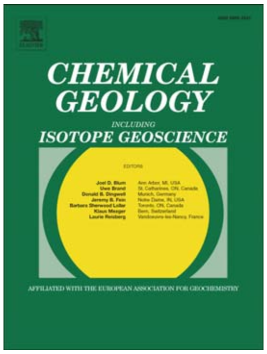

Thallium elemental behavior and stable isotope fractionation during magmatic processes

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Thallium elemental behavior and stable isotope fractionation during magmatic processes

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Abstract

Stable thallium (Tl) isotopes are an extremely sensitive tracer for the addition of small amounts of sediments or materials altered at low temperatures to the source(s) of mantle-derived melts. The ability of Tl to trace such materials is due to the large concentration contrast between the mantle (Tl < 2ng/g) and possible exotic inputs (Tl ~100ng/g to >µg/g), which also often display fractionated Tl isotope compositions. However, the magnitude of Tl isotope fractionation induced by igneous processes alone has not been systematically assessed. Here, two suites of co-genetic magmas, spanning a large range of differentiation, from Hekla, Iceland, and Anatahan, in the Mariana arc, are used to assess the behavior of thallium and its stable isotope variations during magmatic processes. Thallium behaves as a near-perfectly incompatible lithophile element throughout magmatic evolution, mirroring elements such as Rb, Cs, and K. Lavas from Hekla have restricted Cs/Tl ratios and stable Tl isotope compositions, which overlap with mantle estimates. Lavas from subduction-related Anatahan volcano also have a restricted range in Tl isotope composition, which overlaps with Hekla and MORB, demonstrating that fractional crystallisation and partial melting does not fractionate stable Tl isotopes. Subduction environments display variable Cs/Tl, indicating that the subduction process commonly fractionates these two elements. The immunity of thallium stable isotopes to fractionation by magmatic processes coupled with its extreme sensitivity for tracing pelagic sediments, FeMn crusts and low temperature altered oceanic crust highlight its value in elucidating the nature of mantle sources of both oceanic basalts and arc lavas. Critically, meaningful interpretation of thallium isotope compositions need not be restricted to primitive lavas.

Keywords: Thallium, stable isotopes, Hekla, Anatahan, magmatic differentiation

1. Introduction

Geochemical research has unequivocally demonstrated through major, trace and long-lived radiogenic isotopes that intraplate and subduction-related volcanism taps a chemically heterogeneous mantle (e.g., Arculus and Powell 1986; Ellam and Hawkesworth, 1988; Hofmann, 1997; Hofmann and White, 1982; Jackson and Dasgupta, 2008; Stracke et al. 2005; White, 2015; Weaver, 1991; Zindler and Hart, 1986). For example, the addition of sediment, sediment melts, metasomatically enriched mantle, recycled oceanic crust and fluids derived thereof have all been invoked to explain chemical heterogeneity in basaltic lavas. Radiogenic Sr-Nd-Pb-Hf isotopes illustrate clear differences in mantle sources on a global scale. The inherent difficulty in interpretation of radiogenic signatures is that they can be explained by different evolutionary, time-dependent paths, simply by choosing variable source component(s) and elemental partition coefficients. ‘Canonical’ trace element ratios are also often used to ‘see-through’ magmatic processes and examine the inaccessible mantle source, the assumption being that the partitioning of the two ratioed elements is identical in the given phase assemblage. However, the use of trace element ratios to infer mantle sources requires primitive basalts, since crystal fractionation of trace element rich accessory phases (e.g., zircon and apatite) significantly affects many ‘canonical’ ratios. Thus lively debate persists, with starkly contrasting interpretations possible using the same geochemical signatures of primitive basalts (e.g., Samoa: Workmann et al., 2004 versus Jackson et al., 2007).

Stable isotopes offer an alternative perspective to basalt genesis that is independent of uncertainties such as time, source concentrations and elemental fractionation. Stable isotope fractionation is driven by equilibrium and/or kinetic processes. For the former, the magnitude of the effect is proportional to $1/T^2$ (Urey, 1947; Bigeleisen and Mayer, 1947), so that lower temperature environments yield the greatest isotope fractionations, whereas fractionation magnitudes can become vanishingly small at mantle temperatures. In the case of thallium and other heavy elements such as Hg, isotope fractionation that would otherwise be predicted to be very limited given the small relative mass difference between each isotope, is enhanced by nuclear volume effects (e.g., Schauble, 2007).

Small fractionations typical of high temperature processes can be analytically challenging to resolve, however, advances in multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) now enable precise analyses of stable isotope composition of elements spanning the entire periodic table. Resolvable stable isotope fractionations in high temperature magmatic products have been documented in, for example, Si (e.g., Savage et al. 2011), V (Prytulak et al. 2013a, 2017), Cr (Bonnand et al., 2016), Fe (e.g., Williams et al., 2004; Teng et al., 2008), Zn (e.g., Chen et al., 2013), Mo (e.g., Voegelin et al., 2014) and U (Andersen et al., 2015). Here, the geochemical behavior and stable isotope composition of thallium, one of the heaviest naturally occurring elements, is explored to assess its wider applicability to the study of the sources of mantle-derived melts.

1.1 Elemental behavior of thallium

Thallium is a heavy, volatile, highly incompatible trace metal with two oxidation states: Tl^{+} and Tl^{3+}. In highly oxidizing conditions on Earth, Tl can exist as Tl^{3+} (Bately and Florence, 1975; Vink, 1993). Minor Tl^{3+} makes Tl more particle reactive than other alkali metals of similar charge and ionic radii (K, Rb, Cs). During low temperature alteration of basaltic glass, two processes encourage Tl enrichment. First, univalent Tl substitutes for K (along with Cs, Rb) in secondary clays (e.g., Jochum and Verma, 1996), and second, oxidized Tl^{3+} is extracted from seawater by ferromanganese (Fe-Mn) oxides and hydroxides (e.g., Coggon et al., 2014; McGoldrick et al., 1979; Nielsen et al., 2011; Rehkamper and Halliday, 1999). The net result can be orders of magnitude enrichment of Tl in low temperature alteration products and Fe-Mn precipitates (>50 μg/g; e.g., Rehkamper et al., 2002), compared to the mantle (~1-2 ng/g; e.g., Jochum and Verma, 1996; Nielsen et al., 2006a, b; McDonough and Sun, 1995).

There is little study of thallium's behavior in igneous processes compared to other trace elements. Thallium is exclusively univalent in igneous systems, and typically occurs in concentrations on the order of 10's to 100's ng/g. The low abundance of thallium in igneous material is partly responsible for its historical lack of routine determination. The large ionic radius of Tl^+ (1.49 Å) is similar to Rb^+, Cs^+ and K^+ and it is likewise highly incompatible in igneous processes (e.g., Shannon, 1976; Heinrichs et al., 1980); therefore, Tl is concentrated in the continental crust (~ 490 ng/g; Heinrichs et al., 1980) versus the mantle.

There are a few studies reporting Tl partitioning data relevant for igneous systems. These include experimental study of nepheline basanite (Adam and Green, 2006), natural peralkaline granite systems (Bea et al., 1994) and analyses of biotite, K-feldspar and plagioclase from volcanic rocks and granodiorites (Dupuy et al., 1973). Most confirm that thallium substitutes for K^+ in crystallographic sites (e.g., Heinrichs et al. 1980) showing D_{Tl}^{mica} = 3-5 (Adam and Green, 2006), $D_{Tl}^{biotite}$ = 8.6 and $D_{Tl}^{K\text{-}feldspar}$ = 3.7 (Bea et al., 1995). Nielsen et al. (2014) report Tl concentrations below detection limit (<1 ng/g) in olivine, orthopyroxene, clinopyroxene and spinel from the lherz massif in the Pyrenees.

Thallium has been considered both a chalcophile and lithophile element. McGoldrick et al. (1979) suggests that Tl displays chalcophile behavior and follows sulphur in sulphur-saturated magmas. However, study of sulphur-rich ore deposits (Baker et al. 2010) found that Tl retained strong lithophile behavior. Experimentally determined thallium partition coefficients between sulphide liquid and a silicate melt of MORB composition at an oxygen fugacity of FMQ-1, supports chalcophile Tl behaviour during mantle melting ($D_{Tl}^{sulph/sil}$ = 4.1 to 18.8; Kiseeva and Wood 2013). Most recently, Nielsen et al. (2014) have shown that the only phase housing significant Tl in the lherz massif are interstitial sulphides, which yielded variable concentrations from 23 to 430 ng/g. 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, but admitted their Tl data was ‘perplexing’ in that they expected to see indications of fluid mobility, yet Tl did not correlate with ‘fluid-mobile’ elements such as As, Sb and Pb. A study of lavas from the Mariana arc also suggests lithophile, fluid-immobile behavior of Tl, demonstrated by strong co-variation of Tl with La, rather than Ba (Prytulak et al., 2013b). Thus the behavior of Tl during magmatic processes remains ambiguous. It is important to note that Tl partitions strongly into sulfides formed in aqueous low temperature hydrothermal systems (e.g., Xiong, 2007) but this would, classically, not be assigned to chalcophile behavior.

Further study of elemental behavior of Tl in igneous systems is somewhat limited. A key challenge is that large amounts of sample are required to generate precise Tl concentration data, and thus bulk rock analyses can be affected by unintended inclusion of Tl-rich alteration products. However, recent analytical developments using laser ablation to determine precise Tl concentrations in glasses (Jenner and O’Neill, 2012, Jenner et al., 2015; Nielsen and Lee 2013) mitigate this issue and such approaches are poised to considerably advance our knowledge of Tl elemental behavior via rapid expansion of the global database,

1.2 Thallium stable isotopes

Thallium has two stable isotopes: ^{203}Tl (29.5%) and ^{205}Tl (70.5%). Stable isotope compositions are reported relative to the NIST Tl standard SRM997, defined as 0, in parts per ten thousand according to the equation:

$$\varepsilon^{205}\text{Tl} = 10{,}000 \times [(^{205}\text{Tl}/^{203}\text{Tl}_{\text{sample}} - ^{205}\text{Tl}/^{203}\text{Tl}_{\text{SRM997}})/(^{205}\text{Tl}/^{203}\text{Tl}_{\text{SRM997}})]$$

Investigation of stable thallium isotopes was initially motivated by the search for extinct ^{205}Pb, which decays to ^{205}Tl with a half life of ~ 15 My (Rehkämper and Halliday, 1999). However, the first high precision Tl isotope dataset revealed unexpectedly large ^{205}Tl/^{203}Tl variations in a range of natural samples including basalts, meteorites and Fe-Mn crusts (ε^{205}Tl ~ +12 to -2; Rehkämper and Halliday, 1999).

