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## Nuclear field shift effect in isotope fractionation of thallium

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### Abstract:

Environmental transport of Tl is affected by redox reaction between Tl(I) and Tl(III) and ligand exchange reactions of them. In order to deepen the knowledge of Tl chemistry, we investigated fractionation of Tl stable isotopes (<sup>203</sup>Tl and <sup>205</sup>Tl) in a chemical exchange system. Tl isotopes were fractionated in a liquid–liquid extraction system, in which aqueous and organic phases are hydrochloric acid solution and dichloroethane including a crown ether, respectively. After purification by ion-exchange chemistry, the isotope ratio of <sup>205</sup>Tl/<sup>203</sup>Tl in equilibrated aqueous phase was measured precisely by multiple-collector–inductively-coupled-plasma–mass-spectrometry. A large isotope fractionation >1 ‰ was found. Electronic structures of possible Tl species (hydrated Tl<sup>+</sup>, Tl<sup>3+</sup>, and Tl chlorides) were calculated by ab initio methods, and the isotope fractionation factor was theoretically obtained. The isotope fractionation via intramolecular vibrations was calculated to be much smaller than the experimental result. The isotope fractionation via isotopic change in nuclear volume, named the nuclear field shift effect, was calculated to be >1 ‰ in Tl(I)–Tl(III) redox systems and/or ligand exchange systems of Tl(III). The nuclear field shift effect was found to be the major origin of Tl isotope fractionation.

**Keywords:** Thallium ; Isotope fractionation ; Redox ; Ligand exchange ; Nuclear field shift ; Ab initio calculation

## 39 Introduction

40 Thallium is a highly toxic heavy element. Pollution by Tl is found in mining districts and its migration  
41 introduces Tl into surface water, soils, plants, and so on [1]. Environmental transport of Tl is affected by  
42 chemical exchange reactions of related Tl species, that is, redox reaction between Tl(I) and Tl(III) and ligand  
43 exchange reactions of them. The Tl isotope fractionation in the chemical exchange reactions is of interest, since  
44 it may result in the isotopic variation of Tl in nature.

45 The classic theory of isotope effect has been established by Urey, Bigeleisen, and Mayer [2,3]. The  
46 theory originates from the difference in the intramolecular vibrational energies of isotopologues. The theory  
47 predicts the mass-dependent isotope fractionation. The magnitude of isotope effect (isotope enrichment factor,  $\epsilon$ )  
48 is proportional to  $\delta m/mm'$ , where  $\delta m$  means the isotopic mass difference of masses  $m$  and  $m'$  of two isotopes  
49 (prime represents the light isotope). The vibrational isotope effect is predominant in isotope fractionation of light  
50 elements. The isotope effect found in heavy elements has frequently been larger than that expected by the classic  
51 theory. This is now recognized as the nuclear field shift effect [4,5]. The nuclear field shift effect, which results  
52 from the isotopic change in the nuclear size and shape, is larger for heavy elements and it is recognized as the  
53 major origin of the mass-independent isotope fractionation in chemical exchange reactions [4-11], for example,  
54  $\sim 1\%/amu$  (atomic mass unit) fractionation is possible for Hg [6], Tl [6], Pb [7], and U [4,5,8-10]. For middle  
55 heavy elements, Mo [12], Ru [6,12], and Pd [13], 0.05-0.3%/amu of the nuclear field shift effect is estimated.  
56 For light elements such as Ni [14] and Zn [15], the nuclear field shift effect is estimated to be small as  
57 0.02-0.03%/amu.

58 The nuclear field shift effect of Tl is demonstrated in the present study. The isotope fractionation in a  
59 two-phase distribution of Tl was studied, in which an aqueous solution and an organic solution were used. A  
60 macrocyclic compound called crown ether was selected as a complexation agent with Tl. The isotopic ratio of Tl,  
61  $^{205}\text{Tl}/^{203}\text{Tl}$ , was measured precisely by multiple-collector inductively-coupled-plasma mass-spectrometry  
62 (MC-ICP-MS). As supporting information for the isotope separation factor obtained, we performed the  
63 molecular orbital calculations for related Tl complexes. The isotope fractionation via intramolecular vibrations  
64 was estimated as the reduced partition function ratio (RPF) of isotopologues. The contribution of the nuclear  
65 volume to the RPF was also estimated by *ab initio* methods.

