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# Boron and lithium isotopic compositions as provenance indicators of Cu-bearing tourmalines

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## ABSTRACT

The Li and B isotopic compositions of gem-quality Cu-bearing tourmalines were used (1) to distinguish among Paraiba tourmalines from Brazil and Cu-bearing tourmalines from Nigeria and Mozambique; and (2) to identify the likely source of Li and B for these gem-quality tourmalines. The $\delta^{11}$B values of tourmaline from Paraiba, Brazil, range from −42.4‰ to −32.9‰, whereas the $\delta^{11}$B values of Cu-bearing tourmaline from Nigeria and Mozambique range from −30.5‰ to −22.7‰ and −20.8‰ to −19.1‰ respectively. Tourmalines from each locality have relatively homogeneous $\delta^{11}$B values and display no overlap. There is slight overlap between $\delta^{7}$Li values of Paraiba tourmaline (+24.5‰ to +32.9‰) and Cu-bearing tourmaline from Nigeria (+32.4‰ to +35.4‰), and $\delta^{7}$Li values of Cu-bearing tourmaline from Nigeria and Mozambique (+31.5‰ to +46.8‰). Nevertheless, Cu-bearing tourmalines from each locality can be fingerprinted using a combination of their $\delta^{11}$B and $\delta^{7}$Li values. The very small $\delta^{11}$B values are consistent with a non-marine evaporite source, and are among the smallest reported for magmatic systems, expanding the global range of B isotopic composition for tourmaline by 12‰. The corresponding large $\delta^{7}$Li values are among the largest reported, although they are less diagnostic of the source of the Li. The large $\delta^{7}$Li values in conjunction with the small $\delta^{11}$B values suggest a non-marine evaporite or brine as a source for Li and B, either as constituent(s) of the magma source region or, by assimilation during magma ascent. The large range in $\delta^{11}$B and $\delta^{7}$Li values suggests that B and Li isotope fractionation occurred during magmatic degassing and late-stage magmatic-hydrothermal evolution of the granite-pegmatite system.

**Keywords:** tourmaline, isotopes, Paraiba, lithium, boron.

## Introduction

Tourmaline is the largest and most abundant mineralogical sink for B and is hosted in a variety of geological settings. It is a common constituent of granites and granitic pegmatites (e.g. Aurisicchio *et al.*, 1999; Dyar *et al.*, 1999; Novák and Povondra, 1995; Novák *et al.*, 1995, 1999; Selway *et al.*, 1999, 2000*a*,*b*, 2002; Agrosi *et al.*, 2006; Neiva *et al.*, 2007) and a wide variety of metamorphic rocks (e.g. Henry and Dutrow, 1992, 1996; Henry and Guidotti, 1985). Considerable work has been done on the characterization (e.g. Hawthorne *et al.*, 1993; Taylor *et al.*, 1995; MacDonald and Hawthorne, 1995; Bosi, 2008; Bosi and Lucchesi, 2004; Bosi *et al.*, 2004, 2005*a*,*b*; Burns *et al.*, 1994; Bloodaxe *et al.*, 1999; Dyar *et al.*, 1998; Grice and Ercit, 1993; Grice *et al.*, 1993; Francis *et al.*, 1999; Cámara *et al.*, 2002; Schreyer *et al.*, 2002; Ertl and Hughes, 2002; Ertl *et al.*, 2003*a*,*b*, 2004, 2005, 2008; Hughes *et al.*, 2000, 2004; Marschall *et al.*, 2004; Andreozzi *et al.*, 2008; Lussier *et al.*, 2008*a*,*b*, 2009) and understanding (Hawthorne, 1996, 2002; Pieczka, 1999; Bosi, 2008) of site occupancy in tourmaline, and a general understanding of its crystal chemistry is gradually emerging. Water and other fluxing components such as Li and B are central to most

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crystallization models of granitic pegmatites (London, 1986; Thomas *et al.*, 1988; Morgan and London, 1999; Sirbescu and Nabelek, 2003*a*,*b*). The fluxing components may play a critical role in permitting crystallization of pegmatitic melts at low temperature (e.g. <400ºC; Thomas and Klemm, 1997; Webber *et al.*, 1999; Thomas *et al.*, 2000; Nabelek, 2007; Sirbescu *et al.*, 2008).

Tourmaline exhibits a wide range of colours and is a popular gemstone. Copper-bearing elbaites are by far the most valuable of the gem tourmalines, and the highest-quality stones can command up to $20,000/carat. The general chemical formula for tourmaline may be written (Hawthorne and Henry, 1999) as:

