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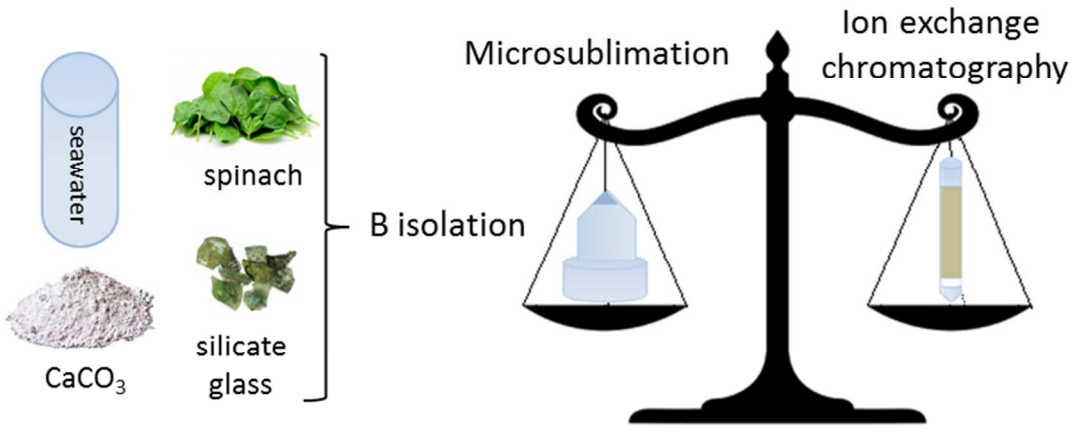
Graphical abstract



20-30 words

Two boron isolation methods, microsublimation and ion exchange chromatography, were compared in terms of B recovery, matrix removal efficiency, accuracy and precision of $\delta^{11}B$, labour intensiveness and costs.

Comparison of microsublimation and ion exchange chromatography for boron isolation preceding its isotopic analysis via multi-collector ICP-MS

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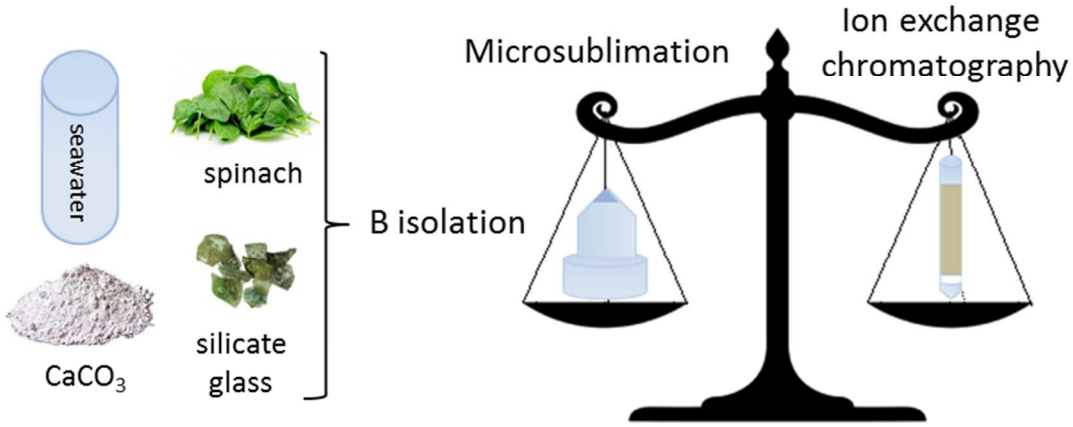

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Abstract

Boron isotopic analysis is of interest in many research fields and for a large variety of sample types. Accurate and precise determination of boron isotope ratios using multi-collector ICP – mass spectrometry or thermal ionization mass spectrometry requires isolation of the target element prior to isotopic analysis, which is accomplished using either ion exchange chromatography or microsublimation. This study systematically compares the two methods in terms of B recovery, procedural blank, matrix removal efficiency, accuracy and precision of the resulting $\delta^{11}B$ values as measured using multi-collector ICP – mass spectrometry, as well as labor intensiveness and costs. For this purpose, four types of sample matrices, *i.e.* 20 g/L Ca aqueous solution, seawater, digests of spinach (100 g/L) and silicate glass (10 g/L), were stripped from their orginal B content and spiked with B of known isotopic composition and were then subjected to both sample preparation methods and subsequent isotopic analysis of the purified B fraction via multi-collector ICP – mass spectrometry. For both methods, the highest (quantitative) B recoveries were obtained for Ca-rich aqueous solution and seawater. For spinach, accurate $\delta^{11}B$ values were obtained after ion exchange chromatography. However, microsublimation was plagued by isotope fractionation, resulting in large offsets (~ 8 ‰) between the experimental results and the corresponding reference values. For glass, B recovery was incomplete, nevertheless absence of fractionation rendered both sample preparation methods suitable. Overall, in absence of isotope fractionation, microsublimation appears advantageous in terms of procedural blanks, matrix removal efficiency, precision (2s) on $\delta^{11}B$ values, labor intensiveness and costs.

Keywords:

Boron, isotope ratio, chromatography, microsublimation, multi-collector ICP-MS.

