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Thallium Mass Fraction and Stable Isotope Ratios of Sixteen Geological Reference Materials

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Thallium stable isotope ratio and mass fraction measurements were performed on sixteen geological reference materials spanning three orders of magnitude in thallium mass fraction, including both whole-rock and partially separated mineral powders. For stable isotope ratio measurements, a minimum of three independent digestions of each reference material was obtained. High-precision trace element measurements (including Tl) were also performed for the majority of these RMs. The range of Tl mass fractions represented is 10 ng g\(^{-1}\) to 16 µg g\(^{-1}\), and Tl stable isotope ratios (reported for historical reasons as \(\varepsilon^{205}\)Tl)

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relative to NIST SRM 997) span the range -4 to +2. With the exception – attributed to between-bottle heterogeneity – of G-2, the majority of data are in good agreement with published or certified values, where available. The precision of mean of independent measurement results between independent dissolutions suggests that, for the majority of materials analysed, a minimum digested mass of 100 mg is recommended to mitigate the impact of small-scale powder heterogeneity. Of the sixteen materials analysed, we therefore recommend for use as Tl reference materials the USGS materials BCR-2, COQ-1, GSP-2 and STM-1; CRPG materials AL-I, AN-G, FK-N, ISH-G, MDO-G, Mica-Fe, Mica-Mg and UB-N; NIST SRM 607 and OREAS14P.

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

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First isolated in 1861 (Crookes 1862, Lamy 1862), thallium is one of the highest atomic mass naturally-occurring elements: a volatile, highly incompatible trace metal, with two oxidation states available in addition to the neutral charge state. Univalent thallium (Tl\(^{+}\)) has a large ionic radius (1.49 Å), comparable to that of the alkali metals potassium, rubidium and caesium, and can therefore substitute for these elements in mineral crystal structures (Shaw 1952, Shannon and Prewitt 1969, Shannon 1976). Trivalent thallium (Tl\(^{3+}\)) can also exist on Earth under highly oxidising conditions (Bately and Florence 1975, Vink 1993), e.g., in the structure of the ferromanganese (Fe-Mn) mineral hexagonal birnessite (Peacock and Moon 2012, Nielsen et al. 2013).
Thallium has two stable isotopes with mass numbers 203 (29.5%) and 205 (70.5%). The relative difference in mass between thallium's two stable isotopes is less than 1%. Because the magnitude of mass-dependent stable isotope fractionations via kinetic and equilibrium processes scales inversely with both overall and relative mass difference (Bigeleisen and Mayer 1947, Urey 1947), it was assumed that there would be little mass-dependent thallium isotope fractionation in nature. Resolvable Tl isotopic differences were therefore thought to arise solely due to decay of the relatively short-lived radioisotope $^{205}$Pb to $^{205}$Tl, with a half-life of about 15 Ma. Initial investigations (Anders and Stevens 1960, Ostic et al. 1969, Huey and Kohman 1972, Chen and Wasserburg 1987, 1994) thus aimed to provide constraints on the delivery and distribution of $^{205}$Pb during the early stages of solar system formation by tracking differences in Tl isotope ratios. These efforts proved unable to resolve variations for a large number of extra-terrestrial and some selected terrestrial materials. This inability was for the most part due to the uncertainties (> 2‰, 2s) associated with TIMS measurement results of Tl (see summary in Nielsen et al. 2017).

As a consequence of initial development of the system in the context of cosmochemistry, where small radiogenic isotope variations are routinely reported using $\varepsilon$-notation, Tl isotope ratios are traditionally reported relative to the Tl reference material NIST SRM 997 (defined as 0) as:

$$\varepsilon^{205}\text{Tl}_{SRM997} = 10,000 \times \left[\left(\frac{^{205}\text{Tl}}{^{203}\text{Tl}}_{\text{sample}} - \frac{^{205}\text{Tl}}{^{203}\text{Tl}}_{\text{SRM997}}\right) / \left(\frac{^{205}\text{Tl}}{^{203}\text{Tl}}_{\text{SRM997}}\right)\right]$$ (1)
Strictly, use of $\varepsilon$-notation is deprecated in favour of $\delta$-notation (Coplen 2011), whereby:

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

(2)

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

The development of multi-collector ICP-MS (MC-ICP-MS) allowed for higher-precision Tl isotope ratio measurements, with precisions > 3–4 times better than those achieved by the best TIMS protocols then reported (0.1–0.2‰, 2σ; Arden 1983). Using these new measurement principles, Rehkämper and Halliday (1999) analysed a number of terrestrial samples in order to define the baseline terrestrial Tl isotope composition for the purpose of comparison with extra-terrestrial materials, again assuming that variations in extra-terrestrial materials would reflect early $^{205}\text{Pb}$ decay. They unexpectedly discovered large variations in Tl isotope ratios for terrestrial materials, from $\varepsilon^{205}\text{Tl}_{\text{SRM997}} -1.8 \pm 1.9$ (2σ) to 11.9 ± 0.5 (2σ).
The natural range of Tl stable isotope variations documented on Earth now exceeds 35 $\varepsilon^{205}\text{TI}_{\text{SRM997}}$ units ("$\varepsilon$-units"; see review in Nielsen et al. 2017). With the exception of volcanic fumaroles and some meteorites (Nielsen et al. 2006a, Baker et al. 2009, 2010b), these variations are best explained by equilibrium isotope effects (Rehkämper et al. 2002, Nielsen et al. 2006c). The magnitude of equilibrium stable isotope variation in Tl exceeds those predicted by classical models of mass-dependent isotope fractionation. Schauble (2007) showed that, for very heavy elements including thallium, variation in nuclear volume means that neutron-rich isotopes tend to be concentrated in more oxidised species. A combination of mass-dependent and nuclear volume effects therefore accounts for the stable isotope fractionation displayed by Tl (e.g., Fujii et al. 2013). Stable isotope variations arising due to this “nuclear field shift effect” (King 1984) have also been documented for other very heavy elements, including Hg (Smith et al. 2005, Xie et al. 2005, Moynier et al. 2013) and U (Fujii et al. 1989a, b, Stirling et al. 2007, Moynier et al. 2013). Additionally, recent calculations (Yang and Liu 2015) suggest that the nuclear volume effects may produce large differences (up to approximately 4‰) for Pb in systems containing Pb$^{4+}$- and Pb$^{2+}$-bearing species.

