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Thallium elemental and isotopic systematics in ocean island lavas

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21 **Abstract**

22 The Earth's mantle exhibits marked chemical heterogeneity, sampled via oceanic basalts. We provide a
23 comprehensive examination of thallium systematics in ocean island basalts (OIB): new high-precision trace
24 element analyses, including Tl, and Tl isotopic compositions for 48 OIB spanning the entire range of
25 observed Sr-Nd-Hf-Pb isotope ratios. All investigated OIB are characterised by ubiquitous Tl depletion
26 requiring OIB mantle sources to have Tl concentrations as low as 0.2 ng/g, which is an order of magnitude
27 lower than estimates for the primitive mantle and similar to Tl concentrations inferred for the depleted
28 mantle. The low Tl concentrations inferred for OIB mantle sources are interpreted to reflect near quantitative
29 removal of Tl during subduction and inefficient Tl recycling into the deeper mantle. If true, the Tl isotopic
30 composition of surface materials may not be readily translated to the mantle sources of OIB.

31 The new OIB dataset shows a >10 ϵ -unit range in primary isotopic variation, from $\epsilon^{205}\text{Tl} = -6.4$ to $+6.6$.
32 However, the majority of samples (32 of 48) are within uncertainty of mantle values ($\epsilon^{205}\text{Tl} = -2 \pm 1$), and
33 show no co-variation with radiogenic isotopic composition. Notably, OIB with only minor Tl depletion (11
34 samples) have Tl isotopic compositions outside the mantle range. The Tl concentration contrast between the
35 mantle and inputs such as sediments and altered basalt is so great that minor additions (<1% by mass) of
36 high-Tl material will dominate the isotopic budget of a lava, with decoupling of Tl and radiogenic isotopic
37 compositions as an expected result. Thallium isotopic compositions of OIB are therefore difficult to link
38 directly to radiogenic isotope variations and the mantle components they may reflect. Indeed, if isotopically
39 distinct Tl from altered oceanic crust and/or sediments were efficiently recycled into the mantle and sampled
40 via OIB, *more* variation in the Tl isotopic composition of OIB would be expected than is observed. The
41 markedly unsystematic primary Tl isotopic variations in OIB therefore likely reflect the residual Tl isotopic
42 composition of subducted material, and/or Tl acquired *en route* to the surface via shallow-level crustal
43 assimilation.

44 **1. Introduction**

45 The majority of intraplate oceanic volcanism is the surface expression of deep-rooted thermochemical
46 upwellings, or 'mantle plumes' (e.g. Morgan, 1971; Hofmann and White, 1982; Montelli et al., 2006). Ocean
47 island basalts (OIB) thus provide a window into geochemical heterogeneity of the otherwise inaccessible
48 deep mantle (e.g. White, 2015). Zindler and Hart (1986) first proposed a classification scheme for oceanic

49 basalts based on the observation that their radiogenic Sr-Nd-Pb isotope ratios vary systematically between a
50 restricted number of isotopic signatures, termed ‘end-members’ or ‘components’. Decades of subsequent
51 work has subdivided or refined the details and interpretations of the radiogenic Sr-Nd-Pb isotopic variability
52 in oceanic basalts (e.g. Weaver, 1991; Chauvel et al., 1992; Hofmann, 1997; Workman and Hart, 2005;
53 Willbold and Stracke, 2006). In general, the chemical variations observed in OIB can be reproduced via
54 mixing of ambient mantle with other components, commonly identified with various recycled crustal
55 lithologies (e.g. Hofmann and White, 1982; Weaver, 1991; Chauvel et al., 1992). Within this framework, it is
56 suggested that the so-called HIMU (high $\mu = {}^{238}\text{U}/{}^{204}\text{Pb}$) signature may represent ancient subducted oceanic
57 crust, isolated for ~2 Ga, while enriched mantle (EM)-type signatures might represent incorporation of
58 heterogeneous continental components in the form of clastic sediments or continental crust eroded at
59 destructive plate margins (e.g. Hofmann and White, 1982; Zindler and Hart, 1986; Chauvel et al., 1992;
60 Hofmann, 1997; Stracke et al., 2003, 2005; Willbold and Stracke 2006, 2010; Stracke, 2012).

61 Inferring mantle source compositions from the radiogenic isotope ratios observed in basalts is challenging,
62 because sampling of the different source components via partial melting depends on a number of factors,
63 such as initial concentrations, melting behaviour, partition coefficients, extent of melt mixing, and time
64 elapsed between parent-daughter fractionation events. As a consequence, it is often difficult to reach
65 unambiguous interpretations of the origins and history of mantle sources.

66 Resolving such ambiguities about the nature and origin of mantle composition and evolution on the basis of
67 radiogenic isotopic variation observed in OIB is necessary to constrain global geochemical cycles and the
68 Earth’s thermal evolution. Stable isotope systematics may provide useful independent constraints, as low-
69 temperature surface environments have the potential to generate resolvable stable isotope fractionations,
70 which might then be traced through subduction recycling into the mantle and subsequently sampled via OIB.
71 Analytical advances have enabled the development and application of a variety of stable isotope systems to
72 igneous rocks, motivated in part by the potential for such systems to act as a tracer of recycled materials.
73 Many of these advances were recently reviewed in Teng et al. (eds), (2017), for stable isotope systems from
74 Li to U. In general, larger isotope fractionations occur in surface environments than magmatic environments,
75 and so a logical aim is to identify the incorporation of recycled surface material by determining whether
76 magmatic rocks carry a stable isotopic signature that is distinguishable from the mantle.

77 **1.2 Thallium: a potential tracer for recycled materials**

78 Thallium is a highly incompatible element, conventionally grouped with the alkali elements due to the
79 similar ionic radii of Tl⁺ and the heavier alkali metals (e.g. Shaw, 1952; Heinrichs et al., 1980). The relative
80 abundance of the two stable isotopes, ²⁰⁵Tl (~70%) and ²⁰³Tl (~30%), is reported as ε²⁰⁵Tl relative to the
81 NIST SRM 997 Tl isotope standard (Rehkämper and Halliday, 1999):

$$82 \quad \epsilon^{205}\text{Tl}_{\text{SRM997}} = 10000 \cdot \left[\left(\frac{{}^{205}\text{Tl}}{{}^{203}\text{Tl}}_{\text{sample}} - \frac{{}^{205}\text{Tl}}{{}^{203}\text{Tl}}_{\text{SRM997}} \right) / \left(\frac{{}^{205}\text{Tl}}{{}^{203}\text{Tl}}_{\text{SRM997}} \right) \right]$$

83 Thallium does not appear to undergo isotope fractionation during the high-temperature igneous processes of
84 partial melting, metasomatism, and anhydrous fractional crystallisation. A systematic study of two co-genetic
85 igneous suites spanning a range of SiO₂ contents from Iceland and the Mariana island arc found a restricted
86 range in ε²⁰⁵Tl (Hekla: ε²⁰⁵Tl from -2.2 to -0.7; Anatahan: ε²⁰⁵Tl from -2.9 to 0.0), and indicates that no
87 analytically resolvable Tl isotope fractionation occurs during anhydrous magmatic differentiation (Prytulak
88 et al., 2017). Fitzpayne et al. (2020) analysed phlogopite mineral separates from highly metasomatised
89 mantle xenoliths, again finding a strikingly restricted range in isotopic composition (ε²⁰⁵Tl = -2.5 ± 1.3 2sd, n
90 = 25). This implies that the Tl isotopic composition of magmatic products should correspond to that of their
91 sources, allowing the use of Tl isotope ratios to disambiguate the history of even evolved igneous rocks.

92 Direct measurements of Tl isotope ratios in mantle peridotites are hindered by their low concentrations (e.g.
93 primitive mantle <4 ng/g: McDonough and Sun, 1995; 4.1 ng/g: Palme and O'Neill, 2014). However, a
94 harzburgite analysed by Nielsen et al. (2015) with ε²⁰⁵Tl = -2.0 ± 0.8 (2sd), is indistinguishable from the Tl
95 isotopic composition of MORB (ε²⁰⁵Tl = -2.0 ± 1.0 2sd; Nielsen et al., 2006a, 2017b), thus suggesting that Tl
96 isotopes are not fractionated by partial melting processes.

97 Thallium elemental systematics in MORB are constrained by several large self-consistent (i.e. samples
98 measured by the same protocols in the same laboratory) datasets collected in recent years, including well-
99 calibrated high-precision Tl concentrations (Jenner and O'Neill, 2012; Nielsen et al., 2014; Yang et al.,
100 2018).

101 Thallium concentrations are generally 100s to 10,000s of ng/g with large isotopic fractionations at the
102 Earth's surface. The continental crust is the main terrestrial host of Tl (~500 ng/g e.g. Rudnick and Gao,
103 2003; Jenner, 2017), with a Tl isotopic composition, inferred via loess, indistinguishable from MORB

104 (Nielsen et al. 2006b). Relative to the mantle, modern altered upper oceanic crust (AOC) has elevated Tl
105 concentrations (~200 ng/g) and light Tl isotopic compositions ($\epsilon^{205}\text{Tl} \sim -20$ to -5 ; Nielsen et al., 2006b,
106 2017b), whereas FeMn sediments have very high Tl contents (>10,000 ng/g) and preferentially incorporate
107 the heavier Tl isotope ($\epsilon^{205}\text{Tl} \sim +5$ to $+15$; review of Nielsen et al., 2017b). The Tl concentration contrast
108 spanning order of magnitude between the mantle and potential recycled components, coupled with the
109 resolvable and opposite directions of isotope fractionation in surface materials relative to the mantle,
110 theoretically makes Tl isotopic compositions extremely sensitive to contributions of recycled surface
111 materials to the mantle. Indeed, previous work investigating subduction settings has shown that Tl isotope
112 ratios of arc lavas can be directly linked to the isotopic composition of materials subducting outboard of the
113 associated trenches (Prytulak et al., 2013; Nielsen et al., 2015, 2016, 2017a; Shu et al., 2017, 2019). By the
114 same reasoning, Tl isotopic compositions may covary with traditional radiogenic isotope ratios in ocean
115 island basalts, used to define mantle components. If some EM-type signatures reflect incorporation of
116 recycled sediments, then isotopically heavy Tl is predicted. Likewise, if the HIMU OIB signature develops
117 via input of AOC then HIMU lavas would be expected to exhibit isotopically light Tl.

118 **1.3 Sample selection and aims**

119 Previous Tl isotope studies of OIB have used the interpretive framework of isotopically heavy thallium
120 indicating FeMn sediments and/or pelagic clays, and isotopically light thallium indicating AOC. Previous
121 work has examined Hawai'i (Nielsen et al., 2006a), the Azores (Nielsen et al., 2007), Iceland (Nielsen et al.,
122 2007; Prytulak et al., 2017), and St. Helena (Blusztajn et al., 2018), documenting a range of $\epsilon^{205}\text{Tl} = -10$ to
123 $+3.9$. This large range is mostly due to variations in rocks from Hawai'i, ascribed to the addition of FeMn
124 sediments, and St Helena, ascribed to the addition of AOC. Thus far, no published studies have examined
125 EM-type lavas, or HIMU lavas from localities other than St Helena. Here, we investigate EM-type lavas and
126 expand the number of HIMU localities, to better characterize the full range of known OIB sources. All
127 selected samples have radiogenic isotope data and show limited evidence of alteration (e.g. low loss on
128 ignition, freshness on inspection of thin section). The 48 new analyses comprise 32 EM-type (13 'EMI', 19
129 other EM) and 16 HIMU lavas (Table 1). We aim to evaluate, on a global scale, the potential relationships
130 between Tl elemental abundances, Tl stable isotopes, and radiogenic isotopic compositions in OIB to
131 investigate the nature of mantle components and the efficiency of Tl cycling between crust and mantle.

132 **2. Methods**

133 Sample digestions and chemical separations were carried out in the MAGIC Laboratories, Imperial College
134 London, as described in Brett et al. (2018). Purified water (resistivity 18.2 M Ω cm from a Milli-Q system)
135 and acids purified via sub-boiling distillation in quartz or PTFE stills were used throughout.

136 **2.1 Trace element determination**

137 While Tl concentrations can be determined during isotope ratio measurements, early studies report
138 uncertainties of 25% (e.g. Rehkämper et al., 2002), improved to ~10% by later work (e.g. Prytulak et al.
139 2013) for relatively high concentration samples >20 ng/g. In contrast, the precision of Tl measurements via
140 ICP-QQQ ('triple-quad' inductively coupled plasma mass spectrometer) is generally <4% RSD, though the
141 uncertainty is higher for samples with lower Tl concentrations. Concentrations for 39 trace elements,
142 including Tl, were obtained at the Open University, UK, using an Agilent 8800 ICP-QQQ following the
143 procedure detailed in Brett et al. (2018).

144 In brief, for most samples approximately 50 mg of powder was weighed into a screw-top Savillex[®] PFA vial.
145 To ensure precise and accurate determination of low Tl concentrations, ~75-100 mg of powder was weighed
146 out for samples G6, FH-01, TH39, HV64, 74-386, and 108B. A 3:1 mixture of concentrated HF and HNO₃
147 was added to the vials, which were then heated to 140 °C for at least 24 hours. Samples were subsequently
148 evaporated to *near* dryness, and dried down from 0.5-1 ml concentrated HNO₃ at 180 °C at least three times
149 in order to destroy insoluble fluorides formed during the initial digestion. Samples were next taken up in 2
150 ml 6M HCl, and refluxed at 120 °C for at least 24 hours, during which time they were ultrasonicated twice
151 for 20 minutes, before being evaporated to complete dryness at 120 °C. 2 ml concentrated HNO₃ and 1 ml
152 water were then added to each sample, followed by refluxing at 140 °C for at least 24 hours. Samples were
153 again evaporated to dryness at 140 °C, before finally being made up to 1000-fold dilution in 2% HNO₃.
154 Sample solutions were aspirated using a quartz microflow nebuliser with an uptake rate of 0.5 ml min⁻¹, with
155 sensitivity on the order of 1-5 x 10⁷ cps per μ g/ml, depending on the element. Two collision/reaction gas
156 configurations were used: no gas, for Tl and most other elements, and O₂, for most Rare Earth Elements (see
157 Brett et al., 2018). In the no gas configuration, oxide levels, measured as CeO⁺/Ce⁺, were kept below 1%;
158 double-charged species, measured as Ce²⁺/Ce⁺, were kept at 1.6%.

159 All elements except Tl were calibrated using the values provided in Eggins et al. (1997) for USGS reference
160 materials (RMs) W-2 and DNC-1. For Tl, USGS RMs BIR-1, BHVO-2 and AGV-1 were used as calibrators,
161 employing the values of Brett et al. (2018). Calibrator materials were run at the beginning of each
162 measurement session. An internal solution standard (with Be, Rh, In, Tm, Re, Bi) was added online to
163 monitor and correct instrumental drift. Drift was further monitored after every five measurements of
164 unknown solutions with a measurement block comprising GSJ RM JB-2, 2% HNO₃, and a repeated unknown
165 sample (G-6).

166 **2.2 Thallium isotope ratio determination**

167 Procedures for Tl separation and subsequent measurement of Tl isotopic compositions followed established
168 protocols. Briefly, all procedures were carried out at the MAGIC Laboratories, Imperial College London.
169 Samples were digested via standard HF-HNO₃ techniques, and Tl isolated from the matrix using a 2-stage
170 ion exchange chromatography procedure detailed in Rehkämper and Halliday (1999) and Nielsen et al.
171 (2004), with modifications as described in Brett et al. (2018). The majority of isotope ratio measurements
172 were performed using a *Nu HR MC-ICP-MS* equipped with 10¹¹ Ω resistors, as low resolution measurements
173 using a ~100 µl/min flow rate nebuliser connected to an *Aridus*, *Aridus II* or *Nu DSN* desolvating system,
174 with Tl solutions ranging in concentration from 2-5 ng ml⁻¹ and a sensitivity of ~800 V/ppm Tl.

