

Appendix

COMPOSITION AND HOMOGENEITY OF THE OLENITE REFERENCE TOURMALINE

A whole rock specimen of about 2x3 cm in size from the Koralpe pegmatite was made available by Andreas Ertl and was collected about 2 cm away from the contact of the pegmatite to its host rock. For more geologic background information see Kalt et al. (2001) and references therein. From this specimen, a 2x1.75x1 mm sized, pale green tourmaline crystal was extracted and cut into halves, of which one half (about 2 mg) was powdered whereas the other half was embedded in a 1-inch epoxy holder and polished. Phase proportions and B isotope ratios of the powdered sample were determined by powder X-ray diffraction and MC-ICP-MS, respectively. Homogeneity in terms of major element chemistry and B isotope ratios were determined by EMP and SIMS analyses on the epoxy mount.

ANALYTICAL CONDITIONS

Powder X-ray diffraction

Powder XRD analysis was performed with a STOE Stadi-P diffractometer equipped with a Cu anode operated at 40 kV and 40 mA, which is located at the GFZ Potsdam. A primary Ge monochromator provided convergent $\text{CuK}\alpha_1$ radiation. Diffraction patterns were recorded with a 7° wide position-sensitive detector in transmission between 5° and $125^\circ 2\theta$ at a step width of $0.01^\circ 2\theta$. Unit-cell parameters, other structural parameters and phase proportions were refined using the GSAS software package for Rietveld refinement (Larson and Von Dreele, 1987). All X-ray reflections of the natural sample could be attributed to olenitic tourmaline, quartz and albite. The initial structural data for olenitic tourmaline were taken from the single crystal structure refinement reported in Kutzschbach et al. (2016). For quartz and albite the structural data from Kihara (1990) and Armbruster et al. (1990) were used, respectively.

EMP analyses

The composition of the olenite RM was determined with wavelength-dispersive X-ray spectrometry (WDX) using a JEOL Hyperprobe JXA-8500F equipped with a thermal field emission gun and 5 spectrometers, which is located at the GFZ Potsdam. A spot size of $10\text{ }\mu\text{m}$ was applied at an accelerating voltage of 10 kV and a beam current of 20 nA. A liquid nitrogen cold trap was used to reduce effects of hydrocarbon contamination. Natural crystals were used as standards: schorl (Al, B), orthoclase (Si, K), hematite (Fe), jadeite (Na), diopside (Ca, Mg), rhodonite (Mn) and rutile (Ti). Counting times on the peaks/background were 20/10 s for Si, 80/40 s for B and 30/15 for all other elements. Background

intensities were collected at higher and lower energies relative to the corresponding K_α line. Raw data were processed by applying a $\phi(\rho Z)$ correction scheme (CITZAF; Armstrong 1995). Under these analytical conditions, the relative precisions (1 RSD) for the major elements are: $\sim 1\%$ for Al, $\sim 1.2\%$ for Si, $\sim 5\%$ for Na and B, $\sim 6\%$ for Ca and $\sim 20\%$ for Fe. For formula calculations the EMP data was normalized to 18 cations at the Y, Z, T and B sites assuming $\text{Fe}_{\text{tot}} = \text{Fe}^{2+}$ and $\text{Mn}_{\text{tot}} = \text{Mn}^{2+}$.

