A rapid, simple, and low-blank pumped ion-exchange column chromatography technique for boron purification from carbonate and seawater matrices

Chen Xu[1*], Hana Jurikova[1], Sophie Nuber[1,2,3], Robert C.J. Steele[1], Molly Trudgill[1,4], Stephen Barker[2], Caroline H. Lear[2], Andrea Burke[1], and James Rae[1]

[1] School of Earth and Environmental Sciences, University of St Andrews, St Andrews, UK.

[2] School of Earth and Environmental Sciences, Cardiff University, Cardiff, UK.

[3] Department of Geosciences, National Taiwan University, Taipei, Taiwan.

[4] Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, France.

Corresponding author: Chen Xu (cx23@st-andrews.ac.uk)

Key Points:

- A new peristaltic pump-based boron ion-exchange column chromatography, achieving 8-fold faster boron separation.
- This technique produces lower total procedure boron blanks than gravity columns.

Abstract

Boron isotopes ratios ($\delta^{11}B$) are used across the Earth Sciences and are increasing analysed by Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS). Accurate $\delta^{11}B$ MC-ICPMS analysis requires boron purification from the sample matrix using ion-exchange column chromatography. However, the traditional gravity-drip column method is time-consuming and prone to airborne contamination due to the long duration and open resin surface. To address these issues, we designed a novel, simple and reliable column chromatography technique called "peri-columns". This method uses a peristaltic pump to generate vacuum on a commonly used column set up. This method uses sealed collection beakers and does not require solutions to pass through pump tubing, minimising contamination. The duration is reduced by eight-fold, processing 12 samples in just 1.5 hours. It also yields low and consistent total procedural blanks (TPBs), averaging 11 pg. The efficiency and efficacy of this method were tested by repeated boron purification from calcium carbonate and high-sodium matrices with international and in-house reference materials (RM). The results matched those obtained with the gravity column method and fell within our laboratorial long-term and international certified values. The mean $\delta^{11}B$ and 2SD (standard deviation) of repeatedly processed NIST 8301f was 14.57 ± 0.26 ‰ (n = 31), NIST 8301c was 24.19 ± 0.33 ‰ (n = 10), STAiG-F1 was 16.20 ± 0.26 ‰ (n = 13) and seawater was 39.52 ± 0.32 ‰ (n = 10). All the components of our techniques are commercially available, and it is easily adaptable to other laboratories and isotope systems.

Plain Language Summary

Scientists use boron isotope ratios to study changes in seawater acidity, atmospheric carbon dioxide levels, pollution, and volatile cycling in the Earth. To measure these changes, they need

to purify boron from a carbonate matrix, such as foraminifera and coral fossils, or seawater, using ion-exchange column chromatography. However, the traditional gravity-drip column method is time-consuming and prone to airborne contamination. To address this issue, we developed a new technique called "peri-columns", where we connect manufactured columns to a peristaltic pump. The pump creates a vacuum, which pulls the liquid through columns faster than gravity. This new method is around eight times faster than the existing gravity method and, due to the shorter timescale and the closed nature of the columns, produces lower levels of contamination. We tested this technique using several international and in-house reference materials and found that it produced the same boron isotope ratios results as the traditional method, but faster and cleaner.

1 Introduction

Boron is significantly fractionated in nature, due to the large mass difference between B isotopes and high geochemical reactivity. This has made it an invaluable tracer of processes ranging from subduction (De Hoog & Savov, 2018; Regier et al., 2023), paleoenvironmental changes in loess–paleosol sequences (Wei et al., 2015), weathering (Ercolani et al., 2019; Muttik et al., 2011), and waste water (Kloppmann et al., 2008). Boron isotopes are also a key tracer in paleoclimate and paleoceanography studies, due to their ability to record oceanic pH and the subsequent determination of oceanic and atmospheric CO_2 (Dai et al., 2022; Foster, 2008; Honisch et al., 2009; Jurikova et al., 2020; Rae et al., 2018; Shankle et al., 2021; Shao et al., 2019).

Over the last 15 years, boron isotope measurements have been increasingly analysed by multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) (Foster, 2008; Foster et al., 2013; Gutjahr et al., 2021; Rae et al., 2018; Stewart et al., 2021). For accurate solution-based MC-ICPMS analysis, boron purification is required to minimise the impact of matrix effects and isobaric interferences from the sample matrix (Chen et al., 2016; Foster et al., 2013; Foster et al., 2018; Gutjahr et al., 2021; Lemarchand et al., 2002; Stewart et al., 2021).

