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Copper isotope fractionation between aqueous compounds relevant to low temperature geochemistry and biology

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Abstract:

Isotope fractionation between the common Cu species present in solution (Cu^{+}, Cu^{2+}, hydroxide, chloride, sulfide, carbonate, oxalate, and ascorbate) has been investigated using both *ab initio* methods and experimental solvent extraction techniques. In order to establish unambiguously the existence of equilibrium isotope fractionation (as opposed to kinetic isotope fractionation), we first performed laboratory-scale liquid-liquid distribution experiments. Upon exchange between HCl medium and a macrocyclic complex, the $^{65}Cu/^{63}Cu$ ratio fractionated by –1.06 to –0.39‰. The acidity dependence of the fractionation was appropriately explained by ligand exchange reactions between hydrated H_2O and Cl^{-} via intramolecular vibrations. The magnitude of the Cu isotope fractionation among important Cu ligands was also estimated by *ab initio* methods. The magnitude of the nuclear field shift effect to the Cu isotope fractionation represents only ~3% of the mass-dependent fractionation. The theoretical estimation was expanded to chlorides, hydroxides, sulfides, sulfates, and carbonates under different conditions of pH. Copper isotope fractionation of up to 2‰ is expected for different forms of Cu present in seawater and for different sediments (carbonates, hydroxides, and sulfides). We found that Cu in dissolved carbonates and sulfates is isotopically much heavier (+0.6‰) than free Cu. Isotope fractionation of Cu in hydroxide is minimal. The relevance of these new results to the understanding of metabolic processes was also discussed. Copper is an essential element used by a large number of proteins for electron transfer. Further theoretical estimates of $\delta^{65}Cu$ in hydrated Cu(I) and Cu(II) ions, Cu(II) ascorbates, and Cu(II) oxalate predict Cu isotope fractionation during the breakdown of ascorbate into oxalate and account for the isotopically heavy Cu found in animal kidneys.

Keywords: Copper, Cupric, isotope fractionation, ligand, quantum chemical calculation

1. INTRODUCTION

Copper has two stable isotopes, ^{63}Cu and ^{65}Cu, with respective average abundances of 69.174% and 30.826% in the reference metal SRM-NIST 976 (Shields et al., 1964). Variations of Cu isotope abundances in natural samples were identified by Walker et al. (1958) using thermal ionization mass spectrometry, but the variability of the mass bias at that time was too large with respect to the natural isotopic availability to qualify Cu isotopes as a potential geochemical or biochemical tracer. The advent of inductively-coupled plasma mass spectrometry (ICP-MS) instruments equipped with a magnetic sector and multiple collection made precise isotopic analysis of Cu possible (Albarède, 2004). Maréchal et al. (1999) published the first measurements of Cu isotope compositions in a variety of minerals and biological materials. The broad range of isotopic variations in Cu ores observed previously (Walker et al. 1958; Shields et al., 1965) was confirmed by subsequent work (Maréchal et al., 1999; Zhu et al., 2000; Albarède, 2004; Klein et al., 2009). Hereafter, the δ notation with

$$\delta^{65}Cu = \left(\frac{([^{65}Cu]/[^{63}Cu])_{sample}}{([^{65}Cu]/[^{63}Cu])_{reference}} - 1 \right) \times 1000 \quad (1)$$

is used throughout.

The narrow range of Cu isotope variation in basalts (Ben Othman et al., 2006; Archer and Vance, 2004; Herzog et al., 2009; Li et al., 2009; Moynier et al., 2010; Bishop et al., 2012) and granites (Li et al., 2009) suggests that high-temperature magmatic processes do not induce large Cu isotope fractionation. As a consequence, it makes Cu isotopes a tracer of choice for the study of sediments and more generally for

73 low-temperature processes such as those involved in soil formation (Bigalke et al., 2010,
74 2011) and in biology (Balter and Zarro, 2011; Weinstein et al., 2011).

75 Substantial isotope fractionation during chemical exchange reactions occurs at
76 room temperature and reflects isotopic differences between the equilibrium constants of
77 Cu isotopologues. Enrichment in ^{65}Cu of up to 0.8‰ was observed during the
78 chromatographic elution of compounds (Matin et al., 1998; Maréchal et al., 1999, 2002;
79 Zhu et al., 2002). The same technique demonstrates isotope fractionation of ~0.4‰
80 upon chromatographic separation of Cu(I) from Cu(II) (Matin et al., 1998; Zhu et al.,
81 2002).

82 At low temperature, Cu isotopic abundances are also affected by inorganic
83 surface processes (physical adsorption/desorption). Isotope separation of up to a few
84 permil upon adsorption/desorption of Cu onto/from inorganic and organic substrates
85 was observed by several groups (Mathur et al., 2005; Balistrieri et al., 2008; Pokrovsky
86 et al., 2008; Navarette et al., 2011).

87 Copper plays very important roles in biology (Lippard and Berg, 1994). The
88 metal centers of the 'blue' copper proteins are divided according to the coordination of
89 the Cu ion into three types that contain one or more copper ions as prosthetic groups
90 (Cowan, 1997). In plastocyanine, cysteine, histidine, and methionine 'residues' bind to
91 Cu and this plays a major role for electron transfer (redox reactions) (Freeman and Guss,
92 2001). In humans, ceruloplasmin is a ferroxidase enzyme involved in the iron cycle,
93 cytochrome c oxidase is involved in electron transfer across the membrane of
94 mitochondrion, and superoxide dismutase protects cells against superoxide. Blue (Cu)
95 proteins are ubiquitous and characterized by their multiple ways of bonding with amino
96 acids. (Cowan, 1997). Coupling of Fe and Cu isotope fractionation has been identified

97 in human blood components (Albarède et al., 2011a) and in mammals (Balter and Zazzo,
98 2011; Albarede et al., 2011b). Depletion of δ^{65}Cu at the permil level was found in plants
99 with respect to soils or nutrient solutions (Weinstein et al., 2011; Jouvin et al., 2012).
100 δ^{65}Cu in enzymes is a few permil negative compared with the Cu isotopic composition
101 of the host soil (Zhu et al., 2002). Positive δ^{65}Cu values up to 1.5‰ also were found in
102 the kidneys of sheep (Balter and Zazzo, 2011) and mice (Albarede et al., 2011b).
103 Contrary to Fe (Hill et al., 2010; Rustad et al., 2010, and references therein), Ni
104 (Fujii et al., 2011a), and Zn (Fujii et al, 2010,2011b; Black et al., 2011; Pons et al.,
105 2011; Fujii and Albarède, 2012), the theoretical prediction of Cu isotope fractionation
106 among ligands (simple inorganic ligands like halide, sulfate, and phosphate ions, and
107 more complex organic ligands as humic acids and phytoplankton exometabolites) in
108 natural waters and biological fluids has only received minimal attention, which is a
109 major hindrance for an informed interpretation of observations. This is the main
110 motivation for the present work.
111 We first demonstrate that equilibrium isotope fractionation of Cu(II) does take
112 place in laboratory-scale experiments. In parallel, we calculated the molecular orbitals
113 of the corresponding Cu species to obtain the reduced partition function ratio (RPFR) of
114 isotopologues. The *ab initio* calculations were then extended to hydrated Cu(II)
115 complexes, hydroxide, sulfate, carbonate, ascorbate, and oxalate. The choice of
116 ascorbate and oxalate was motivated by evidence of isotopically heavy Cu in the
117 kidneys of sheep (Balter and Zazzo, 2011) and mice (Albarède et al., 2011b). Ascorbate
118 is allegedly catabolized into oxalic acid (Chai et al., 2004; Massey et al., 2005;
119 González et al., 2005), which makes some patients develop a condition known as
120 hyperoxaluria and develop kidney stones, a calcium oxalate. The oxalate anions are

known to be strong complexing ligands of Cu(II) (Hayakawa et al., 1973), while ascorbate oxidase, which oxidizes ascorbate into dehydroascorbate (Solomon et al., 1996) is a bis(histidine)copper(II) compound. Applications of our calculations to the understanding of Cu isotope variability in marine sediments and to biological samples are briefly outlined.

2. METHODS

2.1. Extraction experiments and isotopic analyses

Dicyclohexano-18-crown-6 (DC18C6) (>97% purity) is a product of Fluka Chemie GmbH and Cu dichloride (hydrated, 99.9% purity) is a product of Wako Pure Chemical Industries, Ltd. Hydrochloric acid, in which the Cu impurity was certified to be less than 1.9 ppt, was purchased from Kanto Chemical, Co., Inc. Other chemicals were reagent grade.

$CuCl_2 \cdot 2H_2O$ was dissolved in HCl to prepare solutions of 0.1 mol dm^{-3} (M) Cu(II) in 1 to 6 M HCl. DC18C6 was dissolved in 1,2-dichloroethane to prepare a solution of 0.1 M DC18C6. Ten mL aqueous solution were combined with 15 mL organic solution in a glass vial, which was sealed. The two phases were stirred for 30 minutes using a Teflon-coated magnetic bar. After equilibrium was achieved, the two phases were separated by centrifugation at 2,000 rpm for 1 min, and an aliquot of the aqueous solution taken for analysis. A 10 mL aliquot of the organic solution was saved for back extraction of Cu in 15 mL of 0.02 M HCl. The extracted Cu was fully (>98%) recovered in this procedure. All these steps were carried out at 298 K. Copper concentrations in the equilibrated aqueous phase and the back extraction solution were determined by inductively-coupled plasma atomic-emission spectrometry (Thermo

145 Fisher Scientific, iCAP 6300 Duo). Aliquots of these solutions were saved for isotopic
146 analysis.

147 Organic impurities carried over from the extraction step were separated from
148 Cu on AGMP1 anion exchange resin in 7 M HCl as described in Maréchal et al. (1999).
149 Copper isotopic compositions were measured on a Thermo-Finnigan Neptune
150 MC-ICP-MS at Washington University in St. Louis. The samples were introduced by
151 free aspiration in 0.1 M HNO_3 using a Teflon microcentric nebulizer (uptake rate of 100
152 μL/min) and a glass cyclonic spray chamber. Masses 63 and 65 were positioned on the
153 L2 and axial collectors, respectively. Intensities of Zn isotopes (64, 66, 67 and 68) were
154 measured on the collectors L1, H1, H2, H3, respectively. The intensity of ^{62}Ni was
155 monitored in order to correct for the potential interference of ^{64}Ni. Instrumental mass
156 fractionation was corrected by both Zn doping and standard-sample bracketing
157 (Maréchal et al., 1999; Albarède, 2004). The typical external reproducibility of replicate
158 analyses of the same samples carried out during different analytical sessions is 0.10‰
159 (2σ) for $\delta^{65}Cu$.

160

161 **2.2. Computational methods**

162 Orbital geometries and vibrational frequencies of aqueous Cu(II) species were
163 computed using the density functional theory (DFT) as implemented by the Gaussian09
164 code (Frisch et al., 2009; Dannington et al., 2009). The DFT method employed here is a
165 hybrid density functional consisting of Becke's three-parameter non-local hybrid
166 exchange potential (B3) (Becke, 1993) with Lee-Yang-and Parr (LYP) (Lee et al., 1988)
167 non-local functionals. Using the 6-311+G(d,p) basis set or higher is recommended for
168 calculating the Cu complexes by de Bruin et al. (1999). The 6-311+G(d,p) basis set,

which is an all-electron basis set, was therefore chosen for H, C, O, S, Cl, and Cu. Molecules were modeled without any forced symmetry. An 'ultrafine' numerical integration grid was used and the SCF (self-consistent field) convergence criterion was set to 10^{-9}.

