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Direct separation of boron from Na- and Ca-rich matrices by sublimation for stable isotope measurement by MC-ICP-MS

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ABSTRACT

An improved technique for precise and accurate determination of boron isotopic composition in Na-rich natural waters (groundwater, seawater) and marine biogenic carbonates was developed. This study used a 'micro-sublimation' technique to separate B from natural sample matrices in place of the conventional ion-exchange extraction. By adjusting analyte to appropriate pH, quantitative recovery of boron can be achieved (>98%) and the B procedural blank is limited to <8 pg. An additional mass bias effect in MC-ICP-MS was observed which could not be improved via the standard-sample-standard bracketing or the 'pseudo internal' normalization by Li. Therefore a standard other than NBS SRM 951 was used to monitor plasma condition in order to maintain analytical accuracy. An isotope cross-calibration with results from TIMS shows that the space-charge mass bias on MC-ICP-MS can be successfully corrected using off-line mathematical manipulation. Several reference materials, including the seawater IAPSO and two groundwater standards IAEA-B-2 and IAEA-B-3, were used to validate this approach. We found that the δ^{11}B of the reference coral JCp-1 was 24.22 ± 0.28‰, corresponding to seawater pH based on the coral δ^{11}B-pH function.

1. Introduction

Boron has two naturally occurring isotopes ^{10}B and ^{11}B, comprising 19.9 and 80.1% of total B, respectively. Because boron exhibits a single oxidation state in nature, isotopic fractionation between its two stable isotopes is dominated by changes in its coordination number or the ligands present in its coordination sphere [1,2]. Due to relatively large mass difference (10%) between the two isotopes and high volatility, boron isotopic composition ranges from −30 to +60‰ [3] in natural materials and has been used as a tracer for studying continental weathering [4], plate subduction processes [5], and anthropogenic pollution [6]. Furthermore, dissolved boron in seawater primarily includes mononuclear species boric acid (trigonally coordinated) and borate (tetrahedrally coordinated), and the relative proportion of the two species is pH dependant as shown below:

$$B(OH)_3 + H_2O \Leftrightarrow B(OH)_4^- + H^+ \quad (1)$$

The B isotopic composition of marine biogenic carbonates reflects seawater pH [7,8]. These data can be used to constrain estimates of past atmospheric CO_2 concentration (pCO_2) and the oceanic carbonate budget, which in turn is linked to historical climate variation as well as the global carbon cycle [9,10]. However, a major challenge for B stable isotope measurements is instrumental mass fractionation during ^{11}B/^{10}B measurement, and the B blank during the experimental procedures, influences the analytical precision and accuracy [11].

Several methods for purifying B from aqueous solutions have been reported. These include solvent extraction, ion-exchange separation, chelation, B-specific resins, chromatographic separation and conversion to gaseous methyl borate or boron fluoride [12]. Among these methods, the B-specific resin Amberlite IRA-743 is widely used for separation of B from different geological materials [13,14]. Because the measurement of B by thermal ionization mass spectrometry (TIMS) is isobarically interfered by CNO compounds [15] originating from nature and the resin itself, Gaillardet et al. [16] applied 'micro-sublimation' as a second purification step for samples from organic rich matrices. However, the utility of this technique for natural samples has not been adequately tested. During the column separation procedure, the blank signal increases during the infusion of the reagents and is also originates from the resin, thus possibly affecting either the accuracy or precision. Since

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no detectable isotopic fractionation was reported for the 'micro-sublimation' process under acid conditions [16,17], this technique appears promising to replace the conventional column method.

This paper focuses on the experimental approach when using the 'micro-sublimation' technique and reports details on the chemical yield, procedural blank, solvent matrix (HNO_3 and HCl) and solution pH. The single-step B purification tested on natural samples with Na- and Ca-rich matrices shows relatively low experimental blank (2–200 times lower) than the conventional column methods. Reference materials, including Na-rich IAPSO (seawater), IAEA-B-2 and IAEA-B-3 (groundwater), and Ca-rich JCp-1 (coral skeleton), were analyzed and the results were compared to results from $Cs_2BO_2^+$ positive thermal ionization mass spectrometry (P-TIMS).

