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Towards an understanding of thallium isotope fractionation during adsorption to manganese oxides

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20 **Abstract** - We have conducted the first study of Tl isotope fractionation during sorption
21 of aqueous Tl(I) onto the manganese oxide hexagonal birnessite. The experiments had
22 different initial Tl concentrations, amounts of birnessite, experimental durations, and
23 temperatures, but all of them exhibit heavy Tl isotope compositions for the sorbed Tl
24 compared with the solution, which is consistent with the direction of isotope fractionation
25 observed between seawater and natural ferromanganese sediments. However, the magnitude
26 of fractionation in all experiments ($\alpha \approx 1.0002$ to 1.0015 , where $\alpha = {}^{205}\text{Tl}/{}^{203}\text{Tl}_{\text{solid}} /$
27 ${}^{205}\text{Tl}/{}^{203}\text{Tl}_{\text{liq}}$) is smaller than observed between seawater and natural sediments ($\alpha \approx 1.0019$ to
28 1.0021 ; Rehkämper et al., 2002, *Earth. Plan. Sci. Lett.* 197, 65-81). The experimental results
29 display a strong correlation between the concentration of Tl in the resulting Tl-sorbed
30 birnessite and the magnitude of fractionation. This correlation is best explained by sorption of
31 Tl to two sites on birnessite, one with large isotope fractionation and one with little or no
32 isotope fractionation. Previous work (Peacock and Moon, 2012, *Geochim. Cosmochim. Acta*
33 84, 297-313) indicates that Tl in natural ferromanganese sediments is oxidized to Tl(III) and
34 adsorbed over Mn vacancy sites in the phylломanganate sheets of birnessite, and we
35 hypothesize that this site is strongly fractionated from Tl in solution due to the change in
36 oxidation state from aqueous Tl(I). In most experiments, which have orders of magnitude
37 more Tl associated with the solid than in nature, these vacancy sites are probably fully
38 saturated, so various amounts of additional Tl are likely sorbed to either edge sites on the
39 birnessite or triclinic birnessite formed through oxidative ripening of the hexagonal starting
40 material, with unknown oxidation state and little or no isotopic fractionation. Thus each
41 experiment displays isotopic fractionation governed by the proportions of Tl in the
42 fractionated and slightly fractionated sites, and those proportions are controlled by how much
43 total Tl is sorbed per unit of birnessite. In the experiments with the lowest initial Tl
44 concentrations in solution (~ 0.15 - 0.4 $\mu\text{g/g}$) and the lowest concentrations of Tl in the resulting

45 Tl-sorbed birnessite ($\leq 17 \mu\text{g Tl/mg birnessite}$), we observed the largest isotopic
46 fractionations, and fractionation is inversely proportional to the initial aqueous Tl
47 concentration. Again, this correlation can be explained by the simultaneous occupation of two
48 different sorption sites; vacancy sites that carry isotopically fractionated Tl and a second site
49 carrying slightly fractionated Tl. The fractionation factors observed in nature exceed those in
50 the experiments likely because the Tl concentrations in seawater and in ferromanganese
51 sediments are three to four orders of magnitude lower than in our experiments, and therefore
52 the second slightly fractionated sorption site is not significantly utilized. Temperature (6°C to
53 40°C) and experimental duration (3 min to 72 hr) appear to have little or no effects on isotope
54 behaviour in this system.

55

56 **1. Introduction**

57 Ferromanganese (Fe-Mn) marine sediments are commonly used in marine geochemistry
58 to study changes in ocean circulation and variations in the marine source and sink fluxes of
59 the respective elements (Frank, 2002). Slow accumulation and enrichment in many metals
60 allow these rocks to record the elemental and isotopic evolution of the seawater from which
61 they precipitate, and such records are of importance to paleoclimate studies. Traditionally, the
62 focus has been on interpreting past distribution of radiogenic Nd, Hf, Os, and Pb isotope
63 compositions in the oceans. With the advent of MC-ICPMS (multiple collector inductively
64 coupled plasma mass spectrometry), a number of researchers have recently analyzed Fe-Mn
65 crusts and nodules to obtain stable isotope records for metals, including Fe, Zn, Mo, Cd and
66 Tl (Barling et al., 2001; Horner et al., 2010; Levasseur et al., 2004; Maréchal et al., 2000;
67 Rehkämper et al., 2004; Schmitt et al., 2009; Siebert et al., 2003).

68 The interpretation of data obtained for such “unconventional” isotope systems is less
69 straightforward, as they may record either variability in the isotope composition of seawater
70 or changes in the conditions that govern incorporation of the elements into the Fe-Mn mineral
71 assemblages. In order to develop paleoceanographic applications of such records, it is
72 therefore important to obtain (i) a detailed characterization of how specific elements are
73 sorbed by Fe-Mn minerals and (ii) a quantitative and mechanistic understanding of any
74 isotopic fractionation that occurs during this process. This study presents the results of
75 experimental work that was carried out to investigate the sorption of the element thallium (Tl)
76 onto marine Fe-Mn deposits. Such studies are of general interest because temporal shifts in
77 the Tl isotope composition of seawater, as recorded by Fe-Mn crusts, may provide new
78 constraints on past changes in environmental conditions and the Earth’s carbon cycle, and
79 their impact on global climate (Baker et al., 2009; Nielsen et al., 2009a; Rehkämper et al.,
80 2004).

81 Here, we conduct the first investigation aimed at understanding the Tl isotope
82 fractionation observed between seawater and Fe-Mn deposits. Thallium in Fe-Mn deposits is
83 strongly associated with the Mn oxide mineral birnessite (Koschinsky and Hein, 2003;
84 Peacock and Moon, 2012). In addition, XANES and EXAFS studies of Tl sorbed onto
85 birnessite (Bidoglio et al., 1993; Peacock and Moon, 2012) have shown that this process most
86 likely occurs in three steps (Peacock and Moon, 2012). Firstly, monovalent Tl is attracted to
87 the mineral surface as a loosely bound outer-sphere complex. This is followed by surface
88 oxidation to Tl(III) and adsorption as an inner-sphere complex at Mn octahedral vacancy sites
89 present in the phylломanganate sheets of the birnessite. Observation of this process is an
90 important result because theoretical calculations have previously predicted that equilibrium
91 between the two naturally occurring oxidation states of Tl (in vacuo) can generate the large
92 isotope fractionation observed between seawater and Fe-Mn crusts (Schauble, 2007). As
93 such, Peacock and Moon (2012) propose a sorption-oxidation-fractionation mechanism to
94 explain the Tl enrichment and isotope fractionation observed in real marine ferromanganese
95 crusts.

96 To explore whether the mechanism proposed for Tl sorption to birnessite is responsible
97 for natural Tl isotope fractionation we have performed several series of experiments in which
98 we sorbed dissolved Tl(I) onto birnessite. We investigate the Tl isotope effects occurring
99 during the sorption process as a function of time and temperature and for different abundances
100 of sorbed Tl. While the results of these experiments do not exactly reproduce the isotope
101 effects observed in nature, we believe that the outcomes present important clues to the
102 processes behind Tl isotope fractionation during sorption onto Fe-Mn deposits. In conjunction
103 with recently published theoretical aspects of Tl stable isotope fractionation (Schauble, 2007)
104 we employ our experimental results to develop a consistent theory outlining the principal
105 mechanism that likely causes Tl isotope fractionation in marine sediments.

106

107 **2. Background**

108 **2.1. Geochemistry of thallium**

109 The geochemistry of Tl has been the subject of a number of older and more recent
110 publications. In the silicate Earth, Tl is a highly incompatible trace element that is
111 concentrated in K-bearing phases (Heinrichs et al., 1980; Shaw, 1952; Wedepohl, 1974),
112 because it occurs primarily in the form of Tl^+ , which is similar in size to the large monovalent
113 cations K^+ , Rb^+ and Cs^+ . However, unlike the alkali metals, Tl also exhibits chalcophile
114 behaviour in the presence of sulphide melts and S-rich (hydrothermal) fluids (Heinrichs et al.,
115 1980; McGoldrick et al., 1979). A few studies furthermore identified significant enrichments
116 of Tl in volcanic plumes, as Tl is significantly more volatile in volcanic systems than the
117 alkali elements (Gauthier and Le Cloarec, 1998; Hinkley et al., 1994; Patterson and Settle,
118 1987).

