

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/8646907>

Isotopic Fractionation during Diffusion of Transition Metal Ions in Solution

ARTICLE *in* ANALYTICAL CHEMISTRY · MAY 2004

Impact Factor: 5.64 · DOI: 10.1021/ac035296g · Source: PubMed

CITATIONS

45

READS

18

5 AUTHORS, INCLUDING:



Ilia Rodushkin

ALS Scandinavia AB and Lulea University of T...

117 PUBLICATIONS **2,814** CITATIONS

SEE PROFILE



Henrik Andrén

Luleå University of Technology

8 PUBLICATIONS **239** CITATIONS

SEE PROFILE



Dmitry Malinovsky

LGC

39 PUBLICATIONS **896** CITATIONS

SEE PROFILE

Correspondence

Isotopic Fractionation during Diffusion of Transition Metal Ions in Solution

Iliia Rodushkin,^{*,†} Anna Stenberg,[‡] Henrik Andrén,[§] Dmitry Malinovsky,[‡] and Douglas C. Baxter[†]

Analytica AB, Aurorum 10, SE-977 75 Luleå, Sweden, and Division of Applied Geology and Division of Chemistry, Luleå University of Technology, SE-971 87 Luleå, Sweden

Isotope ratios and elemental concentrations were measured in aqueous solutions sampled at varying distances from sources of Fe or Zn ions. The measurements reveal fractionation of isotopes resulting from pure diffusion in solution. Our data demonstrate that diffusion alone can cause changes in $^{56}\text{Fe}/^{54}\text{Fe}$ and $^{66}\text{Zn}/^{64}\text{Zn}$ isotope ratios in excess of -0.3% . These findings thus confirm previous suspicions that transport processes contribute to observed variations in isotopic compositions. Diffusion must therefore be considered when attempting to make inferences from isotope measurements on samples originating from aqueous systems where concentration gradients may develop.

The physical and chemical properties of the isotopes of any given element are mass-dependent.^{1,2} Biological processes and chemical reactions, typically involving phase or redox transitions thus alter the relative abundances of the stable isotopes, most notably for the lighter elements such as C, N, O, and S.¹ Variations in isotopic abundances have recently been documented for transition metals in biological and geochemical materials as well.^{3–9} This has, in turn, led to investigations focused on identifying the underlying mechanisms governing fractionation processes in nature.^{3,9–12}

Although the minor relative mass differences among isotopes of the transition metals may suggest that limited fractionation would be induced by simple chemical reactions, laboratory experiments have demonstrated abiotic variations of several per mil in Fe, Cu, and Zn isotope ratios.^{3,12–14} However, it was noted that additional factors, viz., speciation, ion exchange kinetics, and diffusion, could also affect the observed levels of fractionation. McManus et al.¹⁵ described the fractionation of Mo in sediment pore waters using a reaction–diffusion model, assuming that the isotopes had equal diffusion coefficients and therefore that only authigenic Mo formation was responsible for preferential losses of the lighter isotopes. Thus the need remains to individually characterize potential sources of fractionation before unambiguous interpretation of isotopic variations in nature and, indeed, in laboratory experiments can be realized.

In principle, diffusion is the process most amenable to isolation from other complicating factors. Recent results have demonstrated that substantial fractionation of Li and Ca occurs during diffusion between adjacent molten phases with large differences in initial elemental abundances.¹⁶ Although it has been suspected that diffusion may contribute to observed fractionation effects occurring during the cycling of elements in biological and geochemical systems,^{3,4} the extent of this effect has not previously been quantified for the transition metals at low temperatures. To rectify this situation, model experiments were designed in which the solute could be confined on one side of a boundary, with pure solvent on the other side. After allowing contact between the solute and pure solvent, layers of solvent were sampled and analyzed by inductively coupled plasma mass spectrometry (ICPMS) with respect to concentrations and isotopic compositions.^{5,17} The

* Corresponding author. E-mail: ilia.rodushkin@analytica.se. Telephone: +46-920 289989. Fax: +46-920 289940.