2. Experimental

2.1. Operating conditions, reagents and doping test

Possible contamination from aerosols and dust particles was prevented by conducting all laboratory experiments in a Class-10 positive pressure hood coupled to a B-free ventilation system. Procedures for purifying acids, water and cleaning of PFA vessels (Savillex) were adopted from previous studies with slight modification [11,13,16]. A high-purity Na solution and an in-house synthetic B-free calcium carbonate were prepared for Na- and Ca-doping test. The synthetic $CaCO_3$ was first dissolved in HNO_3 following the same procedure as that of sample dissolution, and was pre-cleaned by micro-sublimation to eliminate potential B contamination. Due to the similarity of isotopic compositions of B in laboratory background with that of the international B isotopic reference material NBS SRM 951, the Ca-rich solution with similar B/Ca ratio as JCp-1 coral was then mixed with 10 μL JABA (10 mg L^{-1} pure B solution, prepared by Aggarwal [18]) for testing the chemical yield test. All blanks, including H_2O (Millipore, two-bottled distilled thereafter), HNO_3 (Merck GR grade treated by Amberlite IRA-743 resin and two-bottle purification processes), HCl (two-bottle distilled from Seastar ultrapure), NH_4OH (two-bottle distilled from Seastar ultrapure) and Na acetate-acetic acid buffer (Merck GR grade treated by Amberlite resin and two-bottle purification) were monitored by sector-field inductively coupled plasma mass spectrometry (Thermo Fisher Scientific, Element 2) operated under low resolution mode (resolving power ~300).

2.2. Sample preparation

Samples of *Porites* sp. coral specimen JCp-1 (GSJ reference material, Japan) and KTP-1 powder (in-house coral standard) were cleaned following the same standard cleaning techniques as those used for boron isotopic analysis. For the routine procedure, 1 mg of individual specimen was immersed in 10 μL H_2O followed by 40 μL 0.3 N HNO_3 (or 0.3 N HCl, for TIMS measurement) for dissolution. The same procedure was adopted for treating 40, 50 and 100 mg samples to investigate sample homogeneity. The pH of the final solution was kept below 3 (always <1 in this study) to ensure that boron was presented as $B(OH)_3$. During this step, impurities were observed in JCp-1 solutions, which were then discarded by siphoning off the supernatant after centrifuging at 8000 rpm for 5 min. Boron was separated from the solutions by micro-sublimation at 98 ± 0.1 °C in a homemade thermostatic hotplate rack in an exhaust hood at 22 °C. In addition, acidified IAPSO seawater and two groundwater standards, IAEA-B-2 and IAEA-B-3, containing about 50 ng B were tested using a similar procedure. For the IAPSO seawater, an aliquot of 12 μL (pH ~ 2) was mixed separately with 0.1 N HNO_3 to a final volume of 50 μL (~2300 mg L^{-1} Na and ~45 ng B) and was used for B purification using the same sublimation procedure.

Table 1
Boron purification procedure using Amberlite IRA-743 anion resin.

Step	Reagent	Volume (μL) × repeat	Purpose
1	H_2O	50 × 2	Rinse
2	0.3 N HNO_3	50 × 2	Cleaning
3	Acetic buffer	50 × 3	Conditioning
4 (check pH value at 5.5 by pH paper)	H_2O	50 × 1	Conditioning
5	Sample (pH ~ 5.5)	50 × 10	Loading
6	H_2O	50 × 2	Elute cations
7	H_2O	100 × 2	Elute cations
8	0.3 N HNO_3	50 × 4	Collect boron
6	0.3 N HNO_3	50 × 1	Tailing check
10	H_2O	100 × 2	Neutralize resin

2.3. Micro-sublimation

Before performing any B isotopic measurements, a microbalance was used to ensure all samples in PFA conical vials (Savillex) did not undergo any mass loss during sublimation. The manual protocol given by Gaillardet et al. [16] was modified slightly to use the same procedure for natural samples. Briefly, a drop of 50 μL sample containing 50 ng B to be analyzed was deposited at the center of the cap of a 5 mL conical vial. To confirm that the pH was less than 3, about 5 μL of each sample was checked using pH-indicator paper (Merck; pH 0-14). The vials were tightly closed in the upside down position on a homemade thermostatic hotplate with a Teflon coated graphite rack, and were then heated for several hours under 98 ± 0.1 °C. In this study, heating durations of 6, 12 and 18 h were tested to evaluate both the recovery and any changes in the isotopic composition. Each sample was diluted with 0.3 N HNO_3 to final volume of 0.5 or 1 mL for MC-ICP-MS measurements.

2.4. Column separation of boron

The conventional bead method was used to evaluate the efficiency of the 'micro-sublimation' technique. Column separation procedure (Table 1) was modified from Foster [19] using Amberlite IRA-743 B-selective resin (Sigma Co.) which was crushed and sieved to 100–200 mesh. The details of the evaluation procedure are given by Lemarchand et al. [17]. A resin volume of 25 μL was packed in a PFA mini-column (I.D. = 2 mm) and the flow rate was controlled at a rate of about 50 μL min^{-1} by a vacuum pumping system. To prevent incomplete washout of sulfur-rich solution and formation of NH_4Cl, ammonia solution was used only for H_2O blank test, while Na acetate-acetic acid buffer was used for both coral (JCp-1 and KTP-1) and acidified IAPSO seawater standard.

