Investigation and application of thallium isotope fractionation

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ABSTRACT

This contribution summarizes the current state of understanding and recent advances made in the field of stable thallium (Tl) isotope geochemistry. High precision measurements of Tl isotope compositions were developed in the late 1990s with the advent of multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) and subsequent studies revealed that Tl, despite the small relative mass difference of the two isotopes, exhibits substantial stable isotope fractionation, especially in the marine environment. The most fractionated reservoirs identified are ferromanganese sediments with ε^{205}Tl ≈ +15 and low temperature altered oceanic crust with ε^{205}Tl ≈ –20. The total isotopic variability of more than 35 ε^{205}Tl-units hence exceeds the current analytical reproducibility of the measurement technique by more than a factor of 70. This isotopic variation can be explained by invoking a combination of conventional mass dependent equilibrium isotope effects and nuclear field shift isotope fractionation, but the specific mechanisms are still largely unaccounted for.

Thallium isotopes have been applied to investigate paleoceanographic processes in the Cenozoic and there is evidence to suggest that Tl isotopes may be utilized as a monitor of the marine manganese oxide burial flux over million year time scales. In addition, Tl isotopes can be used to calculate the magnitude of hydrothermal fluid circulation through ocean crust. It has also been shown that the subduction of marine ferromanganese sediments can be detected with Tl isotopes in lavas erupted in subduction zone settings as well as in ocean island basalts.

Meteorite samples display Tl isotope variations that exceed the terrestrial range with a total variability of about 50 ε^{205}Tl. The large isotopic diversity, however, is generated by both stable Tl isotope fractionations, which reflect the highly volatile and labile cosmochemical nature of the element, and radiogenic decay of extinct ^{205}Pb to ^{205}Tl with a half-life of about 15 Ma. The

difficulty of deconvolving these two sources of isotopic variability restricts the utility of both the ^{205}Pb-^{205}Tl chronometer and the Tl stable isotope system to inform on early solar system processes.

1. INTRODUCTION

The distribution of Tl in natural environments on Earth is controlled in part by its large ionic radius (Tl^{+} = 1.50 A), which is akin to the alkali metals potassium (K), rubidium (Rb) and cesium (Cs) (Heinrichs et al., 1980; Shannon, 1976; Wedepohl, 1974). Thallium's large ionic radius renders it highly incompatible during partial melting and magmatic differentiation, leading to much higher Tl concentrations in the continental crust (Shaw, 1952; Wedepohl, 1995) compared to the mantle (Fig. 1). However, the electron structure of Tl tends to favor covalent bonding, which makes Tl compatible in some sulfides (Genna and Gaboury, 2015; Jones et al., 1993; Kiseeva and Wood, 2013; Nielsen et al., 2011; Nielsen et al., 2014; Wood et al., 2008). In addition to its bonding preferences, Tl has two different valence states: Tl^{+} and Tl^{3+}. Although oxidation of Tl requires a large redox potential (Table 1) the manganese (Mn) oxide birnessite has the ability to adsorb and oxidize Tl at its surface (Bidoglio et al., 1993; Peacock and Moon, 2012) and subsequently incorporate Tl^{3+} more firmly in its structure, which leads to very high concentrations of Tl in marine (Fe) Mn oxides (Fig. 1) (Hein et al., 2000; Nielsen et al., 2013; Peacock and Moon, 2012; Rehkämper et al., 2002; Shaw, 1952). Sorption of Tl onto some clay minerals has also been observed (Matthews and Riley, 1970; McGoldrick et al., 1979; Turner et al., 2010) although it is not clear if this behavior is related to the similarity with alkali metals. Thallium's higher particle-reactivity compared to alkali metals results in low concentrations in rivers and the oceans and thus a higher concentration contrast between the ocean and continental crust compared to elements such as Rb, Cs and K (Bruland, 1983; Flegal and Patterson, 1985; Nielsen et al., 2005b).

Thallium has two isotopes with atomic masses 203 and 205 (Table 1) and abundances of ~30% and ~70%, respectively. This equates to a relative mass difference of <1%. Considering that stable isotope fractionation theory states that the magnitude of isotope fractionation should scale with the relative mass difference of the isotopes (Bigeleisen and Mayer, 1947; Urey, 1947) one would not expect large stable isotope effects for Tl. Hence, it may be surprising that stable isotope investigations for Tl were commenced in the first place. However, the first attempts to measure Tl isotope ratios were not aimed at terrestrial materials. The main reason behind the first Tl isotope studies was the search for potential radiogenic isotope variations due to decay of the now-extinct radioactive isotope ^{205}Pb to ^{205}Tl with a half-life of 15.1 Ma (Pengra et al., 1978), whereas ^{203}Tl is stable and has no radioactive precursor. A number of studies between 1960 and 1994 failed to register resolvable Tl isotope variation for some selected terrestrial and a large number of extraterrestrial materials (Anders and Stevens, 1960; Chen and Wasserburg, 1987, 1994; Huey and Kohman, 1972; Ostic et al., 1969). These investigations were hampered, however, by the relatively large errors (>2‰) associated with the thermal ionization mass spectrometry (TIMS) measurements used at that time. The breakthrough came in 1999 when the first high precision Tl isotope measurements by MC-ICPMS were published (Rehkämper and Halliday, 1999). This technique provided a reduction in the uncertainty of more than an order of magnitude with errors reported at about 0.1-0.2‰ (Rehkämper and Halliday, 1999). With the reduced error bars, analysis of various terrestrial samples revealed large Tl isotope variation in excess of 15 times the analytical reproducibility of the original method, which opened up investigations of Tl isotope fractionation on Earth and in meteorites.

In this contribution, we summarize the knowledge that has been accumulated since 1999 on the stable isotope geochemistry of Tl. Three main environments are discussed: 1) extraterrestrial, 2) the solid Earth, and 3) the marine domain. Throughout these sections, current and notable applications of Tl stable isotopes in geochemical research are incorporated. Finally, potential future studies are suggested that are likely to make Tl isotopes a more quantitative tracer in Earth sciences.

2. METHODOLOGY

2.1. Mass spectrometry

The advent of MC-ICPMS facilitated the development of high-precision Tl isotope ratio measurements. The principal difference to the previous TIMS measurements was the ability to correct for instrumental isotope fractionation that occurs during the measurement (mass bias or mass discrimination). Two-isotope systems are difficult to measure by TIMS because isotope fractionation during volatilization from the filament is both time and mass dependent, which is difficult to correct for. Therefore, precise stable isotope ratios by TIMS are best measured with the use of a double spike (Rudge et al., 2009). However, double spiking can only easily be performed for elements with four or more isotopes (Rudge et al., 2009) and this is the reason why the early Tl isotope studies by TIMS yielded relatively large uncertainties. The great advantage of MC-ICPMS when measuring Tl isotopes (or any two-isotope system) is that, even though the overall magnitude of instrumental mass discrimination is much larger than for TIMS, it can be monitored independently during a measurement and thus corrections can be applied much more precisely than is possible with TIMS. This mass bias correction can be performed because the sample is introduced into the mass spectrometer as a solution (or a desolvated aerosol). Into this solution can be admixed a separate element with a known isotope composition (for Tl this element is Pb) and by assuming that the mass bias incurred for the two elements are proportional, isotope ratios can be determined very accurately and precisely (Nielsen et al., 2004; Rehkämper and Halliday, 1999). For Tl isotope measurements this external normalization with

Pb is always combined with the more conventional standard-sample bracketing technique that is also very common for stable isotope measurements by MC-ICPMS, which produces the most rigorous measurement stability as both instrumental mass bias and machine drift can be corrected for simultaneously. In practice (as is the case for all other stable isotope systems) isotope compositions are conventionally reported by reference to a standard that is defined as zero. For Tl this standard is the NIST 997 Tl metal, such that:

$$\varepsilon^{205}Tl = 10^4 \times (^{205}Tl/^{203}Tl_{sample} - ^{205}Tl/^{203}Tl_{NIST\ 997})/(^{205}Tl/^{203}Tl_{NIST\ 997}) \quad (1)$$

The terminology used for Tl isotope ratios is slightly different from most stable isotope systems, which generally use the δ-notation (variations in parts per 1,000). The reason for this difference is that the Tl isotope system was originally developed as a cosmochemical radiogenic isotope system, which is usually reported using the ε-notation (variations in parts per 10,000). Hence, the original notation was retained in order to facilitate comparisons between cosmochemical and terrestrial data. In addition, the analytical uncertainty on and overall variability of stable Tl isotope ratios make the ε-notation very convenient as most data are thereby shown in whole digits and only a single figure behind the decimal point is needed.

2.2. Chemical separation of thallium

Prerequisites to obtaining precise and accurate stable isotope ratios by MC-ICPMS are the complete separation of the element of interest from the sample matrix as well as 100% recovery. This is important because residual sample matrix in the purified sample can result in isotope effects either present as instabilities that lead to large uncertainties or as reproducible isotopic offsets leading to precise but inaccurate data (Pietruszka and Reznik, 2008; Poirier and Doucelance, 2009; Shiel et al., 2009).

The method for separating Tl from sample matrix when performing isotopic analyses of geologic materials was initially developed by Rehkämper and Halliday (1999). The technique has been modified slightly (Baker et al., 2009; Nielsen et al., 2004; Nielsen et al., 2007) from the original recipe, but the fundamentals have remained unchanged. Only the elution procedure has been optimized in order to remove matrix elements most efficiently (Fig. 2). All techniques outlined in Figure 2 achieve effective Tl separation from sample matrix. However, methods that use HBr during matrix elution allow for collection of Pb from the same column, although this procedure has a tendency to separate Pb less efficiently from Tl due to the strong partitioning of bromide-complexed Pb onto anion exchange resin. The separation technique relies on the fact that Tl^{3+} produces anionic complexes with the halogens (the technique uses either Cl^- or Br^-) in acidic solutions that partition very strongly to anion exchange resins. Conversely Tl^+ does not form strong anionic complexes and thus does not partition at all to anion exchange resins. Therefore, samples are prepared in oxidizing media by adding small amounts of water saturated in Br_2 to the samples already digested and dissolved in hydrochloric acid. This process ensures that all Tl is in the trivalent state, which will adsorb onto the anion exchange resin prepared in a quartz or teflon column. If the Tl oxidation was only partial during bromine addition this would cause loss of Tl and likely result in Tl isotope fractionation. However, the procedure routinely produces quantitative recovery of sample Tl (Prytulak et al., 2013), which documents that all Tl is oxidized from bromine addition. The sample matrix can then be eluted in various acidic media as long as Br_2 is present. Lastly, Tl is stripped from the resin by elution with a reducing solution that converts Tl to the univalent state. The reducing solution used is 0.1M hydrochloric acid in which 5% by weight of SO_2 gas has been dissolved. As SO_2 is not stable in solution for long periods of time it is important to make this solution fresh before performing the chemical separation of Tl.

2.3. Measurement uncertainties and standards

As with most stable isotope measurements by MC-ICPMS, the smallest uncertainties are obtained for pure standard solutions. The most commonly used secondary standard for Tl is a pure 1,000 μg/g standard solution for ICP-MS concentration analyses that was originally purchased from Aldrich. Over more than 10 years this standard has been measured against NIST 997 Tl on seven different mass spectrometers with an average of $\varepsilon^{205}Tl = -0.79 \pm 0.35$ (2sd, n=187). This uncertainty, however, is not necessarily representative of how well samples can be reproduced, mainly because small amounts of sample matrix invariably degrade the measurement precision compared to a pure metal standard even when measuring at the same ion beam intensity. Matrix effects are difficult to quantify and also depend on the sample introduction equipment. However, experiments in which matrix effects were tested by way of doping samples with Tl of a known isotope composition showed no systematic Tl isotope offset due to residual sample matrix (Nielsen et al., 2004). Older studies did find a relationship between sample concentration and measurement uncertainty with the smallest uncertainties obtained for samples with the highest concentrations (Baker et al., 2009; Nielsen et al., 2004; Nielsen et al., 2007; Nielsen et al., 2006a), but the most recent studies have reported external reproducibility for real samples and reference materials that are only slightly worse than what can be achieved for the Aldrich standard (Coggon et al., 2014; Kersten et al., 2014; Nielsen et al., 2015; Prytulak et al., 2013) (Table 2).

In cases where the amount of sample is limited, it can become an important issue how many ions can be measured for a given amount of Tl. Over the last ten years MC-ICPMS instruments have been developed to achieve increased transmission (i.e. the fraction of the ions introduced into the machine that reach the collector) and the most recent instruments have values of >1% for Tl and Pb. This level of transmission routinely produces ion beam intensities of ~20nA for a solution containing 1μg/g Tl and enables Tl isotope analyses on samples as small as 1ng, without notably compromising counting statistics, and an external precision of better than ±1 ε-unit is achievable (Baker et al., 2009; Nielsen et al., 2015; Nielsen et al., 2004; Nielsen et al., 2007; Nielsen et al., 2006a). Smaller sample sizes down to 200pg can still be analyzed on regular Faraday collectors, although precision is significantly degraded to ±3 ε-units (Nielsen et al., 2007; Nielsen et al., 2006a; Nielsen et al., 2009b).

3. THALLIUM ISOTOPE VARIATION IN EXTRATERRESTRIAL MATERIALS

With a half-mass condensation temperature (the temperature at which half of the Tl in the solar nebula was condensed) of 532 K (Lodders, 2003), Tl is classified as a highly volatile element in cosmochemistry. In addition, Tl has also been termed as highly labile (Lipschutz and Woolum, 1988) because it is readily remobilized by processes that are recorded on asteroidal parent bodies and meteroids, including thermal metamorphism and shock heating. Importantly, both properties are conducive to the production of relatively large stable isotope fractionations, and these have been observed for both Tl and other highly volatile elements such as Cd (Wombacher et al., 2008; Wombacher et al., 2003) and Hg (Lauretta et al., 1999; Lauretta et al., 2001) in various extraterrestrial materials.

3.1. The ^{205}Pb–^{205}Tl decay system

The radiogenic Tl isotope variations recorded in meteorites reflect decay of the short-lived radionuclide ^{205}Pb to ^{205}Tl with a half-life of 15.1 Ma (Pengra et al., 1978). Interest in the ^{205}Pb–^{205}Tl decay system and the initial solar system abundance of ^{205}Pb was responsible for driving the first efforts to precisely determine the Tl isotope compositions of natural materials. In detail, the literature documents six attempts to identify radiogenic Tl isotope variations in iron meteorites and chondrites from 1960 to 1995 (Anders and Stevens, 1960; Arden and Cressey, 1984; Chen and Wasserburg, 1987, 1994; Huey and Kohman, 1972; Ostic et al., 1969). Whilst these studies were able to provide an upper limit for the initial solar system ^{205}Pb abundance they were unable to conclusively establish radiogenic Tl isotope variations from the decay of this now-extinct nuclide.

The strong historic interest in the ^{205}Pb–^{205}Tl decay system stems from studies of stellar nucleosynthesis, which indicate that ^{205}Pb is produced primarily or almost exclusively by s-process nucleosynthesis (Blake et al., 1973; Wasserburg et al., 2006; Wasserburg et al., 1994; Yokoi et al., 1985), whereby heavier elements are formed by slow neutron capture in the interior of stars. For astrophysicists, precise constraints on the initial solar system abundance of ^{205}Pb, gained from analyses of meteorites, would hence offer unique clues on the site and operation of s-process nucleosynthesis and the extent to which this process contributed to the freshly synthesized nucleosynthetic material that was delivered to the nascent solar system. In addition, the ^{205}Pb–^{205}Tl decay system is also of interest as a chronometer of volatile depletion as well as core formation and cooling. The latter applications follow from the observation that Pb/Tl ratios are likely to be fractionated by both processes, as (i) Pb, with a half-mass condensation temperature of 727 K (Lodders, 2003), is somewhat less volatile than Tl and (ii) Pb and Tl exhibit different extents of moderately siderophile and chalcophile affinity during metal-sulfide-silicate partitioning (Ballhaus et al., 2013; Jones et al., 1993; Wood et al., 2008).

Despite of the numerous potential applications, only relatively few Tl isotope studies of meteorites have been attempted using the much more precise MC-ICP-MS methods which superseded TIMS measurements following the pioneering study of Rehkämper and Halliday (1999). These investigations were all motivated by the ^{205}Pb–^{205}Tl chronometer but resolved both radiogenic and stable Tl isotope variations in various stony and iron meteorites. A summary of this work, key results, and cosmochemical implications are presented below.

3.2. Chondritic meteorites

3.2.1. Carbonaceous chondrites

Baker et al. (2010b) carried out a comprehensive study of 10 carbonaceous chondrites of groups CI1 (Orgueil), CM2 (incl. Murchison), CR2, CV3 (incl. Allende), and CO3. Two samples were excluded from the evaluation of radiogenic Tl isotope effects as they had fractionated Cd isotope compositions due to thermal processing (Wombacher et al., 2008; Wombacher et al., 2003), and this may have also affected Tl isotopes, whilst four samples were corrected for terrestrial Pb contributions of between 9 and 77% of total Pb, based on measured Pb isotope data.

Overall, the Tl and Pb concentrations of the meteorites varied by more than a factor of 5, between about 20 ng/g (in CR2 chondrites) to 100 ng/g (in Orgueil CI1) for Tl and 340 to 2200 ng/g for Pb. Importantly, the results showed a clear co-variation between Tl and Pb, which was used to derive average carbonaceous chondrite and, by inference, solar system Pb/Tl and ^{204}Pb/^{203}Tl ratios of 22±2 and 1.43±0.14 respectively (uncertainties are 2sd).

Furthermore, the samples revealed a small but significant correlated variability between Tl isotope compositions, with ε^{205}Tl values of −4.0 to +1.2, and ^{204}Pb/^{203}Tl ratios (Fig. 3). A number of observations, in particular unfractionated stable Cd isotope compositions in all the samples, indicate that this correlation is unlikely to be due to stable isotope fractionation from early solar system processes or terrestrial weathering, and is instead most readily explained by in situ decay of ^{205}Pb to ^{205}Tl. Previous ^{53}Mn–^{53}Cr and ^{107}Pd–^{107}Ag studies of bulk carbonaceous chondrites furthermore suggest that the Pb–Tl isochron records volatile fractionation in the solar nebula at close to 4567 Ma (Schönbächler et al., 2008; Shukolyukov and Lugmair, 2006). If this interpretation is correct, then the isochron of Fig. 3 yields the initial ^{205}Pb abundance and Tl isotope composition of the solar system, with values of $^{205}\mathrm{Pb}/^{204}\mathrm{Pb}_{SS,0}$ = (1.0±0.4)x10^{-3} and $\varepsilon^{205}\mathrm{Tl}_{SS,0}$ = −7.6±2.1, respectively. These results provide clear evidence for the existence of live ^{205}Pb in the early solar system. The inferred $^{205}\mathrm{Pb}/^{204}\mathrm{Pb}_{SS,0}$ ratio is close to the upper limit of nucleosynthetic production estimates for AGB stars (Wasserburg et al., 2006) and thus in accord with contributions of such stars to the early solar system budget of freshly synthesized nucleosynthetic matter.

