Tourmaline Reference Materials for the In Situ Analysis of Oxygen and Lithium Isotope Ratio Compositions

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Three tourmaline reference materials sourced from the Harvard Mineralogical and Geological Museum (schorl 112566, dravite 108796 and elbaite 98144), which are already widely used for the calibration of in situ boron isotope measurements, are characterised here for their oxygen and lithium isotope compositions. Homogeneity tests by secondary ion mass spectrometry (SIMS) showed that at sub-nanogram test portion masses, their $^{18}\text{O}/^{16}\text{O}$ and $^{7}\text{Li}/^{6}\text{Li}$ isotope ratios are constant within $\pm 0.27$‰ and $\pm 2.2$‰ (1s), respectively. The lithium mass fractions of the three materials vary over three orders of magnitude. SIMS homogeneity tests showed variations in $^{7}\text{Li}/^{28}\text{Si}$ between 8% and 14% (1s), which provides a measure of the heterogeneity of the Li contents in these three materials. Here, we provide recommended values for $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$ and $\delta^{7}\text{Li}$ for the three Harvard tourmaline reference materials based on results from bulk mineral analyses from multiple, independent laboratories using laser- and stepwise fluorination gas mass spectrometry (for O), and solution multi-collector inductively coupled plasma-mass spectroscopy (for Li). These bulk data also allow us to assess the degree of inter-laboratory bias that might be present in such data sets. This work also re-evaluates the major element chemical composition of the materials by electron probe microanalysis and investigates these presence of a chemical matrix effect on SIMS instrumental mass fractionation with regard to $\delta^{18}\text{O}$ determinations, which was found to be $< 1.6$‰ between these three materials. The final table presented here provides a summary of the isotope ratio values that we have determined for these three materials. Depending on their starting mass, either 128 or 512 splits have been produced of each material, assuring their availability for many years into the future.

Keywords: tourmaline, lithium isotopes, oxygen isotopes, reference materials, SIMS, matrix effect.

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In situ measurement of boron isotope ratios in tourmaline by SIMS and LA-ICP-MS has become a widely used method for investigating fluid–rock interaction in igneous, metamorphic and hydrothermal systems, with important applications to ore genesis studies. Some of this work has been summarised in reviews by Slack and Trumbull (2011), Marschall and Jiang (2011) and in various chapters of the monograph by Marschall and Foster (2018). The rapid growth of B isotope studies on tourmaline is partly due to the availability of well-characterised and demonstrably homogeneous tourmaline reference materials (RMs). Other stable isotope systems that can be applied to tourmaline include H, Li and O, and these have shown their utility in several studies that employed bulk analysis of mineral separates (e.g., Taylor and Palmer 1999, Matthews et al. 2003, Siegel et al. 2016). However, the lack of characterised RMs that are known to be homogeneous at the nanogram to picogram sampling scale has prevented the application of in situ methods to these isotope systems. This is unfortunate, as the combination of two or more isotope systems can reduce ambiguities in models built on laboratory data. In this study, we provide O and Li isotope ratio data for three tourmaline RMs so as to partially meet this need.

Oxygen has three stable isotopes: $^{16}$O, $^{17}$O and $^{18}$O, which have natural abundances of ca. 99.76%, 0.04% and 0.2%, respectively. By convention, the two isotope ratios of oxygen are expressed in delta-notation relative to standard mean ocean water (SMOW) as follows:

$$\delta^{18}O = \left(\frac{^{18}O}{^{16}O_{\text{sample}}} / \frac{^{18}O}{^{16}O_{\text{SMOW}}}\right) - 1 \quad (1)$$

$$\delta^{17}O = \left(\frac{^{17}O}{^{16}O_{\text{sample}}} / \frac{^{17}O}{^{16}O_{\text{SMOW}}}\right) - 1 \quad (2)$$

where the absolute isotope abundance ratio for SMOW is set at $^{18}O/^{16}O = 0.00200520 \pm 0.00000045$ (Baertschi 1976) and $^{17}O/^{16}O = 0.003799 \pm 0.0000008$ (Li et al. 1988). There is abundant literature documenting the utility of oxygen isotopes in identifying fluid provenance, constraining fluid/rock interaction and for isotope-exchange geothermometry (e.g., Valley and Cole 2001, Valley 2003, Sharpe et al. 2016). For most fractionation processes, $\delta^{17}$O shows a close correlation with $\delta^{18}$O. However, small, mass-dependent deviations from such a correlation can now be resolved in terrestrial samples (Barkan and Luz 2005, Pack and Herwartz 2014). Such mass-dependent variations in $\delta^{17}$O are a new tool in understanding oxygen isotope fractionation and/or reservoir-exchange processes (e.g., Herwartz et al. 2015, Sharp et al. 2016). Until now, no certified values are available for any silicate or oxide calibration material for $\delta^{17}$O_SMOW although recent efforts have been made to characterise San Carlos olivine and there are ongoing efforts to standardise the treatment of such data (e.g., Pack et al. 2016, Sharp et al. 2016, Miller et al. 2020, Wostbrock and Cano 2020). Although the efforts presented here do not represent an attempt at an ISO-compliant certification, we nonetheless believe they are a valuable contribution towards addressing this shortage.

Lithium has two stable isotopes, $^6$Li and $^7$Li, with natural abundances of ca. 7.6% and 92.4%, respectively, though their abundance ratio varies considerably in nature. For example, a difference of some 30‰ exists between unaltered MORB and seawater (e.g., Tomascak 2004). The Li isotope system can undergo large fractionation between geological materials (fluids, minerals and melts) during processes including fluid–rock interaction, fluid or melt unmixing, (re)crystallisation and diffusion, making it valuable for many geologic applications (e.g., Teng et al. 2004, Tomascak et al. 2016). Lithium isotope ratios are typically reported in $\delta$-units (‰) with reference to lithium carbonate, LSVEC (now NIST SRM-8545; Flesch and Anderson 1973, Brand et al. 2014) as follows:

$$\delta^7$Li = ($^7$Li/$^6$Li sample/$^7$Li/$^6$Li_SVEC) - 1 \quad (3)$$

where the absolute isotopic abundance ratio for LSVEC is set at $^6$Li/$^7$Li = 0.08215 ± 0.00023 (combined uncertainty at coverage factor $k = 2$; Caplen 2011, Harms and Assonov 2018), equivalent to $^7$Li/$^6$Li ≈ 12.173.

Both oxygen and lithium isotopes in tourmaline can readily be determined by SIMS on polished sample surfaces with a spatial resolution of < 20 µm and analytical repeatabilities at or below ± 1‰ (1σ) in the case of $\delta$Li and better than ± 0.2‰ (1σ) in the case of $\delta^{18}$O. However, in practice such measurements are rarely made due to a lack of suitable tourmaline RMs. For this study, we turned to the widely used Harvard tourmaline suite. Dyar et al. (2001) reported values of $\delta^{18}$O for the tourmaline RMs elbaite, schorl and dravite studied here, albeit prior to the sample splitting done as part of the current investigation. Those analyses were done in one laboratory (Southern Methodist University) only, and no isotope homogeneity tests for O isotopes were carried out at test portion masses relevant for microanalytical applications. Lin et al. (2019) reported values of the Li isotope composition of the Harvard schorl and elbaite materials based on solution nebulisation ICP-MS. Likewise, no isotope homogeneity tests were reported in that study. Finally, Dyar et al. (2001) also reported a single set of 6D values for all three of the materials that are the focus of this current study (see below).

A particular concern in the determination of isotope amount ratios of light elements in tourmaline and other
minerals where a wide major element compositional range exists is the possible presence of a chemical matrix effect. Bell et al. (2009) discussed the chemical matrix effect in the context of SIMS Li isotope measurements in olivine. Because multiple and chemically diverse tourmaline RMs exist for B isotope analysis, workers have been able to demonstrate a small but significant chemical matrix effect in both SIMS (e.g., Kutzschbach et al. 2017, Marger et al. 2020) and ICP-MS applications (Mkavá and Košler 2014). The issue of a matrix effect for the lithium and oxygen isotope SIMS analyses is discussed below.

Materials

Dyar et al. (2001) and Leeman and Tonarini (2001) reported on the major element compositions and chemical homogeneity of three megacystic tourmaline samples from the Harvard Mineralogical and Geological Museum, designated elbaite, schorl and dravite (note: ‘dravite’ is a misnomer, see below). Tonarini et al. (2003) and Gonfiatti et al. (2003) suggested a fourth natural tourmaline (IAEA-B4), which has a major element composition similar to that of the Harvard schorl, as a further RM for in situ chemical and B isotope analyses. We did not have access to large amounts of the B4 material with which to generate metrological splits, so we have not included this material in the current characterisation project. Hence, this study focused exclusively on the three materials described below:

Elbaite (Harvard Mineralogical and Geological Museum #98144): This sample is from a 17.5 g single crystal collected from a granitic pegmatite in Minas Gerais, Brazil.

Schorl (HMGM #112566): This sample is from a 48.4 g single crystal collected from a granitic pegmatite in Zambesi Province, Mozambique (Hutchinson and Claus 1956).

Dravite (HMGM #108796): This sample has been previously described as a 1.66 g single crystal collected from alluvium in Madagascar (Dyar et al. 2001), but this mass seems to be erroneous. Based on its size (Frondel and Biedl 1966), gives 560 g as the mass) and locality, the sample was possibly derived from a granitic pegmatite. Of the amount of material provided to the first author by the Harvard Museum, two large, euhedral crystals with masses of 134 and 194 g remain after producing our metrological splits (see below).

Based on the chemical analyses reported in Dyar et al. (2001) and in this study, the schorl and elbaite samples are appropriately named, whereas the ‘dravite’ term is misleading since this tourmaline has low Al contents, high Ca and an Fe(Fe + Mg) ratio of ~ 0.5, whereby Fe³⁺ dominates and substitutes for Al (Frondel et al. 1966). Using the current nomenclature of Henry et al. (2011), this composition is an intermediate schorl–dravite–feruvite, but in the interests of historical consistency, we will continue to refer to the HMGM #108796 material as ‘dravite’. The chemical classifications of the three materials are shown in Figure 1. We note that the δD (Dyar et al. 2001) and δ¹¹B (Leeman and Tonarini 2001) have already been reported for these materials (see Table 7). More recently, Marger et al. (2020) have reported revised δ¹¹B bulk values for the three tourmaline materials (also shown on Table 7) that are as much as 1.6‰ lower than the values published previously.

We used a riffle splitter in order to generate ~ 100 mg units of < 2 mm fragments from single crystals from each of the three tourmaline specimens; these were placed in 0.5 ml screw-top plastic vials. In total, we generated 256 vials of the elbaite, 128 vials of the schorl and 512 vials of the dravite. In order to give these unique metrological identifiers, each set of splits has been given a Harvard catalogue number that is appended with an additional decimal place (i.e., 98144.1 Elbaite, 112566.1 Schorl and 108796.1 Dravite). With the exception of the wet chemical δLi data, which were performed on fragments removed from the parent samples prior to splitting, all data reported here were made on tourmaline fragments taken from such vials of the split material.