119 Some aspects of the marine geochemistry of Tl are also similar to K and the heavier
120 alkali elements. In seawater, dissolved Tl is generally thought to be monovalent, occurring in
121 the form of Tl^+ , $TlOH^0$ and $TlCl^0$ species (Byrne, 2002; Nielsen et al., 2009a), and it displays
122 a nearly conservative distribution (Bruland, 1983; Flegal and Patterson, 1985). Thallium also
123 appears to be rapidly cycled through marine organisms in the same manner as K (Flegal et al.,
124 1986).

125 However, there are also important differences between Tl and the alkali metals in the
126 oceanic realm. At about 20,000 yr, the marine residence time of dissolved Tl is significantly
127 shorter than those of K and Rb (Bruland, 1983; Rehkämper and Nielsen, 2004). This
128 difference in behaviour appears to be related to the greater reactivity of Tl toward scavenging
129 by authigenic Fe-Mn oxyhydroxides, as evidenced by (i) the high Tl concentrations of
130 ferromanganese deposits, with up to $\sim 100 \mu\text{g/g}$ Tl (Fig. 1), and pelagic clays (Heinrichs et al.,

131 1980; Matthews and Riley, 1969; Rehkämper et al., 2004) and (ii) the observation that the
132 oceans (and to a lesser extent rivers) have Tl to alkali metal ratios that are lower than the
133 continental crust (Bruland, 1983; Nielsen et al., 2005; Rehkämper and Nielsen, 2004; Rudnick
134 and Gao, 2003). The strong affinity of Tl for Fe-Mn oxyhydroxide minerals appears to reflect
135 oxidation of dissolved seawater Tl(I) to Tl(III) on the active surfaces of the Fe-Mn
136 oxyhydroxides (Bidoglio et al., 1993; Peacock and Moon, 2012; Rehkämper et al., 2004;
137 Rehkämper et al., 2002).

138

139 **2.2. Thallium isotopes**

140 Thallium has two stable isotopes, ^{203}Tl and ^{205}Tl , and a number of studies have explored
141 natural isotope fractionations of Tl over the last 10 years. These investigations revealed stable
142 isotope variations in terrestrial samples spanning $35 \epsilon^{205}\text{Tl}$ units, where

$$143 \quad \epsilon^{205}\text{Tl}_{\text{sample}} = 10^4 \times \left(\frac{^{205}\text{Tl}/^{203}\text{Tl}_{\text{sample}} - ^{205}\text{Tl}/^{203}\text{Tl}_{\text{NIST 997}}}{^{205}\text{Tl}/^{203}\text{Tl}_{\text{NIST 997}}} \right) \quad (1)$$

144 and NIST 997 is a standard reference material defined as $\epsilon^{205}\text{Tl} = 0$ (Nielsen et al., 2006b;
145 Rehkämper et al., 2004; Rehkämper et al., 2002). This is a surprising result, as it shows that
146 Tl displays a similar magnitude of stable isotope variability as significantly lighter elements,
147 such as Fe, Zn, and Cd, despite a much smaller relative mass difference of less than 1%. The
148 Tl isotope variability is particularly pronounced in the marine environment. The Tl isotope
149 composition of open-ocean seawater, as determined from analyses of 8 samples from the
150 Atlantic, Pacific and Arctic Oceans, is $\epsilon^{205}\text{Tl} = -5.7 \pm 0.4$ (Nielsen et al., 2004; Nielsen et al.,
151 2006b; Rehkämper et al., 2002). This isotope composition is somewhat lighter than the
152 average composition of the Earth's continental crust and mantle, which are both characterized
153 by $\epsilon^{205}\text{Tl} = -2.0 \pm 0.5$ (Nielsen et al., 2007; Nielsen et al., 2006a; Nielsen et al., 2005). In
154 contrast, Tl-rich basalts from weathered upper ocean crust and Fe-Mn crusts are known to

155 have $\epsilon^{205}\text{Tl}$ values as low or as high as about -20 and +15, respectively (Nielsen et al., 2006b;
156 Rehkämper et al., 2002).

157 Of particular interest are the systematic Tl isotope relationships that were determined for
158 various marine Fe-Mn deposits (Fig. 1). Hydrogenetic Fe-Mn crusts are thought to precipitate
159 directly from seawater, and Tl data are available for the recent growth surfaces of 17 samples
160 from all major ocean basins. These analyses revealed Tl isotope compositions that do not
161 correlate with radiogenic isotope data and display only a narrow range of $\epsilon^{205}\text{Tl}$ values
162 (between of +10 and +14) with a mean result of $\epsilon^{205}\text{Tl} = 12.8 \pm 1.2$ (1sd, n = 17) (Rehkämper
163 et al., 2002). The Fe-Mn crusts thus have Tl isotope compositions that are offset from
164 seawater by a near-constant fractionation factor of $\alpha = 1.0019$
165 ($\alpha = \frac{^{205}\text{Tl}/^{203}\text{Tl}_{\text{FeMn}}}{^{205}\text{Tl}/^{203}\text{Tl}_{\text{sw}}}$). This offset is thought to reflect equilibrium isotope
166 fractionation of Tl during sorption and/or subsequent oxidation of Tl(I) to Tl(III) on the
167 surfaces of Fe-Mn oxyhydroxide particles (Peacock and Moon, 2012; Rehkämper et al., 2004;
168 Rehkämper et al., 2002). However, an alternative explanation whereby the isotopic difference
169 reflects fractionation of Tl between dissolved seawater Tl^+ and Tl^{3+} cannot be ruled out based
170 on the currently available data (Rehkämper et al., 2004; Rehkämper et al., 2002). Regardless
171 of the exact origin, the observed extent of Tl isotope fractionation has recently been shown in
172 a theoretical study (Schauble, 2007) to be in accord with the large equilibrium isotope
173 fractionation that is expected to occur between Tl(I) and Tl(III) due to contributions from both
174 mass dependent and mass independent (nuclear volume or nuclear field shift) isotope effects.

175 Diagenetic Fe-Mn nodules (which include primarily samples of mixed
176 diagenetic/hydrogenetic origin) and hydrothermal Fe-Mn deposits from diffuse fluid flows in
177 the distal parts of hydrothermal systems display significantly more variability in Tl isotope
178 compositions, with $\epsilon^{205}\text{Tl}$ values that range from values of about -6 to +9 (Fig. 1). The origin
179 of this variability is currently unclear and has been ascribed to differences in fluid

180 compositions (seawater vs. diagenetic pore fluids or diffuse hydrothermal flows) or sorption
181 conditions (closed vs. open system Rayleigh fractionation, variable temperatures of
182 hydrothermal fluids) (Rehkämper et al., 2004; Rehkämper et al., 2002). Alternatively, they
183 may also be due to differences in the mineralogy of the manganese oxide phases to which Tl
184 is bound in Fe-Mn sediments (Koschinsky and Hein, 2003; Peacock and Moon, 2012). Whilst
185 the Mn mineralogy of hydrogenetic Fe-Mn crusts is almost completely dominated by
186 hexagonal birnessite, both birnessite and todorokite are present in diagenetic Fe-Mn nodules
187 and hydrothermal deposits (Burns and Burns, 1977).