$$XY_3Z_6(T_6O_{18})(BO_3)_3V_3W \qquad (1)$$

where $X$ = Ca, Na, K, □ (vacancy); $Y$ = Li, Mg, $Fe^{2+}$, $Mn^{2+}$, Zn, Al, $Cr^{3+}$, $V^{3+}$, $Fe^{3+}$, $Ti^{4+}$; $Z$ = Mg, Al, $Fe^{3+}$, $Cr^{3+}$, $V^{3+}$; $T$ = Si, Al, B; $V$ = OH, O and $W$ = OH, F, O. Crystal-structure refinement of Cu-bearing tourmaline from Paraiba, Brazil, showed that the octahedrally coordinated $Z$ site is completely occupied by Al, and Cu is a minor constituent of the octahedrally coordinated $Y$ site (MacDonald and Hawthorne, 1995). Traditionally, the name 'Paraiba' is reserved for bright blue to green Cu-bearing tourmalines from the da Batalha mine in Paraiba state, north-eastern Brazil (Koivula and Kammerling, 1989). Saturated and less-saturated blue and green tourmalines have been mined from other deposits near the da Batalha mine (Fig. 1) in the neighbouring state of Rio Grande do Norte (Shigley *et al.*, 2001), Mozambique (Wentzell, 2004; Laurs *et al.*, 2008) and Nigeria (Smith *et al.*, 2001; Furuya and Furuya, 2007; Breeding *et al.*, 2007). The Mavuco (or Chalaua) mine in the Alto Ligonha pegmatitic district, Mozambique, is the world's largest known deposit of Cu-bearing tourmaline and the colour of these tourmalines is similar to the highest quality tourmalines from Paraiba, Brazil (Laurs *et al.*, 2008). The saturated variety of these gem-quality tourmalines cannot be distinguished from blue-green tourmaline from Paraiba using standard gemological testing or semi-quantitative EDXRF analysis. Trace element analysis using LA-ICP-MS has achieved limited success in distinguishing tourmalines from Brazil, Mozambique, and Nigeria (Abduriyim *et al.*, 2006). However, the Li and B isotopic compositions of tourmaline can be used as powerful geochemical tracers and can provide valuable information regarding magma-volatile relations and the magmatic-hydrothermal evolution of pegmatites. In this study, we use Secondary Ion Mass Spectrometry (SIMS) to measure the stable isotopes of Li and B in Cu-Mn-bearing tourmaline from these localities in order (1) to develop criteria to discriminate their origin, and (2) to identify the source of the fluids that precipitated these minerals.

## Methods

Eight samples of Cu-bearing tourmaline were obtained from the Museum of the Gemological Institute of America. Samples Br1–Br4 are from Paraiba, Brazil, Ng1 and Ng2 are from Nigeria, and Moz1 and Moz2 are from Mavuco, Mozambique. Polished grain mounts of each sample were prepared and the textural homogeneity of the grains was characterized using optical and scanning electron microscopy.

### *Electron-microprobe analysis*

All crystals were analysed using a Cameca SX100 electron microprobe operating in wavelength-dispersive mode with an accelerating voltage of 15 kV, a probe current of 20 nA, and a final beam diameter of 1 μm. The following analysing crystals and standards were used: TAP: albite (Na); andalusite (Al); diopside (Si); LPET: orthoclase (K); diopside (Ca); LTAP: fluororiebeckite (F); forsterite (Mg); LLiF: fayalite (Fe); spessartine (Mn); titanite (Ti); $CuFeS_2$ (Cu). The data were reduced and corrected by the PAP method of Pouchou and Pichoir (1985). Table 1 gives the chemical compositions (mean of three determinations) and formulae calculated with the following assumptions: 31 anions; OH + F = 4 a.p.f.u.; B = 3 a.p.f.u.; $^{Z}Al$ = 6 a.p.f.u.; and Li = $(3 - \Sigma)$ a.p.f.u., iterated to self-consistency.

### *Secondary-Ion Mass Spectrometry*

The isotopic ratios of $^{7}Li/^{6}Li$ and $^{11}B/^{10}B$ were measured using a CAMECA ims 7f secondary ion mass spectrometer (SIMS). The grain and standard mounts were placed in stainless steel sample holders and the entire assembly was placed in the SIMS sample chamber airlock and held at high vacuum for a minimum of 8 h prior to the start of analysis to lessen interference and increase accuracy.

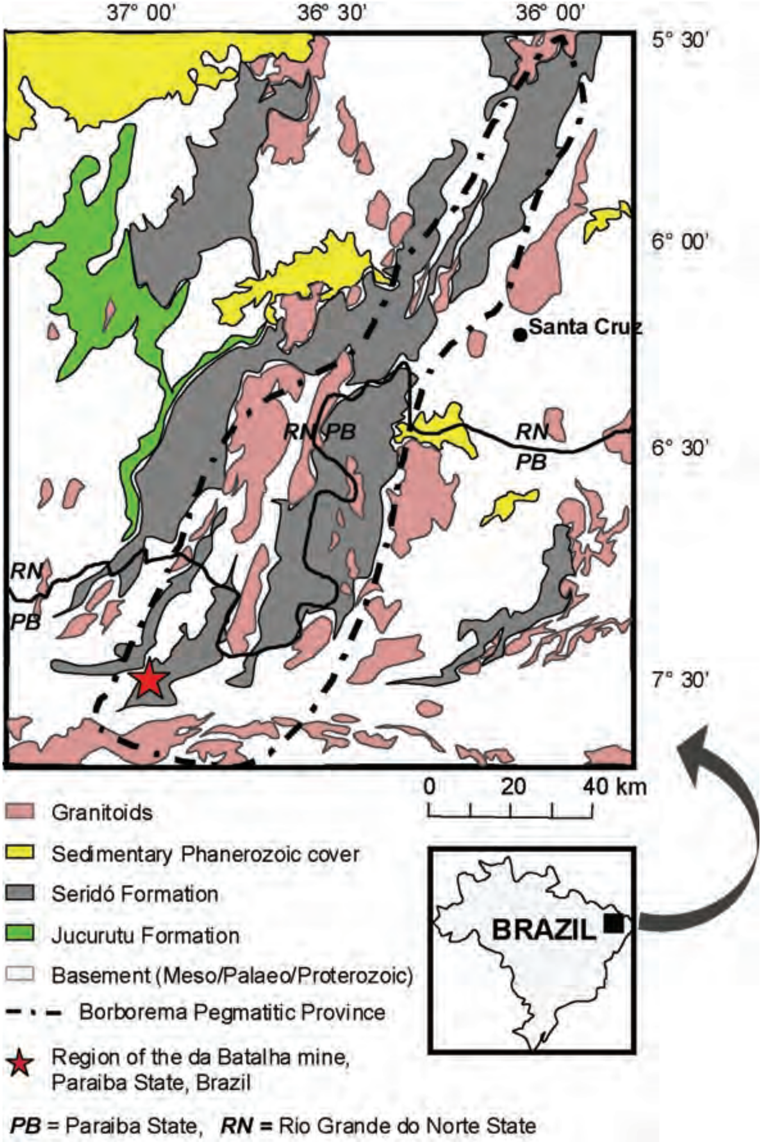

FIG. 1. Geological map of Rio Grande do Norte and Paraiba State, Brazil, showing the location of the Batalha mine (modified from Soares *et al*., 2007).

