmonic vibrational frequencies were evaluated to ensure that imaginary frequencies were absent. Geometries were optimised by including a long-range solvation field approximated using the COSMO solvation model (Klamt and Schurrmann, 1993). Vibrational frequencies, however, were calculated in the absence of the COSMO solvation field, but using the solvated geometries (except for the $Cu(H_2O)_5^{+2}$ complex which yielded several imaginary frequencies at the COSMO geometry). Calculations of vibrational modes for Cu complexes on birnessite were done using the PBE exchange-correlation functional and the relative fractionation was evaluated from the $Cu(H_2O)_5^{+2}$

modes evaluated in the PBE functional. The geometries and vibrational frequencies are given in the Supplemental Data.

The reduced isotopic partition function ratios were then calculated for the harmonic frequencies using the equation of (Bigeleisen and Mayer, 1947). The 65-63 reduced partition function of Cu in a species A, for example, is:

$$^{65-63}\beta_A = \prod_{i=1}^{N} \frac{^{63}U_i \bar{e}^{65}U_i/2 1 - \bar{e}^{63}U_i}{^{63}U_i \bar{e}^{63}U_i/2 1 - \bar{e}^{65}U_i} \tag{1}$$

where

$$U_i = hv_i/kT \tag{2}$$

Here v_i are the vibrational frequencies, in the harmonic approximation, of the independent modes of A; h is Planck's constant; k is Boltzmann's constant and T is temperature. The equilibrium constant for isotope exchange between two chemical species A and B is then $\alpha = \beta_B/\beta_A$; however, since α is very close to 1, the isotopic fractionation (per-mil) between species A and B is

$$\Delta(B - A) = \delta^{65}Cu_B - \delta^{65}CU_A \approx 1000 \ln \alpha = 1000(\ln \beta_B - \ln \beta_A) \tag{3}$$

3. Results

3.1. Surface complexation of Cu on birnessite

Despite a number of studies investigating the local coordination environment of Cu^{2+} in the first Cu-O shell, debate remains as to the coordination number (III-IV fold or V-VI fold) of the vacancy complex, and the ability of Cu to substitute for Mn atoms via incorporation in the mineral structure (Kwon et al., 2013; Little et al., 2014a; Peña et al., 2015; Qin et al., 2017; Sherman and Peacock, 2010). A combination of EXAFS and DFT calculations indicated that Cu^{2+} sorbs predominantly via the formation of III-IV fold coordinated complexes over vacancy sites (Sherman and Peacock, 2010). Initial static ab initio calculations (Sherman and Peacock, 2010) predicted that Cu is in 3-fold coordination over the birnessite vacancy site. However, subsequent calculations (Sherman et al., 2015) which modelled the surface complex with a more complete solvation environment (additional water molecules) predict that Cu forms a tetrahedral complex over the vacancy site. It is clear that explicit inclusion of the longer range solvation environment is necessary to correctly predict the stability and structures of surface complexes. To that end, in the course of the work reported here, we performed ab initio molecular dynamics simulations of Cu on birnessite in a periodic system with 62 H_2O molecules per $Mn_{16}O_{36}H_4$ unit cell (Fig. 1). We confirm that Cu complexed to the vacancy site on birnessite is in 4-fold coordination (3 surface oxygens and 1 inner-sphere H_2O) in an approximately tetrahedral environment. This complex is stable over 50 ps. Significantly, the formation of the surface complex requires that two of the oxygens below the birnessite vacancy site be protonated. If the birnessite vacancy site oxygens are unprotonated, the Cu atoms will occupy the vacancy site. The results confirm the interpretation of the EXAFS of Cu sorbed to synthetic birnessite (Sherman and Peacock, 2010) and Cu associated with natural marine ferromanganese crusts (Little et al., 2014a). Experimentally (Sherman and Peacock, 2010), we find that sorption via surface complexation is favoured at low pH; sorption via structural incorporation occurs only at high pH where the surface oxygens are unprotonated. Our results are at odds with the static periodic calculations of (Kwon et al., 2013) which did not include the degree of explicit solvation used here. In particular, Cu is not in a Jahn-Teller distorted 6-fold coordination
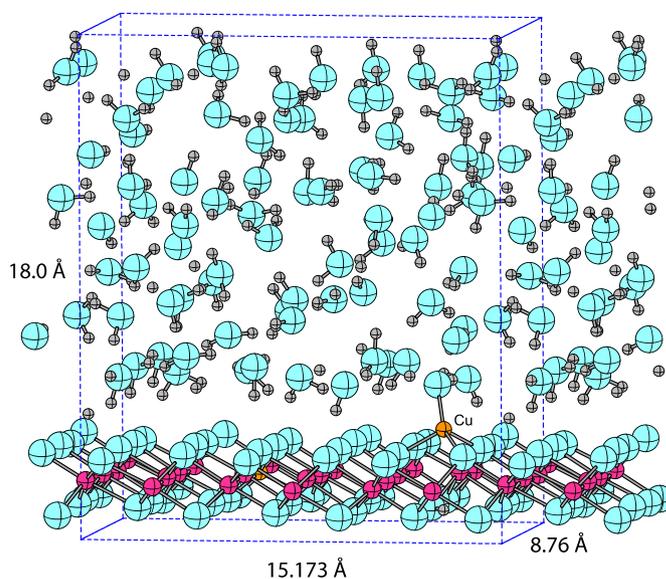
Fig. 1. Snapshot of periodic ab initio molecular dynamics simulation of Cu + 62 H_2O molecules and birnessite layer. The unit cell is indicated by the dashed blue lines and the cell parameters (fixed during the simulation) are given. Red atoms are Mn, blue are O, orange are Cu and grey are H. Note that Cu sorbed as a surface complex is associated with protonation of the MnO_2 oxygen at the base of the vacancy site. If the vacancy site oxygens are unprotonated, sorption occurs via structural incorporation. (For interpretation of the colours in the figure(s), the reader is referred to the web version of this article.)