188 Also of considerable interest are the Tl isotope time-series data that were recently
189 obtained for a number of Fe-Mn crusts (Nielsen et al., 2011; Nielsen et al., 2009a; Rehkämper
190 et al., 2004) and which extend back to the late Cretaceous (Fig. 2). These records are
191 relatively constant for the last 40 Myr but display a dramatic shift in $\epsilon^{205}\text{Tl}$ from values of
192 about +6 at 55 Myr to about +12 at 45 Myr. Both Rehkämper et al. (2004) and Nielsen et al.
193 (2009a) argue that the observed trends are (i) not due to diagenetic alteration and (ii) unrelated
194 to changes in the mineralogy or major element composition of the samples. The trends were
195 therefore interpreted as primary features that record a change in either (i) the isotope
196 fractionation factor of Tl between the Fe-Mn crusts and seawater ($\alpha_{\text{FeMn-sw}}$) or (ii) the Tl
197 isotope composition of the oceans. It is notable that the Cenozoic Tl isotope record is similar
198 in structure to both the benthic foraminiferal $\delta^{18}\text{O}$ curve (Zachos et al., 2001) and the
199 Cenozoic seawater S isotope record determined from marine barites (Paytan et al., 1998),
200 which may suggest causal links between the processes driving the respective isotopic
201 variations (Fig. 2). The $\delta^{18}\text{O}$ curve of benthic foraminifera in the Paleocene and Early Eocene
202 mainly records changes in water temperature between ~ 6 and 12°C (Zachos et al., 2001)
203 whereas the increase in marine S isotopes during the Early Eocene most likely reflects

204 increased pyrite burial rates (Kurtz et al., 2003) and thus a perturbation of the global carbon
205 cycle.

206 Whatever the link with Tl isotopes, it is evident that it is important to obtain an improved
207 understanding of the Tl isotope records preserved in Fe-Mn sediments, as these appear to be
208 linked to significant changes in marine conditions and the Earth's carbon cycle, which may
209 both have an important impact on global climate.

210

211 **3. Experimental methods**

212 **3.1. Batch Tl sorption experiments**

213 Three groups of batch experiments are described in this paper: (1) a time series, with
214 identical concentrations of synthetic birnessite and aqueous thallium and durations ranging
215 from 3 min to 72 hr; (2) a set of experiments at three different temperatures with varied
216 concentrations of birnessite and aqueous Tl; and (3) a set with much lower concentrations of
217 aqueous Tl than the others. For all experiments, hexagonal K-birnessite was synthesized
218 following the methods of Barling and Anbar (2004) by mixing 24 mL of 2 M HCl (distilled)
219 with 0.6 g KMnO_4 and allowing this mixture to react and precipitate while constantly
220 agitated. After 48 hours, the mixture was diluted to ~500 mL with 18.2 M Ω -cm water and
221 then raised to circumneutral pH by addition of NaOH pellets. This suspension was poured
222 through a polyethersulfone filter membrane with 0.45 μm pores. The birnessite was rinsed
223 with 500 mL of 18.2 M Ω -cm water four times, resuspended from the filter with more water,
224 and then suspended in 500 mL of 18.2 M Ω -cm water. A few microliters of 1 M NaOH were
225 added, and a mixture of nitrogen plus 382 ppm CO_2 was sparged through the suspension for a
226 few hours until pH stabilized at ~7. The material was kept wet at all times to avoid
227 recrystallization, and, although the crystals remain stable for long periods, a separate batch
228 was freshly made for each of the three sets of experiments in order to avoid any potential

229 problems from mineralogical transformation over time. An aliquot of the birnessite stock was
230 dried down, dissolved, and analyzed by ICP-MS; from this analysis we know that our
231 birnessite stock contained approximately 0.8 mg of birnessite per gram of stock suspension.
232 Previous batches of birnessite made in the same way were analyzed by X-ray diffraction (J.
233 Post, Smithsonian Institution) and determined to be poorly crystalline hexagonal K-birnessite
234 (Wasylenki et al., 2008).

235 A thallium stock solution with 49.6 $\mu\text{g/g}$ Tl was prepared by dissolving reagent grade
236 TlCl in 18.2 $\text{M}\Omega\text{-cm}$ water with 0.2 M KNO_3 as background electrolyte. This solution was
237 also sparged with nitrogen + 382 ppm CO_2 , and the pH was adjusted to ~ 7 with NaOH. A
238 second Tl stock solution was prepared at 27.0 $\mu\text{g/g}$ Tl for the low Tl concentration
239 experiments.

240 The first set of experiments was performed in order to investigate how quickly Tl
241 isotopic equilibrium was reached. Here, each of six 50 mL polypropylene centrifuge tubes
242 was filled with 25 g of 49.6 $\mu\text{g/g}$ Tl stock solution, 2 g of birnessite suspension, and 18 g of
243 18.2 $\text{M}\Omega\text{-cm}$ water (Table 1). Ionic strength was therefore 0.11 M in each tube and $[\text{Tl}] \approx 28$
244 $\mu\text{g/g}$ (Table 1). All tubes were shaken in a temperature-controlled shaker (Eppendorf
245 Thermomixer R) at 22°C. After shaking for the designated duration, each mixture was filtered
246 through a polyethersulfone membrane with 0.2 μm pores, and both fluid and solid portions
247 were collected for concentration and isotope analysis. A few drops of fluid always stuck to the
248 bottom of the filter assembly, so approximately 0.5-1 g of fluid was lost from each
249 experiment. Hence, to compute the proportion of Tl that sorbed in each experiment, we
250 divided the amount of Tl recovered in the solid portion by the total amount put in the
251 experiment (see section 5.1 for further discussion of sample recovery and mass balance). The
252 loss of fluid has no consequence for the isotope systematics, since all fluids and solids were
253 measured directly for Tl isotope composition.

254 The second set of experiments was designed to investigate how Tl isotope
255 fractionation varies as function of temperature and fraction of Tl sorbed. A range of
256 temperatures that encompasses most of those encountered in the marine environment was
257 chosen. At each temperature (6°, 25°, 40°C), the proportions of Tl and birnessite were varied.
258 In each experiment, an aliquot of 49.6 µg/g Tl stock solution (3 to 10 mL) was mixed with an
259 aliquot of birnessite stock (250 to 2000 µL) plus 18.2 MΩ-cm water in a polypropylene
260 centrifuge tube. These mixtures resulted in [Tl] ≈ 25 µg/g (Table 1). Ionic strength was 0.10
261 M in each experiment, and pH was again ~7. The mixtures were shaken at either 6°, 25°, or
262 40°C. Experiments conducted at 6° C and 25° C ran for 50 and 48 hours, respectively,
263 whereas the 40°C experiments were terminated after just two hours to avoid recrystallization
264 of birnessite to other Mn oxide minerals during the experiment. Experiments that were
265 conducted at 50°C are not included in this paper, as they showed clear signs of change in
266 grain size and aggregation behaviour after 48 hr, presumably because recrystallization of
267 birnessite to another manganese phase had begun.

268 A small, weighed aliquot of each recovered fluid was used for the measurement of Tl
269 concentrations by ICP-MS. Recovered birnessite particles with sorbed Tl were dissolved with
270 warm ~3 M HCl, and a small aliquot of each sample was used for Tl abundance
271 determination. The amounts of Tl in the portions of each experiment and the percentages of Tl
272 sorbed are listed in Table 2. Rigorous propagation of uncertainties is difficult, since the
273 greatest source of error is likely the sample handling, rather than the analytical measurements.
274 Error bars in plots have been propagated from an estimated 5% relative uncertainty on each Tl
275 amount (Prytulak et al., 2013). Further aliquots of each fluid and digested birnessite sample
276 were taken for isotopic analyses, which were performed according to methods described
277 below.

278 The third set of experiments was performed with much lower initial Tl concentrations as
279 it was suspected that the amounts of Tl added to the experiments were partially controlling the
280 observed isotope fractionation factors. Here, about 0.25 g of a 27.0 µg/g Tl stock solution and
281 ~0.5 g of birnessite stock (corresponding to about 0.4 mg of birnessite) were mixed with
282 variable amounts (~15 to 45 g) of a 0.1 M KNO₃ solution (Table 3). These mixtures resulted
283 in starting Tl concentrations between ~0.1 and 0.4 µg/g, two orders lower than in the previous
284 experiments, which ranged from 25 to 28 µg/g Tl. Temperature was 22°C, ionic strength was
285 0.1 M, pH was ~7, and experimental duration was 44 hours. Samples were prepared for Tl
286 isotope analysis using similar methods to those applied in the other experiments.