Introduction

For boron, an element of interest in numerous geological, archaeological, environmental, biological and industrial studies, two stable isotopes, ^{10}B (19.82 %) and ^{11}B (80.18 %) exist and the $^{11}B/^{10}B$ ratio shows natural variation in different environmental compartments. Expressed as a relative difference with respect to the NIST SRM 951 boric acid isotopic reference material, $\delta^{11}B$ covers the range from -30 to +60 ‰ [1]. This large isotopic variation in nature is the result of pronounced isotope fractionation taking place in various processes involved in the biogeochemical cycle of boron, owing to the large relative difference in mass between the two isotopes. Isotope fractionation accompanies a variety of processes, such as weathering [2], adsorption to sediment and suspended particles [3], acid-base equilibrium speciation of boric acid and borate in water [4] and hydrothermal alteration of the oceanic crust [5]. Owing to the high mobility of B in nature and its isotope fractionation, B isotopic analysis aids in answering a broad range of research questions in the fields mentioned above. Besides research into the biogeochemical cycle of B itself, $\delta^{11}B$ determination in natural water bodies allows tracing both natural and anthropogenic sources of boron and investigation of the origin and migration of pollutants [6,7]. Boron co-precipitates in marine carbonates in concentrations typically ranging between 10 and 70 µg/g [8] and its isotopic composition is linked to the pH of the water during the calcification, as a result of the pH-dependent fractionation between $B(OH)_3$ and $B(OH)_4^-$ [9,10]. Hence, $\delta^{11}B$ analysis of marine carbonates provides information on the paleo-pH and ocean acidification [11,12]. Boron also is an essential plant nutrient and acts as a structural component of cell walls [13]. On a global scale, boron deficiency is the most important micronutrient deficiency in plants, causing loss in agricultural yield of certain crops [14]. Hence, studies dealing with the availability of B and its uptake by and translocation within plants benefit

from B isotopic analysis. Furthermore, boron isotopic analysis is an established method for provenancing of food [15]. Finally, B isotopic analysis of Roman glass characterizes the provenance of the natron flux used in its manufacturing [16]. Such source identification sheds light on the technologies used in the production process of glass and the origin of raw materials involved.

High-precision boron isotopic analysis can be accomplished, either with negative [17,18] or positive [19,20] molecular ion thermal ionization mass spectrometry (N-TIMS and P-TIMS, respectively) or with multi-collector inductively coupled plasma - mass spectrometry (MC-ICP-MS) [21,22]. To obtain accurate isotope ratio data, boron needs to be isolated from its concomitant matrix prior to TIMS or MC-ICP-MS analysis. In the case of TIMS, boron needs to be isolated to guarantee sufficient ionization, whereas in MC-ICP-MS, instrumental mass discrimination can only be adequately corrected for when introducing purified solutions of the target element. Two different strategies to obtain matrix-free boron solutions from samples have been described in the literature, *i.e.* ion exchange chromatography and microsublimation. For B isolation via ion exchange chromatography, various procedures exist, all of which make use of one or more anion exchange resin(s), such as the boron-selective Amberlite IRA 743 and/or the strongly basic 1x8 anion exchange resin and/or a cation exchange resin, such as Dowex AG50W-X8. Isolation either relies on the use of a single [23] or more than one [7,9,16,24,25] chromatographic resin(s). Microsublimation, on the other hand, exploits the natural tendency of boric acid to sublimate from 60 °C onwards and was first described for B isolation out of organic-rich solutions by Gaillardet et al. [26]. It was applied as an additional purification step after anion exchange chromatography using Amberlite IRA 743 resin for B isotopic analysis of river waters by Lemarchand et al. [27]. In 2010, Wang et al. described the use of microsublimation as a single step for B isolation from Ca-rich solutions [28]. Since then, a

number of studies have used microsublimation for B isolation preceding isotopic analysis of the target element [6,12,29,30].

However, to date, no study has systematically compared both B isolation methods in terms of their utility and characteristics for the broad range of matrices relevant for B isotopic analysis. In the present work, several evaluation criteria, *i.e.* B recovery, procedural blank, efficiency of removal of matrix elements, accuracy and precision of the $\delta^{11}B$ values subsequently obtained via MC-ICP-MS analysis, as well as labor intensiveness and consumable costs were assessed and compared for the two fundamentally different isolation strategies. Four relevant matrices were selected for this purpose, *i.e.* Ca^{2+}-rich aqueous solution, seawater, plant material and silicate glass.

Materials and methods

Reagents and reference materials

The ultrapure mineral acids Optima® HCl (12 M) and trace metal grade HF (29 M) were purchased from Fisher (Acros Organics, Belgium). Pro analysis grade 14 M HNO_3 (Chem-Lab, Belgium) was further purified by sub-boiling distillation in PFA equipment. Dilutions were prepared using ultrapure water with 18.2 MΩ.cm resistivity, provided by a Milli-Q Element installation (Millipore, France). Certified reference materials were used as a source of sample matrix for seawater, calcium-rich solutions, plant leaves and silicate glass. More specifically, BCR CRM 403 – Trace elements in North Seawater (Institute for Reference Materials and Measurements IRMM, Belgium), NIST SRM 915 calcium carbonate (National Institute for Standards and Technology NIST, MD, USA), NBS SRM 1570 – trace elements in spinach (NIST, MD, USA) and NIST SRM 610 – Trace elements in glass (NIST, MD, USA) were

selected for this purpose. As described further, these materials were stripped from their original B content, after which B with known isotopic composition was added to the digest.

The NIST SRM 951 boric acid isotopic reference material (NIST, MD, USA) was used for calibration of isotope ratio measurements, while the samples were prepared using three $\delta^{11}B$ reference materials, ERM AE120, AE121 and AE122, available from the Federal Institute for Materials Research and Testing (BAM, Germany). The certified $\delta^{11}B$ values of these materials are -20.2, +19.9 and +39.7 ‰, respectively, all with an expanded uncertainty (k = 2) of 0.6 ‰. Lithium carbonate isotopic reference material IRMM-016 (IRMM, Belgium) was used as an internal standard to correct for mass discrimination. Single-element 1 g/L standard solutions were obtained from Inorganic Ventures (VI, USA).

