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

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Abstract - We have conducted the first study of Tl isotope fractionation during sorption of aqueous Tl(I) onto the manganese oxide hexagonal birnessite. The experiments had different initial Tl concentrations, amounts of birnessite, experimental durations, and temperatures, but all of them exhibit heavy Tl isotope compositions for the sorbed Tl compared with the solution, which is consistent with the direction of isotope fractionation observed between seawater and natural ferromanganese sediments. However, the magnitude of fractionation in all experiments ($\alpha \approx 1.0002$ to 1.0015, where $\alpha = \frac{^{205}\text{Tl}}{^{203}\text{Tl}}_{\text{solid}} / \frac{^{205}\text{Tl}}{^{203}\text{Tl}}_{\text{liq}}$) is smaller than observed between seawater and natural sediments ($\alpha \approx 1.0019$ to 1.0021; Rehkämper et al., 2002, Earth. Plan. Sci. Lett. 197, 65-81). The experimental results display a strong correlation between the concentration of Tl in the resulting Tl-sorbed birnessite and the magnitude of fractionation. This correlation is best explained by sorption of Tl to two sites on birnessite, one with large isotope fractionation and one with little or no isotope fractionation. Previous work (Peacock and Moon, 2012, Geochim. Cosmochim. Acta 84, 297-313) indicates that Tl in natural ferromanganese sediments is oxidized to Tl(III) and adsorbed over Mn vacancy sites in the phyllomanganate sheets of birnessite, and we hypothesize that this site is strongly fractionated from Tl in solution due to the change in oxidation state from aqueous Tl(I). In most experiments, which have orders of magnitude more Tl associated with the solid than in nature, these vacancy sites are probably fully saturated, so various amounts of additional Tl are likely sorbed to either edge sites on the birnessite or triclinic birnessite formed through oxidative ripening of the hexagonal starting material, with unknown oxidation state and little or no isotopic fractionation. Thus each experiment displays isotopic fractionation governed by the proportions of Tl in the fractionated and slightly fractionated sites, and those proportions are controlled by how much total Tl is sorbed per unit of birnessite. In the experiments with the lowest initial Tl concentrations in solution (~0.15-0.4 μg/g) and the lowest concentrations of Tl in the resulting
Tl-sorbed birnessite (≤17 μg Tl/mg birnessite), we observed the largest isotopic fractionations, and fractionation is inversely proportional to the initial aqueous Tl concentration. Again, this correlation can be explained by the simultaneous occupation of two different sorption sites; vacancy sites that carry isotopically fractionated Tl and a second site carrying slightly fractionated Tl. The fractionation factors observed in nature exceed those in the experiments likely because the Tl concentrations in seawater and in ferromanganese sediments are three to four orders of magnitude lower than in our experiments, and therefore the second slightly fractionated sorption site is not significantly utilized. Temperature (6°C to 40°C) and experimental duration (3 min to 72 hr) appear to have little or no effects on isotope behaviour in this system.
1. Introduction

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

The interpretation of data obtained for such “unconventional” isotope systems is less straightforward, as they may record either variability in the isotope composition of seawater or changes in the conditions that govern incorporation of the elements into the Fe-Mn mineral assemblages. In order to develop paleoceanographic applications of such records, it is therefore important to obtain (i) a detailed characterization of how specific elements are sorbed by Fe-Mn minerals and (ii) a quantitative and mechanistic understanding of any isotopic fractionation that occurs during this process. This study presents the results of experimental work that was carried out to investigate the sorption of the element thallium (Tl) onto marine Fe-Mn deposits. Such studies are of general interest because temporal shifts in the Tl isotope composition of seawater, as recorded by Fe-Mn crusts, may provide new constraints on past changes in environmental conditions and the Earth’s carbon cycle, and their impact on global climate [Baker et al., 2009; Nielsen et al., 2009a; Rehkämper et al., 2004].
Here, we conduct the first investigation aimed at understanding the Tl isotope fractionation observed between seawater and Fe-Mn deposits. Thallium in Fe-Mn deposits is strongly associated with the Mn oxide mineral birnessite (Koschinsky and Hein, 2003; Peacock and Moon, 2012). In addition, XANES and EXAFS studies of Tl sorbed onto birnessite (Bidoglio et al., 1993; Peacock and Moon, 2012) have shown that this process most likely occurs in three steps (Peacock and Moon, 2012). Firstly, monovalent Tl is attracted to the mineral surface as a loosely bound outer-sphere complex. This is followed by surface oxidation to Tl(III) and adsorption as an inner-sphere complex at Mn octahedral vacancy sites present in the phyllomanganate sheets of the birnessite. Observation of this process is an important result because theoretical calculations have previously predicted that equilibrium between the two naturally occurring oxidation states of Tl (in vacuo) can generate the large isotope fractionation observed between seawater and Fe-Mn crusts (Schauble, 2007). As such, Peacock and Moon (2012) propose a sorption-oxidation-fractionation mechanism to explain the Tl enrichment and isotope fractionation observed in real marine ferromanganese crusts.

