Title | Nuclear field shift effect in the isotope exchange reaction of cadmium using a crown ether

Author(s) | Fujii, Toshiyuki; Moynier, Frédéric; Telouk, Philippe; Albarède, Francis

Citation | Chemical Geology (2009), 267(3-4): 157-163

Issue Date | 2009-09

URL | http://hdl.handle.net/2433/86912

Note | © 2009 Elsevier B.V. All rights reserved.; This is not the published version. Please cite only the published version. この論文は出版社版ではありません。引用の際には出版社版をご確認ご利用ください。
Nuclear Field Shift Effect in the Isotope Exchange Reaction of Cadmium Using a Crown Ether

Toshiyuki Fujii¹, Frédéric Moynier², Philippe Telouk³, and Francis Albarède³

¹Research Reactor Institute, Kyoto University, 2-1010 Asashiro Nishi, Kumatori, Sennan Osaka 590-0494, Japan
²Department of Earth and Planetary Sciences, Washington University in St. Louis, Campus Box 1169, 1 Brookings Drive, Saint Louis, MO 63130-4862, USA
³Laboratoire de Sciences de la Terre, UMR 5570 CNRS, Ecole Normale Supérieure de Lyon, 46, Allee d'Italie, 69364 Lyon Cedex 7, France

*Author to whom correspondence should be addressed
tosiyuki@rrri.kyoto-u.ac.jp
TEL: +81-724-51-2469, FAX: +81-724-51-2634

Keywords: Cadmium; Isotope fractionation; Mass-independent; Nuclear field shift; Crown ether; Solvent extraction
Abstract

Cadmium isotopes were fractionated by the liquid-liquid extraction technique with a crown ether, dicyclohexano-18-crown-6. The isotopic ratios of $^{m}$Cd/$^{111}$Cd (m: 110, 112, 113, 114, and 116) were measured precisely by the multi-collector inductively coupled plasma spectrometry (MC-ICP-MS). When the isotope enrichment factors were calculated, the odd atomic mass isotopes ($^{111}$Cd and $^{113}$Cd) showed excesses of enrichment comparing to the even atomic mass isotopes ($^{110}$Cd, $^{112}$Cd, $^{114}$Cd and $^{116}$Cd). This odd-even staggering property originates from the nuclear field shift effect. The contribution of the nuclear field shift effect to the observed isotope enrichment factor was estimated to be 5 to 30%.
The classic theory of chemical isotope fractionation only predicts mass-dependent isotope effect due to the isotopic difference in vibrational energies of isotopomers (Urey, 1947; Bigeleisen and Mayer, 1947). No exception to that rule was found until the mid-80s. Mass-independent isotope fractionations were first observed for O and S (see a review by Thiemens, 2006). The difference in the symmetry and the densities of states of the activated isotopomers is a possible origin for these mass-independent isotope fractionations (Hathorn and Marcus, 1999). Alternative interpretations have been discussed in review articles (Weston, 1999; Thiemens, 2006). For heavy elements, an anomalous isotope enrichment of $^{235}$U was found in a redox reaction using liquid chromatography (Fujii et al., 1989). Isotope separation factors for even atomic mass isotopes, $^{234}$U, $^{236}$U, and $^{238}$U, showed a mass-dependent trend, while that of $^{235}$U deviated from it. For middle-heavy elements, Nishizawa et al. (1995) found the anomalous isotope fractionation named the odd/even isotope effect, and a similarity between the odd/even isotope effect and the odd-even staggering of $<r^2>$ were pointed out (Nishizawa et al., 1995). To examine the mass-independent isotope effect, the conventional mass-dependent theory was reconsidered by one of the original authors (Bigeleisen, 1996). The original theory has been extended to include correction terms to account for nuclear properties, i.e., nuclear mass, nuclear size and shape, and nuclear spin. The nuclear field shift effect, which results from the isotopic change in the nuclear size and shape, is recognized as the major origin of the mass-independent isotope effect in uranium (Bigeleisen, 1996).

Isotope shifts are well-known energy shifts in atomic spectra (King, 1984;
Aufmuth et al., 1987) and molecular spectra (Tiemann et al., 1982). Basic knowledge of isotope shifts is essential for understanding the isotope effects caused by the nuclear properties. The field shift is an isotope shift which originates from the change of the finite size and angular shape of the nuclear charge distribution when neutrons are added to the nucleus. The isotope shifts result in a displacement in the minimum potential energy of oscillation curve of isotopomers (Bigeleisen, 1996).