Cation/anion exchange chromatography and microsublimation

Chromatographic isolation of B from several matrices was accomplished using a two-step procedure, previously developed for isolating B out of archaeological glass [16]. For this purpose, 0.1 mL sample solution with 0.02 M HCl matrix and containing 4 µg of B was loaded onto the column. In the first chromatographic separation step, 2.5 mL of Dowex AG50W-X8 cation exchange resin (200-400 mesh size, Sigma Aldrich, Belgium) inserted into polypropylene conical columns with a diameter of 0.8 cm and a length of 4 cm (Eichrom technologies, France) was used. This resin was cleaned with 10 mL of 6 M HCl and conditioned using 5 mL of 0.02 M HCl before sample loading. Another 5 mL aliquot of 0.02 M HCl was used for boron elution after sample loading. The eluted boron fraction was subsequently spiked with 1.5 mL of 15 M HF to obtain a 3 M HF matrix. The B fraction was then loaded onto 0.5 mL of 1x8 strong anion exchange resin (200-400 mesh, Eichrom Technologies, France), packed into a 4 cm

polypropylene conical column with a diameter of 0.8 cm (Bio-Rad, Belgium). The resin was pre-cleaned with 10 mL of 6 M HCl and 10 mL of milli-Q water and conditioned with 2 mL of 0.02 M HF. After sample loading, the matrix was removed by washing with 5 mL of an acid mixture consisting of 0.5 M HF and 2 M HCl. Boron was subsequently eluted from the column using 20 mL of 6 M HCl.

For microsublimation, 50 µL of sample digest in 1.4 M HNO_3 medium and containing 0.8 µg of B was deposited as a single drop on the inner side of the lid of a 5 mL Savillex® beaker. The beaker with conical interior and fin legs was screwed on tightly and the closed beaker was incubated upside down on a hotplate at 110 °C for 24 h. The temperature was allowed to decrease to 50 °C before the beakers were removed from the hotplate and unscrewed. The drop attached to the conical interior of the beaker was subsequently diluted to 4 mL with 0.29 M HF.

Preparation of samples with known $\delta^{11}B$

Solid sample matrices, *i.e.* $CaCO_3$, spinach leaves and glass, were first dissolved and/or digested. Calcium carbonate was dissolved in diluted HCl or HNO_3 to prepare 33.3 g/L Ca^{2+} solutions, with a pH of 4.5 or of 0 for chromatography and microsublimation, respectively. The final Ca^{2+} concentration in the spiked samples was 20 g/L.

Two 120 mg aliquots of powdered spinach leaves first underwent a microwave-assisted acid digestion procedure with concentrated HNO_3 in a Milestone Microwave Labstation MLS-1200 mega unit (Milestone s.r.l., Italy). The microwave program consisted of two 1 minute steps with heating at 250 W and 1 minute at zero power, followed by 5 minutes each at increasing powers of 250, 400 and 600 W. After cooling down to room temperature, the digests were subsequently transferred to 15 mL Savillex® PFA beakers, 1 mL of 29 M HF was added and the closed beakers

were incubated on a hotplate for 24 h at 105 °C. The samples were evaporated to dryness at 100 °C and redissolved in 1 mL of 0.02 M HCl.

112 mg of the powdered NIST SRM 610 silicate glass reference material was weighed in a 15 mL Savillex® PFA beaker and subsequently digested using a hotplate procedure, consisting of two steps, both with digestion at 110 °C for 48 h and subsequent evaporation at 70 °C. The acid mixture used in the first step consisted of 6 mL of HF + 2 mL of HNO_3; in the second step, it was 8 mL of *aqua regia*. Finally, the digested glass sample was redissolved in 0.02 M HCl. All sample pretreatment, except for microwave-assisted acid digestion, was carried out in a class-10 clean lab to reduce contamination.

One-mL digests of the sample matrices that contained natural boron, *i.e.* seawater, spinach leaves and silicate glass, were stripped from their original B content using a chromatographic procedure (*cf. supra*). The recovered B-free sample solutions were evaporated to dryness and redissolved in either 0.02 M HCl or 1.4 M HNO_3. The remaining natural B concentration was 6, 26 and < 1 µg/l in seawater, spinach digest and silicate glass digest, respectively, as determined using quadrupole-based ICP-MS after 100-fold dilution. Hence, the fraction of contamination from remaining natural B towards spiked B ranges between < 0.0025 % and 0.16 % for all matrices spiked with either 16 mg/L B for microsublimation or 40 mg/L B for chromatographic isolation. This small fraction of contamination was insignificant as the effects on the $\delta^{11}B$ values of final samples would be biased by 0.1 ‰ in the worst case. Calculations supporting this statement are reported in the supplementary material. The final matrix concentrations of the B-free sample solutions were undiluted seawater, 100 g/L of spinach leaves and 10 g/L of NIST SRM 610 silicate glass.

After dissolution or digestion and removal of natural B (when appropriate), samples were spiked with $\delta^{11}B$ reference materials up to a boron concentration of 40 mg/L for ion exchange chromatography and of 16 mg/L for microsublimation, respectively. Procedural blanks were spiked with Milli-Q water instead. For each type of matrix, 4 solutions for chromatography and 4 for microsublimation were obtained – one free from B and three containing B, with various B isotopic signatures. Each solution was treated in triplicate, such that a total of 24 samples were generated for each matrix.

Concentration determination of boron and matrix elements

Boron recoveries and matrix element concentrations were determined using a Thermo Scientific XSeriesII quadrupole-based ICP-MS instrument (Germany), equipped with a 400 µL/min PFA concentric nebulizer, mounted onto an inert PEEK impact bead spray chamber. A sapphire injector tube was fitted into the plasma torch. Samples for B analysis were diluted 4-fold in 0.29 M HF to a nominal B concentration of 50 µg/L, while 30 µg/L of Be was used as an internal standard to correct for matrix effects and instrument instability. A selection of major matrix elements was determined after 4-fold dilution in 0.28 M HNO_3. For these determinations, Be and Sc (final concentrations: 30 µg/L) were used as internal standards. The selected elements were Al and Si (in silicate glass only); Na, Mg, Mn, Fe and Sr (in seawater, spinach and silicate glass); and Ca (in all matrices). Mn, Fe and Si were measured in CCT mode with the hexapole cell pressurized with He/H_2 collision-reaction gas at a flow rate of 4.5-5 mL/min. External boron calibration standards, with concentrations ranging from 1 to 75 µg/L, were prepared in 0.29 M HF and multi-element external calibration standards, with concentrations ranging from 10 to 250 µg/L for Ca and from 1 to 100 µg/L for the other matrix elements were prepared in 0.28 M HNO_3. Instrument settings and data acquisition parameters are summarized in **Table 1**.