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

2.1. Geochemistry of thallium

The geochemistry of Tl has been the subject of a number of older and more recent publications. In the silicate Earth, Tl is a highly incompatible trace element that is concentrated in K-bearing phases because it occurs primarily in the form of Tl\(^{+}\), which is similar in size to the large monovalent cations K\(^{+}\), Rb\(^{+}\) and Cs\(^{+}\). However, unlike the alkali metals, Tl also exhibits chalcophile behaviour in the presence of sulphide melts and S-rich (hydrothermal) fluids. A few studies furthermore identified significant enrichments of Tl in volcanic plumes, as Tl is significantly more volatile in volcanic systems than the alkali elements. Some aspects of the marine geochemistry of Tl are also similar to K and the heavier alkali elements. In seawater, dissolved Tl is generally thought to be monovalent, occurring in the form of Tl\(^{+}\), TlOH\(^{0}\) and TlCl\(^{0}\) species, and it displays a nearly conservative distribution. Thallium also appears to be rapidly cycled through marine organisms in the same manner as K. However, there are also important differences between Tl and the alkali metals in the oceanic realm. At about 20,000 yr, the marine residence time of dissolved Tl is significantly shorter than those of K and Rb. This difference in behaviour appears to be related to the greater reactivity of Tl toward scavenging by authigenic Fe-Mn oxyhydroxides, as evidenced by (i) the high Tl concentrations of ferromanganese deposits, with up to ~100 \(\mu g/g\) Tl (Fig. 1), and pelagic clays.
1980; Matthews and Riley, 1969; Rehkämper et al., 2004) and (ii) the observation that the oceans (and to a lesser extent rivers) have Tl to alkali metal ratios that are lower than the continental crust (Bruland, 1983; Nielsen et al., 2005; Rehkämper and Nielsen, 2004; Rudnick and Gao, 2003). The strong affinity of Tl for Fe-Mn oxyhydroxide minerals appears to reflect oxidation of dissolved seawater Tl(I) to Tl(III) on the active surfaces of the Fe-Mn oxyhydroxides (Bidoglio et al., 1993; Peacock and Moon, 2012; Rehkämper et al., 2004; Rehkämper et al., 2002).

2.2. Thallium isotopes

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

$$\varepsilon^{205}\text{Tl}_{\text{sample}} = 10^4 \times (\frac{^{205}\text{Tl}_{\text{sample}}}{^{203}\text{Tl}_{\text{sample}}} - \frac{^{205}\text{Tl}_{\text{NIST 997}}}{^{203}\text{Tl}_{\text{NIST 997}}})$$

and NIST 997 is a standard reference material defined as $\varepsilon^{205}\text{Tl} = 0$ (Nielsen et al., 2006b; Rehkämper et al., 2004; Rehkämper et al., 2002). This is a surprising result, as it shows that Tl displays a similar magnitude of stable isotope variability as significantly lighter elements, such as Fe, Zn, and Cd, despite a much smaller relative mass difference of less than 1%. The Tl isotope variability is particularly pronounced in the marine environment. The Tl isotope composition of open-ocean seawater, as determined from analyses of 8 samples from the Atlantic, Pacific and Arctic Oceans, is $\varepsilon^{205}\text{Tl} = -5.7 \pm 0.4$ (Nielsen et al., 2004; Nielsen et al., 2006b; Rehkämper et al., 2002). This isotope composition is somewhat lighter than the average composition of the Earth’s continental crust and mantle, which are both characterized by $\varepsilon^{205}\text{Tl} = -2.0 \pm 0.5$ (Nielsen et al., 2007; Nielsen et al., 2006a; Nielsen et al., 2005). In contrast, Tl-rich basalts from weathered upper ocean crust and Fe-Mn crusts are known to
have $\varepsilon^{205}$Tl values as low or as high as about -20 and +15, respectively (Nielsen et al., 2006b; Rehkämper et al., 2002).

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

Diagenetic Fe-Mn nodules (which include primarily samples of mixed diagenetic/hydrogenetic origin) and hydrothermal Fe-Mn deposits from diffuse fluid flows in the distal parts of hydrothermal systems display significantly more variability in Tl isotope compositions, with $\varepsilon^{205}$Tl values that range from values of about -6 to +9 (Fig. 1). The origin of this variability is currently unclear and has been ascribed to differences in fluid
compositions (seawater vs. diagenetic pore fluids or diffuse hydrothermal flows) or sorption conditions (closed vs. open system Rayleigh fractionation, variable temperatures of hydrothermal fluids) \(^5\)Rehkämper et al., 2004, Rehkämper et al., 2002. Alternatively, they may also be due to differences in the mineralogy of the manganese oxide phases to which Tl is bound in Fe-Mn sediments Koschinsky and Hein, 2003, Peacock and Moon, 2012. Whilst the Mn mineralogy of hydrogenetic Fe-Mn crusts is almost completely dominated by hexagonal birnessite, both birnessite and todorokite are present in diagenetic Fe-Mn nodules and hydrothermal deposits Burns and Burns, 1977.

Also of considerable interest are the Tl isotope time-series data that were recently obtained for a number of Fe-Mn crusts Nielsen et al., 2011, Nielsen et al., 2009a, Rehkämper et al., 2004 and which extend back to the late Cretaceous (Fig. 2). These records are relatively constant for the last 40 Myr but display a dramatic shift in \(\varepsilon^{205}\)Tl from values of about +6 at 55 Myr to about +12 at 45 Myr. Both Rehkämper et al. 2004 and Nielsen et al. 2009a argue that the observed trends are (i) not due to diagenetic alteration and (ii) unrelated to changes in the mineralogy or major element composition of the samples. The trends were therefore interpreted as primary features that record a change in either (i) the isotope fractionation factor of Tl between the Fe-Mn crusts and seawater \(\alpha_{\text{FeMn-sw}}\) or (ii) the Tl isotope composition of the oceans. It is notable that the Cenozoic Tl isotope record is similar in structure to both the benthic foraminiferal \(\delta^{18}\)O curve Zachos et al., 2001 and the Cenozoic seawater S isotope record determined from marine barites Paytan et al., 1998, which may suggest causal links between the processes driving the respective isotopic variations (Fig. 2). The \(\delta^{18}\)O curve of benthic foraminifera in the Paleocene and Early Eocene mainly records changes in water temperature between ~6 and 12°C Zachos et al., 2001 whereas the increase in marine S isotopes during the Early Eocene most likely reflects
increased pyrite burial rates [Kurtz et al., 2003] and thus a perturbation of the global carbon cycle.

