

# Accurate and Precise Determination of Boron Isotopic Ratios at Low Concentration by Positive Thermal Ionization Mass Spectrometry Using Static Multicollection of $\text{Cs}_2\text{BO}_2^+$ Ions

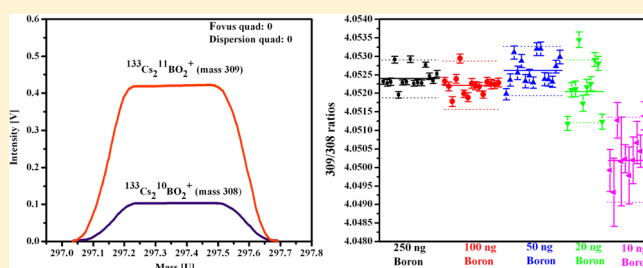
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**ABSTRACT:** A static double-collector system for accurate, precise, and rapid boron isotope analysis has been established by employing a newly fixed Faraday H3 and H4 cup enabling simultaneously collected  $\text{Cs}_2\text{BO}_2^+$  ion beams ( $m/z = 308$  and  $309$ ) on a Finnigan-MAT Triton thermal ionization mass spectrometer of boron (Triton B). The experimental result indicated that  $\text{Cs}_2\text{BO}_2^+$  ion beams ( $m/z = 308$  and  $309$ ) were simultaneously collected using a fixed Faraday H3 and H4 cup without using the "Zoom Quad" function and reduced accelerating voltage. Furthermore, the method enabled the measurement of samples containing as little as 20 ng of boron. An analysis of the National Institute of Standards and Technology standard reference material (NIST SRM) 951 standard showed external reproducibility (2RSD) of  $\pm 0.013\%$ ,  $\pm 0.013\%$ , and  $\pm 0.019\%$  for 100, 50, and 20 ng of boron, respectively. The present method of static multicollection of  $\text{Cs}_2\text{BO}_2^+$  ions is applicable to a wide field of boron isotopic research that requires high precision and accuracy to analyze samples with low boron concentrations, including pore fluids, foraminifera, rivers, rainwater, and other natural samples.



Boron has two naturally occurring isotopes,  $^{10}\text{B}$  (19.9%) and  $^{11}\text{B}$  (80.1%).<sup>1</sup> A relatively large mass difference (10%) between the two isotopes and high volatility results in significant boron isotopic variation from  $-70\%$ <sup>2</sup> to  $+75\%$ <sup>3</sup> in natural materials; thus, boron isotopes have numerous applications in geochemistry, isotope hydrology, oceanography, environmental sciences, cosmology, and nuclear technology.<sup>4–24</sup> Correspondingly, the analytical methods for boron isotope analysis have been significantly developed and improved to permit the study of various types of samples with high precision within the limitations of the instruments.

The isotopic composition of boron can be analyzed by numerous mass spectrometric techniques, e.g., positive ion thermal ionization mass spectrometry (PTIMS),<sup>25–37</sup> negative ion thermal ionization mass spectrometry (NTIMS),<sup>9,38–43</sup> glow discharge mass spectrometry (GDMS), inductively coupled plasma source mass spectrometry (ICPMS), multi-collector inductively coupled plasma mass (MC-ICPMS),<sup>44–48</sup> secondary ion mass spectrometry (SIMS), laser vaporization mass spectrometry, and spark source mass spectrometry. Among these, PTIMS and MC-ICPMS are the two most popular mass spectrometric techniques that are used to determine the isotope ratios of boron in different samples.<sup>9,37</sup>

PTIMS differs from ICPMS in that it analyzes boron in the form of  $\text{M}_2\text{BO}_2^+$ , rather than an elemental form ( $\text{B}^+$ ). In contrast to MC-ICPMS, PTIMS has no memory effect and is thus very useful for determining boron isotope ratios in samples with varying  $^{10}\text{B}$  content, as required in nuclear technology. PTIMS is the most widely used mass spectrometric technique for determining boron isotope ratios due to its inherent capability of providing high-precision isotope ratios.

In PTIMS, the boron in the sample is converted into positively charged metaborate ions ( $\text{BO}_2^+$ ) that are not solely present as  $\text{BO}_2^+$  but exist in the form of alkali or metal metaborate cations, including  $\text{K}_2\text{BO}_2^+$ ,<sup>49</sup>  $\text{Na}_2\text{BO}_2^+$ ,<sup>31,32</sup>  $\text{Cs}_2\text{BO}_2^+$ ,<sup>25</sup>  $\text{Rb}_2\text{BO}_2^+$ ,<sup>33</sup> and  $\text{Li}_2\text{BO}_2^+$ .<sup>50</sup> The  $\text{Cs}_2\text{BO}_2^+$ –graphite method described by Xiao et al.<sup>25</sup> achieved high signal intensity and stability and thereby permits the precise analysis of the boron isotopic composition.