The isotope enrichment factor due to intramolecular vibrations can then be evaluated from the reduced partition function ratio (*s*/*s*')*f* (Bigeleisen and Mayer, 1947), also noted β,

$$ln\frac{s}{s'}f = \sum\left[ln\,b(u_i') - ln\,b(u_i)\right] \tag{2}$$

where

$$ln\,b(u_i) = -ln\,u_i + \frac{u_i}{2} + ln\left(1 - e^{-u_i}\right) \tag{3}$$

and

$$u_i = \frac{h\nu_i}{kT} \tag{4}$$

in which ν stands for vibrational frequency, *s* for the symmetry number of the Cu compound, *h* the Planck constant, *k* the Boltzmann constant, and *T* the absolute temperature. The subscript *i* denotes the *i*th mode of molecular vibration, and primed variables refer to the light isotopologue. The isotope enrichment factor due to molecular vibrations can be evaluated from the frequencies (ν) summed over all the different modes. The isotopic difference in the stability constant of chemical reactions is identical to the difference of ln β between related species. For example, a chemical exchange reaction,

$$Cu^{2+} + Cl^- \rightleftarrows CuCl^+, \quad K_{CuCl^+} \tag{5}$$

187

188 with stability constant K_{CuCl^+}, the isotope fractionation between the hydrated Cu^{2+} and

189 $CuCl^+$ is,

$$\ln \frac{K_{CuCl^+}(^{65}Cu)}{K_{CuCl^+}(^{63}Cu)} = \ln \frac{[^{65}CuCl^+]/[^{63}CuCl^+]}{[^{65}Cu^{2+}]/[^{63}Cu^{2+}]}$$

190

$$= \ln \beta_{CuCl^+} - \ln \beta_{Cu^{2+}} \quad (6)$$

191

192 Isotope fractionation also results from the mass-independent nuclear field shift

193 effect (Bigeleisen, 1996; Nomura et al., 1996, Fujii et al. 2009) which is an

194 isotope-dependent shift reflecting that the electronic orbitals do not vanish at the

195 nucleus and depends on the nuclear size and shape (King, 1984). The latest version of

196 quantum chemical models have taken finite-size nuclei into account in *ab initio*

197 calculations (Schauble, 2007; Abe et al., 2008, 2010; Fujii et al., 2010, 2011a,c,d). For

198 light elements such as Ni (Fujii et al., 2011a) and Zn (Fujii et al., 2010), the nuclear

199 field shift effect was found to be small as 0.02-0.03‰/amu. The isotope enrichment

200 factor via the nuclear field shift ($\ln K_{fs}$) is given by

201

$$\ln K_{fs} = \frac{hc}{kT} \nu_{fs} \quad (7)$$

202

203 where ν_{fs} is the nuclear field shift and c the velocity of light.

204 The contribution of the nuclear volume was estimated by the Dirac-Coulomb

205 Hartree-Fock (DCHF) method implemented in the UTChem program (see references in

206 Abe et al., 2008, 2010). We calculated the electronic structure of Cu^0([Ar]3d^{10}4s^1),
207 Cu^+([Ar]3d^{10}), Cu^{2+}([Ar]3d^9) and a few other simple Cu molecules. The Cartesian
208 coordinates of Cu molecules optimized by the Gaussian09 code were supplied to the
209 DCHF calculation. Exponents of basis sets were taken from Faegri's four-component
210 basis for Cu (Faegri, 2001), third-order Douglas-Kroll basis for H and Cl (Tsuchiya et
211 al., 2001), and ANO-RCC for O (Roos et al., 2005). Contraction coefficients were
212 optimized by four-component atomic calculations (Koc and Ishikawa, 1994). After
213 adding some diffuse and polarization functions, the final contraction form of the large
214 component basis sets was (19*s*14*p*9*d*)/[6*s*4*p*3*d*] for Cu, (16*s*11*p*1*d*)/[4*s*3*p*1*d*] for Cl,
215 (14*s*9*p*2*d*)/[3*s*2*p*2*d*] for O, and (8*s*2*p*)/[3*s*2*p*] for H.

216 The effect of nuclear spin can be neglected at equilibrium (Bigeleisen, 1996).
217 Since the present crown ether experiments were run at equilibrium, the kinetic part of
218 this effect also known as the magnetic isotope effect (Epov et al., 2011; Epov, 2011),
219 will not be considered in this work.

220

221 ## 3. RESULTS AND DISCUSSION

222 ### 3.1. Isotope fractionation of Cu by crown ether extraction

223 The Cu(II) species in HCl medium in the laboratory experiment are Cu^{2+},
224 $CuCl^+$, $CuCl_2$, and $CuCl_3^-$ (Brugger et al., 2001), which are related through
225 complexation reaction 5 and the following stepwise reactions, with stability constants
226 K_{species},

$$CuCl^+ + Cl^- \rightleftarrows CuCl_2, \quad K_{CuCl_2} \tag{8}$$

227 and

$$CuCl_2 + Cl^- \rightleftarrows CuCl_3^-, \quad K_{CuCl_3^-} \tag{9}$$

228

229 The presence of $CuCl_4^{2-}$ was reported for highly concentrated HCl and $CuCl_2$ systems
230 (Bell et al., 1973; Neilson, 1982; Tanimizu et al., 2007) or high-temperature systems
231 (Collings et al., 2000) but this higher order of complexation is negligible at the low HCl
232 concentrations and ambient temperature of the present experiments (Brugger et al.,
233 2001).

234 The extraction reaction of Cu(II) with the macrocyclic ligand can be written as,

$$CuCl_2 + L \rightleftarrows CuLCl_2, \tag{10}$$

235

236 where L stands for DC18C6. The distribution ratio *D* is written as,

$$D = \frac{\Sigma[\mathrm{Cu(II)}]_{org}}{\Sigma[\mathrm{Cu(II)}]_{aq}} \approx \frac{[CuLCl_2]}{[Cu^{2+}] + [CuCl^+] + [CuCl_2] + [CuCl_3^-]} \tag{11}$$

237

238 where the subscripts 'org' and 'aq' stand for the organic and aqueous phases,
239 respectively.

240 The isotope separation factor α, between the aqueous and organic phases, is
241 defined as:

$$\alpha = \frac{\sum_k \varphi_{org}^k \left({}^{65}Cu/{}^{63}Cu\right)_{org}^k}{\sum_k \varphi_{aq}^k \left({}^{65}Cu/{}^{63}Cu\right)_{aq}^k} \tag{12}$$

242

where *k* refers to the *k*th compound in the organic and aqueous phases, respectively, and φ is the fraction of total Cu (proper ^{63}Cu) hosted in the *k*th compound. The isotope enrichment factor is defined as $\alpha - 1$. Because α is always close to unity, $\alpha - 1 \approx \ln \alpha$, and 1000 ln α therefore can be approximated by $\Delta^{65}Cu = \delta^{65}Cu_{org} - \delta^{65}Cu_{aq}$. The $\Delta^{65}Cu$ values obtained are shown in Table 1 together with distribution ratios. $\Delta^{65}Cu$ ranged from –1.06 to –0.39‰.

The yield of Cu(II) extraction by crown ethers has been investigated by Yoshio et al. (1980), Nakamura et al. (1982), and Contreras et al. (1993). A study on extraction kinetics showed that equilibrium is achieved within 30 sec (Nakamura et al., 1982). Hydration-dehydration is known to be the rate-limiting step of solvent extraction. The rate constant for H_2O substitution in the inner coordination sphere of Cu^{2+} is quite high in the transition metal series, and it is comparable with that of Li^+ of the alkali metals as observed by Eigen (1963). The isotope exchange rate kinetics of $^7Li/^6Li$ in the crown ether systems has been studied in detail (Jepson and Cairns, 1979; Nishizawa et al., 1984), in which the isotopic equilibrium is achieved within 30-60 sec after contacting aqueous and organic phases. The 30 min stirring period in the present study is therefore considered to be enough to achieve the isotopic equilibrium of Cu. The $\Delta^{65}Cu$ values listed in Table 1 are hence attributable to the equilibrium isotope effect.

Figure 1a shows the mole fractions of Cu species estimated by using the stability constants of reactions 5, 8, and 9 (Brugger et al., 2001). $\Delta^{65}Cu$ was found to vary with HCl molarity (Fig. 1b), a trend that reflects the isotope fractionation of Cu in reactions 5 and 8-10. With increasing HCl molarity, more $CuCl_2$ forms, which in turn results in an increase of *D*. The magnitude of $\Delta^{65}Cu$ shown in Table 1 is similar to that

found in other ligand exchange systems (Matin et al., 1998; Maréchal et al., 1999, 2002; Zhu et al., 2002).

3.2. Contribution of the mass-independent isotope effect

The total electronic energies calculated for Cu isotopes and isotopologues are shown in atomic units (a.u.) in Table 2, in which Cu^{2+} was chosen as the reference. The maximum effect was found to be 0.015‰ for the Cu^0-Cu(I) pair and 0.012‰ for the Cu(I)-Cu(II) pair. The solvent extraction reaction is controlled by ligand exchange of Cu(II). Based on the Cu(II) data in Table 2, the nuclear field shift effect in Cu(II) species is only ~3% of the smallest Δ^{65}Cu value listed in Table 1. The values of Δ^{65}Cu reported in Table 1 are the values for the mass-dependent isotope fractionation and reflect intramolecular vibrations.

3.3. Mass-dependent isotope effects

3.3.1. Hydrated Cu(II) ions

The hydrated Cu(II) ion is generally represented as the hexaaqua complex $Cu(H_2O)_6^{2+}$ (Fig. 2). It is known that $Cu(H_2O)_6^{2+}$ shows the Jahn-Teller distortion effect (Sherman, 2001; Bersuker, 2006). Two Cu-O distances of the vertical axial bond ($Cu\text{-}O_{ax}$) are longer than four Cu-O distances in the equatorial plane ($Cu\text{-}O_{eq}$). The Jahn-Teller effect lowers the symmetry of $Cu(H_2O)_6^{2+}$ from octahedral T_h to D_{2h}. The calculated bond distance of Cu-O and the literature values are shown in Table 3. The bond distances were calculated to be 2.02-2.03 Å ($Cu\text{-}O_{eq}$) and 2.30 Å ($Cu\text{-}O_{ax}$), which are consistent with those reported in the literature (see references in Table 3).

289 After evidence was found that the stable aqueous complex has a fivefold
290 coordination (Pasquarello et al., 2001), the Jahn-Taller effect of $Cu(H_2O)_6^{2+}$ in aqueous
291 solutions has been questioned (Chaboy et al., 2006). The $Cu(H_2O)_5^{2+}$ complex has five
292 identical Cu-O bonds with a length of 1.96 Å, which was identified by neutron
293 diffraction (ND) analysis combined with first-principles molecular dynamics (MD). The
294 common bond distance reflects the rapid switch between the square pyramid and
295 trigonal bipyramid configurations (Pasquarello et al., 2001; de Almeida et al., 2008). In
296 a Car-Parrinello MD simulation (Amira et al., 2005), a square pyramidal geometry with
297 four short (2.00 Å) and one long (2.45 Å) Cu-O bond could be optimized. A similar set
298 of bond distances, four short (1.97 Å) and one long (2.39 Å) Cu-O bond, has been
299 confirmed in an X-ray absorption study (Benfatto et al., 2002). Our calculation of the
300 $Cu(H_2O)_5^{2+}$ geometry also resulted in the square pyramid rather than the trigonal
301 bipyramid of Fig. 2 and Table 4.
302 There is no clearly predominant structure among the four-, five-, and six- fold
303 coordinated Cu(II) ions (Chaboy et al., 2006). In the present study, we tested both the
304 coordination numbers five and six. We also tested a coordination number four to
305 evaluate the possibility of steric hindrance and strong degree of covalency. The
306 optimized structures in Cartesian coordinates are given in Table S1 of the electronic
307 supplement.
308 The intramolecular vibrational frequencies were then calculated for aqueous
309 Cu(II) species with optimized geometries. The ln β [= ln (*s*/*s*')*f*] values for the isotope
310 pair $^{65}Cu/^{63}Cu$ were determined by employing Eqs. 2-4 and are listed in Table 5. The
311 value of ln β of $Cu(H_2O)_5^{2+}$ at 298 K is 0.26‰ larger than that of $Cu(H_2O)_6^{2+}$.
312

313 *3.3.2. Hydrated Cu(II) chlorides*

314 The structure of the hydrated Cu(II) chloride $CuCl_m(H_2O)_n^{2-m}$ is shown in
315 Tables 6 and S1 together with literature values. For the Cu(II) *monochloride*, $CuCl^+$,
316 both fivefold (D'Angelo et al., 1997) and sixfold (Rode and Islam, 1992; Texler et al.,
317 1998) coordination have been reported. The bond distances obtained for the
318 fivefold-coordinated $CuCl(H_2O)_4^+$ reproduce the experimental results of D'Angelo et al.
319 (1997). Though the geometry of sixfold-coordinated $CuCl(H_2O)_5^+$ was optimized within
320 the SCF convergence criterion, this species still showed a few imaginary (negative)
321 frequencies. Tighter convergence criteria may be needed.