66

## 67 Experimental

68 All chemicals were reagent grade. TlCl was dissolved in HCl, and 0.1 mol dm<sup>-3</sup> (M) Tl(I) with various [HCl]  
69 was prepared. The natural potential of each aqueous phase was measured by using two-electrode system. A Pt  
70 wire and a Ag|AgCl electrode were used as working and reference electrodes, respectively. The organic phase  
71 was 0.1 M dicyclohexano-18-crown-6 (DC18C6) in 1,2-dichloroethane. A 7 cm<sup>3</sup> aqueous solution and a 7 cm<sup>3</sup>  
72 organic solution were mixed in a glass vial with a stirrer bar, and the glass vial was sealed. The two phases were  
73 stirred by a magnetic stirrer for 30 min. After the extraction equilibrium was attained, the two phases were  
74 separated by centrifugation. An aliquot of the upper aqueous solution was taken for analysis. These procedures  
75 were carried out at 298 ± 0.5 K. The Tl concentration in the sample solution was analyzed by ICP-AES (Thermo  
76 Fisher Scientific, iCAP 6300 Duo).

77 Organic impurities carried over the extraction were separated from Tl on anion exchange resin  
78 (AG1X8 200-400 mesh) in HBr/HNO<sub>3</sub>. The sample solution was dried up, and then dissolved into a few drops of  
79 9M HBr. This was dried up by heating once more, and then dissolved into 0.5 M HBr again. On the anion  
80 exchange resin in 0.5 M HBr, Tl was strongly adsorbed while organic substances passed through freely. Finally,  
81 Tl was collected in 0.5 M HNO<sub>3</sub>. Since Tl was totally recovered, no isotope fractionation occurs in this  
82 procedure.

83 Solutions of purified Tl (40 ng g<sup>-1</sup> in 0.3 M HNO<sub>3</sub>) were analyzed on a Neptune (Thermo Fisher  
84 Scientific) MC-ICP mass spectrometer at the "Pole Spectrometrie Ocean" (PSO) of Brest. MC-ICP-MS  
85 technique has opened up high precision measurements of stable isotope ratios of heavy elements [16]. Samples  
86 and standards were spiked with Pb isotopic standard NIST981 (National Institute of Standards and Technology)  
87 to achieve [Tl]/[Pb] ~ 4 to correct for mass discrimination. Isotopes <sup>203</sup>Tl, <sup>205</sup>Tl, <sup>206</sup>Pb, and <sup>207</sup>Pb were collected  
88 on Faraday cups and an exponential mass discrimination law [17] using <sup>207</sup>Pb/<sup>206</sup>Pb = 0.91464 was applied to  
89 correct <sup>205</sup>Tl/<sup>203</sup>Tl ratios. Procedural blanks and instrumental background were corrected simultaneously by  
90 measuring on peak zero signals. Analytical uncertainty was 0.04% (2σ). No isobaric interference was observed.  
91 Each sample solution was analyzed 6 times by standard-sample bracketing.

92 The molecular geometries and vibrational frequencies of aqueous Tl(I) and Tl(III) species were  
93 calculated by using the density functional theory (DFT) implemented by the Gaussian03 code [18]. The DFT  
94 method employed here is a hybrid density functional consisting of Becke's [19] three-parameter non-local hybrid  
95 exchange potential (B3) with Lee-Yang-and Parr (LYP) [20] non-local functionals. The 6-31++G\*\* basis set  
96 (all-electron basis set) was chosen for H, O, and Cl. Stuttgart/Dresden effective core potential (SDD)  
97 compensated the relativistic effect [21] was chosen for Tl.

