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An improved procedure for separation/purification of boron from complex matrices and high-precision measurement of boron isotopes by positive thermal ionization and multicollector inductively coupled plasma mass spectrometry

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ABSTRACT

In order to eliminate boron loss and potential isotopic fractionation during chemical pretreatment of natural samples with complex matrices, a three-column ion-exchange separation/purification procedure has been modified, which ensures more than 98% recovery of boron from each step for a wide range of sample matrices, and is applicable for boron isotope analysis by both TIMS and MC-ICP-MS. The PTIMS-Cs₂BO₂⁻-static double collection method was developed, ensuring simultaneous collection of ¹³³Cs₂¹¹B¹⁶O₂⁺ (*m/z* 309) and ¹³³Cs₂¹⁰B¹⁶O₂⁺ (*m/z* 308) ions in adjacent H3–H4 Faraday cups with typical zoom optics parameters (Focus Quad: 15 V, Dispersion Quad: –85 V). The external reproducibilities of the measured ¹¹B/¹⁰B ratios of the NIST 951 boron standard solutions of 1000 ng, 100 ng and 10 ng of boron by PTIMS method are ±0.06‰, ±0.16‰ and ±0.25‰, respectively, which indicates excellent precision can be achieved for boron isotope measurement at nanogram level boron in natural samples. An on-peak zero blank correction procedure was employed to correct the residual boron signals effect in MC-ICP-MS, which gives consistent δ¹¹B values with a mean of 39.66 ± 0.35‰ for seawater in the whole range of boron content from 5 ppb to 200 ppb, ensuring accurate boron isotope analysis in few ppb boron. With the improved protocol, consistent results between TIMS and MC-ICP-MS data were obtained in typical geological materials within a wide span of δ¹¹B values ranging from –25‰ to +40‰.

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1. Introduction

Because of the large range in boron isotopic composition in nature (δ¹¹B, about 100‰) [1], applications of boron isotopic variation have advanced rapidly in a wide range of research fields, including high-temperature and low-temperature geochemical processes, natural anthropogenic pollution sources, wastewater recharge monitoring, paleo-oceanic pH reconstruction, and global biogeochemical cycles [2–16]. For instance, the joint use of nitrogen and boron isotopes in groundwater constrained the origin of

nitrite ions and provided semi-quantification of their contribution to pollution sources [17]. Boron isotopic fractionation in weathering and hydrothermal processes provides new constraints on the origin and evolution of the geothermal fluids that were involved in the formation of altered minerals at the Ries crater (Germany) [18]. The contribution by Vogl and Rosner et al. provided analytically validated methods to determine the boron isotopic composition in plant tissues and water samples, extending the application of boron isotopes to provenance studies of foods [19,20].

General summaries on the detection limits and the major advantages/disadvantages of various techniques (positive thermal ionization mass spectrometry (PTIMS), negative thermal ionization mass spectrometry (NTIMS), secondary ion mass spectrometry (SIMS), and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) etc.) have been published by various authors [16,21–23]. Among these techniques, PTIMS and MC-ICP-MS are evaluated as the most precise and accurate techniques for

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boron isotope determination [24], and NTIMS gives the highest sensitivity to analyze isotopic composition in few nano-grams of boron [25–26]. Initially, $M_2BO_2^+$ ions (M represents alkali metals, e.g. Na, K, Rb, Cs) were observed with PTIMS, and $Na_2BO_2^+$ and $Cs_2BO_2^+$ were employed for boron isotopic composition measurements since 1948 [27–29]. The $Cs_2BO_2^+$ PTIMS method was greatly improved by Xiao et al. who found the intensity of $Cs_2BO_2^+$ emitted from $Cs_2B_4O_7$ can be increased by two orders of magnitude when coating the filament with graphite slurry at low temperatures ($< 700\text{ }^\circ\text{C}$) [30], resulting in an analytical reproducibility of 0.1% (2σ) for samples with more than 1000 ng of B for the international boron standard NIST 951. Later on, the sample loading procedure for determining the $^{11}B/^{10}B$ ratio using sodium metaborate ($Na_2BO_2^+$) was optimized by Rao et al. [31]. To enhance the capacity of high precision isotope measurement in nanogram amounts of boron and eliminate the signal drift correction for the decay of the ion beam, static multicollection techniques have been developed by Nakano et al. [32] and Deyhle [33] on modified mass spectrometers (Finnigan-MAT 261, Germany) where $Cs_2BO_2^+$ ions at m/z 308 and 309 were collected by a specially fixed double collector package after reducing the accelerating voltage from 10 kV to 8 kV. The mass spectrometer modification is necessary in order to separate the two heavy molecular species, with which the external reproducibility of 0.24% for 100 ng B of NIST 951 is superior to the dynamic peak jumping method. The mass spectrometer-induced isotopic fractionation during measurement remains one of the major problems preventing widespread use of the BO_2^- -NTIMS method. In the interest of solving this problem, an approach to normalize $^{11}B^{16}O^{18}O/^{11}B^{16}O^{16}O$ to a fixed $^{18}O/^{16}O$ has been reported by Shen and You [34], but this method has not been widely used because of the difficulty in measuring the small $^{45}BO_2/^{43}BO_2$ ratios and the fact that the $^{18}O/^{16}O$ ratios may vary considerably for different loading conditions [35]. Recently, an internal normalization approach was found to obtain consistent fractionation-corrected $^{11}B/^{10}B$ ratios based on oxygen isotopes determined using ReO_4^- ions measured on the same filament as the sample, and a precision of 0.6% for NIST 951 was achieved regardless of sample size, solution pH, and loading temperature [35]. Ishikawa and Nagaishi showed that the new pretreatment protocol on sample loading increased the ionization efficiency of $Cs_2BO_2^+$ ions, achieving an external reproducibility better than $\pm 0.1\%$ for 50–100 ng B and $\pm 0.2\%$ for 10 ng B [36]. With regard to the isobaric ion interference induced by organic matter on the boron isotope determination by either BO_2^- -NTIMS or $Cs_2BO_2^+$ -PTIMS methods, an optimized procedure with a micro-sublimation technique was established to extract boron from organic matter, which ensures a precise determination of the boron isotopic composition in river water samples containing a few ppb of boron [14,37]. In recent years, MC-ICP-MS is becoming the dominant method for precise boron isotopic analysis with an external reproducibility of $\pm 0.25\%$ [38–41]. Wang et al. corrected the mass bias effect for boron isotopic analysis by MC-ICP-MS using the pseudo internal normalization of lithium isotopic reference (LSVEC), which could achieve an accurate boron isotope analysis for natural waters and marine biogenic carbonates by means of the modified micro-sublimation purification method associated with the high performance and throughput of MC-ICP-MS [42].