[†] Analytica AB.

[‡] Division of Applied Geology, Luleå University of Technology.

[§] Division of Chemistry, Luleå University of Technology.

- (1) Criss, R. E. *Principles of Stable Isotope Distribution*; Oxford University Press: Oxford, U.K., 1999.
- (2) Choppin, G.; Liljenzin, J. O.; Rydberg, J. *Radiochemistry and Nuclear Chemistry*, 3rd ed.; Butterworth-Heinemann: Woburn, MA, 2002; Chapter 2, pp 11–40.
- (3) Roe, J. E.; Anbar, A. D.; Barling, J. *Chem. Geol.* **2003**, *195*, 69–85.
- (4) Beard, B. L.; Johnson, C. M.; Skulan, J. L.; Nealon, K. H.; Cox, L.; Sun, H. *Chem. Geol.* **2003**, *195*, 87–117.
- (5) Maréchal, C. N.; Télouk, P.; Albèrede, F. *Chem. Geol.* **1999**, *156*, 252–273.
- (6) Zhu, X. K.; O'Nions, R. K.; Guo, Y.; Reynolds, B. C. *Science* **2000**, *287*, 2000–2002.
- (7) Ellis, A. S.; Johnson, T. M.; Bullen, T. D. *Science* **2002**, *295*, 2060–2062.
- (8) Walczyk, T.; von Blanckenburg, F. *Science* **2002**, *295*, 2065–2066.
- (9) Zhu, X. K.; Guo, Y.; Williams, R. J. P.; O'Nions, R. K.; Matthews, A.; Belshaw, N. S.; Canters, G. W.; de Waal, E. C.; Weser, U.; Burgess, B. K.; Salvato, B. *Earth Planet. Sci. Lett.* **2002**, *200*, 47–62.

- (10) Beard, B. L.; Johnson, C. M.; Cox, L.; Sun, H.; Nealon, K. H.; Aguilar, C. *Science* **1999**, *285*, 1889–1892.
- (11) Mandernack, K. W.; Bazylnski, D. A.; Shanks, W. C., III; Bullen, T. D. *Science* **1999**, *285*, 1892–1896.
- (12) Matthews, A.; Zhu, X. K.; O'Nions, K. *Earth Planet. Sci. Lett.* **2001**, *192*, 81–92.
- (13) Anbar, A. D.; Roe, J. E.; Barling, J.; Nealon, K. H. *Science* **2000**, *288*, 126–128.
- (14) Maréchal, C. N.; Albèrede, F. *Geochim. Cosmochim. Acta* **2002**, *66*, 1499–1509.
- (15) McManus, J.; Nägler, T. F.; Siebert, C.; Wheat, C. G.; Hammond, D. E. *Geochem. Geophys. Geosys.* **2002**, *3*, 2002GC000356.
- (16) Richter, F. M.; Davis, A. M.; DePaolo, D. J.; Wilson, E. B. *Geochim. Cosmochim. Acta* **2003**, *67*, 3905–3923.

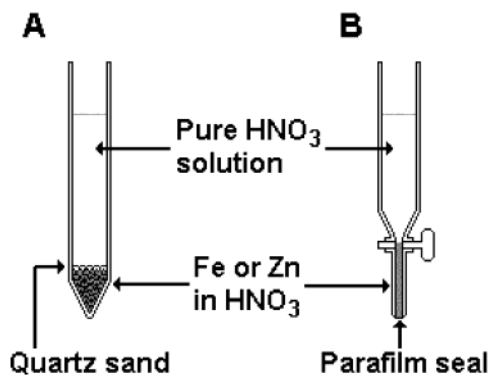


Figure 1. Schematic diagram of the diffusion cells. (A) Acid-washed, polypropylene test tube loaded with 1-cm³ Fe or Zn standard solution. Pure quartz sand was then added to cover the solution, and then pure solvent was dispensed carefully to avoid mixing. (B) Glass buret loaded with standard, after which the tap was closed, the end sealed with Parafilm, and remaining standard thoroughly washed out. Pure solvent was then added and the tap opened to initiate the diffusion experiment.

analyses demonstrate conclusively that diffusion of transition metal ions in solution results in isotopic fractionation.