Although PTIMS using the  $\text{Cs}_2\text{BO}_2^+$ –graphite method has been developed and shown by different research groups to provide the best precision and accuracy, method improvement

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is necessary. Most important among these achievements is the static analysis of  $\text{Cs}_2\text{BO}_2^+$  employing the multicollection technique, as opposed to the conventional peak jumping method, to enable low-concentration boron isotope analysis. Multicollection mass spectrometry is desirable for the  $\text{Cs}_2\text{BO}_2^+$  method for the analysis of small samples, and it has the following advantages in comparison to peak switching mass spectrometry: (1) the data acquisition time is shorter, so smaller sample amounts can be analyzed before the ion beam intensity decays, and (2) the time drift correction for ion beam decay is not necessary. In the  $\text{Cs}_2\text{BO}_2^+$  method, however, the relative mass difference between  $m/z = 308$  and  $309$  is too small to allow simultaneous collection in the general multicollector mass spectrometer. Therefore, data acquisition requires peak switching using a single Faraday cup collector. Many mass spectrometry approaches have been developed to determine boron isotope ratios using the  $\text{Cs}_2\text{BO}_2^+$ –graphite method and static multicollection. Nakano and Nakamura<sup>26</sup> and Deyhle<sup>27</sup> performed studies using a Finnigan-MAT 261/Finnigan-MAT 262 with varying sample concentrations, a piggyback double collector for Pb ( $m/z = 207$  and  $208$ ), a fixed central collector, and a reduced accelerating voltage of  $8\text{ kV}$ . This year, several more efforts have been made to statically analyze  $\text{Cs}_2\text{BO}_2^+$  using Finnigan-MAT Triton mass spectrometry. To simultaneously measure the boron isotopes, He et al.<sup>30</sup> collected  $^{133}\text{Cs}_2^{10}\text{BO}_2^+$  (mass 308) and  $^{133}\text{Cs}_2^{11}\text{BO}_2^+$  (mass 309) using a Faraday L1 and central cup C, respectively. Wei et al.,<sup>29</sup> Trotter et al.,<sup>35</sup> Ishikawa et al.,<sup>36</sup> and Yan et al.,<sup>37</sup> used Faraday H3 and H4 to collect  $^{133}\text{Cs}_2^{10}\text{BO}_2^+$  (mass 308) and  $^{133}\text{Cs}_2^{11}\text{BO}_2^+$  (mass 309). Although the  $\text{Cs}_2\text{BO}_2^+$ –graphite method using static multicollection has improved the analytical precision and reproducibility of geochemical studies, as mentioned above, the “Zoom Quad” function has been used to further focus the two  $^{133}\text{Cs}_2^{10}\text{BO}_2^+$  (mass 308) and  $^{133}\text{Cs}_2^{11}\text{BO}_2^+$  (mass 309) ion beams. The closest cup distance between the Faraday L1 and central cup C or the Faraday H3 and H4 cups still cannot simultaneously collect the ion beams for masses 308 and 309. To achieve real static multicollection, cups H3 and H4 were seamlessly arranged and fixed on a bracket to simultaneously fully collect the ion beams of  $^{133}\text{Cs}_2^{10}\text{BO}_2^+$  (mass 308) and  $^{133}\text{Cs}_2^{11}\text{BO}_2^+$  (mass 309) on our Finnigan-MAT Triton thermal ionization mass spectrometer, and this mass spectrometry was referred to as the Triton boron (Triton B). In this case, the ion beams of  $^{133}\text{Cs}_2^{10}\text{BO}_2^+$  (mass 308) and  $^{133}\text{Cs}_2^{11}\text{BO}_2^+$  (mass 309) were easily simultaneously collected as Pb isotopes that were measured without using “Zoom Quad” and with reduced accelerating voltage on Triton B; moreover, this fixed Faraday H3 and H4 cup did not affect other isotope measurement.

