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Ion-exchange fractionation of copper and zinc isotopes

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Abstract—Whether transition element isotopes can be fractionated at equilibrium in nature is still uncertain. Standard solutions of Cu and Zn were eluted on an anion-exchange resin, and the isotopic compositions of Cu (with respect to Zn) of the eluted fractions were measured by multiple-collector inductively coupled plasma mass spectrometry. It was found that for pure Cu solutions, the elution curves are consistent with a $^{63}Cu/^{65}Cu$ mass fractionation coefficient of 0.46‰ in 7 mol/L HCl and 0.67‰ in 3 mol/L HCl between the resin and the solution. Batch fractionation experiments confirm that equilibrium fractionation of Cu between resin and 7 mol/L HCl is ~0.4‰ and therefore indicates that there is no need to invoke kinetic fractionation during the elution. Zn isotope fractionation is an order of magnitude smaller, with a $^{66}Zn/^{68}Zn$ fractionation factor of 0.02‰ in 12 mol/L HCl. Cu isotope fractionation results determined from a chalcopyrite solution in 7 mol/L HCl give a fractionation factor of 0.58‰, which indicates that Fe may interfere with Cu fractionation.

Comparison of Cu and Zn results suggests that the extent of Cu isotopic fractionation may signal the presence of so far unidentified polynuclear complexes in solution. In contrast, we see no compelling reason to ascribe isotope fractionation to the coexistence of different oxidation states. We further suggest that published evidence for iron isotopic fractionation in nature and in laboratory experiments may indicate the distortion of low-spin Fe tetrahedral complexes.

The isotope geochemistry of transition elements may shed new light on their coordination chemistry. Their isotopic fractionation in the natural environment may be interpreted using models of thermodynamic fractionation. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

Recent developments in multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) have revealed natural variations in the abundance of stable isotopes of Fe, Cu, and Zn in ores, ferromanganese nodules, sediments, and organic samples (Maréchal et al., 1999, 2000; Zhu et al., 2000a, 2000b; Anbar et al., 2000). In particular, the data recently obtained on Cu isotopic variability support previous observations by Walker et al. (1958) and Shields et al. (1965), who, in spite of a relatively poor analytical precision of 1.5‰, reported a range of several per mil in $^{65}Cu/^{63}Cu$ ratios in Cu-bearing minerals. Because transition metals participate actively in multiple biologic and low-temperature inorganic chemical reactions, their isotopic variability offers an unexplored potential as biogeochemical and geochemical tracers (Beard et al., 1999; Maréchal et al., 2000; Zhu et al., 2000a, 2000b). Although mass fractionation on ion-exchange resins has been known for some time, it has so far been thought to be restricted to anions such as borates (Kakihana et al., 1977) or to elements with relatively large mass spreads such as Ca (Russell and Papanastassiou, 1978). In a preliminary study, however, we reported that Cu isotopes can also be fractionated by chromatographic processes (Maréchal et al., 1999). Anbar et al. (2000) extended this observation to include Fe isotopes. These observations may be relevant to the low-temperature inorganic environment and to biologic processes if it can be shown that large fractionation effects are not the result of particular kinetic conditions on ion-exchange columns but rather reflect equilibrium partitioning between solutions and the species adsorbed on the resin. Demonstrating that fractionation of transition element isotopes in the laboratory takes place at equilibrium is required to support the interpretation that the natural isotopic variability of Cu, Zn, and Fe results from equilibrium fractionation and not from kinetic effects.

In this work, we present a study of chemical isotope fractionations of Cu and Zn in laboratory experiments at room temperature. The relative mass difference between ^{65}Cu and ^{63}Cu is approximately the same as between ^{68}Zn and ^{66}Zn, but Cu and Zn have different electronic configurations and different redox behaviors. Cu is mostly present in two oxidation states, Cu(I) and Cu(II), whereas Zn is only present as Zn(II) (Cu[0] and Zn[0] will be disregarded here). Cu(II) is prone to Jahn-Teller distortions in an octahedral field of ligands, while Zn(II) shows no crystal-field effect at all (e.g., Gerloch, 1981; Åkesson et al., 1992a, 1992b; Gerloch and Constable, 1994; Cotton et al., 1999; Figgis and Hitchman, 2000).

In the experiments presented here, we return to the isotopic fractionation on anion-exchange resin in HCl media identified by Maréchal et al. (1999) for Cu. To evaluate whether isotopic fractionation takes place at equilibrium or is a kinetic effect, Cu fractionation between the resin and the HCl solution was also investigated in a batch experiment.

2. ANALYTICAL PROCEDURE

2.1. Chemistry

As in our initial study (Maréchal et al., 1999), we used macroporous, strongly basic anion-exchange resin (Bio-Rad

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AG MP-1, 100 to 200 mesh) consisting of positively charged, quaternary ammonium groups chemically bound to styrene-divinylbenzene copolymers. The AG MP-1 resin has a high porosity (20%). In hydrochloric acid, the active sites of the resin bind to the counter-anion Cl^- that can be reversibly exchanged with other chlorocomplex anions. As discussed below, a solution of Cu or Zn chloride produces predominantly two anionic species: MCl_3^- and MCl_4^{2-}, where M stands for either Cu(II) or Zn(II). Exchanges between these anions and the resin are governed by the following reactions:

$$R - Cl^- + MCl_3^- \overset{K_a}{\longleftrightarrow} R - MCl_3^- + Cl^-$$

$$2(R - Cl^-) + MCl_4^{2-} \overset{K_a}{\longleftrightarrow} 2R - MCl_4^{2-} + 2Cl^-,$$

where K_a and K_b are equilibrium constants. In these reactions, R represents the active sites of the resin matrix. Chlorocomplex species therefore partition between dissolved and resin-bound forms as a function of a distribution coefficient $D = C_r/C_s$, where C_r is the concentration of resin-bound forms per gram of resin (R-MCl_3^- and 2R-MCl_4^{2-}), and C_s is the concentration of dissolved species per milliliter of solution (M^{2+}, MCl^+, MCl_2, MCl_3^-, and MCl_4^{2-}). D is a coefficient characteristic of each metal ion: On AG MP-1 and in hydrochloric acid, D is larger for Zn^{2+} than for Cu^{2+} by a factor varying from ~2 to 60 (van der Walt et al., 1985). Finally, the distribution coefficient constrains the reagent volume v (ml) required for the elution of a substance to its maximum concentration from a column with an interstitial volume V (ml), given as

$$v = V\,(D + 1). \tag{1}$$

The interstitial volume V is the fraction of the volume not occupied by resin and is normally determined by eluting a large molecular weight organic component that is not retained by the resin ($D = 0$). It is independent of the metal ion but varies with the normality of the eluting reagent, whereas the retention volume v also depends on the nature of the metal ion.

The columns used for chromatography were quartz tubes 4.3 cm in length and 0.69 cm in internal diameter packed with AG MP-1 (resin bed volume = 1.6 mL). Pure Zn JMC 3-0749 L and Cu National Institute of Standards and Technology (NIST) 976 standard solutions containing 40 μg of element were used for the experiments. A composite sample of chalcopyrite and sphalerite from a black smoker (NL2206b, Lau Basin, Pacific Ocean) mainly composed of Cu, Fe, Zn, S, SiO_2, Ba, Ca, and Al_2O_3 (Fouquet et al., 1991) was also used for the Cu experiments. A 0.2-mg powdered split of this sample containing ~43 μg of Cu was dissolved and eluted on the resin. The abundances of Cu, Zn, and Fe were comparable. Less than a fraction of a percent of the total resin exchange capacity was used in each experiment. Before loading on the column, the samples were dissolved in 0.2 mL of 3 mol/L HCl + 0.001% H2O2 for Cu NIST 976 experiment, 1 mL of 7 mol/L HCl + 0.001% H2O2 for Cu NL2206b experiment, and 0.2 mL of 12 mol/L HCl for Zn JMC 3 to 0749 L experiment. Cu was eluted in 3 mol/L HCl (4.3 mL) and 7 mol/L HCl (25 mL) solutions mixed with 0.001% H2O2, which serves to prevent reduction of Cu(II) by the resin (van der Walt et al., 1985). The samples were collected in fractions of 0.3 mL of 3 mol/L HCl and fractions of 1 mL of 7 mol/L HCl. The solutions were evaporated to dryness and the residues taken up in 0.1 mL of concentrated HNO_3, then evaporated to dryness again to drive off chloride ions that may create interferences in MC-ICP-MS. The samples were finally dissolved in 0.05 mol/L HNO_3 mixed with 1 ppm of Zn JMC 3-0749 L for isotopic analysis. Zn was eluted in 12 mol/L HCl (58 mL) and collected in fractions of 3 mL. The samples were evaporated to dryness and the residues taken up in concentrated HNO_3, reevaporated, and dissolved in 0.05 mol/L HNO_3 mixed with 1 ppm of Cu NIST 976 for isotopic determinations. Concentrations were determined on aliquots of the Cu and Zn sample solutions. Each fraction was therefore analyzed for both its concentration and isotopic composition. The Cu isotopic composition of the black smoker sample is known from Maréchal et al. (1999): 0.32 ± 0.04‰. Cu NIST 976 and Zn JMC 3-0749 L are standard reference materials. To evaluate how the nature of the complexing anion may affect the results, Cu NIST 976 and Zn JMC 3-0749 L standards were also eluted on AG MP-1 in 0.5 mol/L HNO_3.