![Figure 1](image-url)  
Figure 1. Al-Fe-Mg diagram (molar proportions) showing the composition of the three Harvard tourmaline RMs investigated by this study (see Table 1). The positions of some of the more common tourmaline end members as well as that of the ‘B4’ tourmaline RM (Tonarini et al. 2003) are also indicated. We point the reader to Marger et al. (2019, 2020) for other recent efforts to characterise alternative tourmaline isotope calibration materials.
Table 1. Summary results of homogeneity tests by electron probe microanalysis

|                  | SiO$_2$ | TiO$_2$ | Al$_2$O$_3$ | FeO  | MnO  | MgO  | CaO  | Na$_2$O | K$_2$O | B$_2$O$_3$ | ZnO | Li$_2$O | F    | OH | -O$_2$ = 2F | Total (% m/m) |
|------------------|---------|---------|-------------|------|------|------|------|---------|--------|------------|------|---------|------|-----|-----------------|----------------|
| **Schorl 12566.1** |         |         |             |      |      |      |      |         |        |            |      |         |      |     |                 |                |
| Potdam           |         |         |             |      |      |      |      |         |        |            |      |         |      |     |                 |                |
| Fragment 1       | Mean    | 32.20   | 0.66        | 32.01| 14.87| 0.19 | 0.16 | 2.12    | 0.05   | 10.04      | nd  | nd      | nd  | nd  | 93.34            |                |
|                  | n = 4   | 0.29    | 0.05        | 0.13 | 0.32 | 0.22 | 0.03 | 0.08    | 0.02   | 0.44       | nd  | nd      | nd  | nd  |                  |                |
| 1s (n = 4)       |         | 0.25    | 0.02        | 0.11 | 0.50 | 0.07 | 0.03 | 0.02    | 0.07   | 0.03       | 0.03 | 0.49    |     |     |                 |                |
| Fragment 9       | Mean    | 32.50   | 0.65        | 31.85| 14.15| 1.03 | 0.18 | 0.16    | 2.06   | 0.04       | 10.17| nd      | nd  | nd  | 92.79            |                |
|                  | n = 4   | 0.31    | 0.06        | 0.35 | 0.76 | 0.09 | 0.02 | 0.03    | 0.07   | 0.03       | 0.03 | 0.28    |     |     |                 |                |
| Fragment 12      | Mean    | 32.51   | 0.49        | 32.08| 14.60| 1.07 | 0.22 | 0.14    | 2.12   | 0.04       | 10.37| nd      | nd  | nd  | 93.64            |                |
|                  | n = 4   | 0.59    | 0.07        | 0.18 | 0.50 | 0.18 | 0.03 | 0.03    | 0.06   | 0.03       | 0.03 | 0.22    |     |     |                 |                |
| Fragment 14      | Mean    | 32.48   | 0.68        | 31.61| 14.99| 0.88 | 0.26 | 0.13    | 2.12   | 0.05       | 10.01| nd      | nd  | nd  | 93.21            |                |
|                  | n = 4   | 0.56    | 0.07        | 0.17 | 0.38 | 0.07 | 0.02 | 0.05    | 0.05   | 0.02       | 0.02 | 0.26    |     |     |                 |                |
| Fragment 15      | Mean    | 32.28   | 0.66        | 32.01| 14.13| 1.18 | 0.18 | 0.13    | 2.16   | 0.06       | 10.04| nd      | nd  | nd  | 92.83            |                |
|                  | n = 4   | 0.37    | 0.09        | 0.32 | 0.33 | 0.16 | 0.04 | 0.06    | 0.05   | 0.02       | 0.02 | 0.22    |     |     |                 |                |
| Schorl grand mean| Mean    | 32.37   | 0.63        | 31.99| 14.55| 1.02 | 0.21 | 0.15    | 2.13   | 0.04       | 10.11| nd      | nd  | nd  | 93.21            |                |
|                  | n (n = 24)| 0.44   | 0.10        | 0.30 | 0.60 | 0.17 | 0.04 | 0.04    | 0.07   | 0.03       | 0.37 |         |     |     |                 |                |
|                  | 1s (%)  | 1.37    | 1673        | 0.95 | 4.15 | 1662 | 1988 | 2793    | 3.38   | 5997       | 3.62 |         |     |     |                 |                |
| **Madison**      |         |         |             |      |      |      |      |         |        |            |      |         |      |     |                 |                |
| Fragment 1       | Mean    | 33.43   | 0.54        | 34.33| 15.05| 1.13 | 0.22 | 0.15    | 2.01   | 0.03       | 9.23 | 0.25    | 0.12 | 0.39 | 1.89               | 98.59           |
|                  | n = 4   | 0.06    | 0.02        | 0.13 | 0.08 | 0.06 | 0.01 | 0.07    | 0.06   | 0.06       | 0.64 | 0.06    | 0.02 | 0.55 |                  |                |
| Fragment 2       | Mean    | 33.23   | 0.54        | 34.42| 14.63| 1.23 | 0.21 | 0.14    | 2.03   | 0.05       | 9.30 | 0.32    | 0.12 | 0.44 | 1.49               | 97.96           |
|                  | n = 4   | 0.15    | 0.02        | 0.11 | 0.15 | 0.06 | 0.01 | 0.01    | 0.06   | 0.01       | 0.42 | 0.05    | 0.02 | 0.44 |                  |                |
| Fragment 3       | Mean    | 33.35   | 0.57        | 33.74| 15.52| 1.17 | 0.29 | 0.17    | 2.06   | 0.04       | 10.01| 0.24    | 0.12 | 0.48 | 1.17               | 98.73           |
|                  | n = 4   | 0.02    | 0.06        | 1.52 | 1.59 | 0.22 | 0.19 | 0.05    | 0.16   | 0.01       | 0.43 | 0.06    | 0.10 | 0.13 |                  |                |
| Fragment 4       | Mean    | 33.42   | 0.52        | 34.19| 14.85| 1.19 | 0.19 | 0.13    | 2.02   | 0.04       | 9.77 | 0.28    | 0.12 | 0.39 | 1.51               | 98.46           |
|                  | n = 4   | 0.14    | 0.02        | 0.16 | 0.13 | 0.08 | 0.02 | 0.02    | 0.04   | 0.00       | 0.46 | 0.07    | 0.02 | 0.35 |                  |                |
| Fragment 5       | Mean    | 32.84   | 0.57        | 34.29| 14.57| 1.22 | 0.20 | 0.13    | 1.97   | 0.04       | 10.17| 0.23    | 0.12 | 0.43 | 1.98               | 98.58           |
|                  | n = 4   | 0.16    | 0.02        | 0.05 | 0.12 | 0.04 | 0.01 | 0.01    | 0.06   | 0.01       | 0.81 | 0.13    | 0.01 | 0.56 |                  |                |
| Fragment 6       | Mean    | 33.37   | 0.55        | 34.39| 14.73| 1.20 | 0.18 | 0.13    | 2.05   | 0.04       | 9.34 | 0.26    | 0.12 | 0.42 | 1.68               | 98.28           |
|                  | n = 4   | 0.16    | 0.01        | 0.10 | 0.13 | 0.04 | 0.02 | 0.01    | 0.04   | 0.01       | 0.72 | 0.08    | 0.03 | 0.37 |                  |                |
| School grand mean | SiO₂ | TiO₂ | Al₂O₃ | FeO  | MnO  | MgO  | CaO  | Na₂O | K₂O | B₂O₃ | ZnO  | Li₂O | F   | OH  | -O₂ = 2F | Total (% m/m) |
|------------------|------|------|-------|------|------|------|------|------|-----|------|------|------|-----|-----|----------|----------------|
| Schorl | 33.3 | 0.55 | 342   | 14.9 | 1.19 | 0.21 | 0.14 | 2.02 | 0.04 | 96.4 | 0.26 | 0.12 | 0.43 | 1.62 | 0.18 | 98.43 |
| (n = 24) | 0.25 | 0.03 | 0.60  | 0.67 | 0.10 | 0.08 | 0.03 | 0.08 | 0.01 | 0.65 | 0.08 | 0.05 | 0.49 |      |          |                |
| (n = %) | 0.75 | 5.71 | 1.77  | 4.50 | 8.40 | 37.25| 1780 | 3.99 | 22.49| 674 | 2933 |      |      |      |          |                |
| Dyar et al. (2001) | 33.4 | 0.57 | 331   | 17.3 | 1.20 | 0.21 | 0.11 | 1.92 | 0.02 | 11.4 | nd   | nd   | nd  | nd   | nd       | 87.88 |

| Patsfold |                      | SiO₂ | TiO₂ | Al₂O₃ | FeO  | MnO  | MgO  | CaO  | Na₂O | K₂O | B₂O₃ | ZnO  | Li₂O | F   | OH  | -O₂ = 2F | Total (% m/m) |
|----------|----------------------|------|------|-------|------|------|------|------|------|-----|------|------|------|-----|-----|----------|----------------|
| Fragment 1 | Mean | 33.05 | 1.58 | 2088  | 15.63| 0.08 | 7.86 | 2.41 | 1.60 | 0.10| 96.60| nd   | nd   | nd  | nd   | nd       | 92.79 |
| (n = 4)  | 0.31 | 0.06 | 0.18  | 0.39 | 0.10 | 0.08 | 0.11 | 0.04 | 0.03 | 0.32 |      |      |      |      |          |                |
| Fragment 2 | Mean | 33.39 | 1.52 | 2238  | 13.76| 0.03 | 8.28 | 2.30 | 1.71 | 0.06| 10.44| nd   | nd   | nd  | nd   | nd       | 93.86 |
| (n = 4)  | 0.28 | 0.08 | 0.22  | 0.62 | 0.05 | 0.15 | 0.09 | 0.04 | 0.04 | 0.45 |      |      |      |      |          |                |
| Fragment 3 | Mean | 33.20 | 1.49 | 2231  | 13.91| 0.02 | 8.11 | 2.39 | 1.74 | 0.06| 10.21| nd   | nd   | nd  | nd   | nd       | 93.43 |
| (n = 4)  | 0.29 | 0.17 | 0.20  | 0.13 | 0.04 | 0.13 | 0.08 | 0.07 | 0.04 | 0.26 |      |      |      |      |          |                |
| Fragment 4 | Mean | 33.30 | 1.53 | 2133  | 15.31| 0.00 | 8.14 | 2.59 | 1.47 | 0.06| 9.93 | nd   | nd   | nd  | nd   | nd       | 93.65 |
| (n = 4)  | 0.07 | 0.10 | 0.21  | 0.79 | 0.00 | 0.11 | 0.06 | 0.08 | 0.01 | 0.39 |      |      |      |      |          |                |
| Fragment 5 | Mean | 33.21 | 1.53 | 2087  | 15.47| 0.05 | 8.16 | 2.67 | 1.43 | 0.05| 10.57| nd   | nd   | nd  | nd   | nd       | 93.60 |
| (n = 4)  | 0.33 | 0.08 | 0.28  | 0.63 | 0.05 | 0.20 | 0.08 | 0.05 | 0.02 | 0.34 |      |      |      |      |          |                |
| Fragment 6 | Mean | 33.24 | 1.49 | 2209  | 14.78| 0.08 | 8.25 | 2.29 | 1.76 | 0.10| 10.13| nd   | nd   | nd  | nd   | nd       | 94.20 |
| (n = 4)  | 0.19 | 0.11 | 0.17  | 0.41 | 0.09 | 0.08 | 0.09 | 0.03 | 0.02 | 0.28 |      |      |      |      |          |                |
| Dravite grand mean | 33.16 | 1.52 | 2164  | 14.81| 0.05 | 8.13 | 2.44 | 1.62 | 0.07 | 10.15|      |      |      |      |          | 93.59 |