2.5. Mass spectrometry

All isotopic measurements were carried out using a MC-ICP-MS (Thermo Fisher Scientific, Neptune) at the Isotope Geochemistry Laboratory, National Cheng Kung University (Table 2). To reduce memory effects, 0.3 N HNO_3 was replaced with H_2O, and an additional washing step using 0.05 N NH_4OH solution was used for every 5 analyses (~20 min). To further reduce the blank contribution, the averaged background intensity determined using a 0.3 N HNO_3 blank was subtracted before processing the data using standard-sample bracketing (SSB) approach [20]. Before data collection, baselines were measured with idling and counting times of 10 and 20 s, respectively. One isotopic measurement run, consisting of 60 runs in 10 blocks, required about 2 min. The standard

Table 2
Instrumental operating conditions for MC-ICP-MS analyses.

Mass spectrometer	Neptune
RF power	1200 W
Ar cooling gas flow rate	15.0 L min^{-1}
Ar sample gas flow rate	1.05–1.10 L min^{-1}
Ar auxiliary gas flow rate	0.7 L min^{-1}
Interface cones	Nickel sampler and X-skimmer
Nebulizer type	PFA microflow, 50 μL min^{-1} (Elemental Scientific)
Inlet system	Stable inlet system with PFA Scott or dual-quartz spray chamber
Resolution	Low resolution
Faraday cup	H3 (^{11}B) and L3 (^{10}B)

deviation of repeat analyses (i.e., repeat sample runs) was approximately 4 times that of the standard error of estimate on individual runs. Therefore, this external precision was used for each analysis mass spectrometric data. Repeated analyses of 50 μg L^{-1} NBS SRM 951 resulted in a reproducibility of 0.33‰ (2SD, n = 40) (Table 3). To qualify the accuracy of the instrumental step, two standards, JABA and JABB were also included during the analyses [18].

Because previous studies have found that P-TIMS measurements using $Cs_2BO_2^+$ for B isotopic composition was a high-precision technique [17,21,22], our TIMS analyses were compared with results from MC-ICP-MS. The TIMS isotopic measurements were performed using a Thermal Fisher Scientific TRITON TI at NCKU. The 'Zoom Quad' function was applied to allow the two B isotopes to be measured simultaneously. The filament loading and heating procedures were modified from previous studies [17,22]. The ^{11}B/^{10}B was measured at mass 309/308 when the intensity of $^{133}Cs_2{}^{11}B^{16}O_2^+$ signal reached 800 mV on a Faraday cup (10^{11} Ω). A single mass spectrometric analysis was composed of 100 ratios in 10 blocks and was corrected for ^{17}O contribution by subtracting 0.00079 [23]. The external precision of repeated NBS SRM 951 was 0.36‰ (2SD, n = 20). All values reported in this study are presented in delta notation relative to NBS SRM 951 boric acid standard, where:

$$\delta^{11}B = \left(\frac{(^{11}B/^{10}B)_{Sample}}{(^{11}B/^{10}B)_{Standard}} - 1 \right) \times 1000 \quad (2)$$

The external uncertainty (as two standard deviations of the mean, i.e. 2SD) and the external reproducibility (2SD, long-term collection) are reported both as absolute and as relative (‰) numbers.

3. Results and discussion

3.1. Blank contribution and interference

B concentrations in reagents including H_2O (pre-concentrated from a volume of 100 mL), HNO_3 (13 N), HCl (9 N), acetate-buffer (2 N) and NH_4OH (10 N) solution were less than 10 ppt. Because it is difficult to decrease the B blank from GR grade HCl using the purification system, distilled reagent originated from ultrapure grade HCl (J. T. Baker) was used. An average procedural blank of 55 pg was obtained based on 9 determinations during the column separation step, individual values ranging from 41 to 74 pg and average $\delta^{11}B = -17.6 \pm 9.4$‰. The blank contribution of ~0.1% of a typical sample is negligible compared to the sample loaded on the filament. Similar column procedural blanks were reported by Foster [19] using a micro-column with a 25 μL resin bed. However, the blank

Table 3
Summary of boron isotopic analysis (50 μg L^{-1} B) of NBS 951, synthetic mixture, JABA, JCp-1 and KTP-1 corals, and IAPSO seawater.