322 The Jahn-Teller effect should be detectable in the sixfold-coordinated Cu(II)
323 *dichloride*, $CuCl_2(H_2O)_4$. For a geometry with an axial Cl-Cu-Cl bond, we found two
324 long and two short Cu-O bonds in the equatorial plane (Fig. 2). Our calculation agreed
325 with the bond distances determined experimentally (Neilson, 1982; Tajiri and Wakita,
326 1986). A fivefold coordinated structure was inferred from the experiments of Ansell et
327 al. (1995), and, indeed, we found evidence for a stable fivefold-coordinated
328 $CuCl_2(H_2O)_3$ structure with a distorted square pyramid (Fig. 2).

329 The X-ray diffraction study of Bell et al. (1973) reports the existence of
330 sixfold-coordinated Cu(II) *trichloride*, $CuCl_3(H_2O)_3^-$, which is an average structure of
331 polymerized Cu(II) chlorides in a concentrated $CuCl_2$ solution. The complex has three
332 Cu-Cl and three Cu-O bonds, a very low symmetry, and is unstable. The isolated $CuCl_3^-$
333 anion in solution may have a different structure. There are no reports in the literature of
334 the fivefold-coordinated $CuCl_3(H_2O)_2^-$. Convergence could not be achieved for the
335 square pyramidal nor the trigonal bipyramidal geometry. A smaller coordination
336 number was found for hydrated $CuCl_3^-$ (Collings et al., 2000). Under highly

337 concentrated HCl and $CuCl_2$ conditions, a higher order chlorinated $CuCl_4^{2-}$ exists. It is
338 disputed whether the structure is distorted octahedral $CuCl_4(H_2O)_2^{2-}$ or tetrahedral
339 $CuCl_4^{2-}$ (see references in Table 6). Systematic analysis by the extended X-ray
340 absorption fine structure (EXAFS) technique and Raman spectrometry suggested that a
341 possible structure is the tetrahedral $CuCl_4^{2-}$ (Tanimizu et al., 2007). This supports the
342 existence of fourfold-coordinated $CuCl_3H_2O^-$. The calculation of $CuCl_3H_2O^-$
343 successfully converged.

344 The ln β values of the hydrated chlorides are shown in Fig. 3 and Table 5. As
345 for the hydrated Cu^{2+} case, ln β (298 K) of the fivefold-coordinated $CuCl_2(H_2O)_3$ was
346 found to be 0.26‰ larger than that of the sixfold-coordinated $CuCl_2(H_2O)_4$. A
347 difference of this magnitude is assigned to a stereochemical effect. For the fivefold
348 coordination, the ln β value at 298 K for $Cu(H_2O)_5^{2+}$ is 0.56‰ larger than that of
349 $CuCl_2(H_2O)_3$ (Table 5). Likewise, for the sixfold coordination, the ln β value at 298 K
350 for $Cu(H_2O)_6^{2+}$ is also 0.56‰ larger than that of $CuCl_2(H_2O)_4$ (Table 5). This suggests
351 that, with the same coordination number, exchanging H_2O by Cl^- enhances $^{65}Cu/^{63}Cu$
352 fractionation by approximately the same amount.

353

354 As shown in Fig. 3, ln β decreases when the fraction of H_2O exchanged with
355 Cl^- increases. The variation of $\Delta^{65}Cu$ estimated from the ln β values (298 K) with the
356 molarity of HCl is shown in Fig. 1b. A similar observation was previously made for Ni
357 and Zn isotope fractionation (Fujii et al., 2010, 2011a).

358 The isotopic mass balance is preserved in the extraction system as,

$$\frac{\Sigma[^{65}Cu]}{\Sigma[^{63}Cu]} = \frac{[^{65}Cu^{2+}] + [^{65}CuCl^+] + [^{65}CuCl_2] + [^{65}CuCl_3^-] + [^{65}CuLCl_2]}{[^{63}Cu^{2+}] + [^{63}CuCl^+] + [^{63}CuCl_2] + [^{63}CuCl_3^-] + [^{63}CuLCl_2]} \quad (13)$$

359

360 The mole fractions of related Cu(II) species are evaluated from the values of K_{CuCl^+},

361 K_{CuCl_2}, $K_{CuCl_3^-}$ (Brugger, 2001), and *D* (Eq. 11), all obtained experimentally. Each mole

362 fraction is the sum of fractions of ^{63}Cu and ^{65}Cu isotopologues. The isotopic fractions

363 within the species were estimated from ln β. Since there is no structural information of

364 the Cu-DC18C6 complex in organic solution, β_{CuLCl_2} was set as a free parameter. The

365 results of the calculation are shown in Fig. 1b. The value of ln β_{CuLCl_2} converged to

366 3.35‰. The bold and dotted curves shown in Fig. 1b are the values of Δ^{65}Cu calculated

367 for ln β_{CuLCl_2} = 3.35 ± 0.05‰. The results agree well with the experimental results. An

368 important aspect of the estimation is that the calculation correctly predicts the sigmoidal

369 dependence of ln β on the fraction of H_2O exchanged by Cl^- with increasing HCl

370 molarity.

371

372 **3.4. Application to hydrous geochemistry**

373 In the absence of organic ligands which are known to dominate Cu speciation

374 in seawater (Moffet, 1995; Moffet and Brand, 1996; Hirose, 2006) the free Cu^{2+} ion is

375 dominant in freshwater, while the carbonate complexes $CuCO_3$ and $Cu(CO_3)_2^{2-}$ are

376 dominant in seawater (Albarède, 2004). Copper concentration in seawater increase

377 down the water column, which indicates both the uptake of Cu by plankton and

378 scavenging of Cu by settling particles (Boyle et al., 1977; Bruland, 1980). Dissolved Cu

379 in seawater is isotopically heavy (δ^{65}Cu = +0.9 to +1.5‰) relative to rocks and

380 sediments (0.0 to +0.3‰) and the riverine input (+0.69‰) (Bermin et al., 2006; Vance

381 et al., 2008). It was suggested that this result is attributable to the partitioning of Cu

382 isotopes between a heavy dissolved phase, where Cu is bound to organic ligands, and a
383 light particulate phase, dominated by Fe-Mn oxides (Vance et al., 2008). δ^{65}Cu in
384 Fe-Mn nodules (Albarède, 2004) and encrustations (Little et al., 2010) from the three
385 major ocean basins varies between +0.04 and +0.6‰, which is significantly lighter than
386 the δ^{65}Cu value in seawater (+0.9 to +1.5‰, Vance et al., 2008).

387 Surface seawater also contains various inorganic complexes and carbonates.
388 Speciation of Cu in seawater is very sensitive to the hydrolysis constants. Zirino and
389 Yamamoto (1972) used the cumulative formation constant of $Cu(OH)_2$, log β_2 = 14.3,
390 which, as shown in Fig. S1a (see the electronic supplement), makes Cu speciation in
391 seawater dominated by $Cu(OH)_2$. Mole fractions have been calculated from the set of
392 stability constants recommended by Powell et al. (2007) with the second hydrolysis
393 constant log $*\beta_2 = -16.65$, and the results are shown in Fig. 4a as a function of pH. At a
394 typical seawater pH of 8.22 (Macleod et al., 1994), $CuCO_3$ is the dominant species,
395 while the hydrated Cu^{2+} ion, chloride, sulfate, and hydroxide are subordinate. At pH ≥
396 8.22, $Cu(CO_3)_2^{2-}$ becomes an abundant species. These calculations are only relevant to
397 seawater with no organic ligands.

398 Figure 4b shows the isotope fractionation of Cu(II) among its various species
399 as estimated from their mole fractions and ln β (Tables 5 and 7) at 298 K under
400 conditions typical of seawater. The optimized geometries of the relevant species are
401 shown in Fig. 2 and Table S1 and the temperature dependence of ln β (Table 7) in Fig. 5.
402 The geometry of Cu hydroxides, $CuOH^+$ and $Cu(OH)_2$, were calculated by dissociating
403 H^+ ions from the *fivefold*-coordinated $Cu(H_2O)_5^{2+}$. The positions of OH^- ligands were
404 determined by reference to $CuCl^+$ and $CuCl_2$ (Fig. 2). The structure calculated for both

405 $CuOH(H_2O)_4^+$ and $Cu(OH)_2(H_2O)_3$ converged to a distorted square pyramid. With a
406 H_2O molecule at the vertex of the square pyramid, the bond distance is shorter for
407 $Cu\text{-}OH^-$ (1.8-1.9 Å) than for $Cu\text{-}OH_2$ (2.3-2.4 Å) (see Table S1). This suggests that the
408 stronger Cu-O bonds on the square plane loosen the hydration bond from the vertex.
409 This conclusion is consistent with the known structure of amorphous $Cu(OH)_2$ or
410 $Cu(OH)_2$ colloidal solution, which both show a layer structure of polymerized square
411 planes (Elizarova et al., 1999; Kriventsov et al., 1999).

412 *Fourfold* complexation occurs in both amorphous and crystalline $Cu(OH)_2$. A
413 stable fourfold complexation was also obtained for the Cu(II) carbonates, $CuCO_3(H_2O)_2$
414 and $Cu(CO_3)_2^{2-}$ (Fig. 2 and Table S1). CO_3^{2-} was treated as a bidentate ligand. The
415 structure converged to a distorted square plane. We tested positioning a water molecule
416 above the plane in the initial structure, but it moved out of the inner coordination shell
417 during the calculation. The structural optimization of $CuCO_3OH^-$ was more problematic.
418 Since CO_3^{2-} and OH^- occupy three coordination positions, one water molecule should
419 also bind to Cu(II) at the fourth coordination position, thereby giving the
420 $CuCO_3(OH)H_2O^-$ compound. It was actually found that no water molecule is stable in
421 the inner coordination shell. From the stoichiometry, the stable model molecule may
422 instead be $CuHCO_3(OH)_2^-$. This stable structure, in which HCO_3^- acts as a
423 quasi-bidentate ligand is shown in Fig. 2 and Table S1. The ln β values obtained are
424 shown in Fig. 5 and Table 7. The Cu hydroxides and carbonates have ln β values of
425 4.3-5.2‰ (298 K), in which compounds with higher complexation with OH^- and CO_3^{2-}
426 resulted in ln $\beta \geq 5$‰ (298 K).

427 The structure of hydrated Cu(II) in sulfate solutions was previously
428 investigated by Ohtaki et al. (1976) and Musinu et al. (1983). In $CuSO_4$ solutions, Cu^{2+}

429 is surrounded by disordered ligands (Musinu et al., 1983), which suggests a direct
430 interaction of Cu^{2+} with SO_4^{2-}. We used the structural model of Fe(III) sulfate proposed
431 by Magini (1979) as a reference for $CuSO_4(H_2O)_4$ (Fig. 2 and Table S1), in which SO_4^{2-}
432 is treated as a monodentate ligand, and obtained bond distances of 1.9-2.1 Å for
433 Cu-OH_2 and 2.37 Å for Cu-OSO_3^{2-}. These values agree with the Cu-O bond distances
434 determined by X-ray diffraction (Musinu et al., 1983). The electron donor SO_4^{2-}
435 strongly attracts H^+ and the resulting structure is equivalent to $CuH_2SO_4(OH)_2$ (Fig. 2).
436 The magnitude of ln β for $CuSO_4$ is 5.14‰ at 298 K (Table 7) and matches that of
437 $Cu(CO_3)_2^{2-}$ (Fig. 5).

