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1 **Thallium mass fraction and stable isotope ratios of sixteen geological** 2 **reference materials**

3

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8

9

10 **Abstract.** Thallium stable isotope ratio and mass fraction measurements were performed on sixteen
11 geological reference materials spanning three orders of magnitude in thallium mass fraction,
12 including both whole-rock and partially-separated mineral powders. For stable isotope ratio
13 measurements, a minimum of three independent digestions of each reference material were
14 obtained. High-precision trace element measurements (including Tl) were also performed for the
15 majority of these RMs. The range of Tl mass fractions represented is 10 ng g⁻¹ to 16 µg g⁻¹, and Tl
16 stable isotope ratios (reported for historical reasons as $\epsilon^{205}\text{Tl}$ relative to NIST SRM 997) span the
17 range -4 to +2. With the exception – attributed to between-bottle heterogeneity – of G-2, the
18 majority of data are in good agreement with published or certified values, where available. The
19 precision of mean of independent measurement results between independent dissolutions suggests
20 that, for the majority of materials analysed, a minimum digested mass of 100 mg is recommended to
21 mitigate the impact of small-scale powder heterogeneity. Of the sixteen materials analysed, we
22 therefore recommend for use as Tl reference materials the USGS materials BCR-2, COQ-1, GSP-2,
23 and STM-1; CRPG materials AL-I, AN-G, FK-N, ISH-G, MDO-G, Mica-Fe, Mica-Mg, and UB-N;
24 NIST SRM 607; and OREAS14P.

25

26 **Keywords:** *thallium, stable isotopes, reference materials, powder heterogeneity, sample mass*

28 INTRODUCTION

29

30 First isolated in 1861 (Crookes 1862, Lamy 1862), thallium is one of the highest atomic mass
31 naturally-occurring elements: a volatile, highly incompatible trace metal, with two oxidation states
32 available in addition to the neutral charge state. Univalent thallium (Tl^+) has a large ionic radius
33 (1.49 Å), comparable to that of the alkali metals potassium, rubidium and caesium, and can
34 therefore substitute for these elements in mineral crystal structures (Shaw 1952, Shannon and
35 Prewitt 1969, Shannon 1976). Trivalent thallium (Tl^{3+}) can also exist on Earth under highly
36 oxidising conditions (Bately and Florence 1975, Vink 1993), e.g. in the structure of the
37 ferromanganese (Fe-Mn) mineral hexagonal birnessite (Peacock and Moon 2012, Nielsen *et al.*
38 2013).

39

40 Thallium has two stable isotopes with mass numbers 203 (29.5%) and 205 (70.5%). The relative
41 difference in mass between thallium's two stable isotopes is less than 1%. Because the magnitude of
42 mass-dependent stable isotope fractionations via kinetic and equilibrium processes scales inversely
43 with both overall and relative mass difference (Bigeleisen and Mayer 1947, Urey 1947), it was
44 assumed that there would be little mass-dependent thallium isotope fractionation in nature.

45 Resolvable Tl isotopic differences were therefore thought to arise solely due to decay of the
46 relatively short-lived radioisotope ^{205}Pb to ^{205}Tl , with a half-life of about 15 Ma. Initial
47 investigations (Anders and Stevens 1960, Chen and Wasserburg 1987,1994, Huey and Kohman
48 1972, Ostic *et al.* 1969) thus aimed to provide constraints on the delivery and distribution of ^{205}Pb
49 during the early stages of solar system formation by tracking differences in Tl isotope ratios. These
50 efforts proved unable to resolve variations for a large number of extraterrestrial and some selected
51 terrestrial materials. This inability was for the most part due to the uncertainties ($>2\%$, 2s)
52 associated with TIMS measurement results of Tl (see summary in Nielsen *et al.* 2017).

53 As a consequence of initial development of the system in the context of cosmochemistry, where

54 small radiogenic isotope variations are routinely reported using ϵ -notation, Tl isotope ratios are
55 traditionally reported relative to the NIST Tl reference material SRM 997 (defined as 0) as

56
$$\epsilon^{205}\text{Tl}_{\text{SRM997}} = 10,000 \times [({}^{205}\text{Tl}/{}^{203}\text{Tl})_{\text{sample}} - ({}^{205}\text{Tl}/{}^{203}\text{Tl})_{\text{SRM997}}] / ({}^{205}\text{Tl}/{}^{203}\text{Tl})_{\text{SRM997}}$$

57 Strictly, use of ϵ -notation is deprecated in favour of δ -notation (Coplen 2011), whereby

58
$$\delta^{205}\text{Tl}_{\text{SRM997}} = \delta^{205/203}\text{Tl}_{\text{SRM997}} = [R({}^{205}\text{Tl}/{}^{203}\text{Tl})_{\text{sample}} - R({}^{205}\text{Tl}/{}^{203}\text{Tl})_{\text{SRM997}}] / R({}^{205}\text{Tl}/{}^{203}\text{Tl})_{\text{SRM997}}$$

59 However, since 1999 all published Tl isotope data has been reported using $\epsilon^{205}\text{Tl}_{\text{SRM997}}$, which is
60 strictly equivalent to $\delta^{205}\text{Tl}_{\text{SRM997}}$ in parts per ten thousand. The universal convention of reporting
61 $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ is therefore maintained here for ease of comparison with Tl isotope ratio literature.

62 The development of multi-collector ICP-MS (MC-ICP-MS) allowed for higher-precision Tl isotope
63 ratio measurements, with precisions >3-4 times better than those achieved by the best TIMS
64 protocols then reported (0.1-0.2 ‰, 2s; Arden 1983). Using these new measurement principles,
65 Rehkämper and Halliday (1999) analysed a number of terrestrial samples in order to define the
66 baseline terrestrial Tl isotope composition for the purpose of comparison with extraterrestrial
67 materials, again assuming that variations in extraterrestrial materials would reflect early ${}^{205}\text{Pb}$ decay.
68 They unexpectedly discovered large variations in Tl isotope ratios for terrestrial materials, from
69 $\epsilon^{205}\text{Tl}_{\text{SRM997}} -1.8 \pm 1.9$ (2s) to 11.9 ± 0.5 (2s).

70

71 The natural range of Tl stable isotope variations documented on Earth now exceeds 35 $\epsilon^{205}\text{Tl}_{\text{SRM997}}$
72 units (" ϵ -units"; see review in Nielsen *et al.* 2017). With the exception of volcanic fumaroles and
73 some meteorites (Baker *et al.* 2009,2010b, Nielsen *et al.* 2006a), these variations are best explained
74 by equilibrium isotope effects (Nielsen *et al.* 2006c, Rehkämper *et al.* 2002). The magnitude of
75 equilibrium stable isotope variation in Tl exceeds those predicted by classical models of mass-
76 dependent isotope fractionation. Schauble (2007) showed that, for very heavy elements including
77 thallium, variation in nuclear volume means that neutron-rich isotopes tend to be concentrated in
78 more oxidised species. A combination of mass-dependent and nuclear volume effects therefore
79 accounts for the stable isotope fractionation displayed by Tl (e.g. Fujii *et al.* 2013). Stable isotope
80 variations arising due to this "nuclear field shift effect" (King 1984) have also been documented for

81 other very heavy elements, including Hg (Smith *et al.* 2005, Xie *et al.* 2005, Moynier *et al.* 2013)
82 and U (Fujii *et al.* 1989a,b, Stirling *et al.* 2007, Moynier *et al.* 2013). Additionally, recent
83 calculations (Yang and Liu 2015) suggest that the nuclear volume effects may produce large
84 differences (up to approximately 4‰) for Pb in systems containing Pb⁴⁺- and Pb²⁺-bearing species.

85

86 As of 2018, there are more than 30 studies utilising Tl isotope ratio variations to investigate the
87 natural environment. The utility and versatility of the system lies in the large isotope ratio
88 differences and relatively high mass fractions ($\mu\text{g g}^{-1}$) associated with low temperature
89 environments, in contrast with very low mass fractions and negligible isotope ratio differences in
90 mantle-derived lavas (see review of Nielsen *et al.* 2017, Prytulak *et al.* 2017). Applications include
91 investigations of extraterrestrial materials (Andreasen *et al.* 2009, 2012, Baker *et al.* 2010b, Nielsen
92 *et al.* 2006a, Palk *et al.* 2011); riverine and marine fluxes (Nielsen *et al.* 2004, 2005, 2006c, Owens
93 *et al.* 2016, Rehkämper *et al.* 2002, Rehkämper and Nielsen 2004); anthropogenic mobilization of
94 Tl (Kersten *et al.* 2014, Nriagu 1998, Peter and Viraraghavan 2005, Vaněk *et al.* 2018, Xiao *et al.*
95 2003, 2004); ore exploration (Baker *et al.* 2010a, Hettmann *et al.* 2014); and use as a tracer of
96 contributions to the source regions of igneous materials (Nielsen *et al.* 2006b, 2014, 2015, 2016,
97 Prytulak *et al.* 2013, 2017, Shu *et al.* 2017, Blusztajn *et al.* 2018).

98

99 Despite the breadth of study, literature reports of thallium isotope ratios for geological reference
100 materials have been restricted to three basalts, one andesite and one granite (Table 1), in addition to
101 two ferromanganese sediments, one meteorite and one seawater sample. In response to the growing
102 application of thallium isotopes in Earth systems, we provide the first measurement results of Tl
103 isotope ratios for the bulk rock reference materials COQ-1, GSP-2, ISH-G, MDO-G, STM-1, and
104 UB-N alongside determinations for previously analysed bulk rock reference materials BCR-2,
105 BHVO-2, and G-2. Investigations of emerging stable isotope systems commonly reveal equilibrium
106 inter-mineral isotope fractionations at high temperatures, as reviewed in Teng *et al.* (2017). We
107 therefore also present the first determinations of Tl mass fractions and isotope ratios for the mineral
108 reference materials 14P, AL-I, AN-G, FK-N, NIST SRM 607, Mica-Fe, and Mica-Mg, in an effort

109 to establish an estimate of the possible magnitude of stable isotope ratio variation in phases
110 potentially rich in Tl. These reference materials are intended to be used as matrix-matching RMs for
111 future investigations rather than be interpreted in isolation as indicative of natural Earth processes.
112 A minimum of three separate digestions, separations and measurements were performed for each
113 RM. With the exception of 14P, the reference materials were also analysed for high precision trace
114 element mass fractions, including thallium. We focus on reference materials useful for high
115 temperature applications. Table 2 provides background information on each selected material.