| Madison |                      | SiO₂ | TiO₂ | Al₂O₃ | FeO  | MnO  | MgO  | CaO  | Na₂O | K₂O | B₂O₃ | ZnO  | Li₂O | F   | OH  | -O₂ = 2F | Total (% m/m) |
|---------|----------------------|------|------|-------|------|------|------|------|------|-----|------|------|------|-----|-----|----------|----------------|
| Fragment 1 | Mean | 34.10 | 1.60 | 2340  | 13.89| 0.01 | 8.92 | 2.32 | 1.69 | 0.06| 10.37| bdl  | bdl  | 0.46| 1.93 | 0.19 | 98.55 |
| (n = 4)  | 0.14 | 0.02 | 0.10  | 0.25 | 0.01 | 0.04 | 0.02 | 0.03 | 0.01 | 0.74 |      |      |      |      |      |      |      |
| Fragment 2 | Mean | 33.79 | 1.86 | 2187  | 16.24| -0.02| 8.30 | 2.72 | 1.50 | 0.06| 10.00| bdl  | bdl  | 0.37| 2.43 | 0.16 | 98.99 |
| (n = 4)  | 0.23 | 0.02 | 0.07  | 0.14 | 0.01 | 0.09 | 0.02 | 0.03 | 0.01 | 0.24 |      |      |      |      |      |      |      |
| Fragment 3 | Mean | 34.29 | 1.59 | 2336  | 13.86| 0.03 | 8.93 | 2.32 | 1.72 | 0.06| 9.88 | bdl  | bdl  | 0.50| 2.19 | 0.21 | 98.52 |
| (n = 4)  | 0.15 | 0.04 | 0.19  | 0.24 | 0.01 | 0.12 | 0.02 | 0.07 | 0.01 | 0.22 |      |      |      |      |      |      |      |
| Fragment 4 | Mean | 34.50 | 1.72 | 2341  | 14.28| 0.00 | 8.48 | 2.46 | 1.64 | 0.07| 10.18| bdl  | bdl  | 0.47| 2.07 | 0.20 | 99.07 |
| (n = 4)  | 0.21 | 0.01 | 0.07  | 0.15 | 0.02 | 0.03 | 0.02 | 0.02 | 0.00 | 0.39 |      |      |      |      |      |      |      |
| Fragment 5 | Mean | 33.79 | 1.61 | 2232  | 15.85| 0.00 | 8.27 | 2.53 | 1.59 | 0.07| 9.54 | bdl  | bdl  | 0.38| 2.52 | 0.16 | 98.31 |
| (n = 4)  | 0.18 | 0.03 | 0.09  | 0.14 | 0.02 | 0.15 | 0.04 | 0.06 | 0.00 | 0.17 |      |      |      |      |      |      |      |
| Fragment 6 | Mean | 33.73 | 1.59 | 2250  | 15.66| 0.02 | 8.31 | 2.48 | 1.61 | 0.05| 9.66 | bdl  | bdl  | 0.38| 2.60 | 0.16 | 98.34 |
|                | SiO₂  | TiO₂  | Al₂O₃ | FeO   | MnO   | MgO   | CaO   | Na₂O  | K₂O   | B₂O₃  | ZnO   | Li₂O  | F     | OH   | -O₂ = 2F | Total  |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|---------|--------|
|                |       |       |       |       |       |       |       |       |       |       |       |       |       |       |         |        |
| **Dravite**    |       |       |       |       |       |       |       |       |       |       |       |       |       |       |         |        |
| grand mean     | 0.13  | 0.02  | 0.02  | 0.15  | 0.09  | 0.02  | 0.09  | 0.01  | 0.09  | 0.01  | 0.44  | 0.04  | 0.34  |       | 2F     | 0.34   |
| s (n = 4)      | 34.0  | 1.66  | 22.8  | 14.9  | 0.01  | 8.53  | 2.47  | 1.63  | 0.06  | 9.94  | ball  | ball  | 0.43  | 2.29  | 0.18   | 98.63  |
| **Dyar et al.**|       |       |       |       |       |       |       |       |       |       |       |       |       |       |         |        |
| (2001)         | 0.33  | 0.10  | 0.63  | 1.0   | 0.02  | 0.30  | 0.14  | 0.09  | 0.01  | 0.47  |       |       |       |       |         |        |
| mean           | 34.7  | 1.6   | 22.0  | 14.1  | –     | 8.7   | 2.5   | 1.5   | 0.05  | 10.9  | nd    | nd    | nd    | nd    | –       | 85.23  |
| **Frondel et al.**|       |       |       |       |       |       |       |       |       |       |       |       |       |       |         |        |
| (1966)         | 0.15  | 0.56  | 33.85 | 6.25  | 0.07  | 2.86  | 0.11  | 2.71  | 0.02  | 1.00  | nd    | nd    | nd    | nd    | –       | 95.48  |
| **ELBAITE 98144.1** |       |       |       |       |       |       |       |       |       |       |       |       |       |       |         |        |
|                 |       |       |       |       |       |       |       |       |       |       |       |       |       |       |         |        |
| **Potsdam**    |       |       |       |       |       |       |       |       |       |       |       |       |       |       |         |        |
| Fragment 1     | 35.23 | 0.12  | 35.57 | 5.64  | 0.45  | 0.89  | 0.16  | 2.68  | 0.02  | 10.85 | nd    | nd    | nd    | nd    | –       | 91.60  |
| s (n = 4)      | 35.22 | 0.20  | 35.27 | 6.12  | 0.45  | 1.12  | 0.11  | 2.66  | 0.03  | 10.74 | nd    | nd    | nd    | nd    | –       | 91.92  |
| Fragment 4     | 34.86 | 0.56  | 33.85 | 6.25  | 0.07  | 2.86  | 0.11  | 2.71  | 0.02  | 1.002 | nd    | nd    | nd    | nd    | –       | 91.30  |
| s (n = 4)      | 0.40  | 0.06  | 0.20  | 0.62  | 0.01  | 0.08  | 0.02  | 0.03  | 0.01  | 0.33  |       |       |       |       | –       | 91.90  |
| Fragment 5     | 34.71 | 0.28  | 35.34 | 6.70  | 0.42  | 1.11  | 0.06  | 2.67  | 0.03  | 10.58 | nd    | nd    | nd    | nd    | –       | 91.95  |
| s (n = 4)      | 0.15  | 0.03  | 0.37  | 0.26  | 0.05  | 0.13  | 0.02  | 0.09  | 0.01  | 0.27  |       |       |       |       | –       | 92.56  |
| Fragment 6     | 35.08 | 0.53  | 32.84 | 6.99  | 0.11  | 3.56  | 0.06  | 2.65  | 0.04  | 10.72 | nd    | nd    | nd    | nd    | –       | 91.84  |
| s (n = 4)      | 0.30  | 0.02  | 0.14  | 0.18  | 0.14  | 0.03  | 0.06  | 0.06  | 0.03  | 0.36  |       |       |       |       | –       | 91.85  |
| Fragment 10    | 35.12 | 0.40  | 34.34 | 6.35  | 0.14  | 1.86  | 0.06  | 2.72  | 0.03  | 10.82 | nd    | nd    | nd    | nd    | –       | 91.85  |
| s (n = 4)      | 0.36  | 0.04  | 0.19  | 0.13  | 0.08  | 0.03  | 0.02  | 0.09  | 0.03  | 0.34  |       |       |       |       | –       | 91.85  |
| **Elbaite**    |       |       |       |       |       |       |       |       |       |       |       |       |       |       |         |        |
| grand mean     | 0.40  | 0.17  | 1.03  | 0.55  | 0.20  | 1.02  | 0.06  | 0.08  | 0.02  | 0.45  |       |       |       |       |         |        |
| s (n = 24)     | 34.96 | 0.34  | 34.67 | 6.31  | 0.28  | 1.54  | 0.08  | 2.67  | 0.03  | 10.63 |       |       |       |       |         |        |
| s (%)          | 1.15  | 48.60 | 2.99  | 8.63  | 74.95 | 53.54 | 59.59 | 2.93  | 79.12 | 42.0  |       |       |       |       |         |        |
| **ELBAITE 98144.1 (non-green)** |       |       |       |       |       |       |       |       |       |       |       |       |       |       |         |        |
| **Madison**    |       |       |       |       |       |       |       |       |       |       |       |       |       |       |         |        |
| Fragment 1     | 36.14 | 0.56  | 36.07 | 6.72  | 0.13  | 2.98  | 0.07  | 2.63  | 0.02  | 10.21 | ball  | 1.97  | 1.23  | 0.38  | 0.52   | 98.59  |
| s (n = 4)      | 0.17  | 0.02  | 0.08  | 0.09  | 0.04  | 0.08  | 0.01  | 0.03  | 0.01  | 0.28  |       | 0.02  | 0.35  |       | –       | 98.59  |
| Fragment 2     | 36.01 | 0.64  | 34.91 | 7.22  | 0.11  | 3.74  | 0.06  | 2.63  | 0.03  | 9.27  | ball  | 1.97  | 1.14  | 1.02  | 0.48   | 98.25  |
### Table 1 (continued)