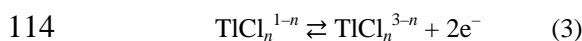
98 The contribution of the nuclear volume was estimated by the numerical multiconfigurational  
 99 Dirac-Coulomb Hartree-Fock (MCDCHF) method implemented in the four-component relativistic atomic  
 100 program package GRASP2K [22] and the Dirac-Coulomb Hartree-Fock (DCHF) method implemented in the  
 101 UTChem program [23]. Calculations of the electronic structure of  $Tl^0([Xe]4f^{14}5d^{10}6s^26p^1)$ ,  $Tl^+([Xe]4f^{14}5d^{10}6s^2)$ ,  
 102  $Tl^{3+}([Xe]4f^{14}5d^{10})$ , and a few simple Tl molecules were performed. Exponents of basis sets are taken from  
 103 Faegri's four-component basis for Tl [24], third-order Douglas-Kroll basis for H and Cl [25], and ANO-RCC for  
 104 O [26]. Contraction coefficients are optimized by four-component atomic calculations [27]. After we added  
 105 some diffuse and polarization functions, the final contraction form of the large component basis sets is  
 106  $[23s21p14d9f]/(8s7p5d3f)$  for Tl,  $(16s11p1d)/[4s3p1d]$  for Cl,  $(14s9p2d)/[3s2p2d]$  for O, and  $(8s2p)/[3s2p]$  for H.  
 107 More details are in the literature [8-10].

108

## 109 Results and Discussion

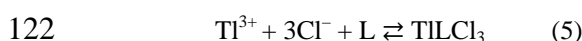
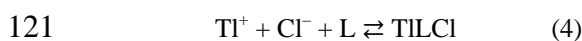
### 110 *Isotope fractionation of Tl by crown ether extraction*

111 Chemical species of Tl(I) and Tl(III) in HCl media considered here are related through the following reactions,



115 where  $n = 3$  of reaction 1 was not found [28]. The stability constants of equilibria 1 and 2 have been reported in  
 116 literatures [28,29]. Complexation proceeds easily in the HCl system. According to the literature data [30] and the  
 117 natural potentials measured, the aqueous phase prepared contains 0.2-0.5% of Tl(III), and the rests are Tl(I).  
 118 Though the present system is mainly controlled by ligand exchange reactions of Tl(I), the redox reaction 3 exists.

119 A few studies on Tl extraction with crown ethers have been reported [31,32]. A neutral ligand  
 120 DC18C6 precedes ion association extraction, and hence the extraction reaction of Tl can be written as,



123 where L stands for DC18C6. The distribution ratio is defined as,

$$124 \quad D = ([Tl(I)] + [Tl(III)])_{org}/([Tl(I)] + [Tl(III)])_{aq} \quad (6)$$

125 where subscripts *org* and *aq* mean the organic and aqueous phases, respectively. Acidity dependence of  $D$   
 126 obtained is shown in Fig. 1a. High extractability of Tl(III) is known for HCl/DC18C6 systems [32]. Tl(I) is not  
 127 extracted from diluted HCl but from concentrated HCl [32]. The steep increase of  $D$  at low [HCl] region is

128 attributable to the extraction of Tl(III). The extraction of Tl(I) becomes significant with the increase of [HCl].  
 129 Anionic species of Tl chlorides form at concentrated HCl region, and this would depress the extraction of both  
 130 Tl(I) and Tl(III). The extraction system is schematically shown in Fig 1b. The extraction behavior of Tl can be  
 131 summarized as,

132 Low acidity: Tl(III) is mainly extracted to the organic phase. Tl(I) remains in the aqueous phase, which is partly  
 133 oxidized to Tl(III).

134 High acidity: Both Tl(I) and Tl(III) are extracted to the organic phase. Higher complexation of Tl ions with Cl<sup>-</sup>  
 135 occurs in the concentrated HCl.

136 Isotope fractionation of Tl found in the equilibrated aqueous phase was evaluated as,

$$137 \quad \delta^{205}\text{Tl} = \left( \frac{[^{205}\text{Tl}]/[^{203}\text{Tl}]_{\text{aq}}}{[^{205}\text{Tl}]/[^{203}\text{Tl}]_{\text{ref}}} - 1 \right) \times 1000 \quad (7)$$

138 where the subscript *ref* means the reference. Isotope ratio <sup>205</sup>Tl/<sup>203</sup>Tl of the starting material was set to be  
 139 (<sup>205</sup>Tl/<sup>203</sup>Tl)<sub>ref</sub>. The δ<sup>205</sup>Tl values obtained are shown in Fig. 2. Analytical errors (2σ) of 6 replicates are shown  
 140 together. Small positive isotope fractionation was observed at high [HCl] region, while large negative isotope  
 141 fractionation at low [HCl] region.