MC-ICP-MS

The boron isotope ratio of the olenite RM presented in this study was analysed at the Isotope Geochemistry Laboratory at the MARUM-Center for Marine Environmental Sciences, University of Bremen (Germany). The analytical procedure is the same as for high-concentrated boron samples detailed in Kutzschbach et al. (2017) and references therein. Certified reference tourmaline IAEA-B4 and NIST SRM 951 were processed with the olenite to monitor the precision and the accuracy of the analytical procedure. Sample dissolution and separation of solid samples followed the procedure described in Romer et al. (2014), which was modified from Kasemann et al. (2001) and Tonarini et al. (1997). About 1 mg of the powdered and homogenised olenite RM was fused with K_2CO_3 in Pt crucibles and the resulting melt cake was dissolved in ultrapure water. For the IAEA-B4 certified reference tourmaline up to 3.5 mg were used. An aliquot of sample solution containing 2-5 μg B was passed through a two-step anion-cation column separation (Romer et al. 2014). Boron loss during separation can result in significant isotopic fractionation. Therefore, each separation step was checked for B loss by collecting 2 ml of the tail fraction. In all cases, more than 99.8 % of the B was collected in the main fraction. The procedural blank had less than 5 ng B with a $\delta^{11}\text{B}$ value of -2.7 ‰ and had no influence on the isotopic composition of the sample. Purified olenite RM and standard reference materials IAEA-B4 and NIST SRM 951 were dissolved in 2% HNO_3 and matched to a 100 ppb B ($\pm 5\%$) NIST SRM 951 reference solution. Boron isotope ratios were analysed repeatedly on MC-ICP-MS Neptune Plus (ThermoFisher Scientific) equipped with the SIS (stable introduction system) and a high-efficiency x-cone using the standard-sample bracketing method and 2% HNO_3 as a baseline for correction. Isotope compositions are reported relative to NIST SRM 951 in the conventional $\delta^{11}\text{B}$ (‰) notation $[\delta^{11}\text{B} = \{[(^{11}\text{B}/^{10}\text{B})_{\text{sample}}/(^{11}\text{B}/^{10}\text{B})_{\text{NIST SRM 951}}] - 1\} * 1000]$. The internal precision of repeatedly analysed reference materials is better than 0.2 ‰ (2 SD). In this study, the analyzed NIST SRM 951 has a $\delta^{11}\text{B}$ value of $-0.1 \pm 0.2\text{ ‰}$ (2 SD). Analyses of certified reference tourmaline IAEA-B4 tourmaline yields $\delta^{11}\text{B}$

values of -8.9 ± 0.1 ‰ (2 SD, $n = 2$), which is in agreement with published values [e.g., 8.97 ± 0.13 ‰ (2 SD) from Kutzschbach et al. 2017; -8.86 ± 0.56 ‰ (2 SD) from Meyer et al. 2008; and -8.71 ± 0.36 ‰ (2 SD) from Gonfiantini et al. 2003] and confirms the accuracy of the analytical procedure. From repeated analysis of fully processed certified reference materials, we estimate that the external precision of $\delta^{11}\text{B}$ is better than 0.2 ‰ (2 SD).

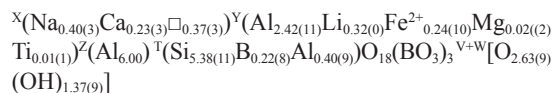
SIMS

Analytical conditions for the SIMS homogeneity test are the same as for session S2 described in the main paper.

RESULTS AND DISCUSSION

EMPA studies reveal that tourmaline appears in intimate intergrowth with albite, quartz and accessory muscovite (Fig. A1). The tourmaline shows a faint patchy zonation with higher FeO, higher SiO_2 and lower Al_2O_3 contents distinguishing the BSE-light areas from the BSE-dark areas. Altogether 46 microprobe analyses were performed across the tourmaline, measuring both BSE-light and BSE-dark areas (Table A1). Variations in B_2O_3 concentrations are within the precision of the EMP and hence are considered constant, whereas variations of Al_2O_3 , FeO and SiO_2 slightly exceed the precision of the microprobe. However, the inhomogeneity of the olenite RM in terms of major elements is small compared to the differences in composition among different tourmaline RM (Fig. 1) and hence, a bias of the SIMS analyses due to intracrystalline chemical variation of the olenite RM is excluded.