438 As shown in Figs. 4a and 4b, at pH ≥ 8.22, the dominant Cu(II) species are
439 carbonates. We found that Cu in $Cu(CO_3)_2^{2-}$ (and $CuSO_4$) is isotopically 0.6‰ heavier
440 than Cu^{2+} ion. At pH = 8.22, the δ^{65}Cu value of $CuCO_3$ is slightly negative –0.17‰,
441 whereas those of $Cu(CO_3)_2^{2-}$ and $CuCO_3OH^-$ are substantially heavier, 0.75‰ and
442 0.58‰, respectively. At high pH, the relevant fractionation factors are
443 $\Delta^{65}Cu[Cu(CO_3)_2^{2-}\text{-}CuCO_3] = 0.92‰$ and $\Delta^{65}Cu[CuCO_3OH^-\text{-}CuCO_3] = 0.75‰$. Copper
444 in carbonates, whether in $CuCO_3$ or in solid solutions with carbonates of other elements
445 should therefore be isotopically light with respect to dissolved Cu.

446 At pH = 8.22, $Cu(OH)_2$ is +0.48‰ heavier than bulk seawater Cu (Fig. 4b). A
447 caveat is the somewhat different fractionation obtained when the cumulative formation
448 constant of $Cu(OH)_2$, log β_2 =14.3 of Zirino and Yamamoto (1972) is used. The major
449 species are $Cu(OH)_2$ and $CuCO_3$, while mole fractions of other species are insignificant
450 (Fig. S1a, Zirino and Yamamoto, 1972). The δ^{65}Cu shift of $Cu(OH)_2$ and $CuCO_3$ at pH
451 = 8.22 with respect to dissolved Cu are +0.02‰ and –0.62‰, respectively (Fig. S1b).

Isotope fractionation may therefore not be seen in Cu(II) hydroxide, but Cu in $CuCO_3$ should nevertheless remain isotopically light with respect to the seawater value.

As sulfides have small ln β values (Fujii et al., 2011b; Pons et al., 2011), sulfate-sulfide and carbonate-sulfide exchange are possibly determinant reactions for Cu isotope fractionation in seawater. $CuHS(H_2O)_4^+$ and $Cu(HS)_2(H_2O)_3$ were calculated with the geometries shown in Table S1. The structures that successfully converged were similar to those of the hydroxides shown in Fig. 2. The ln β values are shown in Fig 5 and Table 7. It is clear that the ln β values of Cu(II) sulfides are smaller than those of all the species shown in Fig. 3. In particular, the ln β values of Cu sulfides are 1.9-2.0‰ smaller than those of Cu sulfate and carbonates. Diagenetic Cu(II)-bearing sulfides are expected to be isotopically lighter than dissolved Cu, while Cu in the water table of sulfide-rich terranes should be heavy (Mathur et al., 2005, 2012).

Isotope fractionation also occurs under reducing conditions through Cu(I)-Cu(II) redox reactions. The ln β values calculated for Cu(I) chlorides and hydrogensulfides are ≤ 2.6‰ at 298 K (Seo et al., 2007), which suggests that Cu(I) complexes preferentially enrich ^{63}Cu and their precipitation results in the enrichment of ^{65}Cu in the fluid.

Cu in sulfides should be isotopically light with respect to dissolved aqueous Cu, and the main form of Cu removal from aquatic systems is Cu sulfide. The heavy isotopic composition of Cu in surface seawater (Vance et al., 2008) and groundwater (Mathur et al., 2012) therefore likely reflects that Cu carbonate complexes are held back in solution, while Cu is precipitated in sulfides. Complexation of Cu(II) with organic matter in surface seawater (Moffett, 1995) should also cause Cu isotope fractionation.

475 Evidence for the large-scale deposition of sediments with isotopically light Cu required
476 by mass balance is, however, still missing.
477
478 **3.5. Application to biological activity**
479 A variety of biological processes may induce Cu isotope fractionation.
480 Pokrosvky et al. (2008) demonstrated that Cu in bacteria is isotopically light relative to
481 the ambient solution. Pokrovsky et al. (2012) further identified S-coordinated Cu(I)
482 complexes at the surface and inside bacterial cells that may preferentially concentrate
483 ^{63}Cu over ^{65}Cu. It is therefore appealing to assign isotope fractionation in biological
484 material to competing Cu(II) and Cu(I) complexation. Mammal physiology is also a
485 cause of Cu isotope fractionation. Albarede et al. (2011a) found a ~1‰ fractionation
486 between human erythrocytes and serum. High δ^{65}Cu values of 1.5‰ were found in the
487 kidney of both sheep (Balter and Zazzo, 2011) and mice (Albarède et al., 2011b) with
488 respect to the rest of the body.
489 Oxalic acid is an ubiquitous toxic organic acid in body fluids. Oxalate is
490 adsorbed in the intestinal track, but the question of the origin of high oxalate contents in
491 urine and plasma found in patients prone to kidney damage is still contentious. This is a
492 genuine medical concern as ascorbate (vitamin C) supplementation has been argued to
493 increase the urinary oxalate levels, and therefore ascorbate may be a risk factor for
494 individuals predisposed to kidney stones (Chai et al., 2005; González et al., 2005;
495 Massey et al., 2005). Ascorbate is efficiently converted to oxalate when the coexisting
496 copper concentration is high (Hayakawa et al., 1973).
497 Hayakawa et al. (1973) suggest that Cu(II) is readily reduced by ascorbic acid
498 (H_2A) to Cu(I),

$$H_2A + 2Cu(II) \rightarrow A + 2Cu(I) + 2H^+ \quad (14)$$

499

500 The ascorbate anion A^{2-} here is oxidized to A, dehydroascorbic acid $C_6H_6O_6$. In the
501 catalytic reaction by a multicopper oxidase, ascorbate oxidase, the oxidation of
502 ascorbate to dehydroascorbate occurs via the disproportionation of the
503 semidehydroascorbate radical (Solomon et al., 1996). The enzymatic reactions may be
504 identical to the catalytic reaction 14.

505 The monohydroascorbate anion HA^- forms a complex with Cu^{2+}, $CuHA^+$.

$$Cu^{2+} + HA^- \rightleftarrows CuHA^+, \quad K_{CuHA^+} \quad (15)$$

506

507 Degradation of ascorbate via dehydroascorbate forms oxalate. A pathway of ascorbate
508 degradation has been proposed by Green and Fry (2005).

509 The oxalic acid also forms a complex with Cu^{2+}, CuC_2O_4.

$$Cu^{2+} + C_2O_4^{2-} \rightleftarrows CuC_2O_4, \quad K_{CuC_2O_4} \quad (16)$$

510

511 The value of the standard redox potential Eh with respect to the standard hydrogen
512 electrode (SHE), E_0, for the Cu redox reaction,

$$Cu^+ \rightleftarrows Cu^{2+} + e^- \quad (17)$$

513

514 is $E_0 = 0.153 + 0.591 \log ([Cu^{2+}]/[Cu^+])$ (Pourbaix, 1974). We used the following acid
515 dissociation constants and equilibrium constants $pK_a = 4.03$ (ascorbic acid), $pK_{a1} =$
516 1.252, $pK_{a2} = 4.266$ (oxalic acid) (Smith and Martell, 1989), $\log K_{CuHA^+} = 2.32$

517 (Jameson et al., 1976), and log $K_{CuC_2O_4}$ = 4.5 (Foreci et al., 1995). Figure 6a shows the
518 mole fractions of Cu^+, Cu^{2+}, $CuHA^+$, and CuC_2O_4 as functions of Eh. The total
519 concentrations of Cu and ascorbic acid are ~10^{-6} M (Lech and Sadlik, 2007) and ~10^{-4}
520 M (Margolls and Davis, 1988), respectively. The pH and Eh in the body are known to
521 be ~7.4 and 0.27 V (van Rossum and Schamhart, 1991). These values were used to
522 estimate the mole fractions of Cu species using the assumption that 10% of ascorbic
523 acid is converted to oxalic acid. We further assumed that no other degradation products
524 were present. Figure 6b shows the speciation as a function of the reaction progress. As
525 expected, oxidation of Cu(I) to Cu(II) proceeds with increasing Eh, which in turn
526 enhances Cu-ascorbate and Cu-oxalate formation. The degradation of ascorbate
527 increases oxalic acid concentration and therefore promotes the production of
528 Cu-oxalate.

529 Figure 6c and 6d show the range of isotope fractionation among Cu species as
530 estimated from their mole fractions and ln β at 298 K (Tables 5 and 8). The optimized
531 geometries of related species are shown in Table S1. Hydrated Cu^+ was treated as free
532 Cu(I). Cu(I) complexes possess simple linear structures (Fulton et al., 2000a,b). Our ln
533 β value of 2.87‰ at 289K for $Cu(H_2O)_2^+$ (Table 8) is consistent with the value of
534 2.89‰ estimated by *ab initio* methods for $CuClH_2O$ (Seo et al., 2007). $Cu(H_2O)_5^{2+}$ was
535 treated as free Cu(II), and its ln β is given in Table 5. For the geometry of Cu(II)
536 ascorbate $CuHA^+$, we used the copper monomer (Ünaleroğlu et al., 2001). The structure
537 calculated for Cu(II) in fivefold coordination with L-ascorbate and H_2O is shown in Fig.
538 2 and Table S1. The value of ln β calculated at 298 K is 3.32‰. The ln β value of
539 D-ascorbate at 298 K (also 3.38‰) is indistinguishable from that of L-ascorbate. The

geometry of Cu(II) oxalate was quite similar to the structure of the hydrated Cu carbonate. It successfully converged to a distorted plane configuration (Fig. 2 and Table S1) and led to large ln β values (Fig.7 and Table 8).

Figures 6c and 6d show the δ^{65}Cu values of the different species relative to the bulk solution as a function of Eh and extent of oxalate formation. Figure 6c shows that, with respect to free Cu(II), free Cu(I) is enriched in the light isotope. When Cu(I) and Cu(II) coexist, the δ^{65}Cu of the total free Cu ions is only slightly lighter than the sum of all the Cu species. The δ^{65}Cu of the Cu ascorbate varies from –1.0 to +0.5‰ when Eh increases from –1 V to +1 V, but its mole fraction remains very small. The prominent feature of Fig. 6c is the heavy isotope enrichment (+0.6 to +2.5‰) of the Cu oxalate relative to total Cu. Figure 6d was drawn for Eh = 0.27 V, which is a typical Eh value of human blood. It is expected that degradation of ascorbate and excretion of oxalate should leave isotopically heavy Cu in the kidney. With respect to food, which has a δ^{65}Cu value of about 0‰ (Balter and Zazzo, 2011), when even trace amounts of oxalate form, it should leave behind copper with a δ^{65}Cu of ~1.4‰. This value is very close to the δ^{65}Cu (of 1.5‰) found in sheep (Balter and Zazzo, 2011) and mice (Albarède et al., 2011b) kidneys. The positive δ^{65}Cu found in kidneys may result from isotopically heavy Cu left in the kidney by the degradation of ascorbic acid. Copper isotopes therefore represent a potential marker of the troubles associated with hyperoxalury and kidney stones.

4. CONCLUSIONS

562 We first demonstrated that Cu isotope fractionation at equilibrium is observed in
563 laboratory-scale experiments. The effect on the $^{65}Cu/^{63}Cu$ ratio of Cu(II) partitioning
564 between HCl and DC18C6 depends on acid molarity. The effect is mainly governed by
565 the mass-dependent fractionations as a result of intramolecular vibrations. The nuclear
566 field shift effect accounts for less than 3% of the mass-dependent fractionation. We then
567 computed the coefficients of isotope fractionation of Cu for several species (hydrated
568 Cu ion, hydroxide, chloride, sulfide, sulfate, carbonate, oxalate, and ascorbate). It was
569 found that Cu in dissolved carbonates and sulfates is isotopically heavier than free Cu
570 and Cu in sulfides. The theoretical estimation of $\delta^{65}Cu$ in ligand exchange between
571 inorganic ligands including carbonate anions may be useful to understand the heavy Cu
572 isotopic compositions found in both seawater and groundwater in the absence of strong
573 organic ligands. Further theoretical estimation of $\delta^{65}Cu$ in hydrated Cu(I) and Cu(II)
574 ions, Cu(II) ascorbates, and Cu(II) oxalate suggests that Cu isotope fractionation during
575 the breakdown of ascorbate into oxalate results in the isotopically heavy Cu found in
576 mammal kidneys.
577

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954

Table 1 Isotopic fractionation of Cu(II) during exchange experiments between HCl medium and a macrocyclic complex.