The field shift is proportional to the isotopic difference in mean-squared nuclear charge radius, $\delta \langle r^2 \rangle$ ($\delta$ means isotopic difference) (King, 1984; Aufmuth et al., 1987). Mean-square radius, $\langle r^2 \rangle$, of an odd atomic mass number isotope (with odd number neutrons) is usually smaller than the value expected from the adjacent isotopes with even atomic mass numbers (with even number neutrons). This unique property is known as the odd-even staggering which can be seen in every element (King, 1984; Aufmuth et al., 1987). The mass-independent isotope effect of uranium (Fujii et al., 1989) possesses the odd-even staggering property, and hence, the anomaly was attributable to the nuclear field shift effect (Bigeleisen, 1996; Nomura et al., 1996).

Similar mass-independent isotope fractionation has also been found in a lighter element, zinc (Nishizawa et al., 1993, 1996, 1998a, 1998b; Fujii et al., 2001). Since employing macrocyclic polyethers in a chemical exchange method is effective to create larger isotope fractionation (Tsuvadze et al., 1996), a crown ether was used as an extractant for a solvent extraction process (Nishizawa et al., 1993, 1996, 1998a) and a cryptand as a stationary phase for liquid chromatography (Nishizawa et al., 1998b; Fujii et al., 2001). In every ligand exchange system, an odd atomic mass number isotope $^{67}$Zn showed the anomalous enrichment property compared to that of the even atomic number isotopes. From these results, we expect that the mass-independent isotope
fractionation can also be found for a congener, cadmium. In this context, we 
fractionated cadmium isotopes by using a liquid-liquid extraction with a crown ether, 
dicyclohexano-18-crown-6 (DC18C6). The mass-independent property of Cd isotope 
fractionation was investigated.

Cadmium isotopic anomalies have been found in few meteoric samples 
(Rosman et al., 1978, 1980). Evaporation on the parent bodies of the meteorites is a 
most probable origin for the Cd isotope fractionation (Rosman et al., 1978, 1980; 
Wombacher et al., 2004, 2008). Wombacher et al. (2004) have studied the isotope 
fractionation during evaporation experiments with a molten Cd. This indicates that the 
simple evaporation just causes the mass-dependent isotope fractionation of Cd 
(Wombacker et al., 2004, 2008). The nuclear field shift effect is considered as a possible 
origin of isotopic anomalies found in several meteoritic samples (Fujii et al., 2006a,b). 
Chemical reactions may have accompanied the formation of these samples, and hence, it 
is interesting whether the mass-independent isotope fractionation occurs in our chemical 
exchange system.

In studies of the Zn isotope effect (Nishizawa et al., 1993, 1996, 1998a, 1998b; 
Fujii et al., 2001), isotopic compositions have been analyzed by ICP quadrupole mass 
spectrometry (ICP-QMS) (Nishizawa et al., 1993), thermal ionization mass 
spectrometry (TIMS) (Nishizawa et al., 1996, 1998a, ), or multiple-collector ICP mass 
spectrometry (MC-ICP-MS) (Nishizawa et al., 1998b; Fujii et al., 2001). In order to 
obtain higher ionization yield, the silica gel method has been adopted for isotopic 
analysis by TIMS (Nishizawa et al., 1996, 1998a, ). In recent analytical studies on Zn 
(Manhès and Göpel, 2003), Cd (Manhès and Göpel, 2003, 2007; Schmitt et al., 2006), 
and Pb (Manhès and Göpel, 2003, 2007) isotopes, it has been pointed that a
mass-independent bias may be created by using the silica gel method. Since the 
mass-independent isotope fractionation of Zn has been confirmed by both TIMS and 
ICP-MS, the anomaly should have been created in the chemical experiments, but the 
pointed uncertainty of the silica gel method in TIMS should be taken care of. Hence, in 
this study, we measured the Cd isotopic composition with a MC-ICP-MS.

2. Experimental

Dicyclohexano-18-crown-6 (over 97% purity) and 1,2-dichloroethane (over 99.8% 
purity) were products of Fluka Chemie GmbH. Cadmium dichloride (hydrated, 
99.999% purity) was purchased from Sigma-Aldrich Co. Hydrobromic acid (twice 
distilled) was purchased from Seastar Chemicals Inc. Hydrochloric acid and nitric 
acid (Merck KGaA) of analytical grade were purified by distillation and supplied for 
experiment.