As of 2018, there are more than thirty studies utilising Tl isotope ratio variations to investigate the natural environment. The utility and versatility of the system lies in the large isotope ratio differences and relatively high mass fractions ($\mu g g^{-1}$) associated with low temperature environments, in contrast with very low mass fractions and negligible isotope ratio differences in mantle-derived lavas (see review of Nielsen et al. 2017, Prytulak et al. 2017). Applications include investigations of extra-terrestrial materials (Nielsen et al. 2006a, Andreasen et al. 2009, 2012, Baker et al. 2010b, Palk et al. 2011); riverine and marine fluxes.
Despite the breadth of study, literature reports of thallium isotope ratios for geological reference materials have been restricted to three basalts, one andesite and one granite (Table 1), in addition to two ferromanganese sediments, one meteorite and one seawater sample. In response to the growing application of thallium isotopes in Earth systems, we provide the first measurement results of Tl isotope ratios for the bulk rock reference materials COQ-1, GSP-2, ISH-G, MDO-G, STM-1, and UB-N alongside determinations for previously analysed bulk rock reference materials BCR-2, BHVO-2 and G-2. Investigations of emerging stable isotope systems commonly reveal equilibrium inter-mineral isotope fractionations at high temperatures, as reviewed in Teng et al. (2017). We therefore also present the first determinations of Tl mass fractions and isotope ratios for the mineral reference materials 14P, AL-I, AN-G, FK-N, NIST SRM 607, Mica-Fe and Mica-Mg, in an effort to establish an estimate of the possible magnitude of stable isotope ratio variation in phases potentially rich in Tl. These reference materials are intended to be used as matrix-matching RMs for future investigations rather than be interpreted in isolation as indicative of natural Earth processes. A minimum of three separate digestions, separations and measurements were performed for each RM. With the exception of 14P, the reference materials were also
analysed for high precision trace element mass fractions, including thallium. We focus on reference materials useful for high temperature applications. Table 2 provides background information on each selected material.

Experimental procedure

Determination of Tl isotope ratios

**Reagents:** All sample digestions and chemical separations were carried out in the MAGIC Laboratories, Imperial College London. Purified water from a Milli-Q® (Merck) system (resistivity 18.2 MΩ cm) was used throughout. HNO₃ (concentrated, ~ 14 mol l⁻¹) and HCl (6 mol l⁻¹) were purified once by sub-boiling distillation in quartz or PTFE stills, whilst ultrapure HF (47–51% ≈ 24 mol l⁻¹) was either purchased from SCP Scientific or prepared in the laboratory from reagent-grade acid by a single distillation step in a PTFE still. Saturated bromine water was prepared by the equilibration of high-purity bromine with purified water in a 125 ml PTFE bottle. Dilute HNO₃ and HCl containing 1–3% v/v saturated bromine water were prepared by adding the appropriate volume of bromine water to the acid immediately before use. A solution of 5–6 % w/w SO₂ in 0.1 mol l⁻¹ HCl ("0.1 mol l⁻¹ HCl–5% SO₂") was used for the reductive elution of Tl from anion-exchange resin. This solution was prepared in a 250 ml PTFE bottle containing 100–200 ml 0.1 mol l⁻¹ HCl, through which was bubbled gaseous SO₂ from a small pressurised cylinder containing liquefied SO₂ (purchased from Sigma Aldrich). The solution was reweighed at regular intervals until the required amount of SO₂ had dissolved in the acid. After preparation, the reagent was stored for a maximum of 1
week for reuse then discarded, as SO\textsubscript{2} oxidises to form sulphate. Finally, a 0.1 mol l\textsuperscript{-1} HNO\textsubscript{3}–0.1\% v/v H\textsubscript{2}SO\textsubscript{4} solution used for sample dilution and subsequent mass spectrometric measurement was made up using distilled-grade concentrated H\textsubscript{2}SO\textsubscript{4} (96\% v/v).

**Sample digestion:** Between 25 mg and 350 mg of reference material powder was accurately weighed into PFA vials (Savillex\textsuperscript{®}), depending on the mass fraction of Tl in the RM. The majority of digestions (exceptions detailed below) were performed on a tabletop hot plate (quoted temperatures are the hot plate temperature setting, unless otherwise specified) at 140 °C for 1–3 days, in an initial mixture of 3 ml HF (24 mol l\textsuperscript{-1}) and ~ 0.3–0.5 ml HNO\textsubscript{3} (14 mol l\textsuperscript{-1}). Samples were then evaporated to near (rather than total) dryness, to minimise formation of insoluble fluorides (Croudace 1980, Yokoyama et al. 1999); taken up in ~ 1 ml of HNO\textsubscript{3} (14 mol l\textsuperscript{-1}); and evaporated to dryness at 180 °C at least three times, to destroy any fluorides formed and to evaporate SiF\textsubscript{4}. Samples were redissolved and evaporated once from 4 ml HCl (6 mol l\textsuperscript{-1}) at 120 °C; redissolved in 2 ml HCl (6 mol l\textsuperscript{-1}) and refluxed at 120 °C for a minimum of 12 h; and finally made up to a 12 ml HCl (1 mol l\textsuperscript{-1}) solution subsequently used to load into the first separation column. The final loading solution of 12 ml HCl (1 mol l\textsuperscript{-1}) for column chromatography was refluxed at 140 °C for a minimum of 12 h. Sample solutions were cooled and 400 μl of saturated Br\textsubscript{2} water was added, then left for a minimum of 3 h to ensure complete oxidation of thallium to its Tl\textsuperscript{3+} state.
Some of the investigated RMs (COQ-1, G-2, GSP-2, ISH-G, MDO-G, STM-1) contain refractory phases such as zircon that may not be completely digested using hot plate dissolution alone. Although thallium is not expected to reside in phases such as zircon, we investigated the potential role of refractory phases on Tl mass fraction and isotope ratio by performing bomb digestions. To this end, approximately 50 mg of powder was accurately weighed into PFA hexagonal bomb vials (Savillex®), to which was added ~0.2 ml HNO₃ (14 mol l⁻¹) and 1.5 ml HF (24 mol l⁻¹). The prepared bombs were sealed tightly and placed in an oven at 150 °C for five days. Subsequent sample processing was identical to that for hot plate digestions.

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

**Chromatographic separation of Tl:** Separation of the Tl fraction from sample matrices largely follows the two-stage ion-exchange procedure devised by Rehkämper and Halliday (1999) and refined by Nielsen *et al.* (2004) (Table 3). The separation technique utilises the two oxidation states of thallium. Oxidised Tl³⁺ adsorbs much more strongly to anion resins than Tl⁺ under a variety of conditions, with a general decrease in distribution coefficients with increasing HCl concentration (Kraus *et al.* 1954). Experimental work by Horne (1958) established that at a temperature of 25 °C the distribution coefficient of Tl³⁺ on Dowex® 1-X8 from aqueous HCl solutions (10⁻³ to 2 mol l⁻¹) has values of D ≥ 10⁵. Under identical conditions the distribution coefficient for Tl⁺ is much smaller; the maximum value (D = 10³)
occurs for 1 mol l$^{-1}$ HCl, and decreases rapidly with small variations in HCl concentration. Horne (1958) also observed that adsorption of Tl$^{3+}$ onto Dowex® 1-X8 from HBr media was too strong to be reliably measured. Thus the ion-exchange procedure employs HCl (at concentrations $\leq$ 2 mol l$^{-1}$) and HNO$_3$ admixed with 1–3% v/v saturated bromine water for sample loading and elution of major and trace elements, to ensure that all Tl remains strongly adsorbed to the resin as Tl$^{3+}$ complexed with chloride and trace bromide present in the bromine solution.