Sample	Method	Matrix[a]	Recovery[b] (%)	δ^{11}B (‰)	2SD[c] (‰)	n
NBS 951	Direct measurement	–	–	0.02	0.33	40
	MS (12 h)	–	>97	0.06	0.42	12
Synthetic mixture	Direct measurement	–	–	25.24	0.44	17
JABA	Direct measurement	–	–	10.52	0.36	7
	MS (12 h)	100 μg L^{-1} Na	97.8	10.76	0.35	2
	MS (12 h)	500 μg L^{-1} Na	97.5	10.51	0.20	2
	MS (12 h)	2000 μg L^{-1} Na	97.2	10.56	0.27	3
	MS (12 h)	5000 μg L^{-1} Na	96.4	10.54	0.41	2
	MS (12 h)	10,000 μg L^{-1} Na	94.7	10.60	0.34	2
	MS (12 h)	500 μg L^{-1} Ca	97.6	10.62	0.25	2
	MS (12 h)	1000 μg L^{-1} Ca	96.9	10.58	0.04	2
	MS (12 h)	4000 μg L^{-1} Ca	97.3	10.78	0.20	2
	MS (12 h)	8000 μg L^{-1} Ca	96.8	10.83	0.16	3
JCp-1	MS (6 h)	Ca-rich	91.1	25.05	0.37	3
	MS (12 h)[d]	Ca-rich	97.6	24.22	0.28	6
	MS (18 h)	Ca-rich	101.6	24.29	0.29	3
	MS (6 h)[e]	Ca-rich	88.4	25.11	0.50	3
	MS (12 h)[e]	Ca-rich	99.1	24.25	0.43	3
	MS (18 h)[e]	Ca-rich	99.6	24.24	0.32	3
	MS (12 h)[f]	Ca-rich	>97	24.21	0.30	4
	Column purification[f]	Ca-rich	>97	24.52	0.37	3
	MS (12 h, 40 mg)	Ca-rich	>97	24.29	1.02	2
	MS (12 h, 50 mg)	Ca-rich	>97	24.27	0.28	8
	MS (12 h, 100 mg)[d]	Ca-rich	>97	24.22	0.28	6
KTP-1	MS (12 h)	Ca-rich	>97	24.34	0.51	4
IAPSO	MS (12 h)	Na-rich	>97	39.64	0.42	12
IAEA-B-2	MS (12 h)	Na-rich	>97	13.86	0.25	6
IAEA-B-3	MS (12 h)	Na-rich	>97	−21.86	0.19	6

[a] All samples were dissolved in 0.3 N HNO_3 except the 0.3 N HCl test. MS refers to samples purified by micro-sublimation.
[b] Data with exact values were quantified by isotope dilution using NBS SRM 952. Others were semi-quantified by comparing the instrumental observed intensity to the bracket standards (expected concentration are referred to the dilution factor from the weighing data).
[c] Uncertainty used here denotes the standard corresponding deviation (σData) as $\sigma^2_{Data} = \sigma^2_{MassSpec} + \sigma^2_{Sample}$.
[d] Using the same dataset.
[e] The JCp-1 samples were dissolved in 0.3 N HCl test.
[f] Coral skeletons were pre-cleaned by 10% NaOCl and 0.0075 N HNO_3 before B extraction and purification.

further decreased (i.e., <8 pg) when applied the micro-sublimation purification.

Although it has been proposed that interference from Ar^{4+} occurs with $^{10}B^{+}$ ion with both ICP-MS and MC-ICP-MS measurements [19,24,25], the ionization potential of Ar^{4+} (5770 kJ mol^{-1}) is much higher than the ionization potential of Ar^{+} (1520 kJ mol^{-1}). Alternatively, Ne^{2+} might be a possible candidate for interference because of its lower ionization potential (i.e., 3952 kJ mol^{-1}) than of Ar^{4+}, affecting both ^{10}B and ^{11}B (by $^{20}Ne^{2+}$ and $^{22}Ne^{2+}$, respectively). In this study, approximately 3 V for $^{20}Ne^{+}$ and 10 mV for $^{21}Ne^{+}$ were associated with a peak of about 20 mV at $m/z = 9.988$ when H_2O was injected. The peak slightly overlapped with ^{10}B and was, therefore, recognized as $^{20}Ne^{2+}$, constituting about 0.6% of $^{20}Ne^{+}$ under a RF power of 1250 W. The interference can be reduced to half by lowering the RF to 1200 W without changing the sensitivity for B measurements. Fortunately, the peak plateau of $^{10}B^{+}$ and the $^{11}B/^{10}B$ ratio were not affected using low resolution mode compared to medium resolution. To obtain higher signal intensity, low resolution mode was used for all B isotopic measurements in this study.