as proposed by Kwon et al. (2013) and hypothesised by Manceau and Nagy (2015). Consequently, we calculated the vibrational partition functions for surface-complexed Cu on birnessite using the cluster shown in Fig. 2.

Aside from sorption by inner-sphere complexation over vacancy sites in birnessite, EXAFS of natural and synthetic Cu birnessite show that Cu also sorbs by incorporation into the manganate layer by occupying the vacancy site to give Cu in 6-fold coordination (e.g., Sherman et al., 2015); Little et al., 2014a). The fraction of vacancy site Cu increases with pH and comprises about 20% of total sorbed Cu at pH 8 in both synthetic (Sherman and Peacock, 2010) and natural (Little et al., 2014a) samples. Cu that is structurally incorporated is easily resolvable in the EXAFS because of the short Cu-Mn distance associated with this complex. However, this structural incorporation (Cu in vacancy site) is proceeded by the surface complex (Cu on vacancy site) and controlled by surface protonation (and varies by pH). As discussed below, the presence of 20-30% structural Cu at high pH will not detract from the conclusions about isotopic fractionation of Cu between dissolved and sorbed species.

As noted above, Peña et al. (2015) and Qin et al. (2017) have argued for Cu complexation on the edge sites of birnessite layers at high loading. Such complexes were not resolved in the EXAFS of synthetic Cu birnessite of (Sherman and Peacock, 2010) nor in the EXAFS of Cu in ferromanganese crusts investigated by Little et al. (2014a). Nevertheless, here we also determined the structure and vibrational modes of a Cu edge complex (Fig. 3). In the edge complex, Cu is in an approximately square-planer arrangement with an additional axial water molecule. Whether such a complex actually forms in marine ferromanganese crusts is unclear.

3.2. Predicted isotopic fractionation between Cu species

As discussed in Sherman (2013), aqueous Cu^{+2} is present as $Cu(H_2O)_5^{+2}$. In freshwater at pH 6, the free aquo-Cu complex is the dominant inorganic Cu species (Turner et al., 1981). However, in seawater inorganic Cu^{+2} is predominantly complexed by
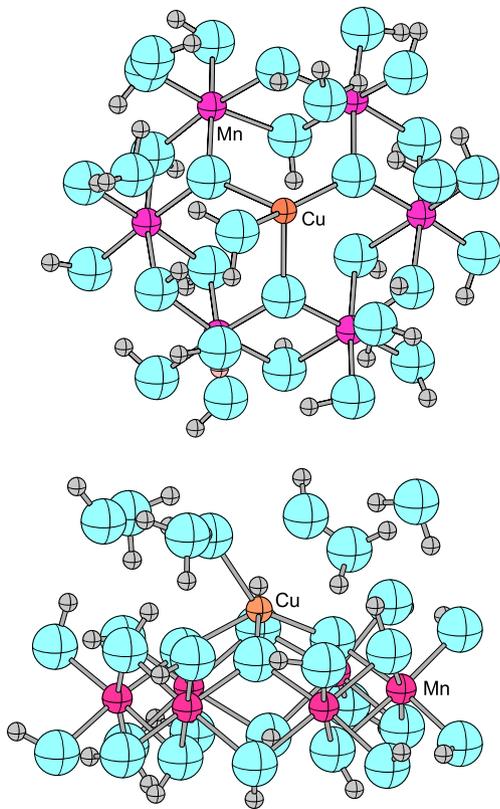
Fig. 2. Cluster used to optimise the structure of Cu complexed over vacancy site and for calculations of the vibrational frequencies.
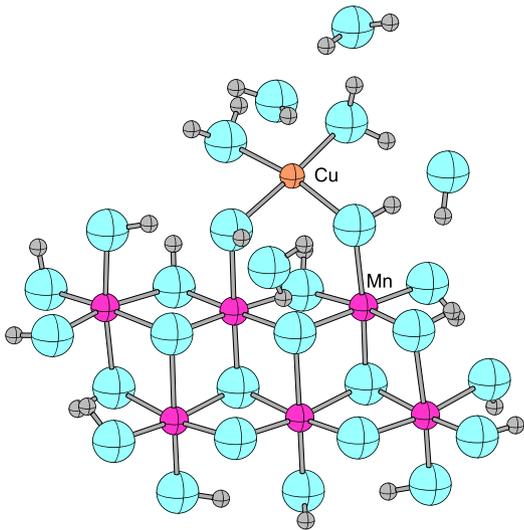