Summary results of homogeneity tests by electron probe microanalysis

|                        | SiO$_2$ | TiO$_2$ | Al$_2$O$_3$ | FeO  | MnO  | MgO  | CaO  | Na$_2$O | K$_2$O | B$_2$O$_3$ | ZnO  | Li$_2$O | F    | OH   | -O$_2$ = 2F | Total (% m/m) |
|------------------------|---------|---------|-------------|------|------|------|------|---------|--------|------------|------|--------|------|------|----------------|----------------|
| **Fragment 3 (n = 4)** |         |         |             |      |      |      |      |         |        |            |      |        |      |      |                |                |
| Mean                   | 36.01   | 0.09    | 0.03        | 0.05 | 0.11 | 0.03 | 0.06 | 0.01    | 0.06   | 10.69      | 0.02 | 1.97   | 1.42 | 0.55 | 0.60          | 98.25          |
| 1s                     | 0.22    | 0.17    | 0.27        | 0.15 | 0.05 | 0.03 | 0.02 | 0.02    | 0.01   | 0.01       | 0.02 | 0.04   | 0.04 | 0.02 | 0.22         |                |
| **Fragment 4 (n = 4)** |         |         |             |      |      |      |      |         |        |            |      |        |      |      |                |                |
| Mean                   | 36.14   | 0.28    | 0.27        | 0.15 | 0.05 | 0.03 | 0.02 | 0.01    | 0.02   | 10.73      | 0.02 | 1.97   | 1.43 | 1.12 | 0.60         | 98.27          |
| 1s                     | 0.23    | 0.02    | 0.02        | 0.13 | 0.11 | 0.03 | 0.03 | 0.01    | 0.01   | 0.01       | 0.01 | 0.02   | 0.02 | 0.05 | 0.29         |                |
| **Fragment 5 (n = 4)** |         |         |             |      |      |      |      |         |        |            |      |        |      |      |                |                |
| Mean                   | 36.16   | 0.30    | 0.30        | 0.13 | 0.11 | 0.03 | 0.03 | 0.01    | 0.01   | 10.91      | 0.00 | 0.01   | 0.01 | 0.01 | 0.85         | 98.39          |
| 1s                     | 0.23    | 0.02    | 0.02        | 0.13 | 0.11 | 0.03 | 0.03 | 0.01    | 0.01   | 0.01       | 0.01 | 0.02   | 0.02 | 0.05 | 0.57         |                |
| Elbaite (green) grand mean | 36.07  | 0.45    | 36.38       | 0.24 | 0.22 | 0.09 | 0.27 | 0.02    | 0.10   | 9.46       | bdl  | 1.97   | 1.43 | 0.39 | 0.48         | 98.73          |
| 1s (n = 4)             | 0.17    | 0.03    | 0.17        | 0.11 | 0.04 | 0.01 | 0.02 | 0.01    | 0.01   | 0.01       | 0.01 | 0.02   | 0.02 | 0.05 | 0.57         |                |
| **Madison**            |         |         |             |      |      |      |      |         |        |            |      |        |      |      |                |                |
| Fragment 1 (n = 4)     | 0.04    | 0.18    | 0.17        | 0.17 | 0.14 | 0.02 | 0.02 | 0.01    | 0.02   | 0.01       | 0.01 | 0.01   | 0.01 | 0.01 | 0.19         | 98.13          |
| Mean                   | 36.20   | 0.17    | 0.17        | 0.14 | 0.05 | 0.03 | 0.03 | 0.03    | 0.04   | 0.02       | 0.04 | 0.02   | 0.04 | 0.02 | 0.19         |                |
| 1s (n = 4)             | 0.05    | 0.01    | 0.01        | 0.09 | 0.09 | 0.03 | 0.04 | 0.04    | 0.04   | 0.04       | 0.04 | 0.04   | 0.04 | 0.04 | 0.25         |                |
| Fragment 2 (n = 4)     | 0.08    | 0.23    | 0.01        | 0.13 | 0.13 | 0.04 | 0.02 | 0.01    | 0.01   | 0.01       | 0.01 | 0.01   | 0.01 | 0.01 | 0.15         |                |
| Mean                   | 35.97   | 0.12    | 0.01        | 0.12 | 0.12 | 0.03 | 0.02 | 0.02    | 0.02   | 10.03      | 0.02 | 1.97   | 1.48 | 1.17 | 0.62         | 98.05          |
| 1s (n = 4)             | 0.08    | 0.01    | 0.01        | 0.12 | 0.12 | 0.03 | 0.02 | 0.02    | 0.02   | 1.03       | 0.02 | 1.97   | 1.48 | 1.17 | 0.62         |                |
| Elbaite (green) grand mean | 35.87  | 0.13    | 0.88        | 0.58 | 0.59 | 0.14 | 0.26 | 0.02    | 0.02   | 9.96       | bdl  | 1.97   | 1.46 | 0.92 | 0.62         | 98.87          |
| 1s (n = 16)            | 0.30    | 0.05    | 0.23        | 0.28 | 0.28 | 0.04 | 0.27 | 0.02    | 0.02   | 0.01       | 0.01 | 0.06   | 0.06 | 0.32 |                |                |
| Elbaite (green)grand mean |         |         |             |      |      |      |      |         |        |            |      |        |      |      |                |                |
| 1s (%)                 | 0.85    | 0.05    | 0.62        | 0.46 | 0.46 | 0.44 | 1.50 | 1.50    | 1.50   | 4.24       | 5.35 | 3.84   | 3.43 | 83.24 | 83.24 | 83.24 |
| **Dyar et al. (2001)** | Mean    | 36.5    | 0.43        | 35.0  | 6.36 | 0.02 | 2.12 | 0.09    | 2.55   | 0.02       | 83.4 | 83.24 | 83.24 | 83.24 | 83.24 | 83.24 |
Table 1 (continued).
Summary results of homogeneity tests by electron probe microanalysis

| NIST SRM 610 glass | SiO₂ | TiO₂ | Al₂O₃ | FeO | MnO | MgO | CaO | Na₂O | K₂O | B₂O₃ | ZnO | Li₂O | F | OH | O = 2F |
|-------------------|------|------|-------|-----|-----|-----|-----|------|-----|------|-----|-----|---|---|------|
| Potsdam           | Mean | 66.49| 0.08  | 1.78| 0.10| 0.10| 008 | 12.40| 0.06| 1.07 | nd  | nd  | nd | nd  | 93.70 |
| 1s (n = 13)       |      | 0.51 | 0.06  | 0.05| 0.10| 0.07| 003 | 0.24 | 0.23| 0.04 | 0.39| 0.24| 0.23| 81.64 |
| 1s (%)            |      | 0.77 | 81.64 | 2.54| 96.73| 1.95| 96.73| 2.54 | 96.73| 1.95 | 96.73| 2.54 | 96.73| 2.54 |
| Jochum et al. (2011) | Preferred | 69.70 | 81.64 | 2.54| 96.73| 1.95| 96.73| 2.54 | 96.73| 1.95 | 96.73| 2.54 | 96.73| 2.54 |

bdl, below detection limits; nd, not determined.

Values are in % m/m; total Fe calculated as FeO; all data reported in Table S1.

Instruments and analytical conditions used: GFZ Potsdam, July 2019, JEOL Hyperprobe JXA-8500F with field-emission cathode and five wavelength-dispersive spectrometers. 10 kV accelerating voltage, 10 nA beam current 8–10 µm beam diameter. Counting times for peaks/background were 60/30 s for B; 2010 s for Fe, Mn and Ti; and 10/5 s for Na, Ca, Mg, Si, Al and K. Calibration materials: schorl (B, Si, Al and Fe), orthoclase (K), diopside (Ca and Mg), rhodonite (Mn), rutile (Ti) and tugtupite (Na). Only Kα lines were used, with the first sequence: B (LDEB), Fe (LIF), K (PETJ), Al (TAP) and Si (PETH); and second: Mn (LIF), Ca (PETJ) and Na (TAP); and last: Ti (LIF) and Mg (TAP). Relative analytical uncertainties (1σ) are ~ 1% for Si, ~ 3% for Al and < 5% for B. Deviation of NIST SRM 610 SiO₂ from the recommended value (Jochum et al. 2011) is due to Si being calibrated on tourmaline. Data reduction used the φ(ρZ) correction scheme (CITZAF; Armstrong 1995). Analyses of UW-Madison in February 2020 by CAMECA SXFive FE with five wavelength-dispersive spectrometers and Praba for EPMA software. Two conditions were utilised: 7 kV accelerating voltage, 40 nA and 10 µm defocused beam for O, B and F; 15 kV, 20 nA and 10 µm defocused beam for the balance of the elements. Counting times were 10 s on peak and 5 s each on two background positions. B was measured with PC2 (98 Å 2d) and O and F with PCO (45 Å 2d) layered synthetic diffractors. A small overlap of Fe L upon F Ka was corrected inside the matrix correction, which was the full PAP phi-ρho-Z. The mass absorption coefficients of Bastin and of Pouchou for the other elements were applied. Calibration materials were as follows: NIST SRM K326 (B), Burma jadeite – London Natural History Museum (Na, Al, Si and O), NIST K411 glass (Mg and Ca), Harvard University haematite (Fe), Asbestos microcline (K), synthetic TiO₂ (Ti), synthetic tephroite (Mn), synthetic ZnO (Zn) and Thomas Range F-topaz (F). The tourmalines fragments and the standards were mounted together in the same mount and carbon-coated with ~ 200 nm of carbon (polished brass colour technique). Minimum detection limits (MDLs) for the following low-concentration oxides for each individual spot analysis were as follows: K₂O, 0.02; CaO, 0.02; TiO₂, 0.03; and ZnO, 0.13% m/m. Differential PHA with wide windows was used for O, B and F, whereas integral PHA was used for the other elements. For the purposes of matrix correction, Li₂O was also input into the composition of the tourmaline fragments, based upon the values presented elsewhere in this paper. After all of the measured oxygen was accounted for by stoichiometric appropriation (including Fe as FeO), any remaining oxygen was assigned to OH. These OH values are considered appropriate for purposes of the matrix correction.

B₂O₃ values from Dyar et al. (2001) are from the GFZ laboratory and should be superseded by those reported here.
Homogeneity assessments

Electron probe microanalysis (EPMA) for major elements

The characterisation study by Dyar et al. (2001) reported homogeneity testing in the form of EPMA traverses across single sections of the original crystals as well as mean values from four independent EPMA laboratories. Most of those reported EPMA measurement results, however, showed very low analytical totals, which can be improved upon by utilising up-to-date EPMA procedures for optimal matrix correction accuracy. Also, there have been no data previously reported describing the chemical heterogeneity between random fragments that are more representative of each of the three materials. For this reason, we conducted new EPMA measurements using a JEOL JXA8500F instrument at the GFZ Potsdam and a Cameca SXFive FE instrument at the University of Wisconsin-Madison, both of which used a single vial of each tourmaline material prepared by riffling during the current investigation. Both laboratories analysed six randomly selected fragments from a single split of each of the three tourmaline materials, whereby each fragment was analysed four times at broadly dispersed locations. In Madison, optically distinct (green vs. non-green) elbaite fragments were recognised and these were analysed separately (Table 1). Additional analyses at GFZ Potsdam were made of the silicate glass NIST SRM 610 for an ‘internal precision’ and repeatability check.

The EPMA measurement results and method descriptions are reported in Table 1, and the full data set is available in Table S1. Variations were found in the degree of homogeneity in these sets of fragments, making it difficult to define unique recommended values for the schorl and the dravite geneity in these sets of fragments, making it difficult to define

Table S1. Variations were found in the degree of homo-

are reported in Table 1, and the full data set is available in

We conclude that schorl 112566.1, dravite 108796.1 and to a certain extent elbaite 98144.1 are suitable for use as EPMA calibration and quality control materials. Any particular fragment composition should fall within the bounds of the reported compositions in Table 1, provided at least 98% m/m of the composition (including Li and OH) is accounted for in the EPMA matrix correction.

SIMS lithium testing

We used the Potsdam Cameca 1280-HR instrument to assess both the Li mass fraction and 8Li heterogeneities in the three tourmaline materials. For this purpose, a mount was made that contained multiple fragments from each of the three tourmaline splits as well as a mm-sized piece of the NIST SRM 610 silicate glass. An additional benefit of this test is that these data contribute towards refining the absolute Li mass fractions reported by Dyar et al. (2001), which showed large discrepancies between analytical methods. However, we specifically note that we do not contribute any further absolute mass fraction data to this discussion.