Cadmium dichloride was dissolved in HCl to create solutions, 0.08 mol dm\(^{-3}\) 
(M) Cd(II) in various [HCl] (=1.6 to 10 M). The organic phase was 0.1 M DC18C6 in 
1,2-dichloroethane. A 3 cm\(^3\) aqueous solution and a 3 cm\(^3\) organic solution were 
mixed in a glass vial with a stirrer bar, and the glass vial was sealed with a stopcock. 
The two phases were stirred by a magnetic stirrer for 30 min. After the extraction 
equilibrium was attained, the two phases were separated by centrifugation (2000 rpm, 1 
min). An aliquot of the upper aqueous solution was taken for analysis. These 
procedures were carried out at 294.0±0.5 K. The Cd concentration in the equilibrated 
aqueous phase was analyzed by ICP-QMS (Thermo Elemental X7).

In order to avoid any matrix effect, possible trace of organic materials from 
DC18C6 was separated from the Cd by adapting our Zn separation technique (Moynier
et al., 2006, 2007) on anion-exchange resin (AG1X8 200-400 mesh) in HBr/HNO₃.

An aliquot of the aqueous phase was once dried by heating at 333 K and then dissolved into 1.5 M HBr. On the anion-exchange resin in 1.5 M HBr, Cd was strongly adsorbed while organic materials went through. Finally, Cd was collected in 0.5 M HNO₃.

A solution containing 200 ppb Cd in 0.05 M HNO₃ was prepared for isotopic analysis. Isotopic ratios of Cd in all samples were analyzed with the MC-ICP-MS Nu plasma 500 HR at ENS Lyon coupled with a desolvating nebulizer Nu DSN-100. 40 ratios in 2 blocks of 20 ratios each, in which the integration time of 1 scan was 10 sec, were measured for each sample. The background was corrected for measuring the ground zero at half-mass positions from the peak prior to data acquisition. The instrumental mass bias was corrected by bracketing each of the samples with standards. The blank from the chemistry is <1ng which is negligible with regards to the large quantity of Cd extracted from the crown-ether experiments (~10mg Cd).

Possible interferences with Pd on the masses 108 and 110 and with In on the mass 113 were verified to be under the detection of the ICP-MS. Because there was no isotopic interference on ¹¹¹Cd, the isotope ratios ⁰⁰⁰Cd/¹¹¹Cd (m : 110, 112, 113, 114, and 116) were measured. Since we were looking for odd-even effects we only selected the more abundant even Cd isotopes (110, 112, 114 and 116) and did not measure the least abundant ones, ¹⁰⁶Cd (1.25%) and ¹⁰⁸Cd (0.89%), which would not have give us additional information. ¹¹⁸Sn was measured to correct isobaric interferences of Sn with Cd on the masses 112, 114, and 116. The interference of ¹¹⁶Sn on ¹¹⁶Cd as beam intensities was less than $2 \times 10^{-4}$, and this was corrected by using the naturally occurring isotopic abundances of Sn. The interferences of Sn on the masses 112 and 114 were also corrected as the same manner, and were negligibly small (less than $4 \times 10^{-6}$ of ¹¹²Cd.
3. Results and discussion

3.1 Extraction reaction for the Cd(II)-crown ether system

Possible species of Cd(II) in HCl media are Cd$^{2+}$, CdCl$^+$, CdCl$_2^-$, CdCl$_3^{−}$, and CdCl$_4^{2−}$, which are equilibrated as the following reactions,

\[ \text{Cd}^{2+} + \text{Cl}^{−} \leftrightarrow \text{CdCl}^+ \]  
(1)

\[ \text{CdCl}^+ + \text{Cl}^{−} \leftrightarrow \text{CdCl}_2 \]  
(2)

\[ \text{CdCl}_2 + \text{Cl}^{−} \leftrightarrow \text{CdCl}_3^{−} \]  
(3)

\[ \text{CdCl}_3^{−} + \text{Cl}^{−} \leftrightarrow \text{CdCl}_4^{2−} \]  
(4)

Stability constants of equilibria 1 to 4 at zero ionic strength are evaluated from the reported values, log $K_1^0 = 2.0$, log $K_2^0 = 0.70$, log $K_3^0 = −0.30$, and log $K_4^0 = −1.2$, respectively (Pivovalov, 2005). From these $K^0$ values, activity of Cl$^−$ (Pivovalov, 2005), and mean activity of CdCl$_2$ (Bromley, 1973), mole fractions of Cd species were estimated as functions of [HCl] (Figure 1). As shown in Figure 1, in our experimental region of [HCl] = 1.6 to 10.0 M, the major species are CdCl$_2^-$, CdCl$_3^{−}$, and CdCl$_4^{2−}$.

