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**Nuclear Field Shift Effect in the Isotope Exchange Reaction of Cadmium Using a Crown Ether**

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23 **Abstract**

24

25 Cadmium isotopes were fractionated by the liquid-liquid extraction technique with a  
26 crown ether, dicyclohexano-18-crown-6. The isotopic ratios of  $^m\text{Cd}/^{111}\text{Cd}$  (m: 110,  
27 112, 113, 114, and 116) were measured precisely by the multi-collector inductively  
28 coupled plasma spectrometry (MC-ICP-MS). When the isotope enrichment factors  
29 were calculated, the odd atomic mass isotopes ( $^{111}\text{Cd}$  and  $^{113}\text{Cd}$ ) showed excesses of  
30 enrichment comparing to the even atomic mass isotopes ( $^{110}\text{Cd}$ ,  $^{112}\text{Cd}$ ,  $^{114}\text{Cd}$  and  $^{116}\text{Cd}$ ).  
31 This odd-even staggering property originates from the nuclear field shift effect. The  
32 contribution of the nuclear field shift effect to the observed isotope enrichment factor  
33 was estimated to be 5 to 30%.

34

35

## 36 1. Introduction

37

38 The classic theory of chemical isotope fractionation only predicts mass-dependent  
39 isotope effect due to the isotopic difference in vibrational energies of isotopomers (Urey,  
40 1947; Bigeleisen and Mayer, 1947). No exception to that rule was found until the  
41 mid-80s. Mass-independent isotope fractionations were first observed for O and S (see a  
42 review by Thiemens, 2006). The difference in the symmetry and the densities of states  
43 of the activated isotopomers is a possible origin for these mass-independent isotope  
44 fractionations (Hathorn and Marcus, 1999). Alternative interpretations have been  
45 discussed in review articles (Weston, 1999; Thiemens, 2006). For heavy elements, an  
46 anomalous isotope enrichment of  $^{235}\text{U}$  was found in a redox reaction using liquid  
47 chromatography (Fujii et al., 1989). Isotope separation factors for even atomic mass  
48 isotopes,  $^{234}\text{U}$ ,  $^{236}\text{U}$ , and  $^{238}\text{U}$ , showed a mass-dependent trend, while that of  $^{235}\text{U}$   
49 deviated from it. For middle-heavy elements, Nishizawa et al. (1995) found the  
50 anomalous isotope fractionation named the odd/even isotope effect, and a similarity  
51 between the odd/even isotope effect and the odd-even staggering of  $\langle r^2 \rangle$  were pointed  
52 out (Nishizawa et al., 1995). To examine the mass-independent isotope effect, the  
53 conventional mass-dependent theory was reconsidered by one of the original authors  
54 (Bigeleisen, 1996). The original theory has been extended to include correction terms to  
55 account for nuclear properties, *i.e.*, nuclear mass, nuclear size and shape, and nuclear  
56 spin. The nuclear field shift effect, which results from the isotopic change in the nuclear  
57 size and shape, is recognized as the major origin of the mass-independent isotope effect  
58 in uranium (Bigeleisen, 1996).

59 Isotope shifts are well-known energy shifts in atomic spectra (King, 1984;

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

66 The field shift is proportional to the isotopic difference in mean-squared  
67 nuclear charge radius,  $\delta\langle r^2 \rangle$  ( $\delta$  means isotopic difference) (King, 1984; Aufmuth et al.,  
68 1987). Mean-square radius,  $\langle r^2 \rangle$ , of an odd atomic mass number isotope (with odd  
69 number neutrons) is usually smaller than the value expected from the adjacent isotopes  
70 with even atomic mass numbers (with even number neutrons). This unique property is  
71 known as the odd-even staggering which can be seen in every element (King, 1984;  
72 Aufmuth et al., 1987). The mass-independent isotope effect of uranium (Fujii et al.,  
73 1989) possesses the odd-even staggering property, and hence, the anomaly was  
74 attributable to the nuclear field shift effect (Bigeleisen, 1996; Nomura et al., 1996).