[HCl] (M)	D	$\Delta^{65}Cu^{a}$ (‰)
1	1.3×10^{-4}	–1.06
2	1.8×10^{-3}	–0.84
3	2.4×10^{-2}	–0.77
4	1.5×10^{-1}	–0.65
5	4.6×10^{-1}	–0.61
6	9.8×10^{-1}	–0.39

[a] Errors are ±0.10‰ for 2σ.

Table 2 Nuclear field shift effect of Cu isotopes and isotopologues at 298 K.

Valence	Species	Total energy (a.u.)		ΔE (a.u.) (10^{-5})	Nuclear Field shift effect (‰)
		^{63}Cu	^{65}Cu		
Cu(0)	Cu^0	–1653.451898480	–1653.451827445	7.1035	–0.014
Cu(I)	Cu^+	–1653.210583752	–1653.210512731	7.1021	0.001
	CuCl	–2114.481787065	–2114.481716036	7.1029	–0.007
	CuH_2O^+	–1729.354508434	–1729.354437410	7.1024	–0.002
	CuOH	–1728.963440770	–1728.963369739	7.1031	–0.010
Cu(II)	Cu^{2+}	–1652.578696630	–1652.578625608	7.1022	0
	$CuCl^+$	–2114.155110496	–2114.155039471	7.1025	–0.003
	CuH_2O^{2+}	–1728.798913392	–1728.798842366	7.1026	–0.004
	$CuOH^+$	–1728.656622258	–1728.656551226	7.1032	–0.011
	CuO	–1728.336259331	–1728.336188299	7.1032	–0.011

[a] The nuclear field shift effect was calculated by $(\delta E_{\text{reference}} - \delta E_{\text{species}})/kT$ at T = 298K. The root-mean-square charge radii $\langle r^2\rangle^{1/2}$ reported for ^{63}Cu (3.8823×10^{-15} m) and ^{65}Cu (3.9022×10^{-15} m) (Angeli, 2004) were used. Cu^{2+} was set as the reference. Energy of photons of 1 a.u. is equal to 4.3597×10^{-18} J.

Table 3 Bond distances determined for $Cu(H_2O)_6^{2+}$.

$Cu\text{-}O_{ax}$ (Å)	$Cu\text{-}O_{eq}$ (Å)	Method[a]	Reference
2.30	2.02-2.03	MO	This study
2.25	2.06	MO	Beagley et al., 1989
2.25	2.05	MO	Åkesson et al., 1992
2.25	2.06-2.07	MO	Breza et al., 1997
2.23-2.26	2.033	MO	Bryantsev et al., 2008
2.46-2.58	1.97-2.09	MD	Liu et al., 2010
2.27	1.94	QM	van Duin et al., 2010
2.24	2.07	QM/MM MC	Marini et al., 1999
2.2-2.3	1.99-2.07	QM/MM MD	Schwenk and Rode, 2003a,b
2.60	1.955	EXAFS	Sham et al., 1981
2.28	2.00	EXAFS	Tajiri and Wakita, 1986
2.3	1.96	EXAFS	Nomura and Yamaguchi, 1988
2.29	1.99	EXAFS	Beagley et al., 1989
2.375-2.413	1.969-1.971	EXAFS	Fulton et al., 2000a,b
2.30	1.955	EXAFS	Persson et al., 2002
2.56	1.99	EXAFS+XANES	Benfatto et al., 2002
2.36	1.96	EXAFS+XANES	Chaboy et al., 2006
2.32	1.96	XANAS	Garcia et al., 1989
≥2.21	1.96	ND	Salmon et al, 1988
2.45	1.95	ND	Okan and Salmon, 1995
2.43	1.94	XRD	Ohtaki and Maeda, 1974
2.339	1.976	XRD	Magini, 1982

[a] MO (molecular orbital), EXAFS(extended x-ray absorption fine structure), MD (molecular dynamics), ND (neutron diffraction), QM(quantum mechanics), MM (molecular mechanics), MC (Monte Carlo), XANES (x-ray absorption near-edge structure), and XRD(x-ray diffraction).

Table 4 Bond distances determined for $Cu(H_2O)_5^{2+}$.

$Cu\text{-}O_{long}$ (Å)	$Cu\text{-}O_{short}$ (Å)	Method[a]	References
2.20	1.99-2.02	MO	This study
2.181	2.011	MO	Bryantsev et al., 2008
2.45	2.00	CPMD	Amira et al., 2005
2.22	2.04-2.07	CPMD	de Almeida et al., 2009
2.31	2.03-2.09	MD	Liu et al., 2010
2.34	1.963	EXAFS	Persson et al., 2002
2.39	1.97	EXAFS+XANES	Benfatto et al., 2002
2.36	1.96	EXAFS+XANES	Chaboy et al., 2006
–	1.96	ND	Pasquarello et al., 2001

[a] CPMD (Car-Parrinello MD)

Table 5 Logarithm of the reduced partition function, ln β, for the pair ^{65}Cu-^{63}Cu. Hydrated Cu(II) ions and chlorides.

Species	Temperature (K)					
	273	298	323	373	473	573
$Cu(H_2O)_5^{2+}$	5.355	4.546	3.905	2.968	1.876	1.290
$Cu(H_2O)_6^{2+}$	5.053	4.288	3.682	2.798	1.767	1.215
$CuCl(H_2O)_4^{+}$	4.906	4.161	3.572	2.712	1.711	1.176
$CuCl_2(H_2O)_3$	4.709	3.988	3.420	2.592	1.633	1.120
$CuCl_2(H_2O)_4$	4.397	3.724	3.193	2.421	1.525	1.046
$CuCl_3H_2O^{-}$	3.530	2.985	2.556	1.933	1.214	0.832

Table 6 Bond distances determined for $CuCl_m(H_2O)_n^{2-m}$.

Possible species	*m*	*n*	Cu-Cl[a] (Å)	Cu-O[a] (Å)	Method	References
$CuCl(H_2O)_4^+$	1	4	2.20	2.04-2.06(3) 2.35(1)	MO	This study
$CuCl(H_2O)_4^+$	1[b]	4	2.29[b]	1.968(3) 2.27(1)	EXAFS	D'Angelo et al., 1997
$CuCl(H_2O)_5^+$	1.1	5.2	2.55	2.00	MC	Rode and Islam, 1992
$CuCl_2(H_2O)_3$	2	3	2.25	2.07-2.08(2) 2.35(1)	MO	This study
$CuCl_2(H_2O)_3$	2.0	3.3	3.1	1.96	ND	Ansell et al, 1995
$CuCl_2(H_2O)_4$	2	4	2.27	2.11(2) 2.43(2)	MO	This study
$CuCl_2(H_2O)_4$	2	4	2.22	2.01(2) 2.28(2)	EXAFS	Tajiri and Wakita, 1986
$CuCl_2(H_2O)_4$	2.8	4.3	2.56	2.05(2) 2.5(2)	ND	Neilson, 1982
$CuCl_3H_2O^-$	3	1	2.22(1) 2.28(2)	2.28	MO	This study
$CuCl_3H_2O^-$	2.1	1	2.28	1.95	EXAFS	Collings et al., 2000
$CuCl_3(H_2O)_3^-$	3.3	2.7	2.43	1.90-1.95	XRD	Bell et al., 1973
$CuCl_4^{2-}$	3.8	0	2.24	–	EXAFS	Tanimizu et al., 2007
$CuCl_4(H_2O)_2^{2-}$	3.8	1.9	2.23	2.18	EXAFS	Tanimizu et al., 2007
$CuCl_4(H_2O)_2^{2-}$	4.2	2.3	2.56	2.05	ND	Neilson, 1982
$CuCl_4(H_2O)_2^{2-}$	3.6	2.4	2.43	1.90-1.95	XRD	Bell et al., 1973

[a] Number of bonds is shown in parentheses.
[b] An additional Cu-Cl bond distance of 2.85 Å reported may be too long to treat as chemical bonding.

Table 7 Logarithm of the reduced partition function, ln β, for the pair ^{65}Cu-^{63}Cu. Cu(II) hydroxides, carbonates, sulfate, and sulfides.

Species	Temperature (K)					
	273	298	323	373	473	573
$CuOH(H_2O)_4^+$	5.307	4.517	3.889	2.967	1.883	1.298
$Cu(OH)_2(H_2O)_3$	5.814	4.966	4.288	3.286	2.098	1.451
$CuCO_3(H_2O)_2$	5.091	4.323	3.715	2.825	1.787	1.230
$Cu(CO_3)_2^{2-}$	6.176	5.239	4.498	3.416	2.158	1.483
$CuHCO_3(OH)_2^-$	5.951	5.075	4.376	3.346	2.130	1.471
$CuSO_4(H_2O)_4$	6.041	5.144	4.430	3.381	2.148	1.481
$CuHS(H_2O)_4^+$	4.002	3.386	2.900	2.194	1.377	0.942
$Cu(HS)_2(H_2O)_3$	3.855	3.264	2.797	2.119	1.333	0.914

Table 8 Logarithm of the reduced partition function, ln β, for the pair ^{65}Cu-^{63}Cu. Hydrated Cu(I) ion, Cu(II) ascorbates, and Cu(II) oxalate.

Species	Temperature (K)					
	273	298	323	373	473	573
$Cu(H_2O)_2^+$, Cu(I)	3.368	2.867	2.468	1.882	1.193	0.822
$CuH(L\text{-ascorbate})(H_2O)_4^+$	3.924	3.324	2.850	2.161	1.362	0.935
$CuH(D\text{-ascorbate})(H_2O)_4^+$	3.989	3.380	2.899	2.199	1.386	0.951
$CuC_2O_4(H_2O)_2$	6.236	5.302	4.561	3.474	2.202	1.516

Figure captions

Figure 1 Mole fractions of Cu species and isotope fractionation of Cu in HCl solutions. a) Distribution of Cu chlorides. The mole fractions were calculated from the stability constants of Brugger (2001). b) Isotope fractionation is shown as $\Delta^{65}Cu = \delta^{65}Cu_{org} - \delta^{65}Cu_{aq}$ upon extraction of Cu by dicyclohexano-18-crown-6 (DC18C6) from the aqueous solution. The solid curves represent our estimates from the ln β values (298 K) of fivefold-coordinated $Cu(H_2O)_5^{2+}$, $CuCl(H_2O)_4^{2+}$, and $CuCl_2(H_2O)_3$, and $CuCl_3H_2O^-$ (Table 5), ln β_{CuLCl_2} (3.35‰), and *D*. The dotted curves represent the effect of ±0.05‰ errors on ln β_{CuLCl_2}.

Figure 2. Molecular structures of hydrated Cu^+, Cu^{2+}, and aqueous Cu(II) species. The structures are drawn using GaussView5 (Gaussian Inc.) (Dannington et al., 2009). Symbol keys: Cu (vermilion), Cl (green), S (yellow), O (red), C (gray), and H (white).

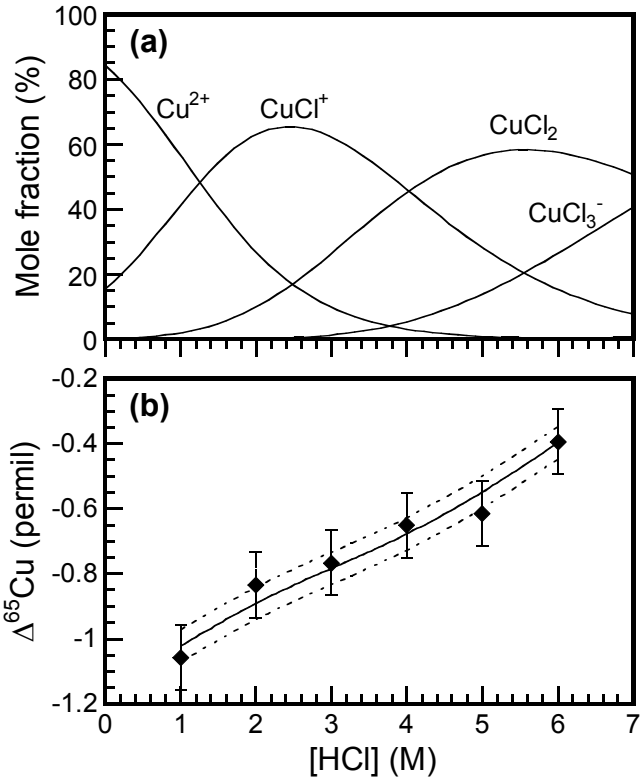
Figure 3. Temperature dependence of ln β. The ln β values of hydrated Cu^{2+} and Cu(II) chlorides (see Table 5) are shown as linear functions of T^{-2}.