Fig. 3. Optimised structure of Cu edge-complex on birnessite.

CO_3^{-2} ions (Turner et al., 1981). Based on the stability constants in Powell et al. (2007), we calculate that the dominant inorganic complexes of Cu^{+2} in seawater are $CuCO_3^0$ (46%), $Cu(CO_3)_2^{-2}$ (21%) and $CuOH^+$ (17.5%). The structures, vibrational frequencies and reduced partition functions for these inorganic complexes were given in Sherman (2013), and from these we can evaluate $\Delta^{65/63}Cu$ for different Cu species relative to the $Cu(H_2O)_5^{+2}$ aquo complex. These are presented in Fig. 4.

Using the optimized cluster that models the surface complex of Cu on birnessite (Fig. 2), we predict a fractionation factor between $Cu(H_2O)_5^{+2}$ and Cu surface complexed on birnessite (Fig. 4). At 25 °C, and assuming all dissolved Cu is present as
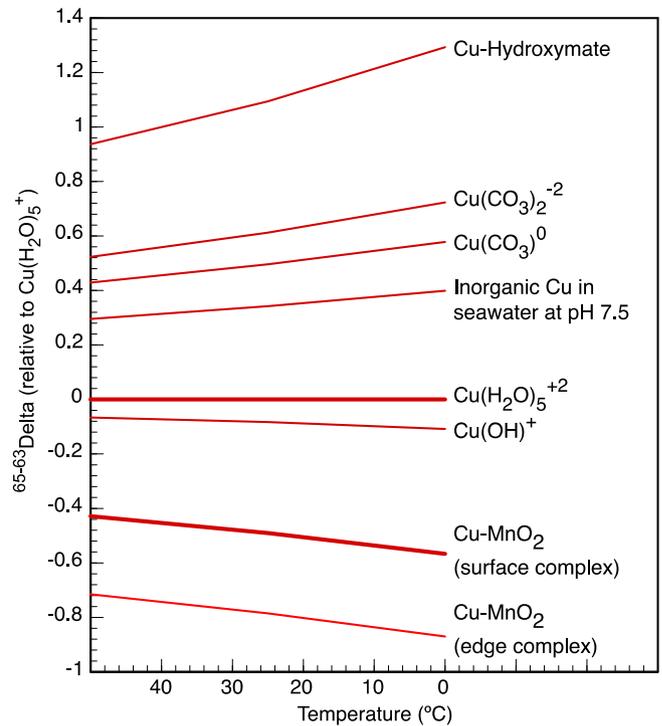

Fig. 4. Calculated isotopic fractionations between species relative to the Cu aquo complex $Cu(H_2O)_5^{+2}$.

the aqueous $Cu(H_2O)_5^{+2}$ complex, we predict that the fractionation between aqueous Cu (as $Cu(H_2O)_5^{+2}$ and surface-complexed Cu will be $\Delta^{65/63}Cu = 0.49‰$ (that is, birnessite will preferentially sorb the light isotope). Our result is in excellent agreement with recently obtained experimentally by Ijichi et al. (2018) where $\Delta^{65/63}Cu_{free-sorbed} = 0.45 \pm 0.18‰$ (n=12). This suggests that the experimental results were in isotopic equilibrium. The agreement between theoretical and experimental results also helps confirm the structural model for the Cu birnessite surface complex. Note that under the pH conditions ($\sim$6) of the experiments, the surface complex greatly dominates over the structural Cu in the birnessite layer (Sherman and Peacock, 2010). The edge-complex (Fig. 3) favours isotopically light Cu even more strongly (Fig. 4) than the surface complex (Fig. 2). The good agreement between the theoretical fractionation due to the surface vacancy complex and the observed fractionation measured by Ijichi et al. (2018), suggests that edge-complexes do not form under the experimental conditions used by Ijichi et al. (2018).

Given the equilibrium (thermodynamic) speciation of Cu in seawater at pH 7.5, we can evaluate the average $\Delta^{65/63}Cu$ between dissolved inorganic Cu in seawater (as 46% $CuCO_3^0$, 21% $Cu(CO_3)_2^{-2}$ and 17.5% $CuOH^+$) and the $Cu(H_2O)_5^{+2}$ complex (Fig. 3). We estimate that the isotopic composition of dissolved inorganic Cu in seawater should be +0.94‰ (at 5 °C) heavier than that of Cu^{+2} sorbed to birnessite via the surface complex over the vacancy site; i.e. complexation by inorganic ligands should enhance the fractionation between dissolved and scavenged Cu.