75 Similar mass-independent isotope fractionation has also been found in a lighter  
76 element, zinc (Nishizawa et al., 1993, 1996, 1998a, 1998b; Fujii et al., 2001). Since  
77 employing macrocyclic polyethers in a chemical exchange method is effective to create  
78 larger isotope fractionation (Tsvadze et al., 1996), a crown ether was used as an  
79 extractant for a solvent extraction process (Nishizawa et al., 1993, 1996, 1998a) and a  
80 cryptand as a stationary phase for liquid chromatography (Nishizawa et al., 1998b; Fujii  
81 et al., 2001). In every ligand exchange system, an odd atomic mass number isotope  $^{67}\text{Zn}$   
82 showed the anomalous enrichment property compared to that of the even atomic number  
83 isotopes. From these results, we expect that the mass-independent isotope

84 fractionation can also be found for a congener, cadmium. In this context, we  
85 fractionated cadmium isotopes by using a liquid-liquid extraction with a crown ether,  
86 dicyclohexano-18-crown-6 (DC18C6). The mass-independent property of Cd isotope  
87 fractionation was investigated.

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

99 In studies of the Zn isotope effect (Nishizawa et al., 1993, 1996, 1998a, 1998b;  
100 Fujii et al., 2001), isotopic compositions have been analyzed by ICP quadrupole mass  
101 spectrometry (ICP-QMS) (Nishizawa et al., 1993), thermal ionization mass  
102 spectrometry (TIMS) (Nishizawa et al., 1996, 1998a), or multiple-collector ICP mass  
103 spectrometry (MC-ICP-MS) (Nishizawa et al., 1998b; Fujii et al., 2001). In order to  
104 obtain higher ionization yield, the silica gel method has been adopted for isotopic  
105 analysis by TIMS (Nishizawa et al., 1996, 1998a). In recent analytical studies on Zn  
106 (Manhès and Göpel, 2003), Cd (Manhès and Göpel, 2003, 2007; Schmitt et al., 2006),  
107 and Pb (Manhès and Göpel, 2003, 2007) isotopes, it has been pointed that a

108 mass-independent bias may be created by using the silica gel method. Since the  
109 mass-independent isotope fractionation of Zn has been confirmed by both TIMS and  
110 ICP-MS, the anomaly should have been created in the chemical experiments, but the  
111 pointed uncertainty of the silica gel method in TIMS should be taken care of. Hence, in  
112 this study, we measured the Cd isotopic composition with a MC-ICP-MS.

113

## 114 **2. Experimental**

115 Dicyclohexano-18-crown-6 (over 97% purity) and 1,2-dichloroethane (over 99.8%  
116 purity) were products of Fluka Chemie GmbH. Cadmium dichloride (hydrated,  
117 99.999% purity) was purchased from Sigma-Aldrich Co. Hydrobromic acid (twice  
118 distilled) was purchased from Seastar Chemicals Inc. Hydrochloric acid and nitric  
119 acid (Merck KGaA) of analytical grade were purified by distillation and supplied for  
120 experiment.

121 Cadmium dichloride was dissolved in HCl to create solutions,  $0.08 \text{ mol dm}^{-3}$   
122 (M) Cd(II) in various [HCl] (=1.6 to 10 M). The organic phase was 0.1 M DC18C6 in  
123 1,2-dichloroethane. A  $3 \text{ cm}^3$  aqueous solution and a  $3 \text{ cm}^3$  organic solution were  
124 mixed in a glass vial with a stirrer bar, and the glass vial was sealed with a stopcock.  
125 The two phases were stirred by a magnetic stirrer for 30 min. After the extraction  
126 equilibrium was attained, the two phases were separated by centrifugation (2000 rpm, 1  
127 min). An aliquot of the upper aqueous solution was taken for analysis. These  
128 procedures were carried out at  $294.0 \pm 0.5 \text{ K}$ . The Cd concentration in the equilibrated  
129 aqueous phase was analyzed by ICP-QMS (Thermo Elemental X7).

130 In order to avoid any matrix effect, possible trace of organic materials from  
131 DC18C6 was separated from the Cd by adapting our Zn separation technique (Moynier

132 et al., 2006, 2007) on anion-exchange resin (AG1X8 200-400 mesh) in HBr/HNO<sub>3</sub>.  
133 An aliquot of the aqueous phase was once dried by heating at 333 K and then dissolved  
134 into 1.5 M HBr. On the anion-exchange resin in 1.5 M HBr, Cd was strongly adsorbed  
135 while organic materials went through. Finally, Cd was collected in 0.5 M HNO<sub>3</sub>.