The obtained distribution ratios, $D = [\text{Cd(II)}]_{\text{org}}/[\text{Cd(II)}]_{\text{aq}}$, are shown in Figure 2 as a function of the activity of HCl, $a_{\text{HCl}}^*$. The $D$ value increases with acidity, then reaches a plateau. The extraction reaction of Cd in the crown ether system is generally written as,

\[ \text{Cd}^{2+} + 2\text{Cl}^{−} + L \leftrightarrow \text{CdLCl}_2 \]  
(5)

where L means ligand, DC18C6. The curve of log $D$ vs. log $a_{\text{HCl}}^*$ can not be
explained by this reaction. This acidity dependence would be attributable to a co-extraction of HCl. The extraction reaction may be rewritten as,

$$n\text{H}^+ + \text{CdCl}_2 + n\text{Cl}^- + \text{L} \leftrightarrow \text{CdLCl}_2 \cdot n\text{HCl}$$  \hspace{1cm} (6)

The stability constant of reaction 6, $K_L$, can be written,

$$K_L = \frac{\gamma_{\text{CdLCl}_2 \cdot n\text{HCl}} \cdot [\text{CdLCl}_2 \cdot n\text{HCl}]}{a_{\text{HCl}}^{2n} \cdot \gamma_{\text{CdCl}_2} \cdot [\text{CdCl}_2] \cdot \gamma_{\text{L}} \cdot [\text{L}]}$$  \hspace{1cm} (7)

where we set the activity coefficients for the organic phase, $\gamma_{\text{CdLCl}_2 \cdot n\text{HCl}}$ and $\gamma_{\text{L}}$, as unities, because the condition of organic phase under the equilibrium would be quite similar. Since $[\text{CdLCl}_2 \cdot n\text{HCl}]$ can be replaced by $[\text{Cd(II)}]_{\text{org}}$, the following equation is obtained.

$$\log [\text{Cd(II)}]_{\text{org}} - \log \gamma_{\text{CdCl}_2} - \log [\text{CdCl}_2] - \log [\text{L}] = 2n \log a_{\text{HCl}} + \log K_L$$  \hspace{1cm} (8)

$[\text{Cd(II)}]_{\text{org}}$ and $[\text{L}]$ are experimentally determined. $\gamma_{\text{CdCl}_2}$ can be calculated by the semi-empirical calculation (Bromley, 1973), and $[\text{CdCl}_2]$ can be calculated from the reported $K^0$ values (Pivovalov, 2005). As shown in Fig. 2, the left hand equation shows a clear linearity to $\log a_{\text{HCl}}$. From the slope and the intercept of this line $K_L=10.4$ and $n=0.7$ were determined, and the determination coefficient was $R^2=0.997$.

The obtained $n$ value suggests that 1 HCl molecule may participate to the extraction reaction 6. The co-extraction of HCl suggests that, in the organic phase, the extracted CdLCl$_2$•HCl may form H$^+$$\cdot$CdLCl$_3$$. According to the reported extraction stoichiometry of H$^+$ and anionic species (Beklemishev et al., 1997), the following extraction may compete with the reaction 6,

$$\text{H}^+ + \text{CdCl}_3^- + \text{L} \leftrightarrow \text{HCdLCl}_3$$  \hspace{1cm} (9)

In a crown ether system, an extraction of anionic species from the concentrated HCl has
been reported (Beklemishev et al., 1997). Thus, extraction of a neutral species (CdLCl₂), co-extraction of the neutral species and HCl, and extraction of anionic species with H⁺ may simultaneously take place in the present system.