3.2.2. Enstatite chondrites

Analyses were carried out on a suite of enstatites chondrites, comprised of three less metamorphosed samples from groups EL3, EH4 and three equilibrated meteorites from groups EH5 and EL6 (Palk et al., 2011). In detail, the EL3 and EH4 enstatite chondrites were found to have much higher volatile contents (of about 40 to 100 ng/g Tl) than the intensely metamorphosed samples of groups EH5 and EL6, which had Tl abundances of only about 5 ng/g Tl. Whilst four of the meteorites displayed moderate to extreme Cd isotope fractionations of up to $\varepsilon^{114/110}$Cd ≈ +70, only a single sample displayed a clearly fractionated Tl isotope composition with ε^{205}Tl ≈ +22. As this sample is known to be highly shocked (with a grade of S5), it is possible that Tl was mobilized and isotopically fractionated during shock metamorphism.

In contrast, all other enstatite chondrites yielded a narrow range of ε^{205}Tl values, with results of between –2.9 and +0.8. Given the limited isotopic variability, the observation of Tl (and more prevalent Cd) stable isotope fractionation, and the presence of terrestrial Pb contamination (in two meteorites) as revealed by Pb isotopes, a robust Pb-Tl isochron could not be obtained for the enstatite chondrites.

3.2.3. Ordinary chondrites

Only a single Pb-Tl study of ordinary chondrites has been attempted, with results reported for samples of groups L and LL (Andreasen et al., 2009). To minimize the problem of terrestrial Pb contamination, only meteorite falls were selected for analysis. Overall, these meteorites displayed a large spread in ^{204}Pb/^{203}Tl ratios from 1.7 to 152, as a result of large variations in Tl concentration (from 0.3 to 19 ng/g), whilst Pb abundances varied by less than a factor of 7. The Tl isotope compositions were also highly variable with ε^{205}Tl values of between about -20 to +15.

Given the observation of large Cd isotope fractionations in ordinary chondrites (Wombacher et al., 2008; Wombacher et al., 2003), the Tl isotope variability was assessed to distinguish radiogenic effects from clearly evident mass dependent Tl isotope fractionations, presumably from mobility and redistribution of Tl during thermal metamorphism. Consequently, the equilibrated LL and L chondrites (of type 4-6) were judged to show no evidence of radiogenic ^{205}Tl, indicating that the high Pb/Tl ratios were established by elemental redistribution after ^{205}Pb was extinct. In contrast, the Tl isotope compositions of unequilibrated LL3 chondrites were interpreted to reflect radiogenic ingrowth of ^{205}Tl, with a Pb-Tl age of about 45 Ma after solar system formation.

3.3. Iron meteorites

Due to the relatively high volatile element contents, IAB irons are the most straightforward iron meteorites for Tl isotope and Pb-Tl isochron analyses. Such measurements were also conducted for IIAB and IIIAB irons, but are significantly more difficult as much larger samples (generally more than 15 g; Nielsen et al. (2006a)) are required to obtain robust Tl isotope data and because the nearly ubiquitous terrestrial Pb contamination is more problematic due to the low meteoritic Pb contents. No data are currently available for the even more volatile depleted irons of groups IVA and IVB.

3.2.1. Non-magmatic IAB complex iron meteorites

Nielsen et al. (2006a) analyzed seven metal samples and five troilite nodules of the IAB main group irons Toluca and Canyon Diablo. The metal samples had Tl concentrations from about 0.03 ng/g to 16.5 ng/g and variable ^{204}Pb/^{203}Tl from about 0.1 to more than 75, equivalent to Pb/Tl ratios of between about 2 and 1200. Notably, the Tl isotope compositions, which ranged between ε^{205}Tl values of about -3 to +23 were observed to correlate with ^{204}Pb/^{203}Tl (Fig. 4). When interpreted as an isochron, this correlation corresponds to initial values of $^{205}\text{Pb}/^{204}\text{Pb}_0$ = (7.3±0.9) x 10^{-5} and $\varepsilon^{205}\text{Tl}_0$ = –2.2±1.5. Alternative explanations for the correlation, such as mixing of variably mass fractionated meteorite components or terrestrial contamination are difficult to reconcile with the results. Troilite nodules from Toluca and Canyon Diablo contain Tl that is generally significantly less radiogenic than the co-existing metal with isotope compositions that are variable and decoupled from $^{204}Pb/^{203}Tl$ (Fig. 4). These effects were interpreted to result from kinetic stable isotope fractionation during diffusion of Tl between metal and sulfide. Given the relatively low Tl contents of the troilites (with about 1.6 to 27 ng/g Tl) and the low overall abundance of sulfides in IAB irons (≤2% of mass), such processes are unlikely to have significantly affected the Tl isotope compositions of the co-existing metal.

Assuming a solar system initial $^{205}Pb/^{204}Pb_{SS,0} = (1.0\pm0.4)x10^{-3}$, as derived from carbonaceous chondrites (Fig. 3), the IAB isochron was established 57 +10/−14 Ma after the start of the solar system (Baker et al., 2010b). In comparison, recent Pd–Ag isochron studies of the same meteorite groups indicate that the Pd-Ag fractionation of IAB irons is only about 15 to 19 Ma younger than carbonaceous chondrites (Carlson and Hauri, 2001; Schönbächler et al., 2008; Theis et al., 2013; Woodland et al., 2005). The Pb–Tl and Pd–Ag ages are thus only barely consistent, within the combined uncertainties, hinting at possible discrepancies between the two ages. Most likely, the relatively young Pb–Tl isochron age of the IAB metals reflects late closure of this isotope system, due to a blocking temperature that is significantly lower than the 1100 K blocking temperature of the Pd-Ag chronometer (Sugiura and Hoshino, 2003) and possibly similar to that of the K–Ar system at 650 K (Renne, 2000; Trieloff et al., 2003). This interpretation is in accord with the highly labile nature of Tl, as opposed to Ag, during thermal processing (Lipschutz and Woolum, 1988).

Also not in accord with the IAB isochron are the results obtained for the anomalous IAB complex iron Mundrabilla (Fig. 4; (Nielsen et al., 2006a)). Two metal samples and a sulfide nodule of this meteorite were characterized by $\varepsilon^{205}Tl$ values of about +30 and +24, respectively. It is likely that the high $\varepsilon^{205}Tl$ found in Mundrabilla is not solely due to rapid radiogenic ingrowth of ^{205}Tl in a high Pb/Tl environment but also reflects, at least in part, significant stable isotope fractionations, most likely associated with volatile loss from or redistribution on the parent body.

3.3.2. Magmatic IIAB and IIIAB iron meteorites

Andreasen et al. (2012) conducted a comprehensive Pb-Tl isochron study of metal samples from six IIAB and six IIIAB iron meteorites. All samples were thoroughly leached prior to dissolution to remove terrestrial Pb contamination. The fraction of primordial Pb was then calculated by assuming that any deviation in the Pb isotope composition of the iron meteorites from primordial Pb is due to residual contributions from terrestrial Pb. The meteorite samples exhibited low and highly variable Tl contents ranging from 0.002 to 0.485 ng/g, with most Tl concentrations at less than 0.02 ng/g. The IIAB and IIIAB iron meteorites are hence, on average, significantly more depleted in Tl than the IAB irons.

The $^{204}Pb/^{203}Tl$ ratios of the meteorites (Fig. 5, (Andreasen et al., 2012)) varied from 0.05 to 5.8 for the IIAB irons (Pb/Tl ≈ 0.8 to 89) and from 1.6 to 14 for the IIIABs (Pb/Tl ≈ 26 to 215). As such, these magmatic irons have $^{204}Pb/^{203}Tl$ ratios that are noticeably less variable than in IABs (Fig. 4), and with many samples not far removed from the chondritic value of $^{204}Pb/^{203}Tl$ = 1.43 (Pb/Tl = 22). The $\varepsilon^{205}Tl$ values of the IIAB and IIIAB irons ranged from –18 to +23 (Fig. 5). The majority of the Tl isotope data, furthermore, display a correlation of $\varepsilon^{205}Tl$ with $^{204}Pb/^{203}Tl$, suggesting that the isotopic variations are primarily governed by decay of ^{205}Pb at variable Pb/Tl ratios.

Further Pb-Tl analyses for metal samples from two IIAB and two IIIAB irons and a IIIAB troilite nodule were reported by Nielsen et al. (2006a). For the IIABs, these data do not support the IIAB errorchron inferred by Andreasen et al. (2012) (Fig. 5). It is possible that this discrepancy arises, at least in part, from the less accurate correction of residual terrestrial Pb contamination that was utilized by Nielsen at al. (2006a) or possibly even minor terrestrial Tl contributions. Alternatively, the non-isochronous behavior of the IIABs analyzed by Nielsen at al. (2006a) may reflect late open system behavior and/or stable isotope fractionation of Tl in some samples. In contrast, the two IIIAB metals and the IIIAB troilite analyzed by Nielsen et al. (2006a) yield results, which are in accord with the IIIAB isochron reported by Andreasen et al. (2012) (Fig. 5).

Assuming that the IIAB data of Andreasen et al. (2012) indeed define a Pb-Tl isochron (Fig. 5), they correspond to an initial $^{205}Pb/^{204}Pb_0$ ratio of $(8.3\pm1.6)\times10^{-4}$. This ^{205}Pb abundance is equivalent to an age of 4 +16/-14 Ma, assuming an initial solar system abundance of $^{205}Pb/^{204}Pb_{SS,0} = (1.0\pm0.4)\times10^{-3}$, as defined by carbonaceous chondrites (Fig. 3) (Baker et al., 2010b). A similar but more uncertain initial ^{205}Pb abundance and a less well-constrained age of 4 +29/-14 Ma was obtained from the IIIAB correlation (Fig. 5). Both iron meteorite isochrons, however, have y-intercepts with initial $\varepsilon^{205}Tl_0$ values that are more negative (at $\varepsilon^{205}Tl_0 = -12\pm1$ for the IIABs) than the initial solar system value of $\varepsilon^{205}Tl_{SS,0} = -7.6\pm2.1$, as defined by the carbonaceous chondrites isochron (Fig. 3). It is conceivable that the observed offset of about 7 ε-units (at the chondritic value of $^{204}Pb/^{203}Tl = 1.43$) between the IIAB and the chondrite isochron reflects a nucleosynthetic isotope anomaly or is caused by stable Tl isotope fractionation. However, nucleosynthetic isotope effects of this magnitude are unlikely for Tl, as they are also not observed for other elements of similar atomic mass, such as Hf, Os, and Pt (Kruijer et al., 2013; Sprung et al., 2010; Walker, 2012; Yokoyama et al., 2007). Thallium isotope data acquired for metal-silicate and sulfide-silicate partitioning experiments furthermore demonstrate that Tl isotope fractionation during metal or sulfide segregation is either very small or absent (Wood et al., 2008).

As a consequence, Andreasen et al. (2012) suggested an alternative interpretation of the carbonaceous chondrite and magmatic iron meteorites isochrons. By discarding the results of all four carbonaceous chondrites, which featured significant quantities of terrestrial Pb contamination (at about 10 to 80% of total measured Pb), a revised carbonaceous chondrite isochron with a significantly steeper but less well-defined slope was obtained. This revised calculation yields $^{205}Pb/^{204}Pb_{SS,0}$ = (2±1)x10^{-3} and $\varepsilon^{205}Tl_{SS,0}$ = –13.6. Using this initial solar system $^{205}Pb_{SS,0}$ abundance, the IIAB and IIIAB isochrons now provide ages of 15 +20/-12 Ma and 14 +32/-15 Ma, respectively. It is unknown, however, whether these ages date core crystallization or are linked to the breakup of the meteorite parent bodies. Likewise the IAB isochron now gives a younger age of 69 +16/-10 Ma after the carbonaceous chondrites, and this may indicate that the Pb-Tl decay system dates the same impact event(s) that are recorded in the ~4.5 Ga Ar-Ar ages of IAB silicate inclusions (Vogel and Renne, 2008). Notably, the revised initial solar system ^{205}Pb abundance of $^{205}Pb/^{204}Pb_{SS,0}$ = (2±1)x10^{-3} is somewhat higher than the upper estimate that was obtained in models of s-process nucleosynthesis by Wasserburg et al (2006). Whether this discrepancy reflects uncertainties in the analytical data, the stellar models, or in the estimates of recent s-process contributions to the solar nebula, remains unclear at present.

3.3. Limitations of the ^{205}Pb–^{205}Tl chronometer

In principle, the ^{205}Pb–^{205}Tl decay system offers many promising applications but translation of this potential has been hindered by a number of factors. (i) Due to the low abundances of Tl in many meteorites, large samples of typically more than 1 g but with >10 g not uncommon, have been used for precise Tl isotope measurements. These requirements make analyses challenging and measurements for highly volatile depleted meteorites (e.g., IVA/B irons and many achondrites) have not been attempted to date. (ii) As a result of the highly labile nature of Tl, isochronous behavior is easily disturbed or fully reset. In addition, remobilization of Tl can be associated with stable isotope fractionation, which hampers unambiguous interpretations. (iii) The pervasive contamination of many meteorites with terrestrial Pb renders the determination of robust primitive $^{204}Pb/^{203}Tl$ ratios (as required for Pb-Tl isochron calculations) and initial $^{205}Pb/^{204}Pb$ values very difficult. Analyses of such contaminated meteorites requires that anthropogenic Pb is removed from samples by thorough cleaning and/or corrections for the effects of contamination must be attempted, based on Pb isotope data. Such corrections, however, can be subject to large uncertainties whilst aggressive cleaning of samples by leaching and/or partial dissolution (as is commonly applied prior to analyses of radiogenic Pb isotope compositions) can lead to partial Tl loss that may be associated with isotope fractionation.

4. THALLIUM ISOTOPE COMPOSITON OF THE SOLID EARTH

4.1. The primitive mantle

The concentration of Tl in the primitive mantle has been estimated as 0.0035 μg/g (McDonough and Sun, 1995) and for the depleted mantle as 0.00038 μg/g (Salters and Stracke, 2004). The challenge associated with evaluating the Tl concentration and isotope composition of the mantle is largely twofold. First, thallium concentrations are vanishingly low, thus grams of material are required to obtain precise concentration and/or isotope measurements by bulk rock dissolution approaches. Minute inclusions of secondary alteration products such as clays that easily incorporate Tl are much more problematic with very large sample sizes, and any such material can drastically affect the determination of both Tl concentration and isotope composition. Second, even though the required sample sizes are large, there is still worrying potential for 'nugget' effects. For example, Nielsen et al. (2014) have shown by laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS) that the only phase housing significant Tl in the Lherz peridotite massif, France, are interstitial sulfides, which yielded variable Tl concentrations from 0.023 to 0.430 μg/g. All other investigated mineral phases (olivine, orthopyroxene, clinopyroxene and spinel) had Tl concentrations below detection limit, restricting the Tl concentration in the vast majority of mantle minerals to < 0.001 μg/g (Nielsen et al., 2014). An experimental study by Kiseeva and Wood (2013) further documents Tl partition coefficients between sulfide liquid and a silicate melt with MORB composition of $D_{Tl}^{sulf/sil} = 4.1$ to 18.8, reinforcing the notion that sulfides are the main host for Tl, at least in the upper mantle. To date, only a single measurement of a mantle xenolith has been published (Nielsen et al., 2015). The sample, a harzburgite from the Eifel volcanic field in Germany, revealed an isotope composition of $\varepsilon^{205}Tl = -2.0 \pm 0.8$ and concentration of 1.05 ng/g. The concentration is, thus, slightly higher than what would be expected based on published estimates of Tl in the depleted mantle (Salters and Stracke, 2004), but given the potential for nugget effects it is unclear if the concentration is necessarily representative of the upper mantle.

Due to the problems associated with direct measurements, Nielsen et al. (2006b) used five fresh, glassy MORBs from different global ocean basins to estimate the Tl isotope composition of the mantle. The homogeneity of the results ($\varepsilon^{205}Tl_{MORB} = -2 \pm 1$; Fig 1) strongly indicates that no large-scale geographic Tl isotopic differences exist in the present day upper mantle uncontaminated by crustal components. Given that these lavas are not derived from identical degrees of melting, the restricted range in ε^{205}Tl strongly suggests that partial melting of the mantle does not fractionate Tl isotopes to an analytically resolvable level. This inference is further supported by the identical Tl isotope composition of these MORBs and the published harzburgite sample (Nielsen et al., 2015) and not unexpected, given the heavy atomic masses of Tl isotopes. However, since stable isotope fractionation has been observed for some lighter elements during mantle melting (e.g., Fe isotopes; (Craddock et al., 2013; Williams et al., 2004)), further Tl isotope analyses of MORB and peridotites are desirable to validate this assumption.

4.2. The continental crust

As discussed, Tl generally follows the alkali metals K, Rb and Cs during melting and fractional crystallization (Heinrichs et al., 1980; Shaw, 1952) resulting in much higher Tl concentrations in the continental crust (~0.5 μg/g) versus the primitive mantle (~0.0035 μg/g) (Heinrichs et al., 1980; McDonough and Sun, 1995; Rudnick and Gao, 2003; Shaw, 1952; Wedepohl, 1995).

Although the chemical affinity with K, Rb, and Cs suggests lithophile behavior, thallium has been considered both a chalcophile and lithophile element. McGoldrick et al. (1979) suggested that Tl displays chalcophile behavior and follows sulfur in sulfur-saturated magmas. In contrast, a study of sulfur-rich ore deposits (Baker et al., 2010a) found that Tl retained strong lithophile behavior in this setting. Noll et al. (1996) assumed that Tl behaved as a chalcophile element and used chalcophile/lithophile element ratios in subduction-related lavas to determine relative fluid mobility of trace elements. They suggested that Tl has a similar bulk partition coefficient to La. However, Tl showed no significant correlation with 'fluid-mobile' and chalcophile elements such as As, Sb and Pb, again casting doubt on its chalcophile affinity in evolving magmatic systems. A study of lavas from the Mariana arc also suggests lithophile, fluid-immobile behavior, demonstrated by strong co-variation of Tl with La, rather than Ba (Prytulak et al., 2013). Thus the elemental behavior of Tl during magmatic processes and the specific controls on its concentration in the continental crust remain ambiguous. This ambiguity is underlined by the strong affinity Tl has for sulfides formed in aqueous low temperature hydrothermal systems (Xiong, 2007), mantle sulfides and early diagenetic pyrite (Nielsen et al., 2011; Nielsen et al., 2014).