136 A solution containing 200 ppb Cd in 0.05 M HNO<sub>3</sub> was prepared for isotopic  
137 analysis. Isotopic ratios of Cd in all samples were analyzed with the MC-ICP-MS Nu  
138 plasma 500 HR at ENS Lyon coupled with a desolvating nebulizer Nu DSN-100. 40  
139 ratios in 2 blocks of 20 ratios each, in which the integration time of 1 scan was 10 sec,  
140 were measured for each sample. The background was corrected for measuring the  
141 ground zero at half-mass positions from the peak prior to data acquisition. The  
142 instrumental mass bias was corrected by bracketing each of the samples with standards.  
143 The blank from the chemistry is <1ng which is negligible with regards to the large  
144 quantity of Cd extracted from the crown-ether experiments (~10mg Cd).

145 Possible interferences with Pd on the masses 108 and 110 and with In on the  
146 mass 113 were verified to be under the detection of the ICP-MS. Because there was no  
147 isotopic interference on <sup>111</sup>Cd, the isotope ratios <sup>m</sup>Cd/<sup>111</sup>Cd (*m* : 110, 112, 113, 114,  
148 and 116) were measured. Since we were looking for odd-even effects we only selected  
149 the more abundant even Cd isotopes (110, 112, 114 and 116) and did not measure the  
150 least abundant ones, <sup>106</sup>Cd (1.25%) and <sup>108</sup>Cd (0.89%), which would not have give us  
151 additional information. <sup>118</sup>Sn was measured to correct isobaric interferences of Sn with  
152 Cd on the masses 112, 114, and 116. The interference of <sup>116</sup>Sn on <sup>116</sup>Cd as beam  
153 intensities was less than 2×10<sup>-4</sup>, and this was corrected by using the naturally occurring  
154 isotopic abundances of Sn. The interferences of Sn on the masses 112 and 114 were  
155 also corrected as the same manner, and were negligibly small (less than 4×10<sup>-6</sup> of <sup>112</sup>Cd



156 or  $^{114}\text{Cd}$  beam intensity).

157

### 158 **3. Results and discussion**

#### 159 *3.1 Extraction reaction for the Cd(II)-crown ether system*

160 Possible species of Cd(II) in HCl media are  $\text{Cd}^{2+}$ ,  $\text{CdCl}^+$ ,  $\text{CdCl}_2$ ,  $\text{CdCl}_3^-$ , and  $\text{CdCl}_4^{2-}$ ,

161 which are equilibrated as the following reactions,



166 Stability constants of equilibria 1 to 4 at zero ionic strength are evaluated from the  
167 reported values,  $\log K_1^0 = 2.0$ ,  $\log K_2^0 = 0.70$ ,  $\log K_3^0 = -0.30$ , and  $\log K_4^0 = -1.2$ ,  
168 respectively (Pivovalov, 2005). From these  $K^0$  values, activity of  $\text{Cl}^-$  (Pivovalov,  
169 2005), and mean activity of  $\text{CdCl}_2$  (Bromley, 1973), mole fractions of Cd species were  
170 estimated as functions of  $[\text{HCl}]$  (Figure 1). As shown in Figure 1, in our experimental  
171 region of  $[\text{HCl}] = 1.6$  to  $10.0$  M, the major species are  $\text{CdCl}_2$ ,  $\text{CdCl}_3^-$ , and  $\text{CdCl}_4^{2-}$ .