3.2. Mass bias correction in MC-ICP-MS analysis

One of the problems of isotopic measurement by MC-ICP-MS is the mass bias effect, which is particularly important for light nuclides such as Li and B. Despite the high precision obtained in this study, our results for NBS SRM 951 had an average $^{11}B/^{10}B$ ratio of 4.7, which generated a $\delta^{11}B$ of about +162‰ regardless of background subtraction (using the certified $^{11}B/^{10}B$ of 4.0436 [26]). This results was, more than 2.4‰ by P-TIMS and −8.2‰ by N-TIMS (using lab-certified value of 4.0528 and 4.010, respectively) but consistent with previous measurements using MC-ICP-MS [20,27]. Some possible factors affecting mass bias in ICP-MS were evaluated by Andrén et al. [28,29], who provided direct evidence of isotopic discrimination mainly due to supersonic expansion of the ion beam taking place at the interface region. Although the mass bias effect remains relatively constant over considerable period of time in our instrument, the correction must be applied in order to increase precision. The correction is generally done using a SSB approach. To test its feasibility, JABA was used for comparison with the P-TIMS certified value. Based on the MC-ICP-MS results, the $\delta^{11}B$ of JABA was 10.52 ± 0.36‰, which is in good agreement with the results from P-TIMS analysis (10.53 ± 0.29‰, No. 14 in [18]). In contrast, during one full day of analyses, slight drift was found without any systematic difference between measurements of a synthetic B solution having $\delta^{11}B = 25.3$‰ which was bracketed by NBS SRM 951. This probably resulted from changes in plasma condition, which may have disturbed the optimal gas flow rate (Fig. 1a and b). In this study, a 'pseudo internal' correction using Li was examined in order to minimize the mass discrimination artifact (30 μg L^{-1} Li, 50 μg L^{-1} B). This approach involved the spiking of the analyte with another non-isobaric element of the same mass range, and has been demonstrated elsewhere for Pb–Tl [30], Cu–Zn [31] and Ag–Cd [32] isotope ratio measurements. Due to difference in the first ionization potential of Li (520.2 kJ mol^{-1}) and B (800.6 kJ mol^{-1}), the optimum analytical gas flow differs between Li and B (Fig. 2a). However, the instrumental mass bias using MC-ICP-MS for determining $^{11}B/^{10}B$ can be corrected by accounting for the constant mass discrimination for Li using the following the equations:

$$\left(\frac{^{7}Li}{^{6}Li}\right)_{true} = \left(\frac{^{7}Li}{^{6}Li}\right)_{measured} \times \left(\frac{M_7}{M_6}\right)^{\beta(Li)} \quad (3)$$

$$\left(\frac{^{11}B}{^{10}B}\right)_{true} = \left(\frac{^{11}B}{^{10}B}\right)_{measured} \times \left(\frac{M_{11}}{M_{10}}\right)^{\beta(Li)} \quad (4)$$

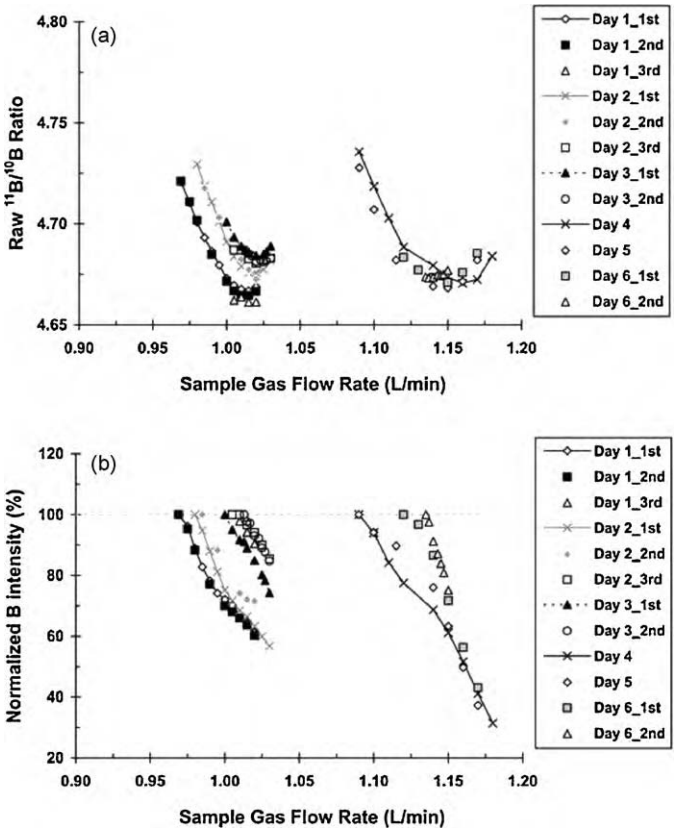

Fig. 1. Plots show effect of sample gas flow rate on (a) NBS SRM 951 $^{11}B/^{10}B$ isotopic ratio, and (b) normalized ^{11}B intensity (normalized by the highest signal). Two 50 μL min^{-1} PFA micro-concentric nebulizers were used spanning from Day 1 to Day 3 (nebulizer A) and from Day 4 to Day 6 (nebulizer B). The optimization of gas flow rate for stable B measurements may generally reduce B intensity approximately 40%. Each second and third gas tuning represents approximately 5 and 10 h after the first tune, respectively.