EXPERIMENTAL SECTION

Diffusion Cells. Experimental conditions were chosen to ensure that no chemical shifts in the isotopic compositions could occur. Two types of diffusion cell were designed (see Figure 1), both permitting the solute to be initially confined on one side of a boundary. (A) A 1-cm³ aliquot of solution, either 10 g L⁻¹ Fe(NO₃)₂ in 0.33 M HNO₃ or 10 g L⁻¹ Zn(NO₃)₂ in 0.84 M HNO₃, was pipetted in the bottom of acid-washed, polypropylene test tubes, and sufficient pure quartz sand was added to completely cover the solution. The sand provided a mechanical barrier that prevented mixing when 9 cm³ of pure solvent, 0.33 or 0.84 M HNO₃, respectively, was carefully dispensed. (B) Acid-washed glass burets were loaded with a few cubic centimeters of solution and sealed at the bottom, and any solution remaining above the tap was thoroughly washed out. A 12-cm³ aliquot of pure solvent was then added and the tap carefully opened after allowing the system to settle. In both types of experiment, the upper ends were sealed and the diffusion cells were stored in a vibration-free, thermostated room maintained at 20.0 ± 0.2 °C. Aliquots of the initial solutions were set aside to be used as standards with which to compare measured isotope ratios for the solvent volumes sampled from the diffusion cells. Type B experiments were used to confirm that the presence of quartz sand in (A) did not result in any unexpected source of isotopic fractionation. Both types of experiment were repeated at least twice; diffusion coefficients and levels of fractionation were reproducible, within experimental error.

Mass Spectrometric Measurements. Blank values were measured on 0.5-cm³ aliquots of pure solvent taken immediately after preparation of each diffusion cell. After 72 h, the remaining solvent was removed in volumes of ~1 cm³. Concentrations of Fe or Zn, as well as a suite of other elements, were then determined by ICPMS using an Element (ThermoFinnigan, Bremen, Ger-

many). Isotopic analyses were then performed by multicollector ICPMS using a Neptune (ThermoFinnigan). For Fe, the Neptune was operated in high-resolution mode ($R \approx 10\,000$) to avoid isobaric interferences from polyatomic ions on the ⁵⁴Fe, ⁵⁶Fe, and ⁵⁷Fe signals.¹⁷ The absence of significant Cr concentrations, i.e., potential ⁵⁴Cr interference on the ⁵⁴Fe signal, was confirmed by measurements using the Element.

Samples and standards for Fe isotope ratio measurement were diluted to a concentration of 5.0 ± 0.5 mg L⁻¹ and spiked to 5.0 mg L⁻¹ with a Ni solution in order to facilitate correction for variations in instrumental mass discrimination using the ⁶⁰Ni/⁶²Ni isotope ratio.¹⁶ For Zn, low resolution could be applied without any measurable interference on the ⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn, and ⁶⁸Zn ion signals. Samples and standards were diluted to a Zn concentration of 1.5 ± 0.15 mg L⁻¹ with addition of 1.0 mg L⁻¹ Cu for mass discrimination correction.⁵ This correction was performed using the exponential mass discrimination model⁵ in the manner described by Woodhead.¹⁸ Although such correction might appear unnecessary, our experience suggests that even minor differences in either elemental or acid concentrations, as may result from dilution of a sample, can actually induce variations in mass discrimination.¹⁷ Data quality can therefore be improved by using Ni or Cu to correct for such variations for Fe and Zn, respectively.