287

288 **3.2. Thallium separation and isotope composition analysis**

289 Before chemical separation of Tl, all samples were evaporated to dryness and re-
290 dissolved in 1 M HCl. Subsequently, 18 MΩ-cm water saturated with ~1% (vol/vol) Br₂ was
291 added in order to oxidize Tl to the trivalent state required for the column chemistry procedure
292 (Rehkämper and Halliday, 1999). Chemical separation of Tl from the sample matrix (mainly
293 Mn and K) was performed with the anion exchange resin AG1-X8 in 100 µL resin bed
294 columns using previously described techniques (Nielsen et al., 2004; Nielsen et al., 2005;
295 Rehkämper and Halliday, 1999).

296 Isotope compositions for time and temperature series were measured on Nu Plasma MC-
297 ICPMS instruments in the MAGIC labs at Imperial College London and Oxford University,
298 respectively, while low-Tl experiments were measured on a Thermo Finnigan Neptune MC-
299 ICPMS at Woods Hole. These analyses applied previously established techniques, whereby
300 the ²⁰⁸Pb/²⁰⁶Pb isotope ratio of an admixed solution of NIST SRM 981 Pb is used to correct
301 for the instrumental mass bias of the measured ²⁰⁵Tl/²⁰³Tl ratio, using the exponential law in
302 combination with standard sample bracketing (Baker et al., 2009; Nielsen et al., 2004;

303 Rehkämper et al., 2002). The corrected $^{205}\text{Tl}/^{203}\text{Tl}$ ratios of the samples are reported here
304 relative to the NIST SRM 997 Tl standard following equation (1)

305 Based on replicate measurements of standard solutions and some of the samples, all
306 analyses are assigned an uncertainty of $\pm 0.3 \epsilon^{205}\text{Tl}$. The precision of the results was
307 furthermore ascertained by repeated analyses of the secondary Aldrich Tl reference material
308 (Nielsen and Rehkämper, 2011; Rehkämper et al., 2002) and solutions of NIST SRM 997 Tl
309 that were processed through the column chemistry. All these tests were consistent with the
310 assigned error of $\pm 0.3 \epsilon^{205}\text{Tl}$. With the most recent generation of MC-ICPMS instruments,
311 precise and accurate Tl isotope data can be generated even for $<1\text{ng}$ of Tl (Nielsen et al.,
312 2007; Nielsen et al., 2006b; Nielsen et al., 2009b) and given that all experimental run products
313 contained $>2\text{ng}$ of Tl, none of the analyses were compromised by low Tl ion beam intensities.
314 The fractionation factors between two samples A and B are expressed in terms of α , where

315
$$\alpha_{A-B} = (^{205}\text{Tl}/^{203}\text{Tl}_A) / (^{205}\text{Tl}/^{203}\text{Tl}_B) \approx (\epsilon^{205}\text{Tl}_A + 10000) / (\epsilon^{205}\text{Tl}_B + 10000). \quad (2)$$

316 The uncertainty on α is the square root of the sum of the uncertainties squared of the two
317 isotopic measurements, which is about ± 0.00004 .

318

319 **4. Results**

320 Results from our experiments are tabulated in Tables 1, 2, and 3 and shown graphically
321 in Figs. 3-6. In all experiments, the isotopic composition of sorbed Tl is heavier than that of
322 aqueous Tl remaining in the fluid. The six time series experiments had nearly identical
323 concentrations of birnessite and Tl (see Table 1), and the resulting proportions of Tl sorbed
324 and dissolved are nearly the same regardless of experimental duration (Table 2). Isotopic
325 fractionation between sorbed and dissolved Tl in these experiments
326 ($\alpha = ^{205}\text{Tl}/^{203}\text{Tl}_{\text{sorbed}} / ^{205}\text{Tl}/^{203}\text{Tl}_{\text{dissolved}}$) is almost constant within analytical uncertainties,
327 although the values show a very slight increase over time from 1.00021 at 3 min to 1.00031

328 after 72 hr (Fig. 3). We note that these fractionations are much smaller than those observed
329 between seawater and natural ferromanganese sediments, and possible reasons for this
330 discrepancy are discussed below.

331 The temperature dependent experiments all had nearly the same initial aqueous [Tl], but
332 varied amounts of birnessite. This led to a wide range in the fraction of sorbed Tl (Fig. 4a)
333 and in the amount of Tl sorbed per milligram of birnessite (Fig. 4b). The isotope fractionation
334 factors in these experiments ranged from $\alpha_{\text{sorbed-dissolved}} \approx 1.0004$ to 1.0007 and are highly
335 correlated with the fraction of Tl sorbed and the amount of Tl sorbed per milligram birnessite.
336 The largest fractionations were recorded for the highest fractions of sorbed Tl, and since these
337 experiments contained more birnessite, the concentrations of Tl in the final solids were lower.

338 Experiments performed with low initial Tl concentrations ($\leq 0.4 \mu\text{g/g}$, rather than ~ 25
339 $\mu\text{g/g}$) exhibit the largest isotope fractionation factors between $\alpha \approx 1.00098$ and 1.00145
340 (Table 3) and are thus closest to agreeing with the fractionation observed between seawater
341 and natural hydrogenetic Fe-Mn crusts ($\alpha \approx 1.0019$ to 1.0022; Rehkämper et al., 2002). The
342 four experiments were performed with nearly identical amounts of birnessite and Tl, but the
343 volume of 0.1 M KNO_3 used to dilute the Tl stock solution varied (Table 1), which means that
344 the starting Tl concentration was the only physical parameter that varied in this set of
345 experiments. The Tl isotope fractionation factor correlates inversely with starting aqueous
346 [Tl], i.e. linearly with $1/[\text{Tl}]$ (Fig. 6), with the largest fractionation observed for the
347 experiment with the lowest initial aqueous [Tl].

348

349 **5. Discussion**

350 **5.1. Assessment of Tl recovery from experiments**

351 Using the measured isotopic compositions and concentrations of our Tl stock solutions
352 (Table 1), we have compared the total amount of Tl put into each experiment to the sum of the

353 amount recovered in the fluid and the solid portions, in order to assess how well Tl was
354 recovered. Note that because we measured the isotopic composition of Tl in every fluid and
355 solid, some loss of Tl from either pool is of no consequence for determining the isotopic
356 fractionation expressed in each experiment, as long as the reasonable assumption is made that
357 the fractions of fluid and solid lost were isotopically identical to those recovered. However,
358 failure to recover all of the Tl in the experiment does introduce some error into our
359 determination of the fraction of Tl sorbed or the amount of Tl sorbed per mg of birnessite, and
360 the error in this case is difficult to quantify rigorously. Therefore, we employ an isotopic mass
361 balance calculation to determine the fraction sorbed in each experiment.

$$362 \quad \epsilon^{205}\text{Tl}_{\text{stock}} = \epsilon^{205}\text{Tl}_{\text{dissolved}} * f_{\text{dissolved}} + \epsilon^{205}\text{Tl}_{\text{sorbed}} * f_{\text{sorbed}} \quad (3)$$

363 Here, $\epsilon^{205}\text{Tl}_{\text{stock}}$, $\epsilon^{205}\text{Tl}_{\text{dissolved}}$ and $\epsilon^{205}\text{Tl}_{\text{sorbed}}$ are the isotope compositions of the stock
364 solution, fluid phase and solid phase Tl, respectively, whilst $f_{\text{dissolved}}$ and f_{sorbed} denote the mass
365 fractions of Tl in the fluid and solid phases and these values add up to 1. Since we know the
366 isotopic compositions of all three components in equation 3 we can determine the fraction
367 sorbed by substituting $f_{\text{dissolved}}$ for $1 - f_{\text{sorbed}}$. The amount of Tl sorbed per mg of birnessite
368 reported in Table 3 is calculated with this method and we use these values throughout all
369 figures.