The lithium isotopic reference LSVEC ($^{7}Li/^{6}Li = 12.1752$) was used to obtain the mass bias factor β(Li). Considering the gas flow rate in Fig. 2b, a long-term average $^{11}B/^{10}B$ ratio for NBS SRM 951 was 4.0520 ± 0.0029, matching closely with the P-TIMS value. The obtained precision of 0.7‰ is larger than the SSB method due to the instrumental mass bias between Li and B is varying within time. This, however, can be further improved to 0.16‰ by normalizing the NBS SRM 915 to the first measurement of each day. With double sample throughput and negligible matrix effect, an external precision of −5.61 ± 0.37‰ (2SD) was achieved using a high-purity B solution (Alfa Aesar), similar to the value calculated using the SSB technique (−5.58 ± 0.31‰), from the same data set. As a result, the results of the Li-doping experiment support the effectiveness of the 'pseudo internal' correction. However, to obtain reliable data, at least one standard other than NBS SRM 951 is strongly recommended for monitoring instrumental performance, applying either the SSB or 'pseudo internal' correction.

3.3. Micro-sublimation test

3.3.1. Working duration and yield

Gaillardet et al. [16] suggested a sublimation interval within 12–14 h at 70 °C. Considering the temperature gradient between the hotplate and the PFA vial, a higher hotplate temperature was conducted in this study. With a well controlled heating facility under higher temperature (98 °C), an interval of 6 h was tested. However, approximately 0.7‰ deviations were observed in both HNO_3 and HCl sets (Table 3), suggesting that the heavier stable

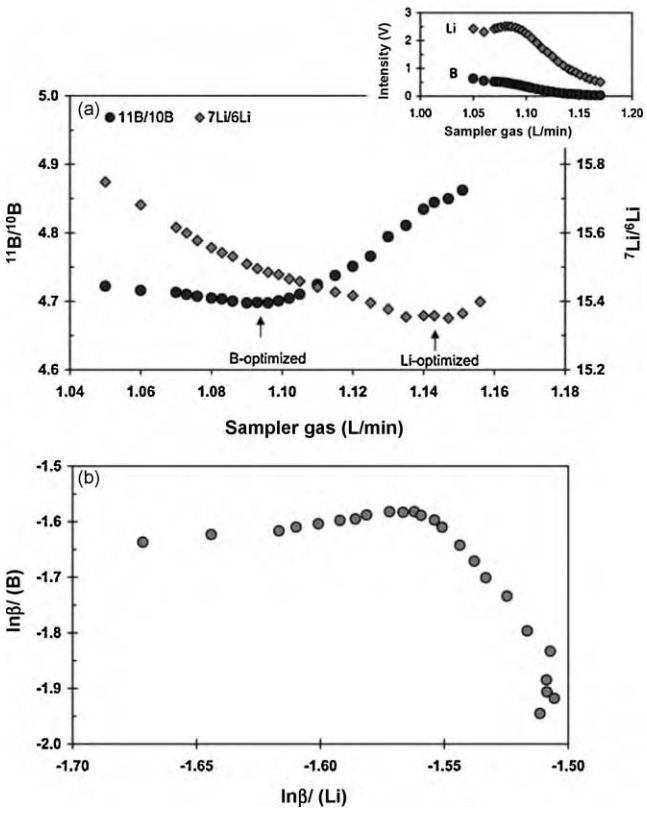

Fig. 2. Plots show the effect of gas flow rate on Li and B isotope ratios. (a) The optimized flow rates for B and Li isotope are different, elucidating that the space-charge effect on these two elements are different. (b) Gas flow tuning for 'pseudo internal' normalization. In this case, the operational gas flow rate was fixed at 1.093 L min^{-1} for both B and Li isotope measurements.

isotope ^{11}B is preferentially enriched in the sublimated drop. The isotope ratios remained rather constant when extending the sublimation time to 18 h. Therefore, the standard sublimation time was fixed at 12 h.

At B concentrations less than 0.025 M, no polymeric species such as $B_3O_3(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$ are formed. Therefore, $B(OH)_3$ is assumed to be the only viable species in aqueous solutions at low pH. Under this condition, no isotopic fractionation of B would occur during complete transformation from liquid to gas phase. However, the formation of borate complexes with cations still needs to be evaluated critically. The effect of salt content on B recovery yield was examined as shown in Table 3. No significant B loss or B isotopic fractionation was observed in the presence of Na ranging from 100 to 5000 mg L^{-1} and Ca from 500 to 8000 mg L^{-1}. In spite of a small portion of B (about 5%) expected to be suppressed during 'micro-sublimation' at a Na level of 10,000 μg L^{-1}, the isotopic composition of sublimated drop remained at constant. Considering the isotopic results from the JCp-1 experiment by dissolving 3 mg powders of each specimen (Table 3), the concentration of the Ca matrix can be as high as 24,000 μg L^{-1}. Based upon the complete yield under salt matrix, reference groundwaters IAEA-B-2 and IAEA-B-3 were repeatedly tested and the results were 13.86 ± 0.25‰ (n = 6) and −21.26 ± 0.19‰ (n = 6) (Table 3), consistent with previous certification [33].