3.2 Isotope fractionation during extraction

The isotope separation factor, between the aqueous and the organic phases, \( \alpha_m \) is defined as:

\[
\alpha_m = \frac{([m\text{Cd}]/[^{111}\text{Cd}])_{\text{org}}}{([m\text{Cd}]/[^{111}\text{Cd}])_{\text{aq}}}
\]  

\( ([m\text{Cd}]/[^{111}\text{Cd}])_{\text{org}} \) and \( ([m\text{Cd}]/[^{111}\text{Cd}])_{\text{aq}} \) are the isotope ratios of \( m\text{Cd} \) relative to \( ^{111}\text{Cd} \) found in the organic and aqueous phases, respectively. Our recent study on mass-independent isotope effect fractionation of Cr created in the crown ether extraction system proved that the isotopic mass balance between two phases was well preserved (Fujii et al., 2008). Hence, we employ \( ([m\text{Cd}]/[^{111}\text{Cd}])_{\text{org}} \) calculated from \( D \), \( ([m\text{Cd}]/[^{111}\text{Cd}])_{\text{aq}} \) and \( ([m\text{Cd}]/[^{111}\text{Cd}])_{\text{init}} \) (the isotope ratios of \( m\text{Cd} \) relative to \( ^{111}\text{Cd} \) in the starting material). \( \delta^{m}\text{Cd} \) is defined as

\[
\delta^{m}\text{Cd} = (\alpha_m - 1) \times 1,000
\]  

As \( \alpha_m \) is almost equal to one, \( \alpha_m - 1 \) (\( =10^{-3} \delta^{m}\text{Cd} \)) \( \approx \ln \alpha_m \). The obtained \( \delta^{m}\text{Cd} \) values are shown in Table 1. For each isotope, the absolute value of \( \delta^{m}\text{Cd} \) decreases and showed a minimum value at 5.2 M HCl. Since the dominant species in the aqueous phase are CdCl₂, CdCl₃⁻, and CdCl₄²⁻ in the experimental acidity region, possible isotope exchange reactions have taken place in
reactions 2, 3, and 4. The isotope exchange reactions have also taken place in the extraction reactions 6 and 9. The acidity dependence of $\delta^m$Cd we observed would be a result of isotopic mass balance corresponding to these reactions.

The conventional mass-dependent theory of the Bigeleisen-Mayer equation (1947) has been extended to include the nuclear field shift effect (Bigeleisen, 1996),

$$\ln \alpha = \frac{hc}{kT} f_s \times a + \frac{1}{24} \left( \frac{h}{2\pi kT} \right)^2 \frac{\delta m}{mm'} \times b$$  \hspace{1cm} (12)

where $f_s$ is the field shift, $a$ scaling factor for the nuclear field shift effect, $b$ the scaling factor for the vibrational mass effect. $m$ and $m'$ are the masses of heavy isotope and light isotope, respectively, and $\delta m$ the difference of masses, $m - m'$. Other symbols mean the usual physical constants. Since the field shift is proportional to the isotopic difference in mean-squared nuclear charge radius (King, 1984; Aufmuth et al., 1987), $\delta <r^2>$, the nuclear field shift effect is totally mass-independent.

The $\delta <r^2>_m$ values of Cd (isotopic difference in mean-square radius, $<r^2>_m - <r^2>_{111}$) (Aufmuth et al, 1987) are given in Figure 3. The $\delta <r^2>_m$ values show a clear odd-even staggering pattern. Similar trends can be seen in our data (Table 1), but magnitudes of the odd-even staggering seem to be smaller. This is because our $\epsilon$ data are sum of mass-dependent and mass-independent isotope effects as shown in Eq. 12. We compare our $\epsilon$ data with $\delta <r^2>$ data as follows. If $m$ of $\delta^m$Cd is an odd atomic mass number, it can be expressed as $\delta^{2n+1}$Cd, while those for adjacent even ones can be expressed as $\delta^{2n}$Cd and $\delta^{2n+2}$Cd. We checked differences between $(\delta^{2n+2}$Cd $- \delta^{2n+1}$Cd) and $(\delta^{2n+1}$Cd $- \delta^{2n}$Cd) by using data given in Table 1. It should be noted that a correction with the reduced mass ($\delta m/mm'$)
is required in order to compare these. The following ratio is evaluated.

\[
R_{\text{odd-even}} = \frac{(\delta_{2n+1}^{\text{Cd}} - \delta_{2n}^{\text{Cd}})}{(\delta_{2n+2}^{\text{Cd}} - \delta_{2n+1}^{\text{Cd}})} \left( \frac{m_{2n+1} - m_{2n}}{m_{2n+1}m_{2n}} \right) \left( \frac{m_{2n+2} - m_{2n+1}}{m_{2n+2}m_{2n+1}} \right)
\]

(13)

where \(m_{2n+i}\) (\(i = 0, 1, \text{ or } 2\)) means mass of isotope with mass number \((2n+i)\). If \(R_{\text{odd-even}}\) shows unity, this means that the observed isotope fractionation is totally mass-dependent.