Lithium mass fraction evaluation: Our SIMS analyses used a ∼ 25 pA 16O primary beam focused to a ∼ 2 µm diameter spot with a total impact energy of 23 keV. Data were collected using a 10 µm raster, thereby assuring a flat-bottom crater geometry. Each analysis was preceded by a 170 s pre-sputtering using a 2 nA primary beam and a 20 µm raster in order to locally remove the conductive gold coat and to suppress any surface contamination; actual data collection used a 10 µm raster, which was compensated with the instrument’s dynamic transfer option. Prior to data collection, we completed automatic centring routines on the field aperture in X and Y. The mass spectrometer was operated at a mass resolution of MΔM ≈ 3700, which is more than adequate to resolve both the 6Li 1H + ion from 7Li + and the 27Al 1H + ion from the 28Si mass station. A 2000 x 2000 µm square field aperture, equivalent to a 20 x 20 µm field of view, and a 150 µm contrast aperture were used. The energy window was set to a 40 eV width,
and no offset voltage was applied. Data were collected using a 40-µm-wide entrance slit and a 280-µm-wide exit slit running in mono-collection mode using the ETP pulse counting system, to which a synthetic 46.2 ns dead time was applied using a delay circuit in our pre-amplifier. A single analysis consisted of twenty cycles of the peak stepping sequence $^7\text{Li}^+$ (2s), $^{28}\text{Si}^+$ (2s). A single analysis, including pre-sputtering, auto-centring and data acquisition, required 7 min. We conducted 116 such analyses over the course of one automated analysis sequence. Using these analytical conditions, we had a typical $^{28}\text{Si}^+$ count rate of around 50000 ions per second. The total amount of material removed during data acquisition was very small; our best estimate of the volume of the sputter crater, based on white light profilometry, is $\sim 3.2$ µm$^3$, equivalent to a test portion mass of $\sim 10$ pg. The data set from this experiment, along with the Li mass fractions based on the calibration using the NIST SRM 610 glass, is shown in Table S2. The equivalent $\text{Li}_2\text{O}$ mass fractions in % m/m, along with other determinations from Dyar et al. (2001), are also given in Table 2. We explicitly note that the Li mass fractions reported here are not robust as the NIST SRM 610 silicate glass is, at best, a poor matrix match for the tourmalines we investigated.

**Lithium isotope evaluation:** Because Li mass fraction varied by a factor of 1000 between the elbaite and dravite materials (Table 2), it was not possible to run all three SIMS $^8\text{Li}$ homogeneity experiments under identical conditions. To accommodate such large differences in mass fractions, we modified the $^{16}\text{O}^+$ primary current, the ion detection system and the total count times, with the goal of achieving better than ±0.2‰ (1σ) measurement repeatability precision (internal precision) on the individual analyses. Hence, the test portion masses, as determined by white light profilometry, also varied between materials. A summary of the specific analytical conditions is included in Table 3.

A common feature of all three sets of $^7\text{Li}^+/^6\text{Li}^+$ SIMS data is that the primary beam was operated in Gaussian mode with a total impact energy of 23 keV. Tests using a K¨ohler mode primary beam showed poor repeatability, and we therefore abandoned this approach. Pre-sputtering employed either a 20 or 30 µm raster, which was reduced to a 15 × 15 µm raster during data collection. The dynamic transfer option of the instrument was used to actively compensate for this rastering. Automatic beam centring on the field aperture in both X and Y was conducted before each analysis. The mass spectrometer was operated with a 40 eV energy window, using no energy offset, in conjunction with a mass resolving power $M/\Delta M > 1900$. Data were recorded in multi-collection mode employing an NMR field control system. Ions were collected using the L2 and H2.

### Table 2.
Summary of SIMS homogeneity tests for lithium mass fraction and new working value

|                | $^7\text{Li}^+/^6\text{Si}^+$ | Precision $^b$ | Li2O ( % m/m) |
|----------------|-------------------------------|----------------|----------------|
|                | This study $^c$ | Dyar 1 | Dyar 2 | Dyar 3 | Dyar 4 |
| SCHORL 112566.1 | Mean | 0.1403 | 0.81% | 0.1176 | 0.09 | 0.107 | 0.071 | nr |
| 1s (n = 30) | 0.0105 | 7.4 |
| % RSD $^a$ | 0.0087 | 7.4 |
| DRAVITE 108796.1 | Mean | 0.00207 | 1.94% | 0.00177 | nr | 0.017 | 0.00095 | 0.0013 |
| 1s (n = 28) | 0.00028 | 13.6 |
| % RSD $^a$ | 0.00024 | 13.6 |
| ELBAITE 98144.1 | Mean | 2.12 | 0.27% | 1.92 | 1.33 | 0.098 | 0.30 | nr |
| 1s (n = 36) | 0.21 | 9.8 |
| % RSD $^a$ | 0.19 | 9.8 |
| NIST SRM 610 | Mean | 0.0567 | 0.68% |
| 1s (n = 19) | 0.0015 | 2.6 |
| % RSD $^a$ | 0.0015 | 2.6 |

$^a$ Repeatability from $n$ repeat measurements. See Table S2 for information about the distribution of SIMS results.

$^b$ Mean ‘internal precision’ from twenty cycles per measurement (1SE).

$^c$ Lithium mass fractions calibrated from NIST SRM 610 glass, recommended $\text{SiO}_2$ value 69.4% m/m and Li 468 µg g$^{-1}$ (Jochum et al. 2011). $\text{SiO}_2$ values for tourmalines used in calculation are the mean of Potsdam and Madison values (see Table 1).

$^d$ Lithium mass fractions reported by Dyar et al. (2001) based on (1) PIGE, (2) flame AAS, (3) SIMS and (4) ICP-AES.

nr, not reported.
trollies for $^{6}$Li and $^{7}$Li, respectively; the actual detectors used varied between the experiments depending on Li mass fraction in the tourmaline RMs (see Table 3); for those experiments using electron multipliers, we did an automatic voltage scan prior to each analysis so as to minimise drift due to aging of the first dynode. Analytical points were dispersed over multiple fragments in the epoxy mount, and additionally, several points were placed closely together on a single fragment of the same tourmaline material as a ‘drift monitor’ (DM) in order to test for a time-dependent drift in the ion detection system. After setting all points, the analysis sequence of all non-DM points was randomised. Making the reasonable assumption that the RMs are homogeneous in isotopic composition within a confined area of a few hundred micrometres, the results of ‘drift monitor’ determinations can also be used to quantify the repeatability of the given analytical design. The results from the lithium isotope ratio homogeneity tests of the three tourmaline materials are shown in Table 3, and the full set of results is available in Table S3.

The Li homogeneity assessment on the schorl material presented a special case in two respects. Firstly, the Li mass fraction in schorl is similar to that of the NIST SRM 610 silicate glass (Table 2). We therefore conducted interspersed $^{7}$Li/$^{6}$Li determinations on this glass as a comparison test for the repeatability, whereby we assume that the NIST SRM 610 synthetic glass is homogeneous over the few hundred micrometres used for this assessment. Secondly, the schorl material was particularly challenging from the perspective of the ion count rates that it provided. Under the requirement that the $^{16}$O- primary beam current was in the range between 20 and 0.5 nA, it was found that one of the Li isotopes inevitably provided a count rate in the gap between optimum performance of our FC using a 1011 $\Omega$ resistor and the Hamamatsu pulse counting system (this ‘gap’ is roughly between $2 \times 10^6$ and $2 \times 10^5$ counts per second). Ultimately, we elected to use a compromise where the $^{7}$Li signal was towards the low end of the optimal range for our FC amplifier ($3.9 \times 10^6$ cps) and the $^{6}$Li signal was slightly above the optimal range for our pulse counting system ($3 \times 10^5$ cps). An automatic voltage scan conducted on the Hamamatsu electron multiplier prior to each analysis was able to compensate the drift in the detector at the 0.5‰ level over the six hours run duration. We have not investigated how large this drift would have been without applying the detector voltage correction.

**SIMS oxygen testing**

We assessed the $\delta^{18}$O heterogeneity of the three tourmaline materials with the Potsdam Cameca 1280-HR
instrument. These analyses employed $^{133}$Cs$^+$ primary ion beam with a total impact energy of 20 keV and $\sim$2.5 nA beam current focused to a ca. 5 µm diameter spot on the polished sample surface. Each analysis was preceded by a 2.5 nA, 60 s pre-sputtering in conjunction with a 20 µm raster. All analysis points were within 8 mm of the centre of the sample mount. Negative secondary ions were extracted using a $-10$ kV potential applied to the sample holder, with no offset voltage applied, in conjunction with a 40 eV wide energy window, which was mechanically centred at the beginning of the measurement session. Normal-incidence, low-energy electron flooding was used to suppress sample charging. Each analysis was preceded by an automatic centring routine for the instrument’s field aperture in both X and Y and the centring of the beam on the contrast aperture in the Y direction only. A square 5000 x 5000 µm filed aperture, equivalent to a 50 x 50 µm field of view, a 400 µm contrast aperture, and a 114-µm-wide entrance slit and a 500-µm-wide exit slits were used for this fully automated data collection sequence. The instrument was operated in multi-collection Faraday cup mode using the instrument’s NMR field stabilisation circuitry. The ion count rate on the $^{16}$O$^+$ peak was typically $2 \times 10^9$ cps. Each analysis consisted of twenty integrations of 4 s duration each. Data were collected using a 10 µm x 10 µm primary beam raster, thereby assuring a flat-bottom crater, for which the dynamic beam transfer option of the secondary ion optics was used to compensate. The analytical stability was monitored by interspersed measurements of the NIST SRM 610 silicate glass that was embedded in the same 1-inch-diameter sample mount. Using this approach, we detected an analytical drift amounting to 0.013 ‰ per hour over the course of the 16.6 h of continuous data acquisition. The analytical repeatability for the $n = 29$ determinations on the NIST SRM 610 glass drift monitor was $/C6^0.33$‰ ($1 \text{s}$ ($n = 29$)), which improved to $/C6^0.21$‰ after applying a linear drift correction (Table 4, Table S4). The analytical repeatability on all three of the Harvard tourmalines was similar to this value (Table 4), and hence, we conclude that no major oxygen isotope heterogeneity is present in any of the three tourmaline RMs. The volume of a single crater that was produced under these conditions was determined to be 115 µm$^3$ using white light profilometry, including the pre-sputtering and beam centring processes, equivalent to a test portion mass of $\sim350$ pg (based on a density of $\rho = 3.0$ g cm$^{-3}$ for tourmaline).

| Sample     | $^{18}$O/$^{16}$O (meas.) | $^{18}$O/$^{16}$O (corr.) | Precision $^a$ | IMF $^d$ | IMF uncert. $^e$ |
|------------|---------------------------|---------------------------|----------------|----------|------------------|
| SCHORL 112566.1 | 0.00201780 | 0.00201709 | 0.11‰ | 0.99630 | 0.030 |
| RSD$^a$ | 0.27‰ | 0.27‰ |  |
| DRAVITE 108796.1 | 0.00202194 | 0.00202103 | 0.10‰ | 0.99785 | 0.1 |
| RSD$^a$ | 0.25‰ | 0.22‰ |  |
| ELBAITE 98144.1 | 0.00202725 | 0.00202645 | 0.11‰ | 0.99825 | 0.0 |
| RSD$^a$ | 0.30‰ | 0.22‰ |  |
| NIST SRM 610 | 0.00203007 | 0.00202942 | 0.10‰ | 1.0 |  |
| RSD$^a$ | 0.33‰ | 0.21‰ |  |

All data are reported in Table S4.

$^a$ Repeatability from $n$ measurements ($1 \text{s}$).

$^b$ Corrected for linear drift based on NIST SRM 610 measurement results (see text for details).

$^c$ Mean ‘internal precision’ from $n$ cycles (1SE).

$^d$ $^{18}$O/$^{16}$O instrumental mass fractionation (measured ratio/true), based on the grand mean $\delta^{18}$O values indicated in Table 6.

$^e$ Uncertainty in ‰ of the recommended $\delta$ value of this material (see Table 7).