116

117 **EXPERIMENTAL PROCEDURE**

118

119 *Determination of Tl isotope ratios*

120

121 **Reagents:** All sample digestions and chemical separations were carried out in the MAGIC
122 Laboratories, Imperial College London. Purified water from a Milli-Q® (Merck) system (resistivity
123 18.2 MΩ cm) was used throughout. HNO₃ (concentrated, ~14 mol l⁻¹) and HCl (6 mol l⁻¹) were
124 purified once by sub-boiling distillation in quartz or PTFE stills, whilst ultrapure HF (47–51% ≈ 24
125 mol l⁻¹) was either purchased from SCP Scientific or prepared in the laboratory from reagent-grade
126 acid by a single distillation step in a PTFE still. Saturated bromine water was prepared by the
127 equilibration of high-purity bromine with purified water in a 125 ml PTFE bottle. Dilute HNO₃ and
128 HCl containing 1–3% v/v saturated bromine water were prepared by adding the appropriate volume
129 of bromine water to the acid immediately before use. A solution of 5–6 % w/w SO₂ in 0.1 mol l⁻¹
130 HCl ("0.1 mol l⁻¹ HCl–5% SO₂") was used for the reductive elution of Tl from anion-exchange
131 resin. This solution was prepared in a 250 ml PTFE bottle containing 100–200 ml 0.1 mol l⁻¹ HCl,
132 through which was bubbled gaseous SO₂ from a small pressurised cylinder containing liquefied SO₂
133 (purchased from Sigma Aldrich). The solution was reweighed at regular intervals until the required
134 amount of SO₂ had dissolved in the acid. After preparation, the reagent was stored for a maximum
135 of 1 week for reuse then discarded, as SO₂ oxidises to form sulphate. Finally, a 0.1 mol l⁻¹ HNO₃–

136 0.1% v/v H₂SO₄ solution used for sample dilution and subsequent mass spectrometric measurement
137 was made up using distilled-grade concentrated H₂SO₄ (96 % v/v).

138

139 **Sample digestion:** Between 25 mg and 350 mg of reference material powder was accurately
140 weighed into PFA vials (Savillex[®]), depending on the mass fraction of Tl in the RM. The majority
141 of digestions (exceptions detailed below) were performed on a tabletop hotplate (quoted
142 temperatures are the hotplate temperature setting, unless otherwise specified) at 140 °C for 1-3
143 days, in an initial mixture of 3 ml HF (24 mol l⁻¹) and ~0.3–0.5 ml HNO₃ (14 mol l⁻¹). Samples were
144 then evaporated to near (rather than total) dryness, to minimise formation of insoluble fluorides
145 (Croudace 1980, Yokoyama *et al.* 1999); taken up in ~1 ml of HNO₃ (14 mol l⁻¹); and evaporated to
146 dryness at 180 °C at least three times, to destroy any fluorides formed and to evaporate SiF₄.
147 Samples were redissolved and evaporated once from 4 ml HCl (6 mol l⁻¹) at 120 °C; redissolved in 2
148 ml HCl (6 mol l⁻¹) and refluxed at 120 °C for a minimum of 12 hours; and finally made up to a 12
149 ml HCl (1 mol l⁻¹) solution subsequently used to load into the first separation column. The final
150 loading solution of 12 ml HCl (1 mol l⁻¹) for column chromatography was refluxed at 140 °C for a
151 minimum of 12 hours. Sample solutions were cooled and 400 µl of saturated Br₂ water was added,
152 then left for a minimum of 3 hours to ensure complete oxidation of thallium to its Tl³⁺ state.

153

154 Some of the investigated RMs (COQ-1, G-2, GSP-2, ISH-G, MDO-G, STM-1) contain refractory
155 phases such as zircon that may not be completely digested using hotplate dissolution alone.
156 Although thallium is not expected to reside in phases such as zircon, we investigated the potential
157 role of refractory phases on Tl mass fraction and isotope ratio by performing bomb digestions. To
158 this end, approximately 50 mg of powder was accurately weighed into PFA hexagonal bomb vials
159 (Savillex[®]), to which was added ~0.2 ml HNO₃ (14 mol l⁻¹) and 1.5 ml HF (24 mol l⁻¹). The prepared
160 bombs were sealed tightly and placed in an oven at 150 °C for five days. Subsequent sample
161 processing was identical to that for hotplate digestions.

162

163 The massive magmatic sulphide 14P was digested on a hot plate at 130°C for a minimum of 12
164 hours in ~5 ml HNO₃ (3 mol l⁻¹), after the protocol of Nielsen *et al.* (2011). Samples of 14P were
165 then evaporated to near dryness at 155 °C and redissolved in 12 ml HCl (1 mol l⁻¹). The solution
166 was then centrifuged and detrital residue was discarded.

167

168 **Chromatographic separation of Tl:** Separation of the Tl fraction from sample matrices largely
169 follows the two-stage ion-exchange procedure devised by Rehkämper and Halliday (1999) and
170 refined by Nielsen *et al.* (2004) (Table 3). The separation technique utilizes the two oxidation states
171 of thallium. Oxidised Tl³⁺ adsorbs much more strongly to anion resins than Tl⁺ under a variety of
172 conditions, with a general decrease in distribution coefficients with increasing HCl concentration
173 (Kraus *et al.* 1954). Experimental work by Horne (1958) established that at a temperature of 25 °C
174 the distribution coefficient of Tl³⁺ on Dowex[®] 1-X8 from aqueous HCl solutions (10⁻³ to 2 mol l⁻¹)
175 has values of $D \geq 10^5$. Under identical conditions the distribution coefficient for Tl⁺ is much
176 smaller; the maximum value ($D = 10^3$) occurs for 1 mol l⁻¹ HCl, and decreases rapidly with small
177 variations in HCl concentration. Horne (1958) also observed that adsorption of Tl³⁺ onto Dowex[®] 1-
178 X8 from HBr media was too strong to be reliably measured. Thus the ion-exchange procedure
179 employs HCl (at concentrations ≤ 2 mol l⁻¹) and HNO₃ admixed with 1-3% v/v saturated bromine
180 water for sample loading and elution of major and trace elements, to ensure that all Tl remains
181 strongly adsorbed to the resin as Tl³⁺ complexed with chloride and trace bromide present in the
182 bromine solution.

183

184 Collection of the thallium fraction is accomplished using a solution of 0.1 mol l⁻¹ HCl–5% SO₂ (see
185 **Reagents**). This reduces Tl³⁺ to Tl⁺, whereby the latter can be readily eluted from the column.
186 Yields of >95% are routinely achieved (Nielsen *et al.* 2004, Rehkämper and Nielsen 2004), with no
187 isotopic fractionation of the separated Tl with respect to the original sample (Rehkämper *et al.*
188 2002, Nielsen *et al.* 2004).

189

190 Here the resin used is AG[®] 1-X8 (200–400 mesh) anion resin. The resin is cleaned prior to use in 4
191 mol l⁻¹ HNO₃ (3 times), 18 MΩ cm water (3 times), quartz-distilled 6 mol l⁻¹ HCl (once), and again
192 in 18 MΩ cm water (3 times); finally, the resin is stored in quartz-distilled HCl (0.1 mol l⁻¹).

193 Between each stage of cleaning the resin is left to stand for five days with intermittent shaking. A
194 fresh resin bed is prepared for each separation and a two-stage process is used (i) to ensure
195 complete elution of other ions and particularly of Pb, and (ii) to minimise the amount of sulphuric
196 acid present prior to measurement.

197

198 Table 3 outlines the two-step chromatographic procedure. Briefly, the first stage of separation
199 utilises quartz columns with an inner diameter 6 mm, fitted with quartz wool plugs for support of
200 the resin bed, which is filled with 1000 µl resin (wet volume). Once collected in acid cleaned PFA
201 vials, the Tl fraction is evaporated at 200 °C, which leaves <20 µl residual concentrated H₂SO₄,
202 formed via oxidation of SO₂ used during collection of Tl. The sample is then re-dissolved in a few
203 drops (~0.1 ml) of concentrated HCl (12 mol l⁻¹), and evaporated again at 200 °C to reduce the
204 amount of residual H₂SO₄. Subsequently, the Tl fraction is dissolved in 1.5 ml HCl (1 mol l⁻¹) and
205 refluxed for 12 hours at 140 °C. Once cooled, 60 µl of saturated Br₂ water is added to this solution;
206 the sample is then left for a minimum of 3 hours to ensure complete oxidation of all Tl ions to the
207 Tl³⁺ state.

208

209 The second stage of chromatographic separation is a scaled-down version of the first column, to
210 provide a final “clean-up” of matrix elements from the Tl fraction. Shrink-fit PFA columns fitted
211 with polypropylene frits are filled with 150 µl resin. Once collected, the Tl fraction is evaporated to
212 near dryness on a hotplate set at 200 °C, leaving <10 µl residual concentrated H₂SO₄. The residue is
213 taken up in a few drops (~0.1-0.3 ml) HNO₃ (14 mol l⁻¹) and evaporated to dryness at 200 °C three
214 times, in order to remove as much of the remaining sulphuric acid and chloride ions as possible.