Batch equilibration experiments were also carried out in duplicate using a Cu JMC 400882 B standard solution. The experimental conditions were similar to those used by van der Walt et al. (1985) for the determination of trace element distribution coefficients. About 250 mg of dried AG MP-1 were poured together with ~25 mL of a 7-mol/L HCl solution containing 0.001% H_2O_2 and 0.2 milli-equivalents of Cu(II) (e.g., ~6.5 mg of Cu) in a Teflon beaker. About 10% of the total exchange capacity of the resin was used in this experiment. The beaker was placed on a very slow rotating plate weakly tilted to ensure gentle mixing of the resin and the liquid. The mixture was left for 22 h under a laminar flow hood, and then the resin was separated by filtration on a quartz column, collecting the acidic solution in a beaker without washing. The resin was then rinsed with 15 mL of 0.5 mol/L HNO_3 and the resin-bound Cu collected in another beaker. The solutions were evaporated to dryness and the residues dissolved in concentrated HNO_3, reevaporated, and redissolved in 0.05 mol/L HNO_3 mixed with 1 ppm of Zn JMC 3-0749 L for isotope analysis. Aliquots of the samples were used for Cu concentration analysis.

2.2. Mass Spectrometry

Isotopic abundance were measured by MC-ICP-MS (Plasma 54, VG Elemental). The instrumental mass bias was corrected with respect to the isotopic composition of a standard of a different element added to the sample (Zn for Cu samples, Cu for Zn samples; Maréchal et al., 1999). We used the Zn JMC 3-0749 L and Cu NIST 976 solutions as standard references. Standards were run alternately with the samples and the isotopic compositions of the samples expressed relative to the isotopic composition of the standard in a delta (per mil) notation:

$$\delta^{65}Cu = \left[\frac{(^{65}Cu/^{63}Cu)_{sample}}{(^{65}Cu/^{63}Cu)_{NIST\ 976}} - 1\right] \times 1000 \tag{2}$$

$$\delta^{68}Zn = \left[\frac{(^{68}Zn/^{66}Zn)_{sample}}{(^{68}Zn/^{66}Zn)_{JMC\ 3\text{-}0749\ L}} - 1\right] \times 1000. \tag{3}$$

The analytical precision achieved by this procedure is 0.04‰ at the 2σ level. We chose to measure the $^{68}Zn/^{66}Zn$ ratio instead

Table 1. Elution of Cu from the NL2206b chalcopyrite in 7 mol/L HCl and from the NIST 976 standard in 3 mol/L HCl (+0.001% H_2O_2) on AG MP-1 anion-exchange resin (1.6-mL bed volume). Quantity of Cu recovered in each fraction and its δ^{65}Cu value. The last column shows the cumulated δ^{65}Cu values. Errors on the mean δ^{65}Cu are at the 95% confidence level and were evaluated assuming an error of 5% on the amount of Cu and an error of 0.04 delta units on the δ^{65}Cu of each fraction.

Fraction number	Eluate (mL)	Cu (μg)	δ^{65}Cu (‰)	Cumulative δ^{65}Cu (‰)
Cu NL2206b (chalcopyrite): 7 mol/L HCl + 0.001% H_2O_2				
1	8 to 9	0.00		
2	10 to 11	0.08	8.95	8.95
3	11 to 12	0.43	7.64	7.85
4	12 to 13	1.51	6.12	6.56
5	13 to 14	3.68	4.42	5.18
6	14 to 15	5.30	3.01	4.13
7	15 to 16	8.22	1.48	3.00
8	16 to 17	8.56	–0.08	2.05
9	17 to 18	6.69	–1.59	1.34
10	18 to 19	4.05	–3.05	0.88
11	19 to 20	2.39	–4.26	0.58
12	20 to 21	1.28	–5.54	0.40
13	21 to 22	0.61	–6.84	0.29
14	22 to 23	0.26	–8.17	0.24
15	23 to 24	0.09	–9.16	0.22
16	24 to 25	0.03	–10.09	0.21 ± 0.23
Cu NIST 976: 3 mol/L HCl + 0.001% H_2O_2				
1	1.3 to 1.6	0.00		
2	1.6 to 1.9	0.99	12.58	12.58
3	1.9 to 2.2	3.93	6.95	8.09
4	2.2 to 2.5	10.72	2.65	4.36
5	2.5 to 2.8	11.55	–0.12	2.46
6	2.8 to 3.1	8.39	–2.31	1.33
7	3.1 to 3.4	3.86	–4.56	0.76
8	3.4 to 3.7	1.28	–7.47	0.50
9	3.7 to 4.0	0.44	–9.87	0.39
10	4.0 to 4.3	0.12	–11.74	0.35 ± 0.42

of the ^{66}Zn/^{64}Zn ratio because some Ni interferences with ^{64}Zn were suspected.

Cu and Zn concentrations were determined by either quadrupole ICP-MS (PlasmaQuad, VG Elemental) or MC-ICP-MS (Plasma 54, VG Elemental) using Co as a spike after calibration of the relative ionization efficiency of Cu, Zn and Co.

Table 2. Elution of Zn JMC 3-0749 L in 12 mol/L HCl on AG MP-1 anion-exchange resin (1.6-mL bed volume). Quantity of Zn recovered in each fraction and its δ^{68}Zn value. The last column shows the cumulated δ^{68}Zn values. The error assessment procedure is identical to that for Cu.

Fraction number	Eluate (mL)	Zn (μg)	δ^{68}Zn (‰)	Cumulative δ^{68}Zn (‰)
1	17 to 20	0.01	—	—
2	20 to 23	0.18	—	—
3	23 to 26	1.14	0.50	0.50
4	26 to 29	4.14	0.30	0.34
5	29 to 32	7.38	0.09	0.20
6	32 to 35	8.75	0.05	0.14
7	35 to 38	7.32	–0.13	0.07
8	38 to 41	4.91	–0.18	0.03
9	41 to 44	2.73	–0.34	0.00
10	44 to 47	1.34	–0.42	–0.01 ± 0.08
11	47 to 50	0.57	—	—
12	50 to 53	0.23	—	—
13	53 to 56	0.10	—	—
14	56 to 59	0.03	—	—

Table 3. Fractionation coefficients α calculated from the elution curves using a best fit to Eqn. A1 for each isotope (see text and Appendix). ^{i}v is the retention volume of isotope i and ^{i}s the width of the elution peak.

Sample	HCl (mol/L)	^{i}v (mL)	^{j}v (mL)	^{i}s (mL)	$^{i}_{j}\alpha^{b}$
Cu	i = ^{63}Cu, j = ^{65}Cu				
NIST 976	3	2.6880	2.6896	0.44	1.00067
NIST 976[a]	7	17.3314	17.3392	3.23	1.00046
NL2206b	7	16.6165	16.6259	2.18	1.00058
Zn	i = ^{66}Zn, j = ^{68}Zn				
JMC 3-0749L	12	34.6704	34.6712	4.85	1.00002
Fe	i = ^{54}Fe, j = ^{56}Fe				
Reagent[c]	7	4.7441	4.7454	0.73	1.00029

[a] Data from Maréchal et al. (1999).
[b] Assumed interstitial volume: 0.3 mL.
[c] Data from Anbar et al. (2000).

3. RESULTS

3.1. Chromatographic Experiments

The results of the chromatographic experiments are listed in Tables 1 to 4 and shown in Figures 1 to 4. They show that fractionation of both Cu and Zn isotopes occurs during the elutions. For Cu isotopes in 3 mol/L HCl, the δ^{65}Cu values spread over ≈24‰. Although less fractionation is observed for Zn isotopes with a total range of ≈0.9‰ of δ^{68}Zn values, this is still more than 20 times the analytical precision at the 2σ level. The first fractions of the eluate are systematically enriched in the heavy isotopes (δ^{68}Zn, δ^{65}Cu $\gg$ 0‰), indicating that the light isotopes of Cu and Zn partition more strongly into the resin than the heavier isotopes. The mean isotopic compositions calculated from the compositions of each fraction weighted by that percentage of element agree with that of the starting solution, which indicates essentially full recovery of each experiment.

The elution curve for bulk Cu can be viewed as the result of the compounding of two elution curves of ^{65}Cu and ^{63}Cu for

Table 4. Elution of Cu NIST 976 and Zn JMC 3-0749 L in 0.5 mol/L HNO_3 on AG MP-1 anion-exchange resin (1.6-mL bed volume).