Even though various procedures for boron isotope analysis have been advanced significantly as discussed above, the need for improved methods for boron extraction from complex matrices has been emphasized by Gonfiantini et al. on the basis of the intercomparison of boron isotope and concentration measurement [43], especially for minerals, rocks and clays with high silica and rich metal oxide components. With the boron separation procedure using Amberlite IRA 743 boron-specific resin, acidic sample

solutions have to be adjusted to a pH of ~ 7 – 8 by adding a proper amount of base (e.g. NaOH) before being loaded into the ion-exchange column because the resin mostly adsorbs boron from neutral or weak basic solution. However, strong adsorption of boron by hydroxide precipitates (such as amorphous $Al(OH)_3$, amorphous $Fe(OH)_3$) has been observed [44], and the associated boron isotopic fractionation has been studied in detail by Lemarchand et al. [45]. Therefore, possible boron loss and potential isotopic fractionation cannot be neglected when adjusting acidic sample solutions that contain large amounts of Al, Fe and Mg ions (e.g. geological samples like clay, tourmaline) by adding OH^- directly.

Therefore, more precise and accurate measurement of boron isotopic ratios in natural samples with trace boron contents and complex matrices remains a great challenge because of the following reasons: (i) the purification of natural geological samples with complex matrices (especially for rocks and minerals) is complicated with the potential loss of boron by volatilization or by adsorption; (ii) the potential for mass spectrometer-induced isotopic fractionation, and the potential for isobaric interference. The main objective of this study is to achieve high precision and high accuracy measurements of boron isotopic compositions in natural geological samples, improving in the separation/purification process of boron from complex matrices, establishing of static double-collection PTIMS- $Cs_2BO_2^+$ method without special requirements on instrumental hardware, and evaluating of the dominant effects that cause deviation on $\delta^{11}B$ measurement by the two leading techniques of TIMS and MC-ICP-MS.

2. Experimental section

2.1. Materials

Milli-Q water (Resistivity, $18.2\text{ M}\Omega\text{ cm}$) was used throughout the experiments. Concentrated HCl and HNO_3 were purified twice by sub-boiling distillation. Solutions of NIST 951 boric acid, K_2CO_3 , $NaHCO_3$ (Sigma-Aldrich, SP), EDTA (Sinopharm Chemical Reagents Limited Company, AR), and Cs_2CO_3 (Sinopharm Chemical Reagents Limited Company, SP) have been prepared using Milli-Q water.

2.2. Dissolution of solid geological samples

To ensure the full extraction of boron from solid samples, different chemical manipulation procedures are employed: (1) Solid carbonate samples were soaked in 30% H_2O_2 to remove any organic matter or residues on sample surfaces before being ground to a powder of approximately 100 mesh. Then, 6.0 mol L^{-1} HCl was added to dissolve the sample, followed with a continuous addition of 0.5 mol L^{-1} HCl (several milliliters) until the solution becomes slightly acidic. The insoluble residue in solution was removed by centrifugation, and a weak acidic and transparent solution was obtained for the first ion exchange separation column; (2) Fine tourmaline (a boron-rich aluminosilicate mineral) powder was prepared followed by boron extraction with alkali fusion (tourmaline: $K_2CO_3=1:25$ (wt/wt)) at $950\text{ }^\circ\text{C}$ and the sintered materials were totally dissolved by adding 2.5 mol L^{-1} HCl after being cooled down immediately at room temperature, and the transparent solution that was obtained was ready for the ion-exchange column. The boron blank from the alkali fusion step is 21 ng, and does not significantly contribute to the analytical uncertainty of boron isotopes in tourmaline samples that contain $60\text{ }\mu\text{g g}^{-1}$ of boron on average.

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