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

3. Experimental methods

3.1. Batch Tl sorption experiments

Three groups of batch experiments are described in this paper: (1) a time series, with identical concentrations of synthetic birnessite and aqueous thallium and durations ranging from 3 min to 72 hr; (2) a set of experiments at three different temperatures with varied concentrations of birnessite and aqueous Tl; and (3) a set with much lower concentrations of aqueous Tl than the others. For all experiments, hexagonal K-birnessite was synthesized following the methods of Barling and Anbar [2004] by mixing 24 mL of 2 M HCl (distilled) with 0.6 g KMnO$_4$ and allowing this mixture to react and precipitate while constantly agitated. After 48 hours, the mixture was diluted to ~500 mL with 18.2 MΩ-cm water and then raised to circumneutral pH by addition of NaOH pellets. This suspension was poured through a polyethersulfone filter membrane with 0.45 μm pores. The birnessite was rinsed with 500 mL of 18.2 MΩ-cm water four times, resuspended from the filter with more water, and then suspended in 500 mL of 18.2 MΩ-cm water. A few microliters of 1 M NaOH were added, and a mixture of nitrogen plus 382 ppm CO$_2$ was sparged through the suspension for a few hours until pH stabilized at ~7. The material was kept wet at all times to avoid recrystallization, and, although the crystals remain stable for long periods, a separate batch was freshly made for each of the three sets of experiments in order to avoid any potential
problems from mineralogical transformation over time. An aliquot of the birnessite stock was
dried down, dissolved, and analyzed by ICP-MS; from this analysis we know that our
birnessite stock contained approximately 0.8 mg of birnessite per gram of stock suspension.
Previous batches of birnessite made in the same way were analyzed by X-ray diffraction (J.
Post, Smithsonian Institution) and determined to be poorly crystalline hexagonal K-birnessite

A thallium stock solution with 49.6 μg/g Tl was prepared by dissolving reagent grade
TlCl in 18.2 MΩ-cm water with 0.2 M KNO₃ as background electrolyte. This solution was
also sparged with nitrogen + 382 ppm CO₂, and the pH was adjusted to ~7 with NaOH. A
second Tl stock solution was prepared at 27.0 μg/g Tl for the low Tl concentration
experiments.

The first set of experiments was performed in order to investigate how quickly Tl
isotopic equilibrium was reached. Here, each of six 50 mL polypropylene centrifuge tubes
was filled with 25 g of 49.6 μg/g Tl stock solution, 2 g of birnessite suspension, and 18 g of
18.2 MΩ-cm water (Table 1). Ionic strength was therefore 0.11 M in each tube and [Tl] ≈ 28
μg/g (Table 1). All tubes were shaken in a temperature-controlled shaker (Eppendorf
Thermomixer R) at 22°C. After shaking for the designated duration, each mixture was filtered
through a polyethersulfone membrane with 0.2 μm pores, and both fluid and solid portions
were collected for concentration and isotope analysis. A few drops of fluid always stuck to the
bottom of the filter assembly, so approximately 0.5-1 g of fluid was lost from each
experiment. Hence, to compute the proportion of Tl that sorbed in each experiment, we
divided the amount of Tl recovered in the solid portion by the total amount put in the
experiment (see section 5.1 for further discussion of sample recovery and mass balance). The
loss of fluid has no consequence for the isotope systematics, since all fluids and solids were
measured directly for Tl isotope composition.
The second set of experiments was designed to investigate how Tl isotope fractionation varies as a function of temperature and fraction of Tl sorbed. A range of temperatures that encompasses most of those encountered in the marine environment was chosen. At each temperature (6°, 25°, 40°C), the proportions of Tl and birnessite were varied. In each experiment, an aliquot of 49.6 μg/g Tl stock solution (3 to 10 mL) was mixed with an aliquot of birnessite stock (250 to 2000 μL) plus 18.2 MΩ-cm water in a polypropylene centrifuge tube. These mixtures resulted in [Tl] ≈ 25 μg/g (Table 1). Ionic strength was 0.10 M in each experiment, and pH was again ~7. The mixtures were shaken at either 6°, 25°, or 40°C. Experiments conducted at 6° C and 25° C ran for 50 and 48 hours, respectively, whereas the 40°C experiments were terminated after just two hours to avoid recrystallization of birnessite to other Mn oxide minerals during the experiment. Experiments that were conducted at 50°C are not included in this paper, as they showed clear signs of change in grain size and aggregation behaviour after 48 hr, presumably because recrystallization of birnessite to another manganese phase had begun.

A small, weighed aliquot of each recovered fluid was used for the measurement of Tl concentrations by ICP-MS. Recovered birnessite particles with sorbed Tl were dissolved with warm ~3 M HCl, and a small aliquot of each sample was used for Tl abundance determination. The amounts of Tl in the portions of each experiment and the percentages of Tl sorbed are listed in Table 2. Rigorous propagation of uncertainties is difficult, since the greatest source of error is likely the sample handling, rather than the analytical measurements. Error bars in plots have been propagated from an estimated 5% relative uncertainty on each Tl amount [Prytulak et al., 2013]. Further aliquots of each fluid and digested birnessite sample were taken for isotopic analyses, which were performed according to methods described below.
The third set of experiments was performed with much lower initial Tl concentrations as it was suspected that the amounts of Tl added to the experiments were partially controlling the observed isotope fractionation factors. Here, about 0.25 g of a 27.0 µg/g Tl stock solution and ~0.5 g of birnessite stock (corresponding to about 0.4 mg of birnessite) were mixed with variable amounts (~15 to 45 g) of a 0.1 M KNO$_3$ solution (Table 3). These mixtures resulted in starting Tl concentrations between ~0.1 and 0.4 µg/g, two orders lower than in the previous experiments, which ranged from 25 to 28 µg/g Tl. Temperature was 22°C, ionic strength was 0.1 M, pH was ~7, and experimental duration was 44 hours. Samples were prepared for Tl isotope analysis using similar methods to those applied in the other experiments.