Fraction number	Eluate (mL)	Cu (μg)	δ^{65}Cu (‰)
Cu NIST 976: 0.5 mol/L HNO_3			
1	0.6 to 0.9	0.00	
2	0.9 to 1.2	21.31	0.05
3	1.2 to 1.5	16.23	0.00
4	1.5 to 1.8	2.95	–0.02
5	1.8 to 2.1	0.00	
Fraction number	**Eluate (mL)**	**Zn (μg)**	**δ^{66}Zn (‰)**
Zn JMC 3-0749 L: 0.5 mol/L HNO_3			
1	0.6 to 0.9	0.00	
2	0.9 to 1.2	7.30	–0.03
3	1.2 to 1.5	6.48	–0.02
4	1.5 to 1.8	1.85	0.06
5	1.8 to 2.1	0.00	

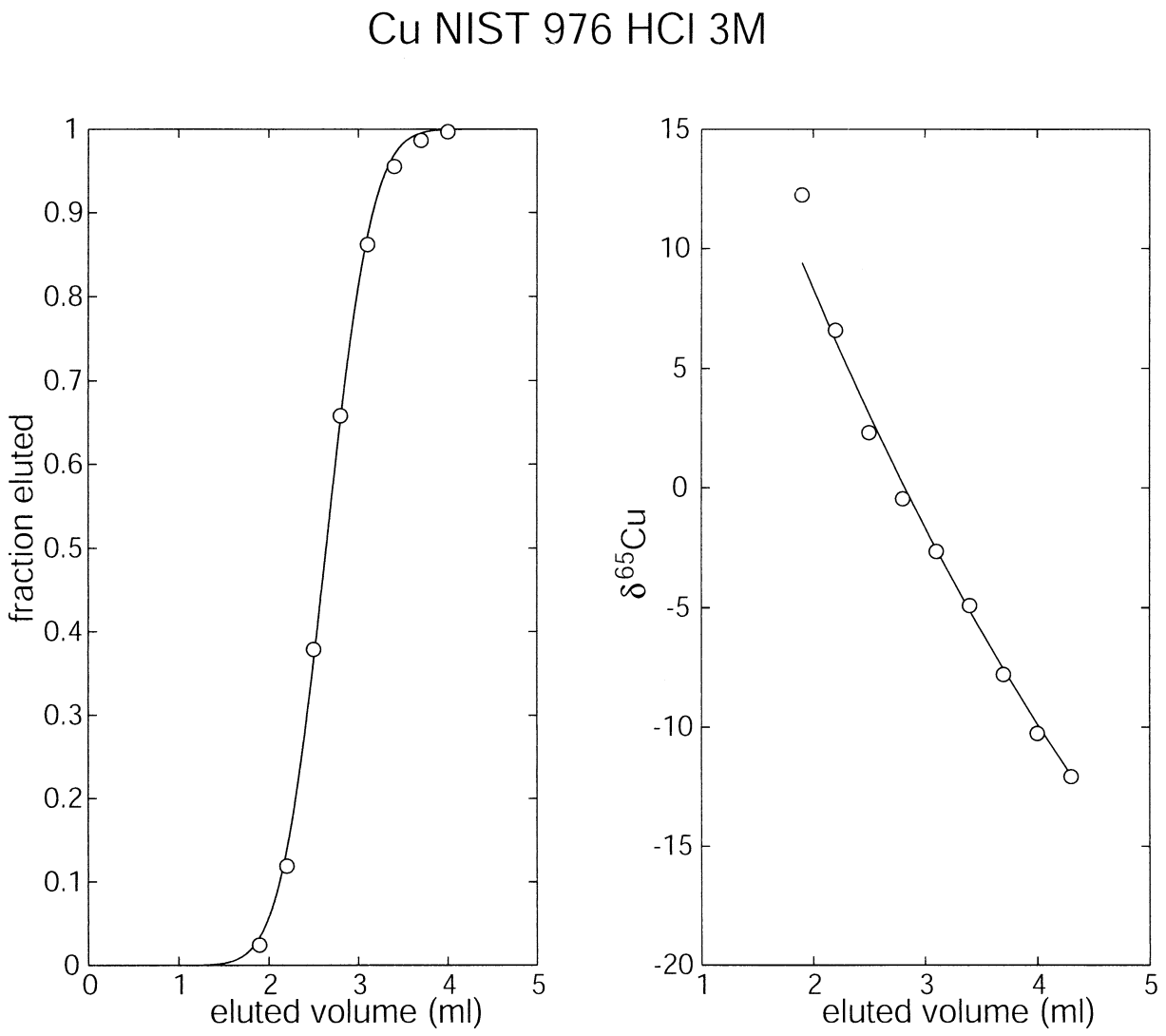

Fig. 1. Left: cumulated fractions of Cu National Institute of Standards and Technology (NIST) 976 standard eluted in 3 mol/L HCl on AG MP-1 resin as a function of the eluted volume. Right: isotopic composition of Cu in individual fractions represented as δ^{65}Cu values with respect to the bulk sample. Open circles represent the measurements, the continuous line model Eqn. A1 (see the Appendix).

Cu and of two elution curves of ^{68}Zn and ^{66}Zn for Zn. The shift between these curves can be evaluated and the isotopic separation factor between the resin and the solution phases determined relative to the distribution coefficients of each isotope. The separation factor ${}^{65}_{63}\alpha_{\mathrm{Cu}}$ for Cu isotopes is defined as

$$ {}^{63}_{65}\alpha_{\mathrm{Cu}} = \frac{D(^{63}\mathrm{Cu})}{D(^{65}\mathrm{Cu})} = \frac{^{63}v - V}{^{65}v - V} = 1 + \frac{^{63}v - {}^{65}v}{^{65}v - V}, \qquad (4) $$

where $D(^{63}\mathrm{Cu})$ and $D(^{65}\mathrm{Cu})$ stand for the distribution coefficients of ^{63}Cu and ^{65}Cu, respectively; ^{63}v and ^{65}v for their retention volume; and V for the interstitial volume of the resin. A similar expression holds for Zn isotopes. To an excellent precision, the shape of the elution curve of each isotope can be approximated by a normal (gaussian) curve (the so-called plate model; e.g., Rieman and Walton, 1970), which is verified in the present experiments (Figs. 1 to 4). The ratio of two normal variables is not distributed as a normal variable, especially when the two variables have different expectations (this is particularly clear in Fig. 4). Contrary to Anbar et al. (2000), we therefore abstained from fitting the isotopic ratios of individual fractions with a normal curve. We instead estimated the retention volumes of each Cu and Zn isotope using an inverse standard normal law based on the data of Tables 1 and 2 (see the Appendix). The fits reproduce the amount of isotope eluted in each fraction to better than 1%.

The results for ^{63}v and ^{65}v for each of the Cu experiments and ^{66}v and ^{68}v for the Zn experiment are presented in Table 3. The interstitial volumes V of the resin for the various elution schemes are not precisely known, but they should represent 10 to 30% of the resin bed (1.6 mL). Therefore, the uncertainty on V does not affect the value of 1-α by more than a few percent (~10% in the worst case of Cu in 3 mol/L HCl). The separation