Since the initial work of Rehkämper and Halliday (1999), study of Tl stable isotopes includes diverse applications such as the tracing of pollutants (Kersten et al., 2014), ore genesis (Baker et al., 2010; Hettmann et al. 2014), cosmochemistry (Nielsen et al., 2006a), paleoceanography (Nielsen et al., 2011), hydrothermal alteration (Coggon et al., 2014; Nielsen et al., 2006b), and seawater chemistry (Baker et al., 2009; Nielsen et al., 2004). Previous work relevant to magmatic systems includes investigation of volcanic aerosols, a peralkaline intrusive complex, eclogites, MORB, Icelandic and Hawaiian picrites, Azorean and arc lavas (Baker et al., 2009; Hettmann et al., 2013; Nielsen et al. 2006c, 2007, 2009a, 2016a; Prytulak et al. 2013b). The Tl isotope composition of the mantle is estimated at ε^{205}Tl = -2 ± 1 (2sd) based on analysis of 5 MORB glasses from different ocean basins (Nielsen et al., 2006b, c), and assuming no isotope fractionation during partial melting. Note that the very low mantle abundances and likely influence of sulphides has hampered reliable bulk peridotite analyses.

In addition to orders of magnitude enrichment in Tl compared to igneous materials, low temperature oxidizing processes also can produce large Tl isotope fractionation (e.g., Coggon et al., 2014; Nielsen et al., 2006b; Rehkämper et al., 2002; 2004; see review in Nielsen et al., 2016b). Two vectors of isotope fractionation are apparent. Pelagic clays and Fe-Mn crusts generally display heavy Tl isotope compositions (+5 to +15; Rehkämper et al., 2004; Nielsen et al., 2009) with an aspect of secular variation in ε^{205}Tl, likely reflecting changing seawater compositions. On the other hand, ocean crust that has been altered at low temperatures by circulating hydrothermal fluids have ε^{205}Tl as light as -16 (Coggon et al., 2014; Nielsen et al. 2006b).

In contrast, Tl exists only as Tl^+ in high temperature igneous materials. Theoretical calculations taking into account mass-dependent nuclear volume effects predict only a -0.05 fractionation factor between Tl^+ and a neutral atomic vapor at 1000^0C (Schauble, 2007). Thus, if ε^{205}Tl of lavas differs from the mantle (as represented by MORB) it may reflect the presence of isotopically fractionated Tl from surficial (low temperature) sources. Nielsen et al. (2006c) applied this concept to interpret Hawaiian picrites with positive ε^{205}Tl as having assimilated Fe-Mn crusts in their source. Prytulak et al. (2013b) explored the possibility that, given the distinct directions of Tl isotope fractionation, ε^{205}Tl may be able to distinguish inputs of low temperature fluid altered material from Fe-Mn sediments in lavas from the Mariana arc. No deviant isotope signatures were detected in the Mariana lavas, likely due to the surprisingly constant ε^{205}Tl of the local sediment and altered oceanic crust inputs at the Mariana subduction zone (Prytulak et al., 2013b). These sediments have much less extreme Tl isotope composition than previously investigated sediments (e.g., Rehkämper et al., 2002, 2004) and altered crust from the Ocean Drilling Program Holes 504B, 896A and U1301B (Coggon et al., 2014; Nielsen et al., 2006b). Recent study of the Aleutian arc, however, has documented along-strike changes in Tl isotope composition that mirror changing subducting sediment compositions on the downgoing plate (Nielsen et al., 2016a).

The underlying assumption in using ε^{205}Tl as a tracer of sediments or altered material in the source of mantle-derived lavas is that magmatic processes do not significantly fractionate stable Tl isotopes. The lack of Tl isotope fractionation has been inferred based on analysis of loess (as a proxy for evolved continental material) and one analysis of a potassic dike, both of which have ε^{205}Tl similar to MORB (Nielsen et al., 2005; Nielsen et al., 2016b). Given that resolvable fractionation during magmatic processes is being increasingly documented in many stable isotope systems, it is important to systematically evaluate the effect that such processes have on Tl and Tl isotopes.

Ideal targets for investigating the effects of magmatic processes on stable isotope fractionation are chemically well-characterised co-genetic suites of lavas spanning a range of differentiation products. Two previous studies are of particular relevance (Baker et al., 2010; Hettmann et al., 2014).

Hettmann et al. (2014) investigated Tl abundances and isotope variations in the Ilimaussaq peralkaline intrusive complex in Greenland. This location has an extensive hydrothermal overprint and contains rare Tl-rich minerals such as thalcusite, djerfisherite and chalcothallite and is therefore not directly applicable to the magmatic processes forming MORB, OIB and arc lavas. However, Hettmann et al. (2014) present mineral separate Tl isotope data, thus their data have relevance when considering effects of equilibrium inter-mineral isotope fractionation. Light elements such as Li, and Si and some transition metal elements such as Fe document resolvable equilibrium isotope fractionation, whereby minerals display a distinct isotope signature compared to their surrounding assemblage (e.g., Si: Savage et al., 2011; Fe: Williams et al., 2004; Li: Jeffcoate et al., 2007). In contrast, Tl-rich amphiboles in Hettmann et al. (2014) show ε^{205}Tl virtually indistinguishable from MORB (ε^{205}Tl = -3.7 to -1.7) suggesting that equilibrium inter-mineral isotope fractionation has a limited role.

Baker et al. (2010) present analyses of dacitic to rhyolitic magmas from the Collahuasi Formation in Chile. The focus of the study was on the relation of Tl and ε^{205}Tl to the Collahuasi porphyry copper deposit and, similar to the Ilimaussaq complex, there is a strong hydrothermal overprint, resulting in a range of ε^{205}Tl from -5.1 to +0.1. Thus there is a paucity of information on Tl elemental and isotope compositions in evolving magmatic systems unaffected by hydrothermalism.

This study presents two suites of lavas from tectonically distinct locations (Hekla, Iceland, and Anatahan, Mariana intra-oceanic arc) to assess:

1) The elemental behavior of thallium during magmatic processes

2) The extent of ε^{205}Tl variation induced by magmatic processes

2. Magmatic suites

2.1 Hekla: geologic and geochemical background

Hekla is a ridge shaped volcano in South Iceland (Fig. 1a). It is unusual in that it erupts large volumes of silicic material compared to the dominantly basaltic volcanism typical of Iceland. Hekla erupts lava with a range of SiO_2 from ~45 to ~72 wt% (e.g., Chekol et al., 2011; Savage et al., 2011; Sigmarsson et al., 1992). The basalts are sometimes termed high Fe-Ti basalts (Sigmarsson et al., 1992) and are phenocryst poor (<10%), consisting of olivine, plagioclase, and clinopyroxene (Chekol et al., 2011; Sigmarsson et al., 1992). Whilst dacitic lavas are aphyric, basaltic andesites have <5% phenocrysts consisting of plagioclase, olivine, clinopyroxene, titanomagnetite, and apatite (Chekol et al., 2011; Sigmarsson et al., 1992). None of these mineral phases are expected to incorporate significant Tl.

Major and trace element geochemistry appears consistent with crystal fractionation at first glance, although closer scrutiny reveals mixing of magma from distinct sources along the fractionation path. Basaltic andesites are genetically related to basalts by ~60% fractional crystallization of olivine, plagioclase, clinopyroxene and titanomagnetite (Sigmarsson et al., 1992). The amount of crystal fractionation is consistent with slightly lower δ^{18}O in basalts (4.6 to 4.8‰) versus basaltic andesites (4.8 to 5.0‰) (Sigmarsson et al., 1992). The relationship of basaltic andesites to dacites is less straightforward. Sigmarsson et al. (1992) noted the increase in Th/U ratios from basaltic andesite to dacite (in the absence of actinide-rich fractionating phases); coupled with variations in ^{238}U-^{230}Th-^{226}Ra isotopes argues against further crystal fractionation of basaltic andesites to form Hekla's dacites. Instead, U-series, oxygen isotopic, and experimental constraints are most consistent with the generation of dacites by partial melting of metabasalts and metagabbros that have experienced high temperature alteration (e.g., Sigmarsson et al., 1992; Thy et al. 1990; Chekol et al. 2011). Dacitic $\delta^{18}O$ are not significantly lower than mantle values (Eiler et al., 2001), thus arguing against low temperature hydrothermal alteration of the metabasalts and metagabbros. This is consistent with the lack of geothermal activity at Hekla. The metabasalts and metagabbros presumably melt in response to heating by ascending basaltic magmas generated by mantle melting. Lastly, Hekla's rhyolites have been explained by 15-20% crystal fractionation from dacites (Sigmarsson et al., 1992).

Genetically related basalts and basaltic andesites have homogeneous long-lived Sr-Nd-Pb-Hf isotope compositions, which overlap with MORB (e.g., Chekol et al., 2011; Sigmarsson et al., 1992). Dacites analysed by Sigmarsson et al. (1992) do not have significantly different Sr-Nd isotope compositions from Hekla basalts. However, more recent Sr-Nd-Pb-Hf isotope determinations by Chekol et al. (2011) reveal higher $^{87}Sr/^{86}Sr$ and lower $^{143}Nd/^{144}Nd$ in dacites compared to basalts and basaltic andesites, which they interpret as re-melting altered crustal material, consistent with previous suggestions (e.g., Sigmarsson et al., 1992). Therefore Hekla erupts lavas that have experienced crystal fractionation, mixing and partial melting of two distinct sources (mantle and altered mafic crust).

Hekla has been investigated for Fe and Li stable isotopes by Schuessler et al. (2009). They found no variation in Li isotopes throughout the magmatic sequence, which is consistent with no significant interaction with seawater, again in agreement with inferences based on $\delta^{18}O$ and ^{238}U-^{230}Th-^{226}Ra isotopes. Basaltic to dacitic lavas have stable Fe isotopes that are indistinguishable from other terrestrial basalts (Schuessler et al., 2009); however, Hekla rhyolites have heavier δ^{56}Fe, correlating with indices of differentiation, which Schuessler et al. (2009) attribute to crystal fractionation of the dacitic magma and subsequent settling of isotopically light titanomagnetite by Rayleigh fractionation. Dauphas et al. (2014) subsequently confirmed with direct Nuclear Resonance Inelastic X-ray Scattering (NRIXS) measurements that differences in the co-ordination environment of Fe between oxides and silicate melts induces isotope fractionation, resulting in an isotopically heavy liquid relative to oxide phases.

We present fourteen lavas from Savage et al. (2011) to explore their Tl abundance and stable isotope compositions. The samples were originally investigated for stable Si isotopes variations and revealed the first resolvable high temperature igneous fractionation of silicon isotopes (Savage et al., 2011), defining the δ^{30}Si 'igneous array'. Savage et al. (2011) propose that this array forms by progressive removal of isotopically light mafic phases such as olivine and clinopyroxene. The samples have also been analysed for stable V isotopes and display a striking range of ~ 2‰, correlating with indices of differentiation and again linked to differences in bonding environment of V in minerals and melts and, in this case, are proposed to strongly reflect the fractionation of oxide phases (Prytulak et al., 2017). Finally, the samples have also been analysed for Zn and Mo stable isotopes (Chen et al., 2013; Yang et al., 2015), with both systems demonstrating negligible isotope fractionation with progressive differentiation. Thus Hekla is arguably one of the best-characterised igneous natural laboratories in which to place Tl concentration and isotope measurements into context.