3.2. Thallium separation and isotope composition analysis

Before chemical separation of Tl, all samples were evaporated to dryness and re-dissolved in 1 M HCl. Subsequently, 18 MΩ-cm water saturated with ~1% (vol/vol) Br$_2$ was added in order to oxidize Tl to the trivalent state required for the column chemistry procedure (Rehkämper and Halliday, 1999). Chemical separation of Tl from the sample matrix (mainly Mn and K) was performed with the anion exchange resin AG1-X8 in 100 µL resin bed columns using previously described techniques (Nielsen et al., 2004; Nielsen et al., 2005; Rehkämper and Halliday, 1999). Isotope compositions for time and temperature series were measured on Nu Plasma MC-ICPMS instruments in the MAGIC labs at Imperial College London and Oxford University, respectively, while low-Tl experiments were measured on a Thermo Finnigan Neptune MC-ICPMS at Woods Hole. These analyses applied previously established techniques, whereby the $^{208}$Pb/$^{206}$Pb isotope ratio of an admixed solution of NIST SRM 981 Pb is used to correct for the instrumental mass bias of the measured $^{205}$Tl/$^{203}$Tl ratio, using the exponential law in combination with standard sample bracketing (Baker et al., 2009; Nielsen et al., 2004).
The corrected $^{205}\text{Tl}/^{203}\text{Tl}$ ratios of the samples are reported here relative to the NIST SRM 997 Tl standard following equation (1). Based on replicate measurements of standard solutions and some of the samples, all analyses are assigned an uncertainty of $\pm 0.3 \, \varepsilon^{205}\text{Tl}$. The precision of the results was furthermore ascertained by repeated analyses of the secondary Aldrich Tl reference material and solutions of NIST SRM 997 Tl that were processed through the column chemistry. All these tests were consistent with the assigned error of $\pm 0.3 \, \varepsilon^{205}\text{Tl}$. With the most recent generation of MC-ICPMS instruments, precise and accurate Tl isotope data can be generated even for $<1\text{ng}$ of Tl and given that all experimental run products contained $>2\text{ng}$ of Tl, none of the analyses were compromised by low Tl ion beam intensities.

The fractionation factors between two samples A and B are expressed in terms of $\alpha$, where

$$\alpha_{A:B} = \left(\frac{^{205}\text{Tl} / ^{203}\text{Tl}_A}{^{205}\text{Tl} / ^{203}\text{Tl}_B}\right) \approx \left(\varepsilon^{205}\text{Tl}_A + 10000\right) / \left(\varepsilon^{205}\text{Tl}_B + 10000\right).$$

The uncertainty on $\alpha$ is the square root of the sum of the uncertainties squared of the two isotopic measurements, which is about $\pm 0.00004$.

## 4. Results

Results from our experiments are tabulated in Tables 1, 2, and 3 and shown graphically in Figs. 3-6. In all experiments, the isotopic composition of sorbed Tl is heavier than that of aqueous Tl remaining in the fluid. The six time series experiments had nearly identical concentrations of birnessite and Tl (see Table 1), and the resulting proportions of Tl sorbed and dissolved are nearly the same regardless of experimental duration (Table 2). Isotopic fractionation between sorbed and dissolved Tl in these experiments ($\alpha = \frac{^{205}\text{Tl} / ^{203}\text{Tl}_{sorbed}}{^{205}\text{Tl} / ^{203}\text{Tl}_{dissolved}}$) is almost constant within analytical uncertainties, although the values show a very slight increase over time from 1.00021 at 3 min to 1.00031.
after 72 hr (Fig. 3). We note that these fractionations are much smaller than those observed between seawater and natural ferromanganese sediments, and possible reasons for this discrepancy are discussed below.

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

Experiments performed with low initial Tl concentrations (\( \leq 0.4 \mu g/g \), rather than ~25 \( \mu g/g \)) exhibit the largest isotope fractionation factors between \( \alpha \approx 1.00098 \) and 1.00145 (Table 3) and are thus closest to agreeing with the fractionation observed between seawater and natural hydrogenetic Fe-Mn crusts (\( \alpha \approx 1.0019 \) to 1.0022; Rehkämper et al., 2002). The four experiments were performed with nearly identical amounts of birnessite and Tl, but the volume of 0.1 M KNO\(_3\) used to dilute the Tl stock solution varied (Table 1), which means that the starting Tl concentration was the only physical parameter that varied in this set of experiments. The Tl isotope fractionation factor correlates inversely with starting aqueous [Tl], i.e. linearly with 1/[Tl] (Fig. 6), with the largest fractionation observed for the experiment with the lowest initial aqueous [Tl].

5. Discussion

5.1. Assessment of Tl recovery from experiments

Using the measured isotopic compositions and concentrations of our Tl stock solutions (Table 1), we have compared the total amount of Tl put into each experiment to the sum of the
amount recovered in the fluid and the solid portions, in order to assess how well Tl was
recovered. Note that because we measured the isotopic composition of Tl in every fluid and
solid, some loss of Tl from either pool is of no consequence for determining the isotopic
fractionation expressed in each experiment, as long as the reasonable assumption is made that
the fractions of fluid and solid lost were isotopically identical to those recovered. However,
failure to recover all of the Tl in the experiment does introduce some error into our
determination of the fraction of Tl sorbed or the amount of Tl sorbed per mg of birnessite, and
the error in this case is difficult to quantify rigorously. Therefore, we employ an isotopic mass
balance calculation to determine the fraction sorbed in each experiment.

\[ \varepsilon_{205}^{\text{stock}} = \varepsilon_{205}^{\text{dissolved}} f_{\text{dissolved}} + \varepsilon_{205}^{\text{sorbed}} f_{\text{sorbed}} \]  