We had previously hypothesized that sorption of Cu on birnessite should result in the enrichment of heavy Cu isotopes in the surface complex (Little et al., 2014a), based on the change in coordination environment of the Cu^{2+} atom and the shortening of bond lengths between aqueous and sorbed Cu^{2+} (Kwon et al., 2013; Little et al., 2014a; Manceau and Nagy, 2015; Peña et al., 2015; Sherman and Peacock, 2010). However, experimental results (Ijichi et al., 2018) and the theoretical predictions obtained here show that qualitative predictions of isotopic fractionation based on

changes in coordination number and bond lengths are not reliable guides for the small degree of fractionation associated with metal sorption on manganese oxides.

4. Application to the Oceans

Analysis of the Cu isotope composition of seawater is challenging (Bermin et al., 2006; Vance et al., 2008; recently reviewed in Little et al., 2018). Nevertheless, recently collected data for different ocean basins from several laboratories converge on a homogeneous deep ocean Cu isotope composition of $+0.66 \pm 0.19‰$ (Baconnais et al., 2019; Boyle et al., 2012; Little et al., 2018; Takano et al., 2014; Thompson and Ellwood, 2014). By comparison to this seawater value, Fe-Mn crust and nodule samples are isotopically light (Albarède, 2004; Little et al., 2014b), implying an isotopic offset $\Delta^{65}Cu_{sw\text{-}fmc} \approx 0.35‰$. This result differs substantially (by 0.59‰) from the predicted inorganic fractionation. However, Cu speciation in seawater is not inorganically controlled. Instead, dissolved Cu is strongly complexed by organic ligands (e.g., Coale and Bruland, 1988; Moffett and Dupont, 2007). There is evidence that organic complexation of dissolved Cu is ubiquitous throughout the world oceans, including in deep waters, suggesting that Cu-binding ligands are refractory and long-lived (e.g., Heller and Croot, 2014; Jacquot and Moffett, 2015; Moffett and Dupont, 2007).

However, organic complexation cannot explain the discrepancy between the predicted inorganic isotopic fractionation and that observed in the oceans. Experiments and theory suggest that organic Cu-binding ligands preferentially complex heavy isotopes (Bigalke et al., 2010; Ryan et al., 2014; Sherman, 2013; Sherman et al., 2015). For example, Sherman (2013) and Sherman et al. (2015) find that organic ligands such as hydroxymate, malonate and histidine favour the heavy isotope over inorganic free Cu^{2+} ($\Delta^{65}Cu_{complex\text{-}free}$) by $+0.75$ to $1.5‰$. If such ligands are indicative of those in the marine environment, then the equilibrium fractionation between dissolved Cu in seawater and sorbed Cu in birnessite should be as high as $\Delta^{65/63}Cu_{sw\text{-}fmc} = +1.7$ to $2.4‰$.

In experiments using a Donnan membrane, Ryan et al. (2014) found a strong correlation between the logarithms of the stability constants (log K) of organic Cu complexes with the magnitude of isotope fractionation, with $\Delta^{65}Cu_{complex\text{-}free}$ values ranging from $+0.14$ to $+0.84‰$ for a range of log K of 8 to 25. Given the typical range of published conditional stability constants for Cu-binding ligands in seawater, at about 11.5 to 14 (Coale and Bruland, 1988; Heller and Croot, 2014; Leal and Van Den Berg, 1998; Moffett and Dupont, 2007), this relationship implies a $\Delta^{65/63}Cu_{complex\text{-}free}$ in seawater of approximately $+0.2$ to $0.5‰$ (Ryan et al., 2014). Even with these smaller degrees of isotopic fractionation, we would still predict that the equilibrium fractionation between dissolved (organically complexed) and Cu sorbed to ferromanganese crusts should be much greater than that observed, at $+1.1$ to $1.6‰$.

Our predicted isotopic fractionation of Cu sorbed to birnessite neglects the contribution of Cu occupying the vacancy site in the birnessite structure. In both synthetic birnessite near pH 8 (Sherman and Peacock, 2010) and natural marine ferromanganese crusts (Little et al., 2014a), structural Cu comprises about 20-30% of total sorbed Cu. Structural Cu would be isotopically heavier than surface complexed Cu. However, any isotopic fractionation between surface-complexed and structurally incorporated Cu cannot explain the observed $\Delta^{65/63}Cu_{sw\text{-}fmc}$ fractionation unless the fractionation between surface complexed and structurally incorporated Cu is greater than 3‰. Such a large fractionation between surface complexed and structurally incorporated Cu is physically unreasonable; fractionations of such magnitude require a change in oxidation state (Cu^+ vs. Cu^{+2}) or a drastic change in the ligand (Cl^- vs OH^-) in the Cu coordination environment (Sherman, 2013). Moreover, if dissolved Cu in the oceans is complexed by organic ligands, the fractionation between surface-complexed and structural Cu would need to be on the order of 6‰ if the observed bulk $\Delta^{65/63}Cu_{sw\text{-}fmc}$ reflects isotopic equilibrium.