The lack of resolvable isotope differences in global MORB suggests that negligible Tl isotope fractionation occurs during moderate degrees of partial melting (15-20%). Given the evolved bulk composition of the continental crust, it is necessary to consider the impact of further igneous processes on Tl stable isotope fractionation. Though stable isotope fractionation has been documented during igneous processes for relatively heavy elements such as iron (e.g. Williams et al., 2004; Williams et al., 2009), the small relative mass difference between the isotopes of Tl in combination with little or no redox chemistry for Tl in igneous systems, favor negligible Tl isotope fractionation during magmatic processes. Several studies found that the isotope composition of the average upper continental crust, represented by loess, is indistinguishable from MORB, with both exhibiting a value of ε^{205}Tl = -2.0 ± 0.5 (Nielsen et al., 2007; Nielsen et al., 2006b; Nielsen et al., 2005b; Nielsen et al., 2006c). The uniform isotope composition of the continental crust is further supported by data obtained for an ultrapotassic dike from the Tibetan Plateau (ε^{205}Tl = -2.3 ± 0.5), which represents a melt originating from the sub-continental lithospheric mantle (Williams et al., 2001). Finally, Nielsen et al., (2016) recently determined ε^{205}Tl in a suite of co-genetic basalts through andesites from a single volcano on Atka Island in the Aleutian arc. Thallium concentrations display strong positive co-variation with K_2O wt%, as expected for an incompatible element during fractional crystallization. Although the lavas range in $\varepsilon^{205}Tl$ from -2.3 to +0.7, the isotope values do not co-vary with Tl concentration and the variability is instead attributed to subduction zone inputs. Hence, on balance, there is little evidence to suggest that melting or fractional crystallization imparts analytically resolvable Tl isotope fractionation and therefore the bulk continental crust can be characterized by $\varepsilon^{205}Tl_{CONTCRUST} = -2 \pm 1$ (Fig. 1).

5. THALLIUM ISOTOPE COMPOSITION OF SURFACE RESERVOIRS

5.1. Volcanic degassing

Due to its low boiling point (Table 1), Tl is significantly enriched in volcanic gasses and particles compared with the geochemically analogous alkali metals (Baker et al., 2009; Gauthier and Le Cloarec, 1998; Hinkley et al., 1994; Patterson and Settle, 1987). Consequently, volcanic plumes provide a large Tl flux from igneous to surface environments on Earth, with an estimated flux to the oceans of 370 Mg/a (Baker et al., 2009; Rehkämper and Nielsen, 2004). The behavior of Tl isotopes during degassing in volcanic systems was investigated by Baker et al. (2009), who identified significant isotope variations. The most likely form of isotope fractionation to occur during degassing is kinetic isotope fractionation, where the light isotope is enriched in the gas phase during evaporation. The extent of kinetic isotope fractionation between two phases is determined by the relative magnitude of the atomic or molecular velocities, where $\alpha = (m_1/m_2)^\beta$ and β varies from 0.5 (in the case of a vacuum) down to values approaching 0 (Tsuchiyama et al., 1994). Hence, even though the relative mass difference between the two Tl isotopes is small, the maximum kinetic $\alpha_{liq\text{-}vap}$ is 1.0049, equivalent to a fractionation factor of 49 ε-units. An isotopic difference of this magnitude exceeds the stable Tl isotope variability currently known for Earth and should hence be readily detectable. However, contrary to the expectation of a gas phase enriched in light isotopes, Baker et al. (2009) found no systematic enrichment of either ^{203}Tl or ^{205}Tl in volcanic emanations compared with average igneous rocks. Despite large isotopic differences between individual samples, the isotope compositions of 34 samples of gas condensates and particles from six separate volcanoes showed an average of ε^{205}Tl = -1.7 ± 2.0. This value is indistinguishable from average igneous rocks (Nielsen et al., 2007; Nielsen et al., 2006b; Nielsen et al., 2005b; Nielsen et al., 2006c; Nielsen et al., 2016; Prytulak et al., 2013) and suggests that degassing as a whole does not significantly alter that Tl isotope composition of degassed lavas. The Tl isotope variation of volcanic emanations was interpreted to reflect the complex evaporation as well as condensation processes that occur in volcanic edifices (Baker et al., 2009), and which eventually produce no net isotope fractionation between Tl in the magma and the Tl transported into the atmosphere and surface environments on Earth.

5.2. Weathering and riverine transport of Tl

Stable isotope fractionation during weathering is often monitored via measurements of isotope ratios in the dissolved and particulate phases in rivers. For example, elements like lithium and molybdenum have been shown to display significant isotopic variation between different rivers and rocks of the continental crust (e.g. Archer and Vance, 2008; Huh et al., 1998; Pogge von Strandmann et al., 2010). Numerous kinetic and equilibrium processes can potentially affect the stable isotope budgets of rivers, and as such it is difficult to predict isotope fractionation during weathering. In general, Tl is soluble in aqueous solution and should be readily mobilized during weathering. However, the tendency for Tl to partition into potassium rich minerals and manganese oxides (Heinrichs et al., 1980) suggests that the transport of Tl into the ocean may be less efficient. Nielsen et al. (2005b) measured the Tl isotope compositions of dissolved and particulate components for a number of major and minor rivers and found that these generally display values similar to those observed for continental crust. The average value for dissolved riverine Tl is ε^{205}Tl = -2.5 ± 1.0 (Nielsen et al., 2005b), with particulate matter (ε^{205}Tl = -2.0 ± 0.5) being indistinguishable from the dissolved phase (Table 3). Although there are clearly resolvable differences in riverine Tl isotope compositions that were inferred to be related to variations in catchment lithoiogies, the majority of rivers including the worlds largest, the Amazon, display ε^{205}Tl values similar to average continental crust. These data strongly imply that there is little or no Tl isotope fractionation associated with continental weathering processes.

Natural unpolluted Tl abundances in rivers are generally very low and vary between 1 and 10 pg/g (Cheam, 2001; Nielsen et al., 2005b). An estimated global average dissolved riverine concentration of 6±4 pg/g (or 30±20 pmol/l) results in a flux to the oceans of 230 Mg/yr. In the study of Nielsen et al. (2005b) three rivers exhibited Tl isotope compositions significantly lighter (at ε^{205}Tl = -6 to -4) than average continental crust (Table 3). The lower ε^{205}Tl values were interpreted to reflect weathering of marine carbonates that are a main constituent of the drainage areas for these rivers. Relatively light Tl isotope compositions are expected for such carbonates based on analyses of modern seawater, which is characterized by ε^{205}Tl = -6.0 ± 0.3 (Nielsen et al., 2004; Nielsen et al., 2006c; Owens et al., 2016; Rehkämper et al., 2002). However, marine carbonates including carbonate oozes (Rehkämper et al., 2004), corals (Rehkämper, unpublished data) and foraminifera (Nielsen, unpublished data) exhibit very low Tl concentrations. This implies that weathering of marine carbonates will only have a strong impact on the Tl inventories of rivers that predominantly drain such lithologies and will not strongly affect the total global budget of Tl transported by rivers to the oceans.

5.3. Anthropogenic mobilization of Tl

Similar to its periodic table neighbors Hg, Cd, and Pb, Tl is also readily volatilized by high-temperature processes, such as combustion. As a consequence, the most important global source of anthropogenic Tl are atmospheric emissions from processes such as pyrite roasting, cement production and coal burning, and associated solid wastes. In addition, Tl release with wastewater from ore processing plants can have a significant impact on terrestrial aquatic system (Nriagu, 1998; Peter and Viraraghavan, 2005).

Like its elemental neighbors, Tl also has a high acute and chronic toxicity to mammals, including humans. Due to the low concentrations of Tl in most natural and manufactured materials, and its limited use in consumer products or industrial processes, anthropogenic Tl emissions to the environment are fortunately generally low. They only represent a significant health hazard in the vicinity of significant emission sources, particularly when aided by bioaccumulation in the food chain (Nriagu, 1998; Peter and Viraraghavan, 2005). Such a case of chronic Tl poisoning was reported for the inhabitants of a rural village in the Lanmuchang area of Guizhou Province, China. The village is situated in close proximity to a massive vein of Tl mineralization that has a protracted history of artisanal mining (Xiao et al., 2003; Xiao et al., 2004). The health effects seen in the villagers (including muscle and joint pain, hair loss, and disturbance or even loss of vision) were traced to the consumption of local crops (particularly highly Tl-enriched green cabbage), which are grown on soils with elevated Tl concentrations from past mining activities (Xiao et al., 2004; Xiao et al., 2007).

The isotopic signature of Pb, which is highly variable due to radiogenic ingrowth from the decay of U and Th isotopes, has long been used to fingerprint anthropogenic Pb emissions to the environment, particularly from the use of leaded gasoline (Alleman et al., 1999; Rosman et al., 1994; Settle and Patterson, 1982). Following the advent and more widespread application of MC-ICP-MS, a number of studies demonstrated that similar fingerprinting is also feasible for Hg and Cd emissions, based on analyses of the stable isotope compositions of these elements (Rehkämper et al., 2012; Ridley and Stetson, 2006). More recently, an investigation by Kersten et al. (2014) demonstrated, for the first time, that Tl stable isotope compositions can also be used as a tracer of anthropogenic Tl emissions to the environment.

In the study of Kersten et al. (2014), Tl isotope data were used to link the high Tl contents of agricultural soils to past emissions of cement kiln dust (CKD) from a nearby cement plant in Lengerich, northwest Germany. In detail, it was shown that the soils were contaminated by Tl emissions that occurred in the 1970's, when the cement plant utilized pyrite-roasting waste with high Tl contents as a cost-effective, S-rich additive during cement production, a process that involves combustion processes at temperatures of more than 1000º C. To arrive at this conclusion, contaminated soil samples from three vertical profiles with up to 1 m depth were analyzed for both Tl concentrations and isotope compositions. When viewed in a diagram of ε^{205}Tl versus inverse Tl concentration (1/[Tl]), the soil data are strongly indicative of a binary mixing relationship (Fig. 6). The mixing endmembers were inferred to be the geogenic background, as defined by isotopically light soils with ε^{205}Tl ≈ -4 at depth, and the Tl emissions, represented by Tl-enriched topsoils with a distinctly heavier isotopic signature of ε^{205}Tl ≈ 0. This conclusion is further corroborated by Tl isotope compositions of ε^{205}Tl $\approx \pm 0$ that were obtained for (i) a CKD sample taken at the time of the inferred Tl emissions and (ii) a pyrite, which was sourced from the same Weggen deposit in Germany as the pyrite roasting waste that was added to the cement raw mix prior to combustion in the kiln (Fig. 6).

Additional analyses were carried out by Kersten et al. (2014) for soil and crop samples from the Lanmuchang area (Guizhou Province) in China. These measurements revealed significant isotope fractionation between soils, with a high natural Tl background characterized by ε^{205}Tl ≈ +0.4, and locally grown cabbage, which displayed ε^{205}Tl values of between –2.5 and –5.4. This demonstrates that biological isotope fractionation and subsequent remineralization of Tl from organic material cannot be responsible for the heavier Tl isotope signatures that were found in the Lengerich topsoil. Rather, the high Tl contents and associated heavier isotope signatures seen in the vicinity of the Lengerich cement plant are most reasonably explained by Tl emissions that were released during cement production (Kersten et al., 2014).

5.4. The isotope composition of seawater

In the oceans, Tl is a conservative, low-level trace element with an average dissolved concentration of 13±1 pg/g (64±5 pmol/l) (Flegal and Patterson, 1985; Nielsen et al., 2006c; Rehkämper and Nielsen, 2004; Schedlbauer and Heumann, 2000). The seawater average is thereby slightly higher than the dissolved Tl abundances of most rivers (see section 5.2). Based on a thorough review of the marine input and output fluxes of Tl, Rehkämper and Nielsen (2004) concluded that the oceans are currently at steady state and that Tl has a residence time of ~21 ka, which is consistent with a number of previous studies (Flegal and Patterson, 1985; Flegal et al., 1989). With an inferred marine residence time that is more than an order of magnitude longer than the ocean mixing time and a conservative distribution, Tl should exhibit an invariant isotope composition in seawater. Analyses of Arctic, Atlantic and Pacific seawater confirm this prediction (Nielsen et al., 2004; Nielsen et al., 2006c; Rehkämper et al., 2002). In particular, a recent data set for about 50 samples covering the GEOTRACES GA10 transect in the Atlantic across 40°S shows no Tl isotope variation, with an overall average of ε^{205}Tl = -6.0±0.3 (Owens et al., 2016). The invariance of the GA10 data is remarkable because a number of different water masses are present in this transect (Antarctic Bottom Water, North Atlantic Deep Water, Antarctic Intermediate Water) that are sourced from very disparate regions of the ocean. Therefore, these analyses confirm that the open ocean is homogenous with respect to Tl isotopes within current measurement uncertainties.

It may be somewhat surprising that the oceans are significantly enriched in ^{203}Tl compared to the continental crust and the mantle (see Section 4) with an average value of ε^{205}Tl = -6.0±0.3 (Nielsen et al., 2004; Nielsen et al., 2006c; Owens et al., 2016; Rehkämper et al., 2002). Hence, it is required either that the marine sources of Tl are isotopically light compared to the continental crust and mantle or that the outputs are fractionated towards heavy isotope compositions relative to seawater. Rehkämper and Nielsen (2004) showed that the most significant marine inputs for Tl are from rivers, high-temperature hydrothermal fluids, mineral aerosols, volcanic emanations and sediment pore water fluxes at continental margins. In contrast, there are only two important marine Tl sinks, namely Tl adsorption by the authigenic phases of pelagic clays and uptake of Tl during low-temperature alteration of oceanic crust. The relative magnitudes and isotope compositions of these fluxes are summarized in Table 4. In the following sections, we outline the main observations that follow from an assessment of these fluxes.

6. THE MARINE MASS BALANCE OF THALLIUM ISOTOPES

6.1. Thallium isotopes in marine input fluxes

As riverine and volcanic input fluxes were already discussed in previous sections, we will here focus on high-temperature hydrothermal fluids, mineral aerosols and sediment pore water fluxes from continental margins.

6.1.1. High temperature hydrothermal fluids

In hydrothermal systems where temperatures exceed ~150°C it has been shown that Tl behaves much like the alkali metals Rb and K (Metz and Trefry, 2000), and is leached from the oceanic crust by circulating fluids. The efficiency of this leaching process is roughly 90%, as shown by Ce/Tl ratios in the sheeted dike complex of ODP Hole 504B that are ~10 times higher than in pristine MORB (Fig. 7). This results in end-member high temperature hydrothermal fluids that exhibit Tl concentrations almost 500 times higher compared to ambient seawater (Metz and Trefry, 2000; Nielsen et al., 2006c). We can estimate the flux of Tl into the oceans (M_{Tl}) from high-T hydrothermal fluids by combining the average Tl concentration of MORB with the flux of ocean crust leached by high-T fluids, assuming 90% leaching efficiency:

$$M_{Tl} = F_{oc\ leach} \times [Tl]_{oc} \times f_{Tl\ leach} \quad (2)$$

Here, $F_{oc\ leach}$ is the annual production rate of ocean crust that is leached by high-T fluids, $[Tl]_{oc}$ is the Tl content of the crust prior to leaching, and $f_{Tl\ leach}$ is the fraction of Tl leached from the rocks during alteration. The annual production rate of ocean crust leached by high-T fluids is comprised of ~$1.24\pm0.16\times10^{16}$ g/a of MORB crust and ~$0.76\pm0.10\times10^{16}$ g/a of cumulate lower ocean crust with Tl concentration estimated at 25% of the fresh MORB value (Mottl, 2003; Nielsen et al., 2006c).

It was previously thought that Tl partitioned similarly to Cs during mantle melting (Jochum and Verma, 1996; Nielsen et al., 2006b), which, based on an assumed Cs/Tl ≈ 6, yielded a Tl content of ~3 ng/g for fresh MORB. However, more recent data has shown that Tl is much more compatible during mantle melting because it partitions into sulfides (Kiseeva and Wood, 2013; Nielsen et al., 2014). Although there is a relatively large database for Tl concentrations in fresh MORB (Jenner and O'Neill, 2012; Nielsen et al., 2014), the global average Tl concentration for MORB is best determined by combining the constant Ce/Tl = 1110±330 for MORB with >6% MgO (Nielsen et al., 2014) with the global weighted average Ce concentration for MORB of 14.86±1.26 μg/g (Gale et al., 2013), because Ce data for MORB have a complete global coverage. This combination yields a global average Tl concentration in MORB of 13.4±4.2 ng/g, which is similar to the value obtained by averaging all available Tl data for MORB (12±8ng/g) (Jenner and O'Neill, 2012; Nielsen et al., 2014). Inserting the three parameters into equation (2) produces an annual Tl flux into the ocean from high-T hydrothermal fluids of 170±60 Mg/yr.

Due to the relatively high temperatures involved (300-400°C), isotope fractionation is not expected to be significant. This inference was confirmed by Nielsen et al. (2006c), who determined the Tl isotope composition of hydrothermal fluids from the East Pacific Rise and Juan de Fuca Ridge. All samples had Tl isotope compositions identical to that of average MORB, thus supporting the interpretation that extraction of Tl from the oceanic crust is not associated with isotope fractionation. The chemical and isotopic behavior inferred for Tl from hydrothermal fluids is furthermore in accord with the results of a study of oceanic crust altered by high temperature hydrothermal fluids from ODP Hole 504B. The latter work revealed Tl concentrations for basalts and dikes that were much lower than expected for depleted ocean crust whilst the Tl isotope compositions were identical to average MORB (Nielsen et al., 2006c).

6.1.2. Mineral aerosols

There are no direct investigations of Tl abundances or isotope compositions for mineral aerosols deposited in the oceans. Based on studies of windborne loess sediments deposited on land, Nielsen et al. (2005b) concluded that the average abundance of Tl in dust deposited in the oceans is about 490±130 ng/g. The main uncertainty in determining the Tl flux to the oceans is from estimating the fraction of Tl that is released from the dust into seawater, following deposition and partial dissolution. By comparison with a number of other elements, Rehkämper and Nielsen (2004) concluded that about 5-30% of the Tl transported in aerosol particles would dissolve in seawater, resulting in an annual Tl flux of 10 – 150 Mg/yr.

It may be reasonable to assume that the bulk Tl isotope composition of the material transported to the ocean is identical to loess, and thereby also the continental crust, with $\varepsilon^{205}Tl$ = -2 (Nielsen et al., 2005b). However, it is unknown whether dust dissolution is associated with isotope fractionation. Schauble (2007) has shown that significant equilibrium Tl isotope fractionations will be produced primarily by chemical reactions that involve both valence states, Tl^{+} and Tl^{3+}. Based on the strongly correlated behavior of Tl, Rb, Cs and K in the continental crust, univalent Tl should be dominant in mineral aerosols. Thermodynamic calculations of the valence state of Tl in seawater also predict that all Tl is univalent in this reservoir (Nielsen et al., 2009a). In addition, continental weathering processes, which are ultimately controlled by aqueous dissolution of silicates and are therefore in some ways analogous to the partial dissolution of dust in seawater, induce no detectable Tl isotope fractionations (Nielsen et al., 2005b). Hence, we infer that isotope fractionation is unlikely to be significant during the dissolution of mineral aerosols in seawater.

6.1.3. Benthic fluxes from continental margins

It has long been known that pore waters, which seep into the oceans from reduced continental margin sediments, are rich in Mn (Elderfield, 1976; Sawlan and Murray, 1983). As Tl has a high affinity to Mn oxides (Koschinsky and Hein, 2003) and is more soluble in seawater than Mn, it has been inferred that such pore waters may be an important source of dissolved marine Tl (Rehkämper and Nielsen, 2004). However, there are currently no direct data available for sediment pore fluids to constrain either the average Tl concentration or isotope composition of these benthic fluxes. An estimate was therefore derived indirectly, based on (1) Tl/Mn ratios observed in ferromanganese nodules that were known to have precipitated from pore waters (Rehkämper et al., 2002), combined with (2) estimates for benthic Mn fluxes (Heggie et al., 1987; Johnson et al., 1992; Sawlan and Murray, 1983). Taken together, these data yield a Tl flux of 5 – 390 Mg/a, and a best estimate of 170 Mg/a (Rehkämper and Nielsen, 2004), which constitutes a substantial fraction of the total Tl flux to the oceans (Table 4).