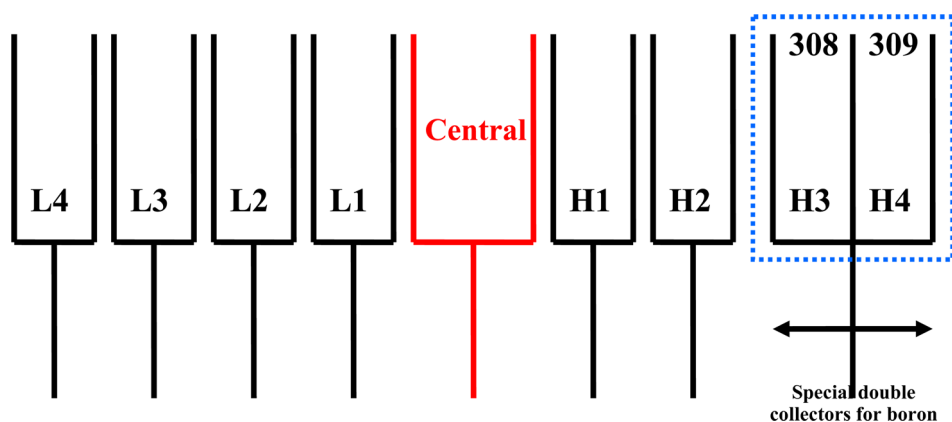
In this paper, we present a true static multicollection method for boron isotope measurement using  $\text{Cs}_2\text{BO}_2^+$  ions with custom-designed double Faraday collectors of H3 and H4 using our mass spectrometer. This method enabled the high-precision isotopic analysis of boron quantities as small as  $20\text{ ng}$ . We also present analytical results for seawater and Foraminifera materials. These results demonstrate the validity of the method for obtaining highly precise and accurate data.

## EXPERIMENTAL SECTION

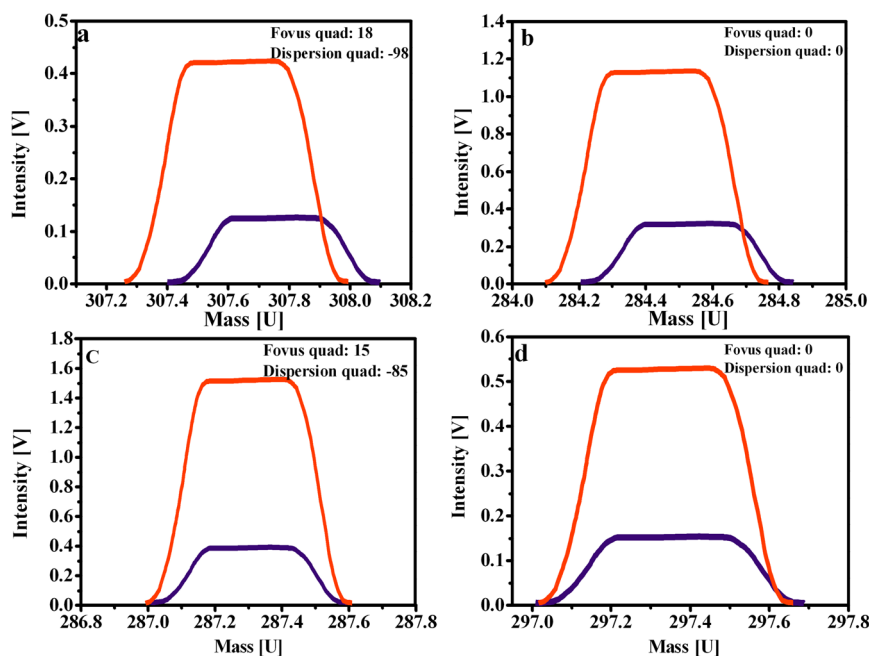
**Reagents and Materials.** The following were used: Ta ribbon,  $0.0249\text{ mm}$  thick,  $1.00\text{ mm}$  wide,  $18.00\text{ mm}$  long, and  $99.98\%$  pure, H. Cross Company; Milli-Q  $\text{H}_2\text{O}$ ,  $18.2\text{ M}\Omega$  at  $25$