370

371 **5.2. Thallium sorption sites**

372 Thallium sorbed to hexagonal birnessite has previously been shown to be oxidized to
373 Tl(III), with Tl sorbed as an inner-sphere complex over Mn vacancies in the phylломanganate
374 sheets, and this difference in Tl oxidation state between solution and solid could well drive
375 isotopic fractionation (Peacock and Moon, 2012). In similar sorption experiments to those
376 here, it has been shown that Ni also sorbs to birnessite as an inner-sphere complex over Mn
377 vacancies (Manceau et al., 2007; Peacock and Sherman, 2007) and it has been estimated that

378 crystalline birnessite can accommodate ~1.4 wt% Ni via this sorption mechanism (Peacock,
379 2009). This corresponds to 0.24 mmol Ni/g birnessite. If the molar capacity for Tl at this site
380 were the same, then the maximum concentration of Tl in Tl-sorbed birnessite would be
381 approximately 5 wt% (or ~53 μg Tl sorbed per g birnessite). Our experiments were performed
382 using poorly crystalline birnessite, which has a larger surface area and therefore might have a
383 higher sorption capacity than that estimated based on the Ni experiments described above.
384 Additional uncertainty should also be considered given that Tl and Ni also sorb via somewhat
385 different processes (only Tl is oxidized during the sorption process). However, we estimate
386 that vacancy sites are unlikely to accommodate more than 5-15 wt% Tl. All of our
387 experimental products have more than 14 wt% Tl associated with the solid (up to 32 wt%),
388 which leads us to hypothesize that some Tl in our experiments is sorbed over vacancy sites,
389 but additional Tl is sorbed in a different manner. The overall isotope fractionation we observe
390 in our experiments would then be a combination of strongly fractionated, inner-sphere-over-
391 vacancy Tl and another pool of Tl with unknown oxidation state that is unfractionated or only
392 slightly fractionated from solution (hereafter designated as 'slightly fractionated').

393 If the amount of sorbed Tl in our experiments exceeds the sorption capacity of sites over
394 Mn vacancies, what could the other sorbed species be? A comprehensive answer to that
395 question is beyond the scope of this study, but Tl(I) may be able to sorb loosely, as an outer-
396 sphere complex, and/or strongly, as an inner-sphere complex onto MnOH sites located at the
397 edges of the phylломanganate sheets (hereafter referred to as 'edge sites'). Neither of these
398 sorption mechanisms is expected to result in oxidation of Tl(I) to Tl(III) (Peacock and Moon,
399 2012), and thus little or no fractionation of isotopes is expected to occur between this pool of
400 sorbed Tl and Tl remaining dissolved in solution. The latter mechanism of inner-sphere
401 sorption to edge sites has been observed previously for Ni on vernadite at high Ni surface
402 loading, when the vacancy sites are saturated (Manceau et al., 2007).

403 Even though Tl and Ni both sorb to birnessite as inner-sphere complexes at Mn vacancy
404 sites, only Tl sorption involves oxidation of the sorbing species and coupled reductive
405 dissolution of the birnessite phase (Peacock and Moon, 2012). This difference in oxidation
406 between Tl and Ni is important because it has been shown that oxidation of redox-active
407 metals at hexagonal birnessite surfaces (our starting material) can induce a rapid structural
408 ripening and conversion to triclinic birnessite and potentially todorokite (Bargar et al., 2005;
409 Learman et al., 2011; Webb et al., 2005), which leads to a dramatic decline in the oxidative
410 capacity of the Mn oxide (Learman et al., 2011). Triclinic birnessite and todorokite still have
411 the potential to sorb significant amounts of Tl, but do not cause any Tl oxidation (Peacock and
412 Moon, 2012) and hence are unlikely to be associated with Tl isotope fractionation. Thus our
413 slightly fractionated Tl could be at least partially located at sorption sites of triclinic birnessite
414 or todorokite that continuously form while the hexagonal birnesiste vacancy sites become
415 occupied.

416 We also considered the possibility that birnessite may continue to oxidize additional Tl(I)
417 to Tl(III), even if all above-vacancy sites are saturated, and that the excess oxidized Tl could
418 precipitate as Tl_2O_3 . However, experimental evidence to date shows that phylломanganates
419 (triclinic birnessite) and tectomanagnates (todorokite), both devoid of vacancy sites, are
420 unable to oxidise Tl, and thus oxidative sorption of Tl is associated with vacancy site sorption
421 only (Peacock and Moon, 2012). We also conducted a scaled-up version of one of our 25 °C
422 experiments (Tl-25-01, with 63% of Tl sorbed and a final solid with 17 wt% Tl) to produce
423 enough solid for X-ray diffraction analysis, but the resulting diffraction pattern (not shown)
424 had only broad peaks consistent with poorly crystalline birnessite, with none of the peaks
425 expected for Tl_2O_3 .

426 Based on the above discussion, we conclude that Tl in our experiments is sorbed to at
427 least two different sites, one of which is as an inner-sphere complex over vacancies in

428 hexagonal birnessite. The remaining Tl could either be sorbed as outer-sphere complexes, as
429 inner-sphere complexes to edge sites and/or associated with triclinic birnessite or todorokite
430 that continuously form due to electron transfer processes occurring as part of the Tl oxidative
431 sorption at vacancy sites.

432

433 **5.3. Time and temperature dependent experiments**

434 The first-order observation for all experiments is a heavier isotopic composition of Tl
435 sorbed onto birnessite relative to that left in solution. This sense of fractionation is consistent
436 with Tl isotope data for natural marine ferromanganese crusts (Fig. 1), which all exhibit heavy
437 isotope compositions compared to the seawater from which they precipitated (Rehkämper et
438 al., 2004; Rehkämper et al., 2002). Because the sorbed Tl is heavier, we infer right away that
439 the fractionation cannot be simply a kinetic effect, whereby lighter Tl sorbs more rapidly.
440 Rather, the fractionation we see in experiments and nature involves at least one equilibrium
441 step, possibly a Rayleigh process, or a combination of kinetic and equilibrium effects.

442 In our time series experiments (Fig. 3), the data indicate a slight increase in the
443 magnitude of fractionation over the first 24 hours. This suggests that a small kinetic isotope
444 effect may overprint an equilibrium fractionation in our shortest duration experiments, but
445 such a small, short-lived effect is very unlikely to have any importance in fractionations
446 recorded in marine ferromanganese sediments and is not discussed further.

447 The fractionation factors we observe in the time series experiments ($\alpha_{\text{sorbed-dissolved}} =$
448 1.00021 to 1.00031) are all much lower than those observed between natural samples and
449 seawater (Fig. 1), where $\alpha_{\text{FeMn-seawater}} \approx 1.0020$ for hydrogenetic Fe-Mn crusts and $\alpha_{\text{FeMn-seawater}}$
450 ≈ 1.0006 to 1.0015 for diagenetic Fe-Mn deposits (Rehkämper et al., 2004; Rehkämper et al.,
451 2002). Our time series fractionation factors are also smaller than theoretical predictions of

452 equilibrium fractionation between Tl(I) and Tl(III) in vacuo ($\alpha \approx 1.0025$ - 1.0027 at 22°C)
453 (Schauble, 2007).

454 The most likely explanation for the discrepancy between our experimental results and
455 those from nature and theory is that the solids in our experiments contain several orders of
456 magnitude more Tl than in nature (1 – 30 wt% vs. 0.001-0.01 wt% (Hein et al., 2000;
457 Rehkämper et al., 2002)) and hence other sorption sites appear to be utilized (see section 5.2.)

458 Other potential explanations could be that the experiments were conducted at different
459 pH and ionic strength than the conditions of Fe-Mn crust precipitation. Since pH strongly
460 affects the sorption capacity of solids, it is also possible that isotope fractionation is affected
461 by variable pH. We did not vary the pH of our experiments (all were conducted at pH ~ 7) and
462 it is therefore not possible with our present data set to evaluate if pH has a strong effect on Tl
463 isotope fractionation during sorption to birnessite. Our experiments contain 0.1 M KNO_3 , but
464 seawater contains ~ 0.5 M NaCl . Thallium is therefore initially present as Tl^+ in our
465 experiments, but may exist as a combination of Tl^+ , $\text{TlOH}^0_{(\text{aq})}$ and $\text{TlCl}^0_{(\text{aq})}$ in seawater
466 (Byrne, 2002; Nielsen et al., 2009a). Whether the difference in coordination chemistry for Tl
467 as a function of ionic strength and $[\text{Cl}^-]$ could influence fractionation during sorption of Tl (or
468 any other metal) to such a large extent is so far unknown and should be a focus of future
469 studies.