We can use two distinct approaches to estimate the average Tl isotope composition of pore waters. The first utilizes published Tl isotope data for the various components that may supply pore waters. The second relies on the Tl isotope compositions of sediments, which contain a component that was precipitated from pore waters. The application of these approaches is summarized below.

There are three principle components, from which Tl could be mobilized and incorporated into sedimentary pore waters. (1) Labile Tl associated with riverine particles (Nielsen et al., 2005b). (2) Thallium adsorbed onto clay minerals from seawater (Matthews and Riley, 1970). (3) Thallium bound to authigenic Mn-oxides that precipitated from seawater as part of pelagic red clays (Rehkämper et al., 2004). All three will be present in continental margin sediments in various proportions depending on sedimentation rate and proximity to estuaries, where high sedimentation rates will tend to dilute the Mn-oxides, as authigenic precipitation should remain fairly constant. Hence, assuming that there is no isotope fractionation associated with the release of Tl into pore waters, the isotope composition of each component provides bounds on the composition of pore waters.

The labile components in riverine particles have been shown to be isotopically similar to the continental crust and river waters and are thus characterized by ε^{205}Tl = -2 (Nielsen et al., 2005b). Matthews and Riley (1970) showed that Tl is readily adsorbed onto some clay minerals (in particular illite) where most Tl is exchanged with K. Because of the required charge balance for adsorption reactions, Tl adsorption onto clays is unlikely to be associated with any Tl reduction/oxidation and should thereby exhibit only minimal or no isotope fractionation (Schauble, 2007). Since Tl adsorption by clay minerals will take place primarily within the marine environment, this component should inherit the Tl isotope composition from seawater of ε^{205}Tl = -6.0.

Thallium that is precipitated with Mn oxides onto sedimentary particles has been shown to have a significantly heavier isotope composition than the seawater from which the mineral forms (Rehkämper et al., 2004; Rehkämper et al., 2002). The origin of this isotope fractionation is discussed in section 5 below. Theoretically, the pure MnO_2 mineral to which Tl is bound should have approximately the same isotope composition as the surfaces of Fe-Mn crusts, which display ε^{205}Tl ≈ +13 (Fig. 8). However, leaching experiments conducted on shelf sediments with HCl and hydroxylamine hydrochloride indicate that the labile Tl on sediment particles features somewhat lower ε^{205}Tl values of between +3 to +7 (Nielsen et al., 2005b; Rehkämper et al., 2004). These lower values could reflect contributions from components other than Fe-Mn oxides, particularly Tl incorporated into carbonates or adsorbed to clay minerals, with both presumably characterized by negative ε^{205}Tl. Nevertheless, it appears reasonable to infer that the Tl associated with marine authigenic Mn in continental margin sediments exhibits ε^{205}Tl ≈ +4 to +10.

In summary, the isotopic data available for these three components indicate that pore waters from continental margin sediments are likely to feature ε^{205}Tl values of about -4 to +6. This range can be compared with the compositions of two different sedimentary archives that form from pore waters. These are diagenetic ferromanganese nodules (which are inferred to originate primarily from pore waters) and early diagenetic pyrite. Rehkämper et al. (2002) analyzed two Mn nodules from the Baltic Sea and these exhibited ε^{205}Tl = -0.2 and -5.2. Nielsen et al. (2011) measured Tl isotopes in pyrites younger than 10 Ma from continental shelf sediments in the Northeast Pacific and the Caribbean and found ε^{205}Tl values of between -1 to +2. Importantly, both ferromanganese nodules and pyrites have Tl isotope compositions that are in accord with the range of values inferred for pore waters based on their constituent components. Taken together (and assuming that there is negligible isotope fractionation between pyrite/Fe-Mn nodules and pore waters) these constraints suggests that benthic fluxes from continental shelf sediments are characterized by ε^{205}Tl ~ -3 to +3, with a best estimate of ε^{205}Tl ≈ 0.

6.2. Thallium isotope compositions of marine output fluxes

6.2.1. Thallium adsorption by the authigenic phases of pelagic clays

There is a significant enrichment of Tl in pelagic clays compared with continental shelf sediments (Heinrichs et al., 1980; Matthews and Riley, 1970; Rehkämper et al., 2004). This enrichment is caused by the adsorption of Tl onto hydrogenetic Fe-Mn oxy-hydroxides and clay minerals (Heinrichs et al., 1980; Matthews and Riley, 1970; McGoldrick et al., 1979). Two independent methods of calculating the Tl flux associated with these authigenic fluxes agree very well and indicate an annual flux of 200-410 Mg/a, with a best estimate of 270 Mg/a (Rehkämper and Nielsen, 2004). If the smaller flux of Tl incorporated into pure Fe-Mn deposits of ~40 Mg/a (Rehkämper and Nielsen, 2004) is also considered, this yields a total marine authigenic Tl flux of 310 Mg/a (Table 4). As discussed in section 6.1.3, the isotope composition of the Tl associated with authigenic phases is best approximated as a mixture of Tl bound to Mn oxides that probably display ε^{205}Tl ≈ +13 and Tl adsorbed onto clay minerals, which likely exhibit the composition of seawater (ε^{205}Tl ≈ -6). Due to the strong enrichment of Mn in pelagic clays, it can be assumed that the majority of authigenic Tl in such sediments originates from Mn oxides and thus may have an isotope composition more akin to Fe-Mn crusts. We can attempt to quantify this effect by performing an isotope mass balance calculation for the modern (core-top) pelagic clays reported in Rehkämper et al. (2004). The bulk isotope composition of these samples is ε^{205}Tl = +3 to +5. About 50% of the Tl in pelagic clays is thought to be of detrital origin (Rehkämper et al., 2004), which is characterized by ε^{205}Tl = -2 (Nielsen et al., 2005b). In order to account for the reported bulk isotope compositions, the authigenic component would thus have to display ε^{205}Tl ~ +8 to +12, and this implies that the authigenic Tl of pelagic clays features an isotope composition that is slightly lighter than pure Fe-Mn deposits. Based on the above considerations we can calculate that ~75-95% of the authigenic Tl in pelagic clays originates from Mn-oxides, whilst the remainder is bound to clay minerals.

6.2.2. Thallium uptake during low temperature hydrothermal alteration

It is well known that alteration minerals produced by interaction between cold (<100°C) seawater and MORB are highly enriched in Tl compared to pristine oceanic crust (Alt, 1995; Jochum and Verma, 1996; McGoldrick et al., 1979), and this leads to a strong Tl enrichment in the upper 500-600m of the oceanic crust (Fig. 7a). It is unclear, however, which alteration mineral(s) are primarily responsible for accommodating the additional Tl. Palagonitization causes substantial deposition of Tl, which has been attributed to partitioning into smectites and other alkali-rich clay minerals (Jochum and Verma, 1996; McGoldrick et al., 1979). In contrast, altered assemblages from IODP Hole U1301B appear to show correlations between bulk Tl and S concentrations, which led to the interpretation that the main carrier phase for Tl during hydrothermal alteration is pyrite (Coggon et al., 2014). Lastly, composites from several depth intervals in Jurassic oceanic crust from ODP Hole 801C showed no clear Tl enrichment and limited isotope fractionation compared with $\varepsilon^{205}Tl_{MORB}$ = -2±1 (Fig. 7). The uncertainties in depositional mechanism, combined with the highly heterogeneous distribution of Tl in low-T altered oceanic crust (Coggon et al., 2014; Nielsen et al., 2006c; Prytulak et al., 2013; Teagle et al., 1996), complicate efforts to estimate the average Tl concentration of low-T altered oceanic crust and determine the annual flux of Tl into this reservoir. Following a conservative approach it was proposed that, on average, the upper 600m of oceanic crust contains 200±150 ng/g of Tl (Nielsen et al., 2006c), although the number is based mostly on inferred values rather than actual data. The Tl concentration estimate is equivalent to an element flux of 225-1985 Mg/a, with a best estimate of ~1000 Mg/yr. The preferred estimate, however, is similar to the combined flux of all marine Tl inputs (Table 4).

Given the uncertainties, it may thus be more reasonable to apply a mass balance approach (which assumes that marine Tl is at steady state) to estimate the Tl flux into low-T altered ocean crust. With a total input flux of 990 Mg/a (Table 4) and an authigenic output flux of 310 Mg/a, the marine Tl budget can be balanced with a low-T alteration output of 680 Mg/a, which is well within the range of values estimated based on Tl concentration data available for low-T altered ocean crust (Table 4). The reconstructed marine Tl mass balance yields a residence time of ~18.5 ka, which is within error of previous estimates of ~21 ka (Flegal and Patterson, 1985; Rehkämper and Nielsen, 2004).

The isotope composition of the low-T alteration output is equally difficult to determine. Nielsen et al. (2006c) observed that, in general, the upper oceanic crust is significantly enriched in isotopically light Tl with the shallowest samples displaying the lightest isotope compositions (Fig. 7b). This isotopic signature was interpreted to reflect closed system isotope fractionation during uptake of Tl from seawater, which gradually becomes more depleted in Tl as it penetrated deeper into the oceanic crust. As shown by a Rayleigh fractionation model in which an isotope fractionation factor of $\alpha = 0.9985$ was applied (Nielsen et al., 2006c), the isotope composition of the total Tl deposited during low-T alteration depends critically on the fraction of Tl that is extracted from the seawater before it is re-injected into the oceans as a low-T hydrothermal fluid. Stripping the fluid of all Tl originally present would imply an isotope composition for the low-T alteration flux that is identical to seawater (ε^{205}Tl = -6), whilst lower degrees of depletion result in lighter isotope compositions.

Based on the isotope fractionation observed for rocks from ODP Hole 504B, it was estimated that extraction of ~50% of the original seawater Tl by ocean crust alteration would yield an average isotope composition of ε^{205}Tl ~ -18 for the Tl deposited during low-T alteration. The application of this approach to obtain a global estimate for the average Tl isotope composition of the low-T alteration flux is fraught with many uncertainties, however, as the database is currently limited to rocks from just three sections of altered ocean crust (504B, 801C, U1301B) and Tl concentration measurements for 3 low-T fluids from the Juan de Fuca ridge (Nielsen et al., 2006c). In principle, average altered upper ocean crust can be characterized by an ε^{205}Tl value of between about -18 to -6. Hence it may again be more appropriate to apply an isotope mass balance approach to obtain a more accurate result. With an isotope composition of ε^{205}Tl ≈ -1.8 for the combined marine Tl input fluxes and an authigenic output flux of ε^{205}Tl ≈ +10, mass balance dictates that the altered basalt flux is characterized by ε^{205}Tl ≈ -7.2 (Table 4). This result is certainly within the range of reasonable values but based on Rayleigh fractionation modeling it requires that more than 95% of seawater Tl is removed by alteration processes, which is not fully supported by the data obtained for ODP Hole 504B (Nielsen et al., 2006c) and IODP Hole U1301B (Coggon et al., 2014). It is unlikely, however, that the results obtained for these two relatively young (<5Ma) sections of oceanic crust are representative for global average ocean crust alteration processes. On the other hand, the Jurassic oceanic crust at ODP Hole 801C was found to have only limited Tl enrichment. This may reflect the low Tl concentration of ambient seawater at the time, as a consequence of enhanced incorporation of Tl into the abundant euxinic sediments of the Jurassic and Cretaceous, during which most of the alteration at ODP 801C took place (Prytulak et al., 2013).

7. CAUSES OF THALLIUM ISOTOPE FRACTIONATION

In general, Tl isotope variations on Earth are fairly limited, with only a few environments displaying significant deviations from the MORB and continental crust value of ε^{205}Tl = -2 (Nielsen et al., 2007; Nielsen et al., 2006b; Nielsen et al., 2005b; Nielsen et al., 2006c). However, the overall magnitude of Tl isotope variations in natural environments on Earth now exceeds 35 ε^{205}Tl-units (Coggon et al., 2014; Nielsen et al., 2006c; Rehkämper et al., 2004; Rehkämper et al., 2002). This variability is substantially larger than what is expected based on classical stable isotope fractionation theory (Bigeleisen and Mayer, 1947; Urey, 1947) and it is therefore important to understand the fundamental processes responsible for the Tl isotope variability.

There are two principle mechanisms by which most stable isotope fractionations are generated – a kinetic route that is associated with unidirectional processes and an equilibrium pathway, which acts during chemical exchange reactions. Both mechanisms should scale with the relative mass difference between the two isotopes of interest. In principle, kinetic isotope fractionation is capable of generating substantial Tl isotope effects (see Section 5.1) and there is evidence that such processes are recorded in volcanic fumaroles and some meteorites (Baker et al., 2009; Baker et al., 2010b; Nielsen et al., 2006a). However, the large Tl isotope fractionations observed between seawater and Fe-Mn oxy-hydroxides are more likely to reflect equilibrium isotope effects (Nielsen et al., 2006c; Rehkämper et al., 2002).

The larger-than-expected Tl isotope effects of equilibrium reactions were shown by Schauble (2007) to be partially caused by the so-called nuclear field shift isotope fractionation mechanism (Bigeleisen, 1996). In short, the fundamental equilibrium isotope exchange equation of Bigeleisen and Mayer (1947) has five components, of which four were deemed negligible.

However, based on unusual isotope fractionation effects observed for uranium (Fujii et al., 1989a; Fujii et al., 1989b), it was concluded that the equilibrium term caused by nuclear field shifts may be important in some cases (Bigeleisen, 1996). Thus, nuclear field shift isotope fractionation is also an equilibrium isotope fractionation term, with a magnitude that scales broadly with the mass of the isotopes and hence is largest for heavy elements (Knyazev and Myasoedov, 2001; Schauble, 2007). The calculations that were carried out for Tl isotopes predict that an equilibrium system with aqueous dissolved Tl^{+} and Tl^{3+} will feature both regular mass dependent and nuclear field shift isotope effects, with isotope fractionation factors that act in the same direction (Schauble, 2007). When combined, these two components can reproduce the approximate magnitude of Tl isotope variation observed on Earth (Schauble, 2007). The calculations are particularly relevant for the isotope compositions determined for Fe-Mn crusts and low-T altered basalts as these represent the heaviest and lightest reservoirs, respectively, found to date. The main requirement for substantial equilibrium Tl isotope fractionation to take place, is a chemical exchange reaction that involves two valence states of Tl (Schauble, 2007), and these could be Tl^{0}, Tl^{+} or Tl^{3+}. However, the calculations of Schauble (2007) also imply that the largest isotope effects are expected if Tl^{3+} is present.

Based on these theoretical considerations, experimental work was conducted to investigate the mechanism for Tl isotope fractionation during adsorption onto hydrogenetic Fe-Mn crusts (Fig. 8) and other Fe-Mn sediments (Nielsen et al., 2013; Peacock and Moon, 2012). The majority of Tl in these deposits is associated with MnO_2 minerals (Koschinsky and Hein, 2003; Peacock and Moon, 2012) and the isotope fractionation is therefore likely to occur at or in such phases. The EXAFS/XANES spectra for Tl sorbed onto Mn-oxides have shown that the MnO_2 phase hexagonal birnessite has the capacity to oxidize Tl^{+} to Tl^{3+}, following Tl sorption as a univalent ion (Bidoglio et al., 1993; Peacock and Moon, 2012). This reaction appears to be associated with isotope fractionation whereas sorption of Tl onto other MnO_2 mineral structures (e.g., todorokite) with less oxidation potential, is not associated with significant isotope effects (Nielsen et al., 2013). Several series of experiments revealed that Tl sorbed to birnessite is systematically enriched in ^{205}Tl (Nielsen et al., 2013), which is in agreement with Tl isotope data for Fe-Mn crusts and seawater (Owens et al., 2016; Rehkämper et al., 2002). However, the experimental isotope fractionation factors measured for aqueous univalent Tl versus Tl sorbed to birnessite were more variable and lower than the constant isotopic fractionation observed between Fe-Mn crusts and seawater (Fig. 8). This discrepancy was interpreted to reflect sorption of Tl to two distinct sorption sites on birnessite: one associated with significant isotope fractionation and one with little or none. If this interpretation is correct, then Tl in natural Fe-Mn crusts either occupies only sorption sites with isotope fractionation or the distribution of Tl between the two types of sites is fairly constant in nature.

In summary, observation (Rehkämper et al., 2002), theory (Schauble, 2007) and experiments (Nielsen et al., 2013) provide a relatively consistent picture of the mechanism responsible for Tl isotope fractionation during sorption to Mn oxides. However, it is still unknown what effects, if any, there are on the magnitude of Tl isotope fractionation during sorption to Mn oxides as a function of temperature, pH, ionic strength or other parameters.

The isotope fractionation effects found in low-T altered ocean crust are much less well understood. In this environment, Tl is extracted from seawater circulating through the ocean crust with an isotope fractionation factor of about $\alpha = 0.9985$ (Coggon et al., 2014; Nielsen et al., 2006c). It is conceivable that these fractionations reflect kinetic isotope effects, for example as a result of more rapid diffusion of the light isotopes from the hydrothermal fluid to the alteration minerals that concentrate Tl. If an equilibrium reaction is responsible, Tl^{3+} is likely to be involved because large equilibrium isotope effects are not expected for reactions without this species (Schauble, 2007). Simple models of Tl speciation in seawater predict that only Tl^{+} is present (Nielsen et al., 2009a) and this implies that the hydrothermal processes, which deposit Tl in the oceanic crust should produce Tl^{3+}. This inference is in accord with the observation that Tl^{3+} has a much lower aqueous solubility than Tl^{+} (Nriagu, 1998) and this implies that trivalent Tl should be deposited during hydrothermal alteration. However, these conclusions strongly contradict observations, which demonstrate that low-T hydrothermal alteration generally occurs at conditions that are more reducing than those prevalent in the open ocean (Alt et al., 1996). In addition, isotope fractionation calculations indicate that oxidized Tl should be enriched in ^{205}Tl (Schauble, 2007), which is at odds with the light Tl isotope signatures observed in altered basalts.

In summary, the large Tl isotope variability observed in the marine environment is most likely produced by a combination of conventional mass dependent and nuclear field shift equilibrium isotope fractionation processes. Contributions from kinetic isotope effects are also possible, but primarily for Tl incorporation during low-T ocean crust alteration. In order to reproduce the magnitude of equilibrium isotope fractionation observed for natural samples, reduction-oxidation processes, in which oxidized Tl^{3+} plays a central role, are predicted to be important.

8. APPLICATIONS OF THALLIUM ISOTOPES

8.1. Studies of Tl isotopes in Fe-Mn crusts

Hydrogenetic Fe-Mn crusts grow on hard substrates that experience little or no regular detrital sedimentation, for example on seamounts where ocean currents prevent gravitational settling of particles (Hein et al., 2000). They precipitate directly from the ambient water mass in which they are bathed and feature growth rates of a few mm/Ma (Eisenhauer et al., 1992; Segl et al., 1989; Segl et al., 1984). This implies that samples with a thickness exceeding 10 cm may provide a continuous seawater record for the entire Cenozoic (the last ~65 Ma). Over the last 20 years, extensive investigations of Fe-Mn crusts have been conducted to infer changes in the radiogenic isotope compositions of various elements in deep ocean waters (e.g. Frank, 2002; Lee et al., 1999). Depending on the marine residence time for the element investigated, the isotopic variability has mainly been interpreted as reflecting changes in ocean circulation patterns or the marine source and/or sink fluxes (Burton et al., 1997; van de Flierdt et al., 2004).