Solution MC-ICP-MS analysis of $\delta^7$Li

Lithium isotope compositions were determined on acid-digested sample solutions by MC-ICP-MS in four laboratories: Woods Hole Oceanographic Institution, the University of
Table 5. Summary results of δ7LiSVEC by solution ICP mass spectrometry, values in ‰.

| Material   | Laboratory | Dissolution | No. of analyses | δ7Li (mean) ‰ | δ7Li (range) ‰ | 1σ  | Lin et al. (2019) b |
|------------|------------|-------------|----------------|--------------|----------------|-----|-------------------|
| SCHORL 112566.1 | Bremen      | 1           | 5              | 5.71         | 5.52–5.88      | 0.13 |                    |
|            | Maryland    | 1           | 2              | 4.24         | 4.22–4.26      | nd  |                   |
|            | Maryland    | 2           | 2              | 4.81         | 4.64–4.98      | nd  |                   |
|            | Bristol     | 1           | 2              | 5.64         | 5.60–5.72      | nd  |                   |
|            | Bristol     | 2           | 2              | 5.71         | 5.64–5.78      | nd  |                   |
|            | Woods Hole  | 1           | 4              | 5.52         | 5.35–5.70      | 0.15|                   |
|            | Woods Hole  | 2           | 4              | 5.29         | 4.70–5.66      | 0.37|                   |
| DRAVITE 108796.1 | Bremen      | 1           | 2              | 10.99        | nd             | nd  | 6.47 ± 0.20       |
|            | Maryland    | 1           | 2              | 8.72         | 7.97–9.35      | nd  |                   |
|            | Maryland    | 2           | 1              | 8.78         | 8.21–9.34      | nd  |                   |
|            | Bristol     | 1           | 3              | 10.17        | 10.10–10.25    | 0.07|                   |
|            | Bristol     | 2           | 2              | 10.24        | 10.14–10.35    | nd  |                   |
|            | Woods Hole  | 1           | 1              | 9.67         | nd             | nd  |                   |
|            | Woods Hole  | 2           | 1              | 10.24        | nd             | nd  |                   |
| ELBIAE 98144.1 | Bremen      | 1           | 5              | 7.10         | 6.94–7.28      | 0.13|                   |
|            | Maryland    | 1           | 2              | 6.04         | 5.84–6.24      | nd  |                   |
|            | Maryland    | 2           | 2              | 6.87         | 6.64–7.11      | nd  |                   |
|            | Bristol     | 1           | 3              | 7.18         | 7.12–7.24      | nd  |                   |
|            | Bristol     | 2           | 2              | 7.71         | 7.62–7.81      | nd  |                   |
|            | Woods Hole  | 1           | 4              | 7.13         | 6.80–7.34      | 0.23|                   |
|            | Mean a      |              |                | 7.12 ± 0.24  | 7.07 ± 0.22    |     |                   |

nd, not defined. 1σ repeatability values only reported for those aliquots with ≥ 3 mass spectrometer determinations.

See Table S5 for a complete report of all individual results.

a Median of n = 6 or 7 independent dissolutions with 15E based on the 1σ reproducibility divided by √(n - 1).

b Values in ‰ reported by Lin et al. (2019) for comparison based on n = 3 determinations using microdrilling and wet chemical methods; uncertainty estimates are 1σ.

Maryland, the University of Bristol and the University of Bremen. The only information exchanged between the laboratories prior to analysis concerned the approximate Li mass fractions in the tourmalines and the need for a prolonged, high-pressure dissolution in order to achieve complete digestion. Each laboratory performed one or two independent dissolutions of separate aliquots of each RM, and in all but a few cases, the separate dissolution samples were analysed between two and five times each. The analytical technique descriptions for each of the participating laboratories are given below, a summary of the results along with the final recommended values are shown in Table 5, and a compilation of all the data is given in Table S5. We note that the Li isotope analyses of elbaite #98144 at the University of Bristol were previously published by Ludwig et al. (2011). Independent of our study, Lin et al. (2019) reported Li isotope values for the Harvard schorl #112566 and elbaite #98144 analysed by solution ICP-MS. Their results are also shown in Table 5.

Woods Hole Oceanographic Institution: Multiple tourmaline fragments with a total mass between 1 and 10 mg were crushed and then digested in steel-clad PTFE bombs under pressure at 120 °C in a mixture of 1.5 ml HF and 0.5 ml concentrated HNO₃ for 2 days. The dried samples were taken up in 9 ml 1 mol l⁻¹ HNO₃ with 80% methyl alcohol from which the Li fraction was separated by ion chromatography using a 10 ml AG SOW X8 (200–400 mesh) column (see Tomascak and Carlson 1999). The Li cuts were analysed with a Thermo Finnigan NEPTUNE MC-ICP-MS using sample/calibrator bracketing with NIST SRM 8545 (see Rosner et al. 2007). The total Li blank of this procedure was < 0.5 ng, which is negligible for the elbaite and schorl materials and less than 1% of the Li recovered from an analysis of the dravite material. Since the isotopic composition of the blank can be assumed to be in the natural terrestrial range, we conclude that a 1% Li contribution from the blank does not significantly impact the determined δ7Li values. The measurement repeatability precision (within-run or internal precision) of each 7Li/M⁴ Li measurement was < 0.1‰ (2SE). Multiple analysis of sample solutions for schorl and elbaite gave repeatabilities < 0.4‰ (2σ, n = 4); the dravite solutions were measured only once. The δ7Li values from individual solution aliquots (schorl and dravite) deviated by less than 0.8‰ (Table 5). Rosner et al. (2007) estimated the trueness of the δ7Li values from this procedure
Table 6.
Summary results of oxygen isotope ratio analyses by gas-source mass spectrometry

| Material | Laboratory | Session | n b | 618O SMOW Mean | 618O SMOW Range c | 617O SMOW Mean | 617O SMOW Range c |
|----------|------------|---------|-----|----------------|-------------------|----------------|-------------------|
| SCHORL 112566.1 | Cape Town | 1 | 2 | 9.59 | 9.54-9.64 | | |
| | Cape Town | 2 | 2 | 9.75 | 9.66-9.83 | | |
| | Milton Keynes | 1 | 2 | 9.71 | 9.68-9.74 | 5.07 | 5.05-5.08 |
| | Milton Keynes | 2 | 2 | 9.71 | 9.71-9.71 | 5.07 | 5.06-5.08 |
| | Madison | 1 | 2 | 9.76 | 9.74-9.77 | | |
| | Madison | 2 | 2 | 9.63 | 9.58-9.67 | | |
| | Keyworth | 1 | 2 | 9.49 | 9.74-9.61 | | |
| | Keyworth | 2 | 2 | 9.65 | 9.33-9.97 | | |
| | Keyworth | 3 | 1 | 9.46 | | | |
| | E. Kilbride | 1 | 3 | 9.70 | 9.59-9.78 | | |
| | Göttingen | 1 | 1 | 9.81 | | 5.12 | |
| | Göttingen | 2 | 2 | 9.70 | 9.47-9.81 | 5.06 | 4.93-5.12 |
| | Grand Mean a | | | 9.66 ± 0.03 | | 5.08 | |
| Dyar et al. (2001) | Cape Town | 1 | 2 | 10.01 | 9.98-9.99 | | |
| | Cape Town | 2 | 2 | 10.04 | 9.90-10.12 | | |
| | Milton Keynes | 1 | 1 | 10.04 | | 5.38 | |
| | Milton Keynes | 2 | 2 | 10.07 | 10.02-10.12 | 5.27 | 5.24-5.29 |
| | Madison | 1 | 2 | 10.19 | 10.17-10.20 | | |
| | Madison | 2 | 2 | 10.01 | 9.99-10.02 | | |
| | Keyworth | 1 | 2 | 9.75 | 9.50-10.00 | | |
| | Keyworth | 2 | 2 | 10.62 | 10.59-10.74 | | |
| | E. Kilbride | 1 | 4 | 9.92 | 9.80-9.99 | | |
| | Göttingen | 1 | 3 | 10.13 | 10.12-10.16 | 5.29 | 5.28-5.31 |
| | Grand Mean a | | | 10.07 ± 0.08 | | 5.31 | |
| | | | | 10.03 ± 0.02 | | | |
| Dyar et al. (2001) | Cape Town | 1 | 2 | 13.71 | 13.69-13.73 | | |
| | Cape Town | 2 | 2 | 13.74 | 13.71-13.77 | | |
| | Milton Keynes | 1 | 2 | 13.81 | 13.77-13.85 | 7.21 | 7.18-7.23 |
| | Milton Keynes | 2 | 2 | 13.87 | 13.87-13.87 | 7.24 | 7.23-7.25 |
| | Madison | 1 | 3 | 13.87 | 13.81-13.92 | | |
| | Madison | 2 | 2 | 13.96 | 13.84-14.08 | | |
| | Keyworth | 1 | 1 | 14.52 | | | |
| | Keyworth | 2 | 2 | 12.72 | | | |
| | Keyworth | 3 | 1 | 13.73 | | | |
| | E. Kilbride | 1 | 4 | 13.54 | 13.20-13.79 | | |
| | Göttingen | 1 | 3 | 13.94 | 13.82-14.00 | 7.27 | 7.20-7.31 |
| | Grand Mean a | | | 13.76 ± 0.13 | | 7.24 | |
| | | | | 13.89 ± 0.02 | | | |
| Dyar et al. (2001) | UWG-2 gmt | Cape Town | 4 | 5.76 | 5.69-5.87 | | |
| | Milton Keynes | 4 | 5.75 | 5.69-5.80 | 2.98 | 2.96-3.01 |
| | Madison | 4 | 5.80 | 5.75-5.91 | | | |
| | Keyworth | 3 | 5.49 | 5.07-5.98 | | | |
| | E. Kilbride | 9 | 5.75 | 5.63-5.87 | | | |
| | Göttingen | 15 | 5.77 | 5.62-5.90 | 2.99 | 2.93-3.06 |

See Table S6 for a complete report of all individual results.

a Simple mean of n = 10, 11 or 12 independent sessions with 1SE based on the reproducibility divided by \(\sqrt{n - 1}\).

b Number of independent determinations during the given measurement session (day).

c Range only reported for those determinations containing \(\geq 2\) determinations.

University of Maryland: Tourmaline fragments having total masses ranging between 0.2 and 13.6 mg were lightly crushed and then cleaned for 1.5 min in an ultrasonic bath using high-purity (Milli-Q) water (18.2 MΩ cm resistivity). Two separate dissolution aliquots were obtained using the following procedure. Sample digestion took place in steel-clad PTFE bombs at 160 °C under pressure in a 3:1 mixture of concentrated HF and concentrated HNO3. The dried residue was refluxed with concentrated HNO3 dried again.
and repeatedly refluxed with concentrated HCl until all fluorides were converted into chlorides and clear solutions were obtained. The final dried residue were taken up in 1 ml 4 mol l⁻¹ HCl, and the Li fraction was separated by ion chromatography in columns loaded with Bio-Rad AG 50w-x12 (200–400 mesh) using the procedure described by Rudnick et al. (2004). Lithium loss during column chemistry was monitored by taking an additional 2 ml cut after the Li cut from each column. The total loss during this study was between 0.6% and 1.3% of the total Li in the sample, which does not affect the Li isotopic composition significantly (Marks et al. 2007). Lithium isotope analyses were made on a Nu-Plasma MC-ICP-MS instrument (for details, see Teng et al. 2004). Each analysis was bracketed by measurements of a standard solution of the Li carbonate RM NIST SRM 8545, and the ⁶Li/⁷Li value for the analysis was calculated relative to the average of the two bracketing runs. The total procedural blank during the course of the study was equivalent to a voltage of 4 mV for ⁷Li⁺ ions. This compares with a voltage of 1–1.5 V obtained for a solution with 50 µg l⁻¹ Li at a 40 µl min⁻¹ uptake rate, resulting in a sample/blank ratio of ~ 300. The measurement repeatability precision (‘internal or within-run precision’) of ⁷Li/⁶Li measurements based on two blocks of twenty ratios each was generally ≤ 0.2‰ (2s). The intermediate measurement precision of the method (over a period of two years), based on > 100 analyses of a purified NIST SRM 8545 standard solution, is ≤ 1.0‰ (2s, see Teng et al. 2004). Analytical trueness was monitored during each session by multiple measurements of two reference solutions: seawater IRMM-016 (Qi et al. 1997) and an in-house UMD-1 quality control material (a purified Li solution from Alfa Aesar®). The results for both reference solutions agree within uncertainties with previously published values. Two measurements of the nepheline syenite RM STM-1 yielded +3.2 and +4.1‰, which are within the range of previously published values (Halama et al. 2008). The long-term bias of Li isotope measurements in the Maryland laboratory was monitored by multiple analyses of the BHVO-1 basalt RM, which gave 4.4‰ ± 0.7 (1SE), which is in good agreement with published values (4.3–5.8‰; James and Palmer 2000, Chan and Frey 2003, Bouman and Elliott 2004, Rudnick et al. 2004).