3.3.2. Effect of pH

Boron is present as boric acid in aqueous solution at low pH, whereas at high pH, boron exists predominately in the form of borate. By changing pH of the drop before sublimation, we found that $\delta^{11}B$ is approximately 0.7‰ heavier ($P < 0.005$, t-test) at neutral pH than at pH <2 (Table 3, Fig. 3a). At pH 12, the $\delta^{11}B$ of sublimated samples increased to an average value of ~43‰, nearly 19‰ heavier than the bulk B isotopic composition. These effects can be attributed to the preferential sublimation of the different forms. We compared the empirical and theoretically derived pH using the following equations [34]:

$$[H^+] = K_B \times \frac{[B(OH)_3]}{[B(OH)_4^-]} \quad (5)$$

$$\varepsilon_B = \left(\frac{R_{B(OH)_3}}{R_{B(OH)_4^-}} - 1 \right) \times 10^3 = (\alpha_B - 1) \times 10^3 \quad (6)$$

$$\delta^{11}B_{B(OH)_4^-} = \frac{\delta^{11}B_T \cdot B_T - \varepsilon_B \cdot [B(OH)_3]}{[B(OH)_4^-] + \alpha_B \cdot [B(OH)_3]} \approx \delta^{11}B_T - \varepsilon_B \cdot \frac{[B(OH)_3]}{B_T} \quad (7)$$

$$\delta^{11}B_{B(OH)_3} = \delta^{11}B_{B(OH)_4^-} + \varepsilon_B \quad (8)$$

Here a pK_B value of 9.2 was used, resulting in a K_B of 6.31 × 10^{-10}. R is the isotope ratio of the corresponding boron species, and the isotope fractionation factor α of 1.027 [35,36] was used. Using Eqs. (6)–(8) the fractionation coefficient ε_B and the $\delta^{11}B$ of boric acid and

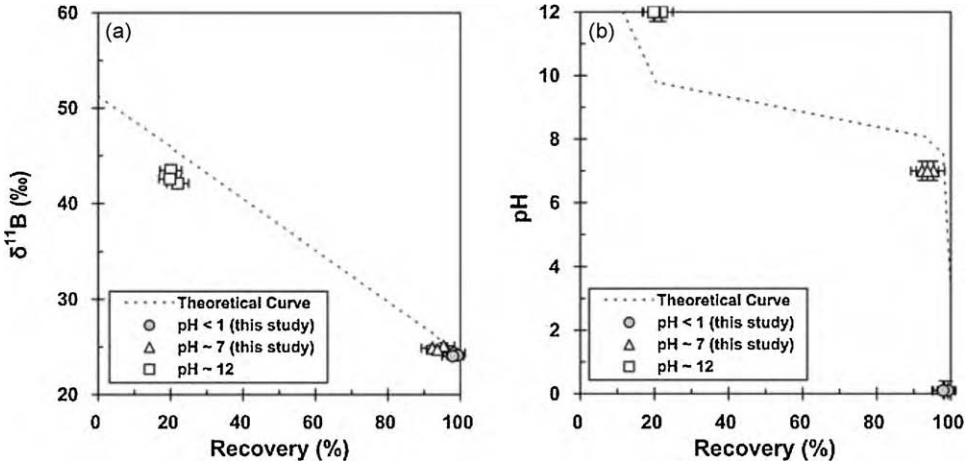

Fig. 3. B-isotopic composition of dissolved coral JCp-1 reference standard after micro-sublimation followed by treatment at three different pH. (a) B-isotopic ratios are reported in per mil relative to NBS SRM 951 and are plotted with respect to the original solution pH. Recovery is calculated by substituting into the calibration equation. Each X error bar shows quantitative uncertainty, while Y error bar represents the external precision 0.3‰ (2SD) derived by replicate analyses on MC-ICP-MS. The dotted line is the theoretical $\delta^{11}B$ calculated adopting fractionation factor α = 1.027 [35]; (b) By comparison with the theoretical curve, distribution of the empirical $\delta^{11}B$ under different pH conditions supports the assumption of preferential sublimation of $B(OH)_3$.