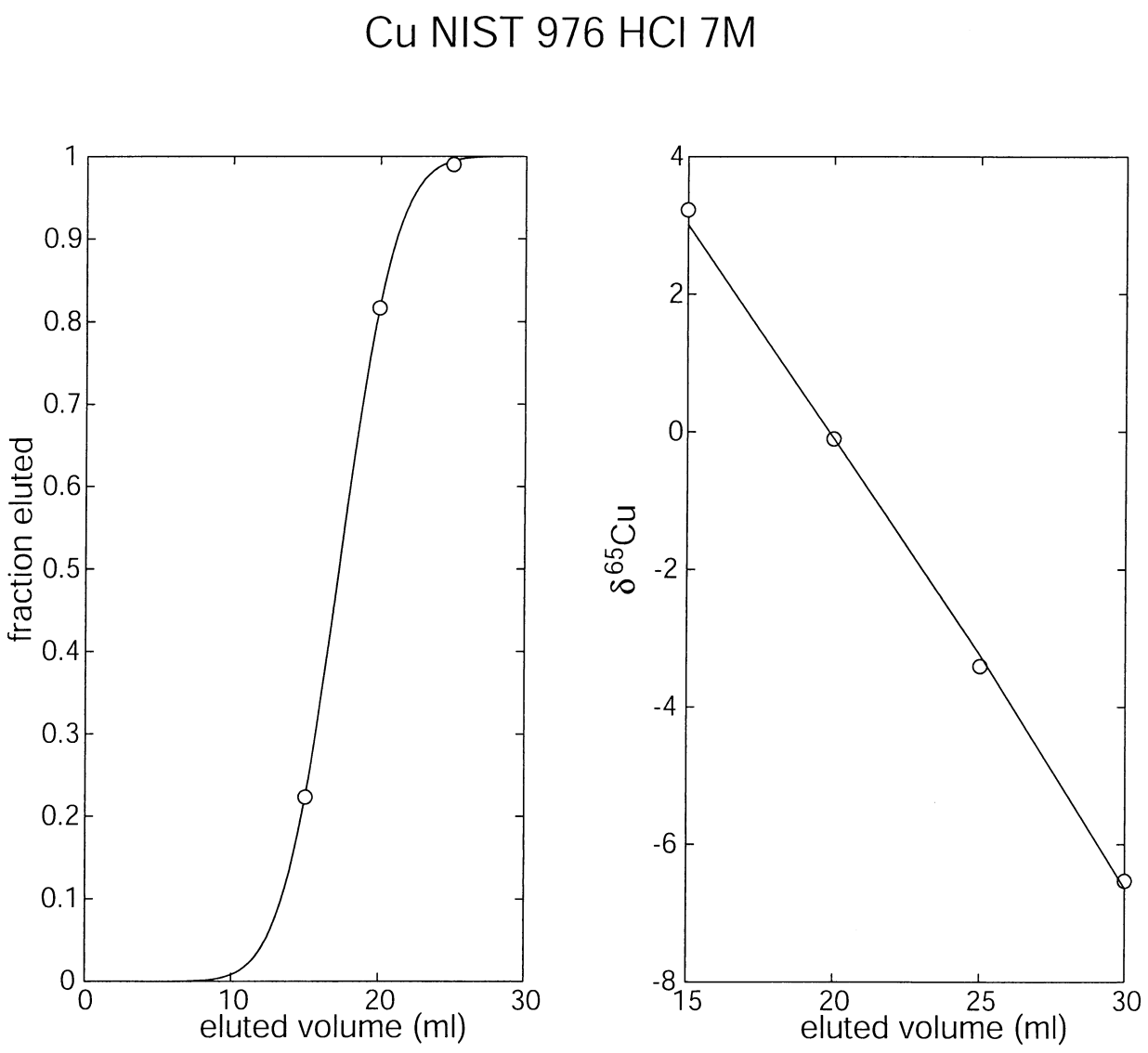

Fig. 2. Same as Figure 1 but in 7 mol/L HCl (data from Maréchal et al., 1999).

factors, reported in Table 3, are surprisingly large for pure Cu (NIST 976) in 3 mol/L HCl, with ${}^{65}_{63}\alpha_{Cu} = 1.00067$. Pure Cu eluted in four fractions using 7 mol/L HCl by Maréchal et al. (1999) gave a ${}^{65}_{63}\alpha_{Cu}$ value of 1.00046. Likewise, we obtained a smaller but significant value of ${}^{68}_{66}\alpha_{Zn} = 1.000024$ (Fig. 4). The chalcopyrite sample NL2206 eluted in 7 mol/L HCl gives a value of ${}^{65}_{63}\alpha_{Cu} = 1.00058$, higher than that of the NIST standard. For each experiment, the error function model used to represent the elution curve fits the isotopic data well (Figs. 1 to 4). Small shifts observed in the frontal and rear fractions are probably due to the small quantities of material analyzed. For comparison, we used the same method to the Fe data of Anbar et al. (2000) and obtained ${}^{56}_{54}\alpha_{Fe} = 1.0003$. This value is higher than that published by these authors (1.0001), probably because their Fe elution curve is strongly asymmetrical, which is not the case for the theoretical gaussian model.

The elution experiments for pure Cu and Zn in 0.5 mol/L HNO_3 medium show no measurable isotopic fractionation. Although the number of fractions collected was small, the amount of metal recovered in each of them was large enough to ensure that the isotopic compositions were measured to their full precision.

3.2. Equilibrium Experiment

The results of the batch equilibrium experiment for Cu JMC 400882 are reported in Table 5. A reproducible isotopic fractionation is observed between the liquid and the resin phases, with a delta difference of 0.4‰ (10 times the analytical precision). As expected, it was found that $\delta^{65}Cu_r < \delta^{65}Cu_s$, which signals that the Cu adsorbed on the resin (r) is enriched in light isotopes with respect to the Cu in solution (s). The cumulated δ^{65}Cu value of the resin-bound and dissolved Cu weighted by the fraction of Cu in each phase sums to 0.60‰ (experiment A)

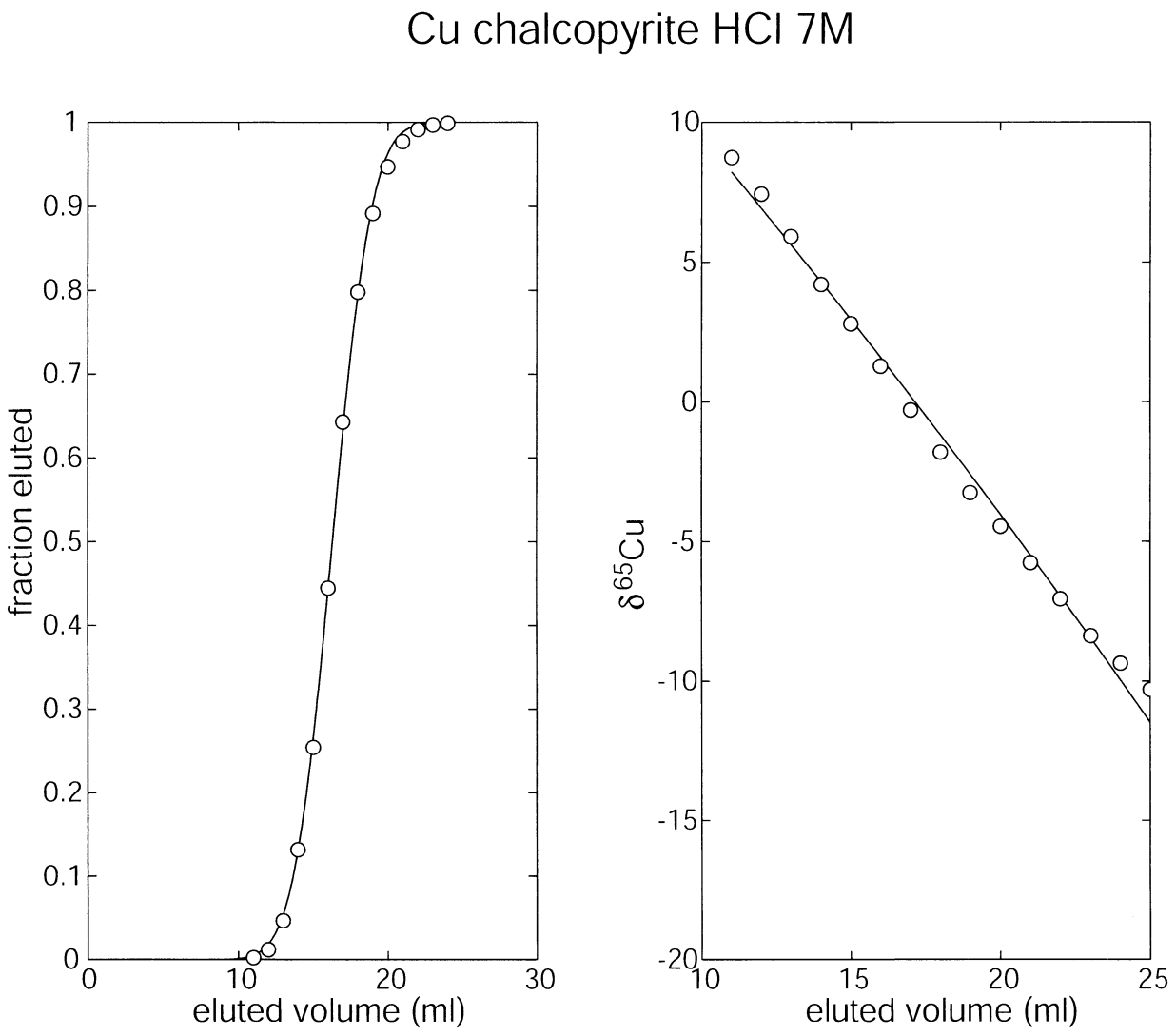

Fig. 3. Same as Figure 2 but for chalcopyrite NL2206b.

and 0.58‰ (experiment B), in agreement with the value of 0.60 ± 0.04‰ of the starting Cu JMC 400882 B solution added to the resin. Cu recovery can therefore be considered as essentially quantitative. The fractionation factor α can be related to $\delta^{65}Cu_r$ and $\delta^{65}Cu_s$ through

$$ {}^{63}_{65}\alpha_{Cu} = \frac{D(^{63}Cu)}{D(^{65}Cu)} = \left(\frac{\delta^{65}Cu_s + 1000}{\delta^{65}Cu_r + 1000}\right). \quad (5) $$

For each experiment, we found that ${}^{65}_{63}\alpha_{Cu} = 1.0004$, in agreement with the chromatographic experiment on pure Cu in 7 mol/L HCl, which indicates that the Cu isotope fractionation in the elution experiments is not significantly dependent on kinetic factors and takes place essentially at equilibrium.