For isotope combinations, \(^{110}\text{Cd}-^{111}\text{Cd}-^{112}\text{Cd}\) and \(^{112}\text{Cd}-^{113}\text{Cd}-^{114}\text{Cd}\), \(R_{\text{odd-even}}\)'s were calculated. The obtained \(R_{\text{odd-even}}\) values are shown in Figure 4. In the same manner with Eq. 13, \(R_{\text{odd-even}}\) for \(\delta<r^2>\) was also calculated, which is shown together. The \(R_{\text{odd-even}}\) values show clear deviation from unity. This proves that the isotope fractionation of \(\text{Cd}\) contains the mass-independent isotope effect. The mass-independent property may have been caused by the nuclear field shift effect.

In order to confirm that the nuclear field shift effect had taken place, we present isotopic anomalies in \(\varepsilon\) unit. \(\varepsilon_m\) is defined as parts per 10,000 deviation from the mass dependent line drawn for a pair of even atomic mass isotopes, \(^{110}\text{Cd}\) and \(^{114}\text{Cd}\). For comparison, the \(\delta<r^2>\) values were also normalized by the same manner. Figure 5 shows a representative example for the 2.8 M acidity case. As shown in Figure 5, the normalized values for \(\varepsilon\) show a quite similar trend to those for \(\delta<r^2>\). Similar trends were found for all acidity conditions. Hence, it can be concluded that the mass independent isotope fractionation of \(\text{Cd}\) originated from the nuclear field shift effect.

As this study was performed under a constant temperature; Eq. 12 can be simplified as,
where $A$ and $B$ are also scaling factors. By applying Eq. 14 to the $\varepsilon_m$ data, the scaling factors $A$ and $B$ were determined for each acidity condition. Contributions of the nuclear field shift effect, $\delta<r^2>_m A / \varepsilon_m$, and that of mass effect, ${(m-111)/m \times 111} \times B / \varepsilon_m$, were evaluated. These contributions on $\varepsilon_m$ are shown in percent unit (Figure 6). The contribution of the nuclear field shift effect (averaged value) was 5%($\delta^{110}\text{Cd}$), 30%($\delta^{112}\text{Cd}$), 17%($\delta^{113}\text{Cd}$), 20%($\delta^{114}\text{Cd}$), or 17%($\delta^{116}\text{Cd}$), and no drastic change of this ratio could be seen in the experimental acidity region. These contributions are reproduced in Figure 7 as functions of $\delta m/\varepsilon_m$'. The direction of the nuclear field shift effect was same with that of the mass effect, and the magnitude of the mass effect was larger than that of the nuclear field shift effect. This suppresses the mass-independent property of the nuclear field shift effect. By increasing the nuclear field shift effect and/or decreasing the mass effect, the mass-independent property will approach to the profile of $\delta<r^2>$. Moreover, if the mass effect has a similar magnitude with an inverse sign to the nuclear field shift effect, an intensive mass-independent property like Figure 5 should appear. Under this extreme condition, the small change of the ratio of the nuclear field shift effect vs. the mass effect results in the drastic change of the mass-independent profile.

There are two ways to change the ratio of the nuclear field shift effect vs. the mass effect. The first way is to change the fractions of chemical species by controlling acidity, ionic strength (concentrations of cation and anion and acidity), and concentration of extractant. Since each isotopic exchange reaction (e.g., for reactions...
1 to 6) may have a specific ratio of the nuclear field shift effect \textit{vs.} the mass effect, this ratio in the total isotope effect should be affected by the fractions of species, but, changing acidity was less effective for the case of cadmium.