175 The limited availability of powder for some OIB samples, coupled with low Tl concentrations, required
176 measurement of solutions with Tl concentrations of <1 ng/ml. Measurements of these low-concentration
177 analytes on the *Nu HR MC-ICP-MS* are less precise than those of solutions with 2-5 ng/ml Tl. Measurements
178 on a *Nu Plasma II MC-ICP-MS* during the later phase of the project have significantly increased sensitivity
179 compared to the *Nu HR MC-ICP-MS*. For Tl, sensitivity on the *Nu Plasma II* was routinely well in excess of
180 1000 V/ppm at the same measurement conditions. Otherwise, the method for isotope ratio determination on
181 the *Nu Plasma II* was identical to the *Nu HR*, as described in Brett et al. (2018).

182 A secondary Tl isotope reference solution from Aldrich ('Aldrich Tl solution'), first characterised by
183 Rehkämper and Halliday (1999), is routinely used (>2000 measurements across at least seven laboratories;
184 Nielsen et al., 2017b) to monitor machine performance. At least two measurements of the Aldrich Tl solution
185 were performed at the beginning and end of each session, with additional measurements performed

186 throughout, typically after every 6 unknown samples. Additionally, a well-characterised USGS reference
187 material (typically BCR-2, though AGV-2 and BHVO-2 were also used) was processed through the complete
188 sample preparation procedure with every batch of 10 samples prepared for MC-ICP-MS analysis.

189 **Powder leaching tests.** Thallium can be concentrated in secondary clays and ferromanganese coatings. To
190 assess possible effects of secondary, low-temperature alteration processes on Tl isotopic composition,
191 powder leaching experiments were performed. Samples with isotopic compositions that differed from
192 average MORB by more than 3 ϵ units, as determined on unleached powders, were chosen for these leaching
193 experiments.

194 The leaching protocol followed the cold acid leaching of Weis and Frey (1991). Approximately 10 ml 6M
195 HCl was added to 100-300 mg of a sample powder, and the suspension was ultrasonicated for 30 minutes.
196 After settling for at least 30 minutes, the leachate was drawn off and discarded, and a further ~10 ml 6M HCl
197 was added to samples, which were then ultrasonicated again for 20-30 minutes. This process was repeated
198 until the leachate ran clear (a minimum of 3 cycles), and was then repeated a further 2 times with purified
199 water in place of HCl. Leached powders were then evaporated, digested, separated and measured in the same
200 manner as unleached powders.

201 **3. Results**

202 **3.1 Trace element concentrations**

203 Table 2 lists key major and trace element concentrations for the 48 OIB samples. Thallium concentrations
204 range from 7 to 235 ng/g. The full dataset of 39 elements is provided in Electronic Annex 1 along with
205 results for the reference materials measured contemporaneously with the OIB samples. Trace element
206 concentrations obtained for repeated measurement of BCR-2 and JB-2 are in good agreement with accepted
207 values (Electronic Annex 2). For most elements, RSDs are generally <3%; for Tl, RSDs are <7% for 34
208 samples, and >10% for 5 samples (Electronic Annex 2).

209 Many samples have existing trace element data published on the same powders (Electronic Annex 2, 3), and
210 there is generally good agreement with previous work. We emphasize that the new data pays particular
211 attention to the calibration of Tl concentration measurements, and is therefore be used throughout the
212 remainder of this work.

213 3.2 Thallium isotope ratios

214 Table 2 presents the Tl isotopic composition of the 48 global OIB measured in this study, highlighting
215 samples with isotopic compositions determined for both leached and unleached powders. Thallium isotopic
216 compositions range from -6.4 to +6.6 and do not co-vary with Tl concentrations (Fig. 1). The quoted
217 uncertainties take into account the measurement instrument and signal intensity, and are reported as the
218 highest of (1) the uncertainty for repeat analyses of BCR-2 on the *Nu HR*, (2) the uncertainty for repeated
219 measurements of the Aldrich Tl solution on the *Nu Plasma II*, or (3) the uncertainty for repeat analyses of a
220 given sample.

221 The long-term intermediate precision of the Aldrich Tl solution measured on the *Nu HR* contemporaneously
222 with OIB samples was $\epsilon^{205}\text{Tl} = -0.8 \pm 0.4$ (2sd; $n = 211$, 14 sessions, 4 years), calculated using the average
223 $\epsilon^{205}\text{Tl}$ values obtained during each measurement session due to the large number of analyses. Unleached
224 digestions of USGS reference materials AGV-2 (1), BCR-2 (10) and BHVO-2 (2) yielded $\epsilon^{205}\text{Tl}$ values of -
225 2.9 ± 0.5 (2sd; $n = 3$, 1 session), -2.6 ± 0.5 (2sd; $n = 21$, 4 sessions), and -1.2 ± 0.8 (2sd; $n = 3$, 1 session) for
226 measurements with signal intensity on mass 205 > 1 V. For measurements of BCR-2 (4 digestions) with
227 signal intensity < 1 V, $\epsilon^{205}\text{Tl} = -2.5 \pm 1.3$ (2sd; $n = 21$, 3 sessions). For both Aldrich solution and USGS
228 RMs, many of these determinations were first reported in Brett et al. (2018) and the values obtained are in
229 good agreement with previous compilations (Nielsen et al., 2017b; Prytulak et al., 2017).

230 The average obtained for the Aldrich Tl solution on the *Nu Plasma II* was $\epsilon^{205}\text{Tl} = -0.8 \pm 0.8$ (2sd; $n = 28$, 2
231 sessions, 2 months), with the higher uncertainty reflecting both the smaller number of analyses and the lower
232 concentration of solutions. One unleached dissolution of BCR-2 yielded $\epsilon^{205}\text{Tl} = -3.1 \pm 0.8$ (2sd; $n = 1$),
233 while one leached dissolution yielded $\epsilon^{205}\text{Tl} = -2.1 \pm 0.8$ (2sd, $n = 1$), demonstrating that our leaching
234 procedure does not introduce resolvable $\epsilon^{205}\text{Tl}$ fractionations.

235 3.3 Assessing secondary effects on Tl isotope ratios

236 **Melt evolution.** Many stable isotope systems display isotope fractionation during fractional crystallisation
237 (e.g. Teng et al., 2017). Thallium behaviour has been previously been investigated using two cogenetic suites
238 with invariant radiogenic isotopic compositions from different tectonic settings: Hekla, Iceland, and
239 Anatahan, Marianas (Prytulak et al., 2017). Neither suite fractionates hydrous phases, nor do they exhibit

240 resolvable Tl isotope fractionation during differentiation. Rader et al. (2018) show that hydrous K-rich
241 phases such as micas can exhibit distinct Tl isotopic compositions ($\epsilon^{205}\text{Tl}$ from -12.1 to +5.3) coupled with
242 significant Tl enrichments ($>5 \mu\text{g/g}$). As such, while it is not possible to completely rule out crystallisation-
243 induced fractionation, it is highly unlikely for the OIB studied here. With the caveat that our samples are not
244 genetically related, there is no systematic variation of $\epsilon^{205}\text{Tl}$ with inferred or observed phenocryst phases or
245 with MgO content in the current dataset (Fig. S1). We thus do not exclude any samples on this basis.

246 **Degassing.** Magmatic degassing can induce kinetic Tl isotope fractionation (Baker et al., 2009), theoretically
247 producing residues with heavy Tl isotopic compositions and low Tl concentrations relative to incompatible
248 refractory elements in contrast with condensates with isotopically light Tl, though these have yet to be
249 reliably identified in nature. Various ratios have been employed to assess sample degassing, including Th/Tl
250 (Nielsen et al., 2007), Pb/Tl (Rehkämper and Nielsen, 2004; Baker et al., 2009), Cs/Tl (Prytulak et al., 2013)
251 and Ce/Tl (Nielsen et al., 2017a). The use of such ratios is challenging: Nielsen et al. (2017a) note that in arc
252 settings, high Ce/Tl ratios potentially indicative of kinetic processes are still lower than the average value for
253 the upper mantle. In the current dataset, there is no co-variation indicative of degassing between $\epsilon^{205}\text{Tl}$ and
254 relevant trace element concentrations or ratios for samples from individual volcanoes (not shown). This lack
255 of chemical evidence is coupled with a lack of textural evidence for significant degassing, in that samples are
256 thought to have been emplaced during effusive eruptions and show no significant vesicularity. Therefore, no
257 data are rejected on this basis.

258 **Post-depositional effects.** In submarine lavas, both contamination (increasing the Tl contents of the rocks)
259 and alteration (decreasing the Tl contents, via weathering) potentially cause resolvable differences in $\epsilon^{205}\text{Tl}$.
260 As little as $1 \mu\text{g}$ of FeMn oxyhydroxide coating per gram of sample can cause an analytically resolvable shift
261 to heavier isotope signatures, while submarine alteration may efficiently strip Tl (at high temperatures) or
262 add isotopically light Tl (at low temperatures) (Nielsen et al., 2006a). Samples exhibiting very low Tl
263 concentration and $\epsilon^{205}\text{Tl}$ therefore require scrutiny for other evidence of alteration, whereas samples with
264 very high Tl concentration and extreme $\epsilon^{205}\text{Tl}$ require scrutiny for contamination. A good example of the
265 effects of alteration on Tl concentrations and isotopic compositions is provided by the study of Bluzstajn et
266 al. (2018) on St. Helena lavas. In this case, a sample (SH-75) was excluded due to its high Tl concentration
267 (339 ng/g) combined with an isotopic composition of $\epsilon^{205}\text{Tl} = -4.06$ and visual evidence of alteration. The

268 authors consider surficial contamination by secondary clay minerals to be the most likely explanation for
269 these features.

270 All OIB lavas analysed in this study were collected subaerially, although ambiguous records mean that it is
271 unclear if the oldest Rurutu lavas were erupted in a subaerial or submarine environment (Chauvel et al.,
272 1997). One Rurutu lava (RRT-037) shows the highest $\epsilon^{205}\text{Tl}$ value (6.6 ± 0.5 2sd) reported for oceanic basalts
273 thus far, warranting further assessment. However, rather than relying solely on chemical variation to identify
274 such effects, five samples with $\epsilon^{205}\text{Tl}$ signatures significantly different from the mantle value were leached
275 and reanalysed alongside USGS reference material BCR-2. The residues from the cold HCl leach retained
276 1% to 50% of the original Tl, resulting in 0.05 to 1.9 ng/g total Tl available for analysis (~ 6 ng/g for BCR-2),
277 thus resulting in larger analytical errors for $\epsilon^{205}\text{Tl}$ (typically about ± 1 ϵ). Notably, there is no systematic
278 offset in $\epsilon^{205}\text{Tl}$ for the leached relative to the unleached sample powders (Table 2). This provides strong
279 evidence that the positive and negative $\epsilon^{205}\text{Tl}$ end-members in our dataset are not due to surficial
280 contamination. Therefore, we do not exclude any samples on this basis.

281 Assessment of subaerial post-depositional alteration is more challenging. These processes may remove Tl
282 from the sample without significant Tl isotope fractionation. While large fractionations do arise in low-
283 temperature environments, strong mineralogical control is exerted by secondary sulphides in low-T
284 hydrothermally altered oceanic crust (Coggon et al., 2014) and by birnessite in FeMn sediments (Peacock
285 and Moon, 2012; Nielsen et al., 2013). Suspended riverine particulate matter, created through weathering,
286 exhibits $\epsilon^{205}\text{Tl}$ very similar to that of loess, with the oxyhydroxide fraction generally containing only minor
287 Tl that is not isotopically distinct (Nielsen et al., 2005). However, loss on ignition (LOI) is a traditional
288 qualitative indicator of such alteration. All 48 analysed samples have LOI < 4%, and 41 have LOI < 2%. The
289 seven samples with LOI > 2% were described as showing no identifiable petrological evidence of alteration
290 (see Table 1 and references therein). Therefore, no data are excluded on this basis.

291 **4. Discussion**

292 We combine our new dataset with published studies to explore Tl behaviour at constructive plate margins
293 and in intraplate settings. We first revisit the relative compatibility of Tl during mantle melting, then present
294 models of Tl behaviour during MORB and OIB melting. Finally, we examine Tl isotope systematics

295 alongside Sr-Nd-Pb radiogenic isotopic compositions in the global OIB dataset to explore implications for
296 cycling of Tl through the solid Earth.

297 **4.1 Tl elemental systematics**

298 Thallium is highly incompatible during magmatic processes. Absolute Tl concentrations in OIB are thus
299 principally determined by the extent of partial melting and fractional crystallisation. To compare the
300 geochemistry of samples representing different degrees of melting, normalised incompatible element
301 diagrams and ratios of trace elements with similar chemical partitioning are often employed. Quantitative
302 assessment of how similarly two elements partition is theoretically straightforward: in a log-log plot of
303 element concentrations, pairs of elements that partition identically produce a linear trend with a slope of
304 unity (e.g. Sims and DePaolo, 1997). Such assessments are improved by taking into account the uncertainties
305 in concentration for *both* elements (e.g. by using York regressions: York et al., 2004; Reed, 2010). In reality,
306 however, analytical and statistical errors potentially obscure small deviations from linearity, especially
307 between highly incompatible elements. It is therefore important to keep in mind that such relationships are at
308 best indicative of relative compatibility contrasts. For MORB data, Nielsen et al. (2014) calculated that La,
309 Ce, and Pb had partitioning most similar to Tl, with $\log[\text{Tl}] - \log[\text{Ce}]$ yielding a slope of 0.999 ± 0.034 (2sd,
310 $n = 594$). Results for the expanded dataset incorporating Yang et al. (2018) are very similar (Table 3).

311 OIB clearly derive from heterogeneous sources. As such there is no expectation that log-log plots would
312 provide anything other than a very approximate indication of relative partitioning. Indeed, even for samples
313 from a single location there is a marked lack of coherence in log-log diagrams of Tl versus any trace element
314 (not shown). Of all analysed elements, the closest approach to a slope of unity with $\log[\text{Tl}]$ is achieved for
315 $\log[\text{Rb}]$, as found by Dupuy et al. (1973) for acidic volcanic rocks (Table 3). However, the uncertainty is so
316 high that this is not a robust result. While lower uncertainties are achieved for $\log[\text{Ce}]$ and $\log[\text{La}]$, the slope
317 does not approximate unity. Attempting to identify elements with similar bulk partition coefficients to Tl
318 during OIB generation via log-log plots is therefore problematic.

319 **Normalised incompatible element diagrams.** Thallium has been placed both between La and Ce, for low-
320 pressure fractionation of MORB (Jenner, 2017), and between Cs and Rb (Prytulak et al., 2017, following
321 Dupuy et al., 1973). Given the ambiguity regarding placement and the lack of compelling indications from

322 log-log plots, we consider both compatibility orderings for the presentation of OIB data. Incompatible
323 elements normalised to PM abundances are shown in Figure 2 (with normalisation to DM shown in Fig. S2).
324 Notable is the marked negative Tl anomaly compared to other large-ion lithophile elements (47 of 48
325 samples) and REE (all samples). The La-Tl-Ce ordering produces visually similar Tl depletions to elements
326 that are fluid-mobile during subduction processing, particularly Pb. The co-variation is less striking for the
327 Cs-Tl-Rb ordering, which might reflect the larger uncertainties of Cs abundances and/or the inferred greater
328 similarity in fluid-mobile behaviour. Interestingly, the magnitude of the negative Tl anomaly co-varies with
329 absolute Tl abundance, regardless of ordering (Fig. S3). Such co-variation would be anticipated if the
330 ambient mantle contains negligible Tl, such that increasing Tl abundances from exotic source(s) correlate
331 directly with less negative Tl anomalies. In this scenario, the normalising PM (and DM) Tl concentration
332 would be overestimated.

333 **‘Invariant’ trace element ratios.** Ratios of trace elements with similar partitioning are commonly used to
334 ‘see through’ the effects of magmatic evolution: where partitioning is identical, ratios should be identical in
335 source and product. However, selecting a suitable ratio for Tl in OIB is challenging. The Cs/Tl ratio has been
336 used, as partitioning of these two elements and their fluid mobility was assumed to be similar (e.g., Nielsen
337 et al., 2006a; Prytulak et al., 2013; 2017). However, Cs/Tl can be affected by both degassing and possible
338 sequestration of Tl in accessory minerals during subduction (e.g., Prytulak et al., 2013) and although Cs
339 concentration determinations are routinely performed during ICP-MS analyses they often have relatively
340 large errors due to the low abundance of Cs in igneous systems. The Ce/Tl ratio has also been used to assess
341 Tl systematics in igneous settings, and has the advantage of a limited range in MORB (e.g. Nielsen et al.,
342 2014, 2017b). As Tl partitioning is likely different between MORB and OIB regimes, no single ratio will be
343 invariant for both tectonic settings.