$^\circ\text{C}$  from Millipore (Elix-Millipore, U.S.A.); HCl,  $\text{HNO}_3$ , and  $\text{NH}_3\cdot\text{H}_2\text{O}$ , obtained from the Beijing Institute of Chemical Reagent and purified using the Savillex<sup>TM</sup> DST-100 sub-boiling distillation system (Minnetonka, MN, U.S.A.); diluted solutions were prepared with Milli-Q water;  $\text{NaHCO}_3$  solution, saturated sodium bicarbonate solution; graphite slurry, high-purity graphite was added to a mixture of  $80\%$  ethanol and  $20\%$   $\text{H}_2\text{O}$  to obtain a final solution of  $13\text{ mg/g}$  graphite slurry ( $99.9999\%$  pure graphite,  $200\text{ mesh}$ , Alfa Aesar, U.S.A.); cesium carbonate solution, a solution of  $\text{Cs}_2\text{CO}_3$  containing  $12.3\text{ mg/mL}$  Cs ( $99\%$  purity, Merck, Germany); mannitol solution, a solution of mannitol with a concentration of  $18.2\%$  (w/v); boron-specific ion-exchange resin, Amberlite IRA 743 resin ground and screened to  $60\text{--}100\text{ mesh}$ ; ion-exchange resin mixture, prepared from the strong cation resin, Dowex  $50\text{W}\times 8$  ( $200\text{--}400\text{ mesh}$ ) and a weak alkaline anion resin, Ion Exchanger II; ion-exchange column 1,  $4\text{ cm}$  long  $\times$   $3.5\text{ mm}$  i.d. with a  $4\text{ mL}$  reservoir packed with Amberlite IRA 743 resin ( $60\text{--}100\text{ mesh}$ ),  $0.2\text{ mL}$  resin bed volume; ion-exchange column 2,  $4\text{ cm}$  long  $\times$   $8\text{ mm}$  i.d. with a  $10\text{ mL}$  reservoir packed with mixed ion-exchange resin; the column was composed of  $1:1$  (v/v) Ion Exchanger II ( $60\text{--}100\text{ mesh}$ ) and Dowex  $50\text{W}\times 8$  ( $200\text{--}400\text{ mesh}$ );  $2\text{ mL}$  of mixed resin was loaded; boron isotopic reference materials, National Institute of Standards and Technology boric acid standard reference material NIST SRM 951 (formerly NBS SRM 951 of the National Bureau of Standards, U.S.A.).

**Chemical Separation.** Before subjecting the sample to mass spectrometry to determine boron isotopic composition, one of key steps is to separate boron of natural samples from its matrix through a chemical separation and purification.<sup>51</sup> The Foraminifera samples were collected and dried under a lamp after being washed repeatedly with deionized water to remove adhering mud, soluble salts, and remnant seawater. Each dried sample was crushed in an agate mortar, washed again with double-distilled water to remove soluble salts, and then dried. The dried samples were powdered to  $100\text{--}200\text{ mesh}$  and then were washed with boron-free water. For all of the samples, prior to dissolution, organic material was oxidized using a treatment with sodium hypochlorite or  $30\%$   $\text{H}_2\text{O}_2$ . Then, boron in seawater and in dissolution foraminifera was isolated using two chromatographic steps with Amberlite IRA 743 boron-selective resin and a mixed resin composed of cation-exchange resin ( $\text{H}^+$  form) and anion-exchange resin (ion-exchanger II,  $\text{HCO}_3^-$  form).<sup>14</sup> A sample volume corresponding to  $50\text{ ng}$  of B was loaded on a small Teflon PFA column filled with  $200\text{ }\mu\text{L}$  of the Amberlite IRA-743 boron-specific resin ( $125\text{--}250\text{ }\mu\text{m}$ ). The column was rinsed with  $1.5\text{--}2\text{ mL}$  of high-purity water. Then, the boron held by the resin was eluted using  $1.5\text{ mL}$  of  $0.1\text{ mol/L}$  HCl at  $75\text{ }^\circ\text{C}$ . After being cooled to room temperature, the eluant from the column of Amberlite IRA 743 was passed through a mixed ion-exchange resin column at a flow rate of less than  $0.2\text{ mL/min}$ , and after that, the column was eluted using  $1.0\text{--}1.5\text{ mL}$  of high-purity water. The final eluent was collected and evaporated in an oven at  $60\text{ }^\circ\text{C}$  under clean air drawn through four KOH impregnated filters. Then, the samples were microsublimated established by He et al.<sup>14</sup> After microsublimation, the proper amount of  $\text{Cs}_2\text{CO}_3$  was added into the final solution (B/Cs molar ratio of  $1/2$ ). Microsublimation technology coupled with routine ion-exchange purification steps would effectively eliminate the organic matter not only in the sample but also brought by the resin itself which usually reduced signal intensity during TIMS analyses and



**Figure 1.** Double-collector Faraday cup package for  $\text{Cs}_2\text{BO}_2^+$  ions of Triton B. There are six movable platforms (L4–H2) that lie along the focal plane and are equipped with Faraday cup collectors. Two cups (H3 and H4) are doubled on the platforms of 308 and 309 for simultaneous measurement.