The globally uniform Tl isotope compositions observed for the surfaces of Fe-Mn crusts (Fig. 8), imply a constant equilibrium isotope fractionation between seawater and Tl incorporated into the Fe-Mn crusts. Time-dependent variations of Tl isotope compositions in Fe-Mn crusts can be interpreted to reflect either changes in the isotope fractionation factor between seawater and Fe-Mn crusts or the Tl isotope composition of seawater. In principle, both interpretations are feasible, but several lines of reasoning currently favor the latter explanation (Nielsen et al., 2009a; Rehkämper et al., 2004).

Two studies have determined Tl isotope depth profiles for several Fe-Mn crusts, and both identified large systematic changes in Tl isotope compositions (Nielsen et al., 2009a; Rehkämper et al., 2004). The first study produced low-resolution depth profiles for a number of samples. The largest Tl isotope variations were observed for the early Cenozoic (Rehkämper et al., 2004), but the low sampling density and uncertainties in the age models of the crusts precluded a precise determination of the timing and duration of the observed changes. It was furthermore argued that the Fe-Mn crusts record variations in the Tl isotope composition of seawater that were caused by changes in the marine input and/or output fluxes of this element (Rehkämper et al., 2004). The second study generated high resolution Tl isotope time series for two Fe-Mn crusts. Improved age models were applied, which resolved a single large shift in Tl isotope composition, which occurred between ~55 and ~45 Ma (Fig. 9; (Nielsen et al., 2009a)). Based on an improved understanding of the marine input and output fluxes of Tl and their respective isotope compositions, it was proposed that the large shift in the ε^{205}Tl value of seawater reflects a decrease in the amount of authigenic Mn oxides that were deposited with pelagic sediments in the early Eocene (Nielsen et al., 2009a).

It is difficult to assess the underlying mechanism responsible for this global change in Mn oxide precipitation. The strong co-variation of the Tl isotope curve with the sulfur (S) isotope composition of seawater (Fig. 9) may imply, however, that the same mechanism is driving the shift in the isotopic evolution of both stable isotope systems, even though S isotopes are known to be unaffected (at least directly) by changes in Mn oxide precipitation. Baker et al. (2009) proposed that the inferred high Mn oxide precipitation rates for the Paleocene (~65-55 Ma) may be explained by increased deposition of Fe- and Mn-rich volcanic ash particles in the oceans. Such volcanic activity would also supply isotopically light S and this could explain the relatively low δ^{34}S value for seawater at this time. The changes in the Tl and S isotope compositions of the oceans between ~55 and ~45 Ma (Fig. 9) would then be controlled by diminishing volcanic activity (Wallmann, 2001). An alternative model proposes that Mn oxide precipitation is controlled by biological utilization and burial of Mn with organic carbon (Nielsen et al., 2009a). Higher organic carbon burial rates would lead to diminished Mn oxide precipitation rates as less Mn would be available in the water column. Simultaneously, the increased organic carbon burial would result in higher rates of sedimentary pyrite burial, which draws isotopically light S out of seawater (Berner, 1984). In summary, the results of initial paleoceanographic studies indicate that it may be possible to utilize Tl isotopes as a proxy for changes in marine Mn sources and/or Mn oxide precipitation rates back in time.

8.2. Calculation of hydrothermal fluid fluxes using Tl isotopes in the ocean crust

Hydrothermal fluids are expelled from the seafloor (i) at high temperature on mid ocean ridge axes, as fueled by the magmatic energy from the crystallization and cooling of newly produced ocean crust to ~300-400°C and (ii) at lower temperatures on the ridge flanks, as the ocean crust cools further over millions of years. These hydrothermal fluxes play pivotal roles in controlling seawater chemistry, but the magnitude of the high temperature water flux at mid-ocean ridge axes remains widely disputed, whilst the volume of low temperature vent fluids expelled at ridge flanks is essentially unconstrained.

As discussed in sections 6.1.1 and 6.2.2, Tl displays distinct behavior during high and low temperature hydrothermal alteration of the ocean crust. High-T fluids effectively leach Tl from the cooling rocks whereas low-T fluids deposit Tl into the upper part of the oceanic crust. Following Nielsen et al. (2006c), a mass balance equation can be constructed for the high-T hydrothermal fluid flux (F_{hT}):

$$F_{hT} \text{ x } [Tl]_{hT} = M_{Tl} \quad (3)$$

where $[Tl]_{hT}$ is the average Tl concentration of the vent fluids and, as defined in equation (2), M_{Tl} is the annual flux of Tl expelled into the ocean via high-T hydrothermal fluids. When the Tl flux of 170±60 Mg/a determined from equation (2) is combined with $[Tl]_{hT}$ = 6.7±0.7 ng/g (Nielsen et al., 2006c), we obtain a high temperature hydrothermal water flux of 2.5±0.9 x 10^{13} kg/a. This fluid flux corresponds to 50-80% of the heat available at mid-ocean ridge axes from the crystallization and cooling of the freshly formed ocean crust (Mottl, 2003). The difference between the available heat at mid-ocean ridge axes and that expelled via hydrothermal fluids requires that some energy at mid ocean ridge axes is lost via conduction and/or through the circulation of intermediate temperature hydrothermal fluids that do not alter the chemical budgets of Tl in the ocean crust (Nielsen et al., 2006c).

For the low-T hydrothermal fluid circulation flux (F_{lT}), the following mass balance equation was shown to apply (Nielsen et al., 2006c):

$$F_{vz} \times ([Tl]_{avz} - [Tl]_{pvz}) = F_{lT} \times [Tl]_{sw} \times f_{upt} \quad (4)$$

where F_{vz} is the mass flux of newly produced ocean crust that is affected by low-T alteration, $[Tl]_{avz}$, $[Tl]_{pvz}$, and $[Tl]_{sw}$ are the Tl concentrations of the altered volcanic zone basalts, their pristine equivalents and seawater, respectively. The fraction of Tl that is removed from seawater by basalt weathering is denoted by f_{upt}. As discussed in section 6.2.2, $[Tl]_{avz}$ is extremely difficult to assess because the oceanic crust at ODP Holes 504B, 896A and U1301B is younger than 5Ma, which means that hydrothermal alteration is still ongoing at these locations. Analyses of Jurassic oceanic crust at ODP Hole 801C revealed little to no Tl enrichment (Fig. 7), possibly due to much lower Tl concentrations in seawater at the time (Prytulak et al., 2013). A meaningful assessment of Tl accumulation in oceanic crust that experienced complete hydrothermal alteration is hence currently not possible. The Tl enrichment factors observed for rocks from drill holes in young oceanic crust (Fig. 7) are, therefore, likely minimum estimates. The remaining parameters are more easily determined, but the large uncertainty on $[Tl]_{avz}$ generates estimates for the low-T hydrothermal fluid fluxes at ridge flanks that are also highly uncertain at 0.2-5.4 x 10^{17} kg/a (Nielsen et al., 2006c). Using the ridge flank power output of 7.1 TW (Mottl, 2003), it was calculated that such fluids have an average temperature anomaly of only about 0.1 to 3.6°C relative to ambient seawater, which is lower than most flank fluids sampled to date. It is therefore unclear how representative low-T fluids sampled to date are of average low-T ocean crust alteration processes.

In order to improve the utility of Tl mass balance calculations to constrain hydrothermal fluid fluxes it will be essential to obtain more data on altered ocean crust from a number of locations and particularly for older sections of altered oceanic crust. However, Jurassic ocean crust appears to not follow the general pattern of strong Tl enrichment during low-T alteration and this may reflect the particular marine conditions of this era (Prytulak et al., 2013). Analyses of intermediate-age altered oceanic crust (20-100Ma) will provide improved constraints on the behavior of Tl during hydrothermal processes and may thus ultimately yield more reliable Tl-based estimates of global hydrothermal water fluxes.

8.3 High temperature terrestrial applications

8.3.1 Mineral Deposits

The accumulation of Tl via hydrothermal activity and the association of Tl and S, suggests obvious potential applications for Tl elemental systematics and isotope signatures in mineral deposit exploration. The significantly elevated concentrations of Tl in many mineral deposits furthermore allows analyses of mineral separates, which are often at the limits of analytical capabilities in barren igneous systems. Such investigations provide useful information on the magnitude and direction of natural mineral fractionation factors. For example, it is of interest to determine if Tl-enriched minerals have a distinctive Tl isotope ‘fingerprint’ that could dominate bulk rock assays and thus aid exploration activities.

The first economically focused study of thallium and thallium isotopes was undertaken by Baker et al. (2010a), who investigated a porphyry copper deposit hosted in the Collahuasi Formation of northern Chile. These authors examined whole rock andesite, dacite, rhyolite and Cu-porphyry samples. The concentration of thallium was found to vary over an order of magnitude from 0.1 to 3.2 μg/g, correlating with K and Rb, and not Cu, thus indicting that Tl displays lithophile rather than chalcophile behavior in this system (Baker et al., 2010a). The isotope compositions ranged from ε^{205}Tl = -5.1 to +0.1, which is not unusual in terms of the range of ε^{205}Tl seen in barren terrestrial igneous rocks (Fig. 1). The five examined porphyry samples had very restricted ε^{205}Tl values of -1.9±0.1, identical to $\varepsilon^{205}Tl_{MORB}$. Thus there appears little potential for fingerprinting Cu porphyry rocks with Tl isotopes. Furthermore, there were no clear, systematic relationships between ε^{205}Tl and major and trace element data or alteration minerals, which also limits the diagnostic potential for Tl isotopes in Cu porphyry systems.

Hettmann et al. (2014) addressed the magnitude of Tl isotope fractionation between different sulfide melts by examining the Pb-As-Tl-Zn deposit at the Lengenbach quarry in Switzerland. The Lengenbach deposit is notable for its abundance of rare Tl-bearing minerals, including hatchite ($AgTlPbAs_2S_5$) with an extreme thallium concentration of up to 24.8 wt%. The high concentrations of Tl in the ore minerals allowed isotopic analysis of individual mineral phases and thus an evaluation of potential isotope fractionation induced by sulfide melt/mineral partitioning. The overall range of ε^{205}Tl measured in sulfides, sulfosalts and micas spans ε^{205}Tl =

-4.1 to +1.9. As for the Collahuasi deposit, the substantial range in Tl isotope compositions over a geographically restricted area was not accompanied by a clear co-variation with other chemical characteristics or mineralogy. Complicated processes including both hydrothermal and sulfide melt inputs and subsequent formation and dissolution of secondary phases are likely responsible for the general lack of coherent behavior. Certainly, the Tl concentrations documented are amongst the highest measured in natural materials, yet the isotopic variability, whilst large, is again within the range of barren igneous rocks.

Given the significant and resolvable variability in ε^{205}Tl for both examined deposits, there is clearly much to be explored in terms of individual mineral controls on isotope signatures and the potential effects of fluid mineral partitioning at different pH, fO_2 and T. The utility of Tl isotopes to fingerprint economically viable deposits, however, remains to be convincingly demonstrated.

8.3.2 The Tl isotope composition of arc lavas

Subduction related magmas are classically considered to be derived from a depleted mantle wedge, chemically flavored by percent-level addition of sediments and/or fluids released from the subducting slab. Due to the large diversity of Tl concentrations and isotope compositions among these three reservoirs (Fig. 1), Tl isotopes appear to be uniquely suited to disentangle these sources and investigate the petrogenesis of subduction-related lavas. Although back arc spreading may cause the mantle wedge to be more depleted than the source of mid-ocean ridge basalts, to a first order, the depleted upper mantle is a reasonable estimate for the Tl content and isotope composition of the mantle wedge. The Tl concentration of the depleted mantle is orders of magnitude lower than possible inputs to the system in the form of sediments and fluids from the altered oceanic crust (Fig. 1). In addition to the large concentration contrast between ‘background’ mantle and possible inputs, the two most commonly invoked inputs have opposite vectors of isotope fractionation. As discussed in sections 6.2.1 and 6.2.2, pelagic sediments rich in Mn oxides are characterized by positive ε^{205}Tl whilst altered oceanic crust and, by inference, slab fluids derived thereof are expected to yield negative ε^{205}Tl signatures. Thus, even minor addition of Mn oxide rich sediments or low-T altered basalts to a mantle wedge can result not only in analytically resolvable Tl isotope signatures, but also identify the type of input a specific lava has experienced. Finally, Tl isotope measurements may be able to contribute to the debate over the petrogenesis of so-called ‘adakite’ lavas (Kay, 1978), whereby one long-standing hypothesis proposes that they are produced by direct melting of the (altered) basaltic portion of the subducting slab.

The prediction is straightforward: lavas with trace element chemistry indicative of fluid contributions are expected to have light Tl isotope signatures, whilst sediment-influenced lavas are expected to be isotopically heavy. However, Tl isotope measurements of lavas from the Mariana subduction zone display very little isotopic variation, with ε^{205}Tl values from -1.8 to -0.4. One lava falls outside this range, with a heavy ε^{205}Tl of +1.2, which was suggested to be due to volcanic degassing (Prytulak et al., 2013). Hence, even though volcanic degassing broadly speaking has little impact on the Tl isotope composition of lavas and the continental crust (see section 5.1), individual samples may be affected by this process and must be assessed in studies of subaerial volcanism. The remaining data from the Mariana arc are reasonable, in that the measured inputs to the system, including sediments and altered ocean crust from ODP Hole 801C, did not show the same variability of Tl isotope compositions that was documented in similar lithologies elsewhere. In addition, a subsequent study of Mariana forearc serpentinites revealed that Tl sourced from pelagic sediments was released with fluids from the subducting sediments that caused serpentinization of the forearc peridotites (Nielsen et al., 2015). This result suggests that the Tl isotope signature of subducting sediments may be altered in the forearc before they enter the subarc mantle. This process could be an important mechanism of subduction zone cycling for Tl and other trace metals that concentrate in Mn oxides. In summary, the Tl isotope data for Mariana arc lavas demonstrates a situation where isotopically invariant inputs produce similarly invariant outputs. This is a key finding, as it provides evidence that the subduction process itself does not fractionate Tl isotopes (Prytulak et al., 2013).

The only other subduction zone that has been investigated for Tl isotopes is the Aleutian arc (Nielsen et al., 2016). The Aleutians are notable for along strike variation in subduction parameters, such as slab dip, slab velocity, and variable sediment lithologies dominated by volcaniclastic in the East to pelagic clay in the West. In addition, the Aleutians contain the type locality for so-called adakite lavas, from Adak Island, Alaska. Nielsen et al. (2016) analyzed both lavas and sedimentary lithologies outboard of the arc and demonstrated that the $\varepsilon^{205}Tl$ values of the lavas closely follow the sediment values, whereby the latter change systematically along the arc, with the Central Aleutian sediments and lavas showing enrichments in ^{205}Tl relative to the Eastern Aleutians. This finding further strengthens the conclusion that subduction processes do not fractionate Tl isotopes and which are thus useful for tracing inputs that are isotopically distinct from the background mantle. Nielsen et al. (2016) also determined the Tl isotopic composition of the lava originally used to define adakites (Defant and Drummond, 1990; Kay, 1978). As expected, the sample has a light $\varepsilon^{205}Tl$ of -3.3, in general agreement with the hypothesis that adakites incorporate melts from the altered basaltic ocean crust (Nielsen et al., 2016).

8.3.3 The Tl isotope composition of ocean island basalts (OIB)

The recycling of sediments and oceanic crust is a central tenant of mantle geochemistry and has been the subject of intense research over the past 35 years (e.g. Hofmann, 2014). Many investigations focus on ocean island basalts, which are argued to be generated at pressures >2.5GPa in the mantle, and thus significantly deeper than mid-ocean ridge basalts. Though still debated, there is some consensus that many ocean island basalts are produced by anomalously hot mantle plumes, thus offering a reasonable explanation why their locations are independent of tectonic plate boundaries (Hofmann, 2014; Hofmann and White, 1982). Traditional approaches to deduce the nature of OIB mantle sources employ a combination of trace element and radiogenic isotope data to distinguish sediment and/or crustal additions. As radiogenic isotopes reflect the time-integrated parent–daughter trace element ratio, there is inescapable ambiguity associated with their employment, with the same isotope signature permissibly generated by markedly different evolution paths.

Stable isotope analyses offer important complementary constraints to measurements that apply radiogenic isotope systems. Some of the earliest applications of stable isotopes to high temperature geochemistry encompass studies of O and Li to trace processes such as ocean crust alteration (Alt et al., 1986; Chan et al., 2002). However, light elements like O and Li are known to record isotope fractionation even during processes that occur at elevated mantle temperatures (Jeffcoate et al., 2007; Marschall et al., 2007; Williams et al., 2009) and their mantle concentrations are relatively high, such that the isotope composition of a mantle source is not readily affected by admixing of sediment and/or ocean crust (Elliott et al., 2004; Thirlwall et al., 2004). However, the concentration contrast and magnitude of isotope fractionation offered by the Tl isotope system is favorable for overcoming these obstacles.

To date, OIB samples from the Azores, Iceland and Hawaii have been investigated (Nielsen et al., 2007; Nielsen et al., 2006b). As it is unclear whether the Azores basalts were affected by post-eruptional alteration (Nielsen et al., 2007), these data will not be discussed in the following. Samples from Hawaii exhibit the most convincing Tl isotope evidence for the presence of sediments in the mantle source (Fig. 10). In detail, about 8 ppm of pure Fe-Mn sediment is sufficient to explain the positive ε^{205}Tl values of up to +4 recorded in these lavas. Whilst it is unlikely that the Tl isotope variation originates from anything else than Fe-Mn sediment, it is uncertain if this component was acquired by the melts during magma ascent via assimilation of modern marine deposits or if it is a feature of the mantle source. The samples with the heaviest Tl isotope compositions are, however, also characterized by the least radiogenic Pb isotope compositions (Nielsen et al., 2006b) which would argue for an old age of the sedimentary component.

The relatively straightforward interpretation of the Tl isotope data for Hawaii could be considered a "smoking gun" for the presence of recycled sediments in the Hawaiian mantle plume and, indeed, agrees with independent constraints from Hf isotopes (Blichert-Toft et al., 1999). However, results obtained for of a suite of lavas from Iceland strongly indicate that there is some way to go before Tl isotopes can be confidently applied as a unique tracer of crustal recycling within the mantle. Seventeen Icelandic samples, including picrites that span all major eruption centers of the island, exhibit an average $\varepsilon^{205}Tl = -1.6 \pm 1.1$, completely overlapping with $\varepsilon^{205}Tl_{MORB}$. In contrast to the isotopic homogeneity, Cs/Tl ratios vary from 0.3 to 11. The isotopic invariance is perhaps unsurprising given that the thickness of subducted oceanic lithosphere exceeds 30km. Thallium isotope anomalies will be situated in only the uppermost ~500 to 1000m, whilst the remainder of the oceanic crust is expected to be isotopically identical to the ambient mantle. The mantle-like Tl isotope signatures of the Iceland basalts hence do not argue against the presence of recycled ocean crust in the plume source. Of more concern is that the samples display variable Cs/Tl ratios. The large observed Cs/Tl range demonstrates that processes other than the addition of Fe-Mn sediments and low-T altered basalts may alter this ratio. It is conceivable that this includes igneous processes, such as partitioning of Tl into sulfides and/or phyllosilicates, Tl mobilization by magmatic fluids (Nielsen et al., 2007) and/or fractionation by accessory phases in the subducted material (e.g., phengite; (Prytulak et al., 2013)).