344 In the new OIB dataset, Ce/Tl varies over an order of magnitude at a similar degree of magmatic
345 differentiation. While absolute Tl concentrations in OIB vary with MgO content, taken as a measure of the
346 extent of differentiation, Ce/Tl ratios do not (Fig. 3). Therefore, the range of Ce/Tl in OIB likely arises from
347 some combination of source heterogeneity and melting processes. For example, Shu et al. (2019) observed a
348 wide range of Ce/Tl in subducted eclogites, which are geochemically similar to altered subducted oceanic
349 crust that is thought to be a common component in OIB sources. Some authors have noted generally higher

350 Ce/Tl ratios in OIB compared to MORB (Nielsen et al., 2014; Blusztajn et al., 2018). When examining all
351 available data, a clear tectonic distinction between MORB, arc and OIB lavas is apparent (Fig. 4): (1) arc
352 lavas generally exhibit the lowest Ce/Tl and highest Tl concentrations, alongside the most scattered
353 distribution, even when filtered to exclude non-basaltic samples; (2) MORB Ce/Tl clusters around 1140, as
354 previously discussed in Nielsen et al. (2014), and (3) global OIB form a remarkably coherent array that is
355 clearly distinct from MORB, with overlap between the different mantle components defined by radiogenic
356 isotopes. Similar patterns are observed for ratios of Tl with Rb, Cs, La and Pb, though with these latter ratios
357 the different tectonic settings are less clearly distinguished (Fig. S4), motivating the further focus on Ce/Tl
358 systematics.

359 **4.2 Modelling Tl variations in MORB and OIB**

360 The systematic variation of Tl versus Ce/Tl in global MORB and OIB can be explored with simple melting
361 and mixing models (Fig. 5, 6). Fractional, non-modal melting models help explore the contrasting Ce/Tl
362 patterns of MORB and OIB, though simplifying assumptions must be made for several parameters (Tables 4-
363 6). Nielsen et al. (2014) identified constraints for the majority of these parameters for MORB generation, and
364 modelled production of the “near-uniform” Ce/Tl ratio for MORB through variation of S concentrations and
365 associated $D_{\text{sulf/sil}}^{\text{Tl}}$ values. However, subsequent findings warrant some re-evaluation of parameters.

366 While it is clear that Tl is hosted in sulphides to some extent, recent investigations into the partitioning of Tl
367 indicates that it is less strongly chalcophile than previously assumed (e.g. Kiseeva and Wood, 2015; Wood
368 and Kiseeva, 2015; Jenner, 2017; and see Appendix for detailed discussion). We therefore explored $D_{\text{sulf/sil}}^{\text{Tl}}$
369 values between 1 and 25 and present results for $D_{\text{sulf/sil}}^{\text{Tl}} = 10$ (e.g. Kiseeva and Wood, 2013, 2015; see
370 Appendix for detailed discussion). We also consider the effects of variation in $D_{\text{cpx/melt}}^{\text{Ce}}$ between 0.01 and
371 0.8, which encompasses the wide range attributed to differences in mineral chemistry (Table 5; Appendix).

372 **MORB.** The MORB dataset in Figure 5 combines the studies of Jenner and O’Neill (2012), Nielsen et al.
373 (2014) and Yang et al. (2018), excluding samples with MgO < 6wt%, seamounts, back-arc basins and
374 aseismic ridges. These studies yield a combined mean MORB Ce/Tl of 1220 ± 570 (2sd, n = 909).

375 Fractional melting models assuming a spinel lherzolite source with variations in $D_{\text{cpx/melt}}^{\text{Ce}}$ and initial
376 elemental concentration are shown in Figure 5, with the fractional melting model of Nielsen et al. (2014)

377 reproduced in Figure 5a. We explore a range of $D_{\text{cpx/melt}}^{\text{Ce}}$ in Figure 5b, reproducing not only the average
378 Ce/Tl value observed for MORB but also the sense of variation in the data. Compared to the model of
379 Nielsen et al. (2014), the reduced compatibility of Tl in sulphides means that the model is less sensitive to
380 the S concentration of the upper mantle. Considering only variations in the bulk partitioning of Ce, over 80%
381 of MORB samples can be explained with a range of $D_{\text{cpx/melt}}^{\text{Ce}}$ up to ~ 0.35 . Furthermore, about 50% of
382 MORB samples are explained by $D_{\text{cpx/melt}}^{\text{Ce}} \leq 0.2$, while fewer than 2% of MORB samples require $D_{\text{cpx/melt}}^{\text{Ce}}$
383 ≥ 0.8 .

384 We also present the effects of variation in initial Tl and Ce concentration on our melting model (Fig. 5c, 5d;
385 Appendix), with $D_{\text{cpx/melt}}^{\text{Ce}} = 0.1$ (equivalent to bulk $D^{\text{Ce}} = 0.015$, i.e. the average value for peridotite melting
386 calculated by Stracke and Bourdon, 2009). Again, variation in either of these parameters can account for
387 both the average Ce/Tl ratio in MORB and the sense of the observed variation.

388 The models thus highlight two main points.

- 389 1. As previously noted, MORB Ce/Tl exhibits some variation with Tl concentration that exceeds
390 measurement uncertainties (Nielsen et al., 2014). We suggest that Ce/Tl variations in MORB can be
391 explained through a combination of melting effects, a range of $D_{\text{cpx/melt}}^{\text{Ce}}$ associated with variations in
392 the mineral composition of clinopyroxene, and variations in source concentrations of Tl and Ce.
393 Notably, this model does not require that bulk partition coefficients for Ce and Tl be approximately
394 equal, and is nonetheless able to satisfy the constraint that a log-log concentration plot should exhibit
395 a slope close to unity given the observed maximum concentration of Tl in MORB.
- 396 2. Regardless of the chosen value of $D_{\text{cpx/melt}}^{\text{Ce}}$, a model incorporating lower compatibility of Tl in
397 sulphides than previously assumed yields a best fit for a Tl_{DM} abundance of 0.27 ng/g. This value is
398 calculated assuming that (i) samples with the lowest Tl concentrations on average represent the
399 highest degree of melting, i.e. the closest approach to the DM Ce/Tl ratio, and (ii) an average Ce_{DM}
400 of 0.55 $\mu\text{g/g}$ (Workman and Hart, 2005). Our proposed Tl_{DM} is considerably lower than the estimate
401 of Salters and Stracke (2004) of 0.38 ng/g, and much lower than that of Nielsen et al. (2014) of 0.48
402 ng/g.

403 **OIB.** Fractional melting models assuming either a PM or a DM source (Table 4) with up to 15% melting are
404 shown in Fig. 6a. It is immediately apparent that partial melting alone cannot produce the observed OIB
405 Ce/Tl array from a PM or DM source, even for extreme values of $D^{\text{Ce}}_{\text{cpx/melt}}$. The systematics in a plot of
406 Tl/Ce versus Tl (Minster and Allègre, 1978; Fig. S5) emphasise that the observed range exceeds that which
407 can be explained by partial melting and fractional crystallisation alone, consistent with longstanding
408 radiogenic isotopic evidence for the heterogeneous and mixed nature of OIB sources. Notably, variations in
409 S concentration or $D^{\text{Tl}}_{\text{sulf/sil}}$ have no significant effect on model fit, but do affect the required degree of partial
410 melting.

411 To explain the variation in the OIB array we first establish constraints on the mixed source compositions. In
412 this context, solid state mixing is assumed, rather than mixing of partial melts of distinct components.
413 Parameters including partition coefficients and initial elemental concentrations were varied until approximate
414 matches between model output and the observed data array for up to 15% melting were achieved (Fig. 6b).
415 We then incorporate the assumption that OIB lavas are typically the product of ~3-5% melting. In this
416 scenario, the required source materials vary over an order of magnitude in terms of Tl concentration even
417 within a single island (Fig. 6c, 6d). A striking feature of the model is that the majority of the array requires a
418 source that is significantly more enriched in Ce than PM estimates, *without* similar enrichment in Tl. Indeed,
419 most lavas require Tl source concentrations lower than PM estimates, and in some instances more depleted
420 than DM. Of all the OIB samples analysed to date ($n = 93$) only 10 (~11%) require a source Tl concentration
421 >3.5 ng/g, i.e. more enriched in Tl than PM. Notably, although lavas from individual islands require source
422 heterogeneity in terms of Tl concentration, lavas representing distinct radiogenic isotopic compositions have
423 overlapping Ce/Tl ranges.

424 The mixed source concentrations required by the OIB Ce/Tl array can be interpreted as a mantle
425 ‘background’ that is extremely depleted in Tl, with addition of a material characterised by high Ce and
426 heterogeneous Tl concentrations, broadly consistent with models of widespread addition of subducted
427 materials to the mixed OIB source. However, prior to subduction surface materials with high Ce
428 concentrations (e.g. FeMn sediments) also exhibit elevated Tl concentrations that greatly exceed values that
429 can be accommodated by the mixing-melting model. If subducted materials are the exotic addition
430 controlling Ce/Tl systematics in OIB, it is necessary that the majority of Tl must be removed or otherwise

431 lost during subduction processing, rather than being recycled into the deep mantle. A ~20% addition of such
432 ‘subduction-processed oceanic crust’ (Table 6) to mantle strongly depleted in Tl would produce an
433 appropriate mixed OIB source.

434 Recently, Shu et al. (2019) analysed the trace element and Tl isotopic composition of a number of eclogites
435 subducted to a maximum depth of ~90 km before being exhumed, which might represent such ‘subduction-
436 processed’ oceanic crust. This sample suite has an average Ce concentration of 20 $\mu\text{g/g}$ with an average Tl
437 concentration of 55 ng/g (Table 6). While the Ce concentration is consistent with the requirements for our
438 proposed subduction-processed oceanic crust, the Tl concentration is an order of magnitude more than the
439 maximum we invoke to satisfy our constraints on OIB source concentrations. However, as the eclogite
440 samples remained within the stability field of Tl-rich phengite, it is likely that further Tl loss would occur
441 during deeper subduction beyond the phengite stability field.

442 We agree with the findings of Shu et al. (2019) that OIB Ce/Tl systematics indicate widespread incorporation
443 of subduction-processed oceanic crust into the OIB source, which may consist of (ancient, relatively
444 enriched) oceanic crust with variable addition of a continental crust component. The Ce/Tl systematics of
445 OIB thus highlight *similarities*, not differences, between mantle components distinguished by their
446 radiogenic isotopic compositions. The complete overlap between different lavas representing distinct
447 (enriched) mantle end-members strongly implies that a high-Ce, low-Tl material such as subduction-
448 processed oceanic crust is common to OIB sources, and that Tl is near quantitatively removed during
449 subduction.

450 **4.3 Thallium isotopic composition of OIB**

451 The Tl isotopic composition of the mantle is strikingly homogeneous, and no resolvable Tl isotopic
452 fractionation is observed during partial melting or fractional crystallisation. Therefore, the significant Tl
453 isotopic variability observed in global OIB ($\epsilon^{205}\text{Tl}$ -10.0 to +6.6) requires the addition of isotopically distinct
454 material to the lavas. The addition of such material can happen in the source, *en route* to the surface, and/or
455 via subaerial/submarine alteration. We have already argued that alteration does not play a significant role in
456 the new data, and previous work has similarly screened and discounted altered samples.

457 Thallium isotopic compositions were predicted to covary with the Sr-Nd-Pb radiogenic isotopes used to
458 classify mantle components, depending on whether AOC or recycled sediments were the primary contributor
459 of exotic material. However, the elemental systematics of Tl in OIB appear to require highly efficient
460 removal of Tl during subduction, which potentially weakens the link between deep mantle recycling and OIB
461 sources in terms of Tl isotopes. Indeed, the first order observation for our global dataset is that primary Tl
462 isotopic compositions do not co-vary with radiogenic Pb, Sr, Nd, or Hf isotopes (Fig. 7), even within the
463 chemically diverse Marquesas island group. Although the range is large, the average $\epsilon^{205}\text{Tl}$ for HIMU and
464 EM-type lavas overlap within error. For HIMU $\epsilon^{205}\text{Tl} = -2.6 \pm 6.6$ (2s, n = 37), and for EM $\epsilon^{205}\text{Tl} = -1.3 \pm 4.4$
465 (2s, n = 32). The overlap remains even if the comparison is restricted to main-phase St Helena lavas and
466 EMI-type lavas, for which $\epsilon^{205}\text{Tl} = -3.2 \pm 3.1$ (2s, n = 10) and $\epsilon^{205}\text{Tl} = -1.1 \pm 4.0$ (2s, n = 13), respectively.
467 The absence of correlation between Tl isotopic compositions and Sr-Nd-Pb-Hf radiogenic isotope systems is
468 consistent with trace element modelling that requires the mantle sources to be ubiquitously depleted in Tl,
469 likely due to near-quantitative removal of Tl during the subduction process. Elemental parent-daughter pairs
470 for radiogenic isotopes do not show this same level of depletion in OIB sources, and thus Tl and radiogenic
471 Sr-Nd-Pb-Hf isotopic compositions can be easily decoupled, as noted by the first study of Tl isotopic
472 composition in OIB (Nielsen et al. 2006a).

473 However, our finding that Tl isotope systematics may not be a straightforward “fingerprint” of recycled
474 AOC or FeMn sediment to OIB source regions is at odds with previous work. While no variation in Tl
475 isotopic composition was found in lavas from the Azores or Iceland (Nielsen et al., 2007), incorporation of
476 deeply subducted FeMn sediment was invoked to explain variations observed in Hawai’ian picrites (Nielsen
477 et al., 2006a), and HIMU-type St Helena basalts have been argued to show evidence for incorporation of
478 subducted AOC (Blusztajn et al., 2018). In the case of Hawai’i, the absence of correlation between Tl stable
479 and Os radiogenic isotopes was noted, despite the potential for FeMn sediment contributions to control both
480 systems, and ascribed to the very high Tl/Os ratio such sediments exhibit.

481 Our new data provide a basis for re-evaluating the systematics of Tl isotopes in the HIMU mantle
482 endmember. The isotopic criterion most commonly used to distinguish HIMU lavas is their radiogenic Pb
483 isotopic compositions (i.e. $^{206}\text{Pb}/^{204}\text{Pb} > 19.5$), which is commonly interpreted to arise from the subduction of
484 AOC with high $^{238}\text{U}/^{204}\text{Pb}$ ratios (‘high μ ’), that was isolated in the mantle for 1-2 Ga (e.g. Hofmann and

485 White, 1982; Zindler and Hart, 1986; Chauvel et al., 1992; Stracke et al., 2005). While acknowledging
486 decoupling of Tl and Sr-Nd-Hf-Pb isotopes, Blusztajn et al. (2018) argue that Tl isotopic compositions that
487 are generally lighter than those found for MORB combined with Ce/Tl variations provide evidence for the
488 presence of a recycled upper AOC component in the St Helena source, from which up to 90% of Tl (relative
489 to Ce) was stripped during subduction processing. Subsequent work investigated eclogites from Cabe
490 Ortegale and the Raspas Complex, thought to represent the metamorphic equivalents of altered oceanic crust
491 (Shu et al., 2019). The eclogites have a similar range in Tl isotopic compositions as the main phase St.
492 Helena lavas ($\epsilon^{205}\text{Tl} \approx -5.5$ to -1.0), and thus Shu et al. (2019) proposed a genetic link between the two.