Collection of the thallium fraction was accomplished using a solution of 0.1 mol l$^{-1}$ HCl-5% SO$_2$ (see Reagents). This reduces Tl$^{3+}$ to Tl$^+$, whereby the latter can be readily eluted from the column. Yields of > 95% are routinely achieved (Nielsen et al. 2004, Rehkämper and Nielsen 2004), with no isotopic fractionation of the separated Tl with respect to the original sample (Rehkämper et al. 2002, Nielsen et al. 2004).

In this study the resin used was AG® 1-X8 (200–400 mesh) anion resin. The resin was cleaned prior to use in 4 mol l$^{-1}$ HNO$_3$ (three times), 18 MΩ cm water (three times), quartz-distilled 6 mol l$^{-1}$ HCl (once), and again in 18 MΩ cm water (three times); finally, the resin was stored in quartz-distilled HCl (0.1 mol l$^{-1}$). Between each stage of cleaning the resin was left to stand for five days with intermittent shaking. A fresh resin bed was prepared for each separation and a two-stage process was used (i) to ensure complete elution of other ions and particularly of Pb, and (ii) to minimise the amount of sulfuric acid present prior to measurement.
Table 3 outlines the two-step chromatographic procedure. Briefly, the first stage of separation utilised quartz columns with an inner diameter 6 mm, fitted with quartz wool plugs for support of the resin bed, which was filled with 1000 μl resin (wet volume). Once collected in acid cleaned PFA vials, the Tl fraction was evaporated at 200 °C, which left < 20 μl residual concentrated H₂SO₄, formed via oxidation of SO₂ used during collection of Tl. The sample was then re-dissolved in a few drops (~ 0.1 ml) of concentrated HCl (12 mol l⁻¹), and evaporated again at 200 °C to reduce the amount of residual H₂SO₄. Subsequently, the Tl fraction was dissolved in 1.5 ml HCl (1 mol l⁻¹) and refluxed for 12 h at 140 °C. Once cooled, 60 μl of saturated Br₂ water was added to this solution; the sample was then left for a minimum of 3 h to ensure complete oxidation of all Tl ions to the Tl³⁺ state.

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

**MC-ICP-MS isotope ratio measurements:** The use of PFA beakers and the high evaporation temperature of H₂SO₄ means that it was not possible to remove all H₂SO₄ from the Tl fraction by evaporation. Nielsen et al. (2004) demonstrated that analytical artefacts of up to 1 ε-unit can be generated if H₂SO₄ is present in samples but not in bracketing
calibrators. Therefore, all sample residues were dissolved in 1 ml of 0.1 mol \( l^{-1}\) HNO\(_3\)-0.1% v/v concentrated H\(_2\)SO\(_4\) for isotopic analysis. The mass bias-corrected \(^{205}\text{Tl}^{/}\text{203}\text{Tl}\) ratio is essentially independent of the concentration of H\(_2\)SO\(_4\) up to 1% v/v (Nielsen et al. 2004). Reference solutions were prepared using the same batch of 0.1 mol \( l^{-1}\) HNO\(_3\)-0.1% v/v concentrated H\(_2\)SO\(_4\) to minimise matrix mismatch between samples and reference solutions. Isotopic ratio measurements were carried out using a Nu Instruments (HR) MC-ICP-MS in low-resolution mode at the MAGIC Laboratories, Imperial College London. Sample introduction systems used over the course of this study included the Aridus, Aridus II and Nu Instruments DSN (Desolvation Nebuliser System), coupled with either PTFE or glass nebulisers, with measured uptake rates between 70 and 120 \( \mu l \) min\(^{-1}\). Samples were run in a sequence using a Cetac autosampler. Dedicated PFA autosampler vials were used for all reference and wash solutions. Sample solutions were made up in 3 ml acid-cleaned PP autosampler vials.

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

The ion beams at \( m/2 \) 202 (Hg\(^+\)), 203 (Tl\(^+\)), 204 (Pb\(^+\) with possible Hg\(^+\) interference), 205 (Tl\(^+\)), 206 (Pb\(^+\)), 207 (Pb\(^+\)) and 208 (Pb\(^+\)) were monitored simultaneously with the Faraday collectors L2, L1, Ax, H1, H2, H3 and H4, all fitted with \( 10^{11} \) \( \Omega \) resistors. Data collection was
performed in three blocks of twenty cycles with 5 s integrations with the electrostatic energy analyser (ESA) deflected for a 15 s electronic baseline at the beginning of each block.

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

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

**MC-ICP-MS Tl mass fraction estimates:** Estimates of thallium mass fractions were acquired during MC-ICP-MS measurements of Tl isotope ratios by comparison of ion beam intensities between reference solutions of known mass fraction and unknown samples, assuming chemical separation returns 100% thallium yields. In detail, the Tl mass fractions were estimated based on measurements of Pb/Tl mass fraction ratios using the known absolute mass of NIST SRM 981 Pb added to sample and reference solutions. However, these measurements are sensitive to small variations in sample dilution, which may occur during sample preparation due to (i) small variations between pipette tips and pipettes; (ii) differences in the volume consumed during initial concentration checks of the diluted sample (for standard-matching purposes); (iii) variations how long a sample is left to stand in the autosampler before a measurement is made (i.e., how much evaporation occurs prior to measurement).

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

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

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

**Method:** Approximately 50 mg of each RM was weighed accurately into PFA vials, to
which a 3:1 mixture of HF (24 mol l⁻¹):HNO₃ (14 mol l⁻¹) was added. The solutions were
treated ultrasonically for 20 min after initial addition of the acids, then placed on a hot plate
at 160 °C for at least 24 h. Sample solutions were further treated ultrasonically for 20 min
twice during the initial digestion. Solutions were then evaporated to near dryness,
redissolved in 2 ml of HCl (6 mol l⁻¹), and refluxed at 120 °C for at least 24 h. The solutions
were next evaporated to complete dryness at 120 °C, redissolved in 1 ml of HNO₃ (14 mol l⁻¹)
and then evaporated at 180 °C. The last step was repeated a minimum of three times, or
until the colour of the residue changed from white to brown, which indicates that fluorides
formed from the initial HF digestion have been destroyed. Samples were then transported

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to the Open University as HNO$_3$ (14 mol l$^{-1}$) solutions, and transferred into acid-cleaned PP bottles, where an appropriate amount of purified H$_2$O was added to each to achieve a 1000-fold dilution of the original sample mass in an HNO$_3$ matrix (0.14 mol l$^{-1}$).

