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Thallium isotope systematics in volcanic rocks from St. Helena – Constraints on the origin of the HIMU reservoir

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ABSTRACT

It is generally accepted that subduction of the oceanic crust plays an important role in creation of mantle heterogeneity. HIMU (stands for high $\mu = (^{238}U/^{204}Pb)$) is a rare and probably not volumetrically large mantle component, which is sampled at St. Helena in the Atlantic and in the Cook-Austral Islands in the South Pacific. Previous studies that used radiogenic isotopes have specifically invoked subducted hydrothermally altered oceanic crust (AOC) as a significant component in the source of HIMU. However, because radiogenic isotopes are affected by both parent-daughter fractionation and time that cannot be independently determined, it is difficult to unambiguously use these tracers to determine the source material of the HIMU reservoir.

Thallium isotopes can be used to identify the involvement of sediments rich in Mn oxides or AOC, because these two components exhibit high Tl concentrations and highly fractionated Tl isotope compositons, whereas the upper mantle is depleted in Tl and homogenous with respect to Tl isotopes. Here we report Tl isotope data for a suite of St. Helena lavas previously characterized to investigate if the HIMU mantle reservoir can be linked to AOC. Samples show large Tl isotopic variation, from $\varepsilon^{205}Tl = -9.8$ to $\varepsilon^{205}Tl = +3.9$ and do not correlate with Sr, Nd, Hf or Pb isotopes. Eight samples have $\varepsilon^{205}Tl$ lighter than the mantle value ($\varepsilon^{205}T = -2$), with the lightest values similar to those observed for modern AOC. These features are consistent with the presence of different proportions of recycled oceanic crust in the source of St. Helena mantle source. Our results, therefore, support previous studies that inferred AOC as a significant component in the HIMU mantle reservoir and show that the Tl isotopic system can be used as a powerful tracer to detect contributions of AOC in the creation of mantle heterogeneities.

1. Introduction

It has long been recognized that there may be a link between the introduction of oceanic lithosphere into the mantle at subduction zones and the formation of mantle plumes (e.g. Hofmann and White, 1982). Cold, dense ocean crust could sink as deep as the core mantle boundary (CMB) and thereby, in time, feed the mantle sources of plume volcanism. This interpretation is corroborated by seismic studies, which have revealed that at least some subducted slabs reach the CMB (e.g. van der Hilst et al., 1997) and that some plumes rise from CMB (e.g. French and Romanowicz, 2015). However, the next step in understanding the specific fate of subducted slabs and what exact material is returned to the surface of the Earth has thus far been elusive. The main reason for this short-coming is that the commonly employed radiogenic isotope tracers (Sr, Nd, Pb, Hf and Os isotopes) which are instrumental in characterizing mantle heterogeneity on a small and large scale are influenced by the source composition, chemical fractionations that occurred during or after subduction, and the residence time of the subducted components in the mantle. An accurate assessment of these parameters is difficult and any attempt to identify the exact nature of the materials, which are responsible for the distinct radiogenic isotope signatures of ocean island basalts (OIBs), is thus problematic.

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One of the isotopically most unusual mantle domains is called HIMU (stands for high μ = ($^{238}U/^{204}Pb$)) and is characterized by more radiogenic Pb isotope compositions than other OIBs (Zindler and Hart, 1986). The most extreme and readily identifiable HIMU lavas occur on St. Helena in the Atlantic and in the Cook-Austral Islands in the South Pacific (White, 1985). Classically, HIMU has been linked to subduction of low-temperature altered oceanic crust (AOC) (e.g. Chauvel et al., 1992), because low-temperature hydrothermal alteration of the oceanic crust leads to strong enrichment in U over Pb (e.g. Bach et al., 2003). However, in order to explain the Pb isotope composition of HIMU it is additionally required that modification of AOC during subduction occurred (e.g. Stracke et al., 2003). Specifically, preferential loss of Pb over U and Th is needed in order to develop sufficiently high μ-values in the subducted material to generate the observed Pb isotope compositions. However, this raises the question as to whether AOC is required to generate the HIMU mantle source or whether strong modification of generic subducted oceanic crust (altered or not) in subduction zones alone could explain the creation of the HIMU reservoir. Quantifying the answer to this question is difficult, partially because of our incomplete understanding of the chemical mass balance in the subducting slab during subduction, but also because the ages of the subducted materials in the deep mantle are highly uncertain.

Stable isotope tracers provide an appealing alternative for the detection and characterization of discrete slab components. They generally do not become strongly modified at high temperature in subduction zones or the mantle and are impervious to time. There are exceptions to this rule as it for example has been suggested that elements like O, Li or U record isotope fractionation even during processes that occur at elevated mantle temperatures (e.g. Marschall et al., 2007; Williams et al., 2009; Andersen et al., 2015). Stable isotope fractionations are generally most pronounced at low temperature, with large variations often observed in AOC and marine sediments (e.g., Teng et al., 2017). Any mantle plume containing these recycled components therefore has the potential to exhibit characteristic stable isotope variation that can be traced directly back to sediments and/or AOC. The extent of these effects will primarily be a function of the nature of the recycled materials and how diluted with ambient mantle they have become over time.

The stable isotope geochemistry of thallium (Tl) is ideally suited to address the origin of subducted recycled material in mantle plumes, because Tl is isotopically fractionated during sorption to manganese oxides that are ubiquitous in pelagic marine sediments (Rehkämper et al., 2004) and in the oceanic crust that has been hydrothermally altered at temperatures below ~100 °C (low-T AOC) (Nielsen et al., 2006b). The two components display highly disparate Tl isotope compositions (reported as $\varepsilon^{205}Tl = 10{,}000 \times (^{205}Tl/^{203}Tl_{sample} - ^{205}Tl/^{203}Tl_{SRM\ 997}) / (^{205}Tl/_{203TlSRM\ 997})$) with AOC characterized by $\varepsilon^{205}Tl \sim -15$ to -5 (Nielsen et al., 2006b) and pelagic sediments often displaying values of $\varepsilon^{205}Tl \sim +2$ to $+8$ (Nielsen and Rehkämper, 2011; Nielsen et al., 2017b). In contrast, most other environments on Earth including the depleted MORB mantle (DMM), the continental crust and detrital sediments all display essentially invariant Tl isotope compositions ($\varepsilon^{205}Tl \approx -2 \pm 1$) (Nielsen et al., 2017b). Furthermore, both pelagic sediments and low-T AOC are highly enriched in Tl compared to the primitive mantle (Nielsen et al., 2006b). Therefore, admixing of either of these two components to the mantle, even in minor quantities, should produce anomalous Tl isotope compositions.

Here we use Tl isotopes to investigate the origin of HIMU lavas erupted at St. Helena that were previously studied in great detail both petrologically and geochemically (Kawabata et al., 2011; Hanyu et al., 2014). We show that lavas from St. Helena generally display Tl isotope compositions that are lighter than the DMM, which suggests that low-T AOC was involved in the generation of the HIMU mantle.

2. Methods

Approximately 200–300 mg of rock samples were dissolved in a 3:1 mixture of concentrated HF + HNO_3 on a hotplate at 100 °C for at least 24 h. Following this step they were dried down and fluxed several times with concentrated nitric acid and hydrochloric acid until the fluorides that formed during dissolution could no longer be seen.