Boron isotopic analysis

The B isolates obtained from the samples were diluted to 150 µg/L of B in 0.29 M HF. Samples with a B recovery < 75 % were not diluted prior to isotopic analysis. Li isotopic standard was spiked to each sample to a final concentration of 100 µg/L. Likewise, 150 µg/L of NIST SRM 951 B isotopic reference material was used as an external standard, measured in a sample-standard bracketing approach. Also this external standard was spiked with 100 µg/L of IRMM-016 Li. Boron and Li isotope ratios were measured using a Thermo Scientific Neptune MC-ICP-MS instrument, operated in dynamic mode with 3 s idle time between each B and Li measurement cycle. Sample introduction was accomplished using a 50 µL/min PFA concentric nebulizer, mounted onto a PFA Scott-type spray chamber. A sapphire injector tube was inserted into the plasma torch. Instrument settings and data acquisition parameters are shown in **Table 1**. The cup configuration and amplifier resistance selected for each cup are provided in **Table 2**. To correct for mass discrimination, both internal correction using the admixed Li isotopic standard and external correction, *i.e.* via sample-standard bracketing, were applied. As samples pre-treated using chromatography contained HCl after elution, Li-spiked isotopic calibration standards were prepared in 2 M HCl to adequately correct for mass discrimination using the common analyte internal standardization (CAIS) method. This approach was first described for quadrupole-based ICP-MS [31] and its appropriateness in mass discrimination correction of MC-ICP-MS data was recently demonstrated for B and Sb isotope ratios [32]. Briefly, an isotopically certified standard of an element with similar characteristics as the analyte element with respect to mass discrimination, *i.e.* the common analyte, is spiked to all samples and standards. Subsequently, the linear relation between the observed isotope ratio for the analyte and the observed isotope ratio for the common analyte in the standards is used to calculate a correction factor for all samples

individually, based on the experimentally determined ratio for the common analyte. All calculations involved in mass discrimination correction are described in detail in the **electronic supporting information.** For selected sample series, the three replicate sub-samples that underwent the isolation procedure separately, were analyzed on different days. In addition, for randomly selected samples, two additional replicate isotope ratio measurements were performed during the same measurement day, to evaluate the respective contributions of sample preparation and instrument stability to the variation in determined $\delta^{11}B$ values.

A statistical method published by ERM was applied to decide whether experimental results significantly differed from certified values [33]. The method is based on a comparison between (1) the absolute value of the difference between average experimental result and certified value (Δ_m) and (2) the expanded uncertainty of Δ_m taking into account the combined uncertainty of experimental result and certified value (U_Δ). If $\Delta_m > U_\Delta$, a significant difference between experimental and certified value is expected.

Results and discussion

Sample throughput, labor intensiveness and costs

Within one sample pretreatment session, typically 24 samples were dealt with, either via chromatography or via microsublimation. A total of 96 samples were processed in this project, 48 via ion exchange chromatography and 48 via microsublimation. The total time of lab work required to handle 24 samples via microsublimation was 190 minutes, while ion exchange chromatography required 465 minutes. These time budgets include the total time required for the purification process and the subsequent cleaning of reusable material, such as columns and Savillex® beakers. Due to the higher volumes of purified acid necessary for ion exchange

chromatography, the costs of consumables are substantially higher for chromatography than for microsublimation.

Removal efficiency of matrix elements, B recovery and procedural blank via ion exchange chromatography and microsublimation

In general, matrix elements are efficiently removed by both isolation methods from all sample matrices. For the Ca-rich solution, none of the purified samples contained Ca^{2+} in a concentration higher than the LOD of 110 µg/l. **Table 3** shows elemental concentration data in undiluted purified samples, obtained from seawater, spinach and silicate glass matrices. Only for Na in the B isolates from seawater samples and for Si in the B isolate from silicate glass samples, a clear difference was observed between the remaining matrix element concentration after ion exchange chromatography and microsublimation, respectively, whereby microsublimation resulted in a more efficient removal. In seawater samples, the Na^+ concentration was lower than 50 µg/L in microsublimated samples, except for 1 out of 12 samples that showed a concentration still below the LOQ of 170 µg/L, while chromatographically purified samples contained up to 230 µg/L of Na^+. Silicate glass samples all contained 1 to 2 mg/L of silicon after chromatographic purification, while no remaining Si was detected in microsublimated samples. In addition, also for Fe and Mg, (smaller) differences in remaining concentrations were noticed between chromatography-purified and microsublimated silicate glass samples. In spinach samples, the Sr concentration was a factor of 3 to 4 higher when chromatography was used. In all other sample sets, very similar matrix element concentrations were observed.

Boron recoveries obtained from seawater and Ca-rich solution were high for both microsublimation and chromatography. Concentrations ranged between 163 and 207 µg/L B in the final 20 mL solutions after chromatography and between 184 and 214 µg/L B in the final 4

mL solutions after microsublimation. This resulted in overall boron recoveries between 81 and 107 %, with the 10th to 90th percentile in-between 90 and 104 %, respectively, for Ca and seawater matrices. In spinach and silicate glass matrices, B recoveries were lower and more variable, with individual boron concentrations ranging between 154 and 198 µg/L B in the final 20 mL solutions after chromatography and between 122 and 207 µg/L B in the final 4 mL solutions after microsublimation. This corresponds to a boron recovery between 61 and 103 % for microsublimation and between 79 and 99 % for chromatography for spinach and silicate glass matrices.