University of Bristol: The determinations on each of the three RMs were based on between 1 and 2 mg of material that was finely powdered, from which two separate aliquots were dissolved in the following three steps: first, with a combined dissolution in a 2:6:1 ratio of concentrated HF-HNO₃-HClO₄ (where the perchloric acid is included to inhibit the formation of insoluble Li fluorides, see Ryan and Langmuir 1987), followed by concentrated HNO₃ and then 6 mol l⁻¹ HCl. The dissolution process incorporated repeated ultrasonication. The dissolved samples were passed through two high-aspect-ratio cation-exchange columns (AG50W X12), using dilute HCl as eluant based on the approach of James and Palmer (2000), and described in detail by Marshall et al. (2007) and Pogge von Strandmann et al. (2011). The Li fractions were measured using a Thermo Finnigan Neptune MC-ICP-MS, with sample bracketing using a solution of NIST SRM 8545 (Jeffcoate et al. 2004). Samples were analysed two or three times during the given sequence. The measurement repeatability precision (‘internal or within-run precision’) was typically better than ±0.2‰ (2s). The intermediate measurement precision (i.e., over a long-term period of 4 years) for the Bristol laboratory was ≤ 0.3‰ (2s), based on analyses of silicate rock RMs BHVO-2 and BCR-2 (δ⁷Li = 4.7 ± 0.2‰; n = 31 and δ⁷Li = 2.6 ± 0.3‰; n = 18, respectively, all uncertainties 2s; Pogge von Strandmann et al. 2011).

University of Bremen: Values of δ⁷Li of the three tourmaline materials were determined in the Isotope Geochemistry Laboratory at the MARUM – Center for Marine

| Table 7. Compilation of reference values for the three Harvard tourmaline materials |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| LiO₂ mass fraction (%) | δ⁷Li-VEC (%) | δ¹⁸O_SMOW (%) | δ¹⁷O_SMOW (%) | δD b (%) | δ¹⁸B c (%) | δ¹¹B d (%) |
| School I 112566.1 | 0.118 ± 0.009 | 5.52 ± 0.23 | 9.66 ± 0.03 | 5.08 | -92.4 | -125.6 |
| Dravite 108796.1 | 0.00177 ± 0.00024 | 10.17 ± 0.34 | 10.02 ± 0.08 | 5.31 | -47.3 | -6.6 |
| Elbaite 98144.1 | 1.92 ± 0.19 | 7.12 ± 0.24 | 13.89 ± 0.02 | 7.28 | -99.4 | -10.4 |

Note: a Values based on SIMS data calibrated using silicate glass NIST SRM 610 – subject to uncontrolled matrix effects.

b Values published by Oyar et al. (2001) on starting materials.
c Values published by Leeman and Tonarini (2001) on starting material.
d Values published by Marger et al. (2020) on starting material.
Environmental Sciences, University of Bremen. Sample digestion, separation and purification of lithium were modified after Moriguti and Nakamura (1998). Between 3 and 15 mg of crushed tourmaline sample were digested at 170 °C in 2 ml HNO₃ mixture (5:1) in steel-clad PTFE bombs, dried at 80 °C, repeatedly re-dissolved in 2 ml of 2 mol l⁻¹ HNO₃ and dried to convert all fluorides into nitrates. The decomposed samples were finally dissolved in 4 mol l⁻¹ HCl. For the schorl and elbaite materials, five solution aliquots per sample were taken, each containing between 60 and 220 ng Li; the Li-poor dravite sample could only be analysed once. Each aliquot solution went through a three-step purification procedure using Bio-Rad® AG 50WX8 (200–400 mesh) resin. The first step removed the trivalent matrix elements (e.g., rare earth elements) using Bio-Rad® Bio-Spin columns with 1 ml of the cation-exchange resin and 4 mol l⁻¹ HCl (for conditioning the resin and loading the sample) and 2.8 mol l⁻¹ HCl (to elute Li) as reagents. The second step removed the majority of matrix elements (e.g., Ca and Mg) using Bio-Rad® Poly-Prep columns with 1.4 ml of the cation-exchange resin and 0.15 mol l⁻¹ HCl as reagent. In the third step, Na was separated using Bio-Rad® Bio-Spin columns with 1 ml resin and 0.15 mol l⁻¹ HCl followed by 0.5 mol l⁻¹ HCl in 50% ethanol as reagents. Lithium must be quantitatively separated from the sample matrix, since the loss of only 1% of Li during column separation as well as the presence of Na can result in significant shifts in the Li isotope composition (James and Palmer 2000, Nishio and Nakai 2002, Jeffcoate et al. 2004). Lithium loss during column separation was monitored by testing the collected head and tail fractions of each separation step. The total Li loss was typically < 0.1% of total collected Li and was thus insignificant. Reference materials NIST SRM 8545 (LSVEC Li carbonate, Flesch et al. 1973), ZGI-TB-2 (clay shale), ZGI-GM (granite) and tourmaline IAEA-B-4 (powdered batch, Universit of Cape Town, the Scottish Universities Environmental Research Centre SUERC (East Kilbride) and the National Environmental Isotope Facility of the British Geological Survey (Keyworth). Each laboratory analysed between one and four aliquots of grain fragments from each of the three tourmaline materials, and each analysis involved between one and four separate determinations. Additionally, all laboratories analysed the UWG-2 garnet RM (Valley et al. 1995) as a silicate traceability material. All laboratories reported δ⁷Li values; in addition, the Open University and University of Cape Town laboratories reported δ¹⁸O values. In 2020, Table 6 also shows the previously published δ¹⁸O value of 0.01 ± 0.11‰ (2s, n = 4), indicating that no significant isotope fractionation occurred during the measurement procedure, and confirming the long-term precision for the δ⁷Li value of 0.01 ± 0.18‰ (2s, n = 78). δ⁷Li values of ZGI-TB-2 (-3.4 ± 0.2‰, 2s, n = 2) agree well with published values of ZGI-TB (-3.3 ± 0.4‰, 2s, Romer and Meixner 2014). The ZGI-GM gives a δ⁷Li value of -0.7 ± 0.1‰ (2s, n = 2), which fits well with the published value of -0.9 ± 0.6‰ (2s, n = 2) (Meixner et al 2019). Tourmaline RM IAEA-B4 was also used as a quality control material, yielding a δ⁷Li of 4.3 ± 0.3‰ (2s). Lin et al. (2019) reported a δ⁷Li value of 5.64 for the B4 tourmaline; here, we note that the value reported for schorl and elbaite in that manuscript are likewise higher than our values based on four independent laboratories. The ‘external’ precision of silicate samples was generally ≤ 0.5‰ (2s). The repeatability of the individual δ⁷Li values is reported as two standard deviations based on the five individually analysed sample aliquots.

**Gas-source analyses of oxygen isotopes**

Oxygen isotope ratios were determined by gas-source mass spectrometry using either laser fluorination or stepwise fluorination techniques in six independent laboratories: University of Wisconsin (Madison), the Open University (Milton Keynes), University of Göttingen, University of Cape Town, the Scottish Universities Environmental Research Centre SUERC (East Kilbride) and the National Environmental Isotope Facility of the British Geological Survey (Keyworth). Each laboratory analysed between one and four aliquots of grain fragments from each of the three tourmaline materials, and each analysis involved between one and four separate determinations. Additionally, all laboratories analysed the UWG-2 garnet RM (Valley et al. 1995) as a silicate traceability material. All laboratories reported δ¹⁸O values; in addition, the Open University and University of Göttingen laboratories reported δ¹⁷O results. Analytical technique descriptions for each of the participating laboratories are given below, a summary of the results is given in Table 6, and the compilation of all data is provided in Table S6. These tables also report the results obtained on the UWG-2 garnet traceability material; nearly all of the six participating gas-source laboratories reported a mean value for UWG-2 which was in close agreement with the previously reported value of δ¹⁸O_MOW = 5.8 (Valley et al. 1995). Table 6 also shows the previously published δ¹⁸O working values for the three Harvard tourmalines as reported by Dyar et al. (2001), for the dravite and elbaite materials, good agreement is seen between these previous working values and the new results presented here. Finally, in Table 6 we also report Δ¹⁷O value for the Open...
University and Göttingen data sets, where $\Delta^{17}O$ is defined as follows:

$$\Delta^{17}O = 1000 \cdot \ln \left( \frac{\delta^{17}O}{1000} + 1 \right) - 0.528 \cdot 1000 \cdot \ln \left( \frac{\delta^{18}O}{1000} + 1 \right)$$

with both $\delta^{17}O$ and $\delta^{18}O$ on VSMOW scale. To ensure that $\delta^{17}O$ is on the VSMOW scale, our data are linked via the composition of UWG-2 garnet, taken as $\Delta^{17}O = -0.062\%$, which is 0.01\% lower than that of San Carlos olivine (Miller et al. 2020) that was measured relative to VSMOW2 and SLAP2 to be $\Delta^{17}O = -0.052\%$ (mean of the determinations by Pack et al. 2016, Sharp et al. 2016, Westbrock et al. 2020).

**University of Wisconsin:** Oxygen isotope ratios were measured at the Department of Geoscience, University of Wisconsin-Madison. Aliquots of tourmaline weighing 1.9–3.3 mg were individually heated in a BrF$_5$ atmosphere using a CO$_2$ laser ($\lambda = 10.6\mu$m) at a beam diameter of ~1 mm and a power of ~19 W. Evolved O$_2$ was cleaned cryogenically, converted to CO$_2$ on hot graphite and analysed on mass stations 44, 45 and 46 using a Finnigan MAT 251 gas-source mass spectrometer. Values are reported in standard permil notation relative to VSMOW. The intermediate measurement precision (i.e., over a period of NN months) was 0.04% for $\delta^{17}O$, 0.08% for $\delta^{18}O$ and 0.099% for $\Delta^{17}O$ (note that the uncertainties for $\delta^{17}O$ and $\delta^{18}O$ are highly correlated; see also Westbrock et al. 2020).