Currently, most commonly used methods for boron purification are based on ion exchange, gravity column chromatography (Foster, 2008; Foster et al., 2013; Gutjahr et al., 2021; Stewart et al., 2021), and to a lesser extent microsublimation (Buisson et al., 2021; Misra et al., 2014; Rodríguez-Díaz et al., 2024), batch method (Douville et al., 2010; Lécuyer et al., 2002), and pumped chromatography systems (de la Vega et al., 2020; Wei et al., 2014). The benefit of traditional ion exchange gravity column chromatography techniques lies in the generation of accurate and precise boron isotope data (Gutjahr et al., 2021; Stewart et al., 2021). However, they rely on time-consuming and labour-intensive operation of hand-made gravity columns, with several methodological drawbacks.

Firstly, due to the geometry and small size of hand-made microcolumns, drip rates are slow, and so the process of gravity column chromatography is very time-consuming (~6 - 12 hrs for 12 samples, depending on specifics of column performance and lab temperature). Minimising blank contamination and isotopic fractionation is crucial to obtain accurate boron isotope data (Kubota et al., 2021). While blank contributions from labware and reagents can be relatively easily minimised, for B, the major source of contamination during column chromatography might be airborne (Kubota et al., 2021). The purification procedure is normally undertaken in a low-boron clean hood. However, the potential for fall-in blank from the operator’s sleeves and/or airborne boron flow into the hood by opening and closing the door, may cause random

contamination of the samples during a long operation procedure, which is hard to monitor and mitigate. As such, a shorter operation time should not only increase the lab efficiency but also minimise contamination and isotopic fractionation during the experiment.

Secondly, the flow rate of solutions through the traditional gravity columns maybe inconsistent, due to changes in hydrostatic head pressure and variations in geometry column to column. The Microcolumns are typically hand-made from heat shrinking PFA using a heat gun or oven. The manual demoulding process and hand fitting of the frit will inevitably cause some deformation of the neck, shoulders, and other delicate parts of the column, while hand-fitting of the frit may additionally cause closure of the frit pore space, reducing flow rates. These also cause each column to be individually shaped, rather than identical. These geometric differences may lead to inconsistency in the flow rate of solutions between the microcolumns, with the potential to influence the consistency of the matrix separation.

Thirdly, the efficient flow of the last regent droplet through the resin and frit is hindered by the liquid's surface tension when driven by gravity. This issue, known as the “last drop issue”, may result in inaccurate $\delta^{11}B$ values. Incomplete boron loading or recovery from the Amberlite IRA-743 resin is the leading cause of boron isotope fractionation during the boron purification (Lemarchand et al., 2002). Studies have shown that ^{11}B is more concentrated in the initial elution solution, while ^{10}B is more enriched at the tail (Lemarchand et al., 2002). A 1% loss of the boron at the end of elution can results in a 0.2 ‰ shift in $\delta^{11}B$ for the recovered solution (Lemarchand et al., 2002). Due to this “last drop issue”, achieving quantitative, complete, and efficient recovery of boron from samples can be challenging. Furthermore, it is crucial to maintain the consistent molarity of nitric acid between sample, standards and blanks in the subsequent MC-ICPMS. Inconsistencies can introduce a matrix effect to the instrument, leading to inaccurately measured $\delta^{11}B$ values (Chen et al., 2016; Trudgill, 2023). The presence of residual Milli-Q water in the resin after the matrix wash may lead to dilution of the nitric acid concentration for the subsequent boron elution, which can cause such a matrix effect.

Efforts have been made to optimise the issues addressed above. A novel design in which the microcolumns are directly connected to a peristaltic pump using peristaltic tubing has been developed (Wei et al., 2014). However, while suitable for some applications, the relatively large procedural blank (TPB) produced from this approach (~0.5 ng), perhaps a function of the direct contact of solutions with pump tubing, would be prohibitive for typical marine carbonate boron isotope sample sizes (~2-20ng). Recently, there have been attempts to optimise the boron purification for coral and seawater samples (de la Vega et al., 2020) using prepFAST Multi Collector (prepFAST) automation system. TPB yield from this method is below 60 pg. However, other marine carbonate matrices with lower boron contents, typical of foraminifera, are yet to be tested.

In this study, we developed a highly efficient and low blank peri-column chromatographic system. This system uses a peristaltic pump generated vacuum on commercially available Savillex microcolumns without direct contact with the peristaltic tubing. This method shortens the whole boron purification procedure to 1.5 hours for a batch of 12 samples, which enables the integration of sample purification and mass spectrometry in a single day, increasing lab efficiency. This method also shows notable consistency in column performance, due to the equally manufactured column components. Tests on a range of marine carbonate and seawater samples yield data that match literature values for a variety of RMs (Stewart et al., 2021; Trudgill, 2023), and show improved blank contamination control. In

addition, this novel method also enables highly efficient preparation of boron-free ammonium acetate buffer for boron purification. The simplicity and accessible nature of this configuration allows its application to a variety of laboratories and isotopic systems and simplifies the protocols for boron purification with a lower blank.