Chromatography (86 %) resulted in significantly better recoveries from spinach samples than microsublimation (75 %). Boron isolation through microsublimation also resulted in poor reproducibility for silicate glass matrix solutions. **Table 4** summarizes average B recoveries (n = 3) obtained for the three δ^{11}B reference materials for various matrices using both isolation procedures.

Procedural blanks of both isolation methods were typically lower than the limit of detection, i.e. 0.08 µg/L B in the final solution subjected to MC-ICP-MS analysis. One exception of 0.44 µg/L of B was observed in a microsublimated spinach blank, which corresponds to 1.8 ng of B. Most of the procedural blanks of ion exchange chromatography for silicate glass and spinach matrices were between 0.40 and 0.60 µg/L, corresponding to 8 and 12 ng of B, respectively. All concentrations in procedural blanks are summarized in **Table S4** of the supporting information.

Accuracy and precision of δ^{11}B determinations

Accurate and precise δ^{11}B values were obtained for the NIST SRM 951 bracketing standard over the five months period of measurements performed within this study. Overall, a δ^{11}B value of 0.0

‰ was obtained, with a measurement precision (2s) of 0.3 ‰ (n = 140). On a daily basis (n ≈ 19), $\delta^{11}B$ was always 0.0 ‰, with a measurement uncertainty (2s) varying between 0.2 and 0.5 ‰. These precisions are in good agreement with other studies reporting long-term 2s on the $\delta^{11}B$ values obtained in repeated measurements of NIST SRM 951 boric acid solutions between 0.2 and 0.6 ‰ [12,18,22,23]. **Table 5** shows the $\delta^{11}B$ values derived for the individually spiked samples after removal of the reference materials' matrices, including average and 2s (n = 3). An asterisk indicates a significant difference between the experimentally determined and corresponding certified value.Average $\delta^{11}B$ values obtained for seawater, Ca-rich matrices and silicate glass correspond well with the certified values, both after ion exchange chromatography and microsublimation. However, a small, though significant, positive offset of ~ 1 ‰ was observed for AE120 in silicate glass matrix treated with chromatography and microsublimation. For spinach samples, ion exchange chromatography clearly performed better than microsublimation, with again a ~ 1 ‰ offset for the AE120 standard after chromatography, but large positive offsets of ~ 8 ‰ for all microsublimated spinach samples. While there is no apparent explanation for the ~ 1 ‰ offsets for AE120, the large 8 ‰ offsets in microsublimated spinach samples were clearly due to fractionation. When plotting $\delta^{11}B$ offset vs. B recovery for each of these microsublimated spinach samples, a linear correlation was found with $R^2 = 0.90$. **Figure 1** and **Figure S2** in the supporting information section show the presence and absence of correlation in microsublimated spinach and all other sample types, respectively. This indicates that in the case of spinach matrix, B isotope fractionation occurred during the microsublimation process, whereas for silicate glass samples, the incomplete B recoveries were not accompanied by meaningful isotope fractionation. Also Gaillardet et al. [26] did not observe isotope fractionation upon microsublimation of B with < 50 % recovery out of NaCl solution. A possible explanation

for the fractionation in the spinach samples is that some undigested material remained in the final solutions, causing inhomogeneity and interactions with B isotopes. In general, B isotope fractionation processes are driven by their different partitioning between trigonal and tetragonal species, where ^{11}B is enriched in trigonal species, such as $B(OH)_3$. In this molecule, B forms three covalent bonds with $OH^{\bullet}$, resulting in a trigonal planar geometry. On the other hand, ^{10}B preferentially partitions into tetragonal species, containing 4 covalent bonds, with ^{10}B in the center and the bound species each at the corners of a tetrahedron. Furthermore, ^{10}B preferentially adsorbs to organic matter and clay minerals [34,35]. More specifically, in the case of spinach solutions, ^{10}B is more likely to adsorb to any remaining organic matter or silicate minerals in the solutions and ^{11}B will be prevalent in the sublimating $B(OH)_3$ species. Such partitioning between dissolved and adsorbed state may explain the low recovery and fractionation observed in spinach samples.

In the silicate glass samples, only a minor deviation from the certified values for AE 120 was observed, despite the incomplete B recoveries in all samples. Hence, the silicate matrix may have affected the efficiency of the microsublimation process itself without B partitioning to an adsorbed state and concomitant B isotope fractionation. In a previous study, the absence of fractionation in glass samples treated with ion exchange chromatography was reported by Devulder et al. [16] and is confirmed in the present study.

Two sources of variation contribute to the overall variation in $\delta^{11}B$ for samples that were independently prepared and analyzed, *i.e.* variation due to sample pretreatment and variation due to instrument instability. Variation due to instrument instability can be estimated from the precision (2s) calculated on the basis of replicate measurements of the same sample. **Table 6** shows average $\delta^{11}B$ and precision (2s) on replicate measurements of randomly selected samples