**Figure 2.** Mass scan graphs of 308 ( $^{133}\text{Cs}_2^{10}\text{B}^{16}\text{O}_2^+$ ) and 309 ( $^{133}\text{Cs}_2^{11}\text{B}^{16}\text{O}_2^+$ ) using the static multicollection method using three Faraday cup groups under different parameters in zoom optics: (a) He et al. (ref 30); (b) Yan et al. (ref 37); (c) Yan et al. (ref 37); (d) this study. Parts a–c reprinted with permission from the *Chinese Journal of Analytical Chemistry*.

sometimes resulted in isobaric ion interference when determining boron isotopic ratios. All sample preparation work and column chemistry was carried out in a dedicated flow hood within an overpressured clean lab fitted with boron-free HEPA filters, permitting typical total procedural blanks of <20 pg.

**Mass Spectrometry. Instrumentation.** Isotopic measurements were performed on a Triton thermal ionization mass spectrometer (TIMS; Thermo Fisher Scientific, U.S.A.), installed at the Institute of Salt Lake, Chinese Academy of Sciences. The instrument was equipped with nine Faraday cups. The instrument was retrofitted with a double Faraday collector array with fixed spacing enabling more precise measurements using a static multicollector mode for  $^{133}\text{Cs}_2^{10}\text{BO}_2^+$  (mass 308) and  $^{133}\text{Cs}_2^{11}\text{BO}_2^+$  (mass 309) ions (Figure 1).

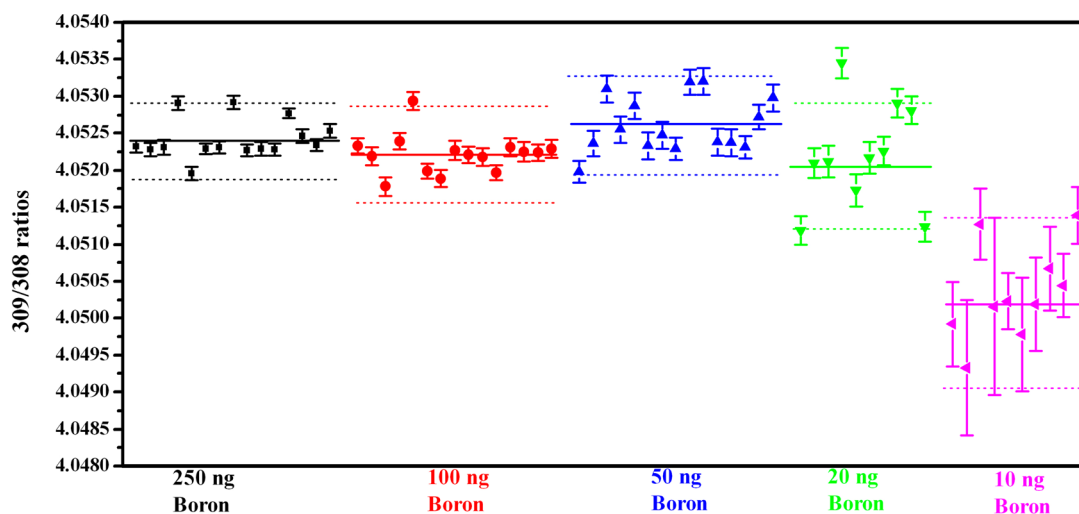
**Sample Loading.** For mass spectrometry, samples were loaded on single tantalum (Ta) filaments. Prior to sample

loading, the Ta filaments were degassed and allowed to oxidize for 3 days in a plastic box to prevent contamination.

First, 2  $\mu\text{L}$  of a graphite/ethanol/water slurry was loaded onto the center of an outgassed single tantalum (Ta) filament. Second, prior to the complete drying of the graphite, the boron sample dissolved in 1  $\mu\text{L}$  of Milli-Q water was loaded on the graphite layer to make a sample–graphite mixture. The filament was then heated until the sample evaporated to dryness at 1.1 A for 2 min. The sample was then introduced into the mass spectrometer.

**Boron Isotopic Composition Analysis.** The boron isotopic compositions in all samples were measured by the PTIMS method using  $\text{Cs}_2\text{BO}_2^+$  ions at masses 308 and 309 with a graphite-loading and Triton magnetic sector thermal ionization mass spectrometer.