On average, the corrected ⁵⁶Fe/⁵⁴Fe, ⁵⁷Fe/⁵⁴Fe, ⁶⁶Zn/⁶⁴Zn, and ⁶⁸Zn/⁶⁴Zn isotope ratios were measurable with standard deviations of approximately ± 0.02, ± 0.04, ± 0.01, and ± 0.02‰, respectively. Note that these standard deviations represent average values for three replicates measured consecutively for the same solution and include the correction for instrumental mass discrimination using the added element. Isotope ratios measured on replicate dilutions of aliquots sampled within 2 cm of the boundary (i.e., concentrations of Fe and Zn > 10 mg L⁻¹) in the diffusion cells could be reproduced to better than twice the aforementioned standard deviations. Therefore, uncertainty bars included in the figures are given at a level of ± 2 standard deviations for $n = 3$ repeated measurements of each solution.

RESULTS AND DISCUSSION

On the basis of the concentration and isotope ratio data, the diffusion coefficients, D , for Fe ions in 0.33 M HNO₃ and Zn ions in 0.84 M HNO₃ could be estimated from least-squares fitting of the solution to Fick's second law of diffusion under the appropriate boundary conditions:¹⁹

$$c/c_i = 1 - \text{erf}[x/(4D\theta)] \quad (1)$$

where c and c_i are the measured and final concentrations at a distance x from the initial boundary, respectively, t is time, and erf denotes the error function. Experimental results for Fe, Zn, and the model are illustrated in Figure 2. The fact that the data points are faithfully described by the model suggests that ionic transport was solely by diffusion and that negligible mixing resulted from the sampling process.

Measured ⁶⁶Zn/⁶⁴Zn and ⁶⁸Zn/⁶⁴Zn ratios, expressed as δ^{66} and δ^{68} , defined as per mil deviations from the initial isotopic composi-

(17) Malinovsky, D.; Stenberg, A.; Rodushkin, I.; Andr n, H.; Ingri, J.;  hlander, B.; Baxter, D. C. *J. Anal. At. Spectrom.* **2003**, *18*, 687–695.

(18) Woodhead, J. J. *Anal. At. Spectrom.* **2002**, *17*, 1381–1385.

(19) Noggle, J. H. *Physical Chemistry*, 2nd ed.; Harper-Collins: New York, 1996; Chapter 9, pp 459–502.

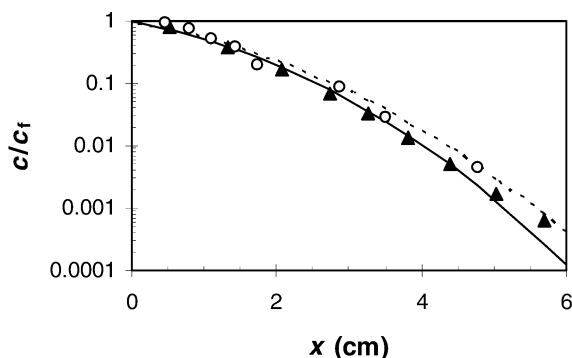


Figure 2. Diffusion of transition metal ions in HNO_3 solutions at 20°C after 72 h. Relative concentrations of Fe (open circles) and Zn (filled triangles) as a function of distance traveled in diffusion cells for experiment type (A). Uncertainties are smaller than the data points. The curves are plotted using $D_{\text{Fe}} = 5.61 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (dashed line) and $D_{\text{Zn}} = 4.71 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (solid line), obtained by solution of the diffusion equation, eq 1, for these particular experiments.