Chemical separation of Tl was performed following the method described in Nielsen et al. (2004). Tl isotopic compositions were measured on a MC-IPCMS Neptune at Woods Hole Oceanographic Institution (WHOI) based on previously described techniques that utilize NIST SRM 981 Pb for mass bias correction and standard-sample bracketing (Nielsen et al., 2004.).

Total procedural blanks throughout this study were around 2 pg, which is insignificant in comparison to the lowest analyzed Tl content of 3.5 ng. The USGS reference basalt standard BHVO-1 was also analyzed with every set of unknowns and had isotopic compositions of $\varepsilon^{205}Tl = -3.34 \pm 0.35$ ($n = 8$; 2sd), in excellent agreement with previous work ($\varepsilon^{205}Tl = -3.5 \pm 0.5$, Nielsen et al., 2015). The long-term 2sd uncertainty of the Tl isotope measurements is estimated to be around 0.5 $\varepsilon^{205}Tl$ units (Nielsen et al., 2015).

Trace element concentrations were measured by ICPMS and were previously reported for all but three samples by Kawabata et al. (2011). Three samples (SH-75, SH-76 and SH-77) were analyzed in a similar way as in Kawabata et al. (2011) and their results are provided here for the first time.

3. Results

Thallium concentration and Tl isotopic compositions for 24 samples are presented in Table 1 and Fig. 1. Concentrations in samples from St. Helena vary from 5 to 339 ng/g and show general negative trend with Mg#. $\varepsilon^{205}Tl$ vary in a large range from, −9.8 to +3.9, but do not correlate with indices of fractional crystallization (Fig. 1). Eight out of twenty-four samples have $\varepsilon^{205}Tl < -2$, which is lighter than the typical mantle, and four samples have heavy $\varepsilon^{205}Tl > 0$ (Fig. 1). Samples in this study vary from primitive ([MgO] around 16 wt%, [SiO_2] around 44 wt %) to very differentiated ([MgO] close to 0 wt%, [SiO_2] around 61 wt%). A plot of Mg# versus $\varepsilon^{205}Tl$ (Fig. 1) reveals the existence of three groups of samples: a very evolved group (Mg# < 0.2) with $\varepsilon^{205}Tl$ between −3.5 and +3.6, an evolved group (Mg# 0.30–0.45) and $\varepsilon^{205}Tl$ between −5.4 and +3.9, and a primitive group with Mg# 0.55–0.72 and $\varepsilon^{205}Tl$ in the range of −9.8 to −1.3. The samples studied here have previously been shown to fall into three age groups: Early magmatism ~12–11 Ma (lower shield of the NE volcano), main phase magmatism ~10–9 Ma (main shield of the NE volcano, lower and main shield of the SW volcano), late stage magmatism ~9–7 Ma (upper shield of the SW volcano and late intrusives) (Hanyu et al., 2014). It is notable that the three groups are characterized by distinct ranges in Tl isotopes (Fig. 1), whereby the early magmatism covers the largest range ($\varepsilon^{205}Tl = -9.8$ to +3.9), the main phase magmatism is characterized by a relatively narrow range of negative values ($\varepsilon^{205}Tl = -5.4$ to −1.0), and the late stage magmatism is represented by values mostly heavier than DMM ($\varepsilon^{205}Tl = -3.5$ to +3.6). No correlations were found between Tl isotopes and radiogenic isotope compositions of Sr, Nd, Hf or Pb (Fig. 2).

4. Discussion

4.1. Secondary processes affecting Tl isotopes and concentrations

It is critical to identify and exclude from consideration samples that have been modified by secondary processes in order to discuss only the primary mantle source signature of lavas from St. Helena. Thallium isotope compositions and concentrations can potentially be affected by processes such as degassing, subaerial alteration and submarine hydrothermal alteration (Nielsen et al., 2016). In addition, assimilation of wall rock and fractional crystallization prior to eruption can obscure the Tl concentration source signal. In the following we discuss each of these processes and identify the samples that likely represent the Tl isotope and concentration signatures in the St. Helena mantle source.

Table 1
Tl isotopes and selected trace elements concentrations for St.Helena lavas.

Sample no.	Rock type	Magmatic phase	ε^{205}Tl	Tl	Rb	Cs	Ce	Pb	Sr	Th
SH-10	Basalt	M	− 2.04	0.010	15.9	0.15	67.1	1.73	539.25	3.76
SH-24	Tephrite Basanite	M	− 5.04	0.046	16.2	0.15	59.0	1.42	458.93	2.93
SH-25	Basalt	M	− 2.05	0.008	12.9	0.10	51.3	1.16	351.95	2.56
SH-38	Basalt	M	− 2.26	0.018	13.1	0.11	53.8	1.69	486.87	2.76
SH-58	Trachybasalt	M	− 5.37	0.038	28.8	0.39	107	2.47	794.79	5.41
SH-59	Basaltic trachyandesite	M	− 1.57	0.055	55.8	0.52	154	5.04	762.70	10.87
SH-62	Trachybasalt	M	− 1.01	0.037	35.1	0.37	130	3.06	843.72	6.87
SH-75	Basalt	M	− 4.06	0.339	7.5	0.04	79.2	1.03	341.21	2.29
SH-76	Trachybasalt	M	− 4.23	0.035	28.8	0.20	110	2.94	727.07	5.80
SH-77	Trachyandesite	M	− 1.63	0.260	65.1	0.33	200	6.20	547.73	12.36
SH-84	Basalt	M	− 4.45	0.040	15.6	0.22	62.2	1.41	469.27	3.22
SH-86	Basalt	M	− 2.46	0.005	8.4	0.06	43.4	0.82	276.54	2.27
SH-90	Picrobasalt	M	− 3.84	0.025	11.4	0.07	51.5	1.13	429.66	2.71
SH-32	Basalt	E	3.88	0.027	18.0	0.21	71.6	1.78	558.64	3.60
SH-35	Picrobasalt	E	− 1.33	0.007	10.3	0.28	42.9	0.94	318.93	2.17
SH-45	Tephrite Basanite	E	− 9.81	0.051	15.8	0.17	60.8	1.38	454.72	19.74
SH-45*			− 10.02	0.039						
SH-30	Trachyte	L	− 1.17	0.143	107.9	1.15	233	9.71	217.33	19.69
SH-42	Trachyte	L	− 0.53	0.167	127.3	1.72	252	10.77	92.41	22.67
SH-43	Trachybasalt	L	3.64	0.023	40.4	0.19	169	3.66	796.48	8.21
SH-49	Basalt	L	− 2.43	0.045	22.7	0.18	90.2	2.18	627.41	4.96
SH-70	Trachyte	L	− 1.36	0.055	104.7	1.02	186	10.56	515.38	21.68
SH-93	Trachyandesite	L	− 3.45	0.038	60.7	0.26	168	5.73	718.60	13.13
SH-99	Trachybasalt	L	1.87	0.029	28.2	0.24	101	2.55	659.76	5.70

Tl, Rb, Sr, Cs, Ce and Pb content (in ppm) after Kawabata et al. (2011), except new results for samples.
SH75,76 and 77. *-repetition. Magmatic phase: M-main, E-early, L-late.