172 The obtained distribution ratios,  $D = [\text{Cd(II)}]_{\text{org}}/[\text{Cd(II)}]_{\text{aq}}$ , are shown in Figure  
173 2 as a function of the activity of HCl,  $a_{\text{HCl}}$ . The  $D$  value increases with acidity, then  
174 reaches a plateau. The extraction reaction of Cd in the crown ether system is generally  
175 written as,



176 where L means ligand, DC18C6. The curve of  $\log D$  vs.  $\log a_{\text{HCl}}$  can not be

177 explained by this reaction. This acidity dependence would be attributable to a  
 178 co-extraction of HCl. The extraction reaction may be rewritten as,



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

$$K_L = \frac{\gamma_{\text{CdLCl}_2 \bullet n\text{HCl}} [\text{CdLCl}_2 \bullet n\text{HCl}]}{a_{\text{HCl}}^{2n} \gamma_{\text{CdCl}_2} [\text{CdCl}_2] \gamma_L [\text{L}]} \quad (7)$$

180

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

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

185  $[\text{Cd(II)}]_{\text{org}}$  and  $[\text{L}]$  are experimentally determined.  $\gamma_{\text{CdCl}_2}$  can be calculated by the  
 186 semi-empirical calculation (Bromley, 1973), and  $[\text{CdCl}_2]$  can be calculated from the  
 187 reported  $K^0$  values (Pivovalov, 2005). As shown in Fig. 2, the left hand equation  
 188 shows a clear linearity to  $\log a_{\text{HCl}}$ . From the slope and the intercept of this line  
 189  $K_L=10.4$  and  $n=0.7$  were determined, and the determination coefficient was  $R^2=0.997$ .  
 190 The obtained  $n$  value suggests that 1 HCl molecule may participate to the extraction  
 191 reaction 6. The co-extraction of HCl suggests that, in the organic phase, the extracted  
 192  $\text{CdLCl}_2 \bullet \text{HCl}$  may form  $\text{H}^+ \bullet \text{CdLCl}_3^-$ . According to the reported extraction  
 193 stoichiometry of  $\text{H}^+$  and anionic species (Beklemishev et al., 1997), the following  
 194 extraction may compete with the reaction 6,



195 In a crown ether system, an extraction of anionic species from the concentrated HCl has

196 been reported (Beklemishev et al., 1997). Thus, extraction of a neutral species  
197 ( $\text{CdLCl}_2$ ), co-extraction of the neutral species and HCl, and extraction of anionic species  
198 with  $\text{H}^+$  may simultaneously take place in the present system.

199

### 200 3.2 Isotope fractionation during extraction

201 The isotope separation factor, between the aqueous and the organic phases,  $\alpha_m$   
202 is defined as:

$$\alpha_m = \frac{([\text{mCd}]/[^{111}\text{Cd}])_{\text{org}}}{([\text{mCd}]/[^{111}\text{Cd}])_{\text{aq}}} \quad (10)$$

203

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

211

$$\delta^{\text{mCd}} = (\alpha_m - 1) \times 1,000 \quad (11)$$

212

213 As  $\alpha_m$  is almost equal to one,  $\alpha_m - 1 (=10^{-3} \delta^{\text{mCd}}) \approx \ln \alpha_m$ .

214

215 The obtained  $\delta^{\text{mCd}}$  values are shown in Table 1. For each isotope, the  
216 absolute value of  $\delta^{\text{mCd}}$  decreases and showed a minimum value at 5.2 M HCl. Since the  
217 dominant species in the aqueous phase are  $\text{CdCl}_2$ ,  $\text{CdCl}_3^-$ , and  $\text{CdCl}_4^{2-}$  in the  
experimental acidity region, possible isotope exchange reactions have taken place in

218 reactions 2, 3, and 4. The isotope exchange reactions have also taken place in the  
 219 extraction reactions 6 and 9. The acidity dependence of  $\delta^m\text{Cd}$  we observed would be a  
 220 result of isotopic mass balance corresponding to these reactions.

221 The conventional mass-dependent theory of the Bigeleisen-Mayer equation  
 222 (1947) has been extended to include the nuclear field shift effect (Bigeleisen, 1996),

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

223

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

230 The  $\delta\langle r^2 \rangle_m$  values of Cd (isotopic difference in mean-square radius,  $\langle r^2 \rangle_m -$   
 231  $\langle r^2 \rangle_{111}$ ) (Aufmuth et al, 1987) are given in Figure 3. The  $\delta\langle r^2 \rangle_m$  values show a clear  
 232 odd-even staggering pattern. Similar trends can be seen in our data (Table 1), but  
 233 magnitudes of the odd-even staggering seem to be smaller. This is because our  $\epsilon$  data  
 234 are sum of mass-dependent and mass-independent isotope effects as shown in Eq. 12.  
 235 We compare our  $\epsilon$  data with  $\delta\langle r^2 \rangle$  data as follows.