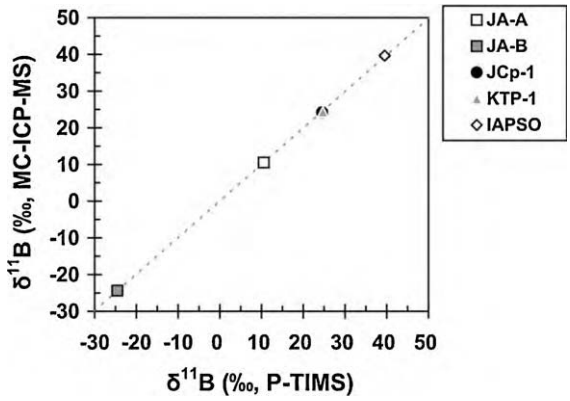

Fig. 4. Comparison of isotopic compositions of JABA (open square), JABB (grey square), GSJ JCp-1 standard (black circle), in-house KTP-1 (grey triangle), and IAPSO seawater (open diamond) determined by MC-ICP-MS and P-TIMS. Dash line represents a slope of 1. Note that δ^{11}B value of IAPSO is adopted from Spivack and Edmond [23]. Plotted are data of samples purified by micro-sublimation for 12 h. All analytical error bars (2SD) are within symbol size.

borate can be derived. A plot of pH versus the chemical yield, interestingly, shows good agreement between the experimental results and the theoretical calculations (Fig. 3b). These results show that solution pH is likely a key factor affecting the recovery of boron and thus absolute isotope ratio, which must be borne in mind when using this separation technique.

3.4. MC-ICP-MS and TIMS cross-calibration

Since mass bias and space-charge effects in MC-ICP-MS may deteriorate analytical results samples were cross-checked using P-TIMS analysis to confirm the accuracy. Several samples including high-purity B solutions, JABA and JABB, and two coral powders, JCp-1 and KTP-1, were analyzed by MC-ICP-MS and the results were compared to the TIMS results. The results from MC-ICP-MS showed δ^{11}B values of 10.52 ± 0.36 and -24.36 ± 0.20‰ for JABA and JABB, respectively (Fig. 4), and agreed well with our previous TIMS measurements (No.14 in [18]) and with results from MC-ICP-MS [19] (also No. 3 in [18]). Similarly, the isotopic ratios for coral specimens JCp-1 and KTP-1 are 24.22 ± 0.28‰ and 24.34 ± 0.51‰, respectively, using MC-ICP-MS, within uncertainties of TIMS measurements (24.52 ± 0.36‰ and 24.68 ± 0.48‰) (Fig. 4). It is also interesting to note that the δ^{11}B of the two coral samples corresponded to seawater pH value of ~8.2, agreeing with modern field data. The preliminarily test for the IAPSO seawater (Table 3) was also in good agreement with previous results reported by Spivack and Edmond [23]. It is worthwhile to point out that under conditions with extremely high Na concentration (e.g., brine) formation of sodium borate may suppress the sublimation efficiency and cause considerable B isotopic fractionation. In that case, it is recommended to dilute the sample appropriately before sublimation. In this preliminary test, the use of a X-skimmer cone in the MC-ICP-MS results in an increase in sensitivity threefold higher than with a H-skimmer cone, reducing the sample amount to 10–15 ng, nearly 20% of the P-TIMS sample-size requirement.

Finally, a simple comparison of B isotope homogeneity of the reference coral JCp-1 revealed no visible B isotopic difference with size between 50 and 100 mg, though the values are scattered by when the amount is reduced to 40 mg (Table 3). A sample size greater than 100 mg is thus suggested for inter-laboratory comparison experiment.

4. Conclusions

The method presented here allows for quantitative purification of B (10–50 ng) from complex Ca- and Na-rich matrices, and high precision B isotopic analysis in natural and synthetic samples. In combination with the improved 'micro-sublimation' technique, a high chemical yield can be achieved with additional advantages of less procedural blank (~8 pg) and easy operation. Based upon our experiments, the micro-sublimation technique can accommodate matrices containing more than 24,000 $\mu g\,L^{-1}$ Ca and at least 5000 $\mu g\,L^{-1}$ Na without detectable loss of B. Moreover, samples sublimed in either HNO_3 or HCl did not affect B recovery, which should be beneficial to both TIMS and MC-ICP-MS. Reference seawater IAPSO, groundwaters IAEA-B-2 and IAEA-B-3 had δ^{11}B values of 39.64 ± 0.42, 13.86 ± 0.25 and -21.26 ± 0.19‰, respectively, consistent with previous results. The δ^{11}B of Ca-rich coral JCp-1 and an in-house KTP-1 were certified as 24.22 ± 0.28 and 24.34 ± 0.51‰, respectively, which recorded faithfully the present seawater pH. By means of the new purification method associated with its high performance and high throughput of MC-ICP-MS, accurate B isotope analysis for natural waters and low-B marine biogenic carbonates such as foraminifera and fish otoliths can also be achieved, thus advancing applications in source tracing, paleo-pH reconstruction and biochemical studies.

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