After the studies of Wei et al.<sup>29</sup> and Trotter et al.,<sup>35</sup> the instrument was retrofitted with a double Faraday collector array with fixed spacing enabling more precise measurements using a



**Figure 3.**  $^{11}\text{B}/^{10}\text{B}$  ratios measured for NIST SRM 951 with sample sizes of 250, 100, 50, 20, and 10 ng of boron using the  $\text{Cs}_2\text{BO}_2^+$ -PTIMS in this study.

static multicollector mode for  $\text{Cs}_2\text{BO}_2^+$ . The simultaneous measurement of masses 308 and 309 is otherwise not possible using the conventional Faraday collection system in the earlier generation instrument due to the small relative mass difference. The Faraday cups were configured to measure mass 308 ( $^{133}\text{Cs}_2^{10}\text{BO}_2^+$ ) and 309 ( $^{133}\text{Cs}_2^{11}\text{BO}_2^+$ ) in the H3 and H4 double-cup array, with the center cup set at 295 (maximum, 300 amu). Data were acquired in 10 blocks of 100 cycles when the intensity of 309 reached  $\sim 0.5$  V. The intensity ratios of the ion beams at masses 308 and 309 ( $R_{309/308}$ ) were calculated. The  $^{11}\text{B}/^{10}\text{B}$  ratio was calculated as  $R_{309/308} - 0.00078$ .<sup>52</sup> The isotopic composition of boron was expressed as the  $\delta^{11}\text{B}$  value according to the following formula:  $\delta^{11}\text{B}$  (‰) =  $[(^{11}\text{B}/^{10}\text{B})_{\text{sample}} / (^{11}\text{B}/^{10}\text{B})_{\text{std}} - 1] \times 1000$ , where the standard material was NIST SRM 951.

Unlike previous studies,<sup>26,27</sup> the data were acquired using a special double-cup system primarily because the Triton TIMS is capable of the static multicollection of  $\text{Cs}_2^{10}\text{BO}_2^+$  (308)/ $\text{Cs}_2^{11}\text{BO}_2^+$  (309) ions.

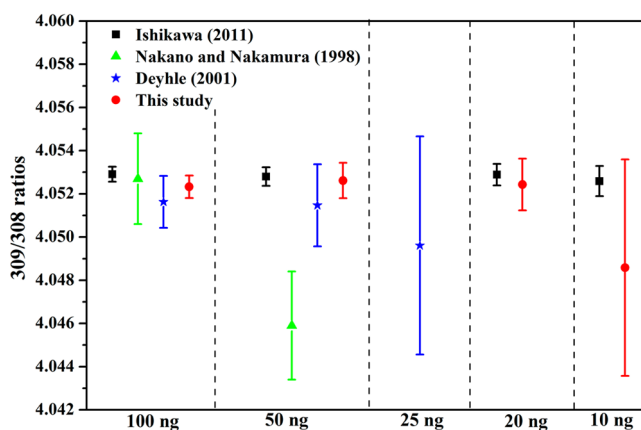
## RESULTS AND DISCUSSION

**Mass Scan Graphs of 308 ( $^{133}\text{Cs}_2^{10}\text{BO}_2^+$ ) and 309 ( $^{133}\text{Cs}_2^{11}\text{BO}_2^+$ ) by Applying the Static Multicollection Method.** Figure 2 shows mass scan graphs of 308 ( $^{133}\text{Cs}_2^{10}\text{BO}_2^+$ ) and 309 ( $^{133}\text{Cs}_2^{11}\text{BO}_2^+$ ) using the static multicollection method using three Faraday cup groups under different zoom optics parameters.

Due to the small relative mass difference between  $m/z = 308$  and  $m/z = 309$ , simultaneous data collection was not possible using conventional multicollection mass spectrometers. To conduct multicollector measurements of 308 ( $^{133}\text{Cs}_2^{10}\text{BO}_2^+$ ) and 309 ( $^{133}\text{Cs}_2^{11}\text{BO}_2^+$ ), the Faraday cups were configured to measure masses 308 and 309 in the L1 and C double-cup (Figure 2a) or H3 and H4 double-cup (Figure 2, parts b and c) array with zoom optics. As shown in Figure 2d, the multicollectors enable both isotopic ion currents of interest ( $^{133}\text{Cs}_2^{10}\text{BO}_2^+$  and  $^{133}\text{Cs}_2^{11}\text{BO}_2^+$ ) to be collected simultaneously without zoom optics.

**Accuracy and Reproducibility of Boron Isotope Measurements for NIST 951 Standard.** Thirty-six analyses of 25 ng of NIST 951 over a period of 1 year were carried out using static multicollection method. A series of NIST 951

standards containing 250, 100, 50, 20, and 10 ng of boron was analyzed too. And the results are shown in Figure 3. Figure 4 shows a comparison of these results with the results that were obtained using the static multicollection methods that were investigated in the previous studies.