236 If  $m$  of  $\delta^m\text{Cd}$  is an odd atomic mass number, it can be expressed as  $\delta^{2n+1}\text{Cd}$ ,  
 237 while those for adjacent even ones can be expressed as  $\delta^{2n}\text{Cd}$  and  $\delta^{2n+2}\text{Cd}$ . We  
 238 checked differences between  $(\delta^{2n+2}\text{Cd} - \delta^{2n+1}\text{Cd})$  and  $(\delta^{2n+1}\text{Cd} - \delta^{2n}\text{Cd})$  by using data  
 239 given in Table 1. It should be noted that a correction with the reduced mass ( $\delta m/mm'$ )

240 is required in order to compare these. The following ratio is evaluated.

$$R_{\text{odd-even}} = \frac{(\delta^{2n+1}\text{Cd} - \delta^{2n}\text{Cd}) / \left( \frac{m_{2n+1} - m_{2n}}{m_{2n+1}m_{2n}} \right)}{(\delta^{2n+2}\text{Cd} - \delta^{2n+1}\text{Cd}) / \left( \frac{m_{2n+2} - m_{2n+1}}{m_{2n+2}m_{2n+1}} \right)} \quad (13)$$

241

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

245 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  
 246 were calculated. The obtained  $R_{\text{odd-even}}$  values are shown in Figure 4. In the same  
 247 manner with Eq. 13,  $R_{\text{odd-even}}$  for  $\delta\langle r^2 \rangle$  was also calculated, which is shown together.  
 248 The  $R_{\text{odd-even}}$  values show clear deviation from unity. This proves that the isotope  
 249 fractionation of Cd contains the mass-independent isotope effect. The mass-independent  
 250 property may have been caused by the nuclear field shift effect.

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

259 As this study was performed under a constant temperature; Eq. 12 can be  
 260 simplified as,

$$10^{-3} \delta^m \text{Cd} = \delta \langle r^2 \rangle_m \times A + \frac{m-111}{m \times 111} \times B \quad (14)$$

261

262 where  $A$  and  $B$  are also scaling factors. By applying Eq. 14 to the  $\epsilon_m$  data, the scaling  
 263 factors  $A$  and  $B$  were determined for each acidity condition. Contributions of the  
 264 nuclear field shift effect,  $\delta \langle r^2 \rangle_m A / \epsilon_m$ , and that of mass effect,  $\{(m-111)/m \times 111\} B / \epsilon_m$ ,  
 265 were evaluated. These contributions on  $\epsilon_m$  are shown in percent unit (Figure 6). The  
 266 contribution of the nuclear field shift effect (averaged value) was 5% ( $\delta^{110}\text{Cd}$ ),  
 267 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  
 268 ratio could be seen in the experimental acidity region. These contributions are  
 269 reproduced in Figure 7 as functions of  $\delta m / m m'$ . The direction of the nuclear field shift  
 270 effect was same with that of the mass effect, and the magnitude of the mass effect was  
 271 larger than that of the nuclear field shift effect. This suppresses the mass-independent  
 272 property of the nuclear field shift effect. By increasing the nuclear field shift effect  
 273 and/or decreasing the mass effect, the mass-independent property will approach to the  
 274 profile of  $\delta \langle r^2 \rangle$ . Moreover, if the mass effect has a similar magnitude with an inverse  
 275 sign to the nuclear field shift effect, an intensive mass-independent property like Figure  
 276 5 should appear. Under this extreme condition, the small change of the ratio of the  
 277 nuclear field shift effect vs. the mass effect results in the drastic change of the  
 278 mass-independent profile.

279 There are two ways to change the ratio of the nuclear field shift effect vs. the  
 280 mass effect. The first way is to change the fractions of chemical species by controlling  
 281 acidity, ionic strength (concentrations of cation and anion and acidity), and  
 282 concentration of extractant. Since each isotopic exchange reaction (*e.g.*, for reactions

283 1 to 6) may have a specific ratio of the nuclear field shift effect vs. the mass effect, this  
284 ratio in the total isotope effect should be affected by the fractions of species, but,  
285 changing acidity was less effective for the case of cadmium.