215

216 **MC-ICP-MS isotope ratio measurements:** The use of PFA beakers and the high evaporation

217 temperature of H₂SO₄ means that it is not possible to remove all H₂SO₄ from the Tl fraction by
218 evaporation. Nielsen *et al.* (2004) demonstrated that analytical artefacts of up to 1 ε-unit can be
219 generated if H₂SO₄ is present in samples but not in bracketing standards. Therefore, all sample
220 residues were dissolved in 1 ml of 0.1 mol l⁻¹ HNO₃-0.1% v/v concentrated H₂SO₄ for isotopic
221 analysis. The mass bias-corrected ²⁰⁵Tl/²⁰³Tl ratio is essentially independent of the concentration of
222 H₂SO₄ up to 1% v/v (Nielsen *et al.* 2004). Reference solutions were prepared using the same batch
223 of 0.1 mol l⁻¹ HNO₃-0.1% v/v concentrated H₂SO₄ to minimise matrix mismatch between samples
224 and reference solutions. Isotopic ratio measurements were carried out using a Nu Instruments (HR)
225 MC-ICP-MS in low resolution mode at the MAGIC Laboratories, Imperial College London.
226 Sample introduction systems used over the course of this study include the Aridus, Aridus II and Nu
227 Instruments DSN (Desolvation Nebuliser System), coupled with either PTFE or glass nebulisers,
228 with measured uptake rates between 70 and 120 μl min⁻¹. Samples are run in a sequence using a
229 Cetac autosampler. Dedicated PFA autosampler vials are used for all reference and wash solutions.
230 Sample solutions are made up in 3 ml acid-cleaned PP autosampler vials.

231

232 Thallium has only two stable isotopes, precluding the possibility of isotopic spiking. Sample-
233 standard bracketing was therefore employed by interspersing unknown samples between analyses of
234 NIST SRM 997 (defined as $\epsilon^{205}\text{Tl}_{\text{SRM997}} = 0$) at the same mass fraction and with the same acid matrix
235 (i.e., a “matching standard”).

236

237 The ion beams at m/z 202 (Hg⁺), 203 (Tl⁺), 204 (Pb⁺ with possible Hg⁺ interference), 205 (Tl⁺), 206
238 (Pb⁺), 207 (Pb⁺) and 208 (Pb⁺) were monitored simultaneously with the Faraday collectors L2, L1,
239 Ax, H1, H2, H3 and H4, all fitted with 10¹¹ Ω resistors. Data collection was performed in three
240 blocks of 20 cycles with 5s integrations with the electrostatic energy analyser (ESA) deflected for a
241 15s electronic baseline at the beginning of each block.

242

243 An external means of monitoring and correcting for mass bias must be employed when measuring

244 an element with only two stable isotopes. In the case of thallium, samples and standards are doped
245 with NIST SRM 981 Pb. The certified $^{208}\text{Pb}/^{206}\text{Pb}$ isotope amount ratio is used to carry out on-line
246 correction for mass discrimination of the measured $^{205}\text{Tl}^+/^{203}\text{Tl}^+$ ratio during the measurement. The
247 Pb/Tl mass fraction ratio of samples and standards was between 3 and 4, and matched to within
248 15%, as variations in the Pb/Tl mass fraction ratio may cause real or apparent changes in the mass
249 bias response of Pb and Tl (Rehkämper and Mezger 2000). This methodology is analogous to the
250 use of Tl doping when performing Pb isotope ratio measurements via MC-ICP-MS (e.g. Rehkämper
251 and Mezger 2000, White *et al.* 2000). Typical instrument sensitivity was between 600 and 900V per
252 $\mu\text{g g}^{-1}$ of Pb or Tl. The repeatability of bracketing SRM 997 reference solutions degrades
253 significantly with $^{205}\text{Tl}^+$ beam intensities below 1V. Therefore, sample solutions were prepared with
254 typical Tl mass fractions of 3-5 ng g^{-1} and Pb mass fractions between 15-20 ng g^{-1} .

255

256 Machine performance is monitored by measurement of a Tl secondary standard solution obtained
257 from Aldrich and first characterised by Rehkämper and Halliday (1999) (“Aldrich Tl solution”),
258 which has subsequently been analysed repeatedly (>2000 times) in at least seven laboratories
259 worldwide (see compilation of Nielsen *et al.* 2017). A minimum of three measurements of the
260 Aldrich Tl solution were performed at the beginning and end of each measurement session, and
261 periodically throughout - typically every four to six unknown sample measurements. A well-
262 characterised USGS RM (typically BCR-2) was processed through the complete sample preparation
263 procedure with every batch of samples prepared for MC-ICP-MS analysis. Thallium mass fractions
264 and $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ values were compared against in-house and inter-laboratory long-term averages, to
265 assess trueness and long-term precision.

266

267 **MC-ICP-MS Tl mass fraction estimates:** Estimates of thallium mass fractions were acquired
268 during MC-ICP-MS measurements of Tl isotope ratios by comparison of ion beam intensities
269 between reference solutions of known mass fraction and unknown samples, assuming chemical
270 separation returns 100% thallium yields. In detail, the Tl mass fractions were estimated based on
271 measurements of Pb/Tl mass fraction ratios using the known absolute mass of NIST SRM 981 Pb

272 added to sample and reference solutions. However, these measurements are sensitive to small
273 variations in sample dilution, which may occur during sample preparation due to (i) small variations
274 between pipette tips and pipettes; (ii) differences in the volume consumed during initial
275 concentration checks of the diluted sample (for standard-matching purposes); (iii) variations how
276 long a sample is left to stand in the autosampler before a measurement is made (i.e. how much
277 evaporation occurs prior to measurement).

278

279 Materials such as the sulphide 14P cannot reasonably be analysed for trace elements on quadrupole
280 or sector field ICP-MS instruments dedicated to silicate analyses due to memory effects associated
281 with very high iron and sulphur mass fractions. It is also difficult to calibrate and matrix-match this
282 type of material. This is not, however, a concern when measuring a purified Tl fraction via MC-
283 ICP-MS. Thus, the Tl mass fraction of 14P is reported based on the estimations made during MC-
284 ICP-MS isotopic ratio measurement, with correspondingly higher uncertainty. Overall, the trueness
285 of such Tl mass fraction estimates have been improved from ~25% (Rehkämper *et al.* 2002,
286 Rehkämper and Nielsen 2004) to ~5-10% (e.g. Prytulak *et al.* 2013, Shu *et al.* 2017) provided care
287 is taken during sample handling. However, ICP-MS analysis with well-characterised calibrating
288 standards and/or standard addition techniques returns the least biased and most precise Tl mass
289 fraction data.

290

291 *Determination of Tl mass fraction by ICP-MS/MS ('ICP-QQQ-MS' or 'triple quad')*

292

293 Reference material digestions were undertaken in the MAGIC Laboratories at Imperial College
294 London, using the same reagents employed for isotope analyses.

295

296 **Method:** Approximately 50 mg of each RM was weighed accurately into PFA vials, to which a 3:1
297 mixture of HF (24 mol l⁻¹):HNO₃ (14 mol l⁻¹) was added. The solutions were ultrasonicated for 20
298 minutes after initial addition of the acids, then placed on a hotplate at 160 °C for at least 24 hours.
299 Sample solutions were further ultrasonicated for 20 minutes twice during the initial digestion.

300 Solutions were then evaporated to near dryness, redissolved in 2 ml of HCl (6 mol l⁻¹), and refluxed
301 at 120 °C for at least 24 hours. The solutions were next evaporated to complete dryness at 120 °C,
302 redissolved in 1 ml of HNO₃ (14 mol l⁻¹), and then evaporated at 180 °C. The last step was repeated
303 a minimum of three times, or until the colour of the residue changed from white to brown, which
304 indicates that fluorides formed from the initial HF digestion have been destroyed. Samples were
305 then transported to the Open University as HNO₃ (14 mol l⁻¹) solutions, and transferred into acid-
306 cleaned PP bottles, where an appropriate amount of purified H₂O was added to each to achieve a
307 1000-fold dilution of the original sample mass in an HNO₃ matrix (0.14 mol l⁻¹).

308

309 **ICP-QQQ-MS measurement:** Trace element mass fraction determinations including thallium were
310 undertaken at the Open University, UK, with an Agilent 8800 ICP-QQQ-MS inductively-coupled
311 plasma mass spectrometer. Sample solutions were aspirated using a quartz microflow nebuliser with
312 an uptake rate of 0.5ml min⁻¹. Machine sensitivity was on the order of 1 – 5 x 10⁷ cps per µg ml⁻¹,
313 depending on the element. The Agilent 8800 has a collision/reaction cell (Octopole Reaction
314 System, ORS), which separates two quadrupoles. The first quadrupole is used as a mass filter to
315 ensure that only specific masses enter the ORS; reactions can therefore be targeted to remove on-
316 mass interferences. The second quadrupole can be used in either mass-shift or on-mass mode,
317 depending on if the analyte or interference reacts with the gas. We employ two collision/reaction
318 gas configurations to undertake measurements: no gas in the collision cell or O₂ gas in the cell.
319 Thallium was analysed in the ‘no gas’ mode, with oxide levels (measured as CeO⁺/Ce⁺) kept below
320 1% and double charged species (Ce²⁺/Ce⁺) at 1.6%. All other elements were similarly measured
321 except for most rare earth elements (La, Pr, Ce, Nd, Sm, Gd, Ho, Tb, Dy, Er, Yb, Lu), which were
322 reacted with O₂ gas for a mass shift measurement.

323

324 **Selection and assessment of calibrating standards:** Calibrating standards were run at the
325 beginning of each measurement session. Additionally, an internal solution standard consisting of
326 Be, Rh, In, Tm, Re, and Bi was added online to all standard and unknown solutions to monitor and
327 correct instrumental drift. Drift was further monitored every five unknown measurements with a

328 measurement block consisting of BIR-1 (a separate digestion to that used in the initial calibration
329 block), HNO₃ (0.3 mol l⁻¹), and a repeated unknown sample.