142

#### 143 *Estimation of Tl isotope effect by ab initio methods*

144 Firstly, we estimated the magnitude of the conventional mass effect. In order to evaluate the respective  
 145 strength of mass-dependent effects, some quantum chemical calculations of the vibrational energies of the  
 146 aqueous Tl(I) and Tl(III) species were performed. Coordination number of hydrated Tl species was set to 4-6  
 147 according to the literatures [33-36].

148 The structures of Tl<sup>+</sup>, Tl<sup>3+</sup>, and their hydrated chlorides were optimized and then intramolecular  
 149 frequencies of these species were calculated in order to evaluate δ<sup>205</sup>Tl. The isotope enrichment factor due to the  
 150 intramolecular vibrations can be evaluated from the reduced partition function ratio (RPF) [3], (s/s')*f*,

$$151 \quad \ln (s/s')f = \sum [\ln b(u_i') - \ln b(u_i)] \quad (8)$$

$$152 \quad \ln b(u_i) = -\ln u_i + u_i/2 + \ln(1 - e^{-u_i}) \quad (9)$$

$$153 \quad u_i = hv_i/kT \quad (10)$$

154 where *v* means vibrational frequency. The subscript *i* stands for the *i*th molecular vibrational level with primed  
 155 variables referring to the light isotopologue. The isotope enrichment factor due to the molecular vibration can be  
 156 evaluated from the frequencies (*v*) summed over all the different modes. The RPFs obtained for the isotope pair  
 157 <sup>203</sup>Tl-<sup>205</sup>Tl at 298 K are shown in Table 1. The reported RPFs calculated for hydrated Tl<sup>+</sup> and Tl<sup>3+</sup> at 298 K [6]

158 are shown together. Our calculations show quite good agreement with the reported values. Though the structure  
159 of the Tl-crown complex is not clear, a similar magnitude of the RPFs may be expected.

160 The acidity dependence of  $\delta^{205}\text{Tl}$  shown in Fig. 2 results from ligand exchange and/or redox reactions  
161 of Tl(I) and Tl(III) species. The RPFs of Tl(I) are ranged in 0.02-0.08‰. The difference is only 0.06‰. The  
162 RPFs of Tl(III) are ranged in 0.37-0.44‰. The difference is also 0.07‰. These values due to ligand exchange  
163 reactions are too small to distinguish as the isotope fractionation. The maximum difference in RPFs between  
164 Tl(I) and Tl(III) species is 0.42‰. This magnitude due to redox reaction is 10 times smaller than  $\delta^{205}\text{Tl}$  found in  
165 low [HCl] region. The results indicate that the conventional mass effect is not the major origin of Tl isotope  
166 fractionation in our experimental system.

167 The nuclear field shift is an isotope shift in orbital electrons [37]. This results from the isotopic  
168 difference in the nuclear size and shape. For example, the root-mean-square charge radii  $\langle r^2 \rangle^{1/2}$  of  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$   
169 are  $5.4664 \times 10^{-15}$  m and  $5.4763 \times 10^{-15}$  m [38], respectively. The nuclear charge distribution gives an electric field,  
170 and its isotopic difference shifts the atomic energy levels, also displacing the electronic molecular states. The  
171 nuclear field shift effect  $\ln K_{\text{fs}}$  can be written.

$$172 \quad \ln K_{\text{fs}} = hc\nu_{\text{fs}}/kT \quad (11)$$

173 where  $\nu_{\text{fs}}$  means nuclear field shift, and  $hc\nu_{\text{fs}}$  is the isotopic displacement of electronic energy level  $\delta E$  due to the  
174 nuclear field shift. In the present study, the total electronic energies at the ground states of  $\text{Tl}^0$ ,  $\text{Tl}^+$ , and  $\text{Tl}^{3+}$  were  
175 calculated for different isotopes with different nuclear charge radii. Calculations for a few simple Tl molecules  
176 were also tested. The molecular structures were optimized by the similar method to obtain RPFs.