Isotope ratios for Li and B were measured using a ~20 μm 10 nA primary beam of O$^-$ ions. A mass resolving power of ~1300 for Li and B was sufficient to limit isobaric interferences to <0.1‰. The sample-accelerating voltage and electrostatic analyser in the secondary column were set to accept +10 kV, and an energy window of ±50 volts as well as a 300 s pre-sputter was used. Ions were detected with an ETP electron multiplier coupled with an ion-counting system with an overall deadtime of 25 ns. The following species were detected sequentially by switching the magnetic field: $^6$Li$^+$ and $^7$Li$^+$ during one session to collect the Li isotopic ratios, and $^{10}$B$^+$ and $^{11}$B$^+$ during a separate session to measure the B isotopic ratios. All Li and B isotopic data are

TABLE 1. Chemical compositions (wt.%) of tourmaline from Brazil, Nigeria and Mozambique.

| | Bra1* | Bra2* | Bra3* | Bra4* | Ng1* | Ng2* | Moz1* | Moz2* |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 37.45 | 36.58 | 37.03 | 36.23 | 37.33 | 36.45 | 36.75 | 37.34 |
| $Al_2O_3$ | 40.75 | 42.22 | 40.72 | 41.02 | 41.04 | 41.17 | 40.54 | 42.52 |
| $TiO_2$ | 0.08 | 0.01 | 0.02 | 0.01 | 0.02 | 0 | 0.01 | 0 |
| FeO | 0.09 | 0.01 | 0.02 | 0 | 0.03 | 0.22 | 0.01 | 0 |
| MnO | 0.53 | 1.23 | 2.65 | 1.89 | 2.65 | 2.39 | 3.30 | 0.82 |
| MgO | 0.17 | 0 | 0.11 | 0 | 0.01 | 0.01 | 0 | 0 |
| CuO | 1.04 | 0.81 | 1.44 | 1.48 | 0.78 | 0.01 | 0.28 | 0.24 |
| CaO | 0.35 | 0.29 | 0.27 | 0.33 | 0.09 | 0.35 | 0.22 | 0.35 |
| $Na_2O$ | 2.01 | 1.88 | 2.24 | 2.07 | 2.30 | 2.08 | 2.20 | 1.83 |
| $K_2O$ | 0.02 | 0.01 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.01 |
| F | 1.43 | 0.94 | 1.34 | 1.32 | 1.02 | 1.26 | 1.24 | 0.95 |
| $Li_2O$** | 1.91 | 1.73 | 1.63 | 1.64 | 1.70 | 1.73 | 1.66 | 1.89 |
| $B_2O_3$** | 10.98 | 11.00 | 11.02 | 10.88 | 11.06 | 10.91 | 10.92 | 11.11 |
| $H_2O$** | 3.11 | 3.35 | 3.17 | 3.13 | 3.33 | 3.17 | 3.18 | 3.38 |
| Sub total | 99.92 | 100.06 | 101.68 | 100.02 | 101.38 | 99.77 | 100.33 | 100.44 |
| less O≡F | 0.60 | 0.40 | 0.56 | 0.56 | 0.43 | 0.53 | 0.52 | 0.40 |
| Total | 99.32 | 99.66 | 101.12 | 99.46 | 100.95 | 99.24 | 99.81 | 100.04 |
| Formula calculations | | | | | | | | |
| Si | 5.927 | 5.778 | 5.84 | 5.787 | 5.867 | 5.807 | 5.85 | 5.839 |
| Al | 0.073 | 0.222 | 0.16 | 0.213 | 0.133 | 0.193 | 0.15 | 0.161 |
| $\Sigma T$ | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| $^{[4]}Al$ | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 |
| B | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| $^{[6]}Al$ | 1.528 | 1.638 | 1.409 | 1.509 | 1.468 | 1.537 | 1.455 | 1.675 |
| $Ti^{4+}$ | 0.01 | 0.001 | 0.002 | 0.001 | 0.002 | 0 | 0.001 | 0 |
| $Fe^{2+}$ | 0.012 | 0.001 | 0.003 | 0 | 0.004 | 0.029 | 0.001 | 0 |
| $Mn^{2+}$ | 0.071 | 0.165 | 0.354 | 0.256 | 0.353 | 0.322 | 0.445 | 0.109 |
| Mg | 0.04 | 0 | 0.026 | 0 | 0.002 | 0.002 | 0 | 0 |
| $Cu^{2+}$ | 0.124 | 0.097 | 0.172 | 0.179 | 0.093 | 0.001 | 0.034 | 0.028 |
| Li | 1.216 | 1.099 | 1.034 | 1.053 | 1.075 | 1.108 | 1.063 | 1.189 |
| $\Sigma Y$ | 3.001 | 3.001 | 3 | 2.998 | 2.997 | 2.999 | 2.999 | 3.001 |
| Ca | 0.059 | 0.049 | 0.046 | 0.056 | 0.015 | 0.06 | 0.038 | 0.059 |
| Na | 0.617 | 0.576 | 0.685 | 0.641 | 0.701 | 0.642 | 0.679 | 0.555 |
| $\Sigma X$ | 0.676 | 0.625 | 0.731 | 0.697 | 0.716 | 0.702 | 0.717 | 0.614 |
| OH | 3.284 | 3.53 | 3.332 | 3.333 | 3.493 | 3.365 | 3.376 | 3.53 |
| F | 0.716 | 0.47 | 0.668 | 0.667 | 0.507 | 0.635 | 0.624 | 0.47 |