Thus, the rather small $\Delta^{65}Cu_{sw\text{-}fmc}$ offset presents a paradox, suggesting that Cu in Fe-Mn crusts is out of isotopic equilibrium with deep seawater – a surprising finding. It is possible that natural organic Cu ligands in seawater are not associated with isotopic fractionation, but we consider this unlikely, given the lines of experimental and theoretical evidence suggesting otherwise (Bigalke et al., 2010; Ryan et al., 2014; Sherman, 2013; Sherman et al., 2015; Fujii et al., 2013).

Interestingly, the labile (leachable) fraction of oceanic particulate matter has an isotopic composition very similar (at about $+0.4‰$; Little et al., 2018) to that observed in Fe-Mn crusts. In fact, similar $\delta^{65}Cu$ values (at about $+0.3‰$) have been observed in the authigenic fraction of all marine sediments analyzed to date (Little et al., 2017). One possibility to explain the small $\Delta^{65}Cu_{sw\text{-}fmc}$ offset, therefore, is that the primary source of Cu to Fe-Mn crusts is not seawater, but sinking particulate organic matter (POM), and that Fe-Mn crusts retain Cu that is released from these organic-rich particles during oxic diagenesis without isotopic fractionation. However, very little POM survives the transit from its production in the sunlit upper ocean to the deep sea (e.g., Martin et al., 1987), and we consider it unlikely that sinking POM is the dominant supply route of Cu to Fe-Mn coatings.

Little et al. (2017) proposed two alternative explanations for the observed consistent isotopic offset between authigenic and seawater Cu. First, they suggest an equilibrium isotope fractionation between isotopically heavy Cu complexed to strong organic ligands and isotopically light Cu sorbed to particles (Little et al., 2017). However, for sorption to birnessite, we have shown that such an equilibrium isotope fractionation should lead to $\Delta^{65}Cu_{sw\text{-}fmc} = +1.1$ to $2.4‰$, much larger than observed in the ocean (at about $+0.35‰$). Second, Little et al. (2017) suggest equilibrium isotope fractionation in the aqueous phase between an isotopically heavy ligand-bound pool and the particle reactive free Cu^{2+} species, followed by quantitative scavenging of the free Cu^{2+} species by particulates (of any type). Experimental estimates for $\Delta^{65/63}Cu_{complex\text{-}free}$, of $+0.2$ to $0.5‰$ at the log K of typical seawater ligands (Ryan et al., 2014), would be consistent with observed oceanic $\Delta^{65/63}Cu_{sw\text{-}fmc}$ (at about $+0.35‰$). The concentration of free Cu^{2+} is very low in seawater (e.g., Jacquot and Moffett, 2015) so quantitative (and irreversible?) scavenging of this species to Fe-Mn crusts is plausible, if somewhat surprising, given their slow-growth rates.

Another possible resolution to the paradox is that the inorganic isotope fractionation factor for Cu sorption on birnessite is not expressed because Fe-Mn coatings are not purely inorganic precipitates. Diverse communities of microbial life have been found living in and on marine Fe-Mn coatings and nodules (e.g., Shiraishi et al., 2016; Tully and Heidelberg, 2013; Blöthe et al., 2015). Rates of biological Mn(II) oxidation are orders of magnitude higher than those of inorganic oxidation, and most known Mn oxidisers are thought to use multicopper oxidase enzymes (e.g., Tebo et al., 2004), which would be supported by the high Cu content of marine Fe-Mn nodules (Shiraishi et al., 2016).

Structurally, Mn biooxides are closely related to synthetic δ-MnO_2 (Villalobos et al., 2003), which is also the dominant form of Mn oxide found in Fe-Mn coatings (Post, 1999). This structural similarity implies a similar Cu sorption mechanism on synthetic and bio-δ-MnO_2, and similar isotopic fractionation; indeed, similar binding mechanisms have been observed for Fe-Mn crusts and in synthetic sorption experiments (Sherman and Peacock, 2010; Little et al., 2014b). However, an important difference between biooxides and inorganic δ-MnO_2 may be the presence of extracellular polymeric substances (EPS) produced by Mn(II) oxidising bacteria,

which can affect the sorptive properties of the biooxide (Tebo et al., 2004). The presence of EPS may also influence the isotopic fractionation associated with Cu sorption (Coutaud et al., 2018), even if the ultimate mineral binding site of the Cu is apparently unaffected (Little et al., 2014a).