177 The  $\ln K_{\text{fs}}$  values calculated are shown in Table 2. The reference is  $\text{Tl}^0$ . In  $K_{\text{fs}}$  values calculated by  
178 another DCHF method [6] are shown together. Our calculations agreed with the reported data. The nuclear field  
179 shift effect is attributable to the probability density of electrons at nucleus, and hence, drastic change in the  
180 electron configuration should cause a larger effect. A drastic case here is the  $\text{Tl}^+-\text{Tl}^{3+}$  redox reaction. The  
181 difference of  $\ln K_{\text{fs}}$  values between  $\text{Tl}^+$  and  $\text{Tl}^{3+}$  is 2.8‰. At low [HCl] region, Tl(III) is extracted in the organic  
182 phase and the major valence of Tl species in the aqueous phase is Tl(I). Since we measured the isotope  
183 fractionation in the aqueous phase, the isotope effect close to  $-2.8$ ‰ would be observed as  $\delta^{205}\text{Tl}$ . The  
184 conventional mass effect as mentioned above is expected to be  $\sim 0.42$ ‰ for the  $\text{Tl}^+-\text{Tl}^{3+}$  redox reaction. Totally  
185  $\delta^{205}\text{Tl}$  of  $-3.2$ ‰ is expected. Hence, the isotope fractionation of  $-3$  to  $-4$ ‰ at low [HCl] region is possible by the  
186 isotope effect in the  $\text{Tl}^+-\text{Tl}^{3+}$  redox reaction. With the increase of [HCl], Tl(I) is extracted and this would have  
187 depressed  $\delta^{205}\text{Tl}$ . The ion association of Tl with  $\text{Cl}^-$  would have changed  $\ln K_{\text{fs}}$ . It should be noted that the

188 complexation of Tl with DC18C6 also creates the nuclear field shift effect during the extraction. The  $\ln K_{fs}$   
189 values of hydration ( $H_2O$ ) and covalent bonding ( $O^{2-}$ ) are shown in Table 2. Dehydration and complexation with  
190 DC18C6 occur in the Tl extraction. If the coordination property of O donors of DC18C6 is similar to that of  
191 hydrated water, the nuclear field shift effect in the DC18C6 complexation is insignificant due to the small  
192 change in  $\ln K_{fs}$ . Conversely, the covalency of Tl-DC18C6 complex would result in a possible nuclear field shift  
193 effect.

194

#### 195 *Conclusions*

196 Thallium isotopes were fractionated in HCl/DC18C6 solvent extraction system.  $\delta^{205}Tl > 1\text{‰}$  was observed. The  
197 conventional mass-dependent isotope fractionation estimated by the DFT calculation was smaller than the  
198 experimental results. The nuclear field shift effect was estimated by the *ab initio* method including a finite  
199 nuclear model. The magnitude of nuclear field shift effect in the  $Tl^+ - Tl^{3+}$  redox reaction calculated was  $> 1\text{‰}$   
200 and similar to  $\delta^{205}Tl$  experimentally obtained. Therefore, the nuclear field shift effect is most probable origin of  
201 Tl isotope fractionation.

202

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*Table 1.* Logarithm of the reduced partition function,  $\ln(s/s^*)f$ , for isotope pair  $^{203}\text{Tl}$ - $^{205}\text{Tl}$  at 298 K.

		$10^3 \ln(s/s^*)f$
Tl(I)	$\text{Tl}(\text{H}_2\text{O})_6^+$	0.063 (0.07 <sup>a</sup> )
	$\text{TlCl}(\text{H}_2\text{O})_5$	0.078
	$\text{TlCl}_2(\text{H}_2\text{O})_4^-$	0.083
	$\text{TlCl}_4^{3-}$	0.019
Tl(III)	$\text{Tl}(\text{H}_2\text{O})_6^{3+}$	0.423 (0.65 <sup>a</sup> )
	$\text{TlCl}(\text{H}_2\text{O})_5^{2+}$	0.424
	$\text{TlCl}_2(\text{H}_2\text{O})_4^+$	0.444
	$\text{TlCl}_3(\text{H}_2\text{O})_2$	0.400
	$\text{TlCl}_4^-$	0.375

<sup>a</sup> Reference [6].

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Table 2. Nuclear field shift effect,  $\ln K_{fs}$ , for isotope pair  $^{203}\text{Tl}$ - $^{205}\text{Tl}$  at 298 K.