4. DISCUSSION

4.1. Principles of Isotopic Fractionation

Although solutions differ from gases by the strong electrical field generated by the presence of polar solvent molecules and neighboring ions, the general theory of isotopic fractionation among gaseous molecules (Urey, 1947; Bigeleisen and Mayer, 1947; McQuarrie, 1973; Richet et al., 1977; O'Neil, 1986) hints at the possible factors that may account for the present results. In the manner of Urey (1947), we consider a typical exchange reaction:

$$ \nu_A A_1 + \nu_B B_2 \Leftrightarrow \nu_A A_2 + \nu_B B_1, $$

where A and B are molecules exchanging two isotopes of a same elements; the subscripts 1 and 2 denote the molecules with the light and heavy isotopes, respectively; and ν stands for the appropriate stoichiometric coefficient. For example, exchange of copper isotopes between the double and quadruple chlorocomplexes is described by the following reaction:

$$ {}^{63}CuCl_2^0 + {}^{65}CuCl_4^{2-} \Leftrightarrow {}^{65}CuCl_2^0 + {}^{63}CuCl_4^{2-}. $$

The equilibrium constant K for this reaction is given by

$$ K = \left(\frac{Q_{A_2}}{Q_{A_1}}\right)^{\nu_A} \Big/ \left(\frac{Q_{B_2}}{Q_{B_1}}\right)^{\nu_B}, \quad (6) $$

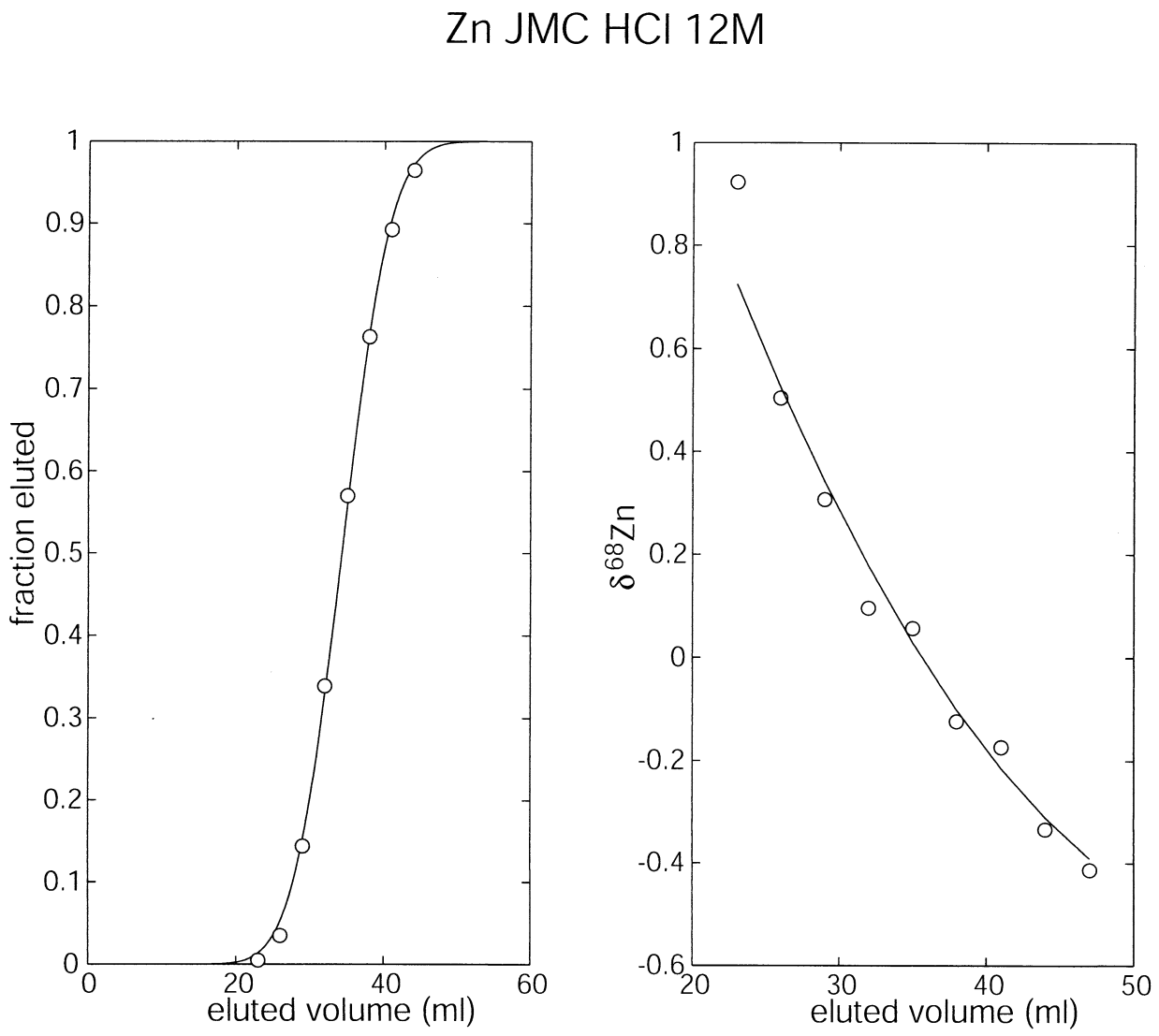

Fig. 4. Left: cumulated fractions of Zn JMC 3-0749 L standard eluted in 12 mol/L HCl on AG MP-1 resin as a function of the eluted volume. Right: isotopic composition of Zn in individual fractions represented as δ^{68}Zn values with respect to the bulk sample. Open circles represent the measurements, the continuous line model Eqn. A1 (see the Appendix).

where Q stands for the reduced partition function of each molecule. For polyatomic molecules, the ratio of reduced partition functions is, to a good approximation (Urey, 1947; Bigeleisen and Mayer, 1947):

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \prod_{i=1}^{3n-6} \frac{u_{2i}}{u_{1i}} \frac{e^{-u_{2i}/2}}{e^{-u_{1i}/2}} \frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}}, \tag{7}$$

where σ stands for the symmetry number of the molecule (the degeneracy of quantum rotational states in its point group) and n for the number of atoms in the molecule. The variable u_i is defined as $u_i = h\ \nu_i/kT$, where ν_i is the ith fundamental vibrational frequency and is normally obtained by infrared and Raman spectroscopy, T is the temperature, and h and k are the Planck and Boltzmann constants, respectively. A and B have

Table 5. Concentrations and isotopic compositions of Cu JMC 400882 B in the 7 mol/L HCl batch equilibration experiments. The solution was equilibrated for 22 h with the resin. The coefficient of isotopic fractionation is similar to that derived from the chromatographic experiment using also pure Cu (1.00046) in the same medium (Table 3).

Sample	Cu (mg)	δ^{65}Cu (‰)	${}^{63}_{65}\alpha_{Cu} = \frac{D(^{63}Cu)}{D(^{65}Cu)}$
Experiment A			
Starting solution	6.29	0.60	
Solution	5.65	0.66	
Resin	0.96	0.25	1.00041
Experiment B			
Starting solution	6.56	0.60	
Solution	5.77	0.63	
Resin	0.74	0.23	1.00040

been dropped from the subscripts since this equation holds for each molecule. We recognize in this expression the product of three terms in u_i corresponding to the rotational, zero-point, and upper vibrational level energy. The dependence of u_i on the symmetry of the molecule and masses of its atoms is apparent through the Teller-Redlich product rule. This rule expresses fundamental symmetry relationships among the normal coordinates of the compounds and relates the principal moments of inertia I_A, I_B, and I_C of the compound to the mass M of the molecule and to the mass m of its constituent atoms through

$$\prod_{i=1}^{3n-6} \frac{u_{2i}}{u_{1i}} = \left(\frac{I_{A_2} I_{B_2} I_{C_2}}{I_{A_1} I_{B_1} I_{C_1}}\right)^{1/2} \left(\frac{M_2}{M_1}\right)^{3/2} \left(\frac{m_1}{m_2}\right)^{3n/2}. \quad (8)$$

(We note that only one isotope is exchanged.)

As pointed out by Urey (1947), the symmetry numbers of isotopically substituted compounds with only one exchangeable atom are identical because the corresponding ratio σ_1/σ_2 is equal to unity and does not contribute to isotopic fractionation. Fractionation may therefore result from three effects: the symmetry of the compound through the numbers σ for more than one exchangeable atom, the mass m of the atoms constituting the compounds (and their resulting effect on the molecular masses M), and the principal moments of inertia (which describe the distribution of masses in the molecule around the principal axes of rotation).