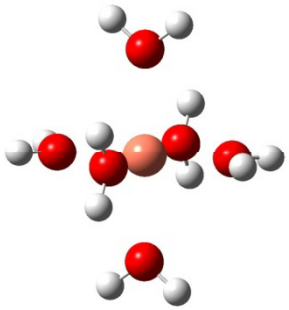
Figure 4. Mole fractions of Cu(II) species and Cu isotopic variations as functions of pH at 298 K. a) Mole fractions of Cu species, b) Species $\delta^{65}Cu$ relative to the bulk solution. Literature values of formation constants at ionic strength I = 0.70 M (Powell et al., 2007) were used for the calculations. Σ[Cu(II)] was set to 10^{-9} M and it was assumed that the system was in equilibrium with air having a CO_2 fugacity of $10^{-3.5}$ bar (1 bar = 10^5 Pa) (Powell et al., 2007). We further assumed log $K[CO_2(g) = CO_2(aq)]$ = –1.5 (Morel and Hering, 1993) and concentrations of Cl^- = 0.55 mol kg^{-1} and SO_4^{2-} = 0.029 mol kg^{-1} (Macleod et al., 1994).

Figure 5. Temperature dependence of ln β. The ln β values of hydrated Cu(II) hydroxides, carbonates, sulfate, and sulfides (see Table 7) are shown as linear functions of T^{-2}.

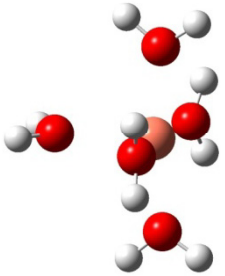
Figure 6. Mole fractions of Cu(I) and Cu(II) species and Cu isotopic variations as functions of Eh and extent of oxalate formation at 298 K. pH and total Cu concentration were set to be 7.4 and 1 μM, respectively a) Mole fractions of Cu species as functions of Eh. Concentrations of ascorbate and oxalate were set to 90 μM and 10 μM, respectively. b) Mole fractions of Cu species as functions of proportion of oxalate formed. Eh was set to be 0.27 V. c) δ^{65}Cu relative to the bulk solution as functions of Eh. Conditions are identical to those of a, and d) δ^{65}Cu relative to the bulk solution as functions of extent of oxalate formation. Conditions are identical to those of b.

Figure 7. Temperature dependence of ln β. The ln β values of hydrated Cu^{+} and Cu(II) oxalate and ascorbate (see Table 8) are shown as linear functions of T^{-2}. The ln β values of pentaaqua Cu^{2+} (see Table 5 and Fig. 3) are shown together.

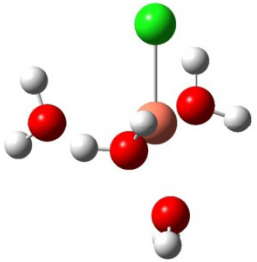

(a)
Mole fraction (%)
100
80
60
40
20
0
Cu2+
CuCl+
CuCl2
CuCl3-
(b)
Δ65Cu (permil)
-0.2
-0.4
-0.6
-0.8
-1
-1.2
0
1
2
3
4
5
6
7
[HCl] (M)



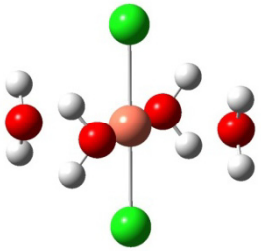
a) $Cu(H_2O)_6^{2+}$



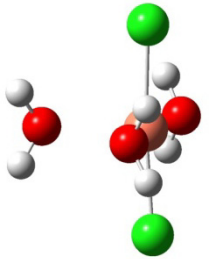
b) $Cu(H_2O)_5^{2+}$



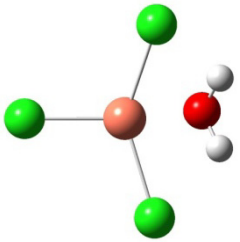
c) $CuCl(H_2O)_4^{+}$



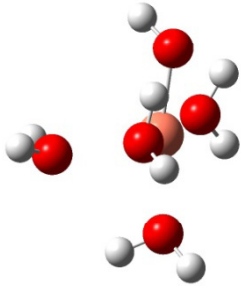
d) $CuCl_2(H_2O)_4$



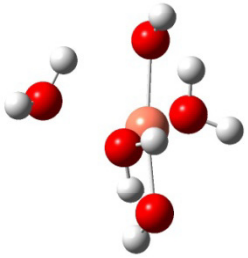
e) $CuCl_2(H_2O)_3$



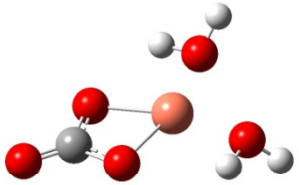
f) $CuCl_3H_2O^{-}$



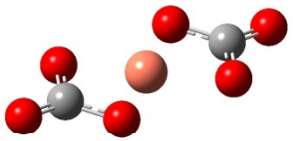
g) $CuOH(H_2O)_4^{-}$



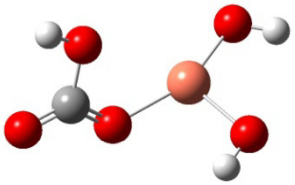
h) $Cu(OH)_2(H_2O)_3$



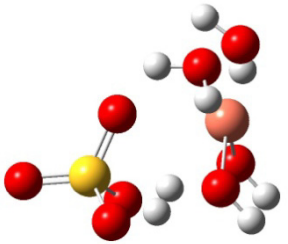
i) $CuCO_3(H_2O)_2$



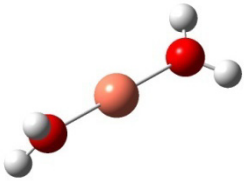
j) $Cu(CO_3)_2^{2-}$



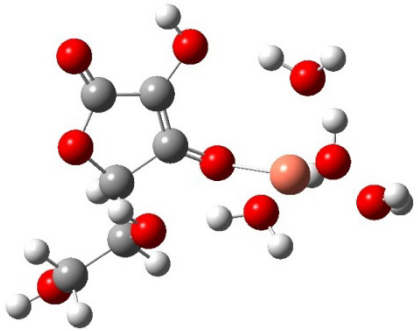
k) $CuHCO_3(OH)_2^{-}$



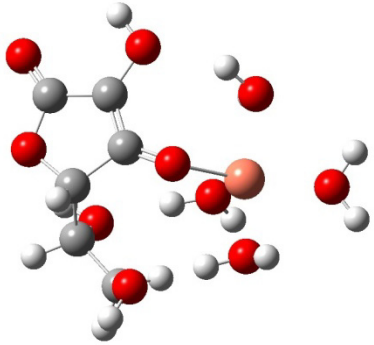
l) $CuSO_4(H_2O)_4$



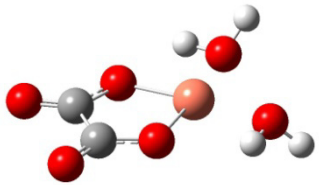
m) $Cu(H_2O)_2^{+}$, Cu(I)



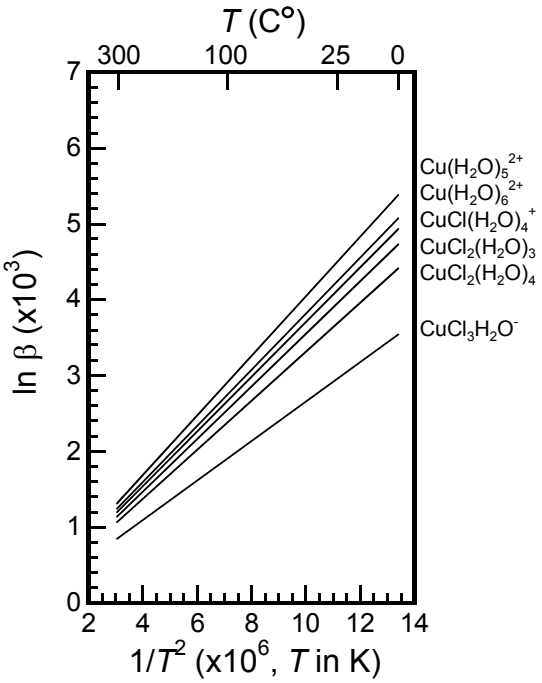
n) $CuHA(H_2O)_4^{+}$
(A: L-ascorbate)

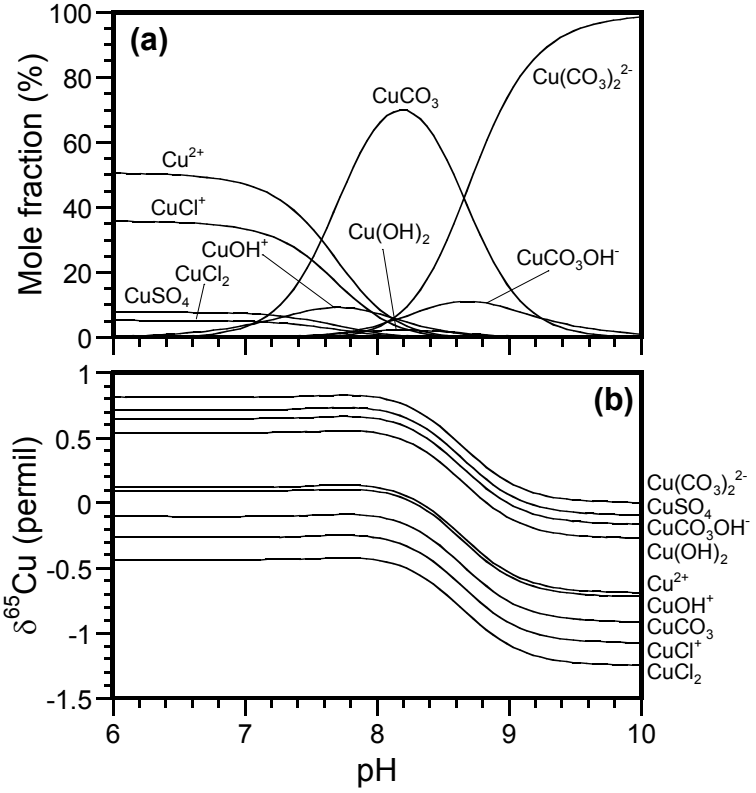


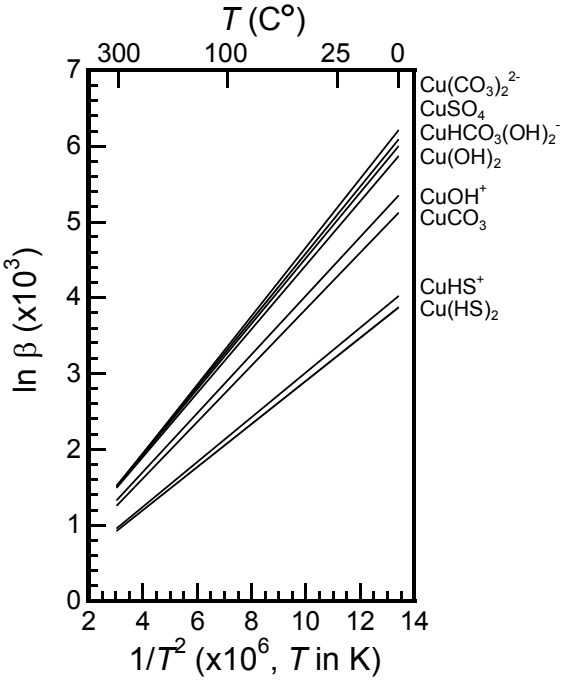
o) $CuHA(H_2O)_4^{+}$
(A: D-ascorbate)