493 This interpretation is complicated by the observation that, for the full OIB dataset (Fig. 8), the majority of
494 HIMU samples have $\epsilon^{205}\text{Tl}$ values that overlap with the range of results obtained for EM-type samples ($\epsilon^{205}\text{Tl}$
495 ≥ -6.5 ; Fig. 8b, 8d). In addition, there is no convincing co-variation of $\epsilon^{205}\text{Tl}$ with Ce/Tl and Ce/Pb for either
496 St Helena lavas (Fig. 8a, 8c) or the complete OIB dataset, with EM-type samples again overlapping the
497 whole range of HIMU-type lavas. While one HIMU-type lava does exhibit the lightest reported Tl isotopic
498 composition of any OIB sampled to date ($\epsilon^{205}\text{Tl} \approx -10$), the broad overlap in $\epsilon^{205}\text{Tl}$ for HIMU- and EM-type
499 OIB does not provide a clear distinction between different mantle end-members based on Tl isotopic
500 compositions alone. It therefore appears that Tl isotopic compositions are decoupled not just from radiogenic
501 isotopes and Tl concentrations, as suggested by Shu et al. (2019), but also – at least on a global scale – from
502 incompatible trace element ratios held to be indicative of AOC contributions.

503 We concur with the conclusion of Blusztajn et al. (2018) that the Ce/Tl ratios of OIB appear to be broadly
504 complementary to those found in island arc lavas. It is therefore necessary to explain *how* Tl isotopic
505 systematics become (apparently) decoupled from Tl elemental systematics. Fitting our model to elemental
506 systematics data requires highly efficient (~99%, relative to Ce) removal of Tl from heterogeneous
507 subducting materials, with only a small proportion of subducted Tl returned to OIB source regions in the
508 deep mantle. Therefore, the low Tl concentrations of the OIB sources produce magmas with Tl signatures
509 that can be readily overprinted by addition of isotopically distinct material.

510 The notion that Tl isotopic compositions distinct from mantle values are due to the input of Tl-rich,
511 isotopically distinct materials can be further examined via the magnitude of the negative Tl concentration
512 anomaly observed for OIB relative to geochemically similar elements. When the magnitude of the Tl

513 anomaly Tl/Tl^* (see caption to Figure 9) is plotted against Tl isotopic composition, samples with $Tl/Tl^* >$
514 ~ 0.5 (calculated relative to Cs and Rb) generally have Tl isotopic compositions that differ from the mantle
515 (Fig. 9a, 9b). As would be expected given the decoupling of Tl and radiogenic isotopic compositions, this
516 pattern is not restricted to or consistent within any one radiogenic isotope end-member, and some samples
517 with $Tl/Tl^* < \sim 0.5$ also display non-mantle values. Ruling out post-depositional isotopic effects, the question
518 that arises is where does the addition of material with non-mantle Tl isotopic compositions take place? The
519 mantle source or *en route* to eruption?

520 Addition of isotopically distinct Tl to the OIB source via residual Tl from a subduction-processed slab and/or
521 addition during ascent through the crust via assimilation of country rock, including sediments and
522 previously-erupted and subsequently altered lavas are both reasonable processes. For example, variation in
523 the extent and type of material assimilated during different stages of magmatism might account for the
524 distinct average Tl isotopic compositions observed by Blusztajn et al. (2018) for St Helena early-, main-, and
525 late-stage lavas. Given the Tl concentration contrast between magma and potential inputs, neither origin for
526 Tl isotope variations – source heterogeneity or assimilation – would necessarily cause resolvable changes to
527 other geochemical markers (e.g. model of Nielsen et al., 2006a; Fig. S6). Caution is therefore advisable when
528 interpreting Tl isotopic compositions of OIB as a direct reflection of the mantle source. However, there is the
529 potential that variable crustal assimilation of isotopically distinct Tl might be identifiable in high resolution
530 studies of lavas from individual volcanic edifices, yielding insight into their magmatic plumbing architecture.

531 **5. Conclusions**

532 Fresh lavas from divergent, convergent and intraplate settings can be distinguished by their distinct
533 systematics in plots of Ce/Tl versus Tl concentrations. The observed patterns can be reproduced by models
534 of fractional, non-modal melting, providing insights into the cycling of Tl through the mantle. The Ce/Tl
535 systematics of MORB can be reproduced by the combined effects of different extents of partial melting and
536 variations in $D_{\text{cpx/melt}}^{\text{Ce}}$ and initial Tl and Ce concentrations, without a significant role for sulfides. In contrast,
537 the Ce/Tl systematics of OIB cannot be generated from a primitive mantle source, but instead require a
538 source that is markedly depleted in Tl (< 1 ng/g) prior to addition of exotic thallium. The requirement for Tl-
539 depleted OIB source regions is consistent with mounting evidence that the extent of present day mantle
540 depletion may be underestimated (e.g. Stracke, 2012; Stracke et al., 2011, 2019; Salters et al., 2011; Salters

541 and Dick, 2002; Cipriani et al., 2004; Sanfillippo et al., 2019). The OIB array can be generated from a
542 depleted mantle source with addition of up to 20% subducted material from which >99% of Tl has been
543 stripped during subduction processing. This suggests that Tl constitutes an extreme example of the behaviour
544 of fluid-mobile elements in subduction zone settings, such that co-variations of Tl with other elements may
545 further constrain elemental subduction zone cycling.

546 Thallium and radiogenic isotopic compositions are decoupled, and Tl isotopic compositions cannot be used
547 in isolation to distinguish between continental and oceanic crust contribution to OIB source regions. The
548 observed decoupling of Tl and radiogenic isotopic compositions most likely reflects (1) the sensitivity of Tl
549 to small variations in the isotopic composition of residual Tl, and/or (2) the extreme Tl concentration contrast
550 between mantle and surface materials. Despite the lack of co-variation with radiogenic isotopes, global OIB
551 display a significant range in primary Tl isotopic compositions which must reflect addition of isotopically
552 distinct material. However, where this Tl addition takes place remains ambiguous. The potential
553 incorporation of Tl-rich materials at crustal levels during magma ascent is a feasible alternative interpretation
554 to the generation of Tl isotopic variability due to incorporation of residual slab-derived Tl at mantle depths
555 following subduction processing.

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563 **Appendix**

564 **I. Elemental concentrations**

565 **MORB.** For Ce concentration, we use the values of Workman and Hart (2005) for Depleted MORB Mantle
566 (DMM), Enriched MORB Mantle (EMM), and the average MORB source. For Tl concentration, we consider
567 previous DMM estimates along with values that provide the best fit for our model.

568 **OIB.** We used the values of McDonough and Sun (1995) as our initial values for PM, then varied
569 concentrations as required to fit our model to the data.

570 **II. Thallium partitioning**

571 **Chalcophilia.** Nielsen et al. (2014) based their values of $D_{\text{sulf/sil}}^{\text{Tl}}$ during MORB melting (18–100) on data
572 from Kiseeva and Wood (2013), who reported $D_{\text{sulf/sil}}^{\text{Tl}} = 4\text{--}24$. However, a growing body of evidence
573 supports the concept that “mixed affinity” behaviour is exhibited by Tl, i.e. elemental behaviour cannot be
574 described as either predominantly chalcophile or predominantly lithophile.

575 Kiseeva and Wood (2015) report $D_{\text{sulf/sil}}^{\text{Tl}}$ of 4–33, and note that “partitioning of most elements is a strong
576 function of the oxygen (or FeO) content of the sulphide”, which “increases linearly with the FeO content of
577 the silicate melt and decreases with the Ni content of the sulphide.” Wood and Kiseeva (2015) go on to state
578 that Tl partitioning does not obey this simple model, nor one extended through consideration of additional
579 parameters: “Despite simple and predictable partitioning behavior for many elements, several important
580 elements (Ni, Cu, Ag, Mn, Tl) show strongly non-linear dependences of $\log D_i$ on $\log[\text{FeO}]$ and we were
581 unable to assign them to any one particular category in terms of affinity for sulfide.”

582 Jenner (2017) calculated that for typical MORB melting $D_{\text{sulf/sil}}^{\text{Tl}} = 7$; Greaney et al. (2017) observe mixed
583 affinity behaviour during magmatic differentiation at Kilauea Iki. Wang et al. (2018) suggested that a
584 significant proportion of the Tl contents of peridotites are hosted in interstitial late-crystallising silicate
585 phases, finding that sulphides typically contribute <30% of the bulk rock Tl budget. These observations are
586 consistent with poor correlation of Tl concentrations with chalcophile element concentrations in most
587 igneous contexts (e.g. Prytulak et al., 2017).

588 **Silicate minerals.** Although Tl is known to be highly incompatible, partitioning of Tl between silicate
589 minerals and melt remains poorly constrained. Nielsen et al. (2014) therefore assumed $D_{\text{min/melt}}^{\text{Tl}}$ identical to
590 $D_{\text{min/melt}}^{\text{Rb}}$ due to the similarity in ionic charge and radius. Tl^+ is well-known to substitute for K^+ in silicate
591 minerals (e.g. Shaw et al 1952), as documented by e.g. Rader et al. (2018), and we also assume similar
592 partitioning behaviour of Rb and Tl in silicate contexts.

593 **III. Cerium partitioning**

594 Although variation in mineral-melt partitioning of Ce between clinopyroxene and basaltic melt (herein
595 $D_{\text{cpx/melt}}^{\text{Ce}}$) is not required to model the MORB Ce/Tl array, it is likely that such variation does exist and does
596 contribute to the observed pattern. The GERM database (as of June 2020) documents a total range in
597 $D_{\text{cpx/melt}}^{\text{Ce}}$ from 0.017 (Frey, 1969) to 0.82 (Vannucci et al., 1998), excluding the values of Nagasawa (1973),
598 which were determined on natural samples showing signs of significant alteration (Uchimizu, 1966).
599 $D_{\text{cpx/melt}}^{\text{Ce}}$ is generally observed to increase with increasing Wollastonite and tetrahedrally-coordinated Al
600 content of clinopyroxene. The data compilation of Sun and Liang (2012) features a range of $D_{\text{cpx/melt}}^{\text{Ce}}$ from
601 0.019 (Salters and Longhi, 1999) to 0.27 (Gaetani and Grove, 1995), excluding the data of Wood and Trigila
602 (2001) determined for highly potassic melts ($D_{\text{cpx/melt}}^{\text{Ce}}$ from 0.48 to 1.31). This information is presented
603 graphically in Figure A1.

604 Johnston and Schwab (2004) additionally determined a $D_{\text{cpx/melt}}^{\text{Ce}}$ value of 0.47 during experiments on the
605 partial melting of peridotite (not shown). Further data for partitioning of REE in the presence of high-Ca
606 clinopyroxenes was compiled by Bédard (2014), though the dataset for terrestrial basalts is limited.

607 While Sun and Liang (2012) provided recommended values for $D_{\text{cpx/melt}}^{\text{Ce}}$ during MORB melting, they note
608 that these values are based on highly simplified thermodynamic models of clinopyroxene that may represent
609 unrealistically restricted mineral composition ranges. We therefore explore a range of $D_{\text{cpx/melt}}^{\text{Ce}}$ from 0.01 to
610 0.8 in our modelling. We do not consider 0.8 a value that is *likely* to be achieved in natural rocks, but it is
611 informative as an end-member scenario.

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879 **Figure captions**

880 **Figure 1:** Plot of $\epsilon^{205}\text{Tl}$ against Tl concentration. There is no covariation. Large symbols: this study. Other
881 data sources: [1] Blusztajn et al. (2018); [2] Prytulak et al. (2017); [3] Nielsen et al. (2007); [4] Nielsen et al.
882 (2006a). * picrites.

883 **Figure 2:** Primitive Mantle-normalised trace element plots. Note that Tl appears twice (highlighted),
884 positioned both between Cs and Rb (Prytulak et al., 2017) and between La and Ce (Jenner, 2017). The
885 ordering otherwise follows that of Willbold and Stracke (2006). For almost all samples there is a clear
886 negative Tl anomaly regardless of position, as emphasised by the averages for each end-member.

887 **Figure 3:** (a) Ce/Tl and (b) Tl concentrations plotted against MgO contents. Thallium is a highly
888 incompatible element, and consequently the absolute abundance co-varies with indices of melt
889 differentiation, such as MgO. However, Ce/Tl ratios do not exhibit co-variation with melt evolution for OIB
890 samples, indicating that Ce and Tl exhibit similar incompatibility with respect to magmatic processes in the
891 mantle. Symbols and data sources as in Figure 1.

892 **Figure 4:** Plot of Ce/Tl ratios versus Tl concentrations in oceanic basalts and subduction zone volcanics.
893 Ce/Tl trends clearly distinguish between tectonic melting regimes for fresh lavas. Note that Hawai 'ian and
894 Icelandic picritic lavas (dark gray) lie off the general OIB trend to lower Tl concentrations, presumably due
895 to the larger degree of melting they represent. Large symbols: this study. Other data sources (see Table 2,
896 Electronic Annex 2): [1] Blusztajn et al. (2018); [2] Prytulak et al. (2017); [3] Nielsen et al. (2007); [4]
897 Nielsen et al. (2006a); [5] Chauvel et al. (2012); [6] Nielsen et al (2016); [7] Nielsen et al. (2017a); [8]
898 Prytulak et al. (2013); [9] Prytulak et al. (2017); [10] Shu et al. (2017); [11] Cox et al. (2019); [12] Jenner
899 and O'Neill (2012); [13] Nielsen et al. (2014); [14] Yang et al. (2018). * picrites.

900 **Figure 5:** (a) MORB melting model of Nielsen et al. (2014), with $\text{Tl}_{\text{DM}} = 0.48 \text{ ng/g}$, $\text{S}_{\text{DM}} = 195 \text{ }\mu\text{g/g}$ and
901 $D_{\text{sulf/sil}}^{\text{Tl}} = 36$ (for other parameters see Table 5). (b) Modified MORB melting model assuming $\text{S}_{\text{DM}} = 100$
902 $\mu\text{g/g}$ and $D_{\text{sulf/sil}}^{\text{Tl}} = 10$; lower $D_{\text{sulf/sil}}^{\text{Tl}}$ increases the melt percentage required to achieve any given Tl-Ce/Tl
903 data pair. In this modified model we permit variation of $D_{\text{cpx/melt}}^{\text{Ce}}$ (see text, Table 5), reproducing both the
904 average MORB Ce/Tl and the sense of variation. Best fit is achieved with a lower Tl_{DM} of 0.27 ng/g ,
905 implying a DM Ce/Tl of ~ 1800 . (c) Modified model with variable Tl (see legend), $\text{Ce} = 0.55 \text{ }\mu\text{g/g}$, $\text{S} = 100$

906 $\mu\text{g/g}$, $D^{\text{Tl}}_{\text{sulf/sil}} = 10$, $D^{\text{Ce}}_{\text{cpx/melt}} = 0.1$ (d) Modified melting model with $\text{Tl} = 0.27 \text{ ng/g}$, variable Ce (see legend;
907 Workman and Hart, 2005), and other values as for subfigure (c). Symbols and data sources as in Figure 4.

908 **Figure 6:** (a) Melting of PM (grey) and DM (black) sources (Table 6) with varying $D^{\text{Ce}}_{\text{cpx/melt}}$. (b) Melting of
909 (i) a hypothetical mixed source with $\text{Tl} = 1 \text{ ng/g}$, $\text{Ce} = 15 \mu\text{g/g}$, and $D^{\text{Ce}}_{\text{cpx/melt}} = 0.8$; and (ii) a hypothetical
910 mixed source with $\text{Tl} = 0.5 \text{ ng/g}$, $\text{Ce} = 5 \mu\text{g/g}$, and $D^{\text{Ce}}_{\text{cpx/melt}} = 0.15$. (c) 3-5% melting of a hypothetical
911 source with $\text{Ce} = 5 \mu\text{g/g}$ and $D^{\text{Ce}}_{\text{cpx/melt}} = 0.1$. Source Tl concentration varies as indicated on figure. (d) As
912 subfigure (c), but instead $\text{Ce} = 15 \mu\text{g/g}$ and $D^{\text{Ce}}_{\text{cpx/melt}} = 0.5$. Symbols and data sources as in Figure 4. All
913 displayed models assume $100 \mu\text{g/g}$ S (Ding and Dasgupta, 2018) and $D^{\text{Tl}}_{\text{sulf/sil}} = 10$. All melting percentages
914 as marked on subfigure (a).