330

331 The USGS reference materials BIR-1, BHVO-2 and AGV-1 were chosen as calibrators for trace
332 element determination of Tl in particular. In addition, RMs W-2 and DNC-1 are used for
333 calibration: for most trace elements (not including Tl) these are well-characterised materials. BIR-1,
334 BHVO-2 and AGV-1 were selected because they are commonly used for analysis of other isotopic
335 systems, i.e. they are well-characterised, and span three orders of magnitude of Tl mass fraction.
336 Only AGV-1 has a USGS listed Tl mass fraction (0.34 µg g⁻¹, recommended value; no uncertainty
337 given). All three RMs have preferred GeoReM (Jochum *et al.* 2005) Tl mass fraction values, per
338 Jochum *et al.* (2016): BIR-1, 2.1 ± 0.7 ng g⁻¹ (n = 13); BHVO-2, 22.4 ± 1.5 ng g⁻¹ (n = 28); AGV-1,
339 337 ± 31 ng g⁻¹ (n = 10) (95% confidence intervals). Specifically, we use Tl mass fractions of: BIR-
340 1, 1.6 ng g⁻¹ (n = 12); BHVO-2, 22 ng g⁻¹ (n = 32); and AGV-1, 349 ng g⁻¹ (n = 13), determined
341 using our own compilation of reported mass fraction data (Appendix 1). All values are within error
342 of the GeoReM recommended values.

343

344 We note that both AGV-1 and BHVO-2 exhibit heterogeneity seen in Pb isotope ratio and mass
345 fraction results, which have been provisionally attributed to contamination during processing using
346 steel mortar and pestle (Weis *et al.* 2006). It has long been suggested that the similarity between
347 properties of Tl and Pb might result in similar behaviours in some geochemical contexts (Lamy
348 1862), but as Tl has historically not been routinely analysed it is not clear whether Tl systematics in
349 these RMs correlate with Pb heterogeneity. We therefore use our compilation of reported Tl mass
350 fractions in these RMs (Appendix 1) to identify and characterise potential Tl heterogeneity in our
351 calibrators.

352

353 We find no identifiable heterogeneity for AGV-1 (n = 13, RSD = 15%). Reported BIR-1 Tl mass
354 fraction results have a notably high RSD (34%); however, this material has a very low Tl mass

355 fraction and is therefore analytically challenging. Consequently, determining whether the high
356 uncertainty reflects powder inhomogeneity or analytical error is not straightforward, and BIR-1
357 remains the best-characterised candidate for a low mass fraction Tl calibrator. For BHVO-2 there is
358 some variation in reported Tl mass fraction between studies: of the 36 reported measurement results
359 (mean mass fraction value of 28 ng g⁻¹; RSD = 58%), a small minority (n = 4) have a mean of 65 ng
360 g⁻¹ (RSD = 7%). The remaining measurement results give a mean of 22 ng g⁻¹ (RSD = 20%). For
361 comparison, BHVO-1 has a reported Tl mass fraction of 46 ng g⁻¹ (RSD = 19%, n = 25). The four
362 anomalous reports of Tl mass fraction in BHVO-2 (Bouman *et al.* 2004, Deegan *et al.* 2012, Deng
363 *et al.* 2013 and Søger *et al.* 2015) are suggestive of either confusion between the two generations
364 of the BHVO RM, or of possible contamination.

365

366 For many trace elements, BHVO-1 and BHVO-2 have USGS listed mass fraction values that are
367 within error of one another. Elements for which this is not true, where analysed, can be used to
368 positively identify instances of confusion between the two generations. For the majority of these
369 elements (notably Sc, Cr, Cu, Zn, Y, Zr and Hf as well as Tl) the mass fractions reported by
370 Bouman *et al.* (2004) as BHVO-2 are highly consistent with listed values for BHVO-1, and
371 disagree with listed values for BHVO-2; the reported Tl mass fraction is 59 ng g⁻¹. Only USGS
372 listed BHVO-2 values are quoted as reference mass fractions for trace element analyses, and these
373 do not include a Tl mass fraction; however, the same paper employs BHVO-1 as a Li isotope RM,
374 suggesting a source of possible confusion. Similar is true for the trace element mass fractions
375 reported by Deng *et al.* (2013), and in this case it appears that the quoted reference Tl mass fraction
376 is *not* for BHVO-2, but instead that given for BHVO-1 by Govarindju (1994). Deng *et al.* (2013)
377 report a Tl mass fraction of 66 ng g⁻¹ for BHVO-2.

378

379 For the two remaining anomalous reports of Tl mass fraction, the trace element pattern is less
380 suggestive of confusion between generations of this reference material. Trace element mass
381 fractions reported by Deegan *et al.* (2012) are on average 10% higher than USGS listed values (2%-
382 20% higher), with the exception of Ta, which is in agreement with the listed value. Two Tl mass

383 fractions are reported for BHVO-2, of 60 ng g⁻¹ and 80 ng g⁻¹. Søger *et al.* (2015) used reference
384 values provided by the Hamburg laboratory that performed sample analysis (pers. comm., 2017),
385 and report a Tl mass fraction for BHVO-2 of 63 ng g⁻¹. These Tl mass fractions are anomalously
386 high for BHVO-2, but are consistent with the listed and compiled values for BHVO-1; however,
387 there is no compelling indication that in these cases confusion between the two generations of
388 powder occurred. These results therefore appear to be best explained by some combination of
389 analytical uncertainty and powder contamination.

390

391 The available data therefore suggest that if BHVO-2 suffers from inhomogeneity with respect to Tl
392 mass fractions, it is not a widespread or common problem. Furthermore, there are very few
393 generally-available igneous standard RMs with low Tl mass fractions. BIR-1, with a Tl mass
394 fraction an order of magnitude lower than BHVO-2, is employed as a calibrator in this study, but as
395 noted presents analytical challenges. The Geological Society of Japan provides three basalt RMs,
396 but all have higher Tl mass fractions than BHVO-2: JB-2 has the lowest Tl mass fraction, reported
397 as 34 ± 3.6 ng g⁻¹ (Jochum *et al.* 2016). As such, BHVO-2 is the best widely-available, well-
398 characterised choice for a low-Tl calibrating standard.

399

400 Trace element mass fractions were generally determined with the chosen geological calibrating
401 standards (AGV-1, BHVO-2, BIR-1). However, partially-separated mineral standards have unusual
402 and, in some cases, extreme trace element mass fractions. For example, a Tl mass fraction of 16 µg
403 g⁻¹ was reported for the biotite Mica-Fe (Table 4), well outside the Tl mass fraction range of the
404 calibrators. Linear extrapolation of the calibration curve is a potential source of error for the
405 reported mass fractions of such high-Tl RMs. Two approaches that are potentially suited to address
406 this concern are (i) isotope dilution ICP-MS (ID-ICP-MS), and (ii) the use of synthetic calibrating
407 reference solutions with known, high Tl mass fractions. The ID-ICP-MS technique was not deemed
408 appropriate, due to the lengthy preparation times required and the possible powder heterogeneity of
409 at least some samples. In other words, obtaining highly accurate trace element mass fraction data
410 for a single dissolution of a potentially heterogeneous material is deemed to be of limited utility. In

411 contrast, the use of synthetic calibrating standards requires significantly less preparation time.
412 However, it is known that the sample matrix can affect the ionisation potential of elements during
413 analysis and, consequently, mass fraction measurement results (e.g. Brown and Milton 2005). To
414 the best of our knowledge it has not previously been established whether using synthetic calibrators
415 results in any systematic effect on measured Tl mass fractions. Therefore, for one analytical session
416 a pure internal trace element reference solution (made from single element plasma grade standards
417 (Alfa Aesar)) was employed as a synthetic calibrating reference solution to assess whether this
418 procedure produced Tl mass fraction data that differed significantly from those obtained with
419 geological calibrators.

420

421 RESULTS AND DISCUSSION

422

423

424 *Determination of Tl mass fraction*

425

426 **Mass fraction measurements by ICP-QQQ-MS:** Table 4 presents the thallium mass fractions
427 determined for RMs in this study, whilst Appendix 2 gives trace element results. Typical precisions
428 reported for Tl in the literature are on the order of 5-15% RSD, compared with <5% RSD for
429 commonly-analysed trace elements. Precision is normally deemed excellent if RSDs are <3% or
430 good if 3-7%.

431

432 RSDs for Tl mass fraction measurement results obtained during this study using ICP-QQQ-MS with
433 geological calibrating standards are calculated as follows. (i) Where the number of measurements n
434 > 4 , the RSD is calculated using the mean and standard deviation of those n analyses. (ii) Where $n =$
435 1 , the reported RSD is based on the within-run standard deviation of the five ICP-QQQ-MS mass
436 scans that comprise each individual analysis. (iii) For $1 < n < 5$, RSDs calculated using method (i)
437 are compared with the within-run standard deviation for each of the n analyses, and the worse of the

438 two precisions is reported.

439

440 With the exception of three RMs (AL-I, AN-G and BIR-1), RSDs for Tl mass fraction measurement
441 results obtained during this study using ICP-QQQ-MS with geological calibrating standards are
442 <7%, and all RSDs except that for BIR-1 are <10% (Appendix 2). We note that RM AN-G has a
443 low Tl mass fraction (10 ng g^{-1} , RSD = 8.1%), making precise measurements technically
444 challenging. Similarly, BIR-1 has a very low Tl mass fraction (1 ng g^{-1}); even for this material, an
445 RSD ($n = 18$) of 21% is achieved. Multiple dissolutions were analysed for trace element mass
446 fractions using ICP-QQQ-MS for BCR-2 (multiple hotplate digestions), BHVO-2 (multiple hotplate
447 digestions measured as unknowns, in addition to the calibrator solution), and GSP-2 (hotplate and
448 bomb digestions). Notably, the hotplate versus bomb dissolution of GSP-2 showed no resolvable
449 variation of Tl mass fraction with digestion method (RSD = 4.5%), suggesting, as expected, that Tl
450 is not hosted in refractory phases present in this material (Appendix 2).