Abbreviations: Bra = Paraiba, Brazil; Ng = Nigeria; Moz = Mavuco, Mozambique.
* Average values based on three analyses per grain. The standard deviation on each value is <1%.
** Calculated values.

presented using standard δ-notation relative to the appropriate international standard, L-SVEC, defined as 12.1163 for $^7Li/^6Li$ (Moriguti and Nakamura, 1998) and NIST 951, defined as 4.0536 for $^{11}B/^{10}B$ (Nakano and Nakamura, 2001; Table 2).

During the measurement process by SIMS, an intrinsic mass-dependent bias is introduced, which is referred to as 'instrumental mass fractionation' (IMF) and typically favours the lower mass isotope. The greatest contributor to IMF is the ionization process, which depends most strongly on sample characteristics (i.e. chemical composition). This is referred to as 'compositionally dependent fractionation' or 'matrix effects' (e.g. Riciputi *et al.*, 1998). Therefore, accurate isotopic analysis by SIMS requires that IMF be corrected by standardizing the IMF using mineral standards

TABLE 2. B and Li isotopic composition of tourmalines from Brazil, Nigeria and Mozambique.

| Sample | $^{11}B/^{10}B_{SIMS}$ | $\delta^{11}B_{NIST951}$ | $2\sigma$ | $^{7}Li/^{6}Li_{SIMS}$ | $\delta^{7}Li_{L\text{-}SVEC}$ | $2\sigma$ |
|---|---|---|---|---|---|---|
| Brazil 1 | 3.7636 | −42.4 | 0.6 | 1.2661 | 31.2 | 1.3 |
| | 3.7649 | −42.0 | 0.6 | 1.2663 | 31.4 | 1.3 |
| | 3.7698 | −40.8 | 0.6 | 1.2633 | 28.9 | 1.3 |
| Brazil 2 | 3.7866 | −36.5 | 0.6 | 1.2578 | 24.5 | 1.3 |
| | 3.7910 | −35.4 | 0.6 | 1.2584 | 25.0 | 1.3 |
| | 3.7944 | −34.5 | 0.6 | 1.2593 | 25.7 | 1.3 |
| Brazil 3 | 3.7826 | −37.5 | 0.6 | 1.2613 | 27.3 | 1.3 |
| | 3.7845 | −37.0 | 0.6 | 1.2642 | 29.7 | 1.3 |
| | 3.7866 | −36.5 | 0.6 | 1.2682 | 32.9 | 1.3 |
| Brazil 4 | 3.8000 | −33.1 | 0.6 | 1.2652 | 30.5 | 1.3 |
| | 3.8007 | −32.9 | 0.6 | 1.2642 | 29.7 | 1.3 |
| Nigeria 1 | 3.8290 | −25.7 | 0.6 | 1.2709 | 35.2 | 1.3 |
| | 3.8317 | −25.0 | 0.6 | 1.2684 | 33.1 | 1.3 |
| | 3.8407 | −22.7 | 0.6 | 1.2696 | 34.1 | 1.3 |
| Nigeria 2 | 3.8160 | −29.0 | 0.6 | 1.2675 | 32.4 | 1.3 |
| | 3.8103 | −30.5 | 0.6 | 1.2708 | 35.1 | 1.3 |
| | 3.8113 | −30.2 | 0.6 | 1.2712 | 35.4 | 1.3 |
| Moz 1 | 3.8549 | −19.1 | 0.6 | 1.2684 | 33.1 | 1.3 |
| | 3.8514 | −20.0 | 0.6 | 1.2687 | 33.4 | 1.3 |
| | 3.8515 | −20.0 | 0.6 | 1.2710 | 35.3 | 1.3 |
| Moz 2 | 3.8485 | −20.8 | 0.6 | 1.2775 | 40.5 | 1.3 |
| | 3.8515 | −20.0 | 0.6 | 1.2829 | 44.9 | 1.3 |
| | 3.8507 | −20.2 | 0.6 | 1.2852 | 46.8 | 1.3 |

Abbreviations: Brazil = Paraiba, Brazil; Moz = Mavuco, Mozambique

that are compositionally similar to the unknown. The SIMS results from the standard are compared to its accepted isotopic composition in order to compute a correction factor that is applied to the unknowns measured during the same analysis session (e.g. Holliger and Cathelineau, 1988; Cathelineau *et al.*, 1990). The NIST 610 standard (Li = 484.6 ppm and B = 357.6 ppm) was used as an internal standard for both Li and B isotope-ratios to correct for mass bias. The spot-to-spot reproducibility (based on 5−7 analyses) on the NIST 610 standard was ±0.6‰ ($1\sigma$) for B and ±1.3‰ ($1\sigma$) for Li. The overall precision and accuracy for each isotope analysis include errors arising from counting statistics of each individual analysis, calibration to a known standard, and uncertainty in deadtime corrections arising from variable count rates. In general, the overall precision was ±0.6‰ ($2\sigma$) for B and ±1.3‰ ($2\sigma$) for Li.