470 There are two conclusions to draw from the second series of experiments, conducted at
471 three different temperatures, with the same initial aqueous $[\text{Tl}]$, but varying amounts of
472 birnessite (Table 1). A clear correlation between fraction of Tl sorbed and isotope
473 fractionation factor is evident in Table 2 and Fig. 4a, but, importantly, temperature seems to
474 have little effect on isotope behaviour. At any given fraction of Tl sorbed, the difference in
475 isotope fractionation between 6° and 40°C is less than 0.0002 in terms of $\alpha_{\text{sorbed-dissolved}}$, with
476 a slight suggestion that a higher magnitude of fractionation occurs at lower temperature, as

477 expected. The magnitude of change in isotope fractionation as a function of temperature is
478 similar to predictions by Schauble (2007), who calculated that $\alpha_{\text{Tl(III)-(I)}}$ should change by
479 ~ 0.0003 between 6° and 40° C.

480 Another observation from Fig. 4a is that the overall fractionation expressed in our
481 experiments is correlated with the fraction of Tl in the experiment that is sorbed to birnessite.
482 This trend could be interpreted to reflect a Rayleigh distillation process, whereby Tl is
483 irreversibly sorbed to birnessite and the fluid continues to evolve to lighter compositions as
484 sorption proceeds. But this conclusion is inconsistent with the much lower fractionation
485 factors recorded for the time dependent experiments at the same fraction of Tl sorbed (Fig.
486 4a). Fig. 4b shows the same experiments with a different choice of independent variable (the
487 number of μg of Tl sorbed per mg of birnessite), and the result is a single trend for the time
488 series and temperature experiments. We did not measure the surface area of birnessite in our
489 experiments, but the mass of birnessite serves as a close proxy. The relationship shown in Fig.
490 4b supports our hypothesis that the fractionations expressed in our experiments reflect
491 different proportions of Tl sorbing in at least two different sites. One of the sites is limited in
492 number, strongly fractionated, and likely represents Tl(III) sorbed over Mn vacancies on
493 $\{001\}$ surfaces (space group $P6_3/mmc$). In contrast, the other sites hold Tl that is only slightly
494 fractionated from dissolved Tl and may comprise Tl sorbed to birnessite edges or triclinic
495 birnessite formed via oxidative ripening (Learman et al., 2011).

496

497 **5.4. Low Tl experiments and sorption site mixing models**

498 To further investigate the relationship between Tl isotope fractionation and the amount of
499 Tl sorbed per unit of birnessite, we conducted the third set of experiments, each with the same
500 amount of birnessite and Tl. These experiments featured varying volumes of fluid (details in
501 Table 1) and initial concentrations of aqueous [Tl] about two orders of magnitude smaller

502 than in the earlier experiments. Results are shown in Table 3 and plotted in Figs. 5 and 6. The
503 concentrations of Tl in the solids (~17 μg Tl per mg birnessite) were the lowest of all the
504 experiments and we observed the highest fractionation factors yet ($\alpha_{\text{sorbed-dissolved}} = 1.0010$ to
505 1.0014), although these values are still smaller than those observed in nature.

506 Figure 5 shows the low-Tl data along with results from the other experiments and the
507 data for natural hydrogenetic ferromanganese crusts from Rehkämper et al. (2002). The shape
508 of the trend formed by all of the data indeed suggests a mixing line between two pools of Tl
509 with different isotopic compositions. We calculated model mixing lines for $\alpha_{\text{sorbed-dissolved}}$ as a
510 function of μg Tl/mg birnessite (x), with three free parameters: the sorption capacity of
511 vacancy sites (sorb-cap), the fractionation factor associated with vacancy sites (vac-frac), and
512 the fractionation factor between dissolved Tl and our hypothesized edge sorption site (edge-
513 frac). For values of μg Tl/mg birnessite smaller than sorb-cap, $\alpha_{\text{sorbed-dissolved}}$ is simply equal to
514 vac-frac because it is assumed that the vacancy sites fill up before any of the edge sites are
515 utilized. For values of μg Tl/mg birnessite greater than sorb-cap, $\alpha_{\text{sorbed-dissolved}}$ is computed as
516 a linear combination of fractionated and slightly fractionated Tl, with all vacancy sites filled
517 up to sorb-cap and the remainder of sorbed Tl on edge sites:

$$518 \quad \alpha_{\text{sorbed-dissolved}} = ((\text{sorb-cap} * \text{vac-frac} + (x - \text{sorb-cap}) * (\text{edge-frac})) / x). \quad (4)$$

519 We present two of our best-fit model curves. Model 1 has a low value for sorb-cap of 5 μg
520 Tl/mg birnessite, vac-frac = 1.0020, and edge-frac = 1.0003. The curve misses some of the
521 temperature dependent data, but fits the rest quite well. Model 2 has a higher sorption capacity
522 of 28 μg Tl/mg birnessite, vac-frac = 1.0023, and edge-frac = 1.0002. This curve fits our
523 high-Tl experiments better, but overestimates the fractionation factors for low-Tl experiments
524 and natural data. This simple model is built on the presumption that the above-vacancy sites
525 are high affinity sites and thus fill first, and all remaining Tl that sorbs does so via edge sites.
526 That we cannot find values for the three parameters that result in a good fit to all data suggests

527 that this presumption is incorrect. Perhaps Tl partitioning onto the two types of sorption sites
528 is simultaneous but the vacancy sites have higher affinity for Tl and thus fill up first. The
529 number of vacancy vs. edge sites, and thus the rate at which the two sorption sites fill, would
530 then depend on the crystallinity of the birnessite, and/or could vary with the amount of sorbed
531 Tl or as a function of aqueous [Tl] (Fig. 6). Such mechanisms are not inconsistent with our
532 high-Tl experiments as, presumably, all vacancy sites are filled and thus these experiments do
533 not inform on the rate at which the two types of sorption sites fill.

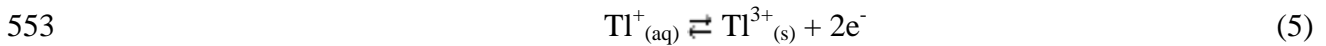
534

535 **5.5. An alternative to sorption site mixing**

536 Figure 6 shows an interesting correlation between the starting concentration of Tl in the
537 low-Tl experiments and the isotope fractionation factor that may shed a bit more light on the
538 factors controlling the observed correlation. These experiments contained essentially the same
539 amount of Tl (6.7 μg) and the same amount of birnessite (0.4 mg), but had different initial
540 aqueous Tl concentrations, since the total volume of the experiments varied. There is a strong
541 linear correlation between the inverse of the initial aqueous [Tl] and fractionation factor (Fig.
542 6). First, we note that the relationship illustrated here serves as more evidence that our data do
543 not reflect a simple equilibrium isotope effect, because the concentration of the solution
544 would not affect the isotope fractionation factor, if a simple equilibrium between just two
545 pools (dissolved and sorbed Tl) was attained. Next, we can use the insight from the EXAFS
546 work of Peacock and Moon (2012) to speculate about an alternative mechanism, other than
547 partitioning of Tl into different sorption sites, that could lead to larger fractionation factors at
548 lower aqueous Tl concentrations.

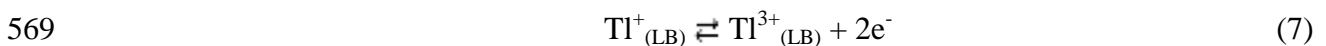
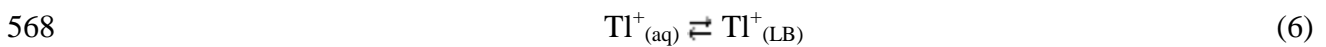
549 We know that birnessite causes surface oxidation of aqueous Tl^+ to Tl^{3+} , which is
550 adsorbed onto the birnessite structure (Peacock and Moon, 2012). In principle, we can

551 therefore construct a simplified isotope exchange reaction that may be predominantly
552 responsible for the Tl isotope fractionation in birnessite:

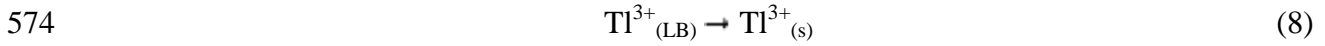


554 In this reaction, an increase in the concentration of Tl in solution will tend to push the
555 equilibrium reaction towards the right, thereby increasing the rate of the forward reaction
556 relative to the reverse process. In this way, higher Tl concentrations in solution could result in
557 longer equilibration times. However, there is no indication in our time series data that the
558 isotope fractionation factor continues to increase for more than ~20 hr (Fig. 3), which would
559 imply that the low-Tl experiments had sufficient time to reach their maximum isotope
560 fractionation as these were conducted at much lower Tl concentrations than the time series
561 (Table 1). Therefore, we cannot explain the variable α in the low-Tl experiments solely by
562 considering reaction (5).