915 **Figure 7:** Plots of $\epsilon^{205}\text{Tl}$ against (a) $^{87}\text{Sr}/^{86}\text{Sr}$, (b) $^{143}\text{Nd}/^{144}\text{Nd}$, (c) $^{176}\text{Hf}/^{177}\text{Hf}$, (d) $^{206}\text{Pb}/^{204}\text{Pb}$, (e) $^{207}\text{Pb}/^{204}\text{Pb}$,
916 (f) $^{208}\text{Pb}/^{204}\text{Pb}$. For OIB samples, there is no co-variation of $\epsilon^{205}\text{Tl}$ and the radiogenic isotope systems
917 commonly used to define mantle components, with the possible exception of $^{143}\text{Nd}/^{144}\text{Nd}$ in Icelandic
918 picrites. Error bars are generally smaller than symbols. Symbols and data sources as in Figure 4.

919 **Figure 8:** Plots of ratios employed to track AOC contributions to OIB source against $\epsilon^{205}\text{Tl}$. (a) Ce/Tl against
920 $\epsilon^{205}\text{Tl}$, showing literature main-phase St Helena lavas and St Helena samples from this study, (b) Ce/Tl
921 against $\epsilon^{205}\text{Tl}$ for all OIB samples, (c) Ce/Pb against $\epsilon^{205}\text{Tl}$ with the same samples as subfigure (a), (d) Ce/Pb
922 against $\epsilon^{205}\text{Tl}$ for all OIB samples. Blusztajn et al. (2018) argued that a sense of correlation for main-phase St
923 Helena lavas indicated a role for subduction-processed AOC in generating the HIMU array. However, this
924 trend is not replicated in HIMU lavas from other localities, and is not unique to HIMU-type lavas. Symbols
925 and data sources as in Figure 4.

926 **Figure 9:** Plot of $\epsilon^{205}\text{Tl}$ against Tl/Tl^* ratios. $\text{Tl}^* = \text{Brett_etal_GCA_Eqn1.pdf}$ or

927 **Brett_etal_GCA_Eqn2.pdf**, where N denotes concentration values normalised to PM (a,c), or DM (b,d).

928 Relative to Cs and Rb, Tl/Tl^* values > 0.5 (for both PM and DM normalisations) are associated with Tl
929 isotopic compositions that are distinct from the mantle range (green band). Relative to La and Ce, it is less
930 clear whether there is any association. Symbols and data sources as in Figure 4.

931 **Figure A1:** $D^{\text{Ce}}_{\text{cpx/melt}}$ values versus CaO in clinopyroxene. This illustrative plot has not been corrected for
932 pressure and temperature, or for other compositional variables including degree of hydration. With the
933 notable exception of Green et al. (2000) and the two McDade studies, which examine melting under strongly

934 hydrous conditions, there is a general sense of increasing Ce compatibility as CaO in cpx increases both
935 within and between studies.

937 **Table 1.** Summary of OIB localities with published Tl concentration and isotopic composition data.

Locality	FOZO/PREMA		EMI		EM		HIMU		
	Hawai'i	Iceland	Gough	Tristan	Marquesas [†]	Azores	St Helena	Rurutu	Tubuai
literature [Tl]	x	x			x	x	x		
literature $\epsilon^{205}\text{Tl}$	x	x				x	x		
$^{87}\text{Sr}/^{86}\text{Sr}$	o	range	x	x	x	x	x	x	x
$^{143}\text{Nd}/^{144}\text{Nd}$	o	x	x	x	x	x	x	x	x
$^{176}\text{Hf}/^{177}\text{Hf}$		range	x	x	x		x		o
Pb isotopes	x	range			x	x	x	x	x
this study			x	x	x		x	x	x
key references	1*	2*,3	4,5	4,5	6	2	4,5,7	8	9

938

939 * picrites.

940 † Note that Marquesas lavas exhibit variable composition covering a very wide range of radiogenic isotopic
941 compositions.

942 x = data exists; o = partial data; range = a range is known, but samples have not been individually analysed.

943 [1] Nielsen et al. (2006a); [2] Nielsen et al. (2007); [3] Prytulak et al. (2017); [4] Willbold and Stracke

944 (2006); [5] Willbold and Stracke (2010); [6] Chauvel et al. (2012); [7] Blusztajn et al. (2018); [8] Chauvel et

945 al. (1997); [9] Chauvel et al. (1992).

Table 2. Key geochemical data for OIB samples analysed in this study.

Sample	MgO* (wt%)	Ce ($\mu\text{g/g}$)	Tl (ng/g)	Ce/Tl	$\epsilon^{205}\text{Tl}$	2sd	Dissolutions	Measurements (n)
<i>Gough (EMI)</i>								
G6	7.94	101	26	3915	0.5	2.2	2	3 (1 NU + 2 NUII)
G102	5.28	107	76	1402	-2.5	0.6	2	3
G117	4.52	113	39	2921	3.8	0.6	1	4
G118	12.97	73.9	49	1495	-0.6	0.5	1	2
G132	5.04	87.1	95	919	-4.6	0.5	1	3
G135	5.85	112	53	2104	-0.6	0.5	1	2
B167	3.39	107	74	1437	-3.2	0.5	1	1
<i>Tristan da Cunha (EMI)</i>								
T16	4.74	134	101	1321	-2.3	0.5	1	2
T60	12.2	60.9	38	1600	-0.3	0.5	1	2
T64	8.91	115	64	1796	-1.1	0.5	1	1
T122	7.28	104	55	1888	-1.2	0.5	1	2
T497	7.61	136	87	1559	-1.2	0.8	2	9
T557	8	112	56	2006	-1.2	1.5	2	7
<i>T557 (leached)</i>					-1.6	0.9	1	1 (NUII)
<i>Fatu Hiva, Marquesas (EM[†])</i>								
FH01	10.6	110	7	16740	0.0	1.3	1	1
FH11	6.8	99.0	26	3837	-3.6	0.8	2	3
FH18	12.2	81.5	32	2554	-1.8	0.5	1	1
<i>Hiva Oa, Marquesas (EM[†])</i>								
HV64	8	81.1	17	4649	0.7	0.5	1	1
HV76	5.14	72.7	63	1162	-0.3	0.7	1	2
<i>Montane, Marquesas (EM[†])</i>								
MT04	5.63	71.6	18	3996	-3.9	1.0	3	3 (2 NU + 1 NUII)
MT08	5.53	82.0	25	3224	0.6	0.5	2	2
<i>Tahuata, Marquesas (EM[†])</i>								
TH4	6.37	108	77	1415	-2.9	0.5	1	1
TH5	7.44	137	66	2064	-0.5	0.5	1	2
TH8	4.67	96.3	24	4045	1.0	0.5	1	1
<i>TH8 (leached)</i>					2.2	0.9	1	1 (NUII)
TH13	6.09	80.7	15	5482	-3.5	0.6	2	4
TH14	8.37	109	177	614	-6.4	0.5	1	4
TH18	6.4	87.6	43	2014	0.4	1.2	2	3 (2 NU + 1 NUII)
<i>TH18 (leached)</i>					-0.2	0.8	1	1 (Nu II)
TH31	5.6	82.1	18	4574	-1.9	1.1	2	2 (1 NU + 1 NUII)
TH39	9.2	81.5	18	4533	4.4	0.9	1	1
<i>Ua Huka, Marquesas (EM[†])</i>								
UH53	0.38	155	235	663	-1.8	0.5	1	4
UH81	7.75	90.4	121	748	-1.9	0.5	2	5
UH89	7.2	89.8	39	2278	-3.5	0.5	1	3
UH93	9.85	72.8	97	753	-1.2	0.5	2	3
<i>St Helena (HIMU)</i>								

H28	6.64	101	26	3936	-0.9	0.5	1	5
H38	15.87	41.3	40	1043	-3.1	0.5	1	2
H64	10.97	61.7	14	4360	-0.7	0.5	1	2
H69	9.09	62.8	94	665	-3.3	0.9	2	9
Rurutu, Austral-Cook (HIMU)								
RRT032	6.02	47.9	45	1073	-6.4	1.3	2	4
RRT037	7.4	59.8	40	1489	6.6	0.5	1	1
<i>RRT037 (leached)</i>					4.9	0.9	1	1 (NUII)
74-386	7.24	56.5	14	4024	-2.3	0.5	2	2
74-390	6.29	74.9	44	1709	-6.3	0.5	1	1
<i>74-390 (leached)</i>					-3.7	0.9	1	1 (NUII)
74-396	7.89	73.9	32	2290	-3.4	0.5	1	3
Tubuai, Austral-Cook (HIMU)								
TBA9	17.9	96.4	18	5371	-2.1	1.2	1	2 (NUII)
K109	15.5	117	19	6108	-5.9	0.5	1	1
108B	10.85	88.4	10	9069	-3.1	0.5	1	2
5433	6.2	145	31	4691	-0.3	0.5	1	2
5434	11.26	84.0	25	3393	-3.5	0.5	1	2
5435	4.85	226	50	4497	-4.8	2.4	2	3 (1 NU + 2 NUII)
5436	9.59	111	12	9279	-2.1	0.5	1	1

948

949 * MgO values per Table 1 and references therein (see Electronic Annex 2b for full details)

950 † Marquesas lavas exhibit variable composition: at a given $^{87}\text{Sr}/^{86}\text{Sr}$ value, lavas from the 'Ua Huka' group
951 (Ua Huka, young Hiva Oa) have higher Nd isotopic compositions, and lavas from the 'Fatu Hiva' group
952 (Fatu Hiva, old Hiva Oa, Montane, Tahuata) have higher $^{206}\text{Pb}/^{204}\text{Pb}$ (see Chauvel et al., 2012; Electronic
953 Annex 2).

954 2sd is quoted as the highest of (1) the uncertainty for repeat analyses of BCR-2 on the *Nu HR*, (2) the
955 uncertainty for repeated measurements of the Aldrich T1 solution on the *Nu Plasma II*, or (3) the uncertainty
956 for repeat analyses of a given sample.

957 **Table 3.** Slopes obtained for York regressions (York et al., 2004) between log[Tl] and log[Element] (see
958 text). For MORB, n = 909 except Cs, for which n = 702. For OIB, n = 48.
959

Element	MORB		OIB	
	slope	2sd	slope	2sd
Ce	0.994	0.030	0.102	0.122
Cs	2.608		2.033	0.571
La	1.285	0.047	0.116	0.136
Pb	0.875	0.021	1.131	0.488
Rb	3.114	0.218	1.091	0.504

960

961 **Table 4.** Modal mineralogy and reaction coefficients used in melting models.

962

mineral	<i>spinel lherzolite (MORB)</i>		<i>garnet lherzolite (OIB)</i>	
	vol proportion (%)¹	melting coefficient²	vol proportion (%)³	melting coefficient³
olivine	0.57	-0.2	0.55	0.08
clinopyroxene	0.13	0.8	0.25	0.81
orthopyroxene	0.28	0.32	0.15	-0.19
spinel	0.02	0.08	-	-
garnet	-	-	0.05	0.3
sulphide	variable	SCSS*	variable	SCSS

963

964 * Sulphur concentration at sulphide saturation for basaltic melts (Liu et al., 2007; Mavrogenes and O'Neill,
965 1999; O'Neill and Mavrogenes, 2002). [1] Workman and Hart (2005); [2] Baker and Stolper (1994) and
966 Wasylenki et al. (2003), as modified by Nielsen et al. (2014); [3] Elliott et al. (2007).

967 **Table 5.** Parameters used in models of MORB and OIB melting.
 968

Variable	Symbol	<i>Nielsen et al. 2014 (MORB)</i>		<i>MORB</i>		<i>OIB</i>	
		Value range	References	Value range	References	Value range	References
<i>Melting</i>							
melt fraction	F	0-16%	-	0-16%	-	0-18%	-
melt increment		0.01%	-	0.1%	-	0.1%	-
pressure (avg)		1.5 GPa	-	1.5 GPa	-	3 GPa	-
temperature (avg)		1350 °C	-	1350 °C	-	1445 °C	-
FeO in melt		~10%	8	~10%	8	~10%	<i>sample data</i>
SCSS		1200 µg/g	9-11	1200 µg/g	9-11	1200 µg/g	9-11
<i>Partition coefficients</i>							
Thallium	D _{cpx/melt}	0.0006	1	0.0006	1	0.0006	1
	D _{opx/melt}	0.00045	1	0.00045	1	0.00045	1
	D _{ol/melt}	4.5 x 10 ⁻⁵	1	4.5 x 10 ⁻⁵	1	4.5 x 10 ⁻⁵	1
	D _{sp/melt}	0	1	0	1	-	-
	D _{gt/melt}	-	-	-	-	0	<i>assumed (3)</i>
	D _{sulf/melt}	18-100	<i>model</i>	1-25	<i>model</i>	1-25	<i>model</i>
	Bulk D	0.0002-0.11		0.0002-0.028		0.0002-0.007	
Cerium	D _{cpx/melt}	0.14	2	0.01-0.8	4-7	0.01-0.8	4-7
	D _{opx/melt}	0.006	2	0.006	2	0.0026	7
	D _{ol/melt}	4 x 10 ⁻⁵	2	4 x 10 ⁻⁵	2	4 x 10 ⁻⁵	2
	D _{sp/melt}	0	<i>assumed</i>	0	<i>assumed</i>	-	-
	D _{gt/melt}	-	-	-	-	0.003	3
	D _{sulf/melt}	0	<i>assumed</i>	0	<i>assumed</i>	0	<i>assumed</i>
	Bulk D	0.02		0.003-0.1		0.002-0.16	

969 [1] Assumed identical to Rb partition coefficients of Donnelly et al. (2004); [2] McDade et al. (2003a); [3]
 970 Adam and Green (2006) were unable to determine a partition coefficient for Tl between garnet and silicate
 971 melt, but for LILE values were very low; [4] Frey (1969); [5] Irving and Frey (1984); [6] Nagasawa et al.
 972 (1969); [7] Matsui et al. (1977); [8] Gale et al. (2013); [9] Liu et al. (2007); [10] Mavrogenes and O'Neill
 973 (1999); [11] O'Neill and Mavrogenes (2002).
 974

975 **Table 6.** Estimated Ce, S and Tl concentrations in potential contributions to OIB source regions.
 976

Reservoirs	Ce ($\mu\text{g/g}$)	References	Tl (ng/g)	References	S ($\mu\text{g/g}$)*	References
DM	0.55	1	0.27-0.48	9; model	0-400	2; model
PM	1.675	2	3.5	2	0-400	2; model
Peridotites	0.020-0.39	3	0.05-3.5	3	76-360	3,12
FeMn sediment (hydrogenetic)	700	8	90000	11	-	-
Subducted eclogites†	20 (1-210)	13	60 (2-350)	13	-	-
Subduction-processed oceanic crust	~10-75	<i>calculated</i>	~2-6	<i>calculated</i>	-	-

977
 978 * Sulphide abundance was converted to S concentration using the assumption that on average mantle
 979 sulphides are 36 wt% S, i.e. dominantly FeNi sulphides. † mean (range). [1] Workman and Hart (2005); [2]
 980 McDonough and Sun (1995); [3] Wang et al. (2018); [4] Sparks (1995); [5] Zuleger et al. (1996); [6] Bach et
 981 al. (1996); [7] Sun and McDonough (1989); [8] Piper (1974); [9] Nielsen et al. (2014); [10] Nielsen et al.
 982 (2006b); [11] Rehkämper et al. (2002); [12] Ding and Dasgupta (2018); [13] Shu et al. (2019).

983 **Supplementary Figures**

984 **Figure S1:** Plot of $\epsilon^{205}\text{Tl}$ against MgO content for samples of this study and from the literature. $\epsilon^{205}\text{Tl}$ does
 985 not vary systematically with melt evolution. As the majority of samples are not cogenetic, two suites of lavas
 986 following common liquid lines of descent (Hekla, Iceland; Anatahan, Marianas) are highlighted, showing
 987 that even at low MgO there is no correlation with $\epsilon^{205}\text{Tl}$. Approximate fields of fractionating phases are
 988 indicated. Data sources: [1] Prytulak et al. (2017); [2] Blusztajn et al. (2018); [3] Nielsen et al. (2007); [4]
 989 Nielsen et al. (2006a). * picrites.

990 **Figure S2:** Depleted Mantle-normalised trace element plots. Here the negative Tl anomaly, while still
 991 present on average, is less pronounced – particularly for EM-type lavas.