2.2 Anatahan: geologic and geochemical background

Anatahan is the southernmost island of the Northern Mariana Island chain of the intra-oceanic Mariana island arc (Fig. 1b). The Izu-Bonin-Mariana system is well studied as it is both an NSF-MARGINS focus site and the location of numerous Ocean Drilling Program Legs and International Ocean Drilling Program Expeditions which characterized subducting sediments, forearc peridotites and ocean crust (e.g., Hussong et al. 1982). Furthermore, a special volume of the *Journal of Volcanology and Geothermal Research* (volume 146) is dedicated to Anatahan, prompted by its first historic eruption in 2003.

Anatahan comprises a single stratovolcanic edifice (Anatahan volcano) of total height 3700m, with one active subaerial vent and as many as 80 submarine vents, concentrated on the east (trenchward) flank of the island (Chadwick et al, 2005). Lavas are predominantly degassed, low-viscosity dacites (Pallister et al, 2005). In spite of this, subaerial eruptions are explosive with style ranging from Plinian to phreatomagmatic. Eruptions from submarine vents are effusive below 1500m above the sea floor, transitioning to explosive eruptions between 1500m and 2000m.

Much of the early work on the petrogenesis of Anatahan lavas was conducted by Woodhead and co-authors (Woodhead & Fraser, 1985; Woodhead, 1988, 1989). The crystallising assemblage includes plagioclase, clinopyroxene, olivine, orthopyroxene and titanomagnetite (Woodhead, 1988, Pallister et al., 2005; de Moor et al., 2005), none of which are expected to incorporate Tl (e.g., Nielsen et al. 2014; 2016). Thin section investigation of prehistoric lavas reveal minimal to negligible alteration (Woodhead, 1988). Anatahan displays little Fe enrichment or depletion at MgO > 4wt% and so can be considered marginally calc-alkaline (with a tholeiitic index (THI) ~ 0.95; after Zimmer et al., 2010). In contrast Hekla is slightly tholeiitic, with THI of 1.1 (Zimmer et al., 2010).

Anatahan erupts a range of products (SiO_2 49 to 66 wt%) similar to Hekla. The large variability is unusual for the Mariana Islands and thus begs examination of possible crustal assimilation versus crystal fractionation for its origin. There are several lines of evidence against crustal contamination. For example, Sr isotopes lack variation, overlap with MORB, and show no correlation with SiO_2 (Wade et al., 2005). Furthermore, oxygen isotopes range from $\delta^{18}O$ values of 5.5 to 6.1 ‰ (Wade et al., 2005), indistinguishable from MORB (Eiler et al., 2001). Moreover, Zr and P variations are consistent with the late saturation of zircon and apatite along the liquid line of descent, and not significant mixing of already saturated crustal melts during fractionation (Wade et al., 2005).

The subducting sediments at ODP Site 801 and 1149 in the Mariana region are chemically well characterized (e.g., Plank and Langmuir 1998, Kelley et al., 2003; Vervoort et al., 2013), including analyses of Tl and Tl isotopes (Prytulak et al., 2013b). Examination of trace element, radiogenic isotope (Sr-Nd-Pb-Hf) and O isotopes led Wade et al. (2005) to suggest that the Anatahan source contains 1-3% of sediment. Mixing calculations by Wade et al. (2005) suggest that sediments in the Anatahan source have elevated Th/La and Ba/La in compared to bulk Site ODP 801 sediments. They attribute the elevated ratios to the loss of the upper 50m of pelagic clays from the subducting column, perhaps by underplating. A suite of 8 well-characterised lavas from Wade et al. (2005), which encompass prehistoric samples from studies by Woodhead and co-authors, were chosen for investigation.

3. Methods

3.1 Major and trace elements

All major and trace elements for Anatahan samples are given in Wade et al. (2005) with the exception of Tl, which are new ICP-MS determinations. Major and some trace elements for Hekla samples are found in Savage et al. (2011). New high precision trace element determinations of Hekla lavas including elements not previously measured by Savage et al. (2011) such as HREE, LREE, Li, Be, Cs, Tl, Hf, and Ta are presented in the electronic annex. New trace element determinations were carried out at LDEO following the analytical protocols of Kelley et al. (2003) and calibration and USGS standard data is found in the electronic annex. ICP-MS measurement of Tl concentrations were calibrated with USGS reference materials as described in Prytulak et al. (2013b).

3.2 Isotope measurement

Thallium isotope separation and measurement was carried out in the MAGIC labs at Imperial College, London. Briefly, samples were dissolved with standard HF-HNO_3 techniques followed by a two-step chemical isolation of thallium from sample matrix following the procedure of Rehkämper and Halliday, (1999) with modification as described in Nielsen et al. (2004).

Thallium fractions were diluted to 4 ng/g, to which NIST SRM 981 Pb standard was added to externally correct for mass bias (for a final Pb/Tl ratio of ~3). Isotope compositions were determined on a NU Instruments HR MC-ICPMS. Samples were bracketed with NIST SRM 997 Tl isotope standard. Data quality was monitored by measurement of USGS reference materials and the Sigma Aldrich Tl solution standard. Through the course of the study, Sigma Aldrich yielded ε^{205}Tl = -0.78 ± 0.31 2sd, in excellent agreement with the long-term reproducibility of this standard (ε^{205}Tl = -0.79 ± 0.35 (2sd, n=187) as compiled by Nielsen et al., 2016b). Total procedural blanks were <4 pg, which is negligible compared to the amount of Tl processed (> 10 ng).

4. Results

Table 1 presents Tl isotope data and selected major and trace elements for Hekla and Anatahan lavas along with USGS reference materials BCR2 and AGV2 measured contemporaneously with Hekla and Anatahan lavas. The thallium isotope compositions of BCR2 and AGV2 agree well with literature values (see Table 1 and compilation in Nielsen et al., 2016b).

4.1 Hekla

The lavas in this study follow the same fractionation path as those from Sigmarsson et al. (1992) and Chekol et al. (2011). Thallium correlates with indices of differentiation such as SiO_2 and MgO (Fig. 2). Thallium abundances range from 20 to 124 ng/g and positively correlate with chemically similar alkali elements K, Rb, Cs and other incompatible elements such as Ce, La and Pb (Fig. 3).

Hekla's total range in ε^{205}Tl is -2.2 to -0.7, with an average of -1.7 ± 0.8 2sd. The two-sigma standard deviation of all 14 lavas is comparable to analytical precision on a single sample (±0.5 epsilon units). Figure 4 shows ε^{205}Tl against Tl concentration and SiO_2 (wt%). There is remarkably little variation in Tl isotopes, with slightly more scatter in the most primitive samples with the lowest Tl concentrations (Table 1).

4.2 Anatahan

Thallium abundances range from 28 to 176 ng/g, very similar to the range in Hekla samples, and again positively correlate with chemically similar alkali elements K, Rb, Cs and other incompatible elements (Fig. 3). The range in ε^{205}Tl for Anatahan is -2.9 to 0, with an average of -1.3 ± 1.6 2sd, which overlaps with Hekla. Sample Anat 9 is slightly anomalous in that it displays enrichment in Rb, K, Pb, Cs and Pb above the fractionation trend of other lavas in the Anatahan sequence (Fig. 3). This sample also displays the heaviest Tl isotope composition (ε^{205}Tl = 0.0; Fig. 4).

5. Discussion

The elemental behavior of thallium during magmatic processes is evaluated, followed by comparison of ε^{205}Tl with the existing literature of igneous Tl isotope compositions. Thallium elemental and isotopic determinations are then discussed in terms of magmatic petrogenesis specific to Hekla and Anatahan. Finally, the broader implications for the use of Tl abundances and ε^{205}Tl as tool in igneous petrogenesis are examined.

5.1 Thallium elemental behavior during magmatic processes

The two lava suites allow assessment of Tl behavior during magmatic differentiation. To a first order, Anatahan Tl abundances are slightly less systematic than Hekla. This is perhaps unsurprising, given that Anatahan is formed in a subduction setting where multiple inputs from sediments and slab are possible, whereas Hekla arguably has a more straightforward mantle source.

5.1.1 Sulphur, sulphides and comparison with chalcophile elements

McGoldrick et al. (1979) suggested that Tl behaves as a chalcophile element, following sulphur in sulphur-saturated magma. Nielsen et al. (2014) have recently provided evidence that, during mantle melting to create MORB, Tl is associated predominantly with sulphides and thus they also infer chalcophile behavior.

Basalts from Hekla have whole rock S contents of 150 to 180 ppm (Fig. 5a). However, olivine and plagioclase hosted melt inclusions in Hekla basalts have 1400 to 2500 ppm S (Moune et al. 2007) and thus they were likely sulphur saturated (e.g., Jugo et al., 2005). Indeed, Moune et al. (2007) show that S is more soluble in Hekla lavas than MORB and attribute the higher solubility to elevated fO_2 in Hekla's source compared to MORB. Moune et al. (2007) further estimate that 78% to 95% of the original sulphur is degassed. The negative correlation of S and Tl abundances in Hekla (Fig. 5a) can likely be attributed to a combination of degassing and sulphide fractionation. The notion of sulphide fractionation is supported petrographically by identification of chalcopyrite in samples HEK12, 14, 17 and 21. In contrast, copper is a chalcophile, non-volatile element and shows a diffuse positive correlation with S contents in Hekla lavas, and no correlation with Tl (Fig. 5b, c).

Anatahan data is currently limited to microprobe SO_2 analyses of matrix glass and glass inclusions in pyroxene and plagioclase from largely dacitic lavas (Pallister et al., 2005) and thus does not span the same compositional range as the Hekla dataset. However, Anatahan shows a convincing negative trend of Cu and Tl abundances (Fig. 5c). This is the opposite of expectations if Tl and Cu are both assumed to be chalcophile and thus partition dominantly into any sulphide phase(s). Finally, MORB show a 3-fold range in Cu at similar Tl concentrations (Fig 5c). The lack of co-variation in bulk rock determinations might be explained by nugget effects of sulphides, but since the database are laser abalation analyses, this is difficult to reconcile. Therefore, although this dataset cannot directly evaluate Tl behavior during partial melting, there is no compelling evidence of thallium behaving as a chalcophile element during magmatic differentiation, even when sulphides are present.