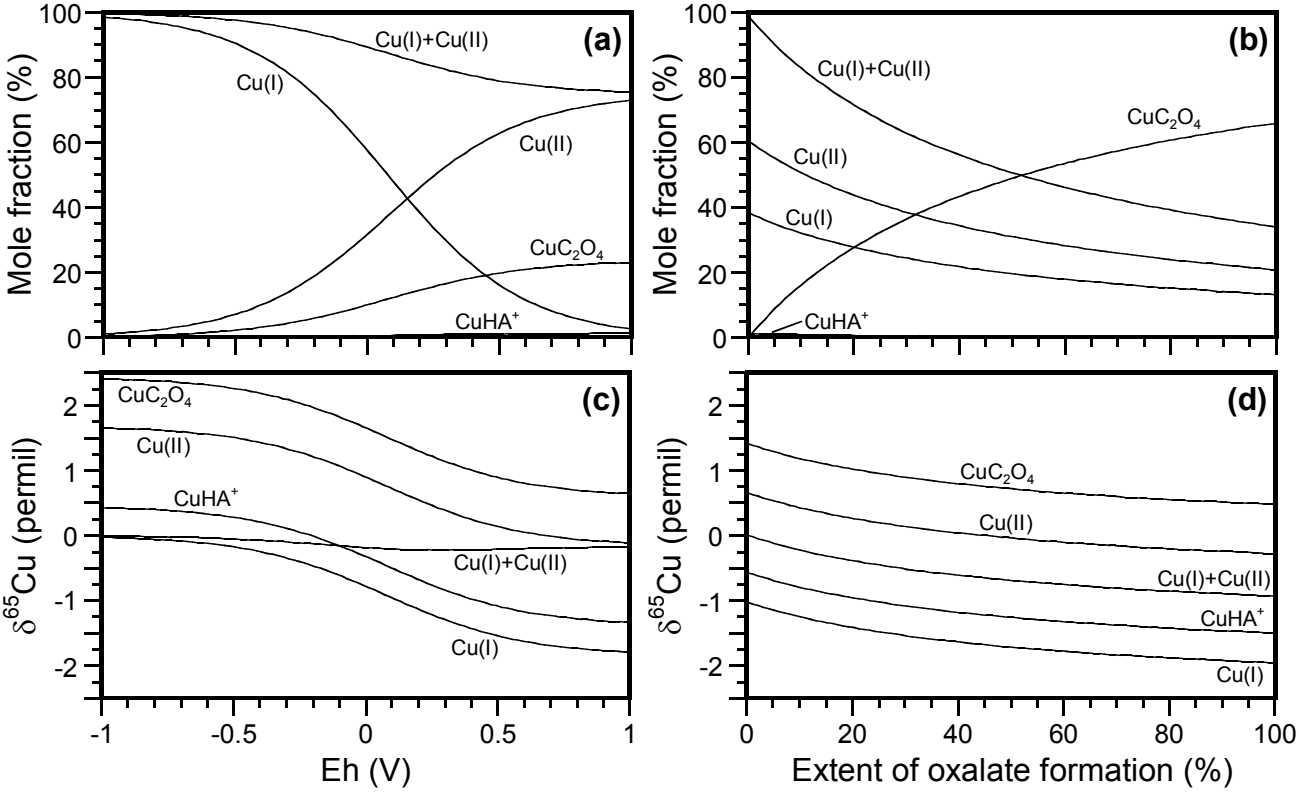


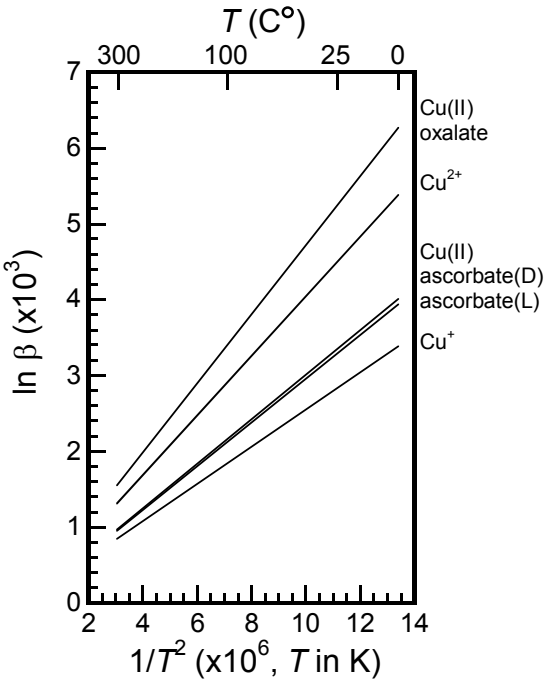
p) $CuC_2O_4(H_2O)_2$


T (C°)
300
100
25
0
7
6
5
4
3
2
1
0
ln β (x10^3)
2
4
6
8
10
12
14
1/T^2 (x10^6, T in K)
Cu(H2O)5 2+
Cu(H2O)6 2+
CuCl(H2O)4 +
CuCl2(H2O)3
CuCl2(H2O)4
CuCl3H2O-


(a)
Mole fraction (%)
100
80
60
40
20
0
Cu2+
CuCl+
CuOH+
CuCl2
CuSO4
CuCO3
Cu(OH)2
Cu(CO3)2 2-
CuCO3OH-
(b)
δ65Cu (permil)
1
0.5
0
-0.5
-1
-1.5
Cu(CO3)2 2-
CuSO4
CuCO3OH-
Cu(OH)2
Cu2+
CuOH+
CuCO3
CuCl+
CuCl2
6
7
8
9
10
pH


T (C°)
300
100
25
0
7
6
5
4
3
2
1
0
ln β (x10^3)
2
4
6
8
10
12
14
1/T^2 (x10^6, T in K)
Cu(CO3)2 2-
CuSO4
CuHCO3(OH)2 -
Cu(OH)2
CuOH+
CuCO3
CuHS+
Cu(HS)2


(a)
(b)
(c)
(d)
Mole fraction (%)
Cu(I)+Cu(II)
Cu(I)
Cu(II)
CuC_2O_4
$CuHA^+$
δ^{65}Cu (permil)
Eh (V)
Extent of oxalate formation (%)


T (C°)
300
100
25
0
7
6
5
4
3
2
1
0
ln β (x10^3)
2
4
6
8
10
12
14
1/T^2 (x10^6, T in K)
Cu(II)
oxalate
Cu2+
Cu(II)
ascorbate(D)
ascorbate(L)
Cu+

Supporting Information

Copper isotope fractionation between aqueous compounds relevant to low temperature geochemistry and biology

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Table S1. Optimized structure Cartesian coordinates of hydrated Cu(I) and Cu(II) ions and Cu(II) complexes. (see Figure 2).

$Cu(H_2O)_5^{2+}$

Element	X	Y	Z
Cu	0.000000	0.000000	0.180286
O	-0.000218	1.972347	0.416359
O	-2.015695	0.000003	0.367094
O	0.000218	-1.972347	0.416359
O	2.015695	-0.000003	0.367094
O	0.000000	0.000000	-2.017628
H	-0.788497	2.520100	0.544468
H	0.787668	2.520277	0.546113
H	-0.787668	-2.520277	0.546113
H	0.788497	-2.520100	0.544468
H	-2.541191	0.000171	1.181710
H	-2.620652	-0.000935	-0.390193
H	2.541191	-0.000171	1.181710
H	2.620652	0.000935	-0.390193
H	-0.000087	0.774145	-2.598417
H	0.000087	-0.774145	-2.598417

$Cu(H_2O)_6^{2+}$

Element	X	Y	Z
Cu	0.000038	-0.000034	0.000063
O	-0.088873	2.019575	0.031113
O	-0.024969	-0.086591	2.300836
O	2.025399	0.080251	0.024068
O	0.088810	-2.019630	-0.031022
O	0.024925	0.086561	-2.300618
O	-2.025376	-0.080204	-0.023865
H	0.668784	2.613652	0.123299
H	-0.902057	2.538568	0.101414
H	0.902001	-2.538615	-0.101323
H	-0.668838	-2.613716	-0.123240
H	-0.067738	0.644710	2.931884
H	0.005459	-0.892336	2.834501
H	-0.005323	0.892306	-2.834292
H	0.067755	-0.644755	-2.931647
H	2.576945	0.077097	0.819263
H	2.591990	0.154602	-0.756953
H	-2.591929	-0.154550	0.757185
H	-2.576976	-0.076949	-0.819023

$CuCl(H_2O)_4^{2+}$

Element	X	Y	Z
Cu	-0.016654	0.212129	-0.176174
Cl	-0.368293	-1.902143	-0.655033
O	-0.263347	-0.047793	1.850095
O	2.209959	-0.237365	0.440996
O	-0.036021	2.218349	0.250375
O	-0.057535	0.711653	-2.157294
H	0.598254	-0.331813	2.193790
H	-0.889110	-0.757015	2.061119
H	0.438028	2.925105	-0.204498
H	-0.248494	2.513422	1.145250
H	3.038932	0.256513	0.412129
H	2.414530	-1.133283	0.138808
H	-0.785481	1.250808	-2.496952
H	-0.059913	-0.113878	-2.668013

$CuCl_2(H_2O)_3$

Element	X	Y	Z
Cu	-0.053962	0.000888	-0.169852
Cl	0.052761	2.249760	-0.117204
Cl	0.050030	-2.247826	-0.115168
O	-0.166668	0.001703	1.905225
O	0.472730	-0.000037	-2.167140

O	-2.337733	0.004542	-0.702549
H	0.114046	0.787034	-2.597917
H	0.111330	-0.785773	-2.598069
H	0.267547	-0.788948	2.253624
H	0.269249	0.791416	2.253590
H	-2.746356	0.783330	-0.306552
H	-2.752723	-0.768865	-0.302717

$CuCl_2(H_2O)_4$

Element	X	Y	Z
Cu	0.000113	-0.000205	0.000036
Cl	0.001187	-2.268694	0.000102
Cl	-0.000962	2.268241	-0.000026
O	0.417498	0.000178	2.071588
O	2.327682	0.000039	-0.692256
O	-0.417251	-0.000257	-2.071517
O	-2.327453	-0.001831	0.692327
H	-2.708483	-0.776704	0.262520
H	-2.710171	0.772049	0.262246
H	0.031352	0.780962	-2.422591
H	0.032951	-0.780315	-2.423107
H	2.709142	-0.774664	-0.262522
H	2.709964	0.774089	-0.262095
H	-0.031968	0.780871	2.422726
H	-0.031827	-0.780407	2.423132

$CuCl_3H_2O^-$

Element	X	Y	Z
Cu	0.009270	0.089718	-0.002037
Cl	2.197046	0.600440	0.407279
Cl	-0.053553	-0.775059	-2.050390
Cl	-2.075181	0.930696	0.398702
O	-0.031900	-0.399468	2.220232
H	-0.770277	0.213170	2.362199
H	0.792853	0.090825	2.362505

$CuOH(H_2O)_4^+$

Element	X	Y	Z
Cu	-0.022412	-0.011572	0.135042
O	2.055857	0.070828	-0.052489
O	-2.050422	0.169765	-0.181485
O	0.159947	1.789601	-0.261094
O	-0.205225	-2.061829	0.224458
O	0.053073	-0.361275	2.421138
H	2.051118	1.010485	-0.319345
H	2.660380	-0.414596	-0.627116
H	-2.204931	0.986925	-0.676734

H	-2.650954	-0.512055	-0.507452
H	-0.097467	2.412135	0.429233
H	-0.047966	-2.399730	1.116909
H	0.091646	-2.725054	-0.410229
H	0.872675	-0.124189	2.873930
H	-0.665321	-0.109440	3.015233

$Cu(OH)_2(H_2O)_3$

Element	X	Y	Z
Cu	-0.258245	-0.086613	-0.062472
O	-0.074679	-0.232907	1.820662
O	2.081764	0.067472	0.259624
O	-0.399476	2.106958	-0.460200
O	-0.677539	0.056454	-1.875154
O	-0.551081	-2.201797	0.273191
H	-0.175399	-0.497968	-2.477903
H	-1.413113	-2.553797	0.027322
H	-0.566410	-1.987168	1.228999
H	2.369866	0.976539	0.124900
H	1.738922	0.025664	1.174903
H	-1.195357	2.594308	-0.223017
H	-0.543869	1.724067	-1.363498
H	-0.468696	0.448284	2.370949