451

452 Analyses employing synthetic calibration reference solutions produced measured Tl mass fractions
453 that are $10 \pm 3\%$ (1s) lower than the exact same sample solutions measured relative to geological
454 reference materials (Figure 1) for all samples except AN-G. This suggests that the presence of a
455 geological matrix alters the ionisation potential of Tl relative to synthetic trace-element reference
456 solutions. Indeed, the $10 \pm 3\%$ (1s) offset in mass fractions observed is apparent even for those
457 materials that fall within the Tl mass fraction range of the geological calibrators employed.
458 Therefore, despite the fact that using geological RMs is a more time-consuming process and that
459 linear extrapolation must be employed with caution, we recommend using geological rather than
460 synthetic calibrators to avoid under-reporting of Tl mass fractions.

461

462 **Mass fraction measurements by MC-ICP-MS:** Mass fraction measurements made during isotope
463 ratio analysis via MC-ICP-MS are indistinguishable from ICP-QQQ-MS results, but show
464 substantial variance (Figure 2) with RSDs (calculated for each material as the RSD of the individual

465 mass fraction measurement results) ranging from about 2% to 54%. For ten of the RMs measured
466 the RSD is <20%, whilst five have >30% RSDs of the mean. This suggests that mass fraction
467 measurements made during MC-ICP-MS isotopic analyses may be suitable for assessing sample
468 heterogeneity. Importantly, there was no resolvable variation of Tl mass fraction with digestion
469 method: for materials analysed following both hotplate and bomb digestion, Tl mass fraction RSDs
470 are <15% (see also Figure 3). This strongly suggests that Tl is not hosted in refractory phases
471 present in these RMs.

472

473 **Comparison with literature data:** Jochum *et al.* (2016) provide GeoReM preferred values for the
474 19 most frequently queried RMs, including AGV-2, BCR-2, BHVO-2 and G-2. Additional
475 literature reports of Tl mass fraction exist for Mica-Fe, BCR-2, GSP-2, G-2, STM-1, and UB-N.
476 These values are reported in Table 4 alongside the mass fraction results obtained over the course of
477 this study. Only the mass fractions determined for GSP-2 and STM-1 differ significantly from
478 published values.

479

480 For AL-I, AN-G, and Mica-Mg only proposed values are available, from the compilation of
481 Govindaraju (1995). No Tl mass fraction estimates are available for COQ-1, trachytes ISH-G and
482 MDO-G, or K-feldspars FK-N and NIST SRM 607. To the best of our knowledge, we provide the
483 first reported values for these reference materials.

484

485 Good agreement between literature reports of Tl mass fractions in these materials and our results,
486 particularly for well-characterised RMs, provide reassurance that the BHVO-2 digestions used as
487 calibrator did not exhibit anomalously high Tl mass fractions. We are confident that the mass
488 fraction data presented are robust.

489

491

492 **Blanks and Reference Solutions:** Due to the low mass fraction of Tl (typically 10s ng g⁻¹) in many
493 rock samples (Table 4), it is necessary that Tl mass fractions of total procedural blanks are below
494 the detection limit of the MC-ICP-MS. This equates to a maximum of 2 pg Tl, where the smallest
495 amount of sample Tl processed was approximately 2.5 ng (for AN-G). The total procedural Tl blank
496 for each batch of samples was determined by dissolving the total procedural blank in 1ml of
497 analysis solution (0.1 mol l⁻¹ HNO₃–0.1% H₂SO₄) and monitoring the intensity of the m/z 205 ion
498 beam. In all cases there was no deviation of the signal from the wash background, indicative of a
499 maximum blank of <1 pg.

500

501 Residual Pb can produce significant errors in the measured ²⁰⁸Pb/²⁰⁶Pb isotope ratio used for
502 correction of mass bias. Thus, any Pb present in the sample solution prior to addition of SRM 981,
503 whether residual from the sample matrix or introduced via contamination, has the potential to affect
504 the precision and repeatability of ε²⁰⁵Tl_{SRM997} measurements. Therefore, to ensure accuracy of
505 measured ε²⁰⁵Tl_{SRM997}, residual Pb mass fractions of below 0.01 ng g⁻¹ were required for every
506 sample solution and for the total procedural blank, as determined from the observed m/z 208 ion
507 beam signal prior to SRM 981 addition. Typical residual Pb mass fractions were approximately
508 equivalent to 1 pg g⁻¹.

509

510 Over the course of this study, over 200 measurement results of the Aldrich Tl solution yield a mean
511 ε²⁰⁵Tl_{SRM997} value of -0.8 ± 0.3 (2s, n = 211; Figure 4), in excellent agreement with the most recent
512 compilation of data from seven laboratories worldwide (Nielsen *et al.* 2017) in which the value is
513 given as ε²⁰⁵Tl_{SRM997} = -0.79 ± 0.35 (2s, n = 187). Due to the large number of analyses, our
514 intermediate precision (2s) is calculated using the average ε²⁰⁵Tl_{SRM997} values obtained for the
515 Aldrich Tl solution during each analytical session.

516

517 **Data quality:** Results for the Tl isotope ratio measurements are given in Table 5. As a minimum of
518 3 isotope ratio measurements were made for each RM, the reported intermediate precision (2s) is
519 based on at least three measurement results obtained following independent sample preparation. For
520 comparison, the typical external reproducibility for multiple digestions performed in multiple
521 institutions of $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ for geological samples is ± 0.5 ϵ -units (see compilation in Nielsen *et al.*
522 2017).

523
524 Literature reports of $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ exist for AGV-2, BCR-2, BHVO-2 and G-2 (Table 1). Of these,
525 BCR-2 has the most widely-reported $\epsilon^{205}\text{Tl}_{\text{SRM997}}$, and can be considered isotopically homogeneous
526 with respect to Tl isotope ratio. The values we obtain for BCR-2 and BHVO-2 are in excellent
527 accord with Prytulak *et al.* (2013, 2017) and Coggon *et al.* (2014), and are indistinguishable from
528 values obtained by Baker *et al.* (2009).

529
530 However, the value we obtain for G-2 is in disagreement with the single previously reported value
531 (Rehkämper and Halliday 1999), in spite of large variance for both measurements. The low
532 precisions and difference in isotope ratio measurement results most likely arise from (i) G-2
533 exhibiting powder heterogeneity in terms of Tl (see subsequent discussion), (ii) analysis of different
534 bottles of G-2, and (c) difficulties with development of the techniques for isotopic analysis of Tl.

535
536 We are therefore confident that the measurement procedure employed has not introduced any
537 systematic bias, and that our $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ values and precisions for previously uncharacterised RMs
538 provide a range where the true value is likely to be. Together with mass fraction measurement
539 results obtained via MC-ICP-MS on the same dissolution, these Tl isotope ratio results are
540 displayed in Figure 3, as mean values for each individual dissolution. There is no correlation of
541 precision with digestion batch or analytical sessions, implying that the better precisions (2s = 0.4-
542 0.6 ϵ -units) are representative of the precision achievable with this analytic approach, whilst the
543 higher measurement results with lower precision (up to 2 ϵ -units) are unlikely to be a consequence
544 of our laboratory techniques or poor measurement precision.

545

546 **Evaluation of reference material heterogeneity:** Despite the demonstrated ability of the analytical
547 techniques to achieve excellent precision, the variances for some samples are surprisingly high,
548 suggesting possible isotopic heterogeneity in the RM powders. Reference materials must be
549 homogeneous in the element system of interest if they are to be used for method development,
550 validation, or interlaboratory comparisons (BIPM et al. 2012). Homogeneity is routinely tested for
551 major elements and some trace elements during RM preparation but heterogeneity for other
552 elements and for isotope systems has been identified in a number of these materials (e.g. BHVO-2:
553 Baker *et al.* 2004, Weis *et al.* 2006, Chauvel *et al.* 2011; SRM 607: Nebel and Mezger 2006).
554 Furthermore, the statistical nature of observed heterogeneity can provide information on the
555 dispersal of an enriched phase or phases through a material. For example, Chauvel *et al.* (2011)
556 discuss the possibility that relatively large, rare Pb-rich microparticles are responsible for the
557 distinctive bimodal distribution of Pb mass fractions in BHVO-2. However, we are not aware of any
558 general assessment of Tl heterogeneity in igneous RMs.

559

560 As Tl⁺ readily substitutes for K⁺ in igneous minerals, it is expected that, if present, K-rich phases
561 will dominate the Tl budget of a rock. Indeed, as shown in Figure 5 for silicate rocks Tl mass
562 fraction correlates with K₂O. Figure 3 presents mean $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ and mass fraction values obtained
563 using MC-ICP-MS for each RM and for each individual dissolution, to aid qualitative assessment of
564 any Tl heterogeneities. There are no resolvable differences in either Tl mass fractions or isotope
565 ratios between bomb and hotplate digestions for the RMs studied, providing evidence that Tl is not
566 hosted in refractory phases. Thus small variations in the proportions of K-rich phases in the powder
567 portion sampled could significantly affect both the mass fraction and isotope ratio of Tl.

568

569 Having performed a minimum of three digestions for isotope ratio measurement of each RM
570 included in this study, we are able to assess whether these materials are heterogeneous for Tl.
571 Examination of the dataset (Figure 3) reveals heterogeneity of mass fraction with weak or no
572 isotope ratio heterogeneity for COQ-1, STM-1, AN-G and Mica-Mg, marked heterogeneity of both
573 isotope ratio and mass fraction for G-2, and possible weak isotope ratio heterogeneity for BHVO-2.