**ICP-QQQ-MS measurement:** Trace element mass fraction determinations including thallium were undertaken at the Open University, UK, with an Agilent 8800 ICP-QQQ-MS inductively coupled plasma-mass spectrometer. Sample solutions were aspirated using a quartz microflow nebuliser with an uptake rate of 0.5 ml min$^{-1}$. Machine sensitivity was on the order of 1–5 $\times$ 10$^7$ cps per µg ml$^{-1}$, depending on the element. The Agilent 8800 has a collision/reaction cell (Octopole Reaction System, ORS), which separates two quadrupoles. The first quadrupole was used as a mass filter to ensure that only specific masses entered the ORS; reactions could therefore be targeted to remove on-mass interferences. The second quadrupole could be used in either mass-shift or on-mass mode, depending whether the analyte or interference reacts with the gas. We employed two collision/reaction gas configurations to undertake measurements: no gas in the collision cell or O$_2$ gas in the cell. Thallium was determined in the ‘no gas’ mode, with oxide levels (measured as CeO$^+/Ce^+$) kept below 1% and double charged species (Ce$^{2+}$/Ce$^+$) at 1.6%. All other elements were similarly measured except for most rare earth elements (La, Pr, Ce, Nd, Sm, Gd, Ho, Tb, Dy, Er, Yb, Lu), which were reacted with O$_2$ gas for a mass shift measurement.

**Selection and assessment of calibrators:** Calibrator materials were run at the beginning of each measurement session. Additionally, an internal solution standard consisting of Be, Rh, In, Tm, Re and Bi was added online to all standard and unknown solutions to monitor
and correct instrumental drift. Drift was further monitored every five unknown measurements with a measurement block consisting of BIR-1 (a separate digestion to that used in the initial calibration block), HNO₃ (0.3 mol l⁻¹), and a repeated unknown sample.

The USGS reference materials BIR-1, BHVO-2 and AGV-1 were chosen as calibrators for trace element determination of Tl in particular. In addition, RMs W-2 and DNC-1 are used for calibration: for most trace elements (not including Tl) these are well-characterised materials. BIR-1, BHVO-2 and AGV-1 were selected because they are commonly used for analysis of other isotopic systems, i.e., they are well characterised, and span three orders of magnitude of Tl mass fraction. Only AGV-1 has a USGS listed Tl mass fraction (0.34 µg g⁻¹, recommended value; no uncertainty given). All three RMs have preferred GeoReM (Jochum et al. 2005) Tl mass fraction values, per 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, 337 ± 31 ng g⁻¹ (n = 10) (95% confidence intervals). Specifically, we used Tl mass fractions of: BIR-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 using our own compilation of reported mass fraction data (Online supporting information Table S1). All values are within error of the GeoReM recommended values.

We note that both AGV-1 and BHVO-2 exhibit heterogeneity seen in Pb isotope ratio and mass fraction results, which have been provisionally attributed to contamination during processing using steel mortar and pestle (Weis et al. 2006). It has long been suggested that the similarity between properties of Tl and Pb might result in similar behaviours in some geochemical contexts (Lamy 1862), but as Tl has historically not been routinely analysed it is
not clear whether Tl systematics in these RMs correlate with Pb heterogeneity. We therefore used our compilation of reported Tl mass fractions in these RMs (Table S1) to identify and characterise potential Tl heterogeneity in our calibrators.

We found no identifiable heterogeneity for AGV-1 \((n = 13, \text{RSD} = 15\%)\). Reported BIR-1 Tl mass fraction results have a notably high RSD (34%); however, this material has a very low Tl mass fraction and is therefore analytically challenging. Consequently, determining whether the high uncertainty reflects powder inhomogeneity or analytical error is not straightforward, and BIR-1 remains the best-characterised candidate for a low mass fraction Tl calibrator. For BHVO-2 there is some variation in reported Tl mass fraction between studies: of the thirty-six reported measurement results (mean mass fraction value of 28 ng g\(^{-1}\); RSD = 58%), a small minority \((n = 4)\) have a mean of 65 ng g\(^{-1}\) (RSD = 7%). The remaining measurement results give a mean of 22 ng g\(^{-1}\) (RSD = 20%). For comparison, BHVO-1 has a reported Tl mass fraction of 46 ng g\(^{-1}\) (RSD = 19%, \(n = 25\)). The four anomalous reports of Tl mass fraction in BHVO-2 (Bouman \textit{et al.} 2004, Deegan \textit{et al.} 2012, Deng \textit{et al.} 2013 and Søager \textit{et al.} 2015) are suggestive of either confusion between the two generations of the BHVO RM, or of possible contamination.

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

For the two remaining anomalous reports of Tl mass fraction, the trace element pattern is less suggestive of confusion between generations of this reference material. Trace element mass fractions reported by Deegan et al. (2012) are on average 10% higher than USGS listed values (2%-20% higher), with the exception of Ta, which is in agreement with the listed value. Two Tl mass fractions are reported for BHVO-2, of 60 ng g\(^{-1}\) and 80 ng g\(^{-1}\). Søager et al. (2015) used reference values provided by the Hamburg laboratory that performed sample analysis (pers. comm., 2017), and report a Tl mass fraction for BHVO-2 of 63 ng g\(^{-1}\). These Tl mass fractions are anomalously high for BHVO-2, but are consistent with the listed and compiled values for BHVO-1; however, there is no compelling indication that in these cases confusion between the two generations of powder occurred. These results therefore appear to be best explained by some combination of analytical uncertainty and powder contamination.
The available data therefore suggest that if BHVO-2 suffers from inhomogeneity with respect to Tl mass fractions, it is not a widespread or common problem. Furthermore, there are very few generally available igneous RMs with low Tl mass fractions. BIR-1, with a Tl mass fraction an order of magnitude lower than BHVO-2, is employed as a calibrator in this study, but as noted presents analytical challenges. The Geological Society of Japan provides three basalt RMs, but all have higher Tl mass fractions than BHVO-2: JB-2 has the lowest Tl mass fraction, reported as 34 ± 3.6 ng g⁻¹ (Jochum et al. 2016). As such, BHVO-2 is the best widely available, well-characterised choice for a low-Tl calibration material.