4.1.1. Assimilation-fractional crystallization processes

Fractional crystallization affects concentrations of trace elements depending on whether they are compatible or incompatible in the crystallizing minerals and thereby also many of the trace element ratios often used to interpret the composition and provenance of the mantle source that lavas are derived from (e.g. Nb/U, Ce/Pb, Rb/Cs, Sr/Y). Given the similarity in charge and ionic ratio of Tl, Rb and Cs these elements are not expected to be significantly fractionated from each other during fractional crystallization (Heinrichs et al., 1980). However, several of the samples investigated here contain almost no Mg, which suggests they underwent large extents of fractional crystallization that would have altered almost every trace element ratio from the original primitive magma. These effects are apparent in the present data set where samples with Mg# < 0.2 display a substantial variation in trace element ratios (e.g. Ce/Pb, Rb/Sr,) compared with more primitive lavas (Fig. 3). In addition, large extents of fractional crystallization releases significant amounts of latent heat, which likely caused assimilation of the oceanic crust the magma passed through or of magma chamber wall rocks. The effects of assimilation could be subtle for Sr, Nd and Hf isotopes since the oceanic crust is only slightly dissimilar to HIMU lavas for these isotopes (e.g. Stracke et al., 2005). However, both Pb and Tl isotopes could be strongly affected due to the large isotopic differences between MORB mantle, modern AOC and HIMU lavas (e.g. Stracke et al., 2005; Nielsen et al., 2006b; Nielsen et al., 2006a). Fractional crystallization, in itself, does not affect Tl isotopes, because Tl is highly incompatible in the major phases precipitated from St Helena lavas (Prytulak et al., 2017; Nielsen et al., 2016). However, given the observed perturbed trace element ratios due to fractional crystallization and potential effects on Pb and Tl isotopes due to assimilation, we conservatively eliminate samples with Mg# < 0.2 from the discussion of the Tl isotope composition of the St Helena mantle source.

4.1.2. Degassing

Thallium is a volatile metal and during magmatic degassing Tl isotopes can experience kinetic fractionation where the light isotope is enriched in the gas phase (Baker et al., 2009). Such processes should produce degassed lavas with low Tl content and heavy Tl isotopes. On the other hand, Baker et al. (2009) found that magmatic fumaroles from six different volcanoes displayed an average ε^{205}Tl ~ − 2 suggesting that overall kinetic isotope fractionation during degassing is rather limited. It is important to emphasize that there is no study which investigated Tl isotope and concentration in degassed rocks. Samples from St. Helena do not show correlation between Tl concentrations and ε^{205}Tl and four samples with heavy Tl isotopic compositions do not have significantly different concentrations compared with samples with typical mantle ε^{205}Tl (Fig. 1).

4.1.3. Posteruption alteration

St. Helena samples in this study vary in age from ~7 to 12 Ma (Hanyu et al., 2014) and, therefore, it is possible that aqueous alteration has affected the concentrations of some trace elements. It has been documented that post eruption subaerial alteration can cause loss of the alkali metals (e.g. Schiano et al., 1993), which might also apply to Tl due to the similarity in ionic charge and radius with the alkali metals (Nielsen et al., 2016; Nielsen et al., 2017). We investigate potential effects from post eruption weathering by examining Th/Cs and Ce/Tl ratios (Fig. 4), both of which should be anomalously high for substantially weathered samples, because Th and Ce are relatively immobile during aqueous alteration whereas Cs and Tl are mobile.

Of the samples not already disregarded due to large extents of fractional crystallization only sample SH-86 displays high Th/Cs and Ce/Tl (~37 and ~8000, respectively), which could be indicative of weathering processes. These ratios are compared to those typically found in other OIB samples, which generally display Th/Cs ~5–30 and Ce/Tl ~1000–5000 (e.g. Willbold and Stracke, 2006; Kokfelt et al., 2006; Nielsen et al., 2006a; Nielsen et al., 2007). We, therefore, infer that SH-86 could have been slightly altered by aqueous fluids and exclude it from the discussion of the St Helena mantle source composition.

Sample SH-75 which is visually altered is characterized by an extremely high Tl content of 339 ng/g and very low Ce/Tl = 233, Cs/Tl = 0.1 and Pb/Tl = 3. These ratios are much higher in all other lavas that are not affected by fractional crystallization/assimilation (Table 1, Fig. 4), which suggests some form of contamination possibly by secondary minerals rich in Tl, but relatively poor in Ce, Cs and Pb. These could be Mn oxides, but given the light Tl isotope composition of this

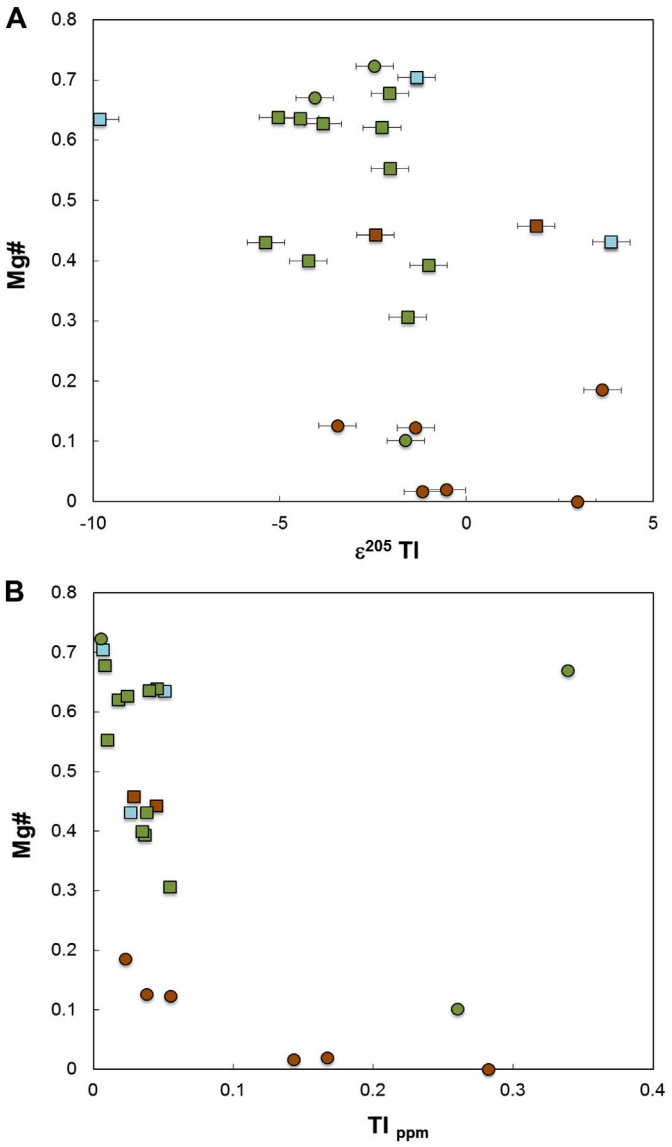

Fig. 1. Mg # versus (A) thallium isotope composition and (B) Tl concentration in lavas from St. Helena. Blue symbols represent samples of early stage magmatism, green main stage magmatism and brown late stage magmatism. Squares symbols represent samples not affected by secondary processes, circles samples which were affected by secondary processes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

sample, the contamination more likely arises from clay minerals or sulfides that can also contain high Tl concentrations (Nielsen et al., 2014). Irrespective of the source of contamination we have decided to eliminate SH-75 from the discussion of the St. Helena mantle source.