5.1.2 LIL, REE elements and the search for ‘canonical’ Tl ratios

Thallium shows positive correlations of variable slopes with highly incompatible elements such as Cs, Rb, K and La (Fig. 3) in all available datasets. The correlative relationships in Hekla’s lavas are in agreement with the study of Baker et al. (2010) who found, even when examining ore deposits with high sulphur contents, that thallium displays lithophile behavior. Similarly in Mariana island arc lavas, Tl co-varies with lithophile fluid-immobile elements (Prytulak et al. 2013b). Likewise, at Anatahan, Tl co-varies with lithophile elements (Fig. 3). Therefore, during magmatic differentiation at Hekla and Anatahan, thallium displays lithophile behavior.

A common means of identifying elements with similar partitioning is to produce log-log plots, whereby the closest slope to ‘1’ has the most similar behavior. Given the limited sample numbers, it is not meaningful to perform this exercise with the current dataset. Thus large, self-consistent databases (Jenner and O’Niell, 2012; Jenner et al., 2015; Nielsen et al., 2014) are used as a guide. The goal is to find an element that is not fractionated from Tl during partial melting and differentiation and thus can be used in conjunction with Tl isotopes to evaluate inputs to the source of mantle-derived melts.

The similar elemental characteristics of Cs and Tl prompted use of Cs/Tl to identify exotic inputs to mantle sources (e.g., Nielsen et al., 2006). However, the use of Cs/Tl is not straightforward in arc lavas, where slab phases such as phengite potentially fractionate Cs from Tl (Prytulak et al., 2013b). Furthermore, Nielsen et al.

(2014) have recently re-evaluated the behavior of Ce, Cs, and Tl, arguing that Ce and Tl have essentially identical partition coefficients during partial melting to create MORB, before the onset of major clinopyroxene fractionation.

Both the Anathan and Hekla datasets have restricted Cs/Tl close to MORB values (Fig. 6a). Despite MORB-like Cs/Tl ratios at Anatahan, other volcanoes in the Mariana arc (Prytulak et al., 2013b) and the Aleutian arc (Nielsen et al., 2016a) display anomalously high Cs/Tl ratios, again suggesting that these two elements can be strongly fractionated from one another in subduction zones. Experimental partition coefficients of Cs and Tl in sheet silicates such as phengite would be extremely useful to further determine the cause of these strikingly elevated ratios.

In contrast to the MORB dataset, Ce/Tl does not remain constant through magmatic differentiation at Hekla, and instead displays a steady decrease, consistent with Tl remaining incompatible whilst Ce is incorporated into fractionating clinopyroxene (Fig. 6b). Intriguingly, Anatahan, Ce/Tl is 335 ± 178 2sd, which is lower than the entire MORB dataset (Ce/Tl = 1280 ± 430 2sd), and instead overlaps with the Tonga back arc basin (221 ± 103 2sd; Jenner et al., 2015) and lavas from the Aleutian arc (426 ± 523 2sd; Nielsen et al., 2016a). The depressed and constant Ce/Tl in subduction-related settings could be a potential indicator of prior melt depletion of the mantle wedge. Future examination of other subduction zones will determine how sensitive Tl and Ce/Tl ratios are to the competing effects of wedge depletion and sediment addition.

Finally, since Nielsen et al. (2014) demonstrate that Pb/Tl ratios are more restricted than Cs/Tl ratios in their MORB database, we also examine Pb/Tl versus Tl concentration (Fig. 6c). Similarly to Ce/Tl, back arc basins once again have significantly lower Pb/Tl ratios than MORB. However, Hekla, Anatahan and the

Aleutian arc datasets all lie at broadly overlapping, elevated Pb/Tl compared to MORB. Hekla again demonstrates systematic decrease in Pb/Tl with progressive differentiation.

Given the observation that Cs/Tl ratios are the most invariant and MORB-like in the Hekla and Anatahan differentiation sequences, Cs/Tl is subsequently used for Tl isotope plots. Clearly, there is much to be explored with Tl elemental systematics in contrasting tectonic settings that is beyond the scope of the current work.

5.2 ε^{205}Tl during magmatic evolution

The successful application of Tl isotopes as tracers of isotopically exotic materials in the mantle source of basalts requires evaluation of the magnitude of Tl isotope fractionation induced by magmatic processes. For both suites of lavas, ε^{205}Tl shows little variation, does not co-vary with indices of magmatic differentiation, and largely overlaps with $\varepsilon^{205}\mathrm{Tl}_{\mathrm{MORB}}$ (Fig. 4).

The major fractionating phases at Hekla and Anatahan are similar (olivine, opx, cpx, magnetite, plagioclase), and none are expected to incorporate significant Tl. One caveat is that all of the fractionating phases in these two sequences are anhydrous. Thus there appears to be no control on ε^{205}Tl that could be ascribed to equilibrium inter-mineral isotope fractionation of anhydrous phases. It should be noted that MORB, Hekla and Anatahan lavas are all relatively high degree mantle melts (~10%). Therefore it is not possible to evaluate if Tl isotope fractionation may occur during *incipient* partial melting with this dataset.

5.3 Implications for petrogenesis of Hekla lavas

Thallium abundances and ε^{205}Tl are used to evaluate models proposed for the formation of basalts, basaltic andesites and dacites at Hekla. Basaltic lavas are thought to represent about 10% melting of the mantle source, based on U and Th (Sigmarsson et al., 1992). The ascent of basaltic liquid is proposed to heat and initiate melting of metabasalts and metagabbros in the Icelandic crust, producing dacites; rhyolites are then generated by crystal fractionation of dacitic magma (Chekol et al., 2011; Schuessler et al., 2009; Sigmarsson et al., 1992). Two observations are useful to examine in the context of Hekla petrogenesis: 1) thallium concentration data are highly systematic, and 2) the entire chemical range of eruptive products has indistinguishable ε^{205}Tl.

Basalts from the 1878 and 1913 eruptions have similar Tl, K, Rb, and Cs concentrations. Likewise, basaltic andesites from 1390, 1970, 1980 and 1991 AD also have remarkably similar Tl, Rb, and Cs contents (Table 1). Since crystal fractionation is responsible for the evolution from basalt to basaltic andesite, relative incompatibilities of the elements can be assessed. Taking the ratio of the concentration in the basaltic andesites to the basalts, the relative incompatibility of the elements is Tl>Cs>Rb>K ≈ La. Furthermore, if thallium is assumed to be perfectly incompatible, constraints can be placed on the maximum amount of crystalisation that occurred to generate the basaltic andesites from the basalts by using the equation:

$$C_l/C_o = F^{(D-1)}$$

where C_l is the concentration in the liquid (basaltic andesite), C_o is the concentration in the source (basalts), F is the amount of liquid remaining, and D is the bulk partition coefficient. Assuming perfectly incompatibility (i.e. $D_o^{Tl} = 0$), basaltic andesites are formed by 58% crystalisation from the basalts, in agreement with Sigmarsson et al. (1992) estimate of 62% crystal fractionation. Dacitic lavas have elevated Tl concentrations compared to other incompatible elements. If Hekla dacites (~120 ng/g Tl) are generated from metabasalts with a Tl concentration ~20 ng/g and $D_0^{Tl} = 0$, they can be formed by 16% partial melting, a value in agreement with melting experiments performed by Sigmarsson et al. (1992). Thus inferences based on elemental Tl systematics are in agreement with previous work.

The invariant ε^{205}Tl in Hekla lavas overlapping with $\varepsilon^{205}\text{Tl}_{MORB}$ places strong constraints on the nature of the mantle source. Critically, if pelagic or Fe-Mn sediments or material altered at low temperature (<150°C) were involved in petrogenesis, then the thallium abundance and isotope compositions would likely be perturbed. Even contributions of less than 1% of low temperature altered crust (e.g., Tl = ~250 ng/g; ε^{205}Tl = -10 to -15; Coggon et al., 2014; Nielsen et al., 2006b) or pelagic clays and/or Fe-Mn sediments (e.g., Tl = >1 μg/g; ε^{205}Tl = +3 to 5; Rehkamper et al., 2002; 2004) to a mantle source (containing ~ 1-2 ng/g Tl) would be detectable in Tl concentration and isotope systematics. Since there are no such observations, Tl isotopes are consistent with the notion that, if metabasalts and metagabbros in the Hekla source were altered, it must have been at high temperatures (e.g., Schuessler et al., 2009; Sigmarsson et al. 1992).

5.4 Implications for petrogenesis of Anatahan lavas

Anatahan lavas derive from a mantle source lacking crustal contamination and incorporating 1-3% sediment from the downgoing Pacific plate, based on radiogenic isotope and trace element systematics (Wade et al., 2005). Previous ε^{205}Tl from the Central Mariana Islands north of Anatahan have ε^{205}Tl overlapping with MORB, with the exception of one lava with heavy Tl isotope composition (GUG13; ε^{205}Tl = +1.2), which may be due to degassing (Prytulak et al. 2013b). Lavas from Anatahan, a single volcanic edifice, span a larger range in ε^{205}Tl than is seen in seven islands of the Central Marianas. Furthermore, the range of ε^{205}Tl and Cs/Tl are greater than observed at Hekla (Fig. 7). Therefore additional processes must be explored to explain the greater ε^{205}Tl variation in Anatahan.

An obvious difference between Hekla and Anatahan are their respective tectonic settings. Anatahan is potentially influenced by sediment and altered oceanic crustal inputs derived from the downgoing slab. Figure 7 shows that the sediments currently subducting outboard the Mariana arc (Prytulak et al., 2013b) sit slightly outside the range of lava compositions; however, they do not have extreme ε^{205}Tl, nor significantly elevated Tl concentrations and thus cannot greatly influence the isotope composition of the lavas (see also Prytulak et al., 2013b).

Sample Anat 9 has the highest ε^{205}Tl value of the Hekla and Anathan datasets (Fig. 4). It is also anomalous in terms of enrichment in elements such as K, Rb, Cs, Tl and Pb (Fig. 2, 3). However, it is also the most evolved in terms of its SiO_2 content. Trace element variations spanning a range of elemental behavior can be visually assessed using normalized incompatible element diagrams (Fig. 8). Thallium is not traditionally plotted on such diagrams, so first its position needs to be justified. Based on relative incompatibilities and our assertion that Tl behaves as a lithophile element during magmatic differentiation, we propose its placement between Cs and Rb, with the rest of the large ion lithophile elements. MORB glasses with less than 1 ng/g Rb from the datasets of Jenner and O'Neill (2012) and Nielsen et al. (2014), yield an average Tl concentration of 7 ng/g. If Tl is assumed to be perfectly to very highly incompatible, then the degree of melting to produce MORB with 7 ng/g Tl from a depleted mantle containing 0.38 ng/g Tl (Salters and Stracke, 2004) is 15-20%, which is consistent with other geochemical and geophysical constraints. Thus we normalize lava compositions to the DMM composition of Salters and Stracke (2004). The spread in trace elements on Fig. 8 relates directly to their degree of differentation. Compared to the other lavas, Anat 9 does not display a particularly anomalous trace element pattern. One interpretation, therefore, is that Tl isotope compositions are more sensitive to perturbation than incompatible trace element concentrations.