563 We can, however, break down the Tl isotope fractionation process into separate reactions
564 that are together responsible for Tl sorption, oxidation and isotope fractionation. Peacock and
565 Moon (2012) have proposed that Tl oxidation likely takes place while Tl^+ is loosely bound
566 (LB) to birnessite as an outer-sphere complex. Thus we can write the following two reactions
567 to account for the Tl isotope fractionation:



570 The oxidation reaction (7) will be followed by adsorption of the oxidized Tl onto the
571 birnessite structure. On the time scale of the experiments, the latter process is probably
572 essentially unidirectional because the trivalent Tl is very strongly bound to the birnessite
573 surface (Peacock and Moon, 2012):



575 Each of these three reactions (6, 7 and 8) account for a separate part of the total reaction
576 (5) whereby aqueous, monovalent Tl is first attracted to a sorption site and loosely bound as
577 an outer-sphere complex with no isotope fractionation (6), then it is oxidized and isotopically
578 fractionated while still loosely bound (7) and lastly adsorbed as an inner-sphere surface
579 complex at the vacancy sites with no isotope fractionation (8). During our experiments we
580 measured the isotopic difference between $\text{Tl}^+_{(\text{aq})}$ and $\text{Tl}^{3+}_{(\text{s})}$, which means we were not directly
581 measuring the isotope fractionation factor in (7), but the sum of the three reactions (6, 7 and
582 8). This limitation is important because the reaction kinetics of all three reactions will
583 determine how much of the isotope fractionation generated in (7) will be expressed in our
584 measurements. For example, we can consider a situation in (7) at isotopic equilibrium where
585 one half of the Tl is trivalent and the other half monovalent. If $\alpha = 1.002$ then we can
586 determine that $\epsilon^{205}\text{Tl}^{3+} = +10$ and $\epsilon^{205}\text{Tl}^+ = -10$, compared with the starting solution. Any
587 $\text{Tl}^{3+}_{(\text{LB})}$ sorbed onto birnessite at this point would have an apparent $\alpha = 1.001$. But at the same
588 time, reaction (6) will drive $\epsilon^{205}\text{Tl}^+$ back toward the isotope composition of the starting
589 solution and thus the relative rates of oxidation (7) and isotope re-equilibration (6) will
590 determine the isotope composition of the $\text{Tl}^{3+}_{(\text{LB})}$, which is what we measure on the birnessite.

591 Using these reaction principles we can understand why the Tl concentration of the
592 starting solution may have such a profound impact on the observed α , because
593 thermodynamics dictate that increased concentrations on the left hand side of a reaction will
594 enhance the rate of the forward reaction relative to the back reaction. The impact of the back
595 reaction in (6) is thereby controlled by the Tl concentration of the solution, which translates
596 directly to isotope fractionation if isotope equilibration is slower in (6) than in (7). If we
597 furthermore assume that reaction (8) is essentially unidirectional at the timescale of our
598 experiments, it can be shown by simple modelling, that the relationship seen in Fig. 6 may

599 result from a dampening of the expressed isotope fractionation, which is enhanced at higher
600 initial dissolved Tl concentrations.

601 Hence, we have two possible explanations for the correlation between isotope
602 fractionation factor and initial solution concentration observed for the low-Tl experiments:
603 namely, a mixing relationship produced by the simultaneous occupation of both vacancy and
604 edge sites by Tl during sorption, or the latter kinetic model. However, given the complexities
605 of the kinetic model, it is debatable whether this can reasonably account for the systematics
606 seen in Fig. 6. Therefore, we currently favour the explanation in which the Tl isotope
607 composition of all our experiments (low- and high-Tl) can be explained by simultaneous
608 occupation of both vacancy and edge sites by Tl during sorption. This mechanism may
609 potentially also operate in nature, which could cause variations in the effective Tl isotope
610 fractionation during sorption to Fe-Mn oxyhydroxides. However, the correlation in Fig. 6
611 would imply that the full isotope fractionation factor (and hence that only vacancy sites are
612 utilized) should occur at solution concentrations below 0.080 $\mu\text{g/g}$, which is more than three
613 orders of magnitude more concentrated than seawater. Thus, based on our data we would
614 predict essentially no variation in isotope fractionation during sorption of Tl from seawater
615 onto birnessite, which is consistent with the almost constant fractionation factor observed in
616 nature between hydrogenetic Fe-Mn crusts and seawater (Rehkämper et al., 2002). On the
617 other hand, given the mineralogical heterogeneity of manganese oxides in diagenetic and
618 hydrothermal Fe-Mn deposits (Burns and Burns, 1977), it is equally expected that Tl isotope
619 fractionation is highly variable in these types of Fe-Mn sediments (Peacock and Moon, 2012).

620

621 **6. Conclusions and outlook**

622 We have conducted the first study of Tl isotope fractionation during sorption of aqueous
623 Tl(I) onto the manganese oxide birnessite. Experiments conducted at high Tl solution

624 concentrations (~25-28 $\mu\text{g/g}$) display relatively small isotope fractionation factors of $\alpha \approx$
625 1.0002 to 1.0007 and Tl concentrations up to 34 wt% (430 $\mu\text{g Tl/mg birnessite}$). We conclude
626 that both fractionated (adsorbed at vacancy sites) and slightly fractionated (sorbed at edge
627 sites or oxidatively formed triclinic birnessite) Tl is associated with the birnessite in these
628 experiments, and the overall fractionation expressed in each experiment reflects the difference
629 between the isotopic compositions of Tl in solution and a weighted combination of the two
630 pools of sorbed Tl.

631 We observe changes of less than 0.0002 in $\alpha_{\text{sorbed-dissolved}}$ when changing the temperature
632 from 6° to 40°C, which is consistent with predictions made from theoretical calculations of Tl
633 isotope fractionation (Schauble, 2007). As such, the temperature dependence of Tl isotope
634 fractionation in Fe-Mn crusts is likely to be negligible as deep ocean water temperatures in the
635 Cenozoic have not varied by more than 10°C (Zachos et al., 2001).

636 Experiments performed at lower Tl solution concentrations (about 0.15 to 0.46 $\mu\text{g/g}$)
637 display higher fractionation factors ($\alpha \approx 1.0010$ -1.0015), which correlate with the reciprocal
638 of initial dissolved Tl concentrations. We cannot presently determine a unique mechanism to
639 explain this correlation. Most likely, the correlation is caused by simultaneous filling of
640 vacancy sites and an unknown sorption site, whereby more monovalent Tl is partitioned to the
641 slightly fractionated with increasing solution concentration. Alternatively, a Rayleigh type
642 distillation process in which the isotope fractionation factor is dampened at increasing
643 solution concentrations may also explain the observed correlation.

644 Our results are consistent with the recently proposed oxidation-adsorption reaction for
645 sorption of Tl onto birnessite (Peacock and Moon, 2012). By combining isotopic and
646 mineralogical considerations we suggest that Tl isotope fractionation for birnessite vacancy
647 sites occurs in three steps: first, aqueous Tl is sorbed as a loosely bound univalent outer-
648 sphere complex, which is then oxidized to Tl(III) and finally adsorbed onto the birnessite

649 structure. Thallium isotope fractionation only occurs during the oxidation reaction, whereby
650 nuclear field shift effects may produce fractionation factors of several permil (Schauble,
651 2007). However, more work is required in order to obtain a full understanding of the
652 mechanisms that produce the large Tl isotope fractionation in nature between Fe-Mn crusts
653 and seawater. In particular, it will be important to ascertain if our hypothesis that two types of
654 sorption sites were occupied in our experiments is correct. In addition, further experiments are
655 needed to investigate the proposed mineralogical control of Tl isotope fractionation during
656 sorption to Fe-Mn deposits (Peacock and Moon, 2012) as well as to assess whether
657 parameters such as pH and ionic strength could affect the Tl isotope fractionation factors.