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

5.2. Thallium sorption sites

Thallium sorbed to hexagonal birnessite has previously been shown to be oxidized to
Tl(III), with Tl sorbed as an inner-sphere complex over Mn vacancies in the phyllomanganate
sheets, and this difference in Tl oxidation state between solution and solid could well drive
isotopic fractionation (Peacock and Moon, 2012). In similar sorption experiments to those
here, it has been shown that Ni also sorbs to birnessite as an inner-sphere complex over Mn
vacancies (Manceau et al., 2007; Peacock and Sherman, 2007) and it has been estimated that
crystalline birnessite can accommodate ~1.4 wt% Ni via this sorption mechanism (Peacock, 2009). This corresponds to 0.24 mmol Ni/g birnessite. If the molar capacity for Tl at this site were the same, then the maximum concentration of Tl in Tl-sorbed birnessite would be approximately 5 wt% (or ~53 µg Tl sorbed per g birnessite). Our experiments were performed using poorly crystalline birnessite, which has a larger surface area and therefore might have a higher sorption capacity than that estimated based on the Ni experiments described above. Additional uncertainty should also be considered given that Tl and Ni also sorb via somewhat different processes (only Tl is oxidized during the sorption process). However, we estimate that vacancy sites are unlikely to accommodate more than 5-15 wt% Tl. All of our experimental products have more than 14 wt% Tl associated with the solid (up to 32 wt%), which leads us to hypothesize that some Tl in our experiments is sorbed over vacancy sites, but additional Tl is sorbed in a different manner. The overall isotope fractionation we observe in our experiments would then be a combination of strongly fractionated, inner-sphere-over-vacancy Tl and another pool of Tl with unknown oxidation state that is unfractionated or only slightly fractionated from solution (hereafter designated as ‘slightly fractionated’).

If the amount of sorbed Tl in our experiments exceeds the sorption capacity of sites over Mn vacancies, what could the other sorbed species be? A comprehensive answer to that question is beyond the scope of this study, but Tl(I) may be able to sorb loosely, as an outer-sphere complex, and/or strongly, as an inner-sphere complex onto MnOH sites located at the edges of the phyllomanganate sheets (hereafter referred to as ‘edge sites’). Neither of these sorption mechanisms is expected to result in oxidation of Tl(I) to Tl(III) (Peacock and Moon, 2012), and thus little or no fractionation of isotopes is expected to occur between this pool of sorbed Tl and Tl remaining dissolved in solution. The latter mechanism of inner-sphere sorption to edge sites has been observed previously for Ni on vernadite at high Ni surface loading, when the vacancy sites are saturated [Manceau et al., 2007].
Even though Tl and Ni both sorb to birnessite as inner-sphere complexes at Mn vacancy sites, only Tl sorption involves oxidation of the sorbing species and coupled reductive dissolution of the birnessite phase (Peacock and Moon, 2012). This difference in oxidation between Tl and Ni is important because it has been shown that oxidation of redox-active metals at hexagonal birnessite surfaces (our starting material) can induce a rapid structural ripening and conversion to triclinic birnessite and potentially todorokite (Bargar et al., 2005; Learman et al., 2011; Webb et al., 2005), which leads to a dramatic decline in the oxidative capacity of the Mn oxide (Learman et al., 2011). Triclinic birnessite and todorokite still have the potential to sorb significant amounts of Tl, but do not cause any Tl oxidation (Peacock and Moon, 2012) and hence are unlikely to be associated with Tl isotope fractionation. Thus our slightly fractionated Tl could be at least partially located at sorption sites of triclinic birnessite or todorokite that continuously form while the hexagonal birnessite vacancy sites become occupied.

We also considered the possibility that birnessite may continue to oxidize additional Tl(I) to Tl(III), even if all above-vacancy sites are saturated, and that the excess oxidized Tl could precipitate as Tl$_2$O$_3$. However, experimental evidence to date shows that phyllomanganates (triclinic birnessite) and tectomanagnates (todorokite), both devoid of vacancy sites, are unable to oxidise Tl, and thus oxidative sorption of Tl is associated with vacancy site sorption only (Peacock and Moon, 2012). We also conducted a scaled-up version of one of our 25 °C experiments (Tl-25-01, with 63% of Tl sorbed and a final solid with 17 wt% Tl) to produce enough solid for X-ray diffraction analysis, but the resulting diffraction pattern (not shown) had only broad peaks consistent with poorly crystalline birnessite, with none of the peaks expected for Tl$_2$O$_3$.

Based on the above discussion, we conclude that Tl in our experiments is sorbed to at least two different sites, one of which is as an inner-sphere complex over vacancies in
hexagonal birnessite. The remaining Tl could either be sorbed as outer-sphere complexes, as inner-sphere complexes to edge sites and/or associated with triclinic birnessite or todorokite that continuously form due to electron transfer processes occurring as part of the Tl oxidative sorption at vacancy sites.

5.3. Time and temperature dependent experiments

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

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

The fractionation factors we observe in the time series experiments ($\alpha_{\text{sorbed-dissolved}} = 1.00021$ to $1.00031$) are all much lower than those observed between natural samples and seawater (Fig. 1), where $\alpha_{\text{FeMn-seawater}} \approx 1.0020$ for hydrogenetic Fe-Mn crusts and $\alpha_{\text{FeMn-seawater}} \approx 1.0006$ to $1.0015$ for diagenetic Fe-Mn deposits (Rehkämper et al., 2004; Rehkämper et al., 2002). Our time series fractionation factors are also smaller than theoretical predictions of
equilibrium fractionation between Tl(I) and Tl(III) in vacuo ($\alpha \approx 1.0025-1.0027$ at 22° C) (Schauble, 2007).

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

Other potential explanations could be that the experiments were conducted at different pH and ionic strength than the conditions of Fe-Mn crust precipitation. Since pH strongly affects the sorption capacity of solids, it is also possible that isotope fractionation is affected by variable pH. We did not vary the pH of our experiments (all were conducted at pH ~7) and it is therefore not possible with our present data set to evaluate if pH has a strong effect on Tl isotope fractionation during sorption to birnessite. Our experiments contain 0.1 M KNO$_3$, but seawater contains ~0.5 M NaCl. Thallium is therefore initially present as Tl$^+$ in our experiments, but may exist as a combination of Tl$^+$, TlOH$_0^{+(aq)}$ and TlCl$_0^{-(aq)}$ in seawater (Byrne, 2002; Nielsen et al., 2009a). Whether the difference in coordination chemistry for Tl as a function of ionic strength and [Cl$^-$] could influence fractionation during sorption of Tl (or any other metal) to such a large extent is so far unknown and should be a focus of future studies.