2 Materials and Methods

2.1 Materials

2.1.1 Standards and reference materials

We used 2ml Savillex Teflon microcolumns with a 5mm diameter capillary packed with 20 µl of crushed and sieved (mesh size 63-150 µm) Amberlite IRA-743 resin (Kiss, 1988) for boron purification. First, we tested the usability of these columns for boron purification using the standard gravity boron column procedure (see Foster et al., 2008). We then optimised the method and assessed the accuracy and reproducibility of $\delta^{11}B$ standard values via peri-column. We tested multiple standards and reference materials with varied matrix types and B/Ca ratios including NIST RM 8301 (Coral) (8301c), NIST RM 8301 (Foraminifera) (8301f) (Stewart et al., 2021), in-house mixed and natural foraminifera standard STAiG-F1, and open ocean seawater from Atlantic Ocean, each of which have been thoroughly characterised within the St Andrews Isotope Group (STAiG) (Trudgill, 2023). All sample preparations were undertaken in the STAiG boron-free clean laboratory at the University of St Andrews.

2.1.2 Buffer reagent

Quantitative absorption of boron from the acid-based sample onto IRA-743 resin can be achieved by raising the pH to 5.5 using a buffer such as ammonium hydroxide, sodium hydroxide, sodium acetate, or ammonium acetate can be added, as demonstrated by Dai et al., 2022; Foster, 2008; Jurikova et al., 2019, and Lemarchand et al., 2002. Marine biogenic carbonate samples, including foraminifera, corals, and brachiopods, are commonly used for boron isotope studies. However, these samples consist mainly of calcite and aragonite, which contain abundant matrix elements such as Ca, Na, and Mg. When the sample is in an alkaline condition, matrix elements can form hydroxide precipitates, which may incorporate boron from the solution, resulting in boron isotopic fractionation (Foster, 2008; Foster et al., 2013; Lemarchand et al., 2002). To prevent the precipitation of hydroxides before loading, the pH of the sample for column loading should be high enough to allow for the binding of boron onto the resin but low enough to avoid the formation of hydroxide precipitates. The buffer regent used in this study is pre-cleaned boron-free ~1.2 M ammonium acetate (de la Vega et al., 2020). This is made from a mixture of 1.4 M ammonium hydroxide and 1.2 M acetic acid. Carbonate samples were dissolved in 0.5 M HNO_3 with an additional 50-100 µl of ultra-pure water (Milli-Q, 18.2 MΩ•cm at 25°C) and then buffered to pH ≈ 5.5 with 1.5 times the volume of the 0.5 M HNO_3 using pre-cleaned boron-free ~1.2 M ammonium acetate. Cleaning of this buffer was also achieved using a peri-column (Table 1).

Table 1. Protocols of the preparation for the boron-free $NH_4CH_3CO_2$ buffer using peri-column described in this study. Note that a pump speed of 85 RPM corresponds to a flows rate of 100 µl/s.

Step	Purpose	Reagent	Pump speed (revolutions per minute)	Collection/Discard
1	Resin pre-clean	2 × 2000 µL 0.5M HNO_3	85	Discard
2	Condition	2 × 2000 µL Milli-Q water	85	Discard
3	Load uncleaned buffer	5 × 2 mL $NH_4CH_3CO_2$ buffer	85	Collect
4	Resin post-clean	2 × 2000 µL 0.5M HNO_3	85	Discard
5	Condition	2 × 2000 µL Milli-Q water	85	Discard

2.1.3 Peri-column chromatographic system setup

The peri-column system (Figure 1a and b) uses a Watson Marlow 205U/CA auto-control multi-channel cassette peristaltic pump with 16 tubing positions, Santoprene 2-stop peristaltic tubing (150 mm bridge, 2.29 mm inner diameter), 2ml Savillex Teflon microcolumns with 20µl of Amberlite IRA 743 resin, and 7 ml Savillex Teflon vials with openings in the lids drilled using a drill bit with a diameter of 3.5 mm to fit the peristaltic tubing and a 6.5 mm bit to seat the column itself (Figure 1c). By pumping out air from the vial headspace, a negative pressure gradient can be created between the vials and the supernatant solution above the resin bed. This allows for solutions to pass quickly and steadily through the resin in the columns without coming into contact with the tubing. To ensure airtightness and consistency of this closed system, customised 2ml Savillex Teflon microcolumns were used instead of the fragile hand-made columns.