4.1.4. Source signal versus shallow processes signature

It is difficult to assess whether the Tl isotope variation that remains in the St. Helena lavas after elimination of samples with likely secondary effects is due to variations in the mantle source or caused by crustal assimilation during magma transport. Oceanic crust, depending on age and extent of alteration, can have very distinct trace element contents and isotopic compositions. However, since HIMU lavas have been hypothesized to originate from subducted AOC, it can be difficult to distinguish between a signature from modern AOC and ancient subducted AOC. One of the most characteristic differences between AOC and HIMU is their Ce/Pb ratio, which is distinctly lower in AOC (Ce/Pb < 20, Bach et al., 2003) than in MORB (Ce/Pb ~25; Hofmann et al., 1986) and in undifferentiated St. Helena lavas (Ce/Pb > 40; Hanyu et al., 2014; Kawabata et al., 2011). The most likely explanation for the generally high Ce/Pb in HIMU lavas is due to the fact that Pb is efficiently removed from the subducted slab during slab dehydration (Stracke et al., 2003; Willbold and Stracke, 2006). We would, therefore, expect different relationships between Ce/Pb and Tl isotopes, if the variation in St Helena lavas was caused by assimilation of modern AOC as opposed to an origin from deeply recycled dehydrated subducted oceanic crust. Here we model the effects of adding these two distinct components to the DMM (Fig. 5) and show that the mixing curves are not compatible with assimilation of modern unmodified AOC. Furthermore, if contamination were to occur as part of an assimilation and fractional crystallization process (AFC), then the more differentiated samples (those with low Mg#) should be the more contaminated by assimilation of AOC and show very light Tl isotopic composition which is not the case (Fig. 1A). Thus, we conclude that the Tl isotopic compositions of our samples most likely represent that of the St Helena mantle source and not of assimilated AOC.

4.2. Elemental behavior of Tl in the mantle and recycled components

We had to remove nine samples that potentially could be affected by assimilation-fractional crystallization processes, degassing, weathering or surficial contamination. The remaining 15 samples are considered representative of the Tl isotope composition variation in the St. Helena mantle source. The Tl concentration of these samples varies from 7 to 55 ng/g with a mean value of 31 ng/g, which is higher than values found in Iceland (~3 ng/g) and Hawaii (~14 ng/g), (Nielsen et al., 2006a; Nielsen et al., 2007). The Tl concentrations for these samples covary with Mg# (Fig. 1B) suggesting that the primitive melt Tl concentration is the primary control of the observed variations.

In order to trace the origin of stable isotope variations it is useful to determine if the element of interest (in this case Tl) is enriched or depleted in the studied mantle source relative to the unmodified DMM. Enrichments, in particular, coupled with distinct isotopic variation are strong indicators of the presence of specific components that may be traced back to, for example, marine sediments or AOC. In order to determine whether a mantle source is enriched or depleted relative to DMM it is expedient to eliminate the effects of melting and small degrees of fractional crystallization by normalizing to an element with similar partitioning during melting and early stages of fractional crystallization. In past studies of Tl isotopes in OIBs the ratio used for this purpose was Cs/Tl (Nielsen et al., 2006a; Nielsen et al., 2007), because it was assumed that the similar ionic radii of these two elements rendered them unfractionated during mantle melting and fractional crystallization. However, it has since been shown that Tl is enriched in mantle sulfides and behaves somewhat like Pb although Tl is not as compatible in sulfides as Pb (Nielsen et al., 2014; Kiseeva and Wood, 2013). Based on several large MORB data sets it was found that bulk partitioning of Tl during melting of the DMM is essentially similar to Ce, even though the two elements are primarily hosted in different minerals, i.e., in sulfide and clinopyroxene, respectively (Nielsen et al., 2014). We, therefore, use Ce as the primary means to monitor enrichment and depletion of Tl in the St. Helena mantle source. The samples investigated here display Ce/Tl ratios significantly higher than MORB (Fig. 6), suggesting that the St. Helena mantle source is significantly depleted in Tl relative to the DMM, AOC and deep-sea sediments. Modern AOC generally displays Ce/Tl between 10 and 1000 (Nielsen et al., 2017), consistent with strong deposition of Tl into the oceanic crust during alteration. Here we report the Tl concentration and isotope composition of the ~109 Ma DSDP 417/418 volcanic zone supercomposite (Staudigel et al., 1995), which exhibits [Tl] = 72 ng/g and ε^{205}Tl = −5.4. Combining the Tl concentration with Ce = 6.19 μg/g (Staudigel et al., 1995) we obtain Ce/Tl = 86 for the DSDP 417/418 supercomposite. These values are entirely consistent with the concentration and isotope data previously reported for younger AOC sections in Holes ODP 504B, ODP 896A and U1301B (Nielsen et al., 2006a;