Although the absolute $\delta^7$Li values for the NIST glasses are controversial, we used the value of +23‰ for NIST 610 (Kasemann *et al.*, 2005). The NIST 610 glass was most similar in matrix to our tourmalines (e.g. large Na, Si and small Fe contents; Table 1). The mass bias for NIST 610 and NIST 612 (Li = 41.54 ppm) is the same, which suggests that matrix effects are negligible for materials, such as tourmaline, with large Li concentrations (Kasemann *et al.*, 2005). However, the mass bias is not the same for materials with small Li concentrations. For example, we analysed BHVO-2G USGS glass standard (Li = 5 ppm) for Li isotopes. Data corrected using the BHVO-2G standard was consistently 20‰ lower than data corrected using the NIST 610 glass standard. The mass-bias difference between NIST 610 and BHVO-2G could also be due to other matrix factors such as the large Na and Si and small Fe contents of the NIST 610 glass. To solve this matrix-related problem, more silica-rich materials need to be studied. The mass bias for B isotope-ratio analysis by SIMS is known to be independent of the matrix (Chaussidon and Appel, 1997).

## Results

### Chemical compositions

The samples generally have similar chemical compositions (Table 1), and all classify as fluor-elbaite (Hawthorne and Henry, 1999). Copper and Mn concentrations vary from 0.01 to 1.48 wt.% CuO and 0.53 to 3.30 wt.% MnO respectively, but there is no direct correlation between Cu and Mn concentrations and the colour of these minerals. Copper and Mn concentrations also vary significantly in tourmaline samples from a single region; for example, tourmaline from Nigeria has CuO ranging from 0.01 to 0.78 wt.%, whereas the MnO in tourmaline from Mozambique varies from 0.82 to 3.30 wt.%. Concentrations of Si, Al, Na and F across all sources, as well as for samples within each individual source, display variations ranging from 36.23 to 37.45 wt.% $SiO_2$, 40.54 to 42.52 wt.% $Al_2O_3$, 1.83 to 2.30 wt.% $Na_2O$ and 0.94 to 1.43 wt.% F. The remaining elements that were measured (Mg, K, Ca, Fe, and Ti) have concentrations <0.35 wt.%.

### B and Li isotopes

The B isotopic composition of the eight samples of Cu-bearing tourmaline ranges from −42.4‰ to −19.1‰ (Table 2). The smallest $\delta^{11}B$ values are from Brazil (−42.4‰ to −32.9‰), whereas the largest values are from Mozambique (−20.8‰ to −19.1‰). Tourmalines from Nigeria have intermediate $\delta^{11}B$ values (−30.5‰ to −22.7‰) (Fig. 2). Tourmalines from Brazil and Nigeria have a similar range in $\delta^{11}B$ values (~8−9‰), whereas tourmalines from Mozambique have a much narrower range in $\delta^{11}B$ values (1.7‰). The $\delta^{11}B$ values of tourmalines in our study are among the smallest values reported for magmatic systems. Based on these data, the B isotopic composition of Cu-bearing tourmaline is distinct for tourmalines from the three major regions that produce the blue-green gem tourmalines.

The Li isotopic composition for the Cu-bearing tourmalines are reported in Table 2 and range from +24.5‰ to +46.8‰. Tourmalines from Brazil have a wide range in $\delta^7Li$ values (+24.5‰ to +32.9‰), whereas $\delta^7Li$ values of tourmaline from Nigeria have a very narrow range (+32.4‰ to +35.4‰). In contrast to the narrow range of B isotopic compositions (−20.8‰ to −19.1‰) of tourmaline from Mozambique, the $\delta^7Li$ values of these tourmalines show the greatest range (+31.5‰ to +46.8‰) (Fig. 2). Although tourmalines from pegmatites generally have high $\delta^7Li$ values (~10‰ to 20‰; e.g. Maloney *et al.*, 2008), the Li isotopic composition of the Cu-bearing tourmalines examined here are among the highest $\delta^7Li$ values reported for magmatic minerals.

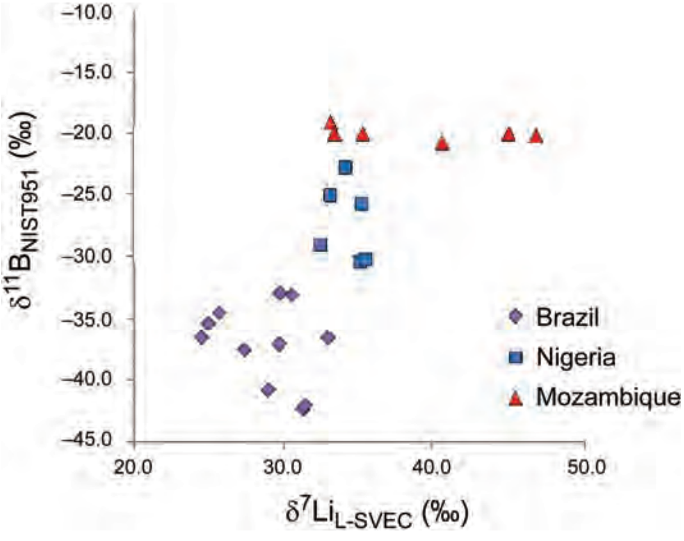

FIG. 2. Variation in $\delta^{11}B$ as a function of $\delta^7Li$ for tourmalines analysed from Paraiba, Brazil, Nigeria and Mavuco, Mozambique. Data are from Table 2.