Trace element mass fractions were generally determined with the chosen geological calibrating RMs (AGV-1, BHVO-2, BIR-1). However, partially separated mineral RMs have unusual and, in some cases, extreme trace element mass fractions. For example, a Tl mass fraction of 16 μg g⁻¹ was reported for the biotite Mica-Fe (Table 4), well outside the Tl mass fraction range of the calibrators. Linear extrapolation of the calibration curve is a potential source of error for the reported mass fractions of such high-Tl RMs. Two approaches that are potentially suited to address this concern are (i) isotope dilution ICP-MS (ID-ICP-MS), and (ii) the use of synthetic calibrating reference solutions with known, high Tl mass fractions. The ID-ICP-MS technique was not deemed appropriate, due to the lengthy preparation times required and the possible powder heterogeneity of at least some samples. In other words, obtaining highly accurate trace element mass fraction data for a single dissolution of a potentially heterogeneous material is deemed to be of limited utility. In contrast, the use of synthetic calibrating standards requires significantly less preparation time. However, it is known that the sample matrix can affect the ionisation potential of
elements during analysis and, consequently, mass fraction measurement results (e.g., Brown and Milton 2005). To the best of our knowledge it has not previously been established whether using synthetic calibrators results in any systematic effect on measured Tl mass fractions. Therefore, for one measurement session a pure internal trace element reference solution (made from single element plasma grade standards (Alfa Aesar)) was employed as a synthetic calibrating reference solution to assess whether this procedure produced Tl mass fraction data that differed significantly from those obtained with geological calibrators.

Results and discussion

Determination of Tl mass fraction

Mass fraction measurements by ICP-QQQ-MS: Table 4 presents the thallium mass fractions determined for RMs in this study, whilst online supporting information Table S2 gives trace element results. Typical precisions reported for Tl in the literature are on the order of 5–15% RSD, compared with < 5% RSD for commonly determined trace elements. Precision is normally deemed excellent if RSDs are < 3% or good if 3–7%.

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

With the exception of three RMAs (AL-I, AN-G and BIR-1), RSDs for Tl mass fraction measurement results obtained during this study using ICP-QQQ-MS with geological calibrators were < 7%, and all RSDs except that for BIR-1 were < 10% (Table S2). We note that RM AN-G has a low Tl mass fraction (10 ng g\(^{-1}\), RSD = 8.1%), making precise measurements technically challenging. Similarly, BIR-1 has a very low Tl mass fraction (1 ng g\(^{-1}\)); even for this material, an RSD (n = 18) of 21% was achieved. Multiple dissolutions were analysed for trace element mass fractions using ICP-QQQ-MS for BCR-2 (multiple hot plate digestions), BHVO-2 (multiple hot plate digestions measured as unknowns, in addition to the calibrator solution), and GSP-2 (hot plate and bomb digestions). Notably, the hot plate versus bomb dissolution of GSP-2 showed no resolvable variation of Tl mass fraction with digestion method (RSD = 4.5%), suggesting, as expected, that Tl is not hosted in refractory phases present in this material (Table S2).

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

**Mass fraction measurements by MC-ICP-MS:** Mass fraction measurements made during isotope ratio analysis via MC-ICP-MS were indistinguishable from ICP-QQQ-MS results, but showed substantial variance (Figure 2) with RSDs (calculated for each material as the RSD of the individual mass fraction measurement results) ranging from about 2% to 54%. For ten of the RMs measured the RSD is < 20%, whilst five have > 30% RSDs of the mean. This suggests that mass fraction measurements made during MC-ICP-MS isotopic determinations may be suitable for assessing sample heterogeneity. Importantly, there was no resolvable variation of Tl mass fraction with digestion method: for materials analysed following both hot plate and bomb digestion, Tl mass fraction RSDs were < 15% (see also Figure 3). This strongly suggests that Tl is not hosted in refractory phases present in these RMs.

**Comparison with literature data:** Jochum *et al.* (2016) provide GeoReM preferred values for the nineteen most frequently queried RMs, including AGV-2, BCR-2, BHVO-2 and G-2. Additional literature reports of Tl mass fraction exist for Mica-Fe, BCR-2, GSP-2, G-2, STM-1, and UB-N. These values are reported in Table 4 alongside the mass fraction results obtained over the course of this study. Only the mass fractions determined for GSP-2 and STM-1 differ significantly from published values.
For AL-I, AN-G, and Mica-Mg only proposed values are available, from the compilation of Govindaraju (1995). No Tl mass fraction estimates are available for COQ-1, trachytes ISH-G and MDO-G, or K-feldspars FK-N and NIST SRM 607. To the best of our knowledge, we provide the first reported values for these reference materials.

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

**Determination of Tl isotope ratios**

**Blanks and reference solutions:** Due to the low mass fraction of Tl (typically tens of ng g\(^{-1}\)) in many rock samples (Table 4), it is necessary that Tl mass fractions of total procedural blanks are below the detection limit of the MC-ICP-MS. This equates to a maximum of 2 pg Tl, where the smallest amount of sample Tl processed was approximately 2.5 ng (for AN-G).

The total procedural Tl blank for each batch of samples was determined by dissolving the total procedural blank in 1 ml of analysis solution (0.1 mol l\(^{-1}\) HNO\(_3\)-0.1% H\(_2\)SO\(_4\)) and monitoring the intensity of the m/z 205 ion beam. In all cases there was no deviation of the signal from the wash background, indicative of a maximum blank of < 1 pg.
Residual Pb can produce significant errors in the measured $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratio used for correction of mass bias. Thus, any Pb present in the sample solution prior to addition of NIST SRM 981, whether residual from the sample matrix or introduced via contamination, has the potential to affect the precision and repeatability of $\varepsilon_{^{205}\text{Tl}_{\text{SRM997}}}$ measurements. Therefore, to ensure accuracy of measured $\varepsilon_{^{205}\text{Tl}_{\text{SRM997}}}$, residual Pb mass fractions of below 0.01 ng g$^{-1}$ were required for every sample solution and for the total procedural blank, as determined from the observed $m/z$ 208 ion beam signal prior to NIST SRM 981 addition. Typical residual Pb mass fractions were approximately equivalent to 1 pg g$^{-1}$.

Over the course of this study, > 200 measurement results of the Aldrich Tl solution yielded a mean $\varepsilon_{^{205}\text{Tl}_{\text{SRM997}}}$ value of -0.8 ± 0.3 (2s, $n = 211$; Figure 4), in excellent agreement with the most recent compilation of data from seven laboratories worldwide (Nielsen et al. 2017) in which the value is given as $\varepsilon_{^{205}\text{Tl}_{\text{SRM997}}} = -0.79 ± 0.35$ (2s, $n = 187$). Due to the large number of analyses, our intermediate precision (2s) was calculated using the average $\varepsilon_{^{205}\text{Tl}_{\text{SRM997}}}$ values obtained for the Aldrich Tl solution during each measurement session.