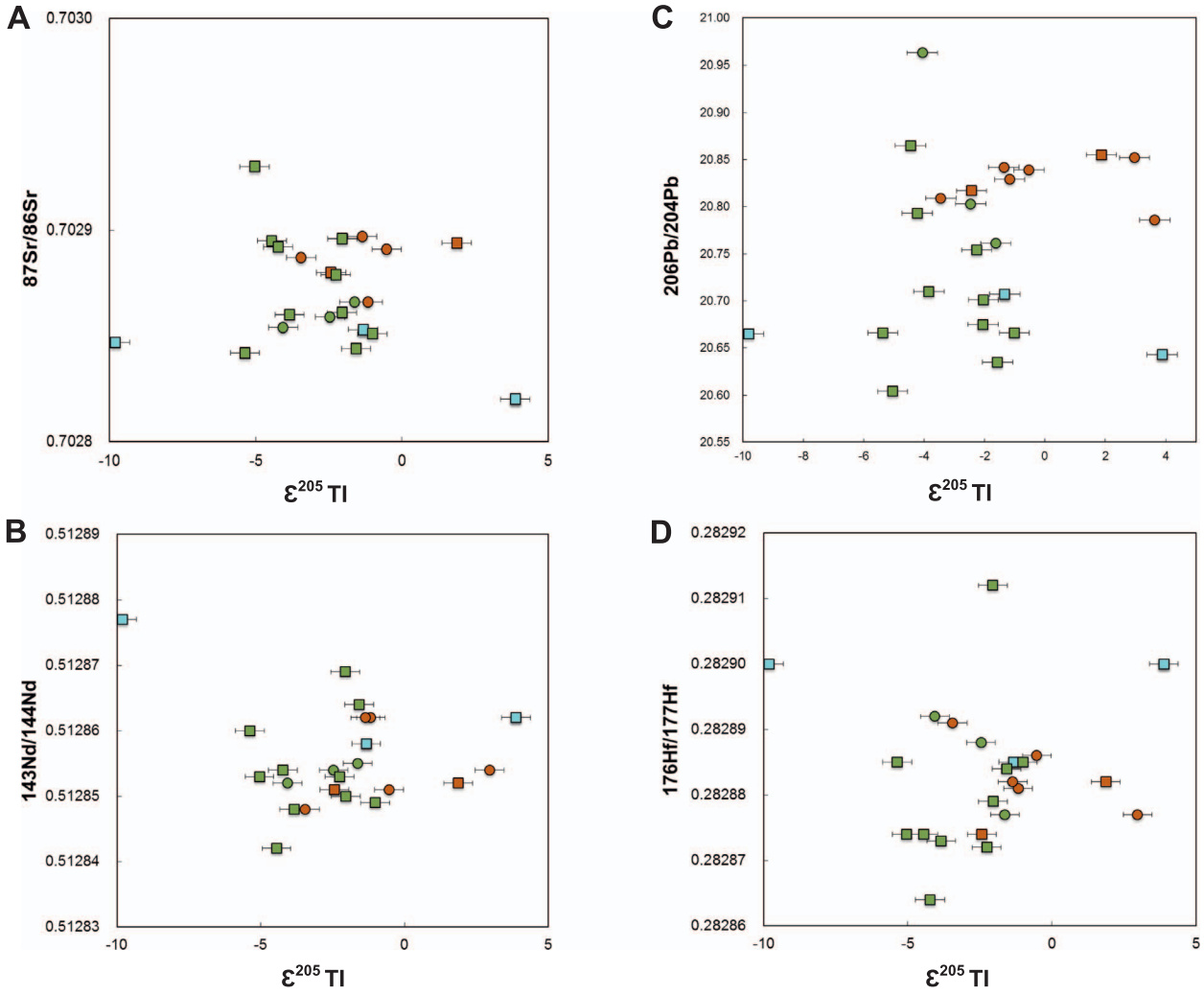

Fig. 2. Thallium isotope composition of St. Helena lavas against (A) Sr isotopes, (B) Nd isotopes, (C) Pb isotopes and (D) Hf isotopes (data from Hanyu et al., 2014). Note strong decoupling between Tl isotopes and Sr,Nd, Pb and Hf isotopes. Symbols as in Fig. 1.

Teagle et al., 1996; Coggon et al., 2014). We note that the Tl isotope composition of AOC must be controlled by the composition of seawater, which has varied in the past (Nielsen et al., 2009; Ostrander et al., 2017). Hence, it is difficult to determine what AOC would have been like during the late Archean/early Proterozoic when the HIMU reservoir was likely subducted into the mantle (Zindler and Hart, 1986; Cabral et al., 2013; Hanyu et al., 2014;). On the other hand we have some basic constraints on the main processes that control the isotope composition of seawater that enable us to make semi-quantitative predictions of ancient seawater and, thereby, ancient AOC and sediments. The Tl isotope fractionation associated with precipitation of Mn oxides is by far the largest isotope effect identified for Tl (Nielsen et al., 2017b) and is the primary control on the Tl isotope composition of seawater. Deposition of Tl during ocean crust alteration fractionates Tl isotopes in the opposite direction, but the overall net fractionation relative to seawater is relatively small at $< 4\ \varepsilon^{205}$Tl-units possibly close to 0 (Nielsen et al., 2006a). In addition, it has recently been shown that Tl deposition into reduced sediments (e.g. those deposited in the Black Sea and Cariaco Basin) record no Tl isotope fractionation relative to the overlying water column (Owens et al., 2017). Therefore, seawater will likely remain lighter than the mantle even when the majority of the ocean experiences anoxic conditions prevalent in the late Archean/early Proterozoic because even minor areas of oxic sediment deposition will translate into an overall isotopically light global Tl seawater reservoir. It is notable that several recent studies on early Proterozoic and late Archean ocean oxygenation have shown that some amount of oxic sedimentation was quite likely (e.g. Olson et al., 2013; Planavsky et al., 2014; Kurzweil et al., 2016). Overall these inferences suggest that late Archean/early Proterozoic AOC should have been lighter than the mantle (e.g. $\varepsilon^{205}\mathrm{Tl} < -2$). In addition, deposition of Tl into AOC would likely also have occurred during these periods, in particular if the enrichment of Tl is related to clay formation or sulfide precipitation (Nielsen et al., 2017b; Coggon et al., 2014), which should not have been hampered by the generally more anoxic conditions of the deep Archean/Proterozoic oceans (Lyons et al., 2014). Collectively, these arguments therefore suggest that ancient AOC should be characterized by low Ce/Tl and light Tl isotopes like we observe today, although the absolute values are not possible to deduct.

Modern sediments generally also display low Ce/Tl ratios (Rehkämper et al., 2004; Nielsen et al., 2016; Shu et al., 2017; Nielsen et al., 2017), because Tl is highly enriched in Mn oxides compared with Ce and because continental crust displays Ce/Tl ~ 70 (Rudnick and Gao, 2003) which is much lower than the mantle. As for AOC, there is no reason to believe that ancient sediments exhibited much higher Ce/Tl ratios than modern counterparts, which underscores that the depletion of Tl relative to Ce in OIBs is likely not a primary feature of subducted materials. Instead the depletion in Tl relative to Ce in OIBs can be explained by more efficient removal of Tl than Ce from the subducting slab, which would lead to high Ce/Tl ratios in the residual slab that is subducted into the deep mantle. This hypothesis is consistent

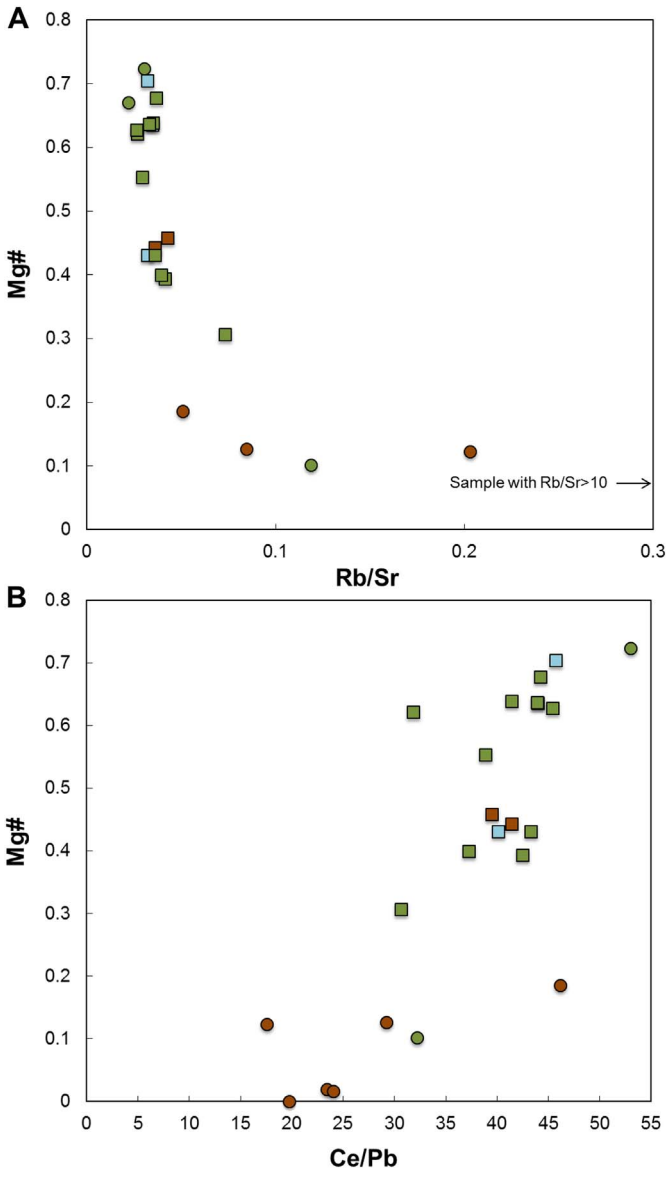

Fig. 3. Mg# ploted against (A) Rb/Sr and (B) Ce/Pb. Note large variations for evolved samples with Mg# < 0.2. Symbols as in Fig. 1.