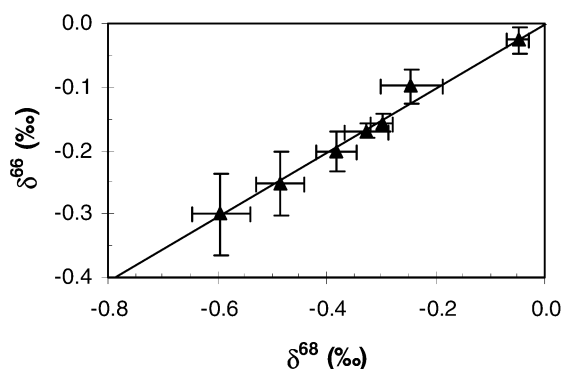


Figure 3. Three-isotope plot for Zn, for the same experiment (type A diffusion cell) as in Figure 2, where the δ values are expressed in per mil. The correlation between δ^{66} and δ^{68} is $\delta^{66} = (0.509 \pm 0.011)\delta^{68}$ with $r^2 = 0.985$. The uncertainty bars are two standard deviations for $n = 3$ replicates of each point.

tion of the standard,^{5,14} are plotted on a three-isotope diagram in Figure 3. These data are consistent with mass-dependent fractionation of the Zn isotopes during the diffusion process, evolving from the initially isotopically homogeneous standard reservoir. Similar conclusions may be drawn from results for Fe using $^{57}\text{Fe}/^{54}\text{Fe}$ and $^{56}\text{Fe}/^{54}\text{Fe}$ ratios. Figure 4 shows the development of the isotopic fractionation gradient between the two most abundant Fe or Zn isotopes. For the data sets shown, Zn fractionation increases more smoothly with diffusion distance than is the case for Fe. Although the same was true for all experiments, we cannot offer any tangible explanation. The trends illustrated in Figures 2–4 were replicated in both types of experiment, (A) and (B).

In Table 1, diffusion coefficients for Fe and Zn derived from our experiments are compared with literature data^{20,21} for these ions in aqueous solutions. The theoretical data, based on limiting ionic conductance values (λ^0), are strictly only applicable at infinite dilution; they are computed using the Nernst–Einstein equation:

$$D = \lambda^0 RT / (|zF|) \quad (2)$$

where R , T , z , and F are the gas constant, absolute temperature,

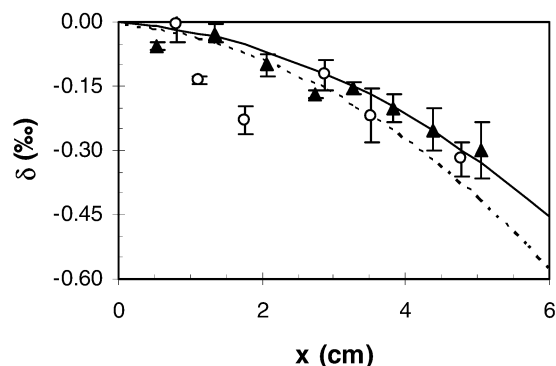


Figure 4. Fractionation of Fe ($^{56}\text{Fe}/^{54}\text{Fe}$ ratio used to calculate δ^{56} ; open circles) and Zn (δ^{66} ; filled triangles) isotopes as a function of diffusion distance (type A diffusion cells), uncertainty bars being two standard deviations ($n = 3$). The curves are given by the ratios $\{1 - \text{erf}[x/(4^{56,66}D_{\text{Fe,Zn}}t)^{0.5}]\} / \{1 - \text{erf}[x/(4^{54,64}D_{\text{Fe,Zn}}t)^{0.5}]\}$ with $[^{56}D_{\text{Fe}}/^{54}D_{\text{Fe}} - 1] = -8.6 \times 10^{-5}$ (dashed line) and $[^{66}D_{\text{Zn}}/^{64}D_{\text{Zn}} - 1] = -5.8 \times 10^{-5}$ (solid line).