To summarise, we make the surprising finding that Cu in Fe-Mn crusts appears to be in isotopic disequilibrium with deep seawater. We suggest that this finding may be due to: a) quantitative scavenging of the free Cu^{2+} species, the latter being isotopically light due to strong organic complexation of Cu in seawater, or b) the possibility that the inorganic fractionation factor on sorption to birnessite is not expressed because Mn(II) oxidation is mediated by microorganisms. If the diversity of scavenging particles in the ocean are either organic-rich or organic-coated (e.g., Mn biooxides coating with EPS), it is plausible that, isotopically, they may behave alike. Future work should investigate the isotopic fractionation associated with biooxides, with incorporation of Cu into the birnessite mineral structure, and with other prevalent marine Mn oxide phases (e.g., todorokite). In addition, it should investigate the isotopic fractionation associated with natural organic ligands, for example, those produced by organisms in culture.

CRediT authorship contribution statement

David M. Sherman: Conceptualization, Methodology, Investigation, Calculations, Software, Writing, Visualization. **Susan H. Little:** Conceptualization, Investigation, Writing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2020.116540.

References

Albarède, F., 2004. The stable isotope geochemistry of copper and zinc. Rev. Mineral. Geochem. 55, 409–427. https://doi.org/10.2138/gsrmg.55.1.409.

Amira, S., Spångberg, D., Hermansson, K., 2005. Distorted five-fold coordination of Cu^{2+}(*aq*) from a Car–Parrinello molecular dynamics simulation. Phys. Chem. Chem. Phys. 7, 2874–2880.

Baconnais, I., Rouxel, O., Dulaquais, G., Boye, M., 2019. Determination of the copper isotope composition of seawater revisited: a case study from the Mediterranean Sea. Chem. Geol. 511, 465–480. https://doi.org/10.1016/j.chemgeo.2018.09.009.

Bermin, J., Vance, D., Archer, C., Statham, P.J., 2006. The determination of the isotopic composition of Cu and Zn in seawater. Chem. Geol. 226, 280–297. https://doi.org/10.1016/j.chemgeo.2005.09.025.

Bigalke, M., Weyer, S., Wilcke, W., 2010. Copper isotope fractionation during complexation with insolubilized humic acid. Environ. Sci. Technol. 44, 5496–5502. https://doi.org/10.1021/es1017653.

Bigeleisen, J., Mayer, M.G., 1947. Calculation of the equilibrium constants for isotopic exchange reactions. J. Chem. Phys. 15, 261–267.

Blöthe, M., Wegorzewski, A., Müller, C., Simon, F., Kuhn, T., Schippers, A., 2015. Manganese-cycling microbial communities inside deep-sea manganese nodules. Environ. Sci. Technol. 49, 7692–7700. https://doi.org/10.1021/es504930v.

Boyle, E.A., John, S., Abouchami, W., Adkins, J.F., Echegoyen-Sanz, Y., Ellwood, M., Flegal, A.R., Fornace, K., Gallon, C., Galer, S., Gault-Ringold, M., Lacan, F., Radic, A., Rehkamper, M., Rouxel, O., Sohrin, Y., Stirling, C., Thompson, C., Vance, D., Xue, Z., Zhao, Y., 2012. GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration. Limnol. Oceanogr., Methods 10, 653–665. https://doi.org/10.4319/lom.2012.10.653.

Bruland, K.W., Middag, R., Lohan, M.C., 2013. Controls of Trace Metals in Seawater, second edition. Treatise on Geochemistry. Elsevier Ltd.

Coale, K.H., Bruland, K.W., 1988. Copper complexation in the northest Pacific. Limnol. Oceanogr. 33, 1084–1101.

Coutaud, M., Méheut, M., Glatzel, P., Pokrovski, G.S., Viers, J., Rols, J.L., Pokrovsky, O.S., 2018. Small changes in Cu redox state and speciation generate large isotope fractionation during adsorption and incorporation of Cu by a phototrophic biofilm. Geochim. Cosmochim. Acta 220, 1–18. https://doi.org/10.1016/j.gca.2017.09.018.

Fujii, T., Moynier, F., Abe, M., Nemoto, K., Albarède, F., 2013. Copper isotope fractionation between aqueous compounds relevant to low temperature geochemistry and biology. Geochim. Cosmochim. Acta 110, 29–44. https://doi.org/10.1016/j.gca.2013.02.007.

Heller, M.I., Croot, P.L., 2014. Copper speciation and distribution in the Atlantic sector of the Southern Ocean. Mar. Chem. 173, 253–268. https://doi.org/10.1016/j.marchem.2014.09.017.

Ijichi, Y., Ohno, T., Sakata, S., 2018. Copper isotopic fractionation during adsorption on manganese oxide: effects of pH and desorption. Geochem. J. 52, e1–e6. https://doi.org/10.2343/geochemj.2.0516.