6. Outlook: ε^{205}Tl as a tracer in mantle-derived melts

Negligible igneous fractionation gives stable Tl isotopes important advantages in their application to mantle geochemistry. First, ε^{205}Tl measurements need not be restricted to primitive material (i.e. basalts) to determine mantle source characteristics, as is required by many geochemical approaches (e.g., trace elements, ^{87}Sr/^{86}Sr, ^{238}U-^{230}Th-^{226}Ra etc.). This significantly expands possible targets to include evolved eruptive products. Second, Hekla has demonstrated that partial melting of different sources (i.e., peridotite versus mafic crust) do not appear to resolvably fractionate Tl isotopes.

6.1 Ocean Island Basalts

There is continued debate over the origin of enriched geochemical signatures in ocean island basalts (e.g., Chauvel et al., 2008; Hart et al., 1992; Jackson and Dasgupta, 2008; Niu and O’Hara, 2003; Pilet et al., 2005; Stracke et al., 2005; Willbold and Stracke, 2010). One long-standing paradigm is that they result from a component of recycled mafic crust (e.g., Hofmann and White, 1982). However, others have suggested a sedimentary origin for enriched geochemical signatures (e.g., Sao Miguel, Azores; Turner et al. (1997) versus Elliott et al. (2007)). Thallium isotopes may provide a novel way to distinguish between these two scenarios. If a contribution of recycled high temperature mafic crust imparts an enriched geochemical signature to OIB, then no stable Tl isotope fractionation is expected. However, if geochemical enrichment is in part from low temperature alteration material or sediments, particularly pelagic clays and FeMn coatings, then Tl isotopes are precisely tuned to detect this signature (e.g., Hawaii; Nielsen et al., 2006c).

Metasomatism is another mechanism to generate enriched geochemical signatures in oceanic basalts (e.g., Pilet et al., 2005). It is unknown what effect metasomatism has on Tl isotopes; however, since metasomatism is a high temperature process, significant Tl isotope fractionation is not expected (e.g., Nielsen et al., 2006b). Thallium will likely be mobilized by metasomatic events and concentrated in K-bearing phases such a phlogopite and amphibole. The similar Tl isotope composition of amphibole and MORB (Hettmann et al., 2014) suggests limited equilibrium inter-mineral fractionation. Thus, Tl elemental enrichments beyond those expected from fractional crystalisation *without* isotope fractionation may be the hallmark of metasomatic processes. Therefore Tl abundances and isotope signatures may be used to clarify arguments for metasomatism versus sedimentary input to create enriched mantle signatures (e.g., Samoa; Workmann et al., versus Jackson et al., 2007).

6.2 Island Arc Lavas

The high concentration of Tl coupled with the wide range of ε^{205}Tl documented in potential sediment and slab inputs make Tl isotopes arguably the most sensitive stable isotope tracer of low temperature materials in both ocean island and arc magmas. The ‘null hypothesis’ demonstrated in the case of the Central Islands of the Marianas where invariant inputs result in invariant outputs strengthens the conclusion of this work that magmatic processes do not fractionate ε^{205}Tl. Furthermore, Tl isotopes appear to track variable sediment input along-arc in the Aleutians (Nielsen et al., 2016a). However, the elemental systematics of Tl may be of even more use than the isotope system. For example, in the Marianas, Pagan island has anomalously high Cs/Tl of >20 (Prytulak et al., 2013b) and Cs/Tl values extend even higher in the Aleutian arc (Nielsen et al., 2016a). Deconvolving the chemical inputs and outputs in subduction systems is complicated. The assessment here, aided by the recent high precision global trace element databases for MORB and back arc basin lavas suggests that thallium can potentially address disparate topics, including sediment addition, wedge depletion, sulphide saturation and the presence of pressure-temperature sensitive phases such as phengite and phlogopite.

7. Summary

Thallium stable isotope compositions are an extremely sensitive isotopic tracer of Fe-Mn and pelagic sediments in the source of oceanic basalts. Since Tl isotopes do not appear to be fractionated by partial melting of recycled crust and are unlikely to be affected by metasomatism, they can be deployed where there is ambiguity about the origin of enriched mantle components and provide key geochemical constraints on the nature of mantle sources. In contrast to many traditional geochemical approaches, evaluation of mantle sources may also be undertaken with evolved lavas. The drawback is that Tl can be *too* sensitive and thus necessitates very careful screening of lavas for post-eruptive alteration.

During magmatic differentiation, Tl behaves as a highly incompatible lithophile element and shows distinct systematics in contrasting tectonic settings that begs further exploration. Thallium elemental and isotopic compositions provide constraints that are consistent with previous studies of Hekla, in terms of the amount of crystal fractionation to produce the lavas and the lack of incorporation of low temperature material in its source. Anatahan volcano spans a greater range in ε^{205}Tl than seven other islands from the Central Mariana Islands, again highlighting the extreme sensitivity of the system to small additions of exotic material.

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Figure Captions

Figure 1: Location of Hekla (a) and Anatahan (b) volcanoes

(a) *Inset*. Grey triangles: major Icelandic volcanoes; black triangle: Hekla. Shaded field: Late Pleistocene/Holocene lava fields. *Main*. Hekla volcano, including sample locations (circles). Modified from Savage et al (2011).

(b) *Inset*. Izu-Bonin-Mariana arc. Contours show water depth in kilometres. Grey triangles: volcanic islands; black triangle: Anatahan; grey markers: non-volcanic islands. Modified from Karig et al (1971). *Main*. Topographic and bathymetric data at Anatahan, modified from the compilation of Chadwick et al., (2005).

Figure 2. a) MgO versus SiO_2. Hekla data sources: Savage et al., (2011); Chekol et al., (2011); Sigmarsson et al., (1992). Anatahan data source: Wade et al., (2005). b) Variation of thallium concentration with SiO_2: [1]Jenner and O’Neill (2012), [2]Nielsen et al., (2014), [3]Jenner et al., (2015), [4]Nielsen et al., (2006c), [5]Nielsen et al., (2007), [6]Prytulak et al., (2013b), [7]Nielsen et al., (2016).

Figure 3 Trace element variation diagrams to assess behavior of thallium during magmatic differentation in MORB, back arc basins and the Hekla and Anatahan datasets. Sample Anat 9 is highlighted and symbols are as in Figure 2b.

Figure 4 Variation of thallium stable isotope composition of the Hekla and Anatahan datasets with Tl concentration (a) and SiO_2 wt% (b). Grey field is the range of

Tl isotope composition in MORB (Nielsen et al. 2006c). Symbols as in Figure 2b.

Figure 5 Variation diagrams to assess indications for chalcophile behavior of thallium during magmatic differentiation. (a) Thallium versus sulphur, (b) sulphur versus copper and (c) thallium versus copper; MORB and back arc basin data are shown for comparison. Symbols as in Figure 2b.

Figure 6 Variation diagrams to assess possible ‘canonical ratios’ involving thallium, including (a) Cs/Tl, (b) Ce/Tl and (c) Pb/Tl. Literature references as in Figure 2b. Note that Azores Pb data are not plotted due to the poor precision of the analyses.

Figure 7 Variation of thallium isotope composition with Cs/Tl ratios. The figure is zoomed in to illustrate details of the Anathan and Hekla datasets. There are other samples, such as lavas from the Aleutians (Nielsen et al., 2016) that plot outside the bounds of the diagram. The grey box is the range of MORB compositions (Nielsen et al., 2006c). Sediment and AOC (altered oceanic crust) samples are from the downgoing plate outboard of the Mariana trench (Prytulak et al. 2013b). Sediment lithologies encompass radiolarian clays, pelagic clays and volcaniclastic material. All other symbols are as in Figure 2b.

Figure 8 Normalised incompatible element diagram for Anatahan lavas with Anat 9 highlighted.

Table 1: Thallium isotope composition and selected major and trace element data

Sample	Age	SiO_2(wt%)	Tl (ppb)	Cs (ppm)	Rb (ppm)	Cs/Tl	ε^{205}Tl	2sd	# Diss	# Measure
Hekla volcano, Iceland										
HEK6	1913 A.D.	46.20	20.3	0.15	12	7.48	-1.9	na	1	1
HEK5	1913 A.D.	46.47	22.0	0.15	12	6.84	-1.1	na	1	1
HEK4	1878 A.D.	46.97	21.7	0.15	12	6.99	-0.7	0.5	2	4
HEK9	1878 A.D.	47.01	23.4	0.16	13	6.82	-2.1	na	1	1
HEK14	1991 A.D.	53.71	48.7	0.32	25	6.49	-1.6	na	1	1
HEK3	1970 A.D.	54.05	53.1	0.32	26	5.97	-2.2	0.4	1	2
HEK8	1970 A.D.	54.59	51.8	0.34	27	6.49	-1.6	0.2	1	2
HEK17	1980 A.D.	54.57	50.6	0.32	26	6.28	-1.9	na	1	1
HEK16	1980 A.D.	54.81	50.6	0.33	26	6.50	-1.8	0.9	2	4
HEK15	1980 A.D.	59.64	59.2	0.44	34	7.36	-1.4	0.8	1	3
HEK21	1390 A.D.	55.64	53.8	0.35	27	6.42	-2.1	0.4	1	3
HEK18	2800 B.P.	68.41	123	0.69	53	5.58	-1.5	na	1	1
HEK1	2800 B.P.	68.71	117	0.67	52	5.71	-1.5	0.7	2	5
HEK19	2800 B.P.	68.88	124	0.71	55	5.74	-2.0	0.5	2	5
Anatahan volcano, Mariana Islands										
AN8		49.28	27.8	0.21	11	8.78	-0.9	0.5	2	5
AN1		51.66	29.7	0.28	12	10.74	-0.7	0.2	1	2
AN2		52.31	44.6	0.24	9	6.34	-2.9	0.6	2	5
04Anat4		54.03	84.3	0.53	20	8.00	-1.4	0.5	2	3
04Anat3		56.35	103	0.60	24	7.93	-1.6	0.9	1	4
04Anat1		59.51	124	0.72	29	7.42	-1.0	0.6	2	5
Anat9		65.06	139	0.94	43	8.83	0.0	0.3	1	3
AN10		63.91	176	0.81	37	7.08	-1.6	0.6	2	5
USGS Reference Materials										
BCR2 (this study)		54.10	257		48		-2.5	0.5	12	25
BCR2 (literature)							*-2.5*	*0.4*		*4*
AGV2 (this study)		59.30	267		69		-2.7	0.2	5	9

AGV2 (literature)	*-3.0*	*0.6*		*8*

Samples measured only once are assigned a 2SD uncertainty of 0.5. # Diss = number of separate dissolutions of the same powder. # Measure = number of isotope ratio measurements on the sample. Literature values for BCR2 and AGV2 are taken from the compilation in Nielsen et al. (2016).