**Data quality:** Results for the Tl isotope ratio measurements are given in Table 5. As a minimum of three isotope ratio measurements were made for each RM, the reported intermediate precision (2s) is based on at least three measurement results obtained following independent sample preparation. For comparison, the typical "external" reproducibility for multiple digestions performed in multiple institutions of $\varepsilon_{^{205}\text{Tl}_{\text{SRM997}}}$ for geological samples is ±0.5 ε-units (see compilation in Nielsen et al. 2017).
Literature reports of $\varepsilon^{205}\text{Tl}_{\text{SRM997}}$ exist for AGV-2, BCR-2, BHVO-2 and G-2 (Table 1). Of these, BCR-2 has the most widely reported $\varepsilon^{205}\text{Tl}_{\text{SRM997}}$, and can be considered isotopically homogeneous with respect to Tl isotope ratio. The values we obtain for BCR-2 and BHVO-2 are in excellent accord with Prytulak et al. (2013, 2017) and Coggon et al. (2014), and are indistinguishable from values obtained by Baker et al. (2009).

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

We are therefore confident that the measurement procedure employed did not introduce any systematic bias, and that our $\varepsilon^{205}\text{Tl}_{\text{SRM997}}$ values and precisions for previously uncharacterised RMs provide a range where the true value is likely to be. Together with mass fraction measurement results obtained via MC-ICP-MS on the same dissolution, these Tl isotope ratio results are displayed in Figure 3, as mean values for each individual dissolution. There is no correlation of precision with digestion batch or analytical sessions, implying that the better precisions (2s = 0.4-0.6 $\varepsilon$-units) are representative of the precision achievable with this analytic approach, whilst the higher measurement results with lower precision (up to 2 $\varepsilon$-units) are unlikely to be a consequence of our laboratory techniques or poor measurement precision.
Evaluation of reference material heterogeneity: Despite the demonstrated ability of the analytical techniques to achieve excellent precision, the variances for some samples are surprisingly high, suggesting possible isotopic heterogeneity in the RM powders. Reference materials must be homogeneous in the element system of interest if they are to be used for method development, validation, or interlaboratory comparisons (BIPM 2012). Homogeneity is routinely tested for major elements and some trace elements during RM preparation but heterogeneity for other elements and for isotope systems has been identified in a number of these materials (e.g., BHVO-2: Baker et al. 2004, Weis et al. 2006, Chauvel et al. 2011; NIST SRM 607: Nebel and Mezger 2006). Furthermore, the statistical nature of observed heterogeneity can provide information on the dispersal of an enriched phase or phases through a material. For example, Chauvel et al. (2011) discuss the possibility that relatively large, rare Pb-rich microparticles are responsible for the distinctive bimodal distribution of Pb mass fractions in BHVO-2. However, we are not aware of any general assessment of Tl heterogeneity in igneous RMs.

As Tl+ readily substitutes for K+ in igneous minerals, it is expected that, if present, K-rich phases will dominate the Tl budget of a rock. Indeed, as shown in Figure 5 for silicate rocks Tl mass fraction correlates with K₂O. Figure 3 presents mean $\epsilon^{205}$Tl$_{NRM997}$ and mass fraction values obtained using MC-ICP-MS for each RM and for each individual dissolution, to aid qualitative assessment of any Tl heterogeneities. There are no resolvable differences in either Tl mass fractions or isotope ratios between bomb and hot plate digestions for the RMs studied, providing evidence that Tl is not hosted in refractory phases. Thus small
variations in the proportions of K-rich phases in the powder portion sampled could significantly affect both the mass fraction and isotope ratio of Tl.

Having performed a minimum of three digestions for isotope ratio measurement of each RM included in this study, we are able to assess whether these materials are heterogeneous for Tl. Examination of the dataset (Figure 3) reveals heterogeneity of mass fraction with weak or no isotope ratio heterogeneity for COQ-1, STM-1, AN-G and Mica-Mg, marked heterogeneity of both isotope ratio and mass fraction for G-2, and possible weak isotope ratio heterogeneity for BHVO-2. AN-G consists primarily of anorthosite (An$_{80}$-An$_{85}$), with hornblende (10–15 % v/v), relict clinopyroxene, and some secondary minerals (Govindaraju 1980). In this rock hornblende is likely the major host of K and therefore of Tl; if the hornblende crystals have identical Tl isotope ratios to the rest of the bulk sample, it follows that Tl isotope ratios will be unaffected by modal proportion of hornblende in any individual dissolution, but the Tl mass fraction will be strongly dependent on the amount of hornblende incorporated into the digested portion. STM-1 contains multiple K-bearing phases including alkali feldspar, nepheline and biotite (Snively et al. 1976), and features a bulk Tl mass fraction two orders of magnitude higher than AN-G. On the basis of three digestions, STM-1 appears to exhibit a bimodal distribution for Tl: two distinct mass fraction populations, with the higher mass fraction possibly weakly associated with an isotopically lighter $\varepsilon^{205}$Tl$_{SRM997}$ signature. This may reflect the existence of at least two distinct hosts of Tl, variably incorporated into the sample portion. In contrast, across four digestions Mica-Mg appears to display a range in both Tl mass fraction and $\varepsilon^{205}$Tl$_{SRM997}$, with no clear systematics; this is consistent with relatively small, frequent microparticles of
several Tl-rich and isotopically distinct phases unevenly dispersed throughout the powdered RM.

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

Petrographic information is not available for BHVO-2, but as a basalt, it is unlikely to contain significant amounts of K-rich phases. We do not observe any evidence for the significant Tl mass fraction variations reported in the literature (Table S1), but do see potential evidence of weak Tl isotope ratio heterogeneity.

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

However, it is unlikely that dissolving larger initial masses would improve the precisions achievable for G-2 and BHVO-2; G-2 in particular exhibits a high variance given initial dissolved masses, suggesting that the discrepancy with the one previous report (Rehkämper and Halliday 1999) arises in large part from powder heterogeneity. Rehkämper and Halliday (1999) are known to have made their analysis using a different vial of G-2, potentially indicating heterogeneity between vials. We therefore recommend against use of G-2 as a Tl reference material. For BHVO-2 the variance for \( \varepsilon^{205} \text{Tl}_{\text{SRM997}} \) is less extreme and, unlike G-2, there is no strong evidence for heterogeneity in Tl mass fraction. We therefore recommend caution when employing BHVO-2 as a Tl isotope reference material, but as it is the only basaltic RM with a Tl mass fraction of \( \sim 20 \) ng g\(^{-1}\), we recognise that it is likely the most appropriate choice for studies involving low-Tl igneous samples. As BHVO-1 and BHVO-2 are distinctly different in terms of both mass fraction and isotope ratio values (Table S1, Table 1), care must be taken to ensure that these materials are not confused if using either as a reference material.