## Discussion

### *Boron isotope systematics*

In minerals and fluids, B is generally bonded to oxygen as tetrahedral or triangular oxysalt complexes. Boron only occurs in one oxidation state in natural materials, and B isotopic fractionation is generally controlled by the partitioning of B isotopes between the tetrahedral and triangular species, where $^{11}$B favours the triangular coordination and $^{10}$B favours the tetrahedral coordination (Palmer and Swihart, 1996; Kotaka, 1973; Kakihana *et al.*, 1977).

In recent years, chemical and B isotopic compositions of tourmaline have been used as a geochemical tracer in studies of ore-genesis and petrogenesis (Palmer and Swihart, 1996; Slack, 1996; Jiang *et al.*, 1997, 2000; Jiang, 1998). The major element compositions of tourmaline typically reflect the environment in which it crystallized (e.g. Henry and Guidotti, 1985; Slack, 1996). Previous B isotope studies show that B isotopes can vary in natural samples and reservoirs by as much as 80‰ (Barth, 1993; Palmer and Swihart, 1996). As a highly mobile element during magmatic and fluid-related processes, B is preferentially enriched in late exsolved volatile-rich fluids, and the exsolution of these fluids leads to depletion of B and other 'fluid mobile' elements in granites (Dingwell *et al.*, 1996; London *et al.*, 2002). In most cases, tourmaline is the only significant B sink in the granite-hydrothermal systems.

Tourmaline is only stable at low pH (Morgan and London, 1989), so triangularly coordinated B is the only stable B species in solution in equilibrium with tourmaline. Therefore, tourmalines should be enriched in $^{11}$B and have high $\delta^{11}$B values. However, tourmalines can have low $\delta^{11}$B values (e.g. Palmer and Slack, 1989). Based on the results of adsorption experiments on clay, Palmer *et al.* (1987) proposed that incorporation of B in aluminosilicates proceeds initially by adsorption of trigonal $B(OH)_3$ onto mineral surfaces. The coordination of the B atom changes from triangular in solution to tetrahedral in the adsorbed species where the adsorbed species is enriched in $^{10}$B. Therefore, the transition from triangular to tetrahedral controls the isotope fractionation, and suggests that B is incorporated into the structure of the mineral without further isotope fractionation, allowing very low $\delta^{11}$B values.

Tourmalines occur in a variety of geological environments (Leeman and Sisson, 1996), and most tourmalines have $\delta^{11}$B values that range from −30‰ to +20‰ (Fig. 3). The majority of tourmalines hosted in granite-pegmatite systems have $\delta^{11}$B values that range from −10‰ to +10‰ (Fig. 3; Barth, 1993), which is characteristic of a granitic source for B. However, not all tourmaline-bearing granitic rocks are the result of B-rich magmas, and tourmaline may be postmagmatic in origin (Dingwell *et al.*, 1996) and reflect isotopically higher or lower $\delta^{11}$B values. Extremely low $\delta^{11}$B values for tourmaline have been reported at Broken Hill, Australia (−27‰ to −23‰; Palmer and Slack, 1989) and the Lavicky leucogranite, Czech Republic (−37.3‰ to −21.3‰; Jiang *et al.*, 2003). As non-marine

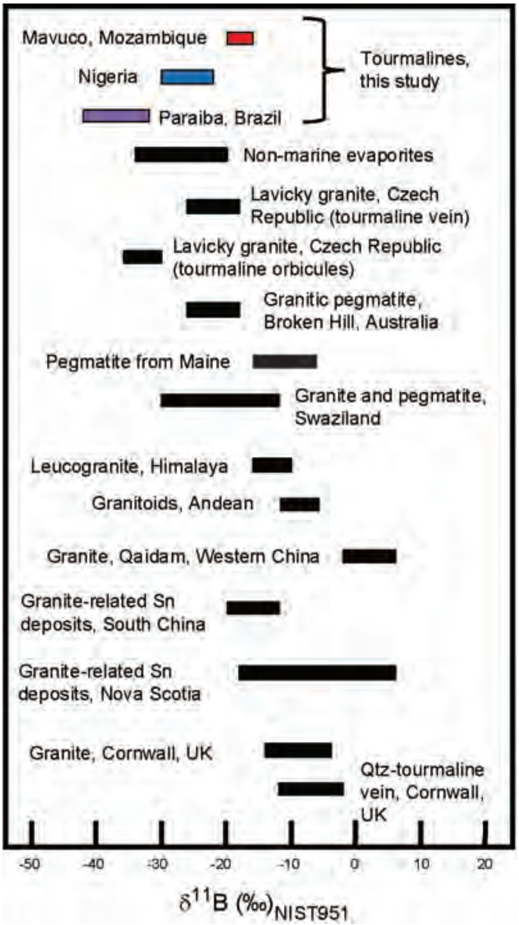

FIG. 3. Comparison of $\delta^{11}$B values of tourmalines from granites, veins and pegmatites in general, together with the results from this study (modified from Jiang *et al.*, 2003).

evaporites are the only known B reservoir with $\delta^{11}B$ values less than −20‰ (Swihart *et al.*, 1986), one explanation for these unusually low $\delta^{11}B$ values is that non-marine evaporites were present at the source region of the sediments and incorporated in the lithification process. The melting of sedimentary rocks produced by non-marine evaporites would therefore produce granitic magmas with lower $\delta^{11}B$ values (Jiang *et al.*, 2003).