and **Table 5** contains individual and average $\delta^{11}B$ values and precision (2s) for independently prepared and analyzed samples. It is clear that the bad precision in Table 5 for microsublimated spinach samples, *i.e.* 2s from 2.4 to 6.3 ‰, was due to the variation in recovery and the concomitant fractionation during sample pretreatment, as a ten-fold better precision, *i.e.* 2s of 0.2 ‰, was observed for replicate measurements of the same microsublimated spinach sample (**Table 6**). However, sample types resulting in higher B recoveries, *i.e.* seawater and Ca^{2+}-rich solution, did not show a worse precision (2s) for independently prepared and analyzed samples (Table 5) compared to replicate measurements of the same samples (Table 6). In fact, the precision (2s) on replicate sample measurements is often as large as or even larger than the precision (2s) for samples that were independently prepared and analyzed. Therefore, for these matrices, the total precision (2s) is mainly dominated by instrument instability, rather than by sample preparation issues. Furthermore, samples originating from seawater and Ca-rich solutions display a $\delta^{11}B$ precision (2s) similar to or up to 8-fold better after microsublimation than after ion exchange chromatography purification. Hence, variation due to instrument instability was higher for chromatographically isolated samples, which could possibly be attributed to the presence of HCl in the samples, potentially affecting instrumental stability. For all samples that underwent purification via microsublimation and for the majority of samples purified via ion exchange chromatography, the precision (2s) on replicate measurements was equal to the precision (2s) established for the NIST SRM bracketing standard results, *i.e.* the 2s varies between 0.1 and 0.6 ‰. Hence, the sample pretreatment methods are reproducible and precision is mainly dominated by instrument instability. Guerrot et al. [36] reported a similar precision of 0.4 ‰ for repeated sample preparations and MC-ICP-MS analyses. For very small B sample masses of 1 ng, Liu et al. [30] reported precisions (2s) between 0.7 and 1.2 ‰ for replicate microsublimation and

subsequent total evaporation NTIMS. Precisions on replicate measurements (2s) higher than 0.6 ‰ in the present study were only observed for samples pretreated with ion exchange chromatography, possibly caused by the presence of HCl in the samples.

Conclusion

Evaluation of microsublimation and ion exchange chromatography for isolation of B from Ca-rich aqueous solution, seawater, plant material and silicate glass matrices allows to draw conclusions in terms of B recovery, procedural blank, matrix element removal efficiency, accuracy and precision of resulting $\delta^{11}B$ values, labor intensiveness and consumable costs. The main advantages and disadvantages of each method are summarized in **Table 7**. Overall, microsublimation is favored in terms of matrix removal efficiency, procedural blank, precision on $\delta^{11}B$ values for replicate samples, labor intensiveness and consumable costs. However, for spinach samples, incomplete B recoveries were accompanied by isotope fractionation, resulting in large (~ +8 ‰) $\delta^{11}B$ offsets, while ion exchange chromatography did not result in isotope fractionation, despite recoveries < 100 %.

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References

[1] M. R. Palmer, G. H. Swihart, *Rev mineral*, 1996, **33**, 709-744.

[2] E. Rose, M. Chaussidon, C. France-Lanord, *Geochim Cosmochim Ac*, 2000, **64**(3), 397–408.

[3] A. J. Spivack, M. R. Palmer, J. M. Edmond, *Geochim Cosmochim Ac*, 1987, **51**(7), 1939-1949.

[4] R. E. Zeebe, *Geochim et Cosmochim Ac*, 2005, **69**(11), 2753–2766.

[5] J. Smith, A. J. Spivack, H. Staudigel, S. R. Hart, *Chem Geol*, 1995, **126**, 119-135.

[6] Y.-C.Liu, C.-F.You, K.-F. Huang, R.-M Wang, C.-H. Chung, H.-C. Liu, *J Asian Earth Sci*, 2012, **58**, 16–23.

[7] D. Widory, E. Petelet-Giraud, A. Brenot, J. Bronders, K. Tirez, P. Boeckx. *Isot Environ Healt S*, 2013, **49**(1), 29–47.

[8] N. G. Hemming, G. N. Hanson, *Geochim Cosmochim Ac,* 1992, **56**, 537-543.

[9] J. C. Gaillardet, C. J. Allègre, *Earth Plan Sc Lett*, 1995, **136**, 665-676.

[10] R. E. Zeebe, A. Sanyal, J. D. Ortiz, D. A. Wolf-Gladrow, *Mar Chem*, 2001, **73**, 113–124.

[11] G. L. Foster, C. H. Lear, J. W. B. Rae, *Earth Plan Sc Lett,* 2012, **341-344**, 243–254.

[12] R. Shinjo, R. Asami, K.-F. Huang, C.-F. You, Y. Iryu, *Mar Geol*, 2013, **342**, 58–64.

[13] T. Koshiba, M. Kobayashi, T. Matoh, *Plant Signal Behav*, 2009, **4**(6), 557–558.

[14] V. M. Shorrocks, *Plant Soil* 1997, **193**(1-2), 121-148.

[15] P. P. Coetzee, F. Vanhaecke, *Anal Bioanal Chem*, 2005, **383**, 977-984, 2005.

[16] V. Devulder, P. Degryse, F. Vanhaecke, *Anal Chem*, 2013, **85**, 12077−12084.

[17] S. K. Aggarwal, B.-S. Wang, C.-F. You, C.-H. Chung, *Anal Chem*, 2009, **81**, 7420–7427.

[18] J. J.-S.Shen, C.-F. You, *Anal Chem,* 2003, **75**, 1972-1977.

[19] A. J. Spivack, J. M. Edmond, *Anal Chem*, 1986, 58, 31−35.

[20] T. Nakano, E. Nakamura, *Int J Mass Spectrom*, 1998, **176**, 13−21.

[21] L. Yang, *Mass Spectrom Rev*, 2009, **28**, 990–1011.

[22] J. K. Aggarwal, D. Sheppard, K. Mezger, E. Pernicka, *Chem Geol*, 2003, **199**, 331– 342.

[23] G. Wei, J. Wei, Y. Liu, T. Ke, Z. Ren, J. Ma, Y. Xu, *J Anal Atom Spectrom*, 2013, **28**, 606–612.

[24] J. Vogl, M. Rosner, W. Pritzkow, *J Anal Atom Spectrom*, 2011, **26**, 861-869.

[25] M. Rosner, W. Pritzkow, J. Vogl, S. Voerkelius, *Anal Chem*, 2011, **83**, 2562–2568.