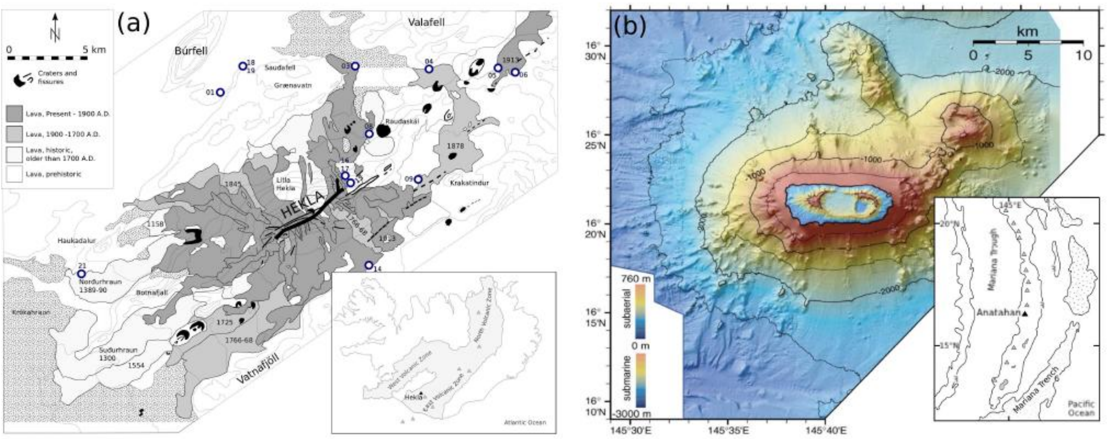

(a)
N
0
5 km
Craters and fissures
Lava, Present - 1900 A.D.
Lava, 1900 -1700 A.D.
Lava, historic, older than 1700 A.D.
Lava, prehistoric
Búrfell
Valafell
Saudafell
Grænavatn
Raudaskál
Litla Hekla
HEKLA
Krakatindur
Haukadalur
Nordurhraun 1389-90
Botnafjall
Sudurhraun 1300
Vatnafjöll
1845
1158
1878
1913
1766-68
1725
1554
01
03
04
05
06
09
14
16
17
18
19
21
West Volcanic Zone
North Volcanic Zone
East Volcanic Zone
Hekla
Atlantic Ocean
(b)
km
0
5
10
-2000
-1000
1000
760 m
subaerial
0 m
submarine
-3000 m
16° 30'N
16° 25'N
16° 20'N
16° 15'N
16° 10'N
145°30'E
145°35'E
145°40'E
145°E
20°N
15°N
Mariana Trough
Anatahan
Mariana Trench
Pacific Ocean

Figure 1

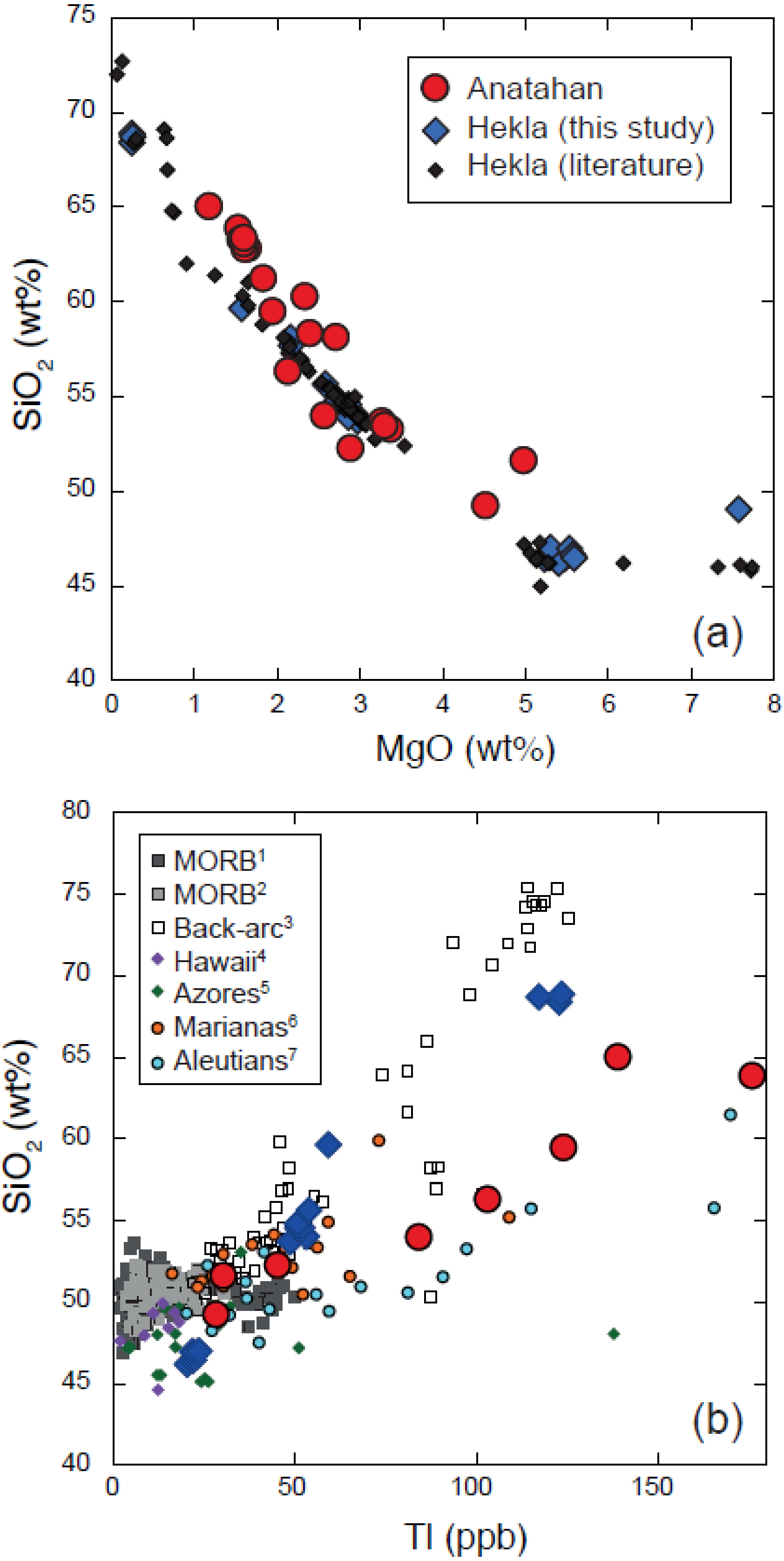

Anatahan
Hekla (this study)
Hekla (literature)
(a)
SiO_2 (wt%)
MgO (wt%)
75
70
65
60
55
50
45
40
0
1
2
3
4
5
6
7
8
MORB^1
MORB^2
Back-arc^3
Hawaii^4
Azores^5
Marianas^6
Aleutians^7
(b)
SiO_2 (wt%)
Tl (ppb)
80
75
70
65
60
55
50
45
40
0
50
100
150

Figure 2

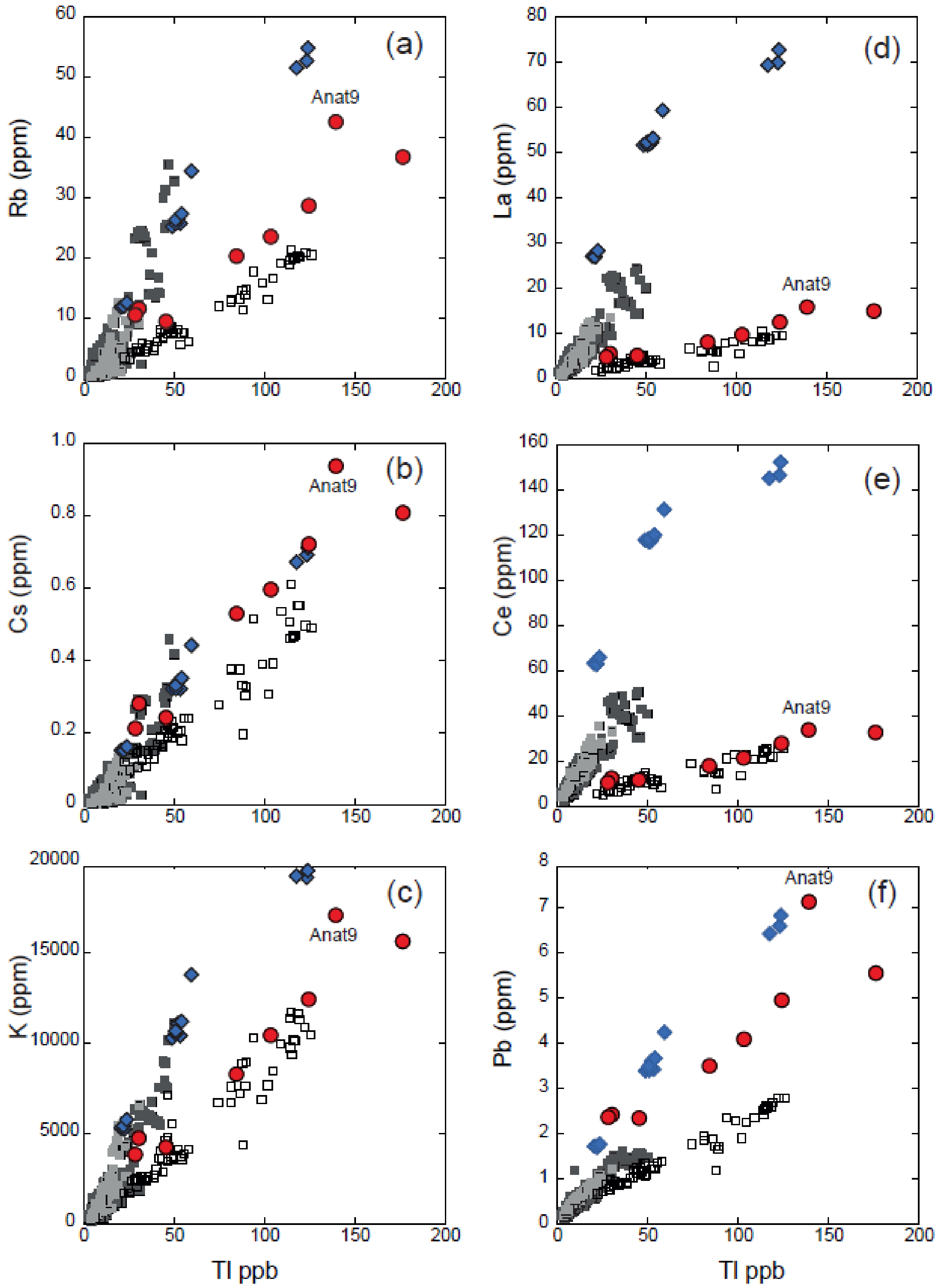
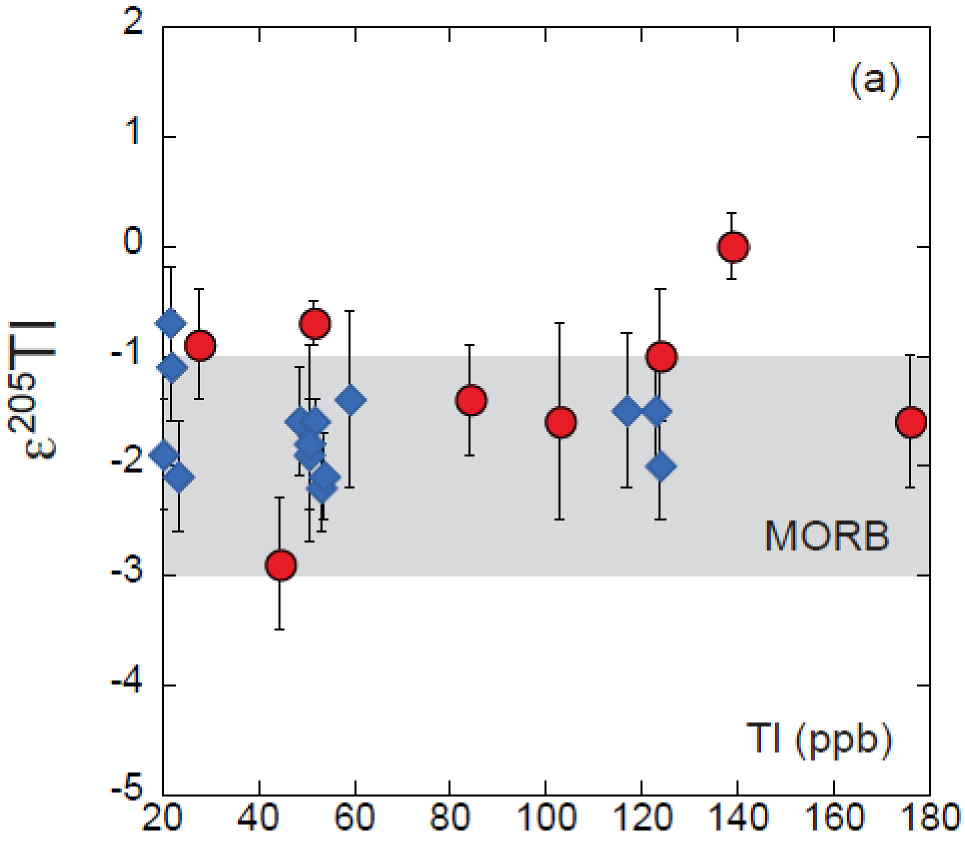