In light of concerns regarding potential inhomogeneous contamination during the generation of RMs, we find no evidence that the overall reported range in \( \varepsilon^{205} \text{Tl}_{\text{SRM997}} \) for the RMs analysed here (5.5 \( \varepsilon \)-units, comparable to that of other natural igneous products: see Nielsen \textit{et al.} 2017) is due to contamination of the samples. In particular, there is no systematic variation of Tl isotope composition with RM provider or date of preparation.
Furthermore, the most isotopically distinct result (serpentinite UB-N: $\varepsilon^{205}\text{Tl}_{\text{SRM997}} = +1.8 \pm 0.4$ 2s) is consistent with the findings of Nielsen et al. (2015). To the best of our knowledge these authors provide the only literature report of $\varepsilon^{205}\text{Tl}_{\text{SRM997}}$ in natural serpentinite samples, and these show similarly heavy Tl isotope compositions, providing indirect validation of our isotopically heavy serpentinite RM.

**Summary**

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

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

The following supporting information is available online:

Table S1. Compilation of literature reports of Tl mass fraction data for relevant RMs.
Table S2. ICP-QQQ-MS trace element measurements obtained during this study.

This material is available as part of the online article from:
(This link will take you to the article abstract).

Figure captions

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

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

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

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

**Figure 5.** Variation of Tl mass fraction with $\text{K}_2\text{O}$ mass fraction for all materials except sulphide 14P. Error bars are smaller than symbols. All $\text{K}_2\text{O}$ data is as listed by the material’s supplier. Tl mass fractions were determined by ICP-QQQ-MS at the Open University.

**Figure 6.** Assessment of relationship between test portion size of dissolved sample and isotope ratio variance (2s). For the digested sample mass, the plotted point represents the mean mass weighted by the number of measurements made per dissolution; error bars represent the full range of masses digested for each sample. Points are coloured according to Tl mass fraction as determined by ICP-QQQ-MS.
Table 1.
Literature MC-ICP-MS Tl isotope ratio data for igneous reference materials

<table>
<thead>
<tr>
<th>Reference material</th>
<th>$\varepsilon^{205}$Tl</th>
<th>2s</th>
<th>Dissolutions a</th>
<th>Measurements b</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGV-2</td>
<td>-1.9</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
<td>Baker et al. (2009)</td>
</tr>
<tr>
<td>AGV-2</td>
<td>-3</td>
<td>0.6</td>
<td>8</td>
<td>15</td>
<td>Prytulak et al. (2013)</td>
</tr>
<tr>
<td>AGV-2</td>
<td>-2.7</td>
<td>0.2</td>
<td>5</td>
<td>9</td>
<td>Prytulak et al. (2017)</td>
</tr>
<tr>
<td>BCR-2</td>
<td>-2.5</td>
<td>0.4</td>
<td>4</td>
<td>19</td>
<td>Prytulak et al. (2013)</td>
</tr>
<tr>
<td>BCR-2</td>
<td>-2.5</td>
<td>0.5</td>
<td>12</td>
<td>25</td>
<td>Prytulak et al. (2017)</td>
</tr>
<tr>
<td>BIR-1</td>
<td>1.1</td>
<td>1.2</td>
<td>6</td>
<td>9</td>
<td>Nielsen et al. (2007)</td>
</tr>
<tr>
<td>BHVO-1</td>
<td>-3.5</td>
<td>0.5</td>
<td>10</td>
<td>16</td>
<td>Nielsen et al. (2015)</td>
</tr>
<tr>
<td>BHVO-1</td>
<td>-3.6</td>
<td>0.4</td>
<td>1</td>
<td>16</td>
<td>Shu et al. (2017)</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>-2.1</td>
<td>0.5</td>
<td>2</td>
<td>2</td>
<td>Baker et al. (2009)</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>-1.5</td>
<td>0.4</td>
<td>2</td>
<td>2</td>
<td>Prytulak et al. (2013)</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>-1.5</td>
<td>0.3</td>
<td>10</td>
<td>n.g.</td>
<td>Coggon et al. (2014)</td>
</tr>
<tr>
<td>G-2</td>
<td>1.3</td>
<td>0.7</td>
<td>1</td>
<td>1</td>
<td>Rehkämper and Halliday (1999)</td>
</tr>
</tbody>
</table>

a Number of independent digestions.
b Number of measurement results.
### Table 2: Reference materials investigated in this study

<table>
<thead>
<tr>
<th>RM</th>
<th>Supplier*</th>
<th>Lithology</th>
<th>Key reference</th>
<th>Reported Tl mass fraction</th>
<th>Reported ε²⁰⁵Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>T4P</td>
<td>OREAS</td>
<td>massive magmatic sulphide</td>
<td>Govindaraju (1984a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AL-I</td>
<td>SARM-CRP/GCNRS</td>
<td>albite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AN-G</td>
<td>SARM-CRP/GCNRS</td>
<td>anorthosite</td>
<td>Govindaraju (1980)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCR-2</td>
<td>USGS</td>
<td>basalt</td>
<td>Wilson (1997a)</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>BV0-2</td>
<td>USGS</td>
<td>basalt</td>
<td>Wilson (1997b)</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>CCOQ-1</td>
<td>USGS</td>
<td>carbonatite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FK-N</td>
<td>SARM-CRP/GCNRS</td>
<td>alkali feldspar</td>
<td>Govindaraju (1984b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G-2²</td>
<td>USGS</td>
<td>granite</td>
<td>Fairbairn et al. (1951)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GSP-2</td>
<td>USGS</td>
<td>granodiorite</td>
<td>Wilson (1998)</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>IH-G</td>
<td>SARM-CRP/GCNRS</td>
<td>trachyte</td>
<td>Gilot et al. (1992)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MDA-G</td>
<td>SARM-CRP/GCNRS</td>
<td>trachyte</td>
<td>Gilot et al. (1992)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mica-Fe</td>
<td>SARM-CRP/GCNRS</td>
<td>biotite</td>
<td>Govindaraju (1979)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mica-Mg</td>
<td>SARM-CRP/GCNRS</td>
<td>phlogopite</td>
<td>Govindaraju (1979)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRM 607</td>
<td>BST</td>
<td>nepheline syenite</td>
<td>Heinrich (1960)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>STM-1</td>
<td>USGS</td>
<td>nepheline syenite</td>
<td>Snowdy et al. (1976)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UB-N</td>
<td>SARM-CRP/GCNRS</td>
<td>serpentinite</td>
<td>Govindaraju (1982)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* OREAS: Ore Research & Exploration Assay Standards (Australia); SARM-CRP/GCNRS: 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.