[26] J. Gaillardet, D. Lemarchand, C. Göpel, G. Manhès, *Geostandard Newslet*, 2001, **25**(1), 67-75.

[27] D. Lemarchand, J. Gaillardet, C. Göpel, G. Manhès, *Chem. Geol*, 2002, **182**, 323–334.

[28] B.-S.Wang, C.-F. You, K.-F. Huang, S.-F. Wu, S. K. Aggarwal, C.-H. Chung, P.-Y. Lin, *Talanta*, 2010, **82**, 1378–1384.

[29] E. Anagnostou, K.-F. Huang, C.-F. You, E. L. Sikes, R. M. Sherrell, *Earth Plan Sc Lett*, 2012, **349–350**, 251–260.

[30] Y.-W. Liu, S. M. Aciego, A. D Jr. Wanamaker, B. K. Sell, *Rapid Commun Mass Sp*, 2013, **27**, 1705–1714.

[31] A. S. Al-ammar, R. M. Barnes, *J Anal Atom Spectrom*, 2001, **16**, 327-332.

[32] V. Devulder, L. Lobo, K. Van Hoecke, P. Degryse, F. Vanhaecke, *Spectrochim Acta B*, 2013, **89**, 20–29.

[33] T. Linsinger. Application note 1 – Comparison of a measurement result with the certified value. European Reference Materials, European Communities, 2005. Available at: http://www.ermcrm.org/ERM_products/application_notes/application_note_1/Documents/erm_application_note_1_english_rev3.pdf

[34] E. Lemarchand, J. Schott, J. Gaillardet, *Geochim Cosmochim Ac*, 2005, **69**(14), 3519–3533.

[35] L. B. Williams, R. L. Hervig, M. E. Wieser, I. Hutcheon, *Chem Geol*, 2001, **174,** 445–461.

[36] C. Guerrot, R. Millot, M. Robert, P. N. Guerrot, *Geostand Geoanal Res*, 2011, **35**(2), 275-284.

Figure captions

Figure 1 - $\delta^{11}B$ offset vs. B recovery from individual spinach samples purified with microsublimation. A linear relation was fitted to the data.

Table 1

Table 1 - Instrumental operation settings for elemental concentration determinations using a Thermo Scientific XSeriesII instrument and B isotope ratio determination with a Thermo Scientific Neptune MC-ICP-MS instrument.

	XSeriesII	Neptune
Intstrumental settings		
RF power (W)	1200	1120-1145[a]
Cool gas flow rate (L/min)	13.0	15.0
Auxiliary gas flow rate (L/min)	0.70	0.70
Nebulizer gas flow rate (L/min)	0.79-0.84[b]	1.035-1.070[a]
He/H_2 CCT gas flow rate (L/min)	0.045-0.050[c,d]	n.a.
Kinetic energy discrimination	3 V[c]	n.a.
Sampler and skimmer cone	Ni, Xt-type	Ni, H-type
Sample uptake rate (mL/min)	0.5	0.05
Torch X-position	149-169[b]	3.300 - 3.710[a]
Torch Y-position	464-494[b]	-2.500 - -2.410[a]
Torch Z-position	43 – 65[b]	0.420 – 0.700[a]
Data acquisition parameters		
Integration time (s)	0.030	4.2
Blocks	3	5
Cycles/block	100	3
Outlier test	n.a.	$\lvert x_i - \bar{x} \rvert > 2\sigma$

[a]: optimized daily for sensitivity and stability;

[b]: optimized daily for sensitivity, stability and $^{156}CeO^+/^{140}Ce^+$ ratio;

[c]: applied in CCT mode only, *i.e.* for concentration determination of Si, Mn and Fe;

[d]: optimized daily for low $^{78}ArAr^+$ background signal (< 10 cps) and highest sensitivity.

Table 2

Table 2 - Cup configuration and amplifier resistance in MC-ICP-MS analysis of B isotope ratios with a Thermo Scientific Neptune

Cup	L4	L2	H4
Amplifier (Ω)	10^{12}	10^{12}	10^{11}
B isotope		^{10}B	^{11}B
Li isotope	^{6}Li		^{7}Li

Table 3

Table 3 - Matrix element concentrations determined after microsublimation or ion exchange chromatography purification. '# < LOD' indicates the number of samples for which a concentration < LOD was obtained.

Element		Ca		Na		Mg		Mn		Fe		Sr		Al		Si	
LOD (undiluted, µg/L)		110		50		3		0.09		2		0.2		2		360	
LOQ (undiluted, µg/L)		360		170		9		0.31		6		0.6		7		1190	
Matrix	Sample preparation	CH	MS	CH	MS	CH	MS	CH	MS	CH	MS	CH	MS	CH	MS	CH	MS
seawater	# < LOD	12	11	0	11	11	8	9	9	0	1	11	11	n.d.	n.d.	n.d.	n.d.
	median (µg/L)	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	LOD	< LOD	< LOQ	< LOQ	< LOD	< LOD	n.d.	n.d.	n.d.	n.d.
	max (µg/L)	< LOD	< LOD	230	< LOQ	< LOQ	< LOQ	< LOQ	0.37	15	20	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.
	min (µg/L)	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	n.d.	n.d.	n.d.	n.d.
spinach	# < LOD	12	12	9	6	9	4	0	0	0	1	0	0	n.d.	n.d.	n.d.	n.d.
	median (µg/L)	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	0.83	0.78	29	19	2.3	0.8	n.d	n.d	n.d	n.d
	max (µg/L)	< LOD	< LOD	< LOQ	< LOQ	< LOQ	< LOQ	1.77	1.77	104	67	2.4	0.9	n.d.	n.d.	n.d.	n.d.
	min (µg/L)	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.67	0.41	15	< LOD	2.2	0.6	n.d.	n.d.	n.d.	n.d.
silicate glass	# < LOD	10	12	10	12	7	8	0	0	0	10	0	0	0	0	0	12
	median (µg/L)	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.96	0.79	9	< LOD	0.6	0.6	13	11	1910	< LOD
	max (µg/L)	< LOD	< LOD	< LOD	< LOD	34	< LOQ	1.38	0.84	19	8	0.6	0.7	17	19	2180	< LOD
	min (µg/L)	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.89	0.77	< LOQ	< LOD	0.6	0.6	10	7	< LOQ	< LOD