Kalt et al. 2001 have reported a homogeneous distribution of Li_2O [0.48(1) wt %], F [0.10(1) wt %] and ZnO [0.05(1) wt %] in tourmalines from the marginal Koralpe pegmatite, from which the olenite RM was sampled (mean and standard deviation, 1 SD, of the three representative analyses of PEG tourmaline given in Kalt et al. 2001; their Table 1). These elements have not been analyzed in our study, but due to its low molecular weight, Li_2O contents are significant and have been considered for formula calculation. Normalizing the averaged microprobe data to 18 cations on the Y, Z, T and B sites, yields the following chemical formula of the olenite RM:



A SIMS B isotope homogeneity test was performed on the same mount by measuring $^{11}\text{B}/^{10}\text{B}$ ratios across the olenite RM

in 3 clusters (one in the center and two at opposite edges). Each cluster consisted of 5 points (15 measurements altogether) whereby within each cluster BSE-dark and BSE-light areas were sampled. No systematic difference between clusters and BSE-light and BSE-dark areas was detected and the mean $^{11}\text{B}/^{10}\text{B}$ is 3.9411(26); 2 SD. This corresponds to a repeatability of 0.66 ‰ (2 RSD), which is in the range of the repeatability obtained for other tourmaline RM (Table 2). Hence, the olenite RM is considered isotopically homogeneous.

Independent determination of the B isotope composition by MC-ICP-MS yielded a $^{11}\text{B}/^{10}\text{B}$ ratio of 4.0384 ± 0.0004 (2 SD) corresponding to a $\delta^{11}\text{B}$ of -1.3 ± 0.1 ‰. The Rietveld refinement of a fraction of the same sample (Dwd: 1.551, $\chi^2 = 0.9724$) results in the following phase proportions: tourmaline 95 (1) wt%, quartz 3 (1) wt% and traces of albite 2 (1) wt%. In contrast to the epoxy mount, muscovite has not been detected. Unit cell parameters of the olenite RM are: $a = 15.7979(5)$ Å, $c = 7.0823(4)$ Å and $V = 1530.8(2)$ Å³. Boron contents of albite and quartz were both below the detection limit during EMP analysis (0.41 wt% B_2O_3), which is taken as a maximum estimate for their B concentrations. In combination with the average B concentration in tourmaline obtained from EMPA (11.36 wt% B_2O_3) and the phase proportions derived by powder, it is calculated more than 99.8 wt% of the total boron is hosted in tourmaline. Hence we are confident that the B isotope ratios obtained by MC-ICP MS derive from the olenite RM only.

TABLE A1. Chemical composition [wt%] of the olenite reference tourmaline derived by EMP

| | BSE-light ^a | BSE-dark ^a | mean (n=46) |
|--|------------------------|-----------------------|-------------|
| SiO_2 | 33.19 | 32.77 | 32.80(60) |
| TiO_2 | 0 | 0.07 | 0.04 (4) |
| B_2O_3 | 10.68 | 11.42 | 11.36(31) |
| Al_2O_3 | 44.52 | 45.67 | 45.60(1.04) |
| FeO | 2.86 | 1.51 | 1.72(0.73) |
| MnO | 0 | 0 | 0.05(5) |
| MgO | 0.04 | 0.28 | 0.07(6) |
| CaO | 1.48 | 1.1 | 1.32(16) |
| Na_2O | 1.18 | 1.41 | 1.24(9) |
| K_2O | 0 | 0.02 | 0.01(1) |
| Li_2O^b | 0.48 | 0.48 | 0.48 |
| H_2O | n.d. | n.d. | n.d. |
| Total | 94.43 | 94.73 | 94.69 |
| FeO # ^c | 0.06 | 0.03 | 0.04 |
| MgO # ^c | 0 | 0.01 | 0 |
| Al_2O_3 # ^c | 0.94 | 0.96 | 0.96 |

^a representative analysis

^b Li_2O content taken from Kalt et al. (2001). See results and discussion section for further information.

^c oxide concentration normalized to $(\text{FeO} + \text{MgO} + \text{Al}_2\text{O}_3)$

n.d. = not determined. numbers in parentheses denote the standard deviation (1 SD)

Figure A1