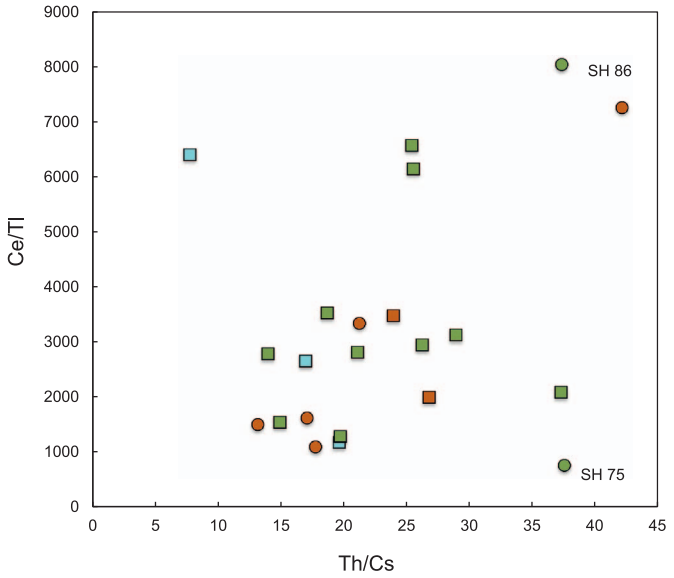

Fig. 4. Ce/Tl plotted against Th/Cs. Two samples with very high and very low Ce/Tl probably were affected by subaerial alteration processes. Symbols as in Fig. 1.

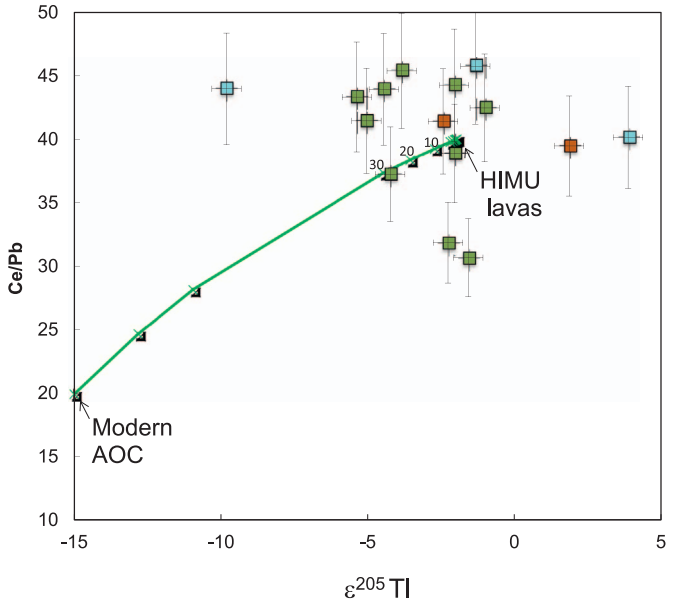

Fig. 5. Thallium isotope composition of St. Helena lavas plotted versus Ce/Pb. Only samples not affected by secondary processes are shown (see text for details and Fig.1 caption). Curve show the relationship that is obtained for mixing between HIMU lavas (ε^{205}Tl = −2 and Ce/Pb of 40) and modern altered oceanic crust (AOC) with ε^{205}Tl = −15 and Ce/Pb = 20. Ticks on the mixing curve show the proportion of AOC in the mixture. It is obvious that mixing between St. Helena lavas and modern AOC cannot reproduce data from this study.

with data from lavas erupted in subduction zones that generally display low Ce/Tl compared with the DMM (Prytulak et al., 2013; Nielsen et al., 2016; Nielsen et al., 2017; Shu et al., 2017). Fractionation of Ce and Tl in subduction zones can be due to fluids in which Tl is more soluble than Ce (Noll et al., 1996) or residual minerals in the subducting slab, such as allanite and monazite (Hermann and Rubatto, 2009; Skora and Blundy, 2010), that are rich in Ce and poor in Tl.

Higher Ce/Tl ratios are systematically found at lower Tl concentrations in OIBs (Fig. 6), which may either imply significant fractionation of Ce and Tl as a function of degree of melting whereby Tl is more incompatible than Ce or that mantle plumes contain considerable Ce/Tl heterogeneities, most likely related to recycled crustal components and Ce/Tl fractionation in subduction zones. High Ce/Tl ratios relative to DMM are ubiquitously observed in OIBs (Fig. 6) which supports the notion that the Tl depletion relative to Ce in OIBs generally reflects the subduction process, rather than Ce/Tl fractionation during OIB mantle melting.

It is important to note that Tl and Ce will likely partition differently when melting a mantle source with very high or low clinopyroxene/sulfide ratios (Nielsen et al., 2014), but given that Ce and Tl are both incompatible elements even moderate degrees of melting (> 3%) will cause only minimal amounts of Ce/Tl fractionation, because the majority of both elements will have entered the melt (Nielsen et al., 2014). Hence, even though some variation in Ce/Tl of the St. Helena samples could be attributed to differences in mantle mineralogy and/or degree of melting, these effects are likely small compared to the influence of the initial source composition.

4.3. Origin of Tl isotope variation in the St. Helena mantle source

After removal of samples potentially modified from their primary trace element ratios or Tl isotope composition, the overall Tl isotope

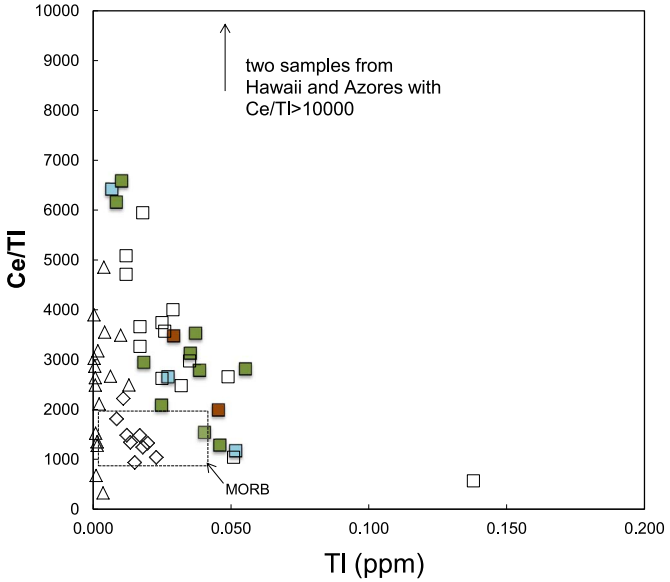

Fig. 6. Ce/Tl plotted against Tl concentration (ppm) for St. Helena lavas. Only samples not affected by secondary processes are shown (see text for details and Fig. 1 caption). In comparison samples from other ocean island basalts (OIBs), Hawaii, open diamonds (Nielsen et al., 2006) Iceland (open triangles) and Azores (open squares) (Nielsen et al., 2007) are shown. MORB field after Nielsen et al. (2014).

variation observed in the St. Helena lavas is $\varepsilon^{205}Tl = -9.9$ to $+3.9$ (Fig. 1). By further subdividing the filtered samples into early, main and late stage magmatism it is evident that the Tl isotope ranges covered in these three groups are the same (except late stage magmatism where the range is somewhat smaller, probably due to the small number of samples left) with and without the samples filtered out (Fig. 1). This fact supports our inference that none of the secondary processes that may have perturbed the Tl isotope and concentration systematics of the lavas caused substantial Tl isotope variations, but more likely affected trace element concentrations and ratios.