Finally, it is prudent to consider three key caveats for the application of Tl isotopes in mantle geochemistry. First, it is likely that the Tl isotope composition of seawater has not remained constant over time (Fig. 9) and the isotope signatures of altered basalts and Fe-Mn sediments are therefore also expected to exhibit temporal variability. Any such variability will obscure the mixing trends that are produced by contamination of the ambient mantle with recycled material. Second, whilst it is unclear when the oceans became sufficiently oxic to support the precipitation of Mn oxides, this probably occurred after ~2.4 Ga (Canfield, 1998). Sediments that were recycled more than 2.4 billion years ago are therefore unlikely to be enriched in Tl associated with Mn oxides and are hence probably characterized by ε^{205}Tl ≈ -2. The isotope fractionation mechanism responsible for the highly negative ε^{205}Tl values of modern altered ocean crusts is yet to be determined. Hence, it is unclear whether such basalts are also isotopically fractionated in ancient environments and if past oceanic crust recycling was able to alter the Tl isotope composition of the mantle. Third, it needs to be acknowledged that Tl can also be *too* sensitive as a tracer. Even much less than 1% of subaerial or submarine contamination by secondary clays or precipitation of Mn oxides can have a drastic impact on the

Tl concentration and isotope signature of a basalt. Great attention must therefore be paid to sample preparation and selection. For example, the careful leaching experiments for submarine samples conducted by Nielsen et al. (2016) should be considered a minimum requirement to establish confidence in the determined ε^{205}Tl isotope signatures of submarine lavas with low Tl concentrations.

9. FUTURE DIRECTIONS AND OUTLOOK

High precision measurements of Tl isotope compositions have only been possible for little more than a decade but despite of this, we have already acquired a surprisingly detailed understanding of the diverse isotopic behavior of this element. Significant gaps in knowledge remain, however.

Most meteorite samples display resolvable variations in Tl isotope compositions with an overall isotopic variability of about 50 ε^{205}Tl. In many samples, the isotopic variation appears to be caused by both radiogenic decay of extinct ^{205}Pb and stable isotope fractionations, which reflect the highly volatile and labile nature of Tl. The difficulty of deconvolving these two sources of isotopic variability restricts the utility of both the ^{205}Pb-^{205}Tl chronometer and the Tl stable isotope system to inform on early solar system processes. Nonetheless, further studies of suitable meteorites (including carbonaceous chondrites) are desirable to better constrain the initial solar system abundance of ^{205}Pb, as this is a unique tracer of freshly synthesized s-process material that was delivered to the nascent solar system.

For the Earth, it is desirable to further expand the Tl isotope and concentration database for various environments, in order to gain a better understanding of the geochemical distribution and cycling of this element. In addition, there are a few crucial investigations that are needed to advance the utility of Tl isotopes as quantitative tracers of past and present geological processes.

First of all, we must fully understand the mechanisms that govern the two major Tl isotope effects observed on Earth, which produce highly fractionated Tl isotope signatures in marine Mn oxides and low-T altered basalts. Experimental studies have shown that Tl oxidation and adsorption to the Mn oxide birnessite is clearly the central processes responsible for the heavy isotope ratios recorded in Mn oxide rich marine sediments (Nielsen et al., 2013; Peacock and Moon, 2012). However, the magnitude of isotope fractionation and the effect of changes in intensive parameters like T, redox potential and ionic strength are presently unknown. Further studies of both natural and synthetic systems that mimic the conditions of Mn oxide precipitation and low-T ocean crust alteration are required to establish the mechanisms controlling Tl isotope fractionation in these two critical reservoirs. This knowledge will not only help expand our appreciation of the physico-chemical processes that cause isotope fractionation in heavy elements, but also enable us to better utilize the Tl isotope system to quantify low-T hydrothermal fluid flow (Nielsen et al., 2006c) and help to unravel the causes of the Tl isotope variations observed in the marine environment over time (Baker et al., 2009; Nielsen et al., 2009a).

Furthermore, it will be important to refine the three applications outlined in section 8. For the paleoceanographic studies, this will include a detailed determination of the magnitude and isotope compositions of the most uncertain marine Tl fluxes. These are the fluxes associated with benthic pore waters, adsorption processes on pelagic clays and low-T hydrothermal alteration. A complete understanding of the modern marine Tl cycle is a prerequisite for good models of past Tl isotope variations. Another aspect of the oceanic Tl isotope evolution that has yet to be investigated are short-term fluctuations, for example on glacial-interglacial time-scales or ocean anoxic events. Since the marine residence time of Tl is about 18.5 ka (Table 4), it should be feasible to observe perturbations of the Tl cycle that occur on geologically rapid time-scales. To this end, a recent study of Tl isotopes in euxinic sediments has revealed no detectable isotope fractionation between seawater and sediment (Owens et al., 2016). This is an important result because such sediments may now enable reconstruction of marine Tl isotope signatures in deep time.

The use of Tl isotopes as a tool in mantle geochemistry is currently limited by scant data. Thallium isotope and concentration data are presently available only for a few OIB and there is a lack of understanding concerning how Tl is cycled through subduction zones. Recent studies that attempted to address such questions through Tl isotope analyses of cratonic eclogites (Nielsen et al., 2009b) and island arc lavas (Nielsen et al., 2016; Prytulak et al., 2013) were unable to conclusively constrain the behavior of Tl and further investigations of rocks from subduction related environments are thus necessary.

The application of Tl isotopes as a tracer of anthropogenic Tl emissions to the environment has been shown to be viable in an initial study (Kersten et al., 2014) and hence shows promise for future investigations. However, whilst Tl is a highly toxic element, it shows low concentrations in most natural materials and is used to only a limited extent in industrial products and processes. Hence, Tl isotopes are unlikely to develop into a widely used tracer of anthropogenic emission, similar to radiogenic Pb isotope compositions, but will be of utility to trace Tl origin and mobility in particular, localized pollution scenarios.

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Table 1: Physical properties of thallium (Nriagu, 1998)

Melting point	577 K
Molar weight	204.38 g
Density	11.85 g/cm^3
Valence states	Tl^0 Tl^+ Tl^{3+}
Redox potentials (V)	
$Tl_{(s)} \rightarrow Tl^+ + e^-$	+0.336
$Tl^+ \rightarrow Tl^{3+} + 2e^-$	-1.28
Ionic radius (Tl^+)	1.50 Å
Ionic radius (Tl^{3+})	0.89 Å
Stable isotopes	^{203}Tl ^{205}Tl

Table 2: Tl isotope and concentration data for geologic reference materials

Standard	Description	ε^{205}Tl	n	Error[a]	Tl conc (ng/g)	Reference
Nod P1	USGS Ferromanganese nodule	0.5	1	0.5	146000	1
Nod A1[b]	USGS Ferromanganese nodule	10.7	6	0.5	108000	1,2
AGV-2	USGS Andesite	-3.0	8	0.6	269	3,4
BCR-2	USGS Columbia River basalt	-2.5	4	0.4	257	3
BHVO-1	USGS Hawaii Basalt	-3.5	10	0.5	37	3,8
BHVO-2	USGS Hawaii Basalt	-1.8	17	0.3	18	3,4,7
BIR-1	USGS Iceland basalt	1.1	6	1.2	1.3	5
NASS-5	Atlantic surface seawater	-5.0	1	1.0	0.0094	2
Allende	Carbonaceous chondrite	-3.1	8	0.5	55	6
BHVO-2G	USGS Basaltic glass	nd			16	9
BCR-2G	USGS Basaltic glass	nd			234	9
BIR-1G	USGS Basaltic glass	nd			2.5	9

References 1: (Rehkämper et al., 2002); 2: (Nielsen et al., 2004); 3:(Prytulak et al., 2013); 4: (Baker et al., 2009); 5: (Nielsen et al., 2007); 6: (Baker et al., 2010b); 7: (Coggon et al., 2014); 8: (Nielsen et al., 2015); 9: (Nielsen and Lee, 2013)

[a] – errors are either 2sd of the population of separate sample splits processed individually ($n \geq 3$) or estimated based on repeat measurements of similar samples (n=1).

[b] – Isotope composition reported for multiple analyses of one large 300mg aliquot dissolved in 6M HCl.

nd - not determined

Table 3: Thallium isotope and concentration data for rivers

Sample	$\varepsilon^{205}Tl_{diss}$	Tl_{diss} (ng/kg)	$\varepsilon^{205}Tl_{part}$	Tl_{part} (ng/kg)
Amazon	-2.3	16.4		
Danube	-6.7	16.4	-2.9	3.6
Doubs	-5.5	3.36		
Eder	-4.2	1.93		
Kalix	-1.6	1.31	-3.8	0.29
Nahe	-2.5	7.03	-1.2	3.7
Nidda	-2.7	1.67		
Nidder	-2.6	2.85	-1.6	0.26
Nile	0.0	3.13		
Rhine Rueun	-6.4	3.61		
Rhine Laufenbg.	-3.0	4.04		
Rhine Speyer	-2.8	5.35		
Rhine Bingen	-2.9	6.71	-2.1	1.3
Rhone	-2.7	6.54	-2.2	36
Volga	-1.1	1.60		

Uncertainty on Tl isotope measurements is ±1 ε^{205}Tl-unit

Exact sample locations are given in Nielsen et al. (2005b)

Table 4: The Tl mass balance of the oceans with estimated source and sink fluxes.

	Range of Tl flux estimates (Mg/a)	Best estimate (Mg/a)		$\varepsilon^{205}Tl$	Ref.
Marine Input Fluxes					
Rivers	76 – 380	230	23%	-2.5	1, 2
Hydrothermal fluids	110 – 230	170	17%	-2	3, 9
Subaerial volcanism	42 – 700	370	37%	-2	6
Mineral aerosols	10 – 150	50	5%	-2	1, 2
Benthic fluxes from continental margins	5 – 390	170	17%	0	1, 7
Total Input Flux	465 – 1850	990	100%	-1.8	
Marine Output Fluxes					
Pelagic clays	240 – 450	310	36%	+10	1, 4, 7
Altered ocean crust	225 – 1985	680	64%	-7.2	1, 3, 7
Total Output Flux	465 –1850	940	100%	-1.8	

	Mass of Tl (Mg)	Steady-state residence time	$\varepsilon^{205}Tl$	
Global Oceans	1.75 (±0.14) x 10^7*	18,500 a	-6.0	1, 3, 5, 8

References 1: (Rehkämper and Nielsen, 2004); 2: (Nielsen et al., 2005b); 3: (Nielsen et al., 2006c); 4: (Rehkämper et al., 2004); 5: (Rehkämper et al., 2002); 6: (Baker et al., 2009); 7: This study; 8: (Owens et al., 2016); 9: This work.

* For a global ocean system with 1.348 x 10^{21} kg, the Tl mass in the oceans is equivalent to an average seawater concentration of 65±5 pmol/kg or 13±1 ng/kg (Rehkämper and Nielsen, 2004).

FIGURE CAPTIONS:

Figure 1: Thallium isotope compositions and concentrations for terrestrial reservoirs relevant to subduction zones and recycled oceanic crust. Note the logarithmic scale for the concentrations. Data sourced from (Nielsen, 2010; Nielsen et al., 2015; Nielsen et al., 2006b; Nielsen et al., 2005a; Nielsen et al., 2006c; Nielsen et al., 2014; Nielsen et al., 2016; Prytulak et al., 2013; Rehkämper et al., 2004; Rehkämper et al., 2002).

Figure 2: Anion exchange separation procedures for Tl. The recipes can be scaled to any amount of resin (RV – resin volume) depending on sample size, though large samples require a second 100µl resin column to ensure that Tl is sufficiently pure. Four different elution procedures are outlined, as published by Baker et al., Nielsen et al. and Rehkämper and Halliday (2009; 2004; 1999).

Fig. 3. Pb–Tl isochron diagram for carbonaceous chondrites (modified from Baker et al., 2010b). Excluded from the plot and isochron calculation are two meteorites that exhibit stable Cd isotope fractionations as well as a sample of Allende Smithsonian due to contamination with terrestrial Pb (Baker et al., 2010b). All error bars are 2sd.

Fig. 4. Pb–Tl isochron diagrams for metal samples (filled symbols) and sulfides (open symbols) of IAB complex iron meteorites, based on the results of Nielsen et al. (2006a). The metal samples of Toluca and Canyon Diablo (CD) delineate a well-defined isochron. The isochron slope is slightly revised from Nielsen et al. (2006a), due to improved corrections for terrestrial Pb. The troilite nodules of these meteorites and metal and sulfide from the anomalous

IAB iron Mundrabilla do not plot on the IAB main group isochron defined by Toluca and Canyon Diablo, presumably due to stable isotope fractionation of Tl. All error bars are 2sd.

Fig. 5. Pb–Tl isochron diagram for metal samples of IIAB (squares) and IIIAB (diamonds) iron meteorites. The large and small symbols, with 2sd error bars, denote the data of Andreasen et al. (2012) and Nielsen et al. (2006a), respectively. The open diamond is for a troilite nodule of Grant IIIAB. Despite of the scatter and some large uncertainties, the results for both groups of magmatic irons display a positive correlation, which is indicative of radiogenic variations in Tl isotope composition from in situ decay of ^{205}Pb. The two errorchron trendlines were calculated from the data of Andreasen et al. (2012) only and correspond to initial $^{205}Pb/^{204}Pb_0$ ratios of $(8\pm2)x10^{-4}$ and $(8\pm4)x10^{-4}$ for the IIABs and the IIIABs, respectively.

Figure 6: Plot of ε^{205}Tl vs. 1/total Tl concentration for soil samples from the vicinity of the Lengerich cement plant in Germany (modified from Kersten et al., 2014). Furthermore shown are results for a pyrite from the Meggen deposit (which is also the ultimate origin of the Tl-rich additive that was used in cement production) and the cement kiln dust (CKD). The linear trend and associated correlation coefficient R^2 were calculated from the soil data only. All error bars are 2sd.

Figure 7: Plots of (a) Ce/Tl and (b) Tl isotopes against depth for different sections of hydrothermally altered oceanic crust. Data compiled from (Coggon et al., 2014; Nielsen et al., 2006c; Prytulak et al., 2013; Teagle et al., 1996). The samples with error bars from ODP 801C

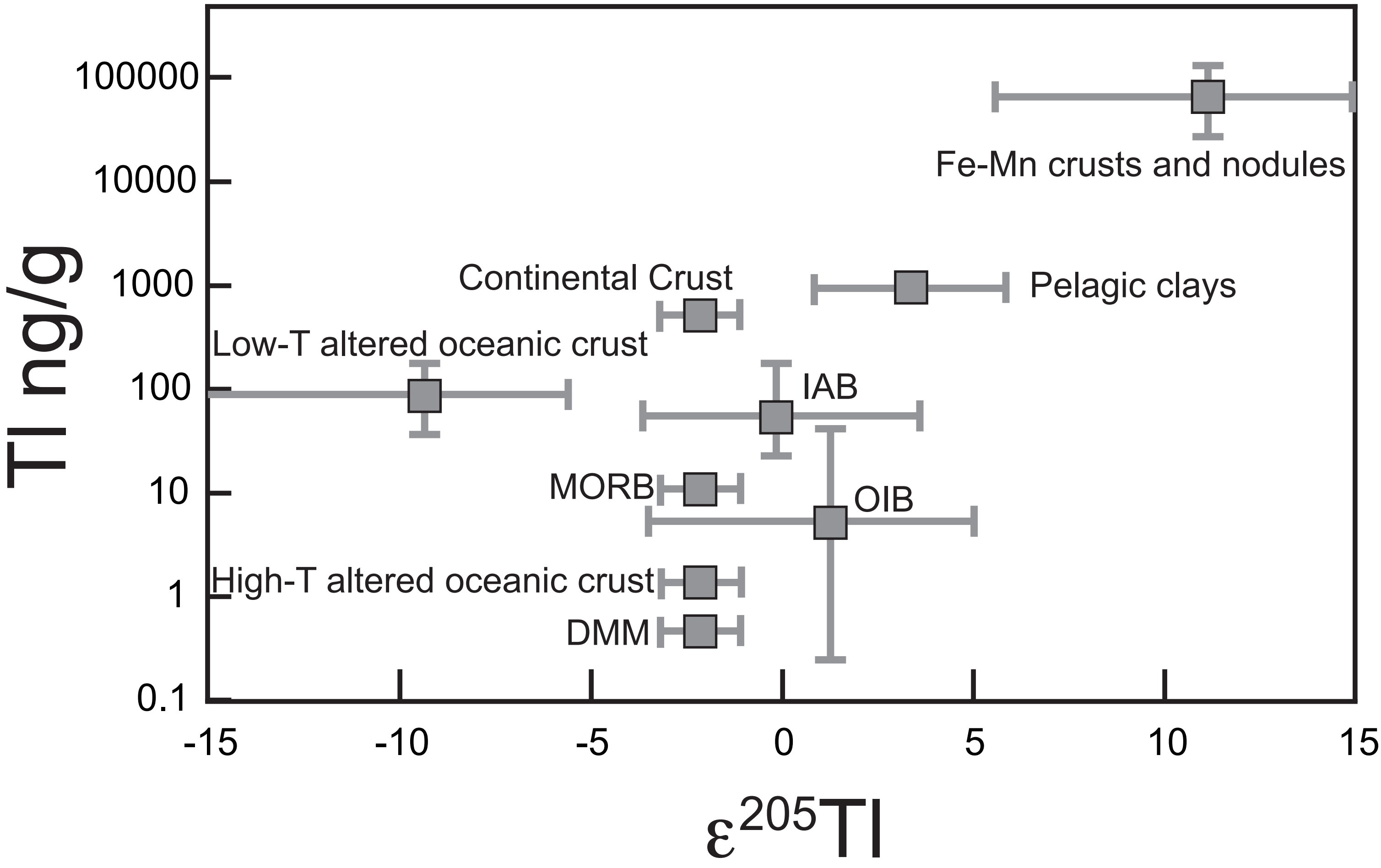
are composites prepared from the lithologies encountered in these depth intervals (Kelley et al., 2003).

Figure 8: Thallium isotope compositions determined for the growth surfaces of hydrogenetic Fe-Mn crusts and seawater. The Fe-Mn crusts precipitate directly from seawater and hence there is an isotope fractionation of ~19 ε^{205}Tl-units (labeled α_{EMP}) between these two reservoirs. Data from (Nielsen et al., 2004; Nielsen et al., 2006c; Owens et al., 2016; Rehkämper et al., 2002). Also shown are the isotope fractionation factors (α_{EXP}) determined for experiments in which the manganese oxide birnessite was equilibrated with an aqueous Tl solution (Nielsen et al., 2013).