1. The symmetry of isotopically substituted compounds may be different for polynuclear complexes. For example, $Cu_2Cl_6^{2-}$ groups formed by paired tetrahedron with a shared edge are known in ionic solids (Cotton et al., 1999). For instance, the symmetry numbers of $^{63}Cu_2Cl_6^{2-}$ and $^{63}Cu^{65}CuCl_6^{2-}$ would be different.
2. Mass effects are apparent in the last two terms of the right-hand side of Eqn. 8. Although they are less prominent than for the lighter isotopes of oxygen or sulfur, the product of the last two terms for Cu and Zn complexes with two to six chlorine atoms deviates from unity by up to several percent.
3. The principal moments of inertia may differ upon isotopic exchange, particularly for polynuclear compounds.

4.2. Speciation in Solution

To understand the isotopic partitioning processes, we need to assess which chlorocomplexes are the most abundant in the solution. The redox potential of the Cu(I)/Cu(II) pair is small enough (0.161 V) that copper is quantitatively oxidized by both the H_2O/H_2O_2 (1.763 V) and the H_2O_2/O_2 (0.695 V) pairs present in the eluent. This contrasts with the incomplete oxidation expected for the Fe(II)/Fe(III) pair (0.771 V) in the same solutions in contact with the atmosphere. Zn has only one state of oxidation in the conditions of the experiments.

Cu and Zn species formed in aqueous solutions of hydrochloric acid are M^{2+}, MCl^+, MCl_2^0, MCl_3^-, and MCl_4^{2-} (where M stands for Cu[II] or Zn[II]), following the reactions

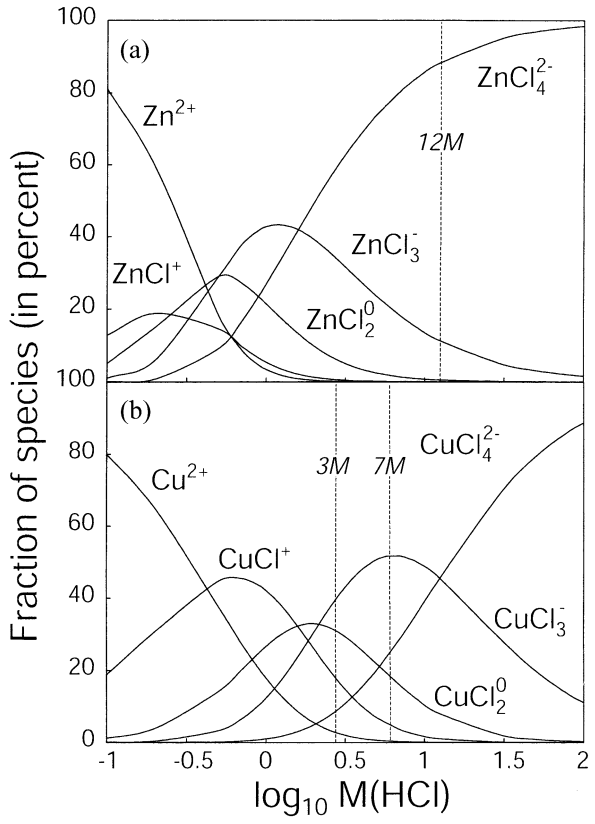

Fig. 5. Calculated distribution of the dissolved species of (a) Cu and (b) Zn in aqueous solution of HCl. We used the stability constants determined at 25°C by Ramette (1986) for Cu (β_1 = 2.36 [0.07], β_2 = 1.49 [0.19], β_3 = 0.69 [0.13], β_4 = 0.055 [0.021]) and by Ashurst (1974) for Zn (β_1 = 1.6, β_2 = 6.3, β_3 = 12.6, β_4 = 7.9). The activity coefficients were assumed to be unity. The dashed lines indicate the working conditions: $\log_{10}$ M(Cl) = 0.5, 0.8, and 1.1 for 3 mol/L, 7 mol/L, and 12 mol/L HCl respectively, where a_{Cl} is the molar concentration of Cl^-.

$$M^{2+} + Cl^- \overset{\beta_1}{\longleftrightarrow} MCl^+$$

$$M^{2+} + 2Cl^- \overset{\beta_2}{\longleftrightarrow} MCl_2$$

$$M^{2+} + 3Cl^- \overset{\beta_3}{\longleftrightarrow} MCl_3^-$$

$$M^{2+} + 4Cl^- \overset{\beta_4}{\longleftrightarrow} MCl_4^{2-},$$

where the β_i's are the compounded stability constants (Ashurst, 1974; Khan and Schwing-Weill, 1976; Bjerrum and Skibsted, 1977; Ramette and Fan, 1983, Ramette, 1986). The distribution of the Cu and Zn species at 25°C was calculated using the constants determined by Ramette (1986) for Cu and Ashurst (1974) for Zn and is shown in Figure 5 and Table 6. The dominating species in strong HCl medium are MCl_2^0, MCl_3^-, and MCl_4^{2-}. Such a distribution disagrees with that of Collings et al. (2000), who evaluated the dissociation constants of Cu(II) chlorocomplexes at 25°C by extrapolating Sverjensky et al.'s (1997) hydrothermal experimental data obtained at 100°C to 450°C. We surmise that this discrepancy is simply due to the

Table 6. Calculated speciation of Cu and Zn in HCl of selected molarities. The stability constants are those of Ashurst (1974) for Zn and Ramette (1986) for Cu. The activity coefficients are unity.

Zn species	12 mol/L HCl	Cu species	7 mol/L HCl	3 mol/L HCl
Zn^{2+}	0.0%	Cu^{2+}	0.2%	2.2%
$ZnCl^{+}$	0.0%	$CuCl^{+}$	3.6%	15.9%
$ZnCl_2$	0.5%	$CuCl_2$	15.9%	30.1%
$ZnCl_3^{-}$	11.6%	$CuCl_3^{-}$	51.5%	41.8%
$ZnCl_4^{2-}$	87.9%	$CuCl_4^{2-}$	28.8%	10.0%

different sets of dissociation constants used by Collings et al. (2000) and in the present work.

4.3. Cu, Zn, Fe Coordination and the Jahn-Teller Effect

In aqueous chloride solutions, Cu^{2+} is six coordinated and forms complexes with an octahedral configuration, Cu^{2+} being surrounded by six oxygens of water molecules and/or chloride ions (Bell et al., 1973; Magini, 1981; Salmon et al., 1988; Ansell et al., 1995, D'Angelo et al., 1997). The Cu(II) complexes therefore can be expressed as $(CuCl_n(H_2O)_{6-n})^{+(2-n)}$, with n varying from 0 to 4. Like other transition metal ions, Zn^{2+} produces hexacoordinated ions when hydrated, e.g., $(Zn[H_2O]_6)^{2+}$, since 6 is known to be the predominant hydration number (Åkesson et al., 1992a, 1994). However, the tendency of this element is to form tetrahedral complexes in the presence of chloride ions (Cotton et al., 1999), and an octahedral to tetrahedral geometry change has been observed by the ultrasonic absorption technique (Silber et al., 1984). Finally, the d^5 Fe(III) ion in the most abundant chlorocomplex, and $FeCl_4^{-}$ is in a tetrahedral configuration (Magini and Radnai, 1979; Anbar et al., 2000).

The octahedral Cu(II) species are not regular, however, and suffer distortion to give a (4 + 2) coordination, with four ligands occupying an equatorial position and two ligands occupying an axial position. This behavior is known as the Jahn-Teller effect, whereby the Cu^{2+} ion placed in a regular octahedral environment will distort the configuration and remove the degeneracy of some of the orbitals (Gerloch, 1981; Beagley et al., 1989; Åkesson et al., 1992a, 1992b). Such an effect is important in the case of Cu(II) complexes because of the asymmetrical electronic occupancy of the two e_g d orbitals of Cu^{2+} ($3d^9$), and the observed distortions are frequently cited to illustrate the Jahn-Teller theorem in transition metal complexes (Gerloch and Constable, 1994; Cotton et al., 1999; Figgis and Hitchman, 2000). The large distortions are predominantly tetrahedral elongations that produce distant axial sites occupied by more weakly bound ions than the ions in the equatorial positions. Jahn-Teller distortion does not exist for d^{10} Zn^{2+} (its five d orbitals are fully occupied). For ferric iron in its most common high-spin configuration, the five electrons distribute themselves symmetrically on the five d orbitals, and no Jahn-Teller effect is expected. To get a significant distortion, the asymmetrical low-spin form of Fe(III) complexes (five electrons on the three t_{2g} orbitals) in a tetrahedral environment is probably more favorable, but how to reach these conditions in a concentrated HCl medium is unknown.