992 **Figure S3:** Tl anomaly exhibits clearer covariation with absolute Tl abundance when calculated relative to
 993 REE than when calculated relative to LILE (with the possible exception of HIMU). Symbols and data
 994 sources as in Figure 5.

995 **Figure S4:** Plot of La/Tl, Pb/Tl, Rb/Tl and Cs/Tl ratios against Tl concentration. Only the La/Tl ratios
 996 distinguishes tectonic settings as clearly as the Ce/Tl ratios. Symbols and data sources as in Figure 5.

997 **Figure S5:** Process identification plot (Minster and Allègre, 1978) of Tl/Ce against 1/Tl. Also shown are
 998 melting patterns (melt fraction $F = 0.0001$ to 1) for DM (Tl = 0.00038 $\mu\text{g/g}$, Ce = 0.772 $\mu\text{g/g}$) and PM (Tl =
 999 0.0035 $\mu\text{g/g}$, Ce = 1.675 $\mu\text{g/g}$), in addition to the fractional crystallisation trend ($F = 1$ to 0.1), assuming bulk
 1000 $D_{\text{Tl}} = 0.02$ and bulk $D_{\text{Ce}} = 0.06$. While most of the variation in OIB is subparallel to the DM melting trend,
 1001 with scatter leaving room for some fractional crystallisation, the observed range significantly exceeds that
 1002 which can be explained simply through a combination of melting and fractional crystallisation. The OIB
 1003 trend therefore requires mixing melts from different sources, one of which cannot contain more than
 1004 negligible Tl (note y-intercept of trend). Symbols and data sources as in Figure 5.

1005 **Figure S6:** Mixing between St Helena HIMU average composition (Blusztajn et al., 2018) and three “AOC”
 1006 values (see Table S1). Ticks correspond to admixture of 10%, 20% and 30% of AOC as labelled for ODP
 1007 504B.

	DM	St Helena average	ODP 504B (~6.6 Ma)	DSDP 417/418 (~109 Ma)	“Modern AOC”
Tl ($\mu\text{g/g}$)	0.00038	0.03	0.25	0.07	<u>0.017</u>
Ce ($\mu\text{g/g}$)	0.772	80.83	4.31	6.19	<u>12</u>
Pb ($\mu\text{g/g}$)	0.0232	2.06	0.36	0.69	<u>0.6</u>
Ce/Pb	33	~40	12	9	20
$\epsilon^{205}\text{Tl}$	-2	~-2	-15	-5.4	-15

1008

1009 **Table S1.** For DM, values are taken from Salters and Stracke (2004), except $\epsilon^{205}\text{Tl}$ (Nielsen et al., 2006a).
 1010 For DSDP 417/418, supercomposite values are taken from Blusztajn et al. (2018) and Staudigel et al. (1995).
 1011 ODP 504B values are taken from Nielsen et al. (2006b) and Bach et al. (2003). “Modern AOC” values are

1012 taken from Blusztajn et al. (2018) or inferred (underlined). St Helena average values are as reported by
1035

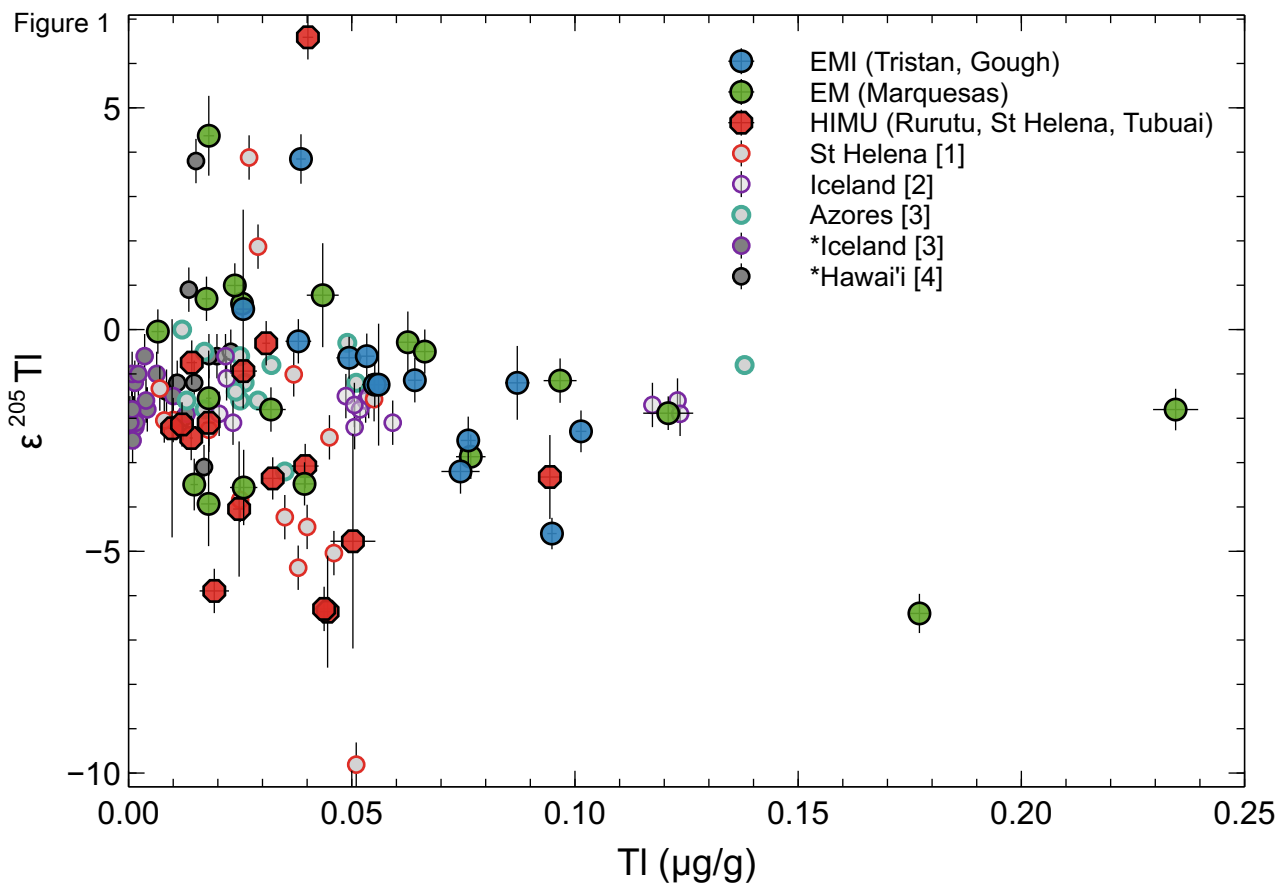


Figure 2

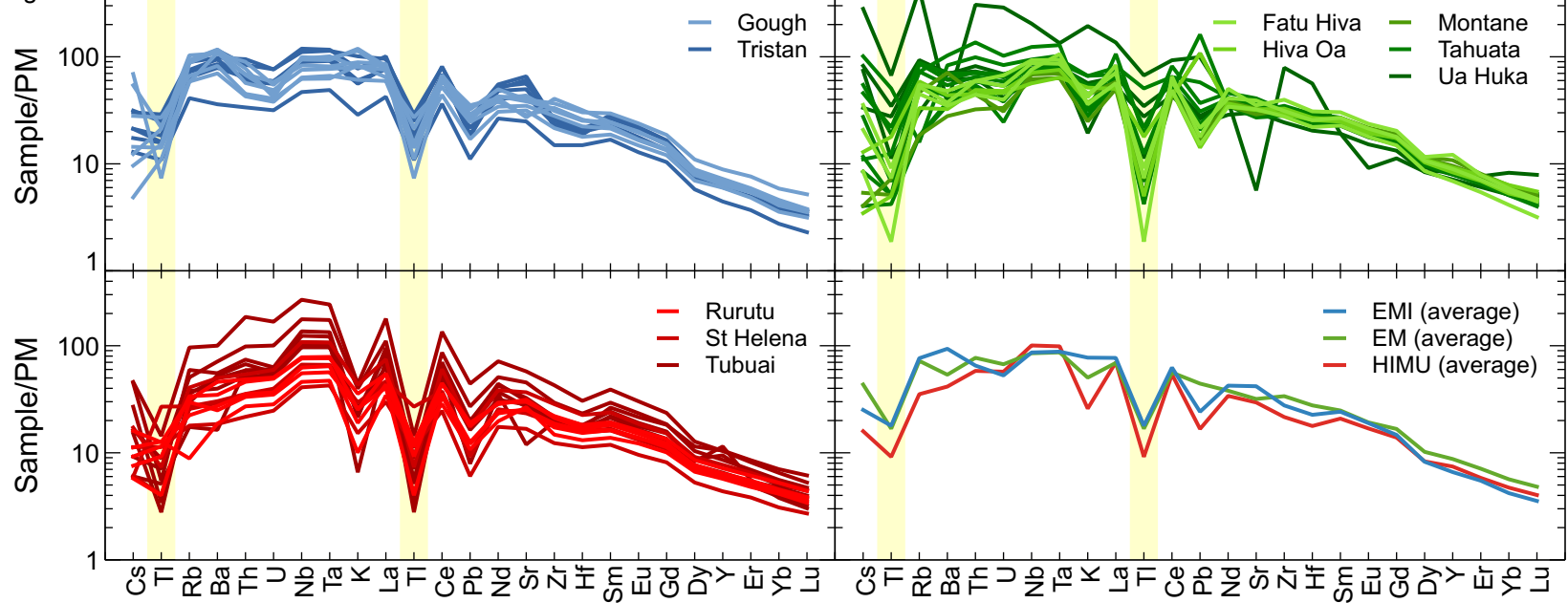
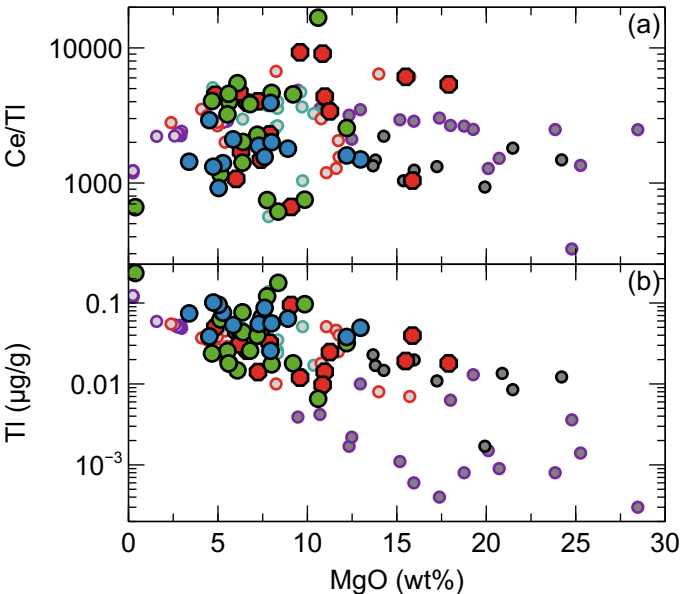


Figure 3

- | | |
|------------------------------------|-----------------|
| ● EMI (Gough, Tristan) | ● St Helena [1] |
| ● EM (Marquesas) | ● Iceland [2] |
| ● HIMU (St Helena, Rurutu, Tubuai) | ● Azores [3] |
| | ● *Iceland [3] |
| | ● *Hawai'i [4] |