Figure 9: The S and Tl isotope composition of seawater over the last 75Myrs. The Tl isotope curve is based on a Fe-Mn crust from the Pacific Ocean and an inferred constant isotope fractionation factor of $\alpha = 1.0019$. The S isotope data are from Paytan et al. (1998, 2004), with ages based on the age model of Kurtz et al. (2003). The chronology of the Tl isotope curve was determined based on Os isotope data (Burton, 2006). Figure modified from Nielsen et al. (2009a).

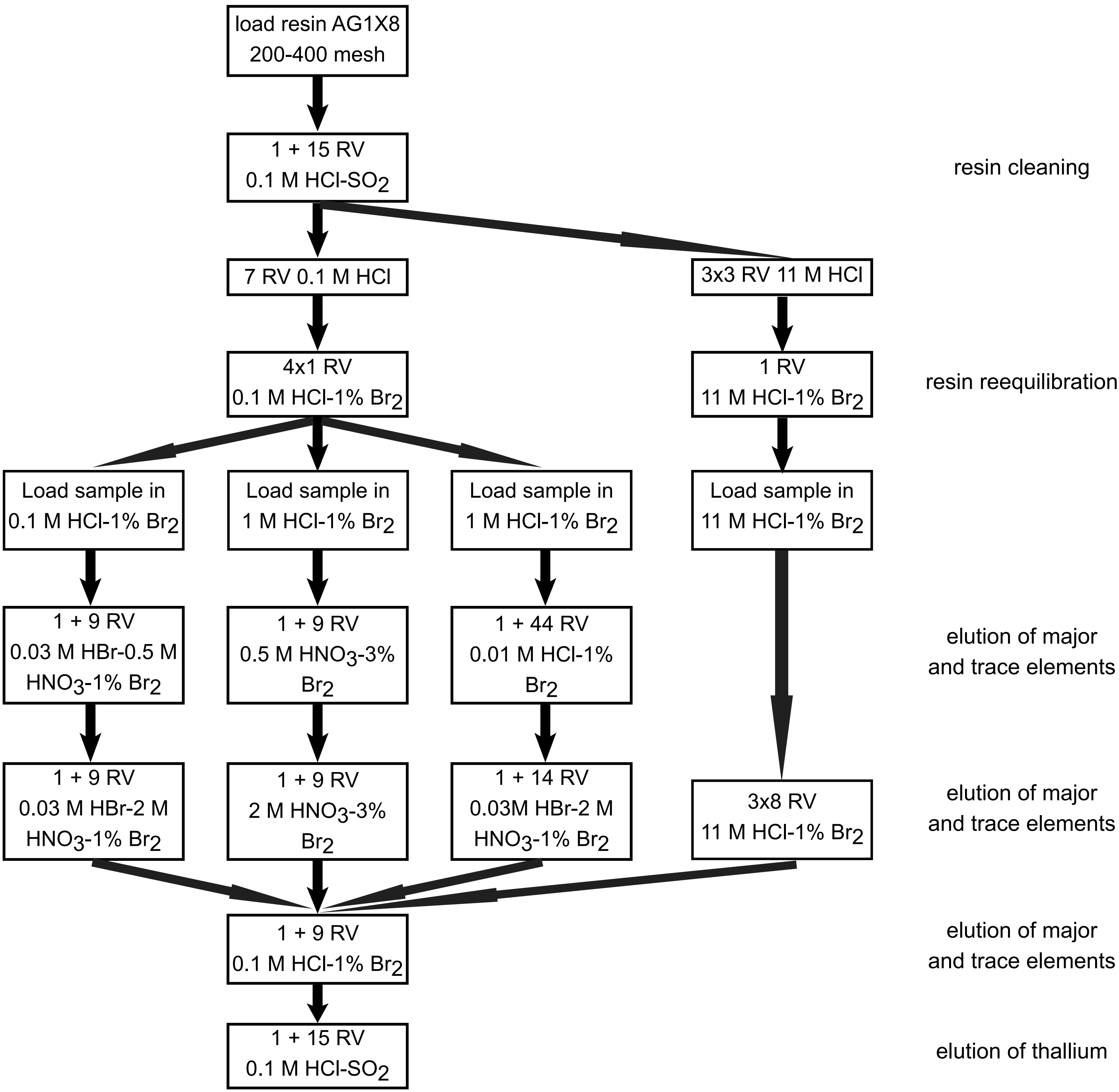
Figure 10: Cs/Tl and Ce/Tl ratios of primitive basalts from Hawaii (Nielsen et al., 2006b) and Iceland (Nielsen et al., 2007) plotted versus Tl isotope composition. Mixing lines between pristine mantle (large pink square), Fe-Mn oxyhydroxides (blue squares) and low-T altered MORB (light green circles) are also shown. The mantle is assumed to be characterized by ε^{205}Tl = -2 (Nielsen et al., 2006b) and Ce, Cs and Tl concentrations of 772 ng/g, 4.2 ng/g and 0.7 ng/g, respectively (Nielsen et al., 2014; Salters and Stracke, 2004). For the Fe-Mn oxyhydroxides, the

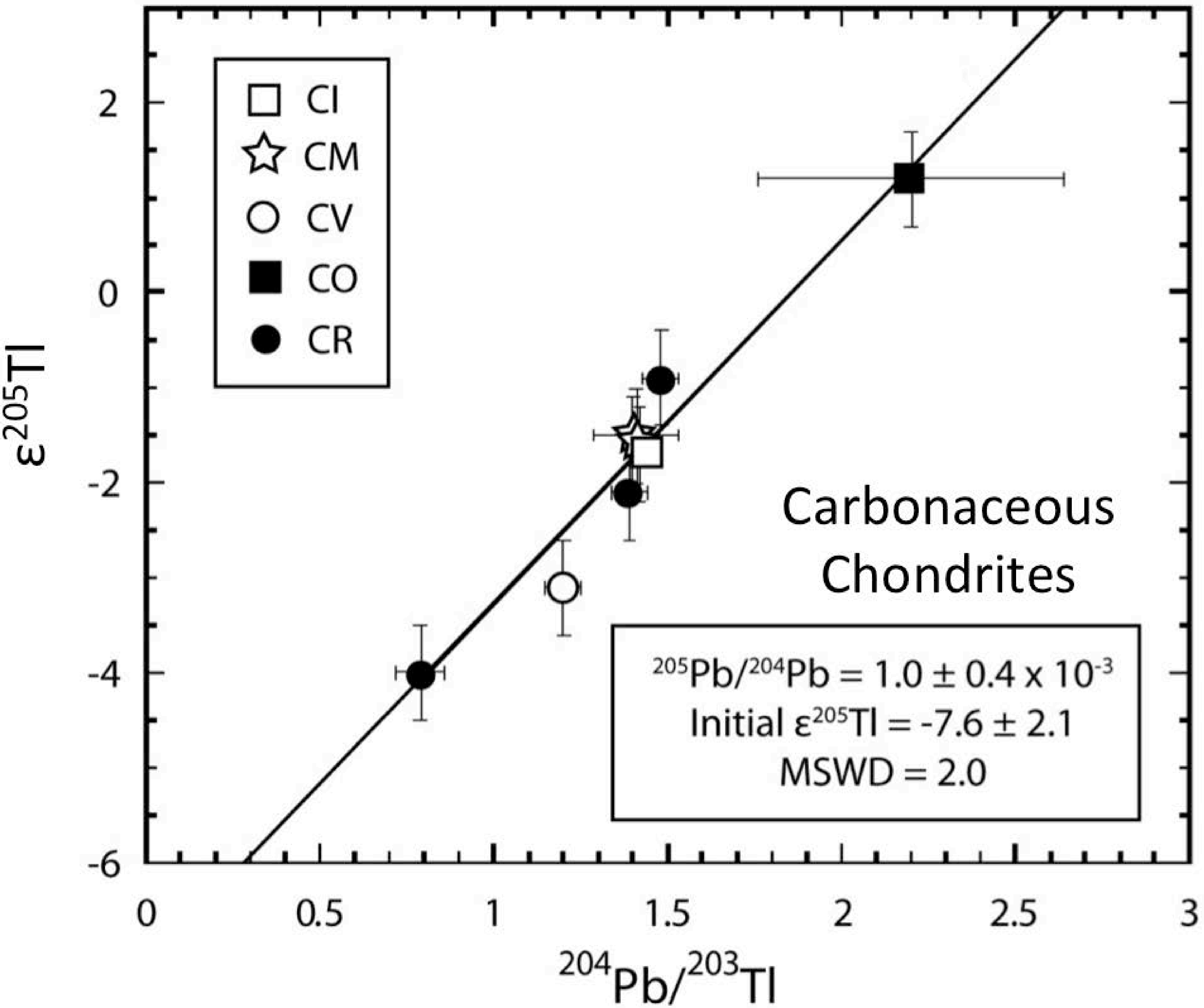
Tl concentration and isotope composition are assumed to be 100 μg/g and ε^{205}Tl = +10, akin to values of modern Fe-Mn crusts and nodules (Hein et al., 2000; Rehkämper et al., 2002). The Cs content of Fe-Mn oxyhydroxides is about 500 ng/g (Ben Othmann et al., 1989). Altered MORB is assumed to be characterized by ε^{205}Tl = -10 and Ce, Tl and Cs concentrations of about 13400ng/g, 200ng/g and 200ng/g, respectively (Gale et al., 2013; Nielsen et al., 2006c). Error bars denote 2sd uncertainties.



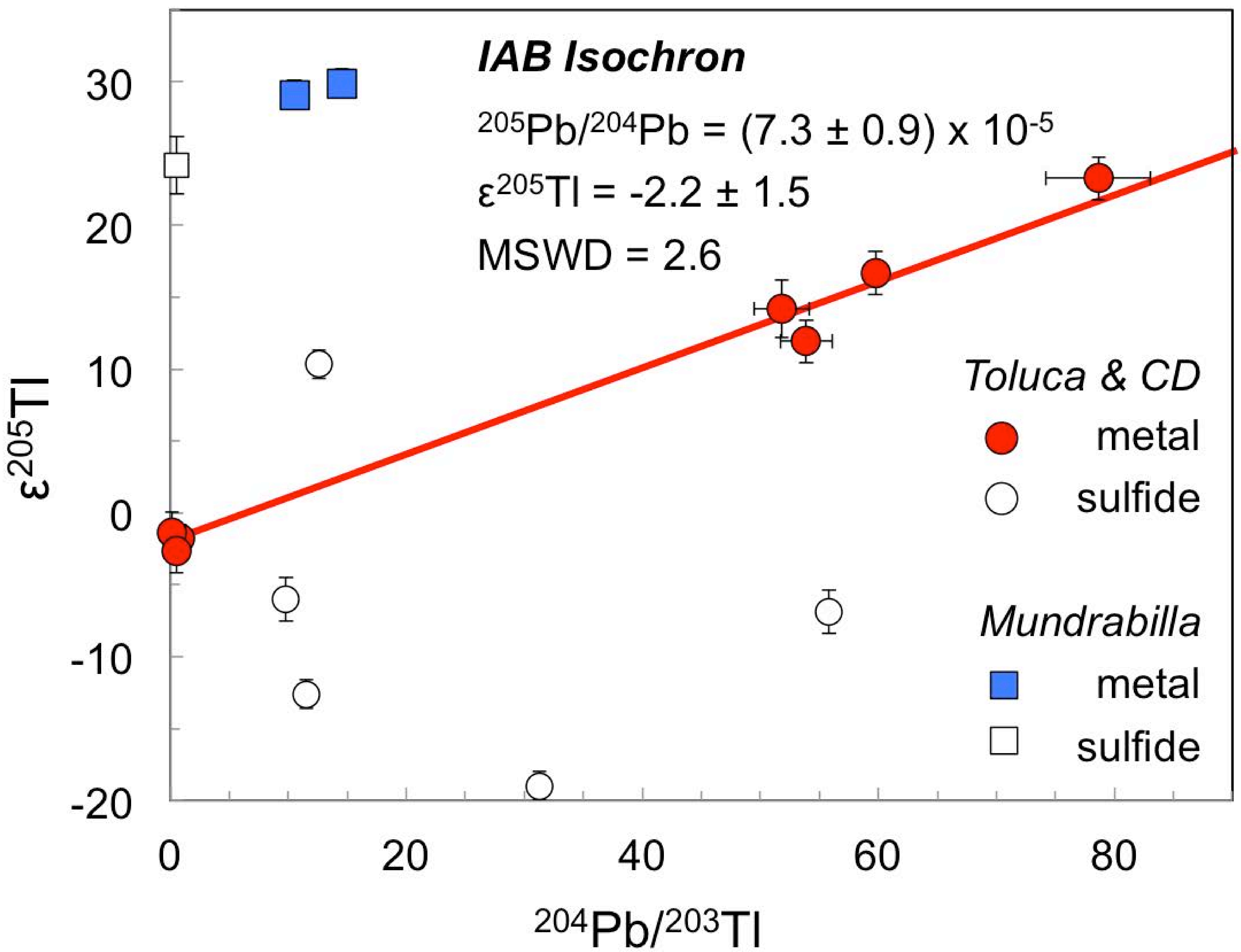
Tl ng/g
100000
10000
1000
100
10
1
0.1
-15
-10
-5
0
5
10
15
ε205Tl
Fe-Mn crusts and nodules
Continental Crust
Pelagic clays
Low-T altered oceanic crust
IAB
MORB
OIB
High-T altered oceanic crust
DMM

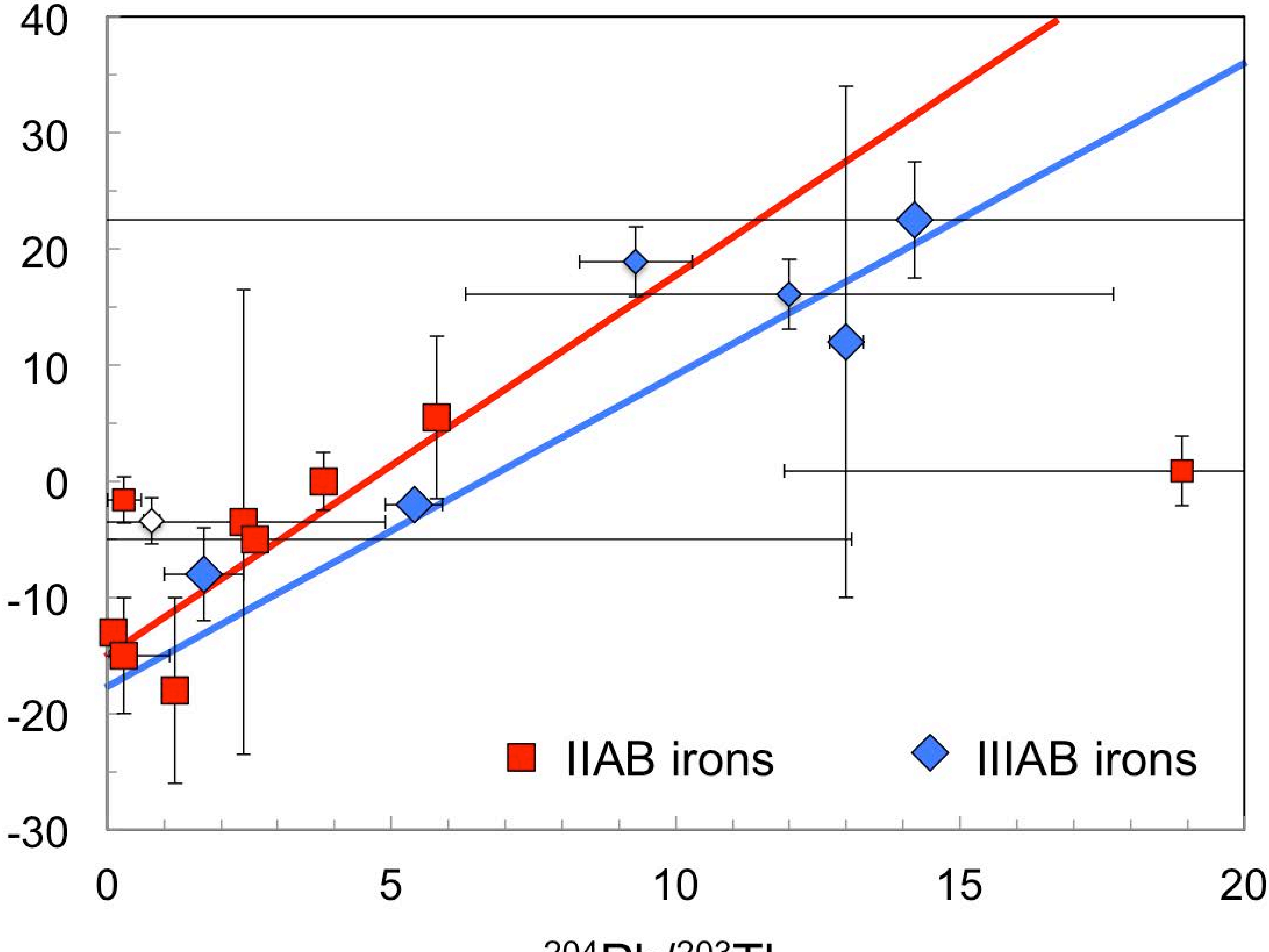
Tl chemistry; RV - resin volume



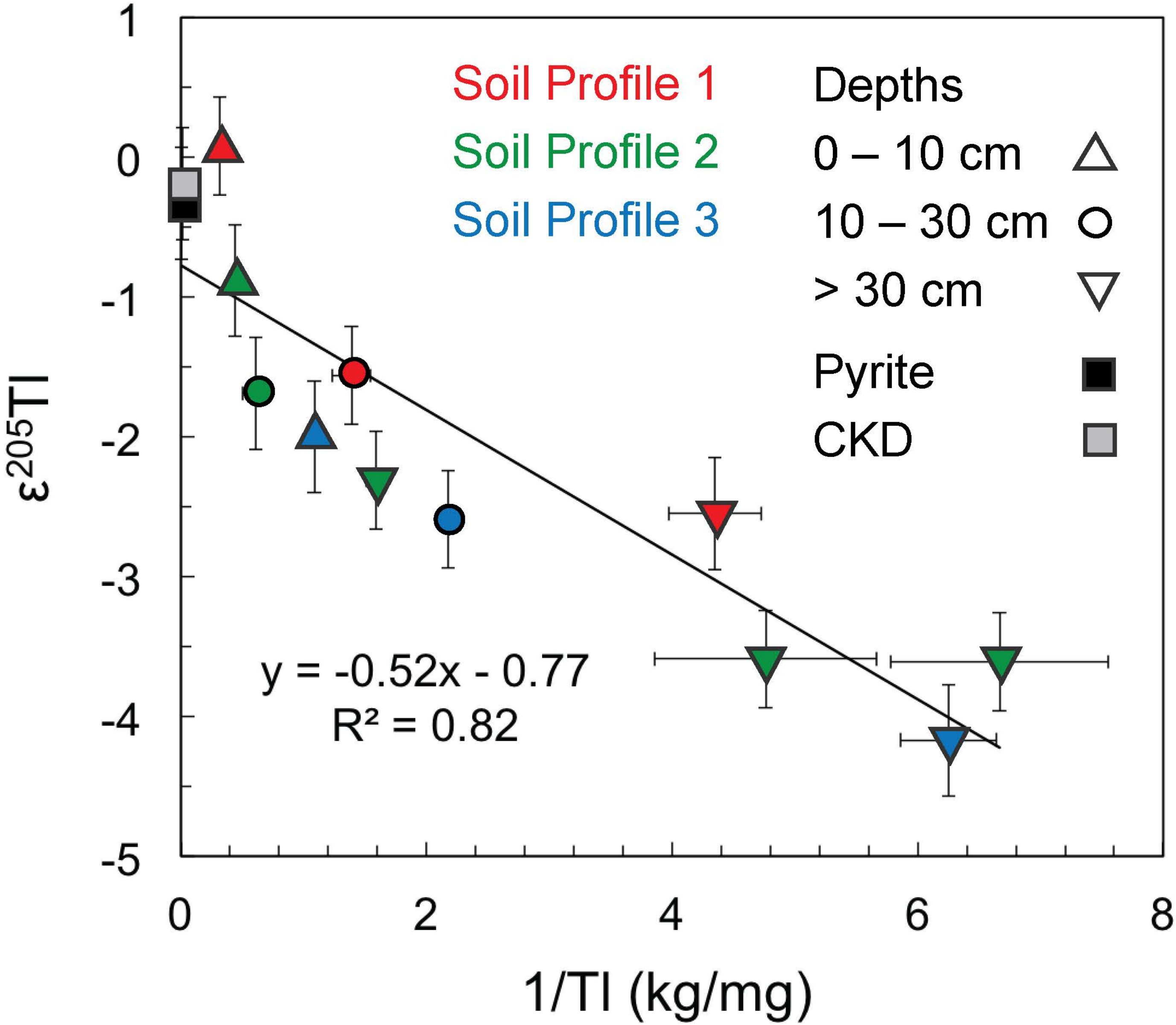


CI
CM
CV
CO
CR
Carbonaceous Chondrites
205Pb/204Pb = 1.0 ± 0.4 x 10-3
Initial ε205Tl = -7.6 ± 2.1
MSWD = 2.0
ε205Tl
204Pb/203Tl
2
0
-2
-4
-6
0
0.5
1
1.5
2
2.5
3