4.4. The Origin of Isotopic Fractionation on Ion-Exchange Resins

Isotopic fractionation has been observed on ion-exchange resin for B isotopes (Kakihana et al., 1977), Ca isotopes (Russell and Papanastassiou, 1978), Ga isotopes (Machlan and Gramlich, 1988), and Fe isotopes (Anbar et al., 2000). As for Cu and Zn isotopes in the present work, these studies show that the distribution coefficient between the resin and the eluant is larger for the light than for the heavy isotope. From the separation factors listed in Tables 3 to 5, several properties stand out:

1. The strong isotopic fractionation of Cu in HCl medium contrasting with the lack of fractionation in HNO_3 medium reflects the dominance of Cu chlorocomplexes (and the nonprevalence of nitrate complexes) in resin-liquid isotopic separation processes.
2. The values of ${}^{65}_{63}\alpha_{Cu}$ obtained from the elution and the equilibrium experiments on pure Cu in 7 mol/L HCl medium are very similar. This indicates that the kinetics of ion exchange are rapid and that isotopic fractionation during elution takes place either at or not too far from equilibrium. This result conforms to the common experience that elution schemes devised with the help of batch partition coefficients are normally very satisfactory.
3. ${}^{65}_{63}\alpha_{Cu}$ increases with decreasing HCl molarity.
4. Zn isotope fractionation between resin and the HCl solution is undoubtedly present but is an order of magnitude less than for Cu.

A further argument in favor of equilibrium is the essentially constant relative dispersion of the elution peak (adopting the Appendix notation, ${}^{i}s/{}^{i}v = 0.15 \pm 0.02$; see Table 3) regardless of the element or the acid normality considered. A similar value was also found for the Fe elution carried out by Anbar et al. (2000).

The fact that Zn isotopes (and to some extent, as shown by Anbar et al., 2000, Fe isotopes) fractionate less than Cu isotopes suggests that mass differences between compounds are not the dominant effect (unless the molecular weight of Zn compounds is much larger than that of Cu compounds, but no evidence exists for that). Likewise, it is unclear how redox reactions could promote isotopic preference for one species with a particular oxidation state of the exchangeable metal. What controls isotopic fractionation is the ratio of partition functions of the same compound in the same oxidation state for two different isotopes, and there is no obvious source of variability in these terms.

In spite of the Jahn-Teller effect being particularly strong for Cu, which also shows the largest isotopic fractionation, the reason why these two features should be related is unclear. Upon tetragonal stretching of octahedral Cu compounds, the Jahn-Teller effect should affect their symmetry number but to the same extent for each isotope. It may change the principal moments of inertia of Cu compounds, but since the Cu atom occupies the center of the distorted octahedron, isotopic substitution is likely to be of very limited importance. Alternatively, Cu compounds may be severely distorted upon adsorption on the surface of the resin so that isotopic substitution changes their principal moments of inertia dramatically. We do

not favor this interpretation, however, because the strongly adsorbed Zn chlorocomplexes are barely isotopically fractionated during elution.

The most appealing interpretation is that isotopic fractionation results from the presence of polynuclear molecules, with Cu occupying two different sites in the compound. For the sake of illustration, let us speculate that the reaction

$$^{63}Cu_2Cl_6^{2-} + {}^{65}Cu_2Cl_6^{2-} \Leftrightarrow 2\ {}^{63}Cu^{65}CuCl_6^{2-}$$

takes place in solution. In such a reaction, both the symmetry number σ and the principal moments of inertia would be different for the molecules on both sides of the reaction, and large isotopic fractionation may therefore be expected. Bell et al. (1973) actually inferred that Cu(II) in chloride solutions forms polynuclear complexes of octahedral structures, but the presence of such associations was rejected by D'Angelo et al. (1997). However, it remains difficult to assess where in particular isotopic fractionation takes place. So far, fractionation of Cu isotopes seems equally probable between species in solution and during Cu absorption on the resin surface.

Strong isotopic fractionation on AG MP-1 resin was also demonstrated by Anbar et al. (2000) for Fe(III). The present work evaluates resin/solution fractionation coefficients of ~1.0003 for Fe and ~1.0004 to 1.0007 for Cu. In contrast to Zn, the existence of polynuclear Fe(III) complexes would also create the conditions for large isotope fractionation.

4.5. Other Effects

Anbar et al. (2000) predicted that because of the conversion of chlorocomplexes into metal ions, Fe isotope fractionation would diminish or even disappear in very dilute acid. Our results show a stronger Cu(II) isotope fractionation for 3 mol/L than for 7 mol/L HCl and therefore fail to confirm this predicted trend for Cu. Such a discrepancy, however, does not necessarily indicate that Anbar et al.'s (2000) model is incorrect. We favor the alternative interpretation that at high HCl molarity and therefore at high ionic strength I of the solution, mass-independent electrostatic forces (Debye-Hückel contribution) take a larger share of the energy than at lower ionic strength. Electrostatic effects may become crucial in seawater ($I = 0.6$) and brines where activity coefficients are particularly large.

The difference between the isotope separation factor obtained for pure Cu in 7 mol/L HCl and for the chalcopyrite sample NL2206 may be due to the absorption of Fe and Zn on the column or to the competition of Cu, Fe, and Zn for chlorocomplexes. It suggests that the isotopic fractionation of transition elements in nature may be complicated by the presence of species competing for the same sites.

Finally, the smaller isotopic fractionation of Zn with respect to Cu in the present chromatographic experiments mirrors the smaller variability of Zn isotope abundances in natural compounds with respect to that of Cu compounds (Shields et al., 1965; Maréchal et al., 1999, 2000; Zhu et al., 2000a). We believe that this agreement is not fortuitous. It is of course far too early to identify the fractionating species in natural environments, but the present experiments have shown that Cu equilibrium fractionation exists and can be reproduced under well-controlled laboratory conditions. Measurable and even large isotopic effects can therefore be anticipated for many multi-isotopic transition metals that are not the product of poorly controlled kinetic effects. Although they are not fully relevant to the present investigation, tetranuclear chlorocomplexes with organic ligands are known (Reim et al., 1995). They hint at possibly strong isotope fractionation in biologic environments or in low-temperature solutions rich in organic products. We anticipate that isotopic effects will be a fresh source of information for the coordination chemistry of transition metals in solutions, low-temperature minerals, and biologic compounds.

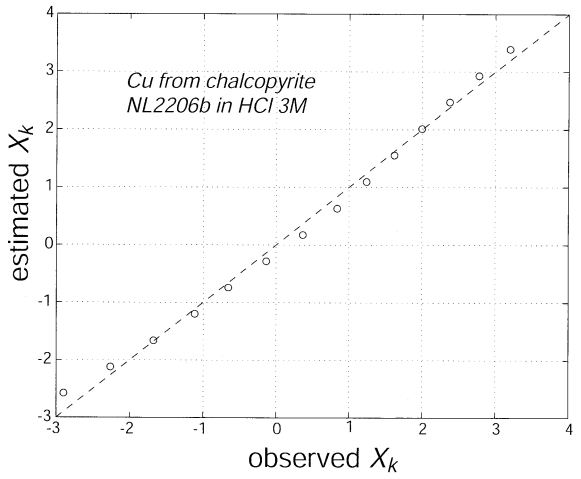

Fig. 6. Example of fit between the observed values and the regressed values (open circles) of $X_k = (v_k - {}^iv)/{}^is$, where v_k is the cumulated volume eluted at step k, ${}^iv$ is the mean (and retention volume for the isotope i), and ${}^is$ is the standard deviation obtained by regressing F_k vs. v_k (Eqn. A2).

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REFERENCES

Åkesson R., Pettersson L. G. M., Sandström M., Siegbahn P. E. M., and Wahlgren U. (1992a) Theoretical ab initio SCF study of binding energies and ligand-field effects for the hexahydrated divalent ions of the first-row transition metals. *J. Phys. Chem.* **96,** 10773–10779.

Åkesson R., Pettersson L. G. M., Sandström M., and Wahlgren U. (1992b) Theoretical calculations of the Jahn-Teller effect in the hexahydrated copper(II), chromium(II), and manganese(III) ions, $(Cu(H_2O)_6)^{2+}$, $(Cr(H_2O)_6)^{2+}$, and $(Mn(H_2O)_6)^{3+}$, and comparisons with the hexahydrated copper(I), chromium(III), and manganese(II) clusters. *J. Phys. Chem.* **96,** 150–156.

Åkesson R., Pettersson L. G. M., Sandström M., and Wahlgren U. (1994) Ligand field effects in the hydrated divalent and trivalent metal ions of the first and second transition periods. *J. Am. Chem. Soc.* **116,** 8691–8704.

Anbar A. D., Roe J. E., Barling J., and Nealson K. H. (2000). Nonbiological fractionation of iron isotopes. *Science* **288,** 126–128.

Ansell S., Tromp R. H., and Neilson G. W. (1995) The solute and aquaion structure in a concentrated aqueous solution of copper(II) chloride. *J. Phys. Condens. Matter* **7,** 1513–1524.