The second way is to change the molecular orbital itself by changing the coordination and bonding circumstances, \textit{i.e.}, changing the types of extractant, counter anion, aqueous and organic solvents. Investigating the second way should be performed with a quantum chemical study on what kind of molecular orbital enlarges the nuclear field shift effect. Recently, the magnitudes of nuclear field shift effects of heavy elements (Tl, Hg, U, and so on) were estimated by employing quantum chemical calculations (Schauble, 2007; Abe, 2008). The growth of their research field will be helpful for further studies on nuclear field shift effect.

As a final note, we present a possibility of the nuclear field shift effect in nature. Cd isotopic anomalies have been observed in the ordinary chondrites Brownfield (H 3.7) and Bishunpur (LL3.1) (Rosman et al., 1978, 1980, 1988). They have pointed out that nucleosynthesis, neutron irradiation, and isotope fractionation in mass spectrometry are disallowed as the origin of these anomalies, however no alternative origin is explained. When normalized to $^{110}\text{Cd}/^{114}\text{Cd}$ these data let anomalies in $^{111}\text{Cd}$ and $^{113}\text{Cd}$, which is similar to what is expected from the nuclear field shift effect (Fig. 5). Therefore field shift effect during chemical exchange reactions on the parent body of these meteorites may be an alternative origin for these Cd isotopic anomalies (Fig. 8).

\textbf{Conclusions}

Cadmium isotopes were fractionated by the liquid-liquid extraction technique with dicyclohexano-18-crown-6. The odd atomic mass isotopes showed excesses of
enrichment comparing to the even atomic mass isotopes. This mass-independent property is attributable to the nuclear field shift effect. The isotope enrichment factors showed an acidity dependence, while the ratio of contributions of the mass effect and the nuclear field shift effect were less sensitive to the acidity change.

\textit{Acknowledgment}

TF thanks Roy Jacobus for his help in improving the English of this paper. The authors thank two anonymous reviewers and the editors, Olivier Rouxel and Mathieu Roskosz, for useful suggestions on the manuscript.
References


Table 1  Isotope fractionation of Cadmium.

<table>
<thead>
<tr>
<th>[HCl] /M</th>
<th>Number of measurement</th>
<th>δ(^{110})Cd</th>
<th>δ(^{112})Cd</th>
<th>δ(^{113})Cd</th>
<th>δ(^{114})Cd</th>
<th>δ(^{116})Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>5</td>
<td>1.19±0.14</td>
<td>−1.48±0.06</td>
<td>−2.64±0.09</td>
<td>−4.07±0.06</td>
<td>−6.51±0.11</td>
</tr>
<tr>
<td>4.0</td>
<td>2</td>
<td>1.21±0.14</td>
<td>−1.40±0.06</td>
<td>−2.62±0.09</td>
<td>−3.95±0.07</td>
<td>−6.35±0.17</td>
</tr>
<tr>
<td>5.2</td>
<td>5</td>
<td>0.12±0.04</td>
<td>−0.14±0.02</td>
<td>−0.23±0.05</td>
<td>−0.37±0.06</td>
<td>−0.59±0.17</td>
</tr>
<tr>
<td>6.4</td>
<td>6</td>
<td>0.31±0.09</td>
<td>−0.38±0.01</td>
<td>−0.71±0.02</td>
<td>−1.07±0.03</td>
<td>−1.71±0.06</td>
</tr>
<tr>
<td>7.6</td>
<td>3</td>
<td>0.63±0.14</td>
<td>−0.76±0.06</td>
<td>−1.40±0.09</td>
<td>−2.11±0.07</td>
<td>−3.40±0.17</td>
</tr>
<tr>
<td>8.8</td>
<td>6</td>
<td>0.28±0.02</td>
<td>−0.33±0.02</td>
<td>−0.62±0.04</td>
<td>−0.93±0.03</td>
<td>−1.50±0.04</td>
</tr>
</tbody>
</table>

Errors are 2σ of experimental uncertainties (the error evaluation procedure can be seen in our previous study (Fujii et al., 2006b)).
Figure captions

Figure 1  Formations of the Cd(II) species in HCl solutions.  The reported stability constants for cadmium species (Pivovalov, 2005), the activity of Cl\(^{-}\) (Pivovalov, 2005), and the mean activity of CdCl\(_2\) (Bromley, 1973) were used for calculation. The reported \(a_{\text{HCl}}\) (Bromley, 1973) was also used. Dissociation of HCl was treated as the complete dissociation. It should be noted that the thermodynamic data (Pivovalov, 2005; Bromley, 1973) used have been determined under 6 mol kg\(^{-1}\) ionic strength.