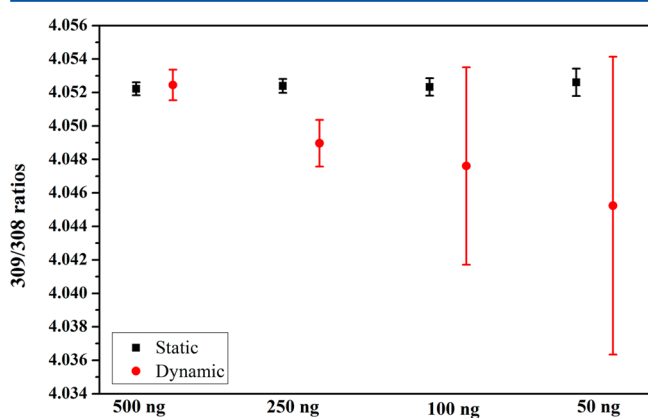
**Figure 4.** Boron sample size and isotope ratios ( $^{11}\text{B}/^{10}\text{B}$ ) of NIST SRM 951 measured by the  $\text{Cs}_2\text{BO}_2^+$ -PTIMS in this study and in previously published studies.

Repeated analyses of 25 ng of boron over a period of 1 year had an average value of  $^{11}\text{B}/^{10}\text{B} = 4.05229 \pm 0.00028$  ( $N = 36$ ), with individual runs having in-run precision (2SE) ranging from 0.00003 to 0.00014. The results from the analyses of 100, 50, and 20 ng of boron were consistent with those of 25 ng of boron. The external reproducibility of the analyses (2RSD) of  $^{11}\text{B}/^{10}\text{B}$  was  $\pm 0.013\%$ ,  $\pm 0.013\%$ , and  $\pm 0.019\%$  for 100, 50, and 20 ng of boron, respectively. The  $^{11}\text{B}/^{10}\text{B}$  ratios obtained in this study are essentially consistent with the reported values of NIST 951 measured by the  $\text{Cs}_2\text{BO}_2^+$ -graphite method (Figure 4). The external reproducibility in this study for 100, 50, and 20 ng samples is 3–9 times better than the most precise results that were previously reported for similar sample amounts.<sup>26,27,36</sup> However, a small bias toward a lower  $^{11}\text{B}/^{10}\text{B}$  ratio exists for 10 ng of boron:  $4.050338 \pm 0.00126$  ( $2\sigma$  mean), with a reproducibility of 0.032% (2RSD), indicating that this is the minimum concentration that can be measured on the

double collector. Hence, 25 ng is considered the optimum amount of NIST 951 for isotopic measurements using the Thermo Fisher Scientific Triton TIMS with the static multicollection of  $\text{Cs}_2\text{BO}_2^+$  ions to obtain the best results with respect to measurement precision and short data acquisition time (approximately 8 min). Considering the average standard  $^{11}\text{B}/^{10}\text{B}$  ratios and reproducibility, the results from this study are superior to the previous results that were obtained using multicollection.<sup>26,27,36</sup>

Static measurement of 309/308 has been achieved by using a “Zoom Quad” mode without the special Faraday array, as mentioned above, and these methods can provide very high internal and external precision for  $^{11}\text{B}/^{10}\text{B}$ . However, our static measurement of 309/308 has the following advantages in comparison to the “Zoom Quad” mode: (1) It was easy to switch from other isotopic measurements to boron isotopic measurement because our static measurement of 309/308 was achieved by changing the physical structure of the Faraday cup, whereas it would spend a lot of time on adjusting parameters to achieve static multicollection of  $\text{Cs}_2\text{BO}_2^+$  ions using “Zoom Quad” mode after other isotopic measurement. (2) Our method provided better long-term stability of NIST 951 standard compared to “Zoom Quad” mode when more than two isotopes were determined in addition to boron isotope.

**Accuracy and Reproducibility of the  $^{11}\text{B}/^{10}\text{B}$  Ratios for NIST SRM 951 Measured by Static Multicollection and the Conventional Peak Jumping Method.** Differences in NIST SRM 951 measurements were examined using static multicollection and the conventional peak jumping method. A series of NIST 951 standards with 500, 250, 100, and 50 ng of boron was analyzed using these two methods. The average duration of one isotopic measurement run was 8 min, and it was 50 min for two methods, including the gain calibration for 10 blocks (100 ratio values). One block of data contained 10 scans. The analytical results are plotted in Figure 5.