Jacquot, J.E., Moffett, J.W., 2015. Copper Distribution and Speciation Across the International GEOTRACES Section GA03. Deep. Res. Part II Top. Stud. Oceanogr., vol. 116, pp. 187–207.

Klamt, A., Schurrmann, G., 1993. COSMO - a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. J. Chem. Soc., Perkin Trans. 2, 799–805.

Koschinsky, A., Hein, J.R., 2003. Uptake of elements from seawater by ferromanganese crusts: solid-phase associations and seawater speciation. Mar. Geol. 198, 331–351. https://doi.org/10.1016/S0025-3227(03)00122-1.

Kwon, K.D., Refson, K., Sposito, G., 2013. Understanding the trends in transition metal sorption by vacancy sites in birnessite. Geochim. Cosmochim. Acta 101, 222–232. https://doi.org/10.1016/j.gca.2012.08.038.

Leal, M.F.C., Van Den Berg, C.M.G., 1998. Evidence for strong copper(I) complexation by organic ligands in seawater. Aquat. Geochem. 4, 49–75.

Little, S.H., Archer, C., Milne, A., Schlosser, C., Achterberg, E.P., Lohan, M.C., Vance, D., 2018. Paired dissolved and particulate phase Cu isotope distributions in the South Atlantic. Chem. Geol. 502, 29–43. https://doi.org/10.1016/J.CHEMGEO.2018.07.022.

Little, S.H., Sherman, D.M., Vance, D., Hein, J.R., 2014a. Molecular controls on Cu and Zn isotopic fractionation in Fe-Mn crusts. Earth Planet. Sci. Lett. 396. https://doi.org/10.1016/j.epsl.2014.04.021.

Little, S.H., Vance, D., Walker-Brown, C., Landing, W.M., 2014b. The oceanic mass balance of copper and zinc isotopes, investigated by analysis of their inputs, and outputs to ferromanganese oxide sediments. Geochim. Cosmochim. Acta 125, 673–693. https://doi.org/10.1016/j.gca.2013.07.046.

Little, S.H., Vance, D., McManus, J., Severmann, S., Lyons, T.W., 2017. Copper isotope signatures in modern marine sediments. Geochim. Cosmochim. Acta 212, 253–273. https://doi.org/10.1016/j.gca.2017.06.019.

Manceau, A., Nagy, K.L., 2015. Comment on "Molecular controls on Cu and Zn isotopic fractionation in Fe-Mn crusts" by Little et al. Earth Planet. Sci. Lett. 411, 310–312. https://doi.org/10.1016/j.epsl.2014.12.028.

Manceau, A., Lanson, M., Takahashi, Y., 2014. Mineralogy and crystal chemistry of Mn, Fe, Co, Ni, and Cu in a deep-sea Pacific polymetallic nodule. Am. Mineral. 99, 2068–2083.

Martin, J.H., Knauer, G.A., Karl, D.M., Broenkow, W.W., 1987. VERTEX: carbon cycling in the northeast Pacific. Deep-Sea Res. 34, 267–285.

Moffett, J.W., Dupont, C., 2007. Cu complexation by organic ligands in the sub-Arctic NW Pacific and Bering Sea. Deep-Sea Res., Part 1, Oceanogr. Res. Pap. 54, 586–595. https://doi.org/10.1016/j.dsr.2006.12.013.

Navarrete, J.U., Borrok, D.M., Viveros, M., Ellzey, J.T., 2011. Copper isotope fractionation during surface adsorption and intracellular incorporation by bacteria. Geochim. Cosmochim. Acta 75, 784–799.

Pasquarello, A., Petri, I., Salmon, P.S., Parisel, O., Car, R., Tóth, É., Powell, D.H., Fischer, H.E., Helm, L., Merbach, A.E., 2001. First solvation shell of the Cu (II) aqua ion: evidence for fivefold coordination. Science 80 (291), 856–859.

Peña, J., Bargar, J.R., Sposito, G., 2015. Copper sorption by the edge surfaces of synthetic birnessite nanoparticles. Chem. Geol. 396, 196–207. https://doi.org/10.1016/j.chemgeo.2014.12.021.

Perdew, J.P., Burke, K., Ernzerhof, M., 1996. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868.

Pokrovsky, O.S., Viers, J., Emnova, E.E., Kompantseva, E.I., Freydier, R., 2008. Copper isotope fractionation during its interaction with soil and aquatic microorganisms and metal oxy(hydr)oxides: possible structural control. Geochim. Cosmochim. Acta 72, 1742–1757. https://doi.org/10.1016/j.gca.2008.01.018.

Post, J.E., 1999. Manganese oxide minerals: crystal structures and economic and environmental significance. Proc. Natl. Acad. Sci. USA 96, 3447–3454.

Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Sjöberg, S., Wanner, H., 2007. Chemical speciation of environmentally significant metals with inorganic ligands Part 2: The Cu2+-OH-, Cl-, CO32-, SO42-, and PO43- systems (IU-PAC Technical Report). Pure Appl. Chem. 79, 895–950. https://doi.org/10.1351/pac200779050895.