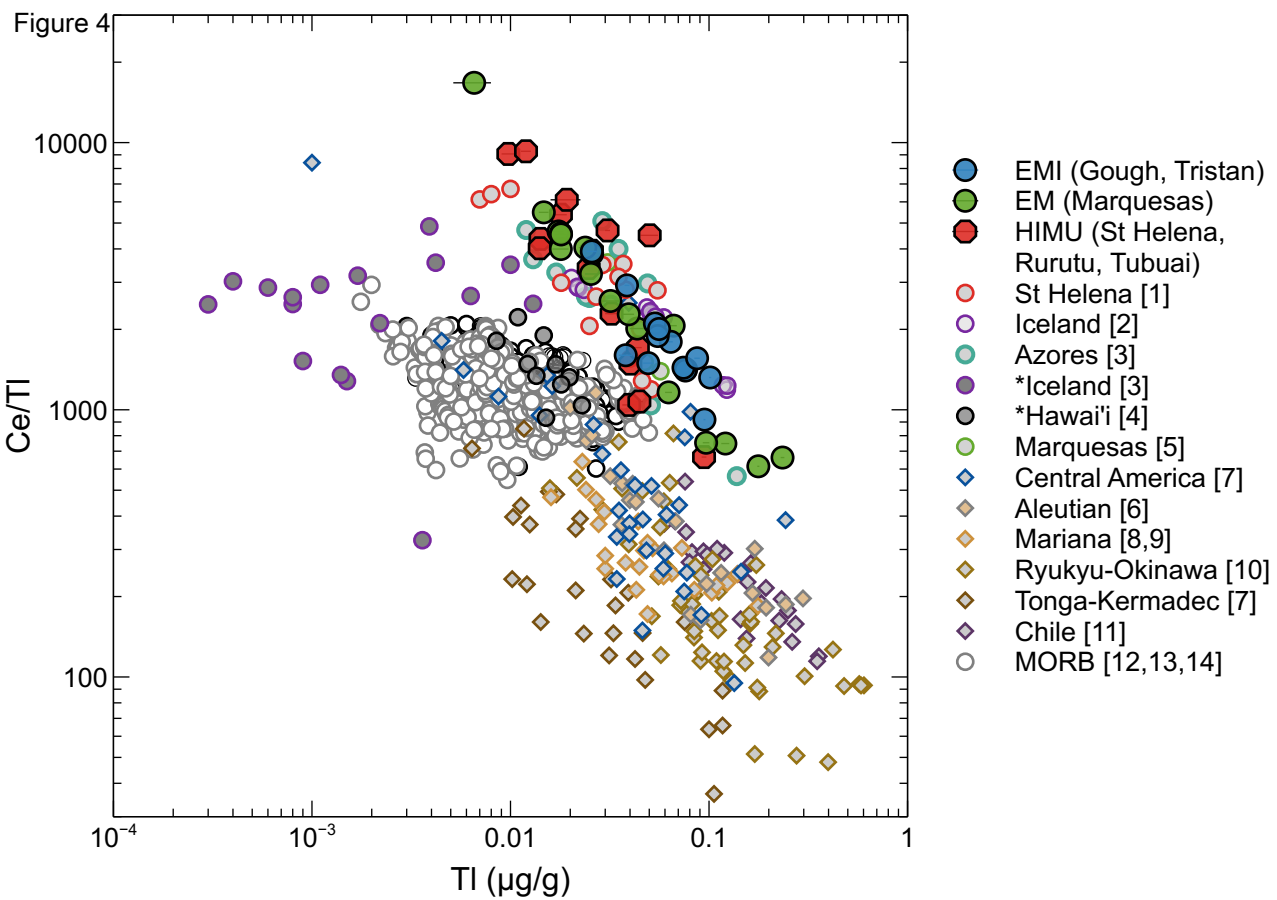
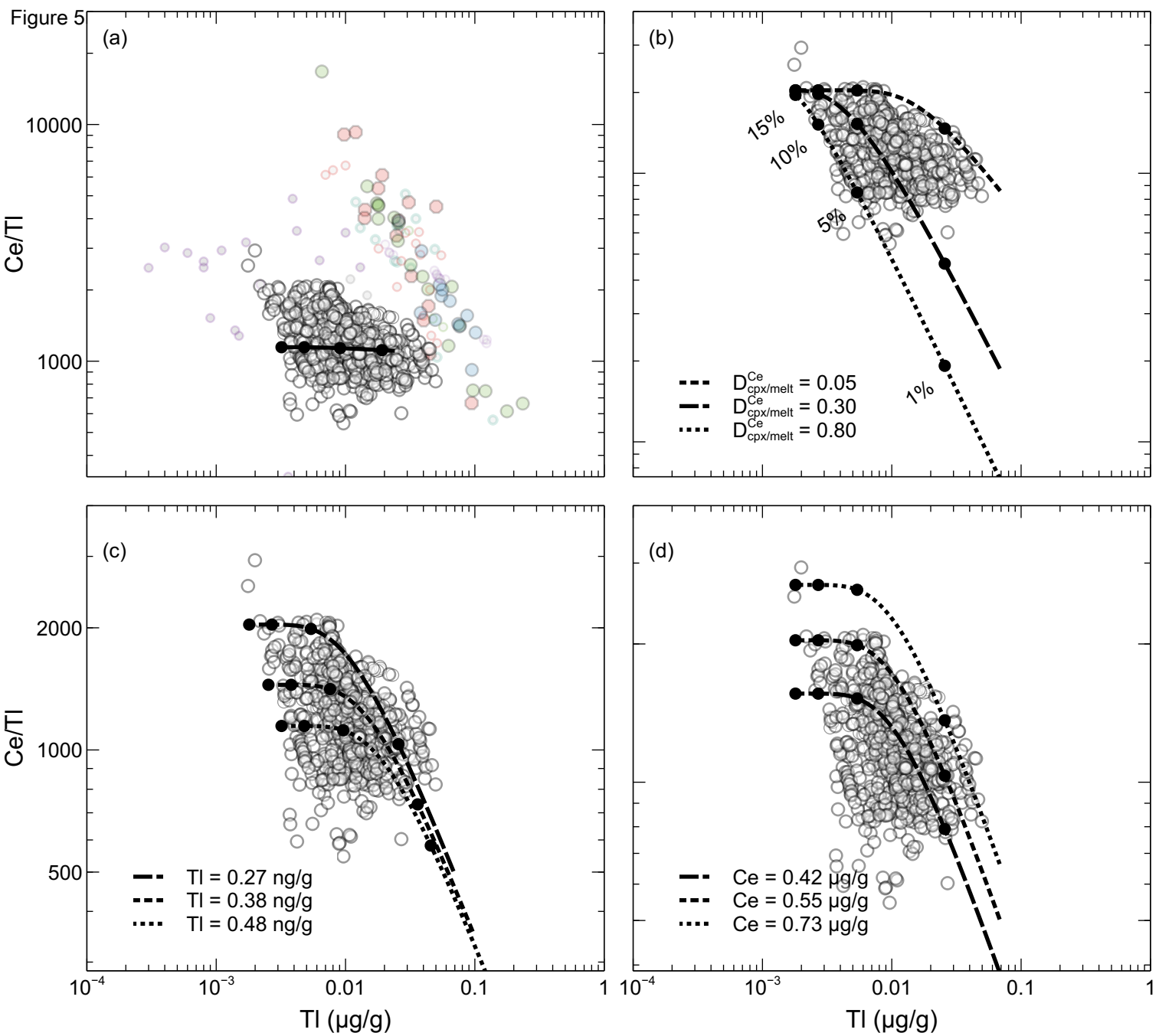
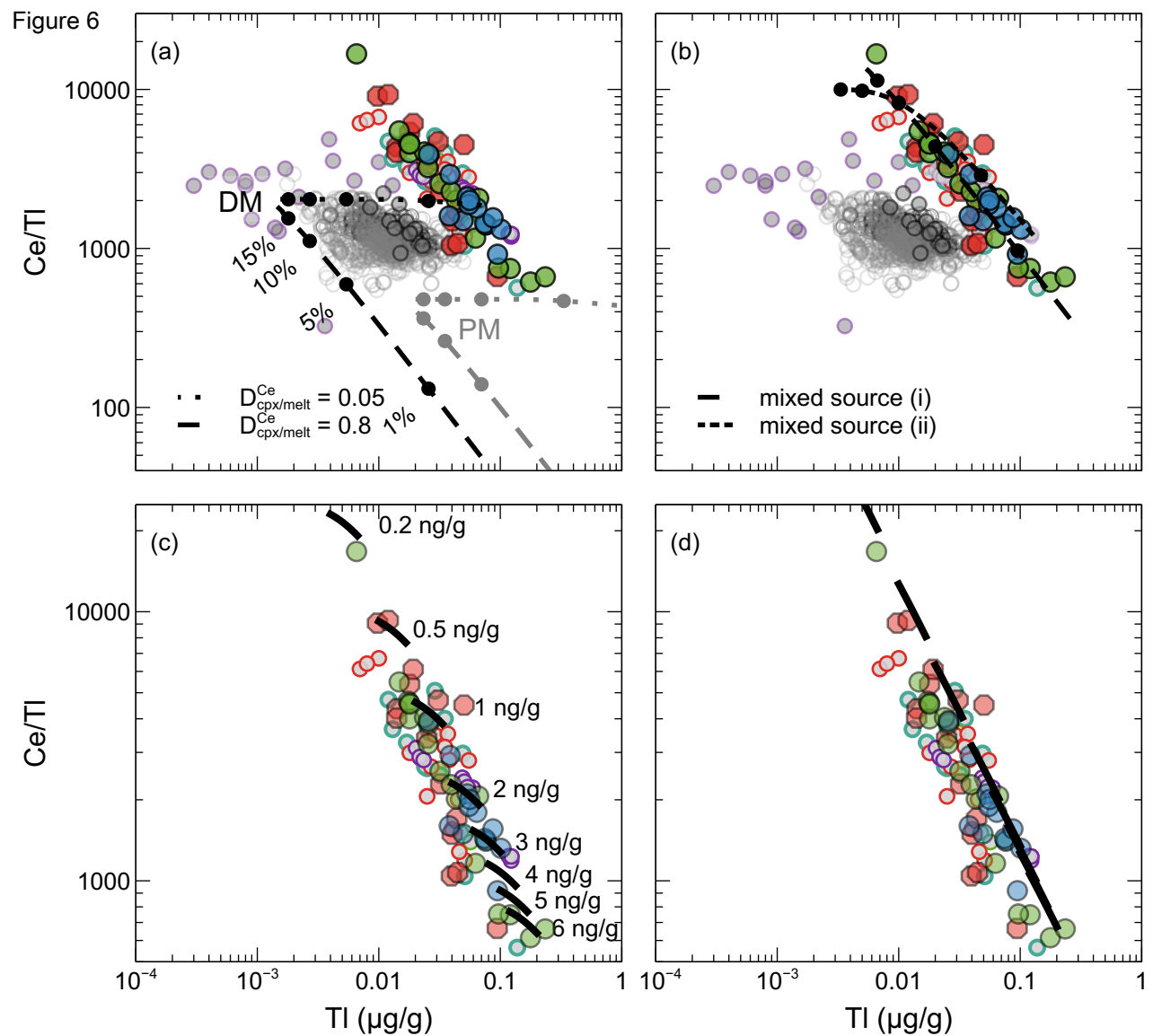