574 AN-G consists primarily of anorthosite (An_{80} - An_{85}), with hornblende (10-15 % v/v), relict
575 clinopyroxene, and some secondary minerals (Govindaraju 1980). In this rock hornblendes are
576 likely the major host of K and therefore of Tl; if the hornblendes have identical Tl isotope ratios to
577 the rest of the bulk sample, it follows that Tl isotope ratios will be unaffected by modal proportion
578 of hornblende in any individual dissolution, but the Tl mass fraction will be strongly dependent on
579 the amount of hornblende incorporated into the digested portion. STM-1 contains multiple K-
580 bearing phases including alkali feldspar, nepheline and biotite (Snively *et al.* 1976), and features a
581 bulk Tl mass fraction two orders of magnitude higher than AN-G. On the basis of three dissolutions,
582 STM-1 appears to exhibit a bimodal distribution for Tl: two distinct mass fraction populations, with
583 the higher mass fraction possibly weakly associated with an isotopically lighter $\epsilon^{205}\text{Tl}_{\text{SRM997}}$
584 signature. This may reflect the existence of at least two distinct hosts of Tl, variably incorporated
585 into the sample portion. In contrast, across four dissolutions Mica-Mg appears to display a range in
586 both Tl mass fraction and $\epsilon^{205}\text{Tl}_{\text{SRM997}}$, with no clear systematics; this is consistent with relatively
587 small, frequent microparticles of several Tl-rich and isotopically distinct phases unevenly dispersed
588 throughout the powdered RM.

589

590 G-2 appears to exhibit significant heterogeneities in Tl mass fraction and isotope ratio. As with
591 STM-1, these heterogeneities appear to be weakly coupled. G-2 is a micaceous granite, known to
592 contain microcline, biotite and muscovite (Fairbairn *et al.* 1951, Chayes and Suzuki 1963, Flanagan
593 1969). These K-rich phases are likely to be the major hosts of Tl in G-2; given the difficulty of
594 ensuring even crushing and even distribution of sheet silicates, it is plausible that small variations in
595 the amount of each phase sampled in any given digestion could account for the coupled
596 heterogeneity seen here.

597

598 Petrographic information is not available for BHVO-2, but as a basalt, it is unlikely to contain
599 significant amounts of K-rich phases. We do not observe any evidence for the significant Tl mass
600 fraction variations reported in the literature (Appendix 1), but do see potential evidence of weak Tl
601 isotope ratio heterogeneity.

602

603 Constraints on the scale of isotope ratio heterogeneities are provided by a comparison of dissolved
604 mass versus the 2s precision of the measurement result of $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ (Figure 6). For samples with
605 higher (known or predicted) Tl mass fractions, smaller masses were digested to yield similar
606 amounts of Tl for measurement. However, it is precisely the samples with high Tl contents and low
607 digested mass that, in general, display the largest variance in the isotope ratio measurements. For
608 most RMs included in this study it appears that weighing out at minimum 100mg of powder might
609 mitigate the effects of small-scale heterogeneity and enable routinely achievable $\epsilon^{205}\text{Tl}_{\text{SRM997}}$
610 measurements with 2s precisions on the order of 0.5 ϵ -units.

611

612 However, it is unlikely that dissolving larger initial masses would improve the precisions achievable
613 for G-2 and BHVO-2; G-2 in particular exhibits a high variance given initial dissolved masses,
614 suggesting that the discrepancy with the one previous report (Rehkämper and Halliday 1999) arises
615 in large part from powder heterogeneity. Rehkämper and Halliday (1999) are known to have made
616 their analysis using a different vial of G-2, potentially indicating heterogeneity between vials. We
617 therefore recommend against use of G-2 as a Tl reference material. For BHVO-2 the variance for
618 $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ is less extreme and, unlike G-2, there is no strong evidence for heterogeneity in Tl mass
619 fraction. We therefore recommend caution when employing BHVO-2 as a Tl isotope reference
620 material, but as it is the only basaltic RM with a Tl mass fraction of $\sim 20 \text{ ng g}^{-1}$, we recognise that it
621 is likely the most appropriate choice for studies involving low-Tl igneous samples. As BHVO-1 and
622 BHVO-2 are distinctly different in terms of both mass fraction and isotope ratio values (Appendix
623 1, Table 1), care must be taken to ensure that these materials are not confused if using either as a
624 reference material.

625

626 In light of concerns regarding potential inhomogeneous contamination during the generation of
627 RMs, we find no evidence that the overall reported range in $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ for the RMs analysed here
628 (5.5 ϵ -units, comparable to that of other natural igneous products: see Nielsen *et al.* 2017) is due to

629 contamination of the samples. In particular, there is no systematic variation of Tl isotope
630 composition with RM provider or date of preparation. Furthermore, the most isotopically distinct
631 result (serpentinite UB-N: $\epsilon^{205}\text{Tl}_{\text{SRM997}} = +1.8 \pm 0.4$ ‰) is consistent with the findings of Nielsen *et*
632 *al.* (2015). To the best of our knowledge these authors provide the only literature report of
633 $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ in natural serpentinite samples, and these show similarly heavy Tl isotope compositions,
634 providing indirect validation of our isotopically heavy serpentinite RM.

635

636 SUMMARY

637

638 Thallium mass fraction and isotope ratio measurements were performed for a comprehensive suite
639 of sixteen geological reference materials, including both bulk rock and partially-separated mineral
640 powders. We provide the first reported Tl mass fraction and $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ (i.e. $\delta^{205}\text{Tl}_{\text{SRM997}}$ in parts per
641 ten thousand) measurement results for geochemical reference materials 14P, Albite AL-I,
642 Anorthosite AN-G, Carbonatite COQ-1, Potash Feldspar FK-N, Trachyte ISH-G, Trachyte MDO-
643 G, and Phlogopite Mica-Mg; and additionally provide the first reported $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ values for
644 Biotite Mica-Fe and Serpentinite UB-N.

645

646 Of the 16 reference materials included, all but G-2 are in principle appropriate for use as Tl isotopic
647 reference materials, provided sufficiently large test portion sizes (minimum 100mg) are chosen for
648 digestion. The $\epsilon^{205}\text{Tl}_{\text{SRM997}}$ represented spans from -3.5 to +1.8, comparable to the range thus far
649 reported in global igneous rocks (e.g. Nielsen *et al.* 2017).

650

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1110 FIGURES

1111

1112 **Figure 1.** Comparison of Tl mass fractions obtained when using geological versus synthetic
1113 calibrators (see text for details). Both sets of measurements were performed using the same ICP-
1114 QQQ-MS instrument (Open University) and on the same solutions. Error bars are smaller than
1115 symbols in most cases.

1116

1117 **Figure 2.** Comparison of Tl mass fractions obtained during MC-ICP-MS isotope analysis and those
1118 determined by ICP-QQQ-MS (using geological reference materials as calibrators). Some error bars
1119 are smaller than symbols.

1120

1121 **Figure 3.** Tl isotope ratios (as $\epsilon^{205}\text{Tl}_{\text{SRM997}}$; error bars: 2s) and Tl mass fractions (error bars indicate a
1122 conservative RSD of 20%) of RMs determined by MC-ICP-MS for (a) whole rock and (b) partially
1123 separated mineral reference materials. Shown are data for each individual digestion and the mean
1124 values for each RM. Thallium mass fraction data obtained via MC-ICP-MS simultaneously with
1125 isotope ratio measurement is used to aid qualitative assessment of material heterogeneity.

1126

1127 **Figure 4.** Tl isotope ratios (as $\epsilon^{205}\text{Tl}_{\text{SRM997}}$) determined for the Aldrich Tl solution, relative to NIST
1128 SRM 997, over the course of 18 analytical sessions. The number of measurements made during
1129 each session is shown in brackets, and the error bars indicate the precision (2s) calculated from
1130 those measurements for each analytical session. The overall long-term intermediate precision of
1131 session averages (2s) is displayed as a grey band.

1132

1133 **Figure 5.** Variation of Tl mass fraction with K_2O mass fraction for all materials except sulphide
1134 14P. Error bars are smaller than symbols. All K_2O data is as listed by the material's supplier. Tl
1135 mass fractions were determined by ICP-QQQ-MS at the Open University.

1136

1137 **Figure 6.** Assessment of relationship between test portion size of dissolved sample and isotope ratio
1138 variance ($2s$). For the digested sample mass, the plotted point represents the mean mass weighted by
1139 the number of measurements made per dissolution; error bars represent the full range of masses
1140 digested for each sample. Points are coloured according to Tl mass fraction as determined by ICP-
1141 QQQ-MS.

1142

Table 1: Literature MC-ICP-MS TI isotope ratio data for igneous reference materials

Reference Material	$\epsilon^{205}\text{Tl}$	2s	# dissolutions	# measurements	Reference
AGV-2	-1.9	0.5	1	1	Baker <i>et al.</i> (2009)
AGV-2	-3	0.6	8	15	Prytulak <i>et al.</i> (2013)
AGV-2	-2.7	0.2	5	9	Prytulak <i>et al.</i> (2017)
BCR-2	-2.5	0.4	4	19	Prytulak <i>et al.</i> (2013)
BCR-2	-2.5	0.5	12	25	Prytulak <i>et al.</i> (2017)
BIR-1	1.1	1.2	6	9	Nielsen <i>et al.</i> (2007)
BHVO-1	-3.5	0.5	10		Nielsen <i>et al.</i> (2015)
BHVO-1	-3.6	0.4		16	Shu <i>et al.</i> (2017)
BHVO-2	-2.1	0.5	2	2	Baker <i>et al.</i> (2009)
BHVO-2	-1.5	0.4	2	2	Prytulak <i>et al.</i> (2013)
BHVO-2	-1.5	0.3	10	n.g.	Coggon <i>et al.</i> (2014)
G-2	1.3	0.7	1	1	Rehkämper and Halliday (1999)

dissolutions: number of independent digestions

measurements: number of measurement results

Table 2: Reference materials investigated in this study

Reference Material	Supplier ^a	Lithology	Key reference	reported TI mass fraction	reported $\epsilon^{205}\text{TI}$
14P	OREAS	massive magmatic sulphide	-		
AL-I	SARM-CRPG/CNRS	albite	Govindaraju (1984a)		
AN-G	SARM-CRPG/CNRS	anorthosite	Govindaraju (1980)		
BCR-2	USGS	basalt	Wilson (1997a)	x	x
BHVO-2	USGS	basalt	Wilson (1997b)	x	x
COQ-1	USGS	carbonatite	-		
FK-N	SARM-CRPG/CNRS	alkali feldspar	Govindaraju (1984b)		
G-2 ^b	USGS	granite	Fairbairn <i>et al.</i> (1951)	x	x
GSP-2	USGS	granodiorite	Wilson (1998)	x	
ISH-G	SARM-CRPG/CNRS	trachyte	Gillot <i>et al.</i> (1992)	x	
MDO-G	SARM-CRPG/CNRS	trachyte	Gillot <i>et al.</i> (1992)		
Mica-Fe	SARM-CRPG/CNRS	biotite	Govindaraju (1979)	x	
Mica-Mg	SARM-CRPG/CNRS	phlogopite	Govindaraju (1979)		
SRM 607	NIST	alkali feldspar	Heinrich (1960)		
STM-1 ^b	USGS	nepheline syenite	Snavelly <i>et al.</i> (1976)	x	
UB-N	SARM-CRPG/CNRS	serpentinite	Govindaraju (1982)		

^a OREAS: Ore Research & Exploration Assay Standards (Australia); SARM-CRPG/CNRS: Service d'Analyse des Roches et des Minéraux - Centre de Recherches Pétrographiques et Géochimiques/Centre National de la Recherche Scientifique (France); USGS: United States Geological Survey.