Qin, Z., Xiang, Q., Liu, F., Xiong, J., Koopal, L.K., Zheng, L., Ginder-Vogel, M., Wang, M., Feng, X., Tan, W., Yin, H., 2017. Local structure of Cu^{2+} in Cu-doped hexagonal turbostratic birnessite and Cu2 + stability under acid treatment. Chem. Geol. 466, 512–523. https://doi.org/10.1016/j.chemgeo.2017.06.040.

Ryan, B.M., Kirby, J.K., Degryse, F., Scheiderich, K., McLaughlin, M.J., 2014. Copper isotope fractionation during equilibration with natural and synthetic ligands. Environ. Sci. Technol. 48, 8620–8626. https://doi.org/10.1021/es500764x.

Sherman, D.M., 2013. Equilibrium isotopic fractionation of copper during oxidation/reduction, aqueous complexation and ore-forming processes: predictions from hybrid density functional theory. Geochim. Cosmochim. Acta 118, 85–97. https://doi.org/10.1016/j.gca.2013.04.030.

Sherman, D.M., Little, S.H., Vance, D., 2015. Reply to comment on "Molecular controls on Cu and Zn isotopic fractionation in Fe–Mn crusts". Earth Planet. Sci. Lett. 411, 313–315. https://doi.org/10.1016/j.epsl.2014.12.027.

Sherman, D.M., Peacock, C.L., 2010. Surface complexation of Cu on birnessite (δ-MnO_2): controls on Cu in the deep ocean. Geochim. Cosmochim. Acta 74, 6721–6730. https://doi.org/10.1016/j.gca.2010.08.042.

Shiraishi, F., Mitsunobu, S., Suzuki, K., Hoshino, T., Morono, Y., Inagaki, F., 2016. Dense microbial community on a ferromanganese nodule from the ultra-oligotrophic South Pacific gyre: implications for biogeochemical cycles. Earth Planet. Sci. Lett. 447, 10–20. https://doi.org/10.1016/j.epsl.2016.04.021.

Takano, S., Tanimizu, M., Hirata, T., Sohrin, Y., 2014. Isotopic constraints on biogeochemical cycling of copper in the ocean. Nat. Commun. 5, 5663. https://doi.org/10.1038/ncomms6663.

te Velde, G., Bickelhaupt, F.M., Baerends, E.J., Fonseca Guerra, C., van Gisbergen, S.J.A., Snijders, J.G., Ziegler, T., 2001. Chemistry with ADF. J. Comput. Chem. 22, 931–967.

Tebo, B.M., Bargar, J.R., Clement, B.G., Dick, G.J., Murray, K.J., Parker, D., Verity, R., Webb, S.M., 2004. Biogenic manganese oxides: properties and mechanisms of formation. Annu. Rev. Earth Planet. Sci. 32, 287–328. https://doi.org/10.1146/annurev.earth.32.101802.120213.

Thompson, C.M., Ellwood, M.J., 2014. Dissolved copper isotope biogeochemistry in the Tasman Sea, SW Pacific Ocean. Mar. Chem. 165, 1–9. https://doi.org/10.1016/j.marchem.2014.06.009.

Tully, B.J., Heidelberg, J.F., 2013. Microbial communities associated with ferro-manganese nodules and the surrounding sediments. Front. Microbiol. 4, 1–10. https://doi.org/10.3389/fmicb.2013.00161.

Turner, D.R., Whitfield, M., Dickson, A.G., 1981. The equilibrium speciation of dissolved components in freshwater and sea water at 25°C and 1 atm pressure. Geochim. Cosmochim. Acta 45, 855–881. https://doi.org/10.1016/0016-7037(81)90115-0.

Van Lenthe, E., Baerends, E.J., 2003. Optimized slater-type basis sets for the elements 1-118. J. Comput. Chem. 24, 1142–1156.

Vance, D., Archer, C., Bermin, J., Perkins, J., Statham, P., Lohan, M., Ellwood, M., Mills, R., 2008. The copper isotope geochemistry of rivers and the oceans. Earth Planet. Sci. Lett. 274, 204–213. https://doi.org/10.1016/j.epsl.2008.07.026.

VandeVondele, J., Hutter, J., 2007. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. J. Chem. Phys. 127, 114105.

VandeVondele, J., Krack, M., Mohamed, F., Parrinello, M., Chassaing, T., Hutter, J., 2005. Quickstep: fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. Comput. Phys. Commun. 167.

Villalobos, M., Toner, B., Bargar, J., Sposito, G., 2003. Characterization of the manganese oxide produced by pseudomonas putida strain MnB1. Geochim. Cosmochim. Acta 67, 2649–2662. https://doi.org/10.1016/S0016-7037(03)00217-5.