Figure 5





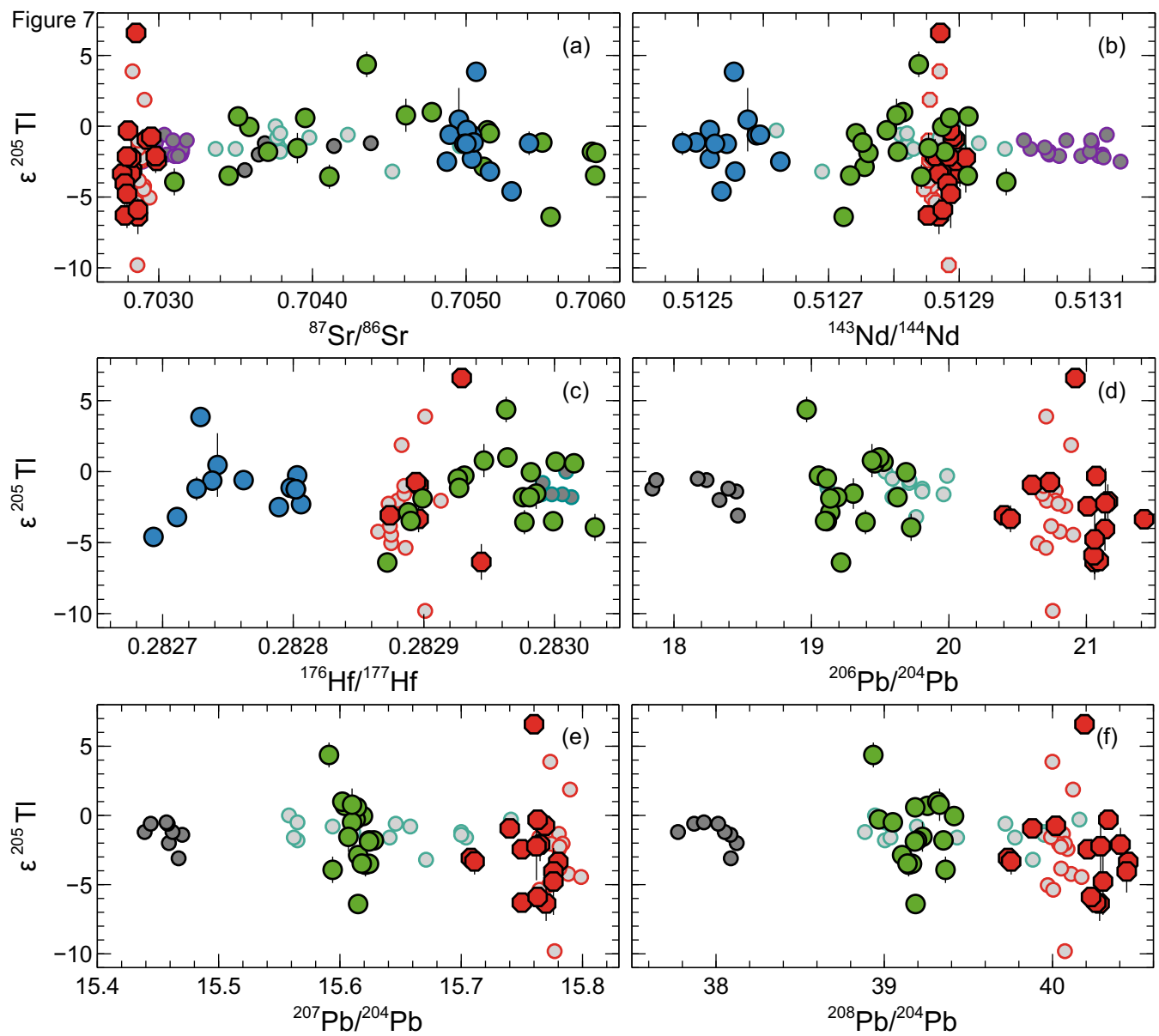


Figure 8

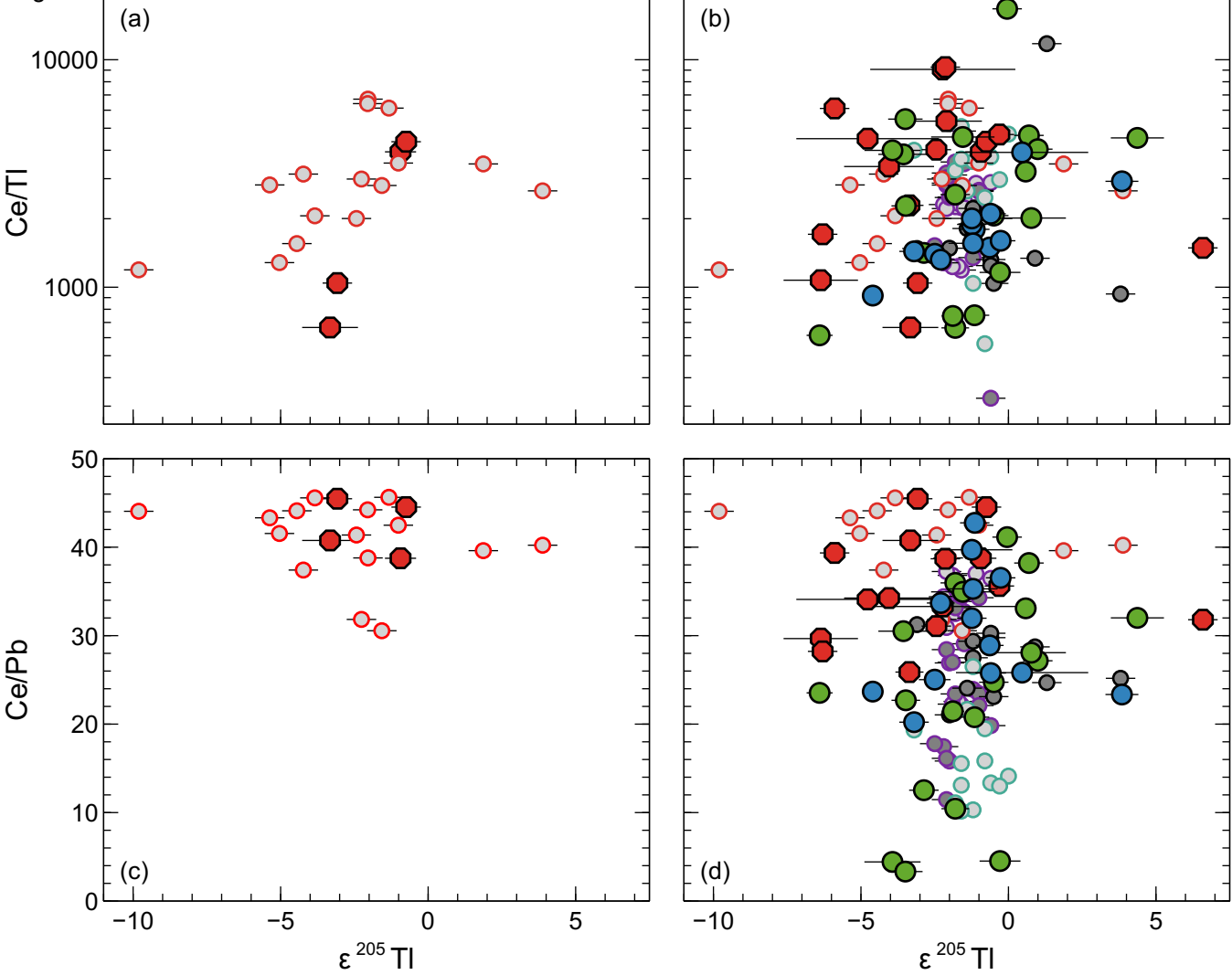


Figure 9

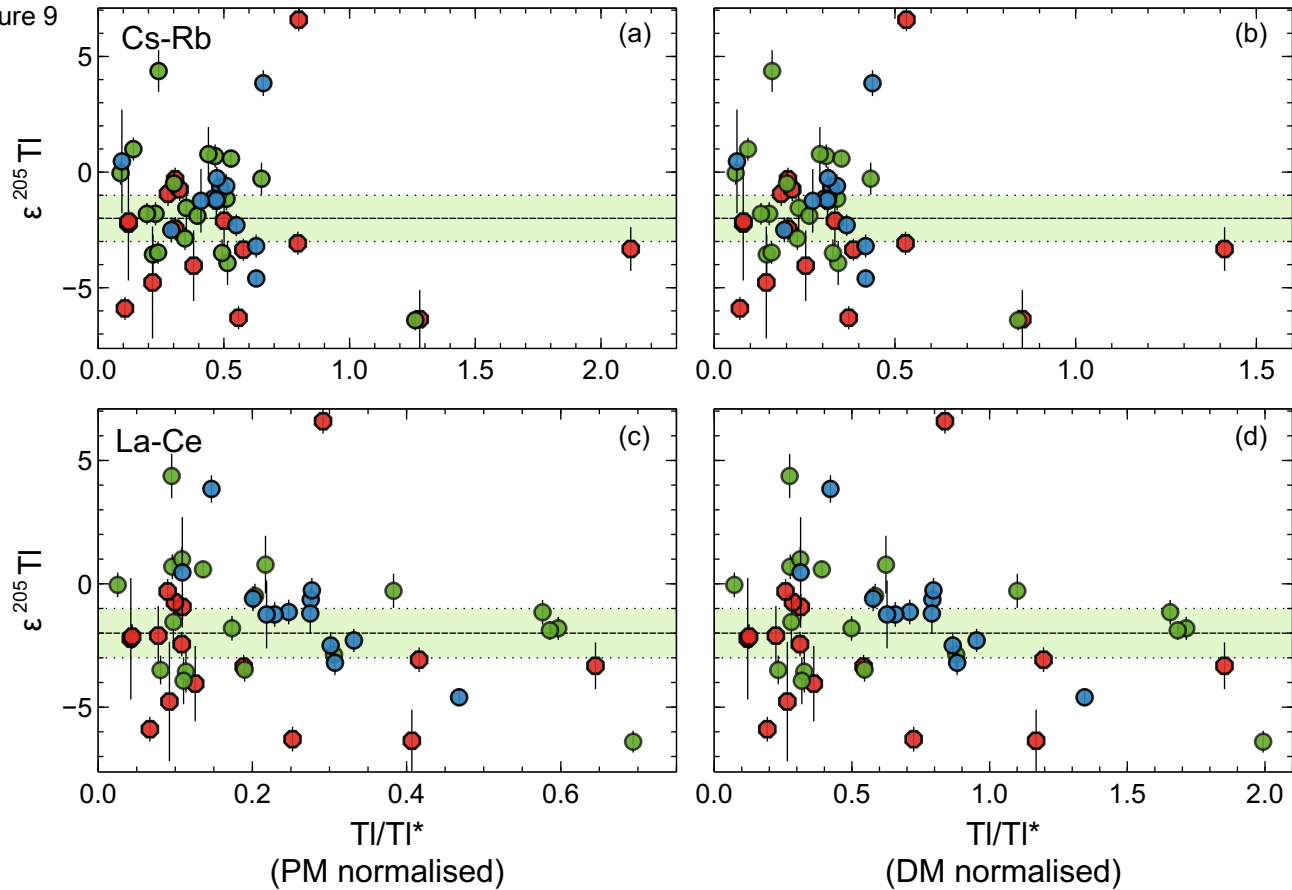
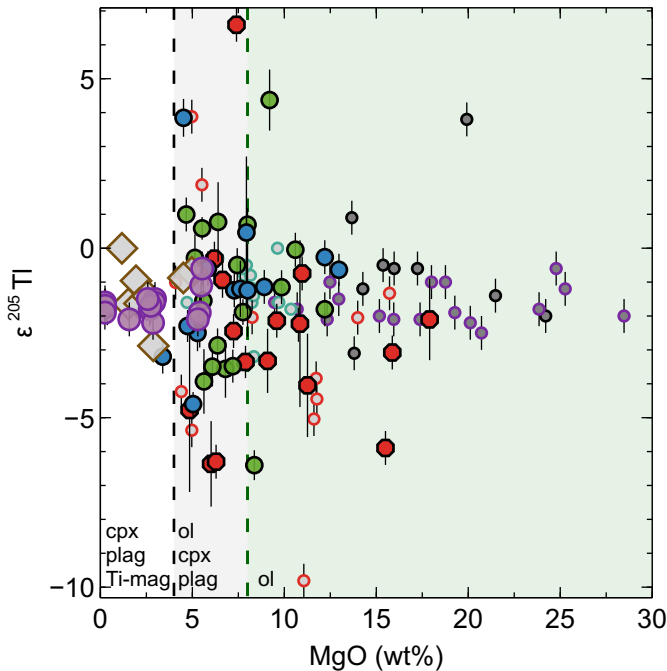
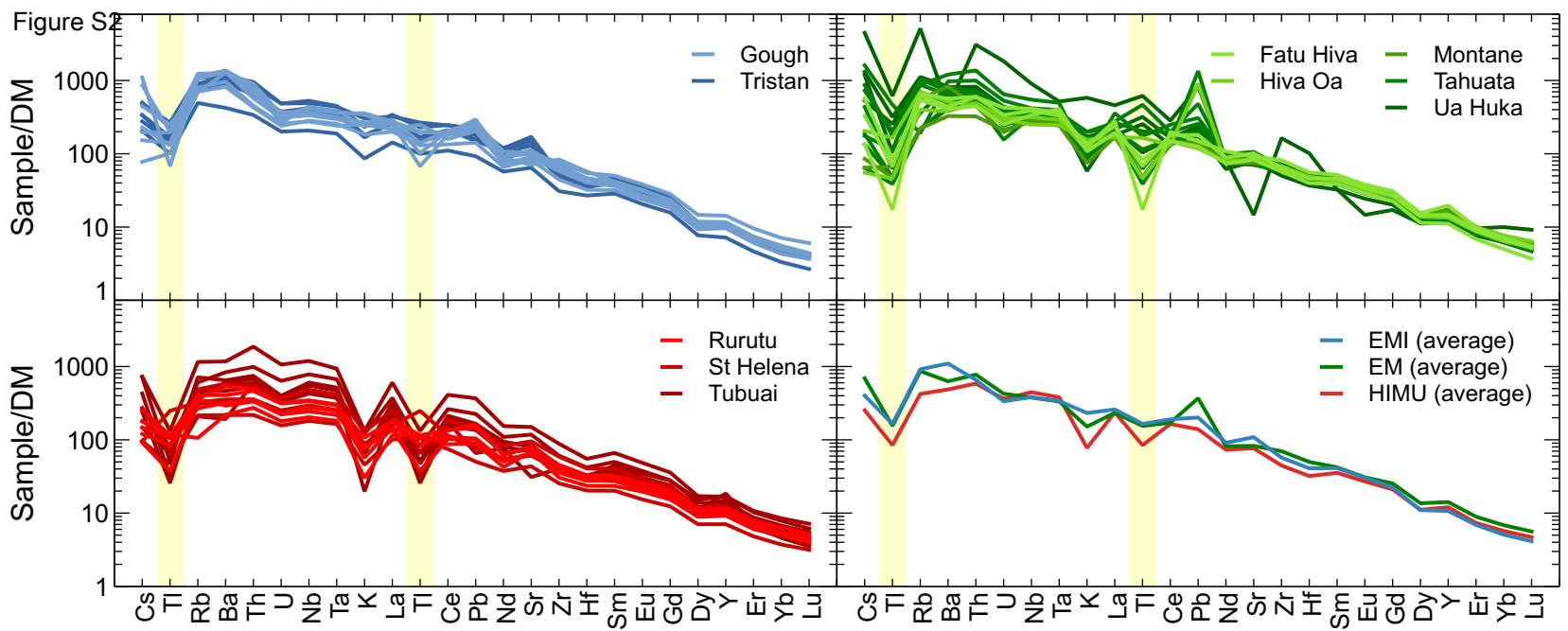
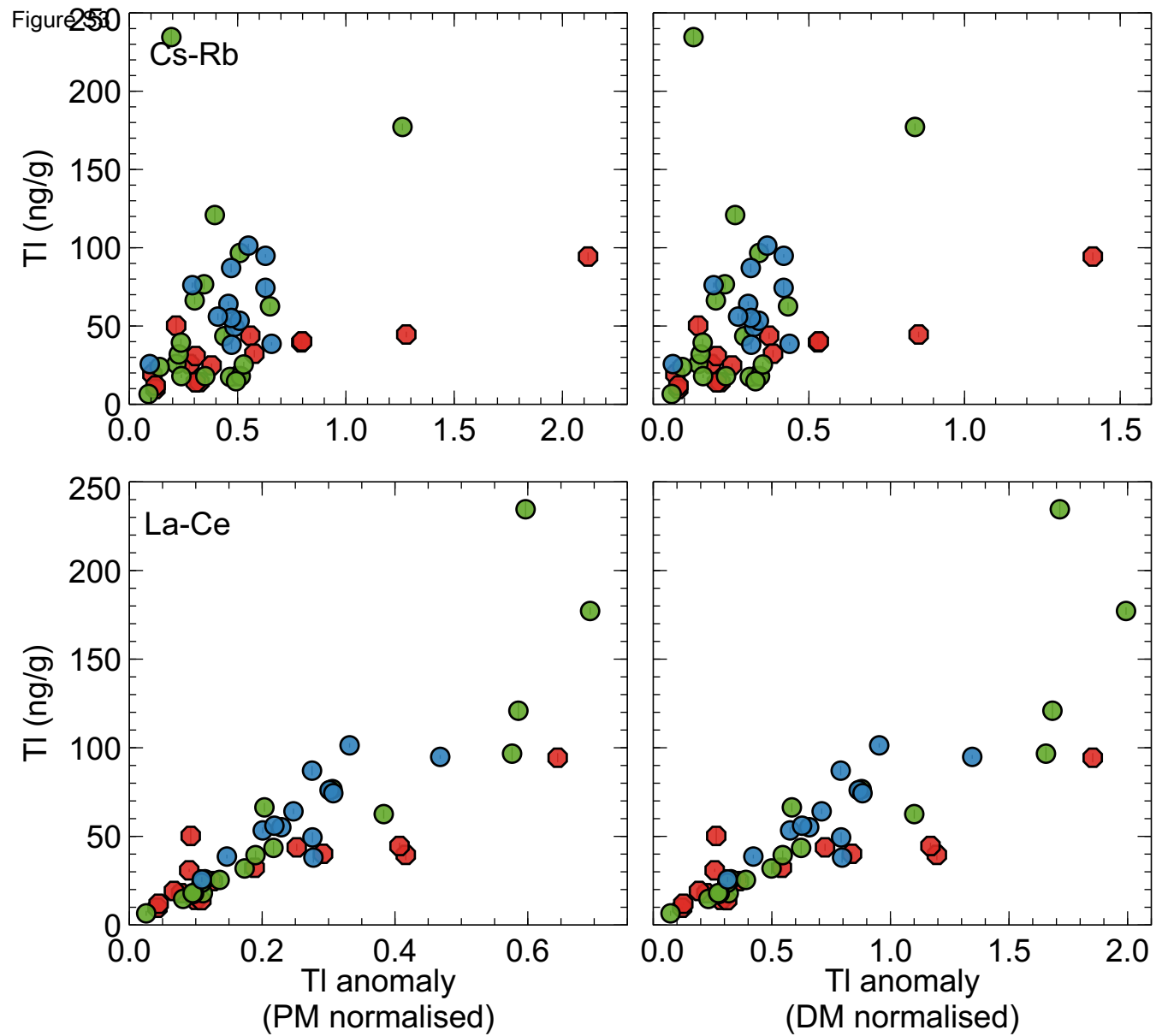


Figure S1







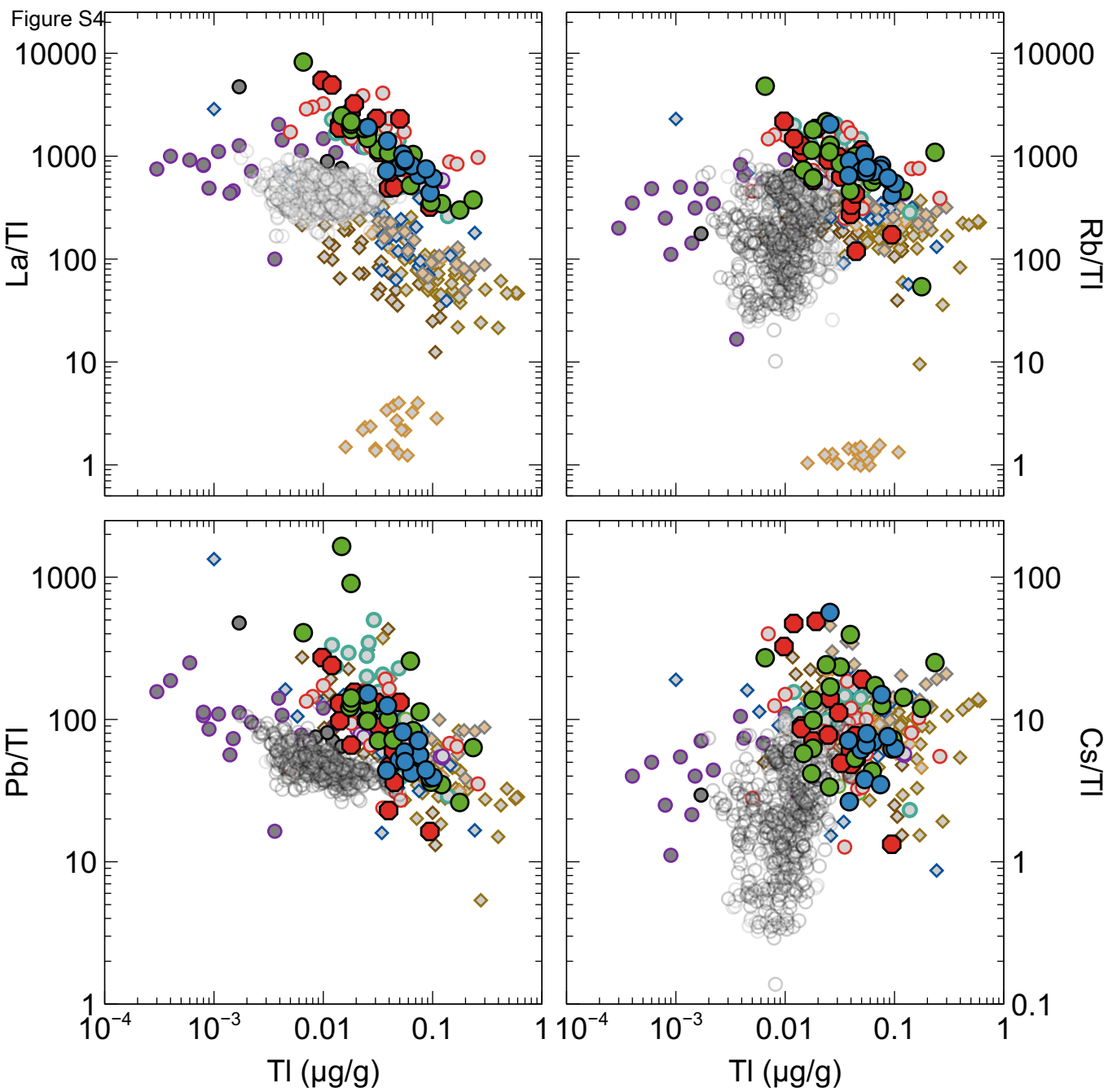


Figure 75

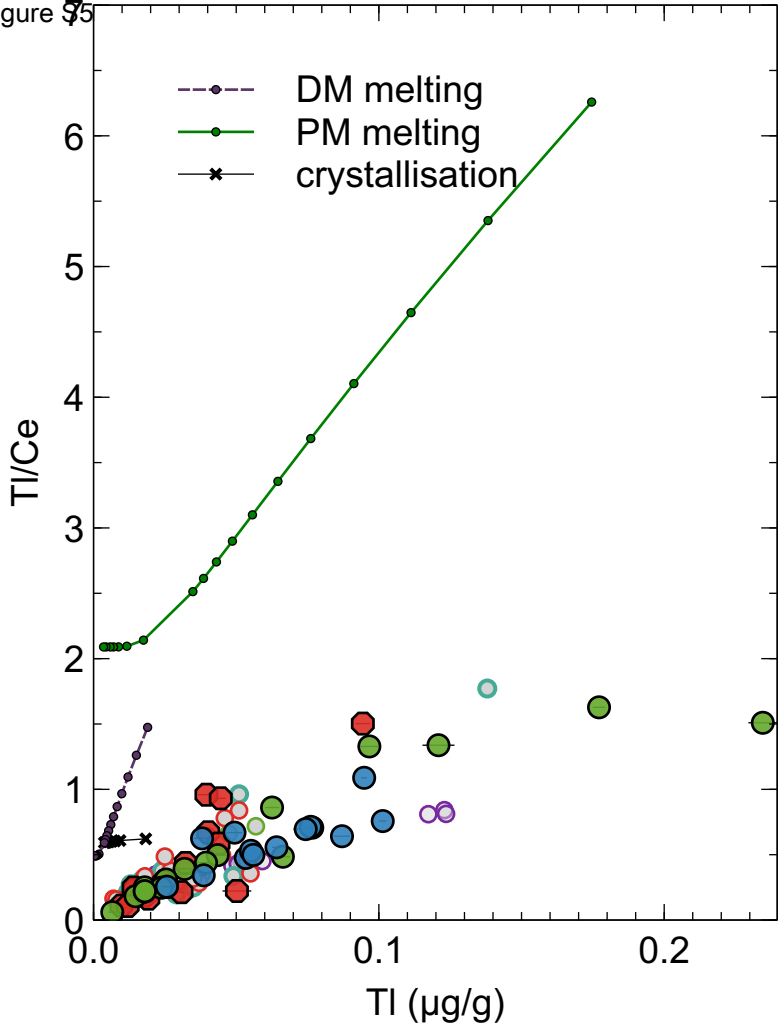


Figure 56