658

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666

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791 **Figure Captions**

792 Fig. 1. Plot of $\epsilon^{205}\text{Tl}$ vs. Tl concentration (note logarithmic scale) for various types of
793 marine Fe-Mn deposits (Rehkämper et al., 2002). The dark and light shaded fields denote the
794 Tl isotope compositions of hydrothermal fluids and seawater, which are characterized by
795 $\epsilon^{205}\text{Tl}$ of -5.7 ± 0.4 and about -2.0 ± 0.5 , respectively (Nielsen et al., 2004; Nielsen et al.,
796 2006b; Rehkämper et al., 2002).

797

798 Fig. 2. Plot of the high-resolution $\epsilon^{205}\text{Tl}$ record obtained for two Fe-Mn crusts from the
799 Pacific Ocean for the Cenozoic (Nielsen et al., 2009a). Shown for comparison are (at the top)
800 the seawater S isotope record from marine barites (Kurtz et al., 2003; Paytan et al., 1998) and
801 (at the bottom) the deep-sea oxygen isotope record from analyses of benthic foraminifera
802 (Zachos et al., 2001; Zachos et al., 2008).

803

804 Fig. 3. (a) Thallium isotope compositions of recovered fluids and solids from time series
805 experiments as a function of experimental duration, in terms of epsilon units, measured
806 relative to NIST 997. (b) Thallium isotope fractionation factors between sorbed and dissolved
807 Tl as a function of experiment duration. There is a small discernible increase in isotope
808 fractionation during the first ~24 hr, after which no change is observed.

809

810 Fig. 4. (a) Fractionation factors for temperature and time series experiments, shown as a
811 function of the fraction of Tl associated with the solid phase. Symbols are defined in the
812 legend. (b) Fractionation factors for the same experiments as a function of $\mu\text{g Tl per mg}$
813 birnessite.

814

815 Fig. 5. Thallium isotope fractionation factors between dissolved and solid Tl plotted
816 versus the amount of Tl sorbed per milligram of birnessite. Also shown are hydrogenetic crust
817 data from Rehkämper et al. (2002) and best-fit mixing lines for strongly fractionated and
818 slightly fractionated Tl in two different sorbed sites. See text for details.

819

820 Fig. 6. Thallium isotope fractionation (α) between dissolved and solid Tl plotted versus
821 the inverse of initial aqueous Tl concentration for low-Tl experiments.

822

823 Table 1: Experimental parameters for variable time and temperature adsorption experiments.

Experiment	Temp (°C)	Duration (hr)	Tl stock* (g)	MnO ₂ stock (g)	H ₂ O (g)	[Tl] start sol. (µg/g)
Tl-3min	22	0.05	25.88	1.93	17.52	28.3
Tl-10min	22	0.16	25.19	2.00	18.11	27.6
Tl-6hr	22	6	24.59	2.00	18.35	27.1
Tl-24hr	22	24	25.50	1.97	17.77	28.0
Tl-48hr	22	48	25.41	1.97	18.02	27.8
Tl-72hr	22	72	25.25	1.98	17.87	27.8
Tl-6-04	6	50	4.92	0.51	4.36	24.9
Tl-6-05	6	50	4.94	0.25	4.62	25.0
Tl-6-06	6	50	2.98	1.01	1.98	24.8
Tl-25-01	25	48	10.37	1.99	8.17	25.1
Tl-25-02	25	48	10.27	1.00	9.13	25.0
Tl-25-03	25	48	10.46	0.50	9.61	25.2
Tl-25-04	25	48	10.75	0.25	9.95	25.5
Tl-40-01	40	2	3.06	0.97	2.01	25.1
Tl-40-02	40	2	5.09	0.51	4.53	24.9
Tl-40-03	40	2	5.09	0.25	4.87	24.7
LowTl-2201	22	44	0.247 [†]	0.50	14.37 [§]	0.464
LowTl-2202	22	44	0.251 [†]	0.50	24.46 [§]	0.277
LowTl-2203	22	44	0.250 [†]	0.50	34.52 [§]	0.195
LowTl-2204	22	44	0.248 [†]	0.50	44.57 [§]	0.150

824 * Stock solution had a Tl concentration of 49.6 µg/g, $\epsilon^{205/203}\text{Tl} = -0.3 \pm 0.3$ (2sd), and 0.1 m KNO₃
 825 for all but the four low-Tl experiments.

826 [†]Tl stock solution had 27.0 µg/g and $\epsilon^{205/203}\text{Tl} = -0.6 \pm 0.3$ (2sd), for the four low-[Tl] experiments,
 827 with no KNO₃.

828 [§]A solution of 0.1 m KNO₃ was used instead of H₂O for the four low-Tl experiments.
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 830

831 Table 2. Thallium mass balance and isotopic compositions of varied time and temperature adsorption
 832 experiments.

Experiment	Total Tl (μg)	Tl in solid (μg)	Tl recovery* (%)	$\mu\text{g Tl/mg}$ birnessite	[Tl] end sol. ($\mu\text{g/g}$)	$\epsilon^{205}\text{Tl}_{\text{diss}}$	$\epsilon^{205}\text{Tl}_{\text{sorb}}$	$\alpha_{\text{sorb-diss}}$
Tl-3min	1284	612	88	418.3	11.5	-1.4	0.7	1.00021
Tl-10min	1249	673	90	414.6	10.0	-1.5	0.7	1.00022
Tl-5hr	1220	669	90	404.3	9.7	-1.6	0.8	1.00024
Tl-24hr	1265	674	89	404.7	10.1	-1.8	1.1	1.00029
Tl-48hr	1260	622	87	379.8	10.4	-1.8	1.3	1.00031
Tl-72hr	1252	681	89	397.4	9.7	-1.9	1.2	1.00031
Tl-6-04	244	89	87	266.7	12.7	-2.4	2.2	1.00046
Tl-6-05	245	50	87	328.1	16.6	-1.5	2.9	1.00045
Tl-6-06	148	115	91	155.5	3.2	-6.6	0.6	1.00072
Tl-25-01	514	324	96	206.9	8.2	-4.3	1.7	1.00060
Tl-25-02	509	195	92	260.8	13.5	-2.2	2.3	1.00045
Tl-25-03	519	105	90	344.2	17.7	-1.4	2.6	1.00040
Tl-25-04	533	51	92	453.2	20.9	-0.9	2.7	1.00036
Tl-40-01	152	113	90	163.2	3.8	-5.5	0.5	1.00061
Tl-40-02	252	85	84	279.0	12.6	-2.2	1.9	1.00041
Tl-40-03	252	51	85	301.3	16.0	-1.2	2.4	1.00036

833 *Computed by adding weighted isotopic compositions of recovered fluid and solid and subtracting
 834 from Tl stock solution's isotopic composition. Minor loss of both solid and liquid occurred for
 835 most experiments. See text for details.
 836

837

838 Table 3: Thallium mass balance and isotopic compositions of experiments performed at low Tl
839 abundances.

Experiment	Total Tl (μg)	Tl in solid (μg)	Tl recov.* (%)	$\mu\text{g Tl}/$ mg birnessite	[Tl] end sol. ($\mu\text{g}/\text{g}$)	$\epsilon^{205}\text{Tl}_{\text{diss}}$	$\epsilon^{205}\text{Tl}_{\text{sorb}}$	$\alpha_{\text{sorb-diss}}$
LowTl-2201	6.67	5.32	80	17	0.00034	-10.6	-0.8	1.00098
LowTl-2202	6.78	4.71	70	17	0.00054	-12.4	-1.4	1.00110
LowTl-2203	6.73	6.43	96	17	0.00050	-13.8	-0.9	1.00129
LowTl-2204	6.68	5.25	79	17	0.00086	-15.2	-0.7	1.00145

840 *Computed by adding weighted isotopic compositions of recovered fluid and solid and subtracting
841 from Tl stock solution's isotopic composition. See text for details.

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