Table 4

Table 4 - Average (n = 3) boron recoveries from various sample types after ion exchange chromatography and microsublimation purification

Matrix	$\delta^{11}B$ reference	Ion exchange chromatography		Microsublimation	
		Average (%)	SD (%)	Average (%)	SD (%)
seawater	AE120	97	3	98	1
	AE121	96	4	94	1
	AE122	94	2	97	3
Ca^{2+} solution	AE120	90	8	103	1
	AE121	96	7	106	2
	AE122	91	3	101	1
spinach	AE120	85	5	75	12
	AE121	88	3	74	3
	AE122	86	3	74	8
silicate glass	AE120	86	2	79	7
	AE121	91	11	94	8
	AE122	79	1	68	9

Table 5

Table 5 - $\delta^{11}B$ values obtained in individual, purified samples, after ion exchange chromatography and microsublimation for the four matrices. An asterisk (*) indicates a significant difference between the average experimentally determined and the corresponding certified value.

Matrix	$\delta^{11}B$	Chromatography					microsublimation				
		A	B	C	$\bar{x}$	2s	A	B	C	$\bar{x}$	2s
seawater	AE120	-20.2	-20.2	-19.6	-20.0	0.7	-20.1	-20.2	-20.2	-20.2	0.1
	AE121	20.2	20.2	20.1	20.1	0.1	19.4	19.5	19.5	19.5	0.1
	AE122	39.9	40.9	40.5	40.4	0.9	38.9	39.3	39.2	39.1	0.5
Ca^{2+} solution	AE120	-20.0	-18.9	-20.0	-19.6	1.3	-20.4	-20.2	-20.4	-20.4	0.2
	AE121	20.7	20.3	20.0	20.4	0.8	n.d.	19.6	19.6	19.6	0.1
	AE122	41.3	40.3	39.8	40.5	1.5	39.6	39.0	39.1	39.2	0.6
spinach	AE120	-18.5	-18.5	-18.5	-18.5*	0.0	-15.1	-13.6	-9.1	-12.6*	6.3
	AE121	20.0	20.0	20.0	20.0	0.0	27.7	27.5	29.7	28.3*	2.4
	AE122	39.4	39.4	39.4	39.4	0.1	47.2	45.3	49.4	47.3*	4.1
silicate glass	AE120	-18.9	-18.7	-18.4	-18.7*	0.6	-18.2	-18.8	-18.6	-18.5*	0.6
	AE121	20.0	20.4	n.d.	20.2	0.6	20.5	20.1	21.5	20.7	1.5
	AE122	n.d.	39.4	39.4	39.4	0.1	39.2	40.4	41.3	40.3	2.1

Table 6

Table 6 - Average (n = 3) $\delta^{11}B$ values (2s) obtained in three replicate MC-ICP-MS analyses of the same sample during the same day

Matrix	$\delta^{11}B$ reference material	Chromatography	Microsublimation
seawater	AE120	-20.4 (0.9) (B)	-20.1 (0.4) (A)
	AE121	20.5 (0.6) (A) 20.6 (1.1) (C)	n.d.
Ca^{2+} solution	AE120	-20.0 (0.1) (A)	-20.3 (0.2) (C)
	AE122	40.0 (0.5) (C)	39.2 (0.6) (A) 39.3 (0.6) (B)
spinach	AE121	20.9 (0.4) (A) 21.1 (0.3) (C)	29.5 (0.2) (C)
silicate glass	AE120	-18.5 (0.3) (B)	n.d.
	AE122	n.d.	40.5 (0.1) (B)

Table 7

Table 7 - Summary of advantages and disadvantages of microsublimation and ion exchange chromatography with respect to the criteria assessed in this study

Criterion	Purification method	Advantage (+)	Disadvantage (-)
Labor intensiveness	Chromatography		High (465 minutes/24 samples)
	Microsublimation	Low (190 minutes/24 samples)	
Consumable costs	Chromatography		High consumables costs
	Microsublimation	Low consumables costs	
Matrix removal efficiency	Chromatography	Efficient matrix removal	Some Na (up to 230 µg/l) and Si (up to 2 mg/l) remaining in certain matrices
	Microsublimation	Complete matrix removal	
B recovery	Chromatography	Complete recovery from Ca-rich solution and seawater	80-90 % recovery from spinach and silicate glass
	Microsublimation	Complete recovery from Ca-rich solution and seawater	60-100 % recovery from spinach and silicate glass
Accuracy $\delta^{11}B$	Chromatography	Accurate $\delta^{11}B$ for all samples in Ca-rich solution and seawater, for the majority of samples in silicate glass and spinach digests	~ 1 ‰ positive offset for AE120 samples in spinach and silicate glass matrices.
	Microsublimation	Accurate $\delta^{11}B$ for all Ca-rich solution and seawater samples, for the majority of samples in silicate glass digests	Large offset (+8 ‰) for all spinach samples, ~ 1 ‰ positive offset for AE120 samples in silicate glass.
Precision $\delta^{11}B$	Chromatography	Majority of $2s \leq 0.6$ ‰	Remaining HCl possibly affects instrument stability, resulting in $2s > 0.6$ ‰
	Microsublimation	$2s \leq 0.6$ ‰; precision not affected by sample preparation procedure	

Figure 1