(a)
Rb (ppm)
0
10
20
30
40
50
60
Anat9
(d)
La (ppm)
0
10
20
30
40
50
60
70
80
Anat9
(b)
Cs (ppm)
0
0.2
0.4
0.6
0.8
1.0
Anat9
(e)
Ce (ppm)
0
20
40
60
80
100
120
140
160
Anat9
(c)
K (ppm)
0
5000
10000
15000
20000
Anat9
(f)
Pb (ppm)
0
1
2
3
4
5
6
7
8
Anat9
0
50
100
150
200
Tl ppb
Tl ppb

Figure 3


(a)
MORB
Tl (ppb)
ε^{205}Tl
2
1
0
-1
-2
-3
-4
-5
20
40
60
80
100
120
140
160
180

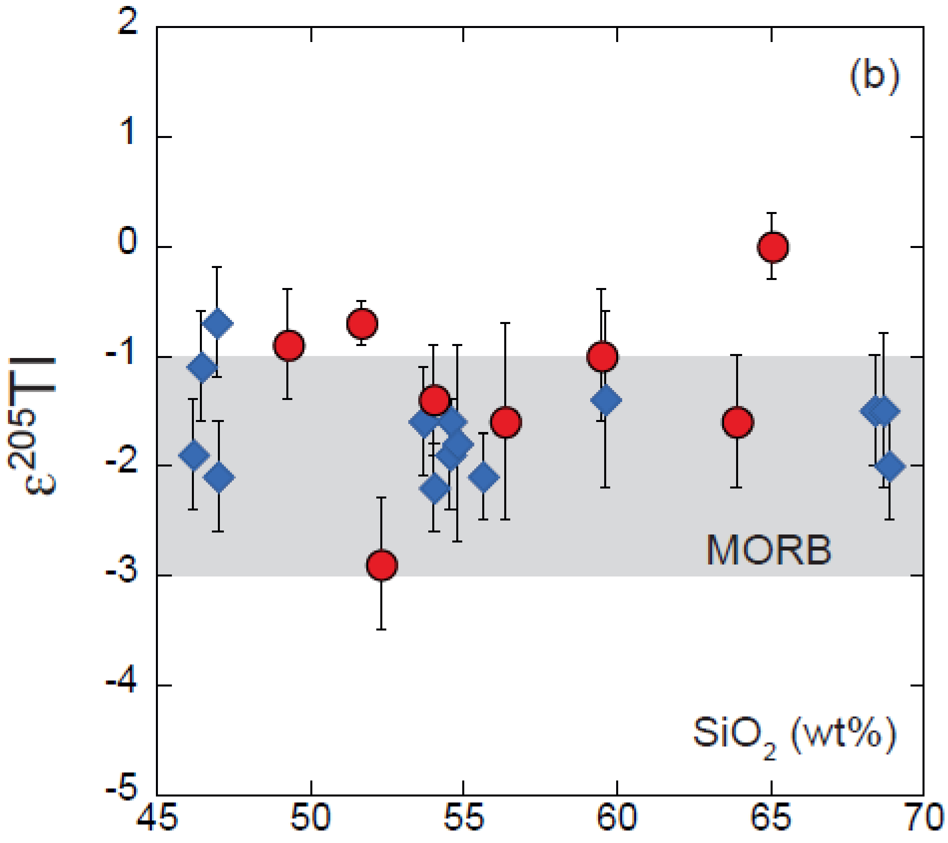

(b)
MORB
SiO$_2$ (wt%)
ε^{205}Tl
2
1
0
-1
-2
-3
-4
-5
45
50
55
60
65
70

Figure 4

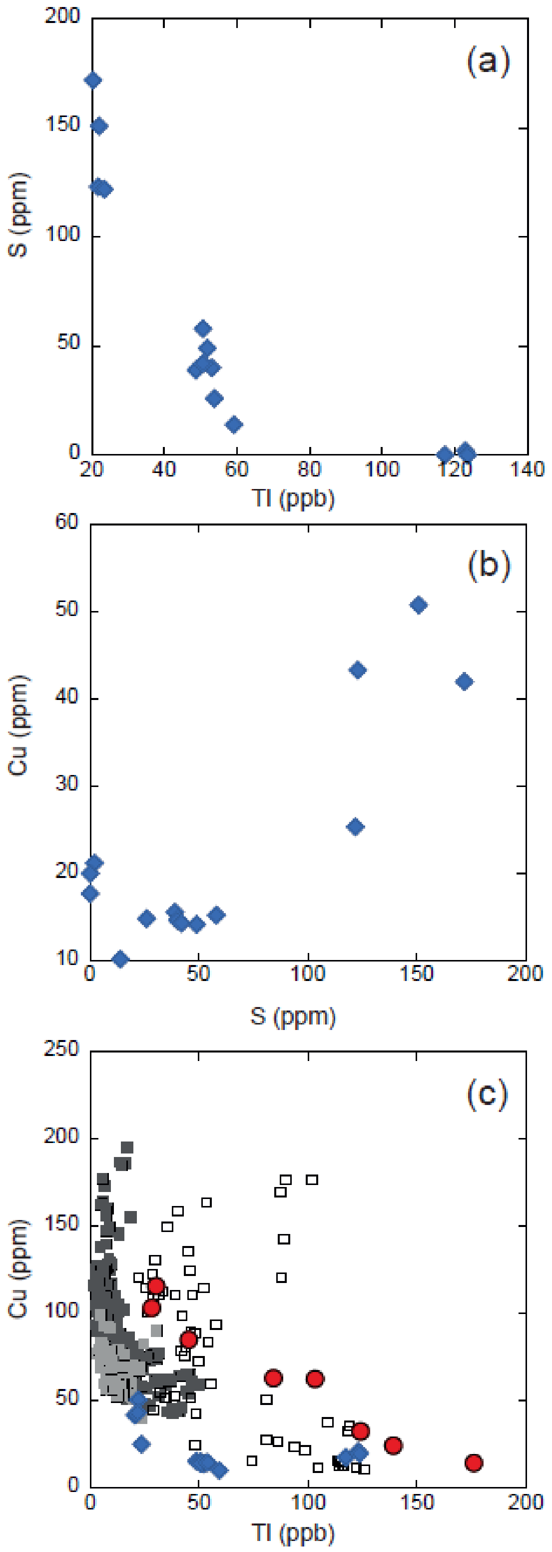

(a)
S (ppm)
200
150
100
50
0
20
40
60
80
100
120
140
Tl (ppb)
(b)
Cu (ppm)
60
50
40
30
20
10
0
50
100
150
200
S (ppm)
(c)
Cu (ppm)
250
200
150
100
50
0
0
50
100
150
200
Tl (ppb)