Figure 2  Distribution ratios of Cd(II). \(D=[\text{Cd(II)}]_{\text{org}}/[\text{Cd(II)}]_{\text{aq}}\), in which [Cd(II)]\(_{\text{org}}\) was determined as [Cd(II)]\(_{\text{init}}\) – [Cd(II)]\(_{\text{aq}}\). Since [CdLCl\(_2\)•\(n\)HCl] is much smaller than [HCl]\(_{\text{init}}\), the consumption of HCl by the co-extraction was neglected. The experimental acidities were [HCl]= 1.6, 2.8, 4.0, 5.2, 6.4, 7.6, 8.8, and 10.0 M, and these were converted into \(a_{\text{HCl}}\) (Bromley, 1973). The unit of concentrations in right ordinate is mol kg\(^{-1}\).

Figure 3  Change in mean-square radius of Cd, \(\delta<r^2>_m\). \(\delta<r^2>_110 = -0.021\pm0.008\), \(\delta<r^2>_112 = 0.119\pm0.024\), \(\delta<r^2>_113 = 0.140\pm0.025\), \(\delta<r^2>_114 = 0.244\pm0.032\), and \(\delta<r^2>_116 = 0.342\pm0.037\). \(\delta<r^2>_m\) values are calculated from reported data (Aufmuth et al, 1987).

Figure 4  \(R_{\text{odd-even}}\) values for isotope combinations \(^{110}\text{Cd}-^{111}\text{Cd}-^{112}\text{Cd}\) and \(^{112}\text{Cd}-^{113}\text{Cd}-^{114}\text{Cd}\). The thin dotted lines show \(R_{\text{odd-even}}\) for \(\delta<r^2>\). (See text for the definition of \(R_{\text{odd-even}}\)).

Figure 5  Correlation between \(\epsilon\) and \(\delta<r^2>\).  Open marks show \(\epsilon_m\) and solid marks \(\delta<r^2>\). The data are normalized for an isotope pair \(^{110}\text{Cd}\) and \(^{114}\text{Cd}\). Errors of \(\delta^{m}\text{Cd}\) are drawn as those of \(\epsilon_m\). For \(\epsilon_{111}\), the largest error (±1.4, see Table 1) found for \(\delta^{m}\text{Cd}\) was used.

Figure 6  Contributions of nuclear field shift effect and mass effect to observed isotope enrichment factor. Open marks show the contribution of mass effect to \(\delta^{m}\text{Cd}\) and solid marks that to \(\delta^{m}\text{Cd}\). These contributions were calculated by employing Eq. 14.

Figure 7  Nuclear field shift effect, mass effect, and sum of these effects. Solid circles show contributions of mass effect, while open circles those of nuclear field shift effect. Open cross marks are sums of mass effects and nuclear field shift effects. These contributions were calculated by employing Eq. 14. \(\delta^{m}\text{Cd}\) is shown in arbitrary unit.

Figure 8  Isotopic variations of Cd in type 3 ordinary condrites. a) Brownfield (Rosman et al., 1980) b) Bishunpur (Rosman and De Laeter, 1988). Open marks show
reported $\varepsilon_m$. $^{111}$Cd data of b) was not reported. Solid marks show $\varepsilon_m$ values estimated by employing Eq. A11 in (Fujii et al., 2006a).
$\log D$ vs. $\log \gamma_{\text{CdCl}_2} - \log [\text{L}]$
\[ R_{\text{odd-even}} = \frac{\delta r_m}{r_2} \]

- For even sets: \( m:110,111,112 \)
- For odd sets: \( m:112,113,114 \)

[HCl] / M vs. \( R_{\text{odd-even}} \) graph.
Normalized $\delta \langle r^2 \rangle / \text{fm}^2$

Mass number
Mass effect

\[ \delta^{110}\text{Cd} \]

Nuclear field shift effect

\[ \delta^{112}\text{Cd} \]

\[ \delta^{113}\text{Cd} \]

\[ \delta^{114}\text{Cd} \]

\[ \delta^{116}\text{Cd} \]
Nuclear field shift effect

Mass effect

Total effect

\[ \delta m / \text{mm} \]

\[ \delta^{\text{m Cd}} / \text{arb.} \]
a) Brownfield

b) Bishunpur