

**Reply to “Re-examination of the boron isotopic composition of tourmaline from the Lavicky granite, Czech Republic, by secondary ion mass spectrometry: back to normal” by H. R. Marschall and T. Ludwig:
Critical comment on “Chemical and boron isotopic compositions of tourmaline from the Lavicky leucogranite, Czech Republic”**

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New SIMS data (Marschall and Ludwig, 2006) indicate that some of the boron isotopic compositions of tourmaline from the Lavicky granite (Czech Republic) previously reported by us (Jiang *et al.*, 2003) are erroneous. The problems are discussed in this paper. This lesson tells us that special cares must be taken when analyzing boron isotopic compositions of solid materials with complex matrices. Sample dissolution, purification of boron via column chemistry, and mass spectrometric measurements have to be carefully evaluated.

Keywords: boron isotopes, tourmaline, analytical problems

INTRODUCTION

The boron isotopic composition of tourmaline from granites and pegmatites is a powerful tracer for petrogenesis, ore-genesis, and geochemical evolution of magmatic- and hydrothermal systems (e.g., Palmer and Swihart, 2002; Slack, 2002). However, the analysis of boron isotope compositions in geological samples, in particular those with complex matrices such as tourmaline, is a challenging task (Gonfiantini *et al.*, 2003; Tonarini *et al.*, 2003). In 2003, we reported extremely negative boron isotope compositions of tourmaline from the Lavicky granite (Jiang *et al.*, 2003), and these values have been proven to be wrong as they are not supported by new SIMS analysis on tourmalines from the same granite (Marschall and Ludwig, 2006). We thank Marschall and Ludwig for pointing out the problem, and will take this lesson into account in our future boron isotope studies.

Recently, we conducted a boron isotope analysis of tourmaline from the Altay No. 3 pegmatite using SIMS (Secondary Ionization Mass Spectrometry) method and have also found similar large discrepancy between our SIMS data and those reported previously by Zhang and Liu (2003) who used acid digestion methods for tourmaline dissolution. We believe that similar problems may have caused these erroneous data in both these different

laboratories. In this paper, we will discuss the possible factors that may affect the accuracy of boron isotope analysis of tourmaline and other solid materials with complex matrices. At the same time, we are planning to re-analyze all tourmaline samples in question together with a tourmaline standard (B4, pegmatitic tourmaline from Elba Island) provided by the International Atomic Energy Agency, using different techniques, in order to determine the exact analytical problems, and to optimize an improved chemical and mass spectrometry protocol for tourmaline analysis.

DISCUSSIONS ON ANALYTICAL METHODS OF BORON ISOTOPIC COMPOSITIONS OF TOURMALINE

Over the last two decades, there has been a rapid increase in the number of studies on the boron isotopic compositions of various geological samples involving a variety of extraction, purification and mass spectrometric methods. Four methods have been employed by various laboratories for boron isotope ratio measurement of tourmaline: (1) a pyrohydrolysis technique for extraction of boron from tourmaline coupled with TIMS (Thermal Ionization Mass Spectrometry) measurement; (2) acid digestion technique, column chemistry, and TIMS measurement; (3) alkaline fusion technique, distillation or column chemistry, and TIMS measurement; (4) SIMS ion probe technique. The first three methods need complex chemical procedures and extensive analytical processing,

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whereas the SIMS method requires minimal sample preparation and also allows us to look at sector zoning within individual mineral grains. However, there are some matrix effects associated with SIMS analyses and the precision is generally not as good as for the TIMS methods.

The pyrohydrolysis technique has been used in several laboratories to extract boron from tourmaline and other solid materials (Spivack and Edmond, 1986; Palmer and Slack, 1989; Aggarwal and Palmer, 1995; Jiang *et al.*, 1999, 2002). In this method, 4–5 mg of tourmaline are placed in a Pt boat and heated to 1400°C in an alumina tube for four hours. Steam is passed over the sample at a rate of ~20 ml/h of water and the condensates are collected using a quartz condenser (Aggarwal and Palmer, 1995). However, this method generally has a slow sample throughput (one sample per day) and requires large volumes of high purity water. Problems are also encountered if impure samples contain high levels of other volatile elements, such as sulfur (Aggarwal and Palmer, 1995). Therefore, acid dissolution method using combinations of HF and HNO₃ and mannitol in closed containers have been used (Ishikawa and Nakamura, 1990; Nakamura *et al.*, 1992). Due to the refractory nature of tourmaline and its low solubility in acid, the alkaline fusion method has been developed for tourmaline decomposition (Tonarini *et al.*, 1997). This method requires extensive purification of the fusion cake before the sample is suitable for TIMS measurement, and the high blanks in the fluxing agents of sodium or potassium carbonates may also invalidate this technique for the low-boron content samples.