There are two conclusions to draw from the second series of experiments, conducted at three different temperatures, with the same initial aqueous [Tl], but varying amounts of birnessite (Table 1). A clear correlation between fraction of Tl sorbed and isotope fractionation factor is evident in Table 2 and Fig. 4a, but, importantly, temperature seems to have little effect on isotope behaviour. At any given fraction of Tl sorbed, the difference in isotope fractionation between 6° and 40° C is less than 0.0002 in terms of $\alpha_{sorbed-dissolved}$, with a slight suggestion that a higher magnitude of fractionation occurs at lower temperature, as
expected. The magnitude of change in isotope fractionation as a function of temperature is similar to predictions by Schauble (2007), who calculated that $\alpha_{\text{Tl(III)-(I)}}$ should change by $\sim 0.0003$ between $6^{\circ}$ and $40^{\circ}$ C.

Another observation from Fig. 4a is that the overall fractionation expressed in our experiments is correlated with the fraction of Tl in the experiment that is sorbed to birnessite. This trend could be interpreted to reflect a Rayleigh distillation process, whereby Tl is irreversibly sorbed to birnessite and the fluid continues to evolve to lighter compositions as sorption proceeds. But this conclusion is inconsistent with the much lower fractionation factors recorded for the time dependent experiments at the same fraction of Tl sorbed (Fig. 4a). Fig. 4b shows the same experiments with a different choice of independent variable (the number of $\mu$g of Tl sorbed per mg of birnessite), and the result is a single trend for the time series and temperature experiments. We did not measure the surface area of birnessite in our experiments, but the mass of birnessite serves as a close proxy. The relationship shown in Fig. 4b supports our hypothesis that the fractionations expressed in our experiments reflect different proportions of Tl sorbing in at least two different sites. One of the sites is limited in number, strongly fractionated, and likely represents Tl(III) sorbed over Mn vacancies on {001} surfaces (space group P6$_3$/mmc). In contrast, the other sites hold Tl that is only slightly fractionated from dissolved Tl and may comprise Tl sorbed to birnessite edges or triclinic birnessite formed via oxidative ripening (Learman et al., 2011).

### 5.4. Low Tl experiments and sorption site mixing models

To further investigate the relationship between Tl isotope fractionation and the amount of Tl sorbed per unit of birnessite, we conducted the third set of experiments, each with the same amount of birnessite and Tl. These experiments featured varying volumes of fluid (details in Table 1) and initial concentrations of aqueous [Tl] about two orders of magnitude smaller...
than in the earlier experiments. Results are shown in Table 3 and plotted in Figs. 5 and 6. The concentrations of Tl in the solids (~17 µg Tl per mg birnessite) were the lowest of all the experiments and we observed the highest fractionation factors yet ($\alpha_{\text{sorbed-dissolved}} = 1.0010$ to 1.0014), although these values are still smaller than those observed in nature.

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

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

We present two of our best-fit model curves. Model 1 has a low value for sorb-cap of 5 µg Tl/mg birnessite, vac-frac = 1.0020, and edge-frac = 1.0003. The curve misses some of the temperature dependent data, but fits the rest quite well. Model 2 has a higher sorption capacity of 28 µg Tl/mg birnessite, vac-frac = 1.0023, and edge-frac = 1.0002. This curve fits our high-Tl experiments better, but overestimates the fractionation factors for low-Tl experiments and natural data. This simple model is built on the presumption that the above-vacancy sites are high affinity sites and thus fill first, and all remaining Tl that sorbs does so via edge sites. That we cannot find values for the three parameters that result in a good fit to all data suggests
that this presumption is incorrect. Perhaps Tl partitioning onto the two types of sorption sites is simultaneous but the vacancy sites have higher affinity for Tl and thus fill up first. The number of vacancy vs. edge sites, and thus the rate at which the two sorption sites fill, would then depend on the crystallinity of the birnessite, and/or could vary with the amount of sorbed Tl or as a function of aqueous [Tl] (Fig. 6). Such mechanisms are not inconsistent with our high-Tl experiments as, presumably, all vacancy sites are filled and thus these experiments do not inform on the rate at which the two types of sorption sites fill.

5.5. An alternative to sorption site mixing

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

We know that birnessite causes surface oxidation of aqueous Tl\(^+\) to Tl\(^{3+}\), which is adsorbed onto the birnessite structure [Peacock and Moon, 2012]. In principle, we can
therefore construct a simplified isotope exchange reaction that may be predominantly responsible for the Tl isotope fractionation in birnessite:

\[
\text{Tl}^+_{(aq)} \rightleftharpoons \text{Tl}^{3+}_{(s)} + 2e^- \tag{5}
\]

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

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

\[
\text{Tl}^+_{(aq)} \rightleftharpoons \text{Tl}^+_{(LB)} \tag{6}
\]

\[
\text{Tl}^+_{(LB)} \rightleftharpoons \text{Tl}^{3+}_{(LB)} + 2e^- \tag{7}
\]