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

294 As a final note, we present a possibility of the nuclear field shift effect in nature.  
295 Cd isotopic anomalies have been observed in the ordinary chondrites Brownfield (H  
296 3.7) and Bishunpur (LL3.1) (Rosman et al., 1978, 1980, 1988). They have pointed out  
297 that nucleosynthesis, neutron irradiation, and isotope fractionation in mass spectrometry  
298 are disallowed as the origin of these anomalies, however no alternative origin is  
299 explained. When normalized to  $^{110}\text{Cd}/^{114}\text{Cd}$  these data let anomalies in  $^{111}\text{Cd}$  and  $^{113}\text{Cd}$ ,  
300 which is similar to what is expected from the nuclear field shift effect (Fig. 5).  
301 Therefore field shift effect during chemical exchange reactions on the parent body of  
302 these meteorites may be an alternative origin for these Cd isotopic anomalies (Fig. 8).

303

### 304 **Conclusions**

305 Cadmium isotopes were fractionated by the liquid-liquid extraction technique with  
306 dicyclohexano-18-crown-6. The odd atomic mass isotopes showed excesses of

307 enrichment comparing to the even atomic mass isotopes. This mass-independent  
308 property is attributable to the nuclear field shift effect. The isotope enrichment factors  
309 showed an acidity dependence, while the ratio of contributions of the mass effect and  
310 the nuclear field shift effect were less sensitive to the acidity change.

311

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316



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**Table 1 Isotope fractionation of Cadmium.**

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

423 Errors are 2 $\sigma$  of experimental uncertainties (the error evaluation procedure can be seen  
424 in our previous study (Fujii et al., 2006b).  
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426

427 **Figure captions**

428 **Figure 1 Formations of the Cd(II) species in HCl solutions.** The reported stability  
429 constants for cadmium species (Pivovarov, 2005), the activity of  $\text{Cl}^-$  (Pivovarov, 2005),  
430 and the mean activity of  $\text{CdCl}_2$  (Bromley, 1973) were used for calculation. The  
431 reported  $a_{\text{HCl}}$  (Bromley, 1973) was also used. Dissociation of HCl was treated as the  
432 complete dissociation. It should be noted that the thermodynamic data (Pivovarov,  
433 2005; Bromley, 1973) used have been determined under  $6 \text{ mol kg}^{-1}$  ionic strength.

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

440 **Figure 3 Change in mean-square radius of Cd,  $\delta\langle r^2 \rangle_{\text{m}}$ .**  $\delta\langle r^2 \rangle_{110} = -0.021 \pm 0.008$ ,  
441  $\delta\langle r^2 \rangle_{112} = 0.119 \pm 0.024$ ,  $\delta\langle r^2 \rangle_{113} = 0.140 \pm 0.025$ ,  $\delta\langle r^2 \rangle_{114} = 0.244 \pm 0.032$ , and  $\delta\langle r^2 \rangle_{116}$   
442  $= 0.342 \pm 0.037$ .  $\delta\langle r^2 \rangle_{\text{m}}$  values are calculated from reported data (Aufmuth et al, 1987).

443 **Figure 4  $R_{\text{odd-even}}$  values for isotope combinations  $^{110}\text{Cd}$ - $^{111}\text{Cd}$ - $^{112}\text{Cd}$  and**  
444  **$^{112}\text{Cd}$ - $^{113}\text{Cd}$ - $^{114}\text{Cd}$ .** The thin dotted lines show  $R_{\text{odd-even}}$  for  $\delta\langle r^2 \rangle$ . (See text for the  
445 definition of  $R_{\text{odd-even}}$ ).

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

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

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

457 **Figure 8 Isotopic variations of Cd in type 3 ordinary chondrites.** a) Brownfield  
458 (Rosman et al., 1980) b) Bishunpur (Rosman and De Laeter, 1988). Open marks show

459 reported  $\epsilon_m$ .  $^{111}\text{Cd}$  data of b) was not reported. Solid marks show  $\epsilon_m$  values estimated by  
460 employing Eq. A11 in (Fujii et al., 2006a).

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