

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 ($\alpha \approx 1.0002\text{--}1.0015$, where $\alpha = {}^{205}\text{Tl}/{}^{203}\text{Tl}_{\text{solid}}/{}^{205}\text{Tl}/{}^{203}\text{Tl}_{\text{liq}}$) is smaller than observed between seawater and natural sediments ($\alpha \approx 1.0019\text{--}1.0021$; Rehkämper et al., 2002, *Earth. Planet. 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 phylломanganate 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 ($\sim 0.15\text{--}0.4 \mu\text{g/g}$) and the lowest concentrations of Tl in the resulting Tl-sorbed birnessite ($\leq 17 \mu\text{g Tl/mg birnessite}$), 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

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experiments, and therefore the second slightly fractionated sorption site is not significantly utilized. Temperature (6–40 °C) and experimental duration (3 min–72 h) appear to have little or no effects on isotope behaviour in this system.

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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 (Maréchal et al., 2000; Barling et al., 2001; Siebert et al., 2003; Levasseur et al., 2004; Rehkämper et al., 2004; Schmitt et al., 2009; Horner et al., 2010).

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 (Rehkämper et al., 2004; Baker et al., 2009; Nielsen et al., 2009a).

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 phyllosilicate 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 (Shaw, 1952; Wedepohl, 1974; Heinrichs et al., 1980), 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 (McGoldrick et al., 1979; Heinrichs et al., 1980). 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 (Patterson and Settle, 1987; Hinkley et al., 1994; Gauthier and Le Cloarec, 1998).

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 (Byrne, 2002; Nielsen et al., 2009a), and it displays a nearly conservative distribution (Bruland, 1983; Flegal and Patterson, 1985). Thallium also appears to be rapidly cycled through marine organisms in the same manner as K (Flegal et al., 1986).

However, there are also important differences between Tl and the alkali metals in the oceanic realm. At about

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