* No longer available for purchase.
Table 3.
Anion exchange separation of Tl (adapted from Nielsen et al. 2004)

<table>
<thead>
<tr>
<th>Step</th>
<th>Eluent</th>
<th>Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Stage I</td>
</tr>
<tr>
<td>load resin</td>
<td>AG&lt;sup&gt;®&lt;/sup&gt; 1-X8 (200–400 mesh) in 0.1 mol l&lt;sup&gt;−1&lt;/sup&gt; HCl</td>
<td>1</td>
</tr>
<tr>
<td>condition</td>
<td>0.1 mol l&lt;sup&gt;−1&lt;/sup&gt; HCl - 5% w/w SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1 + 10</td>
</tr>
<tr>
<td>condition</td>
<td>0.1 mol l&lt;sup&gt;−1&lt;/sup&gt; HCl</td>
<td>1 + 10</td>
</tr>
<tr>
<td>condition</td>
<td>1 mol l&lt;sup&gt;−1&lt;/sup&gt; HCl - 1% v/v Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1 + 3 + 1</td>
</tr>
<tr>
<td>load sample</td>
<td>1 mol l&lt;sup&gt;−1&lt;/sup&gt; HCl - 3% v/v Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>elution (matrix)</td>
<td>0.5 mol l&lt;sup&gt;−1&lt;/sup&gt; HNO&lt;sub&gt;3&lt;/sub&gt; - 3% v/v Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1 + 1 + 1 + 5 + 10</td>
</tr>
<tr>
<td>elution (matrix)</td>
<td>2 mol l&lt;sup&gt;−1&lt;/sup&gt; HNO&lt;sub&gt;3&lt;/sub&gt; - 3% v/v Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1 + 1 + 4 + 10</td>
</tr>
<tr>
<td>elution (matrix)</td>
<td>0.1 mol l&lt;sup&gt;−1&lt;/sup&gt; HCl - 1% v/v Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1 + 1 + 4 + 10</td>
</tr>
<tr>
<td>Tl elution</td>
<td>0.1 mol l&lt;sup&gt;−1&lt;/sup&gt; HCl - 5% w/w SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1 + 1 + 1 + 3 + 9 + 1</td>
</tr>
</tbody>
</table>
Table 4.
Thallium mass fraction data obtained during this study, and comparison with literature data

<table>
<thead>
<tr>
<th>Reference Material</th>
<th>Dissolutions (^a)</th>
<th>Measurements ((n)</th>
<th>[Tl] (ng g(^{-1}))</th>
<th>% RSD</th>
<th>References</th>
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</thead>
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<td><strong>Calibrators</strong></td>
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<tr>
<td>AGV-1</td>
<td>349</td>
<td>14.9</td>
<td>7,8,13,17,24,25,33,34,49,50,53,55</td>
<td>337</td>
<td>4.7</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>2</td>
<td>6</td>
<td>23</td>
<td>4.9</td>
<td>This study*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>22</td>
<td>1,2,5,6,8-10,16,21,23,25-27,30,31,36-41,43,45,48,49,51-53,58</td>
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<td></td>
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<td>22.4</td>
<td>20</td>
<td>28 (GeoReM preferred value)</td>
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<tr>
<td>BIR-1</td>
<td>3</td>
<td>15</td>
<td>1</td>
<td>21</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.8</td>
<td>41</td>
<td>1,8,18,25,32,35,42,46,47,53-56</td>
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<td></td>
<td></td>
<td></td>
<td>2.1</td>
<td>34</td>
<td>28 (GeoReM preferred value)</td>
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<td><strong>Measured reference materials</strong></td>
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<tr>
<td>14P</td>
<td>3</td>
<td>10</td>
<td>100(^\d)</td>
<td>20</td>
<td>This study</td>
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<td>AL-I</td>
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<td>AN-G</td>
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<td>1</td>
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<td>8.0</td>
<td>This study</td>
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<td>BCR-2</td>
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<td>This study</td>
</tr>
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<td></td>
<td>265</td>
<td>13</td>
<td>3,10,12,14,15,19-22,25,26,29,36-38,40,41,43,45,58</td>
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<td>267</td>
<td>13</td>
<td>28 (GeoReM preferred value)</td>
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<tr>
<td>COQ-1</td>
<td>1</td>
<td>7</td>
<td>96</td>
<td>3.9</td>
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<tr>
<td>FK-N</td>
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<td>1</td>
<td>3720</td>
<td>0.5</td>
<td>This study</td>
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<tr>
<td>G-2</td>
<td>1</td>
<td>1</td>
<td>940</td>
<td>6.6</td>
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<td>884</td>
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<td>1500</td>
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<td>0.7</td>
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<td>MDO-G</td>
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<td>1</td>
<td>61</td>
<td>2.0</td>
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<td>Sample</td>
<td>n.</td>
<td>Number of Measurements</td>
<td>Mass Fraction</td>
<td>Reference</td>
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<td>--------------</td>
<td>----</td>
<td>------------------------</td>
<td>---------------</td>
<td>-----------</td>
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<td>Mica-Fe</td>
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<td>1</td>
<td>0.4</td>
<td>This study</td>
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<td></td>
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<td>16800</td>
<td>n.g.</td>
<td>4,11,44</td>
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<td>0.8</td>
<td>This study</td>
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<td>NIST SRM 607</td>
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<td>1</td>
<td>1.1</td>
<td>This study</td>
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<td></td>
<td></td>
<td>2650</td>
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<tr>
<td>STM-1</td>
<td>1</td>
<td>1</td>
<td>1.4</td>
<td>This study</td>
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<td>260</td>
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<td></td>
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</tr>
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<td>UB-N</td>
<td>1</td>
<td>2</td>
<td>4.3</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>41</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* These Tl mass fraction results were obtained for solutions of the calibrator reference materials that were run as unknowns.
† Mass fraction estimated using MC-ICP-MS.

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

<table>
<thead>
<tr>
<th>RM</th>
<th>Dissolutions a</th>
<th>Sessions b</th>
<th>Measurements c</th>
<th>ε(^{205}) Tl</th>
<th>2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>14P</td>
<td>3</td>
<td>1</td>
<td>10</td>
<td>-2.0</td>
<td>0.5</td>
</tr>
<tr>
<td>AL-I</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>-1.5</td>
<td>0.2</td>
</tr>
<tr>
<td>AN-G</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>-2.7</td>
<td>0.4</td>
</tr>
<tr>
<td>BCR-2</td>
<td>3</td>
<td>1</td>
<td>5</td>
<td>-2.4</td>
<td>0.2</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>-1.2</td>
<td>0.7</td>
</tr>
<tr>
<td>COQ-1</td>
<td>3</td>
<td>2</td>
<td>5</td>
<td>-2.3</td>
<td>0.5</td>
</tr>
<tr>
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</table>

\(a\) Total number of independent digestions; (X) gives the number of bomb digestions.

\(b\) Number of measurement sessions during which the RM was analysed.

\(c\) Number of separate analyses.