It is unclear why the Tl isotope compositions of main stage lavas (average value of all lavas $\varepsilon^{205}Tl = -3.1$) are distinct from late stage magmatism (average value of all lavas $\varepsilon^{205}Tl = -0.6$). In the following discussion we do not include the Tl isotope compositions of the early lavas because there are only three such samples in this study and their Tl isotope compositions vary across the entire range of St. Helena. It has been suggested that the early and late stages might represent phases of St. Helena magmatism where the heat flux from the mantle plume was lower than during the main stage of magmatism. Assuming that the recycled material contains a high proportion of pyroxenite (Hanyu et al., 2014), the lower heat fluxes might be hypothesized to produce melts dominated by the recycled component represented by such pyroxenites, because pyroxenite melts at lower temperature than does the ambient peridotite mantle (Hirschmann and Stolper, 1996). In this case, the early and late stages of magmatism should be characterized by the most radiogenic $^{206}Pb/^{204}Pb$ isotope ratios. In addition, we would expect that Tl isotopes in the same lavas would be closest to the HIMU end-member. As such, the generally heavier Tl isotope compositions observed in the early and late stage lavas should represent the most unmodified HIMU mantle component. However, although there is a tendency for late stage magmatism to exhibit some of the more radiogenic Pb isotope compositions (Hanyu et al., 2014), early stage lavas are among the least radiogenic and there is no direct relationship between Pb isotopes and the age of the lavas (Fig. 2). It is, therefore, difficult to conclude that the St. Helena HIMU component is generally associated with heavy Tl isotope values. Instead, it is possible that different portions of the St. Helena plume (e.g. those responsible for the main and late stage magmatism) are associated with Tl isotope compositions lighter (main stage) and heavier (late stage) than the average DMM ($\varepsilon^{205}Tl = -2$). Heavy Tl isotope compositions in OIBs and arc lavas have previously been inferred to reflect addition of sediments rich in Mn oxides that contain high Tl concentrations and heavy Tl isotope compositions (Rehkämper et al., 2002; Prytulak et al., 2013; Nielsen et al., 2006a; Nielsen et al., 2016; Nielsen et al., 2017b). Such a conclusion would be difficult to reconcile with the very radiogenic Pb isotope compositions found in St. Helena. It is difficult to further evaluate the cause of the heavy Tl isotopes observed in the late stage lavas because the majority of late stage magmas likely do not retain their original trace element systematics due to degassing, fractional crystallization and/or assimilation. Hence, effects from assimilation and degassing that could produce heavy Tl isotope values cannot presently be excluded for the late stage lavas and we do not further discuss these in the context of the HIMU mantle source.

The main phase lavas, on the other hand, comprise 10 lavas that are sufficiently primitive that trace element compositions broadly represent those that were extracted from the St. Helena mantle source and no secondary effects that would have altered Tl isotopes could be identified. When plotting Tl isotopes against Ce/Tl ratios for the main phase lavas (Fig. 7) it can be seen that there is a tendency for isotopically lighter samples to be characterized by lower Ce/Tl ratios. This trend is consistent with recycled AOC that before subduction adhered to a coarse mixing line between MORB ($\varepsilon^{205}Tl \sim -2$ and Ce/Tl ~ 1100) and AOC ($\varepsilon^{205}Tl < -6$ and Ce/Tl ~ 200). During subduction between 50 and 90% of Tl could have been lost relative to Ce, which caused the Ce/Tl ratio to increase by a factor of 2–10. The loss of Tl associated with subduction most likely did not cause any significant Tl isotope fractionation given that neither hydrothermal processes at 150–350 °C (Nielsen et al., 2006a; Nielsen et al., 2015) nor igneous melting and fractional crystallization in basaltic systems cause detectable Tl isotope fractionation (Prytulak et al., 2017; Nielsen et al., 2016). Based on these considerations, we conclude that the Tl isotope and concentration systematics in St. Helena lavas strongly implicate subduction-modified AOC in the generation of the HIMU mantle source. These observations are, of course, consistent with for example Pb isotopes in St. Helena lavas that have similarly been explained by preferential loss of Pb relative to U from AOC that had previously been enriched in U relative to Th through hydrothermal alteration (e.g. Bach et al., 2003). Such enrichment processes very likely occurred in the Precambrian but

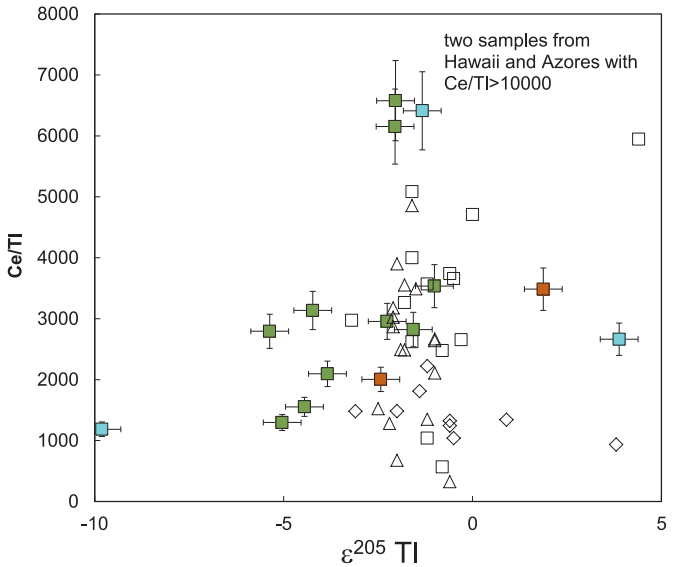

Fig. 7. Thallium isotope composition of St. Helena lavas plotted versus Ce/Tl. Only samples that are not affected by secondary processes (see text for details and Fig. 1 caption) are shown. In comparison samples from other ocean island basalts (OIBs), Hawaii (Nielsen et al., 2006) and Iceland and Azores (Nielsen et al., 2007) are shown. Symbols as in Fig. 6.

probably on a smaller scale then in modern time due to the lower solubility of uranium at low atmospheric oxygen concentrations (Andersen et al., 2015). Based on these arguments it might be expected that Pb and Tl isotopes should correlate in the St. Helena main stage lavas. Although there is a tendency for lighter Tl isotope compositions in the main stage lavas to be associated with more radiogenic $^{206}Pb/^{204}Pb$ (Fig. 2) the trend is not very clear. There are a number of reasons why Pb and Tl isotopes in the HIMU source could have become decoupled. Assuming that the age of the St. Helena mantle source is relatively uniform (and thus variations in Pb isotopes do not reflect variable age), it is first and foremost the amount of U/Pb fractionation both during initial ocean crust alteration as well as during subduction processing that ultimately controls the $^{206}Pb/^{204}Pb$ of the HIMU mantle source. However, none of these two processes may necessarily imply anything about the magnitude of Tl isotope fractionation incurred during ocean crust alteration. Given their different ionic charge and radii (Shannon, 1976), U and Tl deposition into AOC is probably not controlled by the same mineral precipitation reaction and therefore it is theoretically possible to produce AOC with high U/Pb and little Tl isotope fractionation and vice versa. Similarly, the amount of Pb loss from the slab during subduction likely has little to do with the Tl isotope composition of the initial AOC. Hence, the highest U/Pb in deeply subducted AOC is not necessarily associated with the lightest Tl isotope compositions.