$CuCO_3(H_2O)_2$

Element	X	Y	Z
Cu	0.248982	0.000870	-0.001777
O	1.470106	1.668045	-0.237640
O	1.470728	-1.665996	0.239991
O	-1.340955	1.081270	-0.128922
O	-1.338478	-1.082522	0.125223
O	-3.325503	-0.003074	-0.002008
C	-2.117328	-0.001419	-0.001917
H	2.092931	1.971316	0.432853
H	0.791443	2.353819	-0.329161
H	0.791117	-2.351065	0.329900
H	2.096954	-1.971245	-0.426543

$Cu(CO_3)_2^{2-}$

Element	X	Y	Z
Cu	0.000000	0.000000	0.000000
O	1.670093	1.094791	0.000000
O	1.670093	-1.094791	0.000000
O	-1.670093	1.094791	0.000000
O	-1.670093	-1.094791	0.000000
O	3.658669	0.000000	0.000000
O	-3.658669	0.000000	0.000000

C	2.413378	0.000000	0.000000
C	-2.413378	0.000000	0.000000

$CuHCO_3(OH)_2^-$

Element	X	Y	Z
Cu	0.328828	-0.274402	0.333280
O	-0.217938	0.652837	1.889544
O	2.152371	-0.434121	0.505155
O	-1.358315	-0.720389	-0.512057
O	-2.850925	-0.477652	-2.183668
O	-0.850477	0.562886	-2.262179
C	-1.778817	-0.270627	-1.625885
H	2.446380	-0.021985	1.321861
H	-1.181615	0.642755	1.857756
H	-1.280353	0.840660	-3.079424

$CuSO_4(H_2O)_4$

Element	X	Y	Z
Cu	0.747523	-0.018631	0.075914
S	-2.464712	0.089386	0.319198
O	0.888308	1.472448	-1.374296
O	1.260468	-1.547098	-1.216183
O	-1.460921	0.074115	-0.784172
O	-3.860376	0.146652	-0.015297
O	-2.105782	1.314366	1.248990
O	-2.198978	-1.199463	1.194935
O	0.426005	1.463763	1.245656
O	0.334120	-1.521773	1.204522
H	0.822684	1.412610	2.120663
H	0.727408	-1.537786	2.082364
H	-1.070215	1.435319	1.324962
H	-1.181852	-1.395474	1.269655
H	-0.031570	1.461652	-1.687718
H	0.699514	-1.631741	-1.997308
H	0.934346	2.226004	-0.763219
H	0.994031	-2.244346	-0.588664

$CuHS(H_2O)_4^+$

Element	X	Y	Z
Cu	0.005656	0.054181	0.049629
S	0.046759	2.225860	-0.652513
O	2.066189	0.034639	0.017085
O	-2.046642	0.067176	-0.000969
O	-0.098475	-2.084607	0.119384
O	-0.014729	-0.342819	2.333240
H	2.342733	0.886375	-0.359080
H	2.619756	-0.660348	-0.362321

H	-2.350685	0.888640	-0.417416
H	-2.561894	-0.668691	-0.356925
H	0.013829	2.775894	0.581471
H	-0.038801	-2.444466	1.013933
H	0.055219	-2.798994	-0.509691
H	0.752827	-0.111541	2.871191
H	-0.791745	-0.101300	2.852979

$Cu(HS)_2(H_2O)_3$

Element	X	Y	Z
Cu	-0.314974	-0.153083	0.141975
S	-0.177791	-0.026204	2.425827
S	-0.977088	-0.352010	-2.086603
O	2.022133	0.047647	0.018214
O	-0.359897	2.013095	-0.277947
O	-0.584294	-2.264904	0.309083
H	0.260936	-0.547023	-2.586321
H	-1.025393	-2.457587	-0.533692
H	-1.180639	-2.509597	1.028124
H	2.206699	0.965967	-0.211249
H	2.078845	0.012600	0.986178
H	-1.007256	2.546627	0.198468
H	-0.707717	1.864863	-1.179080
H	-0.366876	1.299105	2.585329

$Cu(H_2O)_2^+$, Cu(I)

Element	X	Y	Z
Cu	0.000000	0.000000	0.000000
O	1.917316	0.000000	0.000000
O	-1.917316	0.000000	0.000000
H	2.479474	0.000000	0.785072
H	2.479474	0.000000	-0.785072
H	-2.479474	0.785072	0.000000
H	-2.479474	-0.785072	0.000000

$CuH(\text{L-ascorbate})(H_2O)_4^+$

Element	X	Y	Z
Cu	-2.554119	0.204618	-0.182677
O	2.495659	-1.159318	2.512367
O	2.452051	-0.123655	0.482443
O	0.832979	2.264059	0.187868
O	2.921441	1.402529	-2.662114
O	-0.251520	-1.875139	2.006688
O	-0.902877	-0.653920	-0.701190
O	-1.802772	1.980765	0.480774
O	-2.984382	-1.344893	1.462135
O	-3.638265	-1.258716	-1.373516

O	-4.488981	1.096700	-0.188664
C	0.210170	-0.634730	-0.055714
C	0.533793	-1.180051	1.159370
C	1.917511	-0.858682	1.501999
C	1.476723	0.028661	-0.581649
C	1.324332	1.507831	-0.932285
C	2.611406	2.124521	-1.479680
H	0.282491	-2.124993	2.781107
H	1.856949	-0.495139	-1.462939
H	0.550722	1.582431	-1.699857
H	2.426476	3.184812	-1.685448
H	3.412119	2.041566	-0.733982
H	1.495728	2.278551	0.891165
H	3.769228	1.694906	-3.011156
H	-0.822376	2.131725	0.453305
H	-2.229187	2.799140	0.202579
H	-5.124762	0.619254	-0.737069
H	-4.976734	1.533791	0.518984
H	-2.135960	-1.697050	1.787704
H	-3.557018	-1.253973	2.232088
H	-3.692109	-2.023413	-0.782479
H	-3.169074	-1.562546	-2.161632

CuH(D-ascorbate)$(H_2O)_4^+$

Element	X	Y	Z
Cu	1.338456	0.278439	2.323761
O	0.071296	1.001644	1.087992
O	3.072810	0.897735	1.231687
O	1.773378	-1.729001	1.305373
O	-0.285916	0.071930	3.660925
O	2.706954	0.025220	3.885105
O	1.836297	1.689085	-1.258622
O	0.437176	0.641637	-3.585234
O	-1.131435	-0.102936	-2.109935
O	-0.309048	-2.292050	-0.476613
O	-2.377214	-0.591814	1.927738
C	-0.098546	0.703108	-0.149174
C	0.661040	1.030157	-1.240427
C	0.029557	0.534435	-2.460046
C	-1.310506	-0.058681	-0.671084
C	-1.489555	-1.515966	-0.211950
C	-1.770799	-1.723141	1.289766
H	-2.225667	0.499580	-0.459825
H	-2.314597	-1.919188	-0.807171
H	-0.261507	-2.495742	-1.418672
H	-2.380007	-2.618680	1.425075
H	-0.818875	-1.901148	1.791013

H	-3.309482	-0.757823	2.100138
H	2.102750	1.825492	-2.183748
H	2.843084	1.455503	0.467547
H	3.464206	0.098983	0.853094
H	3.521725	0.542562	3.868942
H	2.519606	-0.218994	4.798761
H	-1.112200	0.003512	3.130698
H	-0.438922	0.769088	4.309435
H	1.151785	-2.028910	0.608694
H	2.088039	-2.518759	1.759410

$CuC_2O_4(H_2O)_2$

Element	X	Y	Z
Cu	0.220299	0.001436	-0.001762
O	-1.136604	0.668638	1.127124
O	-1.137806	-0.672486	-1.125207
O	-3.370391	0.723223	1.234860
O	-3.371751	-0.739772	-1.222759
O	1.501827	0.874109	1.359112
O	1.503177	-0.864008	-1.365652
C	-2.354928	0.396973	0.678715
C	-2.355545	-0.407526	-0.671427
H	0.833390	1.221592	1.973878
H	2.155906	0.391795	1.877813
H	2.155176	-0.378487	-1.884016
H	0.837250	-1.215488	-1.980679

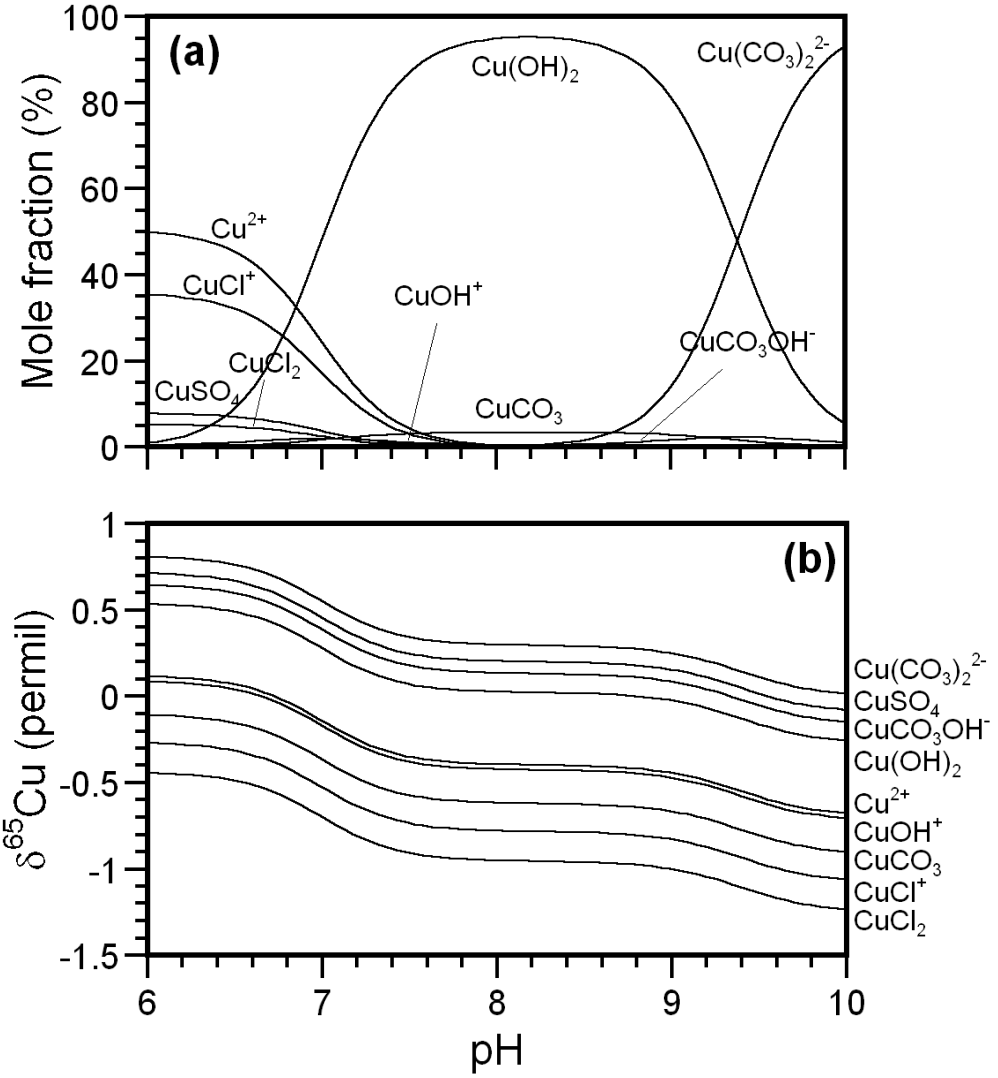

Figure S1. Mole fractions of Cu(II) species and Cu isotopic variations as functions of pH at 298 K. a) Mole fractions of Cu species, b) Species δ^{65}Cu relative to the bulk solution. Conditions are the same with those of Fig. 4 except for second hydrolysis constant. log*β_2 = –16.65 used in Fig. 4 was substituted by log β_2 = 14.3 and ion product pK_W = 14 (ionic strength I = 0).