**Open University (Milton Keynes):** Aliquots of tourmaline weighing 2.0–2.1 mg were heated in a BrF$_5$ atmosphere by laser ($\lambda = 10.6\mu$m) ramped up to ~15 W power. Evolved O$_2$ was prepared through a two-stage cryogenic purification process with an intermediate hot (110 °C) KBr reactor. The purified O$_2$ gas was cryofocused at the entrance of the analyser using zeolite molecular sieve at -196 °C before being analysed by gas-source mass spectrometer (Thermo Finnigan MAT 253). Details of analytical procedures are given in Miller et al. (1999). Values for $\delta^{17}O$ and $\delta^{18}O$ are reported in conventional % notation relative to VSMOW. Typical intermediate measurement precision (i.e., over a period of NN months) was ±0.052% for $\delta^{17}O$, ±0.093% for $\delta^{18}O$, and ±0.017% for $\Delta^{17}O$ (2σ) (Greenwood et al. 2015). Analyses of UWG-2 yielded 5.75 ± 0.06% (1s, n = 4).

**SUERC East Kilbride:** Aliquots of tourmaline weighing between 1.7 and 2.9 mg of tourmaline, and between 1.4 and 3.0 mg of UWG-2 garnet, were pre-fluorinated overnight, under vacuum in the sample chamber. Samples were then individually heated in a ClF$_3$ atmosphere by laser (SYNRAD J48-2 CO$_2$ laser $\lambda = 10.6\mu$m), following the method of Sharp (1990). The evolved O$_2$ was cleaned cryogenically, passed through an online hot mercury diffusion pump, before being converted to CO$_2$ on hot graphite, and analysed by gas-source mass spectrometer (VG SIRA2). Values are reported in conventional permil notation relative to VSMOW. Analyses of the UWG-2 garnet during the measurement session yielded 5.75 ± 0.08% (1s, n = 9). Values were corrected by 0.04% to the accepted value of 5.80 for UWG-2 (Valley et al. 1995).

**BGS (Keyworth):** The tourmalines, weighing between 6.1 and 6.6 mg, were powdered, transferred to pure nickel reaction vessels and furnace-heated to 700 °C in an excess
of BrF₅ for an extended period (> 16 h). The evolved O₂ was cleaned cryogenically, converted to CO₂ on hot graphite and collected under liquid N₂. Oxygen isotope analyses were conducted with a Thermo Finnigan MAT 253 dual-inlet mass spectrometer. Values are reported in standard δ-notation in permil relative to VSMOW calibrated using NBS28 quartz, which has an assigned composition of δ¹⁸O = 9.59‰ (Hut 1987). Analyses of the UWG-2 garnet during the session yielded 5.49 ± 0.46‰ (1σ, n = 3). Values were corrected by 0.31‰ to the accepted value of 5.80‰ for UWG-2 (Valley et al. 1995). It is noted that the Keyworth laboratory does not normally run high-temperature minerals, and fluorination was conducted at a temperature well above the typical 500 °C used in this facility for biogenic silica. This deviation for the Keyworth validated operating protocol may have contributed to the somewhat lower mean δ¹⁸O value (-0.3‰, n = 3) determined on the UWG-2 garnet traceability material.

### Discussion

Table 7 summarises the best available values for stable isotope ratios of the three Harvard tourmaline materials.

#### Major element compositions

With respect to the major element compositions of the three Harvard tourmaline RMs, we believe the best estimates of their major element compositions and their inter-fragment variabilities are provided by the grand means of two EPMA data sets presented in Table 1. In general, the grand means reported from Potsdam and Madison agree well, though biases outside the reported repeatability are also visible for some elements. Both sets of EPMA results provide data that characterise the composition of the tourmalines. We note that the values for B composition determined by EPMA are in excellent agreement with earlier non-EPMA technique data (Dyar et al. 2001). However, due to different analytical EPMA protocols, further examinations of all three tourmaline RMs will be necessary in order to establish recommended values. For the time being, the grand means reported in Table 1 should be considered as working values, subject to possible future refinement.

#### Working values for lithium mass fractions

Based on the observed repeatabilities of our SIMS data as compared with both the (presumably) homogeneous NIST SRM 610 silicate glass and the ‘within-run’ precision of the individual SIMS measurements (Table 2), it appears that significant variability in the Li²O contents is present in all three materials. Furthermore, our 'current best estimate' values for Li contents (Table 7) are derived from a SIMS calibration based on the NIST SRM 610 glass; as such, we do not have a matrix-matched calibration. We conclude that the Li content values presented in Table 7 should only be used as rough indicators and that any values calibrated using these materials should employ multiple grains so as to suppress issues related to the observed sample heterogeneity.

#### Recommended values for lithium isotopes

A comparison of the δ⁷Li values determined by the four laboratories (Table 5) shows good agreement for all three RMs, the only noteworthy observation being the consistently lower δ⁷Li values reported in the University of Maryland data set, which differs by roughly 1‰ from the results reported by Bremen, Bristol and Woods Hole. The source of this phenomenon is unclear, particularly in view of the detailed quality assurance plans implemented by all four bulk analysis laboratories. In total, there are eight repeated pairs of data in our full data set (Table 5), and these have on average a difference of only 0.38‰ between the members of the pairs. Equally, the overall repeatabilities of the SIMS homogeneity assessments were better than ± 0.8‰ (1σ) for both of the Li-rich materials (Table 3). Hence, both the repeatability of our analytical methods and the homogeneity observed by SIMS are significantly better than the observed spread in the result. Based on these observations, we suggest that the median δ⁷Li values based on the individual (n = 6 or 7) bulk δ⁷Li determinations represent the best possible estimates of the true value of the three materials. These are reported in Table 5, and their assigned uncertainties are the repeatabilities of the complete set of determinations divided by \(\sqrt{n - 1}\). We note that our results for schorl and elbaite are roughly 0.9‰ lower than those reported by Lin et al. (2019) (see Table 5).

#### Recommended values for oxygen isotopes

The results of thirty-three δ¹⁸O laser and stepwise fluorination determinations reported by six independent laboratories show excellent agreement for all three of the tourmaline RMs (Table 6). The 'within-run' precision of individual analyses was better than ± 0.1‰ (1σ) for all of the gas-source data (Table S6). With regard to the homogeneity at the picogram sampling scale, our SIMS data (Table 4) yielded repeatabilities similar to those obtained on the NIST SRM 610 silicate glass, which we presume to be isotopically homogeneous at the SIMS sampling scale. We therefore conclude that the recommended δ¹⁸O values reported in Table 7 can be used to calibrate in situ oxygen isotope ratio measurements at
SIMS matrix effects

In the case of the three Harvard tourmaline RMs, it is not possible for us to say anything with regard to SIMS matrix effects related to Li mass fraction determinations as we do not have any independently determined value for the three materials in which we have high confidence. Equally, in the case of $^{7}\text{Li}/^{6}\text{Li}$ determinations we cannot conclude anything meaningful regarding a chemical matrix effect. The large differences in Li mass fractions mean that each of the three RMs had to be run under distinct analytical conditions, preventing any direct comparison. The only thing that can be said concerning a matrix effect is through comparing the schorl RM and the concurrently run NIST SRM 610 silicate glass, which was used as a drift monitor. Kasemann and Jeffcoate (2005) published a solution MC-ICP-MS value of $^{7}\text{Li}_{\text{NIST}} = 32.50 \pm 0.02$ for NIST SRM 610, which is equivalent to an absolute isotope ratio of $^{7}\text{Li}/^{6}\text{Li} = 12.5686$ (see Equation 3). During our homogeneity testing, we obtained on $n = 8$ measurements $^{7}\text{Li}^{*}/^{6}\text{Li}^{*} = 11.8166$ for NIST SRM 610 (Table 3), corresponding to an instrumental mass fractionation (IMF) of $11.8166/12.5686 = 0.94016$. For the concurrently analysed schorl, the IMF value is 0.94993, based on our recommended $^{7}\text{Li} = 5.52$ (Table 7) and the observed average $^{7}\text{Li}^{*}/^{6}\text{Li}^{*} = 11.6273$ (Table 3). Comparison of these IMF values indicates a difference of circa 10% between the schorl and silicate glass matrix. Similar to what has already been demonstrated for SIMS baron isotope data (e.g., Rosner and Wiedenbeck 2008), the use of NIST silicate glass RMs (SRM 610 x series) for calibrating SIMS lithium isotope measurements of tourmaline leads to a grossly biased result.

During our SIMS $^{18}\text{O}$/$^{16}\text{O}$ homogeneity test run, we ran all three of the Harvard tourmaline RMs as well as NIST SRM 610 glass (as drift monitor) during a single analytical sequence under identical analytical conditions. This allows us to evaluate the impact of the various matrices on the SIMS IMF value. For the tourmaline RMs, we used the grand mean $^{8}\text{O}$ values reported in Table 6 in conjunction with the absolute ratio for SMOW of $^{18}\text{O}/^{16}\text{O} = 0.00200520$ (Baertschi 1976). In the case of NIST SRM 610 silicate glass, we used the value reported by Kasemann et al. (2001) of $^{18}\text{O}_{\text{SMOW}} = 10.91$ (see Equation (1) for conversion to absolute isotope ratio). The resulting IMF values for each of these four materials are reported in Table 4. Among the three tourmaline RMs, the maximum difference in IMF is 1.9‰, as seen between schorl and elbaite, with dravite yielding an IMF intermediate between the two. These differences in IMF are large compared with the analytical uncertainties and are similar to variations in IMF reported for oxygen isotope ratio determinations on tourmaline by Marger et al. (2019); that earlier work reported that tourmalines having low iron contents (e.g., elbaite) tend to measure comparatively high $^{18}\text{O}$/$^{16}\text{O}$ SIMS results. This observation suggests that, despite the low uncertainties of the gas-source data and the good repeatability of our SIMS method, the determination of $^{18}\text{O}$ in natural tourmalines at precision levels better than 0.5‰ will be difficult except where there is a close chemical match between the unknown sample and one of these RMs, as has been shown for gemet and other minerals (Valley and Kita 2009, Page and Kita 2010). For the case of NIST SRM 610, the IMF was biased by between 3‰ and 5‰ relative to the dravite and schorl RMs, respectively. This confirms that, at least in the case of SIMS, the use of a silicate glass calibrant is inappropriate for $^{18}\text{O}$ determinations on tourmaline.

Material availability

Since 2014, the three Harvard tourmalines RMs described here have been distributed through IAGEO Limited (www.iageo.com), and it is expected this arrangement will continue on into the future. Vials containing ca. 100 mg of tourmaline (samples HMGM #98144.1, HMGM #112566.1 and HMGM #108796.1) are therefore readily available to the global user community. In the light of the large number of splits that were produced of each of these materials (128 or 512 units) in conjunction with past levels of demand, it is reasonable to expect this resource will last for at least two decades into the future.

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Data availability statement

The data that supports the findings of this study are available in the supplementary material of this article.

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Supporting information

The following supporting information may be found in the online version of this article:

Table S1. Measurement results for tourmaline reference materials by electron probe microanalysis, complete data set.

Table S2. Lithium mass fraction homogeneity test results by SIMS, complete data set.

Table S3. Lithium isotope homogeneity tests by SIMS, complete data set.

Table S4. Oxygen isotope homogeneity test by SIMS, complete data set.

Table S5. Wet chemical lithium isotope ratio measurement results, complete data set.

Table S6. Gas source oxygen isotope ratio measurement results.

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