The Cu-bearing tourmalines in our study are from pegmatites and paleoplacer deposits (which were likely derived from local pegmatite) and have $\delta^{11}B$ values that range from −42.4‰ to −19.1‰. Although all the $\delta^{11}B$ values of the Cu-bearing tourmalines in our study are low and generally reflect a non-marine evaporitic source, the $\delta^{11}B$ values of the tourmalines from Mozambique ($\delta^{11}B \approx -20.0$‰) and Nigeria ($\delta^{11}B \approx -26.6$‰) are generally higher than the values of tourmaline from Paraiba, Brazil ($\delta^{11}B \approx -37.7$‰). These differences in $\delta^{11}B$ values suggest that, at least for the Mozambique and Nigerian tourmalines, there are different degrees of crustal assimilation, or possibly more than one source for B (e.g. magmatic), during the crystallization process that resulted in higher $\delta^{11}B$ values than for the Brazilian tourmalines for which non-marine evaporites seem to be the dominant source of B.

Our values are similar to the $\delta^{11}B$ values reported by Jiang *et al.* (2003) for tourmalines from the Lavicky leucogranite, Czech Republic, and suggest that the source of the B was non-marine evaporites. However, the results by Jiang *et al.* (2003) were challenged by Marschall and Ludwig (2006) who re-analysed tourmalines from the same leucogranite by SIMS and reported $\delta^{11}B$ values from −11.54‰ to −9.76‰. Based on these results, Marschall and Ludwig (2006) suggested that the B came from the granite rather than non-marine evaporites. One possible explanation for the discrepancy in the data of Jiang *et al.* (2003) and Marshall and Ludwig (2006) is the different techniques used to obtain the data. Jiang *et al.* (2003) used Negative Thermal Ionization Mass Spectrometry (N-TIMS) whereas Marshall and Ludwig (2006) used a Cameca 3f SIMS. Jiang (2006) compared TIMS and SIMS data for tourmalines from the Lavicky leucogranite and reported that some of the tourmalines that gave low $\delta^{11}B$ values (e.g. −41‰) using N-TIMS gave higher values (e.g. −9.3‰) using SIMS. However, not all the samples analysed by SIMS produced $\delta^{11}B$ values that were greater than those obtained by N-TIMS; some SIMS $\delta^{11}B$ values were smaller than the N-TIMS values. Jiang (2006) concluded that the lower $\delta^{11}B$ values reported by Jiang *et al.* (2003) may have been due to fractionation during sample preparation and acid digestion. However, Marschall and Ludwig (2006) may have used low mass-resolution during their SIMS analysis and may, as a consequence, have insufficiently resolved the $^{10}BH$ signal which produces an interference with $^{11}B$. This interference would produce artificially elevated $^{11}B$ counts and result in higher $\delta^{11}B$ values. Based on our results, tourmalines from pegmatites can have very low $\delta^{11}B$ values characteristic of a non-marine evaporite source and the values reported by Jiang *et al.* (2003) may be correct.

Although previous studies have shown large $\delta^{11}B$ variations in tourmaline from granites and pegmatites (~30‰), tourmalines from an individual magmatic body generally have a narrow range in $\delta^{11}B$ values (<5‰; Swihart and Moore, 1989; Chaussidon and Albarède, 1992; Smith and Yardley, 1996; Jiang and Palmer, 1998; Tonarini *et al.*, 1998). Our study shows that Cu-bearing tourmalines from Brazil and Nigeria have a wide range in $\delta^{11}B$ values (~8−9‰) whereas Cu-bearing tourmalines from Mozambique have a range in $\delta^{11}B$ values (1.7‰) that is typical of tourmalines from a single magmatic body. There are several possible mechanisms that could produce a range of $\delta^{11}B$ values >5‰ in the tourmalines from our study:

(1) B isotope fractionation can occur during magmatic degassing and magmatic-hydrothermal evolution, where $^{11}B$ is partitioned into the exsolved volatile aqueous fluid, resulting in $^{10}B$ enrichment in the residual melt and magmatic tourmalines (Smith and Yardley, 1996; Jiang and Palmer, 1998);

(2) based on the experimental tourmaline-fluid fractionation factors of Palmer *et al.* (1992), fluctuations in temperature as well as pH could cause a range in $\delta^{11}B$ values (~8−9‰) in tourmalines from Brazil and Nigeria;

(3) mixing between two sources of B (e.g. a primary magmatic source ($\delta^{11}B \approx -10$ to −15‰) and a non-marine evaporite source ($\delta^{11}B \approx -27$‰) (Jiang and Palmer, 1998);

(4) variable water/rock ratios involving the $^{10}B$-rich residual hydrothermal-magmatic fluids, the $^{11}B$-enriched exsolved volatile fluids and the host rocks.

Although currently we cannot determine the exact mechanism that contributed to both the low $\delta^{11}$B values and the wide range in B isotopic composition, it is conceivable that there may be more than one mechanism that produced the anomalous values for Cu-bearing tourmalines (such as fluid mixing and degassing).

### *Lithium isotope systematics*

There has been no comprehensive study of Li isotopes in igneous systems (except where involved purely in mantle melting). Available data show only very limited Li isotope fractionation during crystallization of high-temperature igneous systems (Tomascak *et al*., 1999*a*; Magna *et al*., 2006; Halama *et al*., 2007) and during vapour-liquid separation in hydrothermal systems (Foustoukos *et al*., 2004; Liebscher *et al*., 2007). In general, $^6$Li preferentially occupies sites of higher coordination number involving weaker bonds, whereas $^7$Li preferentially enters sites with lower coordination number (and stronger bonds) (Wunder *et al*., 2007). Therefore, Li isotope geochemistry is similar to B in that there are large isotopic differences between oceanic ($\delta^7$Li +32‰) and mantle reservoirs (Tomascak, 2004).