**Figure 5.**  $^{11}\text{B}/^{10}\text{B}$  ratios measured for NIST SRM 951 with sample sizes of 500, 250, 100, and 50 ng of boron using static multicollection and the conventional peak jumping method.

Figure 5 shows that the results of analytical precision and reproducibility from the static multicollection method are essentially identical to those obtained using the peak jumping method to measure samples containing more than 100 ng of boron.

Figure 5 also illustrates that the results of analytical precision and reproducibility using the static multicollection method are significantly better than those obtained using the peak jumping

method to measure samples with less than 100 ng of boron. Using the static multicollection method, the average duration of one isotopic measurement run was 8 min, including 10 blocks (100 ratio values). This acquisition time is shorter than the 45 min acquisition time required when data are collected in a single Faraday cup. Moreover, dynamic changes in the signals of  $\text{Cs}_2\text{BO}_2^+$  ions were eliminated using the static multicollection method. To measure samples containing less than 100 ng of boron, it is difficult to increase the ion beam intensity of  $m/z = 308$  to  $5 \times 10^{-13}$  A. If the ion beam intensity is increased above this value, it decays rapidly during data collection. It is thus difficult to measure an isotope ratio for samples containing less than 100 ng of boron using the peak jumping method because of the required 45 min data acquisition time. However, the static multicollection technique established in this study can facilitate boron isotope measurement in challenging conditions, such as small samples with rapidly decaying signals.

#### Boron Isotope Measurements of Natural Samples.

**Seawater  $\delta^{11}\text{B}$ .** In the open ocean, boron is a conservative element that is well-mixed with a uniform concentration and isotopic composition. Boron concentrations and isotopic ratios are uniform in the open seawater, with values of 4.5 ppm and 39.6‰, respectively. This homogeneity is explained by the long residence time of boron in seawater (approximately 20 Myr), relative to the time scale of ocean mixing (approximately 1 kyr). An accurate determination of  $\delta^{11}\text{B}_{\text{sw}}$  is critical for precise reconstructions of paleo-pH, as the proxy calibration depends on it. Additionally, seawater is commonly used as an interlaboratory standard.<sup>53</sup> Therefore, a more precise definition of  $\delta^{11}\text{B}_{\text{sw}}$  is desirable.

Five 10 and 20  $\mu\text{L}$  aliquots of South China Sea surface water were processed with Amberlite IRA 743 resin. Boron isotope ratios were investigated by TIMS using the static multicollection of  $\text{Cs}_2\text{BO}_2^+$  ions. The average ( $n = 5$ )  $\delta^{11}\text{B}$  values of 10 and 20  $\mu\text{L}$  samples were  $39.54 \pm 0.08\text{‰}$  and  $39.65 \pm 0.11\text{‰}$ , respectively. The average  $\delta^{11}\text{B}$  value of seawater is generally understood to be 39.5‰, with reported values ranging from 37.7‰ to 40.4‰, with a mean of  $39.46\text{‰} \pm 1.45\text{‰}$  ( $n = 26$ ; 2SD).<sup>53</sup> This large range in published seawater  $\delta^{11}\text{B}$  values may result from differences in column chemistry, mass spectrometric methods, and sample handling. The accuracy and precision of our method was assessed by comparing measured seawater  $\delta^{11}\text{B}$  values to other published results.

**$\delta^{11}\text{B}$  of Planktonic Foraminifera.** Boron isotope ratios were investigated by TIMS using the static multicollection of  $\text{Cs}_2\text{BO}_2^+$  ions on two Foraminifera species: *Globigerinoides ruber* and *G. sacculifer*. The measured  $\delta^{11}\text{B}$  values of these two species were  $22.07\text{‰} \pm 0.03\text{‰}$  ( $n = 4$ ) and  $22.14\text{‰} \pm 0.09\text{‰}$  ( $n = 4$ ), showing an excellent external reproducibility that was comparable to the analyses of SRM 951.

## CONCLUSIONS

A highly sensitive method for measuring boron isotopes as  $\text{Cs}_2\text{BO}_2^+$  using the multicollection method with newly fixed Faraday H3 and H4 cups on a Finnigan-MAT Triton thermal ionization mass spectrometer has been developed. This technique enables us to conduct rapid analysis of boron isotopes with samples containing as little as 20 ng of boron. The static multicollection technique will extend the application of boron isotope analysis to boron-poor natural samples, such as marine carbonates, pore fluids, and rainwater.

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## Notes

The authors declare no competing financial interest.

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