^b No longer available for purchase.

Table 3: Anion exchange separation of Tl (adapted from Nielsen *et al.* 2004)

Step	Eluent	Volume (ml)	
		Stage I	Stage II
load resin	AG® 1-X8 (200–400 mesh) in 0.1 mol l ⁻¹ HCl	1	0.15
condition	0.1 mol l ⁻¹ HCl – 5% w/w SO ₂	1 + 10	0.1 + 1.5
condition	0.1 mol l ⁻¹ HCl	1 + 10	0.1 + 1.5
condition	1 mol l ⁻¹ HCl – 1 % v/v Br ₂	1 + 3 + 1	0.1 + 0.3 + 0.3 + 0.3
load sample	1 mol l ⁻¹ HCl – 3 % v/v Br ₂	-	-
elution (matrix)	0.5 mol l ⁻¹ HNO ₃ – 3% v/v Br ₂	1 + 1 + 1 + 5 + 10	0.1 + 0.1 + 0.1 + 1.5
elution (matrix)	2 mol l ⁻¹ HNO ₃ – 3% v/v Br ₂	1 + 1 + 4 + 10	0.1 + 1.5
elution (matrix)	0.1 mol l ⁻¹ HCl – 1% v/v Br ₂	1 + 1 + 4 + 10	0.1 + 1.5
Tl elution	0.1 mol l ⁻¹ HCl – 5% w/w SO ₂	1 + 1 + 1 + 3 + 9 + 1	0.1 + 1.5

Table 4: Thallium mass fraction data obtained during this study, and comparison with literature data

Reference Material	# dissolutions	# measurements (n)	[Tl] (ng g ⁻¹)	RSD %	References
Calibrators					
AGV-1			349	14.9	7,8,13,17,24,25,33,34,49,50,53,55
			337	4.7	28 (GeoReM preferred value)
BHVO-2	2	6	23	4.9	This study*
			22	20	1,2,5,6,8-10,16,20,21,23,25-27,30,31,36-41,43,45,48,49,51-53,58
			22.4	20	28 (GeoReM preferred value)
BIR-1	3	15	1	21	This study*
			1.8	41	1,8,18,25,32,35,42,46,47,53-56
			2.1	34	28 (GeoReM preferred value)
Measured reference materials					
14P	3	10	100 [†]	20	This study
AL-I	1	2	42	8.3	This study
AN-G	1	1	10	8.0	This study
BCR-2	3	19	306	6.7	This study
			265	13	3,10,12,14,15,19-22,25,26,29,36-38,40,41,43,45,58
			267	13	28 (GeoReM preferred value)
COQ-1	1	7	96	3.9	This study
FK-N	1	1	3720	0.5	This study

G-2	1	1	940	6.6	This study
			888	3.1	18,23,25,26,28,50,57,58
			884	3.0	28 (GeoReM preferred value)
GSP-2	2	4	1500	5.4	This study
			1290	7.9	26,36,58
ISH-G	1	1	790	0.7	This study
MDO-G	1	1	61	2.0	This study
Mica-Fe	1	1	16800	0.4	This study
			16000	<i>n.g.</i>	4,11,44
Mica-Mg	1	1	5270	0.8	This study
SRM 607	1	1	2650	1.1	This study
STM-1	1	1	260	1.4	This study
			220	6.4	17,44
UB-N	1	2	41	4.3	This study
			49	18.3	8,17,46,52,56

* These TI mass fraction results were obtained for solutions of the calibrator reference materials that were run as unknowns.

† Mass fraction estimated using MC-ICP-MS.

dissolutions: number of independent digestions

measurements: number of measurement results

References: (1) Babechuk *et al.* (2010), (2) Babechuk and Kamber (2011), (3) Baker *et al.* (2010), (4) Baranov *et al.* (2002), (5) Barnes *et al.* (2013), (6) Brandl *et al.* (2012), (7) Bolge *et al.* (2006), (8) Chauvel *et al.* (2011), (9) Chauvel *et al.* (2012), (10) Condomines *et al.* (2015), (11) Dampare *et al.* (2008), (12) Deng *et al.* (2013), (13) Eggins *et al.* (1997), (14) Elmaleh *et al.* (2012), (15) Espanon *et al.* (2014), (16) Gale *et al.* (2011), (17) Garbe-Schönberg (1993), (18) Gaschnig *et al.* (2015), (19) Geldmacher *et al.* (2008), (20) Gibson *et al.* (2013), (21) Gómez-Tuena *et al.* (2011), (22) González-Álvarez and Kerrich (2011), (23) He *et al.* (2010), (24) Hettmann *et al.* (2014), (25) Hu and Gao (2008), (26) Hu *et al.* (2013), (27) Jacques *et al.* (2013), (28) Jochum *et al.* (2016), (29) Kamber *et al.* (2005), (30) Kawabata *et al.* (2011), (31) Kirchenbauer *et al.* (2012), (32) Kodolányi *et al.* (2012), (33) Makishima and Nakamura (2006), (34) Makishima *et al.* (2011), (35) Martin *et al.* (2015), (36) Marx and Kamber (2010), (37) Marx *et al.* (2010), (38) McCoy-West *et al.* (2010), (39) Mohan *et al.* (2013), (40) Mori *et al.* (2007), (41) Mori *et al.* (2009), (42) Nielsen *et al.* (2007), (43) Park *et al.* (2012), (44) Parks *et al.* (2014), (45) Prytulak *et al.* (2013), (46) Robin-Popieul *et al.* (2012), (47) Søger *et al.* (2015), (48) Stromsoe *et al.* (2013), (49) Timm *et al.* (2009), (50) Uysal *et al.* (2011), (51) van der Straaten *et al.* (2008), (52) Wang *et al.* (2015), (53) Wehrmann *et al.* (2014), (54) Woodhead *et al.* (2011), (55) Worthington *et al.* (2006), (56) Yu *et al.* (2000), (57) Yu *et al.* (2001), (58) Zhang *et al.* (2012).

Table 5: Thallium isotope ratio measurement results obtained during this study

Reference Material	# dissolutions	# sessions	# measurements	$\epsilon^{205}\text{Tl}$	2s
14P	3	1	10	-2.0	0.5
AL-I	3	3	5	-1.5	0.2
AN-G	3	3	3	-2.7	0.4
BCR-2	3	1	5	-2.4	0.2
BHVO-2	3	3	4	-1.2	0.7
COQ-1	3	2	5	-2.3	0.5
FK-N	3	4	11	-0.1	0.7
G-2	3 (1)	3	10	-2.3	2.0
GSP-2	3 (1)	2	9	-2.5	0.6
ISH-G	3 (1)	3	9	-1.5	0.5
MDO-G	3 (1)	3	7	0.5	0.7
Mica-Fe	3	4	11	-3.4	0.7
Mica-Mg	3	4	12	-0.1	0.9
SRM 607	3	2	9	-3.1	0.8
STM-1	3 (1)	2	10	-2.0	1.1
UB-N	3	3	5	1.8	0.4

dissolutions: total number of independent digestions; (X) gives the number of bomb digestions