Recent work on granitic rocks show a wide range in $\delta^7$Li from −1.4‰ to +11.3‰ (e.g. Bryant *et al*., 2003; Teng *et al*., 2004; Tomascak *et al*., 2003; Sturchio and Chan, 2003; Bottomley *et al*., 2003). Studies that have considered evolved granitic systems (associated with Li mineralization) have found both extremely light and heavy isotopic compositions from −10‰ to +19‰ (Vocke *et al*., 1990; Tomascak *et al*., 1995; Tomascak *et al*., 1999*b*). The range in $\delta^7$Li values for these highly evolved magmatic systems (i.e. pegmatites) may be due to mass fractionation at near-solidus temperatures where significant fractionation may result from different coordination states of Li in coexisting phases that include minerals, melts, and aqueous fluids in relatively low-temperature granitic systems (Wenger and Armbruster, 1991; Teng *et al*., 2006). A possible alternative explanation is that the structure of a hydrous pegmatite melt has more similarity to water than to minerals, and therefore it incorporates $^7$Li preferentially over minerals, in a fashion analogous to the large $^7$Li enrichment in crustal fluids compared to crustal rocks (Tomascak, 2004). As hydrated pegmatite melts pass through the crust from their source, they may acquire elevated $\delta^7$Li values through rapid Li isotopic exchange with the surrounding rocks. A third possible mechanism that can produce Li isotope fractionation is diffusion, as $^6$Li has a greater diffusivity relative to $^7$Li (Lundstrom *et al*., 2001; Richter *et al*., 2003). Diffusion would cause magmas to become enriched in $^6$Li as they interacted with various geological reservoirs of Li.

There have been no direct measurements of Li isotope fractionation between peraluminous silicate melts and aqueous fluids, but it seems probable that Li in a melt should be isotopically heavier because of strong bonds in association with charge balancing of Al that is in tetrahedral coordination (Maloney *et al*., 2008). This inference is supported by empirical observations and Li isotopic analysis of fluid inclusions and quartz from the Tin Mountain pegmatite in the Black Hills (Teng *et al*., 2006), where Li in fluid inclusions has much smaller $\delta^7$Li values than Li in quartz (Maloney *et al*., 2008).

The $\delta^7$Li values of Cu-bearing tourmalines (+24.5‰ to +46.8‰) are some of largest $\delta^7$Li values reported. There are several source reservoirs that can produce extremely high $\delta^7$Li values: marine biogenic carbonates, marine pore waters, lake and river waters, saline groundwater and brines, and continental thermal fluids (Tomascak, 2004). Thus, the high $\delta^7$Li values of Cu-bearing tourmalines are not as diagnostic of the source as the very low $\delta^{11}$B values (which are characteristic of non-marine evaporites). As a hydrated pegmatite melt passes through the crust, it may have interacted with any of these sources that are enriched in $^7$Li to produce tourmalines with high $\delta^7$Li values. However, if the main source of Li is similar to the main source of B, this would suggest that the Li isotopic composition of non-marine evaporites is > +20‰.

The Li isotopic composition of tourmalines from pegmatites can vary by as much as 10‰ and they are generally enriched in $^7$Li (Teng *et al*., 2006; Maloney *et al*., 2008). The apparent large fractionation for these relatively low-temperature igneous systems contrasts with the mineral fractionation in high-temperature igneous systems (Tomascak, 2004). Copper-bearing tourmalines from Brazil have a range in Li isotopic composition of ~8‰, whereas Cu-bearing tourmalines from Nigeria have a much narrower range in $\delta^7$Li values (~3‰). In addition, Cu-bearing tourmalines from Brazil and Nigeria have $\delta^7$Li values that are similar to (or below) the $\delta^7$Li value for seawater (~ +32‰). In contrast, the Li isotopic composition of Cu-bearing tourmalines from Mozambique has a range of ~15‰ and the $\delta^7$Li values are generally higher than seawater. The large range of Li isotopic compositions for Cu-bearing tourmalines may be due to mass fractionation that occurs at near-solidus temperatures, particularly for evolving granitic systems (e.g. Tomascak *et al*., 1995). The Cu-bearing tourmalines are enriched in $^7$Li and therefore it is unlikely that diffusion alone can produce the large $\delta^7$Li values. The large Li isotopic fractionation and the large $\delta^7$Li values of Cu-bearing tourmalines are interpreted as a result of crystallization at sub-solidus temperatures in an evolving hydrothermal-magmatic system.

## Conclusions

The Li and B isotopic compositions of pegmatitic Cu-bearing tourmaline from Brazil and Cu-bearing tourmalines in pegmatites and paleoplacer deposits from Nigeria and Mozambique suggest that:

(1) Using B stable isotopes, we can fingerprint and distinguish between Cu-bearing tourmaline from Paraiba, Brazil ($\delta^{11}$B = −42.4‰ to −32.9‰), Nigeria ($\delta^{11}$B = −30.5‰ to −22.7‰) and Mozambique ($\delta^{11}$B = −20.8‰ to −19.1‰);

(2) The $\delta^{11}$B values for Cu-bearing tourmalines (−42.4‰ to −19.1‰) are among the smallest ever reported for magmatic systems. Based on previous studies and B isotope fractionation, these unusually small values suggest a non-marine evaporitic source for the B. The proposed mechanisms that produce the range in B isotopic composition for these tourmalines include fluid mixing and degassing;

(3) Although there is some overlap between the Li isotopic compositions of tourmalines from Paraiba, Brazil, Nigeria, and Mozambique, the large range in Li isotopic compositions and the high $\delta^7$Li values of Cu-bearing tourmalines are probably due to crystallization at sub-solidus temperatures in an evolving hydrothermal-magmatic system.

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