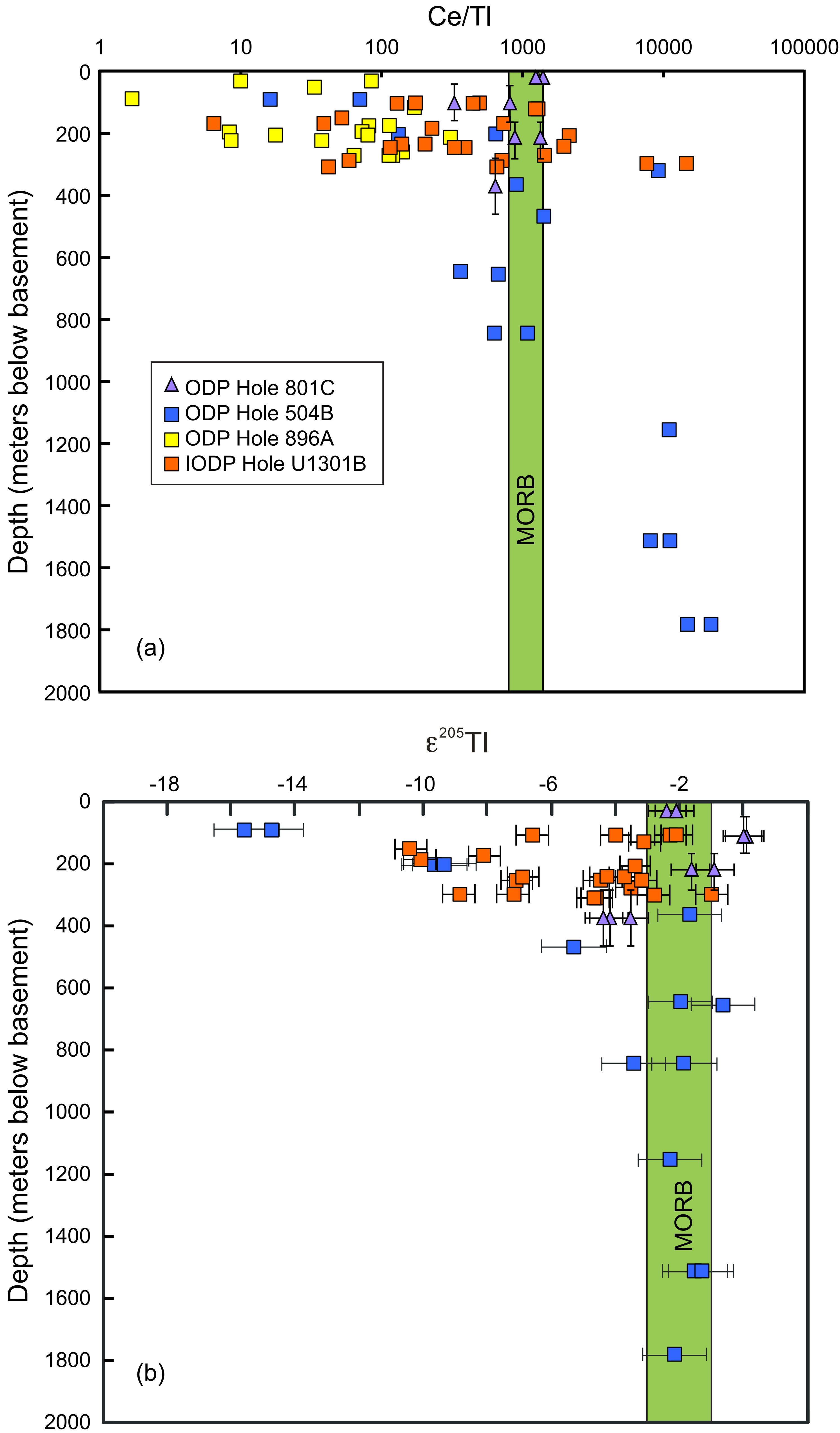

IAB Isochron
205Pb/204Pb = (7.3 ± 0.9) x 10-5
ε205Tl = -2.2 ± 1.5
MSWD = 2.6
Toluca & CD
metal
sulfide
Mundrabilla
metal
sulfide
ε205Tl
30
20
10
0
-10
-20
0
20
40
60
80
204Pb/203Tl



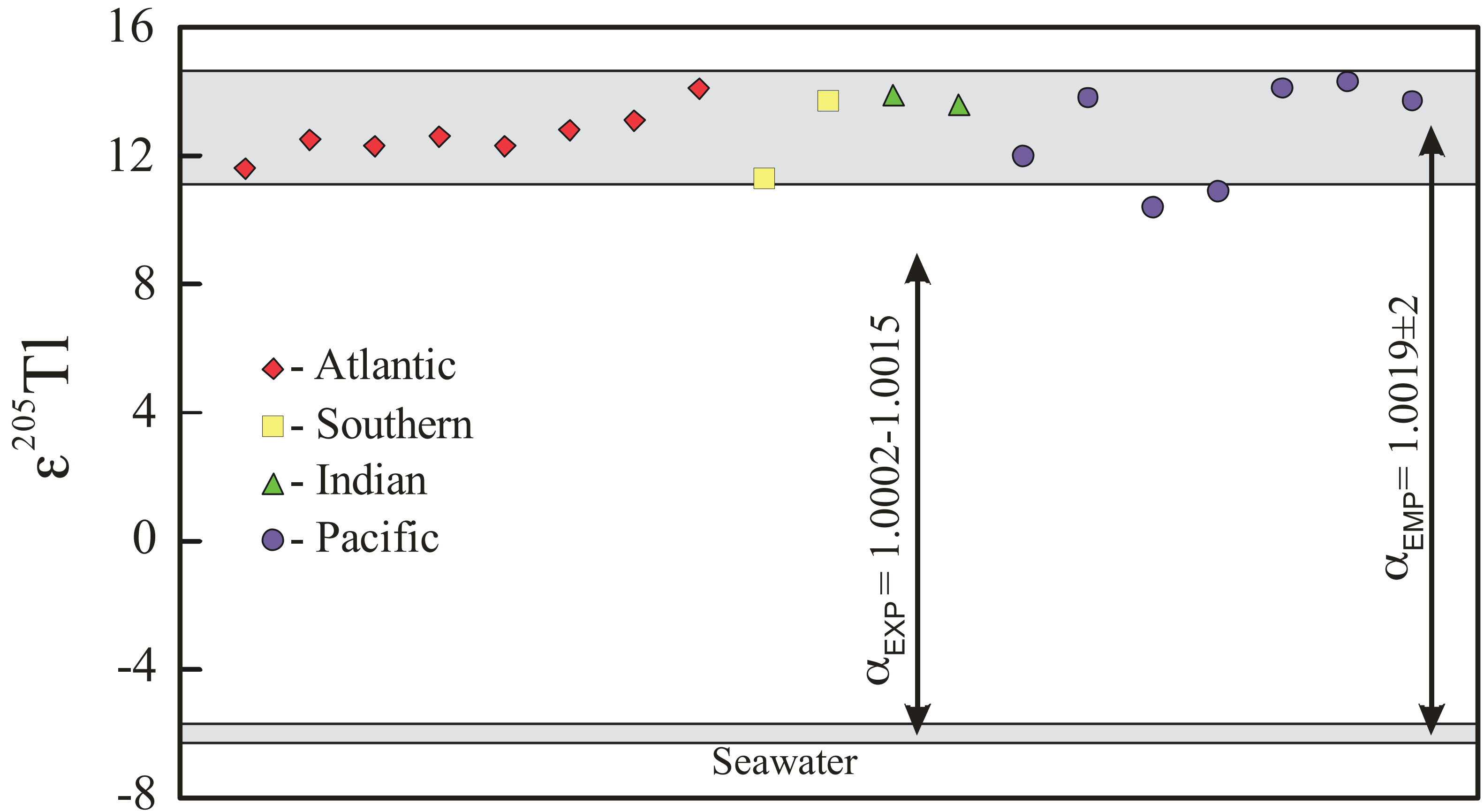
40
30
20
10
0
-10
-20
-30
ε205Tl
0
5
10
15
20
204Pb/203Tl
IIAB irons
IIIAB irons



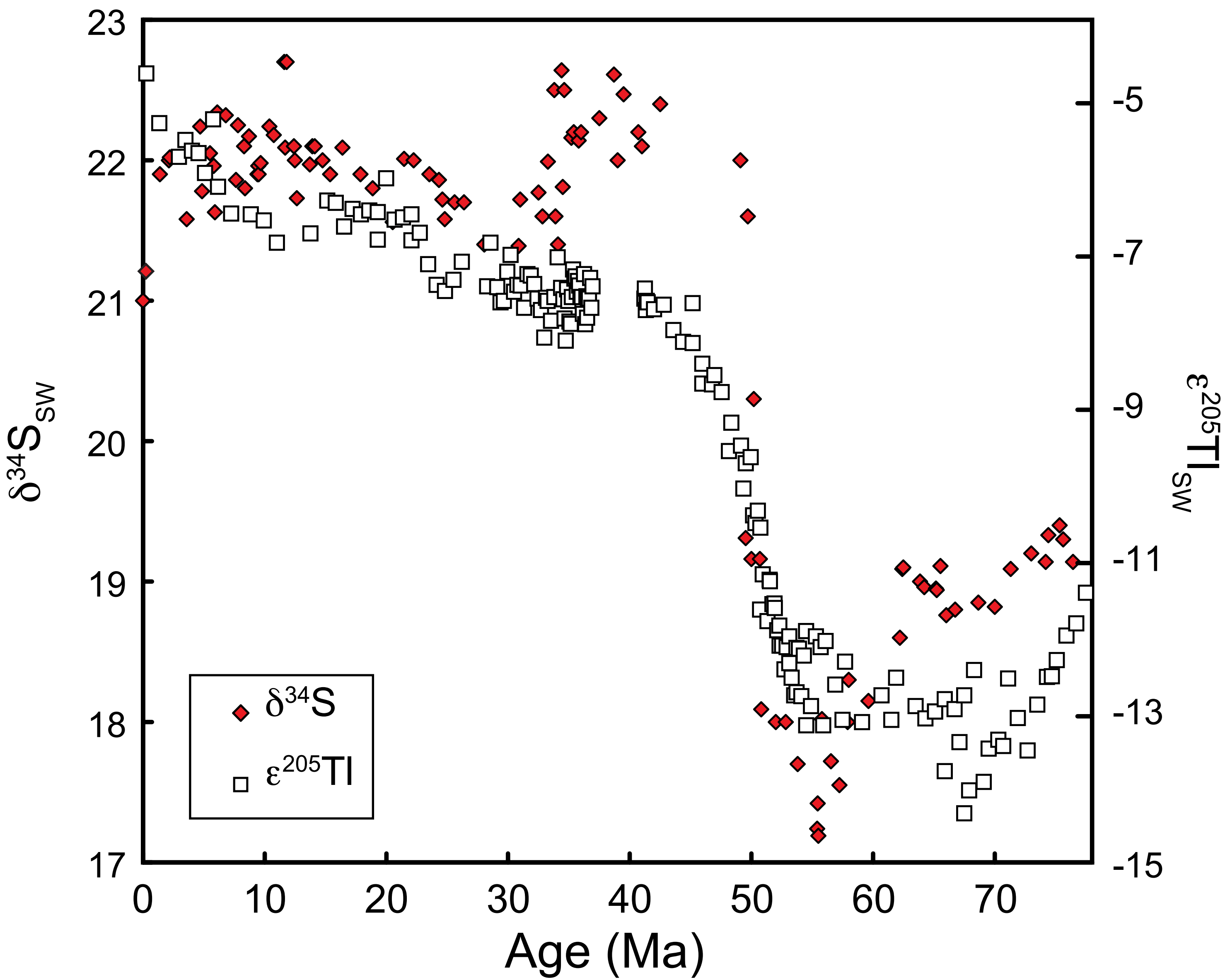
Soil Profile 1
Soil Profile 2
Soil Profile 3
Depths
0 – 10 cm
10 – 30 cm
> 30 cm
Pyrite
CKD
y = -0.52x - 0.77
R² = 0.82
ε205Tl
1/Tl (kg/mg)
1
0
-1
-2
-3
-4
-5
0
2
4
6
8



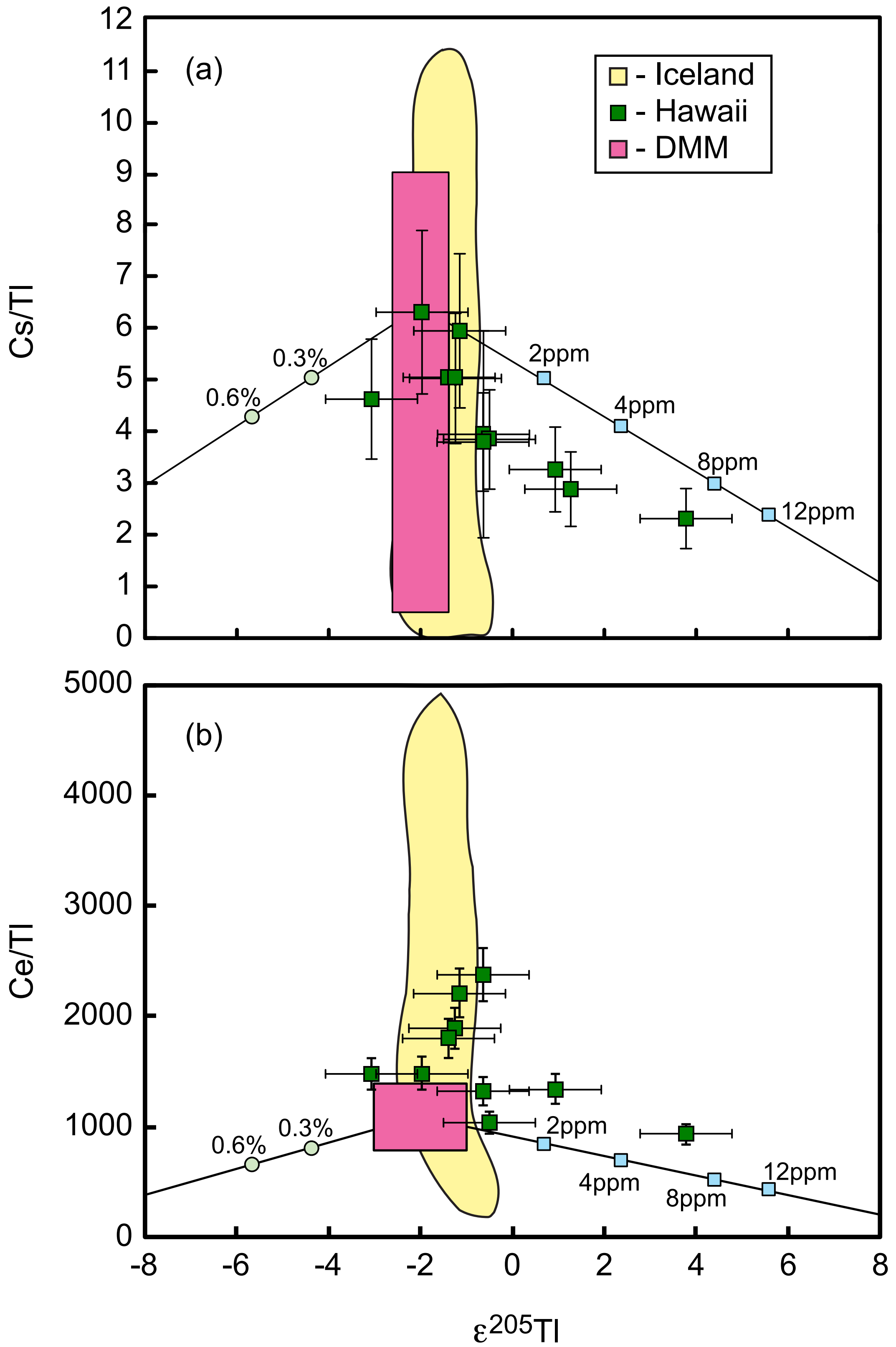
Ce/Tl
1
10
100
1000
10000
100000
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Depth (meters below basement)
ODP Hole 801C
ODP Hole 504B
ODP Hole 896A
IODP Hole U1301B
MORB
(a)
ε^{205}Tl
-18
-14
-10
-6
-2
MORB
(b)



16
12
8
4
0
-4
-8
ε205Tl
- Atlantic
- Southern
- Indian
- Pacific
αEXP= 1.0002-1.0015
αEMP= 1.0019±2
Seawater



23
22
21
20
19
18
17
$\delta^{34}S_{SW}$
-5
-7
-9
-11
-13
-15
$\varepsilon^{205}Tl_{SW}$
0
10
20
30
40
50
60
70
Age (Ma)
$\delta^{34}S$
$\varepsilon^{205}Tl$



(a)
- Iceland
- Hawaii
- DMM
Cs/Tl
0.3%
0.6%
2ppm
4ppm
8ppm
12ppm
(b)
Ce/Tl
0.3%
0.6%
2ppm
4ppm
8ppm
12ppm
ε^{205}Tl