		$10^3 \ln K_{fs}^a$		
		GRASP2K	UTChem	DIRAC04 <sup>b</sup>
Tl(I)	Tl <sup>+</sup>	-0.221	-0.157	-0.22
	TlH <sub>2</sub> O <sup>+</sup>		-0.168	-0.11 <sup>c</sup>
	TlCl		0.004	
	TlO <sup>-</sup>		0.283	
Tl(III)	Tl <sup>3+</sup>	2.568	2.501	2.55
	TlH <sub>2</sub> O <sup>3+</sup>		1.898	1.97 <sup>d</sup>
	TlCl <sup>2+</sup>		-0.677	
	TlO <sup>+</sup>		-0.018	

285 <sup>a</sup> Nuclear field shift effect compared with Tl<sup>0</sup> energy level.

286 <sup>b</sup> Reference [6].

287 <sup>c</sup> Calculated for Tl(H<sub>2</sub>O)<sub>3</sub><sup>+</sup>

288 <sup>d</sup> Calculated for Tl(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>

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291 *Figure captions*

292 Fig. 1 Distribution ratio and extraction scheme of Tl. (a) Distribution ratio of Tl as a function of [HCl]. (b)

293 Simplified schematic of Tl extraction

294 Fig. 2 Isotope fractionation of Tl as a function of [HCl]. Definition of  $\delta^{205}\text{Tl}$  is shown in Eq. 7. The  $\delta^{205}\text{Tl}$  values

295 with  $2\sigma$  analytical errors obtained are,  $-4.14 \pm 0.28\text{‰}$  (2 M HCl),  $-4.27 \pm 0.17\text{‰}$  (3 M HCl),  $0.59 \pm 0.26\text{‰}$  (4 M

296 HCl),  $0.55 \pm 0.20\text{‰}$  (6 M HCl), and  $0.83 \pm 0.28\text{‰}$  (7 M HCl).

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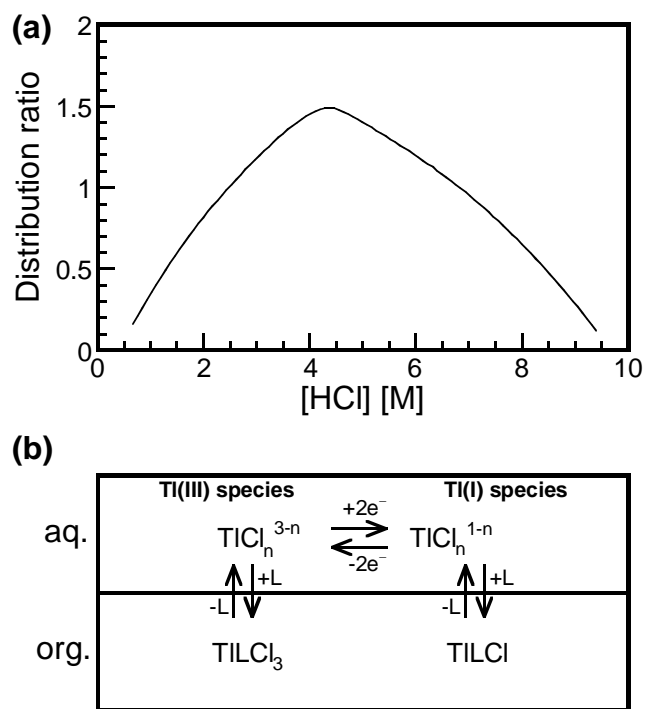
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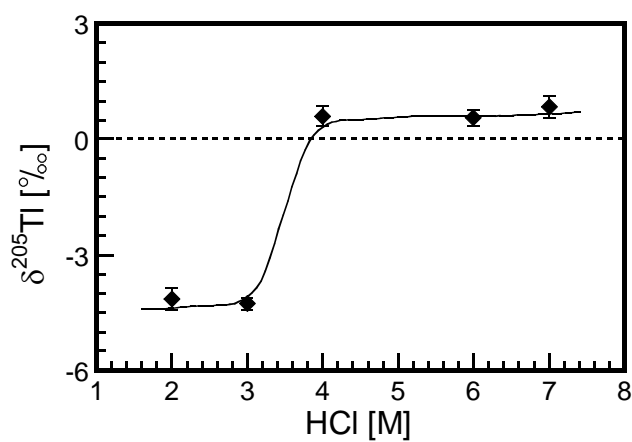
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Figure 1 (Fujii et al.)

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Figure 2 (Fujii et al.)