Table 1. Fe and Zn Diffusion Coefficients at 20°C

medium	diffusion coefficient ($10^{-10} \text{ m}^2 \text{ s}^{-1}$)		ref
	Fe	Zn	
infinite dilution ^a	6.28	6.14	22–24
0.1 M NaNO_3		6.16	21
0.33 M HNO_3	5.78 ± 0.23		this work
0.84 M HNO_3		4.71 ± 0.07	this work

^a Infinite dilution values computed from limiting ionic conductance data at 25°C ,²⁰ recalculated to 20°C using the Stokes–Einstein relation,^{21,22,24} eq 3.

ionic charge, and Faraday constant, respectively. With increasing ionic strength, the mobility of diffusing ions decreases due to short-range electrostatic forces;^{22,23} thus, the lower than infinite dilution values, particularly pronounced for Zn in the more concentrated HNO_3 medium, are in line with expectations. In fact, if the infinite dilution values are corrected in the manner described in Wang,²² we obtain theoretical diffusion coefficients of 5.5×10^{-10} and $4.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for Fe and Zn, respectively, which agree with the experimental data to within $\sim 6\%$.

Using the Stokes–Einstein relation,

$$D = kT / (6\pi\eta r) \quad (3)$$

where k is the Boltzmann constant and η the solution viscosity, the hydrodynamic radius, r , of the hydrated ions can be calculated from estimated diffusion coefficients.²⁴ This results in hydrodynamic radii of $\sim 3.8 \times 10^{-10} \text{ m}$ for Fe in 0.33 M HNO_3 and $\sim 4.6 \times 10^{-10} \text{ m}$ for Zn in 0.84 M HNO_3 . These values are consistent with relatively small degrees of hydration, approximately 6 and 12 water molecules, respectively, indicating that the masses of the diffusing species correspond to about 162 and 280 u for the lightest isotopes of each element.

(21) Zhang, H.; Davison, W. *Anal. Chim. Acta* **1999**, 398, 329–340.

(22) Wang, J. H. *J. Phys. Chem.* **1954**, 58, 686–692.

(23) Anderko, A.; Lencka, M. M. *Ind. Eng. Chem. Res.* **1998**, 37, 2378–2388.

(24) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987; Chapter 11, pp 557–631.

(20) *Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1992–1993; p 5-111.

In the gaseous phase, diffusion coefficients scale as $(1/m_i + 1/M)^{-0.5}$ for an isotope of mass m_i diffusing through a gas of molecular mass M .^{16,23} If this relationship applied to the hydrated ions in aqueous solution, then relative diffusion coefficients of $[^{56}D_{\text{Fe}}/^{54}D_{\text{Fe}} - 1] \approx -6.1 \times 10^{-4}$ and $[^{66}D_{\text{Zn}}/^{64}D_{\text{Zn}} - 1] \approx -2.1 \times 10^{-4}$ would result. In fact, relative values of only -9×10^{-5} and -6×10^{-5} , respectively, are actually observed, the latter values being used to construct the curves in Figure 4. At the onset of diffusion, step-function sources of both Fe^{2+} or Zn^{2+} and NO_3^- exist; thus, NO_3^- must diffuse together with the transition metal ions to maintain electroneutrality.^{19,22–24} These ionic interactions effectively serve to limit the rate of fractionation in solution.

The levels of fractionation measured in these experiments are, quite simply, too small to have been detected previously and would certainly not affect the measurement of diffusion coefficients by tracer methods.²² Nevertheless, lighter isotopes could potentially be enriched by diffusion through, for example, biological membranes or the boundary layer surrounding reactive particles in aquatic environments, even without considering the fact that their reaction rates are kinetically favored^{1,2} as well. Therefore, when

attempting to interpret data acquired in studies of aqueous environments, including biological materials,^{5,8} geochemical systems,^{4–7} and laboratory experiments,^{3,7,9–14} due consideration must be given to the possibility that diffusion may be an important contributing factor to any observed fractionation, as has been suspected.^{3,4}

ACKNOWLEDGMENT

This work was made possible by grants from EU's structural fund for Objective 1 Norra Norrland and Kempestiftelserna. We thank C. Pontér and Analytica AB for technical and financial assistance, as well as E. Engström, Analytica AB, and W. Forsling, B. Öhlander, and J. Ingri of the Center for Isotope and Trace Element Measurement, Luleå University of Technology, for critical comments.

Received for review November 3, 2003. Accepted January 29, 2004.

AC035296G