Tourmaline samples from the Lavicky granite were decomposed using the acid digestion method (HF + HNO₃), purified through column chemistry, and the ¹¹B/¹⁰B ratio determined using the N-TIMS method (Jiang *et al.*, 2003). After publication of these extreme negative $\delta^{11}\text{B}$ values for the Lavicky tourmalines, we noted that an abstract published in *Geochemica et Cosmochimica Acta* (2003, Suppl., A577) also reported very negative $\delta^{11}\text{B}$ values from –41.1 to –9.2 per mil in tourmalines from the Altay No. 3 pegmatite (Zhang and Liu, 2003). These authors used a similar acid digestion and column chemistry to purify boron from the matrix. But the ¹¹B/¹⁰B ratios were measured using P-TIMS (Positive Ion Thermal Ionization Mass Spectrometry) methods (Xiao *et al.*, 1988; Zhang, 2001). Subsequently I obtained several samples from these authors, and have recently completed a SIMS analysis in the Institute for Study of the Earth's Interior, Okayama University, Misasa, Japan. The results also demonstrated that large discrepancy exists for the two samples with very negative $\delta^{11}\text{B}$ values, but two other samples have nearly identical $\delta^{11}\text{B}$ values between the two methods (Table 1). The discovery of this discrepancy alerted us to the need to re-analyze all these samples using the different analytical methods described

Table 1. Comparison between boron isotope data of tourmaline from the Altay No. 3 pegmatite determined by TIMS and SIMS methods

	TIMS ¹⁾	SIMS ²⁾
A-1a	–41.1	–9.3 (21 points analysis from –6.5 to –11.0)
A-2a	–30.9	–12.0 (18 points analysis from –11.0 to –13.0)
A-5a	–10.1	–11.5 (19 points analysis from –9.0 to –14.0)
A-7a	–13.4	–15.6 (8 points analysis from –15.0 to –16.0)

¹⁾Data from Zhang H (2001); ²⁾This study.

above in order to determine the exact problems that caused the sporadic erroneous data, and we were on the way to develop new analytical protocols when Marschall and Ludwig (2006) pointed out our mistakes.

During a laboratory intercomparison study of boron isotope and concentration measurements of standard water and solid samples, a large spread in $\delta^{11}\text{B}$ values was obtained, which forced Gonfiantini *et al.* (2003) to discard a few isolated results that were far different from the others presented in that report. The tourmaline sample (B4) analyzed in this laboratory intercomparison study had a total $\delta^{11}\text{B}$ variation of –7.7 to –14.7 per mil, far beyond the reported analytical precision for each individual method.

We agree with Marschall and Ludwig (2006) that the problems may have arisen during sample preparation using the acid digestion technique. The refractory nature of tourmaline makes this mineral very difficult to dissolve in acid, so that concentrated HF must be used during tourmaline decomposition. In this method, the sample may react with HF to produce highly volatile BF₃ that can be easily lost from the dissolved samples to cause large boron isotope fractionation (Ishikawa and Nakamura, 1990; Nakamura *et al.*, 1992). In order to suppress boron volatilization, mannitol is routinely added during acid dissolution because it forms a stable boron-mannitol complex (Ishikawa and Nakamura, 1990; Nakamura *et al.*, 1992). However, experiments done by Xiao *et al.* (1997) suggested that the presence of mannitol can reduce but not completely suppress the volatilization of boron. They also found an enrichment of ¹¹B in the vapor during the sample evaporation procedure that causes a negative shift of boron isotopic compositions of the sample during evaporation in dilute HCl and alkaline solutions.

In addition to the sample preparation problems, we also cannot totally rule out problems that may have arisen during mass spectrometric measurement. The accuracy during mass spectrometry can be controlled by measuring standard boric acid (Marschall and Ludwig, 2006), but the samples may have a different matrix and contamination may still produce erroneous data in some cases. For example, using P-TIMS methods, Xiao and Wang

(1998) found a serious effect of NO_3^- on the isotopic measurement of boron, which considerably reduced the measured boron isotope ratios of the samples. The presence of mannitol can enhance this problem due to the formation of the Cs_2CNO^+ ion producing ion peaks at masses of 308 and 309. In most cases, the effect of NO_3^- will decay after heating the filaments for 1 h. However, in some cases, the measured 309/308 ratios do not reach the accepted value even after 5 h heating of the filament (Xiao and Wang, 1998). In this later case, erroneously low $^{11}\text{B}/^{10}\text{B}$ ratios may have been obtained for individual samples. It is widely recognized that the effect of organic matter is a serious problem for N-TIMS (Negative Ion Thermal Ionization Mass Spectrometry) measurements of boron isotopes using BO_2^- at masses of 42 and 43 (Hemming and Hanson, 1994; Aggarwal and Palmer, 1995). Organic materials present problems in N-TIMS for two reasons: (1) interference with and suppression of ionization of BO_2^- , (2) occurrence of an isobaric interference on mass 42 which may produce erroneous lower $^{11}\text{B}/^{10}\text{B}$ ratios (Hemming and Hanson, 1994).

It is also important to note that all other tourmaline boron isotope data reported by this author, and from this laboratory, were performed using either SIMS or the pyrohydrolysis technique and include numerous replicates of internal standards. Hence, we have no reason to believe that any of our other published data are incorrect.

CONCLUSIONS

Erroneous data with extremely low $\delta^{11}\text{B}$ values were obtained during analysis of tourmaline from Lavicky granite and Altay pegmatite using an acid digestion technique and TIMS measurements. We thank Marschall and Ludwig for pointing out these problems. The problems most likely occurred during sample preparation, but we also cannot rule out the possibility of problems during mass spectrometric measurement. Further work is needed to determine the exact factors that caused this problem, and we are in the process of testing various techniques for tourmaline boron isotope analysis in our lab.

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