sessions: number of analytical sessions during which the RM was analysed

measurements: number of separate analyses

Figure 1

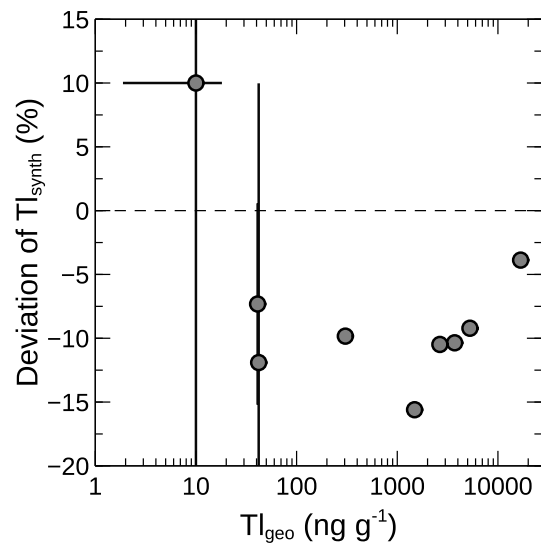


Figure 2

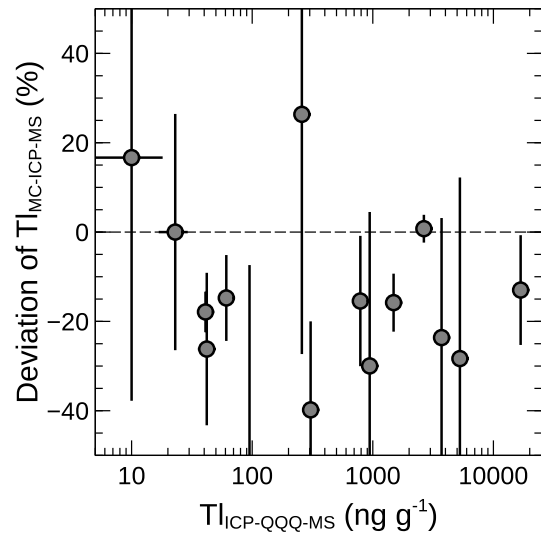


Figure 3a

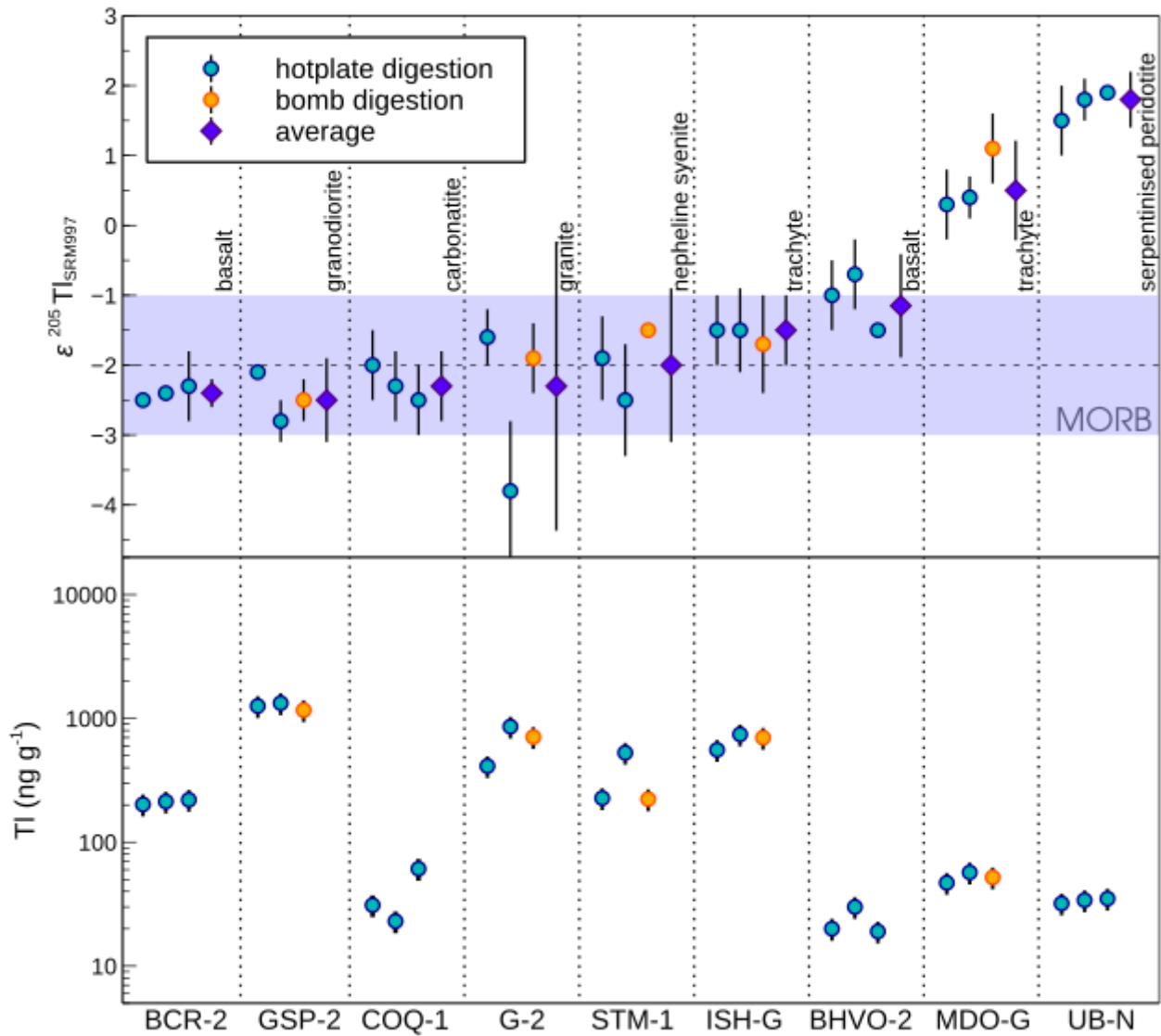


Figure 3b

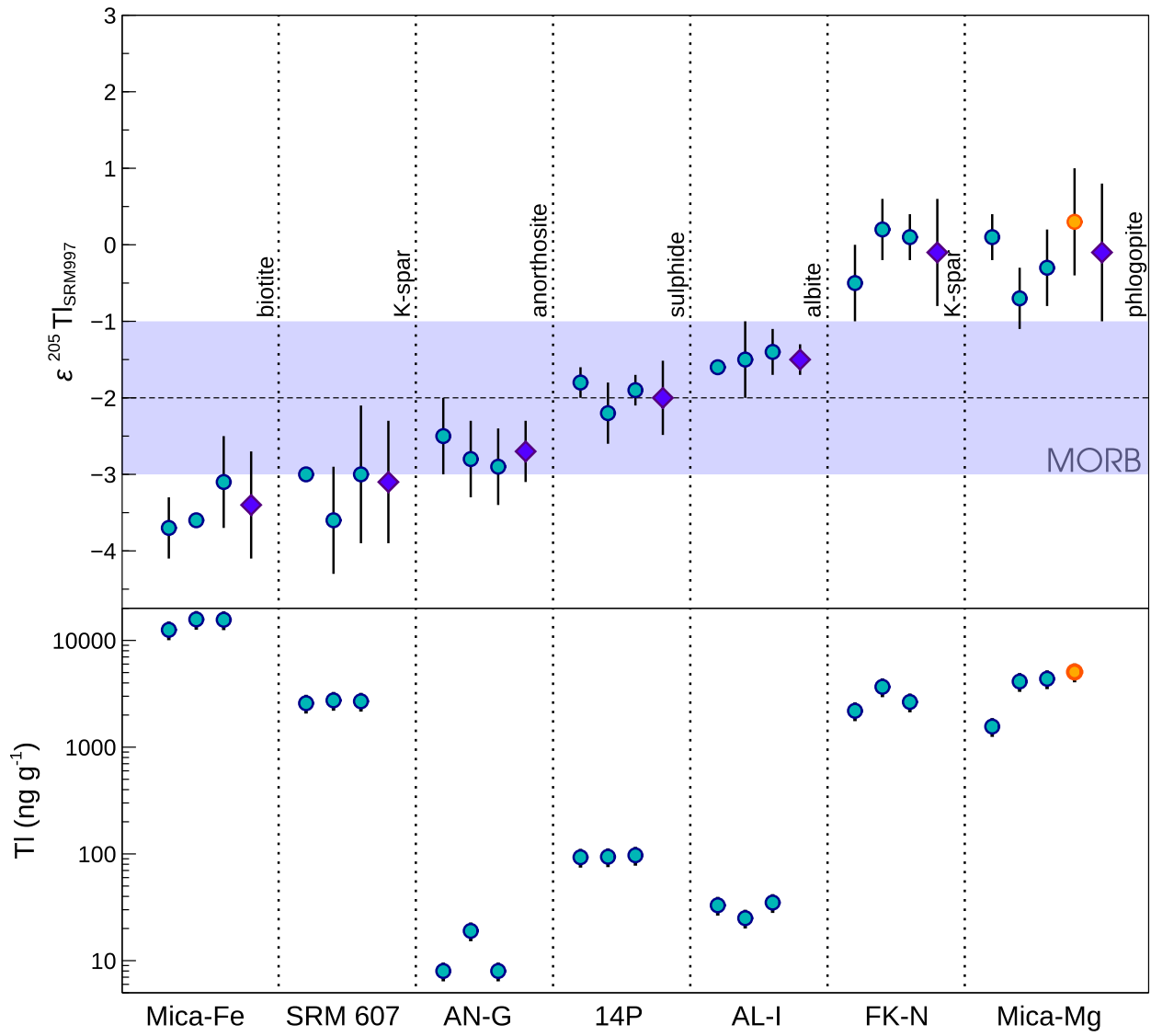


Figure 4

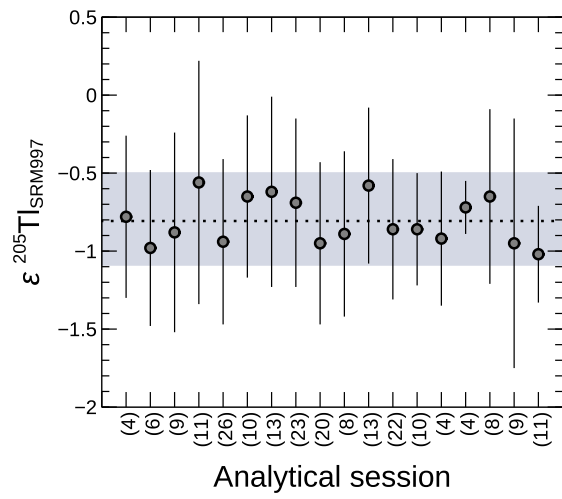


Figure 5

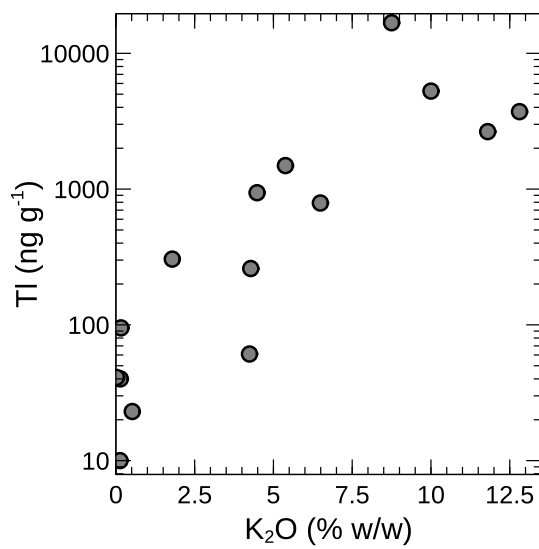


Figure 6