Ashurst K. G. (1974) Formation constants of zinc chloro complexes in perchlorate medium. *Natl. Inst. Metall. Repub. S. Afr. Rep.* **1626,** 38 pp.

Beagley B., Eriksson A., Lindgren J., Persson I., Pettersson L. G. M., Sandström M., Wahlgren U., and White E. W. (1989) A computational and experimental study on the Jahn-Teller effect in the hydrated copper(II) ion. Comparisons with hydrated nickel(II) ions in aqueous solution and solid Tutton's salts. *J. Phys. Condens. Matter* **1,** 2395–2408.

Beard B. L., Johnson C. M., Cox L., Sun H., Nealson K. H., and Aguilar C. (1999) Iron isotope biosignatures. *Science* **285,** 1889–1892.

Bell J. R., Tyvoll J. L., and Wertz D. L. (1973) Solute structuring in aqueous copper(II) chloride solutions. *J. Am. Chem. Soc.* **95,** 1456–1459.

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

Bjerrum J. and Skibsted L. H. (1977) *Acta Chem. Scand. A.* 673–677.

Collings M. D., Sherman D. M., and Ragnarsdottir K. V. (2000) Complexation of the Cu^{2+} in oxidized NaCl brines from 25°C to 175°C: Results from in situ EXAFS spectroscopy. *Chem. Geol.* **167,** 65–73.

Cotton F. A., Wilkinson G., Murillo C., and Bochmann M. (1999) *Advanced Inorganic Chemistry,* 6th ed. John Wiley, New York.

D'Angelo P., Bottari E., Festa M. R., Nolting H. F., and Pavel N. V. (1997) Structural investigation of copper(II) chloride solutions using X-ray absorption spectroscopy. *J. Chem. Phys.* **107,** 2807–2812.

Figgis B. N. and Hitchman M. A. (2000) Ligand Field. Theory and Its Applications. John Wiley, New York.

Fouquet Y., Von Stackelberg U., Charloux J.-L., Donval J.-P., Foucher J.-P., Erzinger J., Herzig P., Mühe R., Wiedicke M., Soaka S. I., and Whitechurch H. (1991) Hydrothermal activity in the Lau back-arc basin: Sulfides and water chemistry. *Geology* **19,** 303–306.

Gerloch M. (1981) The sense of Jahn-Teller distortions in octahedral copper(II) and other transition-metal complexes. *Inorg. Chem.* **20,** 638–640.

Gerloch M. and Constable C. E (1994) *Transition Metal Chemistry*. VCH, Weinheim, Germany.

Kakihana H., Kotaka M., Satoh S., Nomura M., and Okamoto M. (1977) Fundamental studies on the ion-exchange separation of boron isotopes. *Bull. Chem. Soc. Jap.* **50,** 1, 158–163.

Khan M. A. and Schwing-Weill M. J. (1976) Stability and electronic spectra of the copper(II) chloro complexes in aqueous solutions. *Inorg. Chem.* **15,** 2202–2205.

Machlan L. A. and Gramlich J. W. (1988) Isotopic fractionation of gallium on ion-exchange column. *Anal. Chem.* **60,** 37–39.

Magini M. (1981) Hydration and complex formation study on concentrated MCl_2 solutions (M=Co(II), Ni(II), Cu(II)) by X-ray diffraction technique. *J. Chem. Phys.* **74,** 2523–2529.

Magini M. and Radnai T. (1979) X-ray diffraction study of ferric chloride solutions and hydrated melt. Analysis of the iron(III)-chloride complexes formation. *J. Chem. Phys.* **71,** 4255–4262.

Maréchal C. N., Télouk P., and Albarède F. (1999) Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chem. Geol.* **156,** 251–273.

Maréchal C. N., Télouk P., Douchet C., and Albarède F. (2000). Abundance of zinc isotopes as a marine biogeochemical tracer. *Geochem. Geophys. Geosyst.* **1,** paper #1999.GC000029.

McQuarrie D. A. (1973) *Statistical Thermodynamics*. University Science, Mill Valley, CA.

O'Neil J. R. (1986) Theoretical and experimental aspects of isotopic fractionation. In *Stable Isotopes in High Temperature Geological Processes* (eds. J. W. Valley, H. P. Taylor, Jr., and J. R. O'Neil). *Rev. Mineral.* **16,** 1–40.

Ramette R. W. (1986) Copper(II) complexes with chloride ion. *Inorg. Chem.* **25,** 2481–2482.

Ramette R. W. and Fan G. (1983) Copper(II) chloride complex equilibrium constants. *Inorg. Chem.* **22,** 3323–3326.

Reim J., Griesar K., Haase W., and Krebs B. (1995) Structure and magnetism of novel tetranuclear μ_4-oxo-bridged copper (II) complexes. *J. Chem. Soc. Dalton Trans.* 2649–2656.

Richet P., Bottinga Y., and Javoy M. (1977) A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules. *Ann. Rev. Earth Planet. Sci.* **5,** 65–110.

Rieman W., III, and Walton H. F. (1970) *Ion Exchange in Analytical Chemistry*. Pergamon, Oxford, UK.

Russell W. A. and Papanastassiou D. A. (1978) Calcium isotope fractionation in ion-exchange chromatography. *Anal. Chem.* **50,** 1151–1154.

Salmon P. S., Neilson G. W., and Enderby J. E. (1988) The structure of Cu^{2+} aqueous solutions. *J. Phys. C: Sol. State Phys.* **21,** 1335–1349.

Shields W. R., Goldich S. S., Garner E. L., and Murphy T. J. (1965) Natural variations in the abundance ratio and the atomic weight of copper. *J. Geophys. Res.* **70,** 479–491.

Silber H. B., Simon D., and Gaizer F. (1984) Octahedral-tetrahedral geometry changes for zinc(II) in the presence of chloride ions. *Inorg. Chem.* **23,** 2844–2848.

Sverjensky D. A., Shock E. L., and Helgeson H. C. (1997) Prediction of the thermodynamic properties of aqueous metal complexes to 1000°C and 5 kb. *Geochim. Cosmochim. Acta* **61,** 1359–1412.

Urey H. C. (1947) The thermodynamic properties of isotopic substances. *J. Chem. Soc. London* 562–581.

van der Walt T. N., Strelow F. W. E., and Verheij R. (1985) The influence of crosslinkage on the distribution coefficients and anion exchange behavior of some elements in hydrochloric acid. *Solvent Extract. Ion Exchange* **3,** 723–740.

Walker E. C., Cuttitta F., and Senftle F. E. (1958) Some natural variations in the relative abundance of copper isotopes. *Geochim. Cosmochim. Acta* **15,** 183–194.

Zhu X. K., O'Nions R. K., Guo Y., Belshaw N. S., and Rickard D. (2000a). Determination of natural Cu-isotope variation by plasma-source mass spectrometry: Implications for use as geochemical tracers. *Chem. Geol.* **163,** 139–149.

Zhu X. K., O'Nions R. K., Guo Y., and Reynolds B. C. (2000b). Secular variation of iron isotopes in North Atlantic deep water. *Science* **287,** 2000–2002.

APPENDIX

A.1. Fitting the Elution Curves

First, the number of moles of each isotope (^{63}Cu, ^{65}Cu, ^{66}Zn, and ^{68}Zn) eluted with each individual fraction k is calculated from the metal concentration in the fraction and its isotopic composition. This number is turned into a cumulative fraction F_k that can be associated through an error function with a normal reduced variable X_k using the standard relationship:

$$F(X_k) = \frac{1}{2}\left\{1 + \mathrm{erf}\,\frac{X_k}{\sqrt{2}}\right\}. \tag{A1}$$

The reduced random variable X provides the mean retention volume ${}^iv$ of isotope i and the width (standard deviation) ${}^is$ of the elution peak by regressing $X_k = (v_k - {}^iv)/{}^is$ linearly against the total volume v_k that passed through the column at step k using

$$v_k = {}^iv + {}^is\ \sqrt{2}\mathrm{erf}^{-1}F_k. \tag{A2}$$

An example is shown in Figure 6. This procedure draws on the same principles as the Q-Q (quantile-quantile) probability plots. Both inverse error functions and statistical software can be used to obtain the elution parameters.

As a check of the model, the number of moles of isotope i is calculated for each individual fraction k from ${}^iv$ and ${}^is$. Then, the cumulative fraction of Cu or Zn eluted is obtained by addition of the number of moles of all isotopes cumulated over each fraction k (continuous lines in the left-hand sides of Figs. 1 to 4). The $\delta^{65}Cu$ and $\delta^{68}Zn$ values for the different fractions are determined from the ratio of the calculated number of moles of ^{65}Cu, ^{63}Cu, ^{68}Zn, and ^{66}Zn isotopes (continuous lines in the right-hand sides of Figs. 1 to 4).