The oxidation reaction (7) will be followed by adsorption of the oxidized Tl onto the birnessite structure. On the time scale of the experiments, the latter process is probably essentially unidirectional because the trivalent Tl is very strongly bound to the birnessite surface (Peacock and Moon, 2012):
Each of these three reactions (6, 7 and 8) account for a separate part of the total reaction (5) whereby aqueous, monovalent Tl is first attracted to a sorption site and loosely bound as an outer-sphere complex with no isotope fractionation (6), then it is oxidized and isotopically fractionated while still loosely bound (7) and lastly adsorbed as an inner-sphere surface complex at the vacancy sites with no isotope fractionation (8). During our experiments we measured the isotopic difference between $\text{Tl}^{+}(\text{aq})$ and $\text{Tl}^{3+}(\text{s})$, which means we were not directly measuring the isotope fractionation factor in (7), but the sum of the three reactions (6, 7 and 8). This limitation is important because the reaction kinetics of all three reactions will determine how much of the isotope fractionation generated in (7) will be expressed in our measurements. For example, we can consider a situation in (7) at isotopic equilibrium where one half of the Tl is trivalent and the other half monovalent. If $\alpha = 1.002$ then we can determine that $\varepsilon^{205}\text{Tl}^{3+} = +10$ and $\varepsilon^{205}\text{Tl}^{+} = -10$, compared with the starting solution. Any $\text{Tl}^{3+}_{(LB)}$ sorbed onto birnessite at this point would have an apparent $\alpha = 1.001$. But at the same time, reaction (6) will drive $\varepsilon^{205}\text{Tl}^{+}$ back toward the isotope composition of the starting solution and thus the relative rates of oxidation (7) and isotope re-equilibration (6) will determine the isotope composition of the $\text{Tl}^{3+}_{(LB)}$, which is what we measure on the birnessite.

Using these reaction principles we can understand why the Tl concentration of the starting solution may have such a profound impact on the observed $\alpha$, because thermodynamics dictate that increased concentrations on the left hand side of a reaction will enhance the rate of the forward reaction relative to the back reaction. The impact of the back reaction in (6) is thereby controlled by the Tl concentration of the solution, which translates directly to isotope fractionation if isotope equilibration is slower in (6) than in (7). If we furthermore assume that reaction (8) is essentially unidirectional at the timescale of our experiments, it can be shown by simple modelling, that the relationship seen in Fig. 6 may
result from a dampening of the expressed isotope fractionation, which is enhanced at higher initial dissolved Tl concentrations.

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

6. Conclusions and outlook

We have conducted the first study of Tl isotope fractionation during sorption of aqueous Tl(I) onto the manganese oxide birnessite. Experiments conducted at high Tl solution
concentrations (~25-28 µg/g) display relatively small isotope fractionation factors of \( \alpha \approx 1.0002 \) to 1.0007 and Tl concentrations up to 34 wt% (430 µg Tl/mg birnessite). We conclude that both fractionated (adsorbed at vacancy sites) and slightly fractionated (sorbed at edge sites or oxidatively formed triclinic birnessite) Tl is associated with the birnessite in these experiments, and the overall fractionation expressed in each experiment reflects the difference between the isotopic compositions of Tl in solution and a weighted combination of the two pools of sorbed Tl.

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

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

Our results are consistent with the recently proposed oxidation-adsorption reaction for sorption of Tl onto birnessite [Peacock and Moon, 2012]. By combining isotopic and mineralogical considerations we suggest that Tl isotope fractionation for birnessite vacancy sites occurs in three steps: first, aqueous Tl is sorbed as a loosely bound univalent outer-sphere complex, which is then oxidized to Tl(III) and finally adsorbed onto the birnessite
structure. Thallium isotope fractionation only occurs during the oxidation reaction, whereby nuclear field shift effects may produce fractionation factors of several permil [Schauble, 2007]. However, more work is required in order to obtain a full understanding of the mechanisms that produce the large Tl isotope fractionation in nature between Fe-Mn crusts and seawater. In particular, it will be important to ascertain if our hypothesis that two types of sorption sites were occupied in our experiments is correct. In addition, further experiments are needed to investigate the proposed mineralogical control of Tl isotope fractionation during sorption to Fe-Mn deposits [Peacock and Moon, 2012] as well as to assess whether parameters such as pH and ionic strength could affect the Tl isotope fractionation factors.

7. Acknowledgements

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8. References


Figure Captions

Fig. 1. Plot of \( \varepsilon^{205}\text{Tl} \) vs. \( \text{Tl} \) concentration (note logarithmic scale) for various types of marine Fe-Mn deposits [Rehkämper et al., 2002]. The dark and light shaded fields denote the \( \varepsilon^{205}\text{Tl} \) of \(-5.7 \pm 0.4\) and about \(-2.0 \pm 0.5\), respectively [Nielsen et al., 2004; Nielsen et al., 2006b; Rehkämper et al., 2002].

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

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

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

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

Fig. 6. Thallium isotope fractionation \((\alpha)\) between dissolved and solid \( \text{Tl} \) plotted versus the inverse of initial aqueous \( \text{Tl} \) concentration for low-\( \text{Tl} \) experiments.
Table 1: Experimental parameters for variable time and temperature adsorption experiments.

<table>
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<tr>
<th>Experiment</th>
<th>Temp (°C)</th>
<th>Duration (hr)</th>
<th>Tl stock* (g)</th>
<th>MnO$_2$ stock (g)</th>
<th>H$_2$O (g)</th>
<th>[Tl] start sol. (μg/g)</th>
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<td>0.50</td>
<td>34.52§</td>
<td>0.195</td>
</tr>
<tr>
<td>LowTl-2204</td>
<td>22</td>
<td>44</td>
<td>0.248†</td>
<td>0.50</td>
<td>44.57§</td>
<td>0.150</td>
</tr>
</tbody>
</table>