Our results can be compared with previously collected data from Hawaii, Iceland and the Azores (Fig. 7). Samples from these OIBs display Tl isotope compositions that range from $\varepsilon^{205}Tl \sim -3$ to $+5$ and thus comprise no samples that are significantly lighter than DMM. Apart from the relatively restricted number of OIBs sampled, it is interesting to consider why only HIMU appears to retain Tl isotope values that represent AOC. The most likely explanation is that Tl concentrations in sediments, and in particular pelagic clays, are at least an order of magnitude higher than in AOC. Thus, minor amounts of sediments included in recycled oceanic crust will tend to dominate the Tl budget. Given the close spatial proximity before subduction of pelagic clays and AOC, mixing processes at the top of the slab during subduction such as mélange formation (Bebout, 2007) would certainly aid preferential overprinting of the light Tl isotope compositions originally found in AOC. In addition, only the low-T altered oceanic crust (e.g. upper ~600 m of fast spreading crust) exhibits light Tl isotope compositions. High-T hydrothermal alteration in the sheeted dike complex and possibly deeper gabbros removes Tl from oceanic crust (producing high Ce/Tl ratios) with no net isotope fractionation (Nielsen et al., 2006a) and, thus, subduction of these volumetrically larger portions of oceanic crust will not produce any Tl isotope heterogeneity in an OIB. Iceland could be an example of this component where a large range of Ce/Tl is accompanied by almost no Tl isotope variation (Fig. 7).

Data from our study provide evidence that altered upper oceanic crust is indeed involved in the creation of the HIMU mantle endmember and that the Tl isotopic signal from upper altered oceanic crust can survive the subduction processes. The amount of subduction modified AOC needed to explain the Tl isotope data is difficult to assess, because it requires several assumptions regarding the Tl concentration and isotopic composition in the recycled material. As discussed above, the Tl isotope composition of subducted AOC is likely heterogeneous and, therefore, it is not possible to construct binary mixing diagrams between DMM and the recycled material. However, if we make the assumption that the lightest main phase lava ($\varepsilon^{205}Tl = -5.4$, Ce/Tl = 2800) constitutes mixing between a recycled endmember ($\varepsilon^{205}Tl = -6$, Ce/Tl = 3000, [Tl] = 5 ng/g) and DMM ($\varepsilon^{205}Tl = -2$, Ce/Tl = 1100, [Tl] = 0.48 ng/g) then the recycled component makes up about 30% of the source region. This fraction of recycled AOC in the HIMU mantle source is the highest needed by the present data set, but the fraction could easily be less than 10% if, for example, the recycled component was $\varepsilon^{205}Tl \sim -8$, which is still significantly heavier than the lightest values found in modern AOC of $\varepsilon^{205}Tl \sim -15$. Overall, the amount of altered upper oceanic crust that can theoretically explain the Tl isotope variations in St. Helena lavas is very similar to proportions suggested based on radiogenic isotopes (e.g. Hauri and Hart, 1993, Nebel et al., 2013).

4.4. Implications for deep time seawater chemistry

It is generally thought that recycled oceanic crust and sediments that form a critical component in OIB source regions were introduced into the mantle via subduction hundreds of millions to several billions of years ago (e.g. Zindler and Hart, 1986; Hauri and Hart, 1993; Cabral et al., 2013; Hanyu et al., 2014). For St. Helena, recent calculations based on Pb isotopes have suggested that this HIMU source has an age of ~2.0–2.3 Ga (Hanyu et al., 2014). If these ages are correct then our Tl isotope data can also be viewed in the light of the ancient marine environments that must have formed them. In extension of our discussion in Section 4.2. regarding the elemental behavior of Tl in ancient AOC and sediments, we here present some additional, more speculative, implications for the Tl isotope variations observed in HIMU and other OIBs. These should not be seen as definitive conclusions, but rather thoughts that may spur further studies of OIBs and ancient sediments.

The Tl isotope variation in recycled material is strongly influenced by seawater because AOC (with their affinity for light Tl isotopes) and Mn oxides (with their affinity for heavy Tl isotopes) are the two principal output fluxes and only realistic isotope fractionation mechanisms that ultimately control the Tl isotope composition of seawater itself through essentially all of Earth history. If Tl isotope variations found in OIBs, as we currently believe, are linked to recycling of AOC and Mn oxides, then these variations have profound implications for the processes that operated at the time when these components were recycled back into the mantle. First, burial of Mn oxides within deep-sea sediments requires free oxygen at the sediment-water interface (Rue et al., 1997; Ostrander et al., 2017). Hence, the occurrence of heavy Tl isotopes in OIBs suggests that at some parts of the ocean contained at least minor amounts of oxygen at the time of subduction. Second, it is the burial of these Mn oxides that also produces light Tl isotopes in global ocean waters, which ultimately sets the $\varepsilon^{205}Tl$ translated into AOC. Thus, the light Tl isotope values found in St. Helena may also imply that the global ocean had achieved some amount of oxygenation when the HIMU component was formed and subsequently subducted.

Even under a dominantly anoxic Archean atmosphere, as suggested by the mass-independent fractionation of sulfur (MIF-S) record (Farquhar et al., 2000), minor accumulation of O_2 in the marine environment remains highly plausible (Olson et al., 2013, and references therein). In support of this, and more importantly in support of processes capable of imparting Tl isotope fractionation in the Archean, multiple lines of geochemical evidence support the production of Mn oxides in mildly oxygenated oceans even prior to the Great Oxidation Event (GOE) at ~2.33 Ga (e.g. Duan et al., 2010; Planavsky et al., 2014; Kurzweil et al., 2016). This leaves open the possibility of a variable seawater $\varepsilon^{205}Tl$ signatures early in Earth's history, especially during and after the unequivocal rise of atmospheric O_2 associated with the GOE (~2.33 Ga, Luo et al., 2016).

Additionally, the mechanism by which Tl is added to the oceanic crust during alteration potentially offers tantalizing evidence regarding ancient oceans. It has been suggested that Tl deposition during ocean crust alteration is linked to microbially mediated sulfide formation (Coggon et al., 2014). If this hypothesis and the early Proterozoic age for the recycled component in St. Helena are correct, then the light Tl isotope values in St. Helena provide evidence for an active deep biosphere in the oceanic crust over 2 billion years ago. Clearly, it is premature to draw definitive conclusions regarding such environments, but it will be important to further identify the exact processes (biotic or abiotic) by which isotopically light Tl is deposited into oceanic crust. Such studies might well provide important information about the low-T surface processes that may have operated several billions of years ago.

5. Conclusions

We present the first Tl isotope compositions measured on samples from the HIMU mantle end-member found on the island of St. Helena. Many lavas from the main magmatic phase on St. Helena display Tl isotope compositions lighter than the depleted upper mantle value of $\varepsilon^{205}Tl = -2$. These samples provide strong evidence of a recycled upper AOC component in the HIMU source. The overall extent of Tl heterogeneity of the St. Helena source depends on the proportion as well the differences in composition of AOC. Results of this study indicate that recycled upper AOC carries its light Tl-isotope fingerprint via subduction into the mantle. We may expect that Tl isotopic analyses from other OIBs will provide further evidence of oceanic crust involvement in the generation of other mantle end-member components.

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