Figure 5

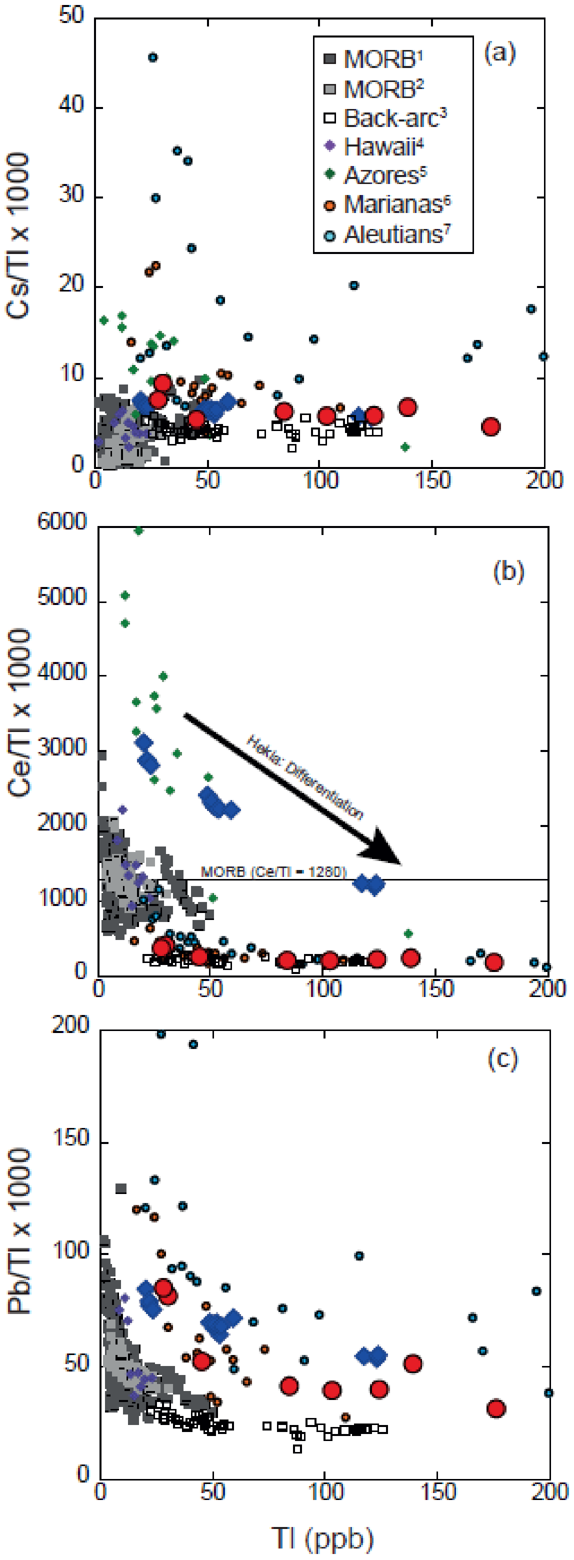

(a)
MORB[1]
MORB[2]
Back-arc[3]
Hawaii[4]
Azores[5]
Marianas[6]
Aleutians[7]
Cs/Tl x 1000
0
10
20
30
40
50
0
50
100
150
200
(b)
Ce/Tl x 1000
0
1000
2000
3000
4000
5000
6000
Hekla: Differentiation
MORB (Ce/Tl = 1280)
0
50
100
150
200
(c)
Pb/Tl x 1000
0
50
100
150
200
0
50
100
150
200
Tl (ppb)

Figure 6

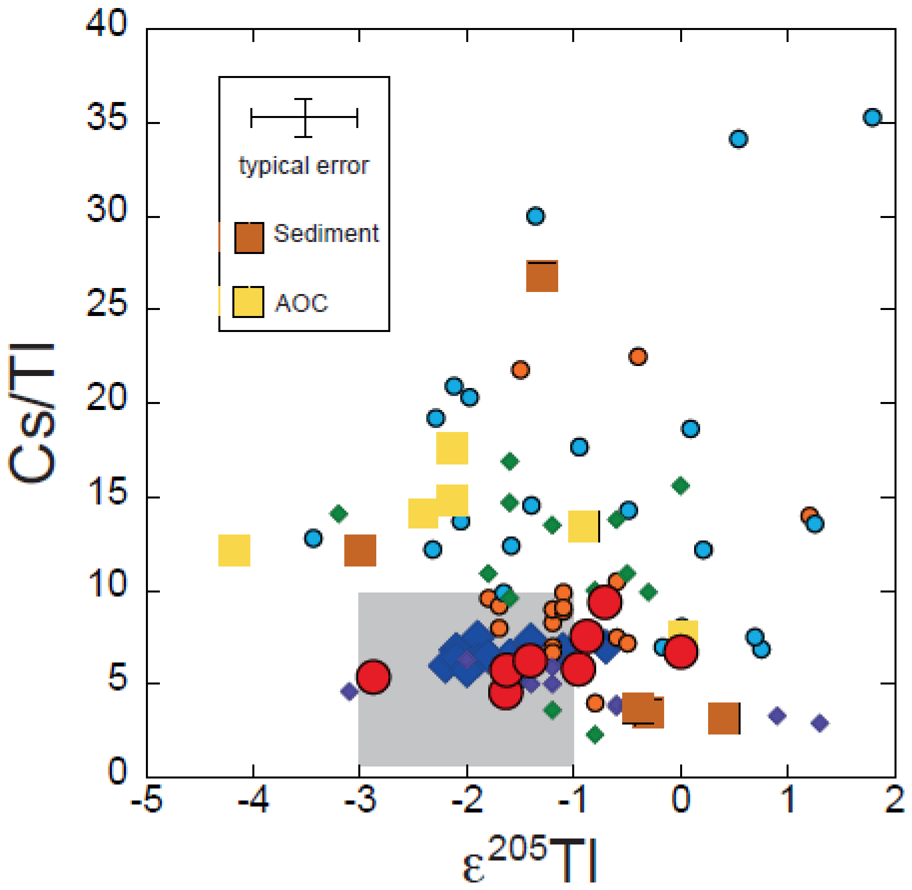

typical error
Sediment
AOC
Cs/Tl
ε^{205}Tl
40
35
30
25
20
15
10
5
0
-5
-4
-3
-2
-1
0
1
2

Figure 7

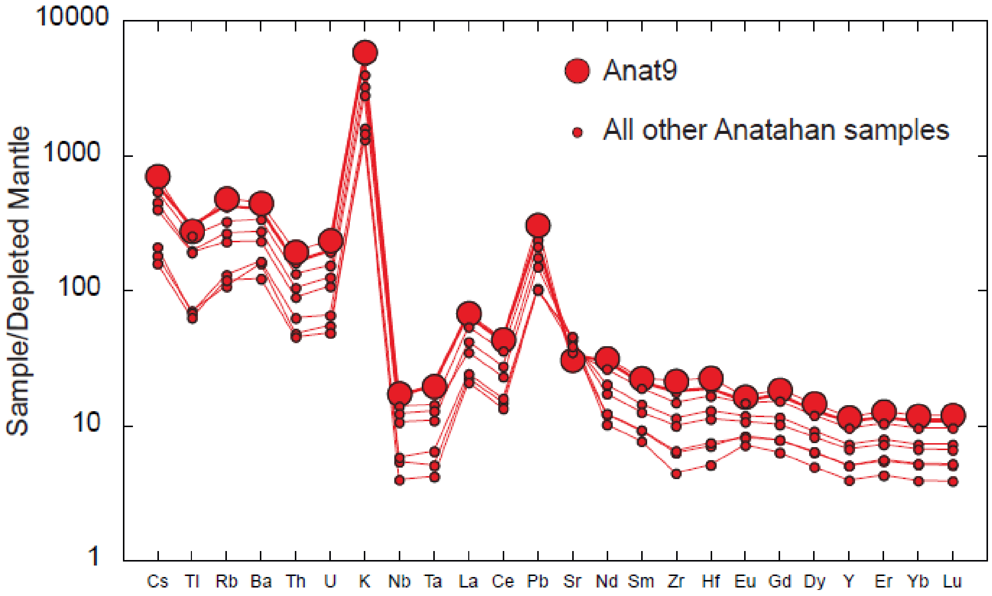
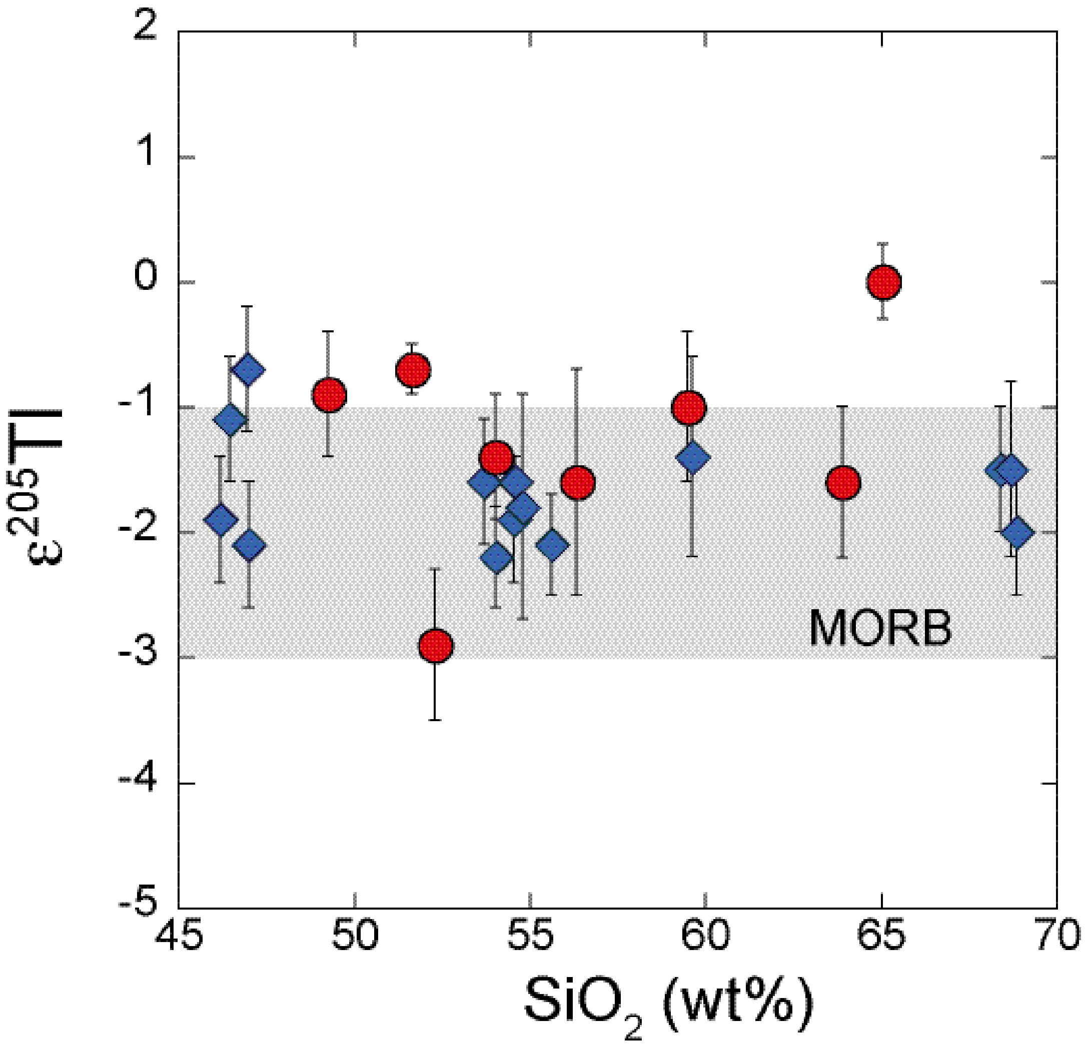

Sample/Depleted Mantle
10000
1000
100
10
1
● Anat9
● All other Anatahan samples
Cs
Tl
Rb
Ba
Th
U
K
Nb
Ta
La
Ce
Pb
Sr
Nd
Sm
Zr
Hf
Eu
Gd
Dy
Y
Er
Yb
Lu

Figure 8



Graphical abstract