*Stock solution had a Tl concentration of 49.6 μg/g, $\varepsilon_{205/203}$Tl = -0.3±0.3 (2sd), and 0.1 m KNO$_3$ for all but the four low-Tl experiments.
†Tl stock solution had 27.0 μg/g and $\varepsilon_{205/203}$Tl = -0.6±0.3 (2sd), for the four low-[Tl] experiments, with no KNO$_3$.
§A solution of 0.1 m KNO$_3$ was used instead of H$_2$O for the four low-Tl experiments.
Table 2. Thallium mass balance and isotopic compositions of varied time and temperature adsorption experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Total Tl (ȝg)</th>
<th>Tl in solid (ȝg)</th>
<th>Tl recovery* (%)</th>
<th>Tl/birnessite (µg/mg)</th>
<th>[Tl] end sol. (µg/g)</th>
<th>ε²⁰⁵Tl_diss</th>
<th>ε²⁰⁵Tl_sorb</th>
<th>α_sorb-diss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-3min</td>
<td>1284</td>
<td>612</td>
<td>88</td>
<td>418.3</td>
<td>11.5</td>
<td>-1.4</td>
<td>0.7</td>
<td>1.00021</td>
</tr>
<tr>
<td>Ti-10min</td>
<td>1249</td>
<td>673</td>
<td>90</td>
<td>414.6</td>
<td>10.0</td>
<td>-1.5</td>
<td>0.7</td>
<td>1.00022</td>
</tr>
<tr>
<td>Ti-5hr</td>
<td>1220</td>
<td>669</td>
<td>90</td>
<td>404.3</td>
<td>9.7</td>
<td>-1.6</td>
<td>0.8</td>
<td>1.00024</td>
</tr>
<tr>
<td>Ti-24hr</td>
<td>1265</td>
<td>674</td>
<td>89</td>
<td>404.7</td>
<td>10.1</td>
<td>-1.8</td>
<td>1.1</td>
<td>1.00029</td>
</tr>
<tr>
<td>Ti-48hr</td>
<td>1260</td>
<td>622</td>
<td>87</td>
<td>379.8</td>
<td>10.4</td>
<td>-1.8</td>
<td>1.3</td>
<td>1.00031</td>
</tr>
<tr>
<td>Ti-72hr</td>
<td>1252</td>
<td>681</td>
<td>89</td>
<td>397.4</td>
<td>9.7</td>
<td>-1.9</td>
<td>1.2</td>
<td>1.00031</td>
</tr>
<tr>
<td>Ti-6-04</td>
<td>244</td>
<td>89</td>
<td>87</td>
<td>266.7</td>
<td>12.7</td>
<td>-2.4</td>
<td>2.2</td>
<td>1.00046</td>
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<tr>
<td>Ti-6-05</td>
<td>245</td>
<td>50</td>
<td>87</td>
<td>328.1</td>
<td>16.6</td>
<td>-1.5</td>
<td>2.9</td>
<td>1.00045</td>
</tr>
<tr>
<td>Ti-6-06</td>
<td>148</td>
<td>115</td>
<td>91</td>
<td>155.5</td>
<td>3.2</td>
<td>-6.6</td>
<td>0.6</td>
<td>1.00072</td>
</tr>
<tr>
<td>Ti-25-01</td>
<td>514</td>
<td>324</td>
<td>96</td>
<td>206.9</td>
<td>8.2</td>
<td>-4.3</td>
<td>1.7</td>
<td>1.00060</td>
</tr>
<tr>
<td>Ti-25-02</td>
<td>509</td>
<td>195</td>
<td>92</td>
<td>260.8</td>
<td>13.5</td>
<td>-2.2</td>
<td>2.3</td>
<td>1.00045</td>
</tr>
<tr>
<td>Ti-25-03</td>
<td>519</td>
<td>105</td>
<td>90</td>
<td>344.2</td>
<td>17.7</td>
<td>-1.4</td>
<td>2.6</td>
<td>1.00040</td>
</tr>
<tr>
<td>Ti-25-04</td>
<td>533</td>
<td>51</td>
<td>92</td>
<td>453.2</td>
<td>20.9</td>
<td>-0.9</td>
<td>2.7</td>
<td>1.00036</td>
</tr>
<tr>
<td>Ti-40-01</td>
<td>152</td>
<td>113</td>
<td>90</td>
<td>163.2</td>
<td>3.8</td>
<td>-5.5</td>
<td>0.5</td>
<td>1.00061</td>
</tr>
<tr>
<td>Ti-40-02</td>
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<td>85</td>
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<td>12.6</td>
<td>-2.2</td>
<td>1.9</td>
<td>1.00041</td>
</tr>
<tr>
<td>Ti-40-03</td>
<td>252</td>
<td>51</td>
<td>85</td>
<td>301.3</td>
<td>16.0</td>
<td>-1.2</td>
<td>2.4</td>
<td>1.00036</td>
</tr>
</tbody>
</table>

*Computed by adding weighted isotopic compositions of recovered fluid and solid and subtracting from Ti stock solution’s isotopic composition. Minor loss of both solid and liquid occurred for most experiments. See text for details.
Table 3: Thallium mass balance and isotopic compositions of experiments performed at low Tl abundances.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Total Tl (ȝg)</th>
<th>Tl in solid (ȝg)</th>
<th>Tl recov.* (%)</th>
<th>μg Tl/mg birnessite</th>
<th>[Tl]</th>
<th>ε²⁰⁵Tl_diss</th>
<th>ε²⁰⁵Tl_sorb</th>
<th>α_sorb-diss</th>
</tr>
</thead>
<tbody>
<tr>
<td>LowTl-2201</td>
<td>6.67</td>
<td>5.32</td>
<td>80</td>
<td>17</td>
<td>0.00034</td>
<td>-10.6</td>
<td>-0.8</td>
<td>1.00098</td>
</tr>
<tr>
<td>LowTl-2202</td>
<td>6.78</td>
<td>4.71</td>
<td>70</td>
<td>17</td>
<td>0.00054</td>
<td>-12.4</td>
<td>-1.4</td>
<td>1.00110</td>
</tr>
<tr>
<td>LowTl-2203</td>
<td>6.73</td>
<td>6.43</td>
<td>96</td>
<td>17</td>
<td>0.00050</td>
<td>-13.8</td>
<td>-0.9</td>
<td>1.00129</td>
</tr>
<tr>
<td>LowTl-2204</td>
<td>6.68</td>
<td>5.25</td>
<td>79</td>
<td>17</td>
<td>0.00086</td>
<td>-15.2</td>
<td>-0.7</td>
<td>1.00145</td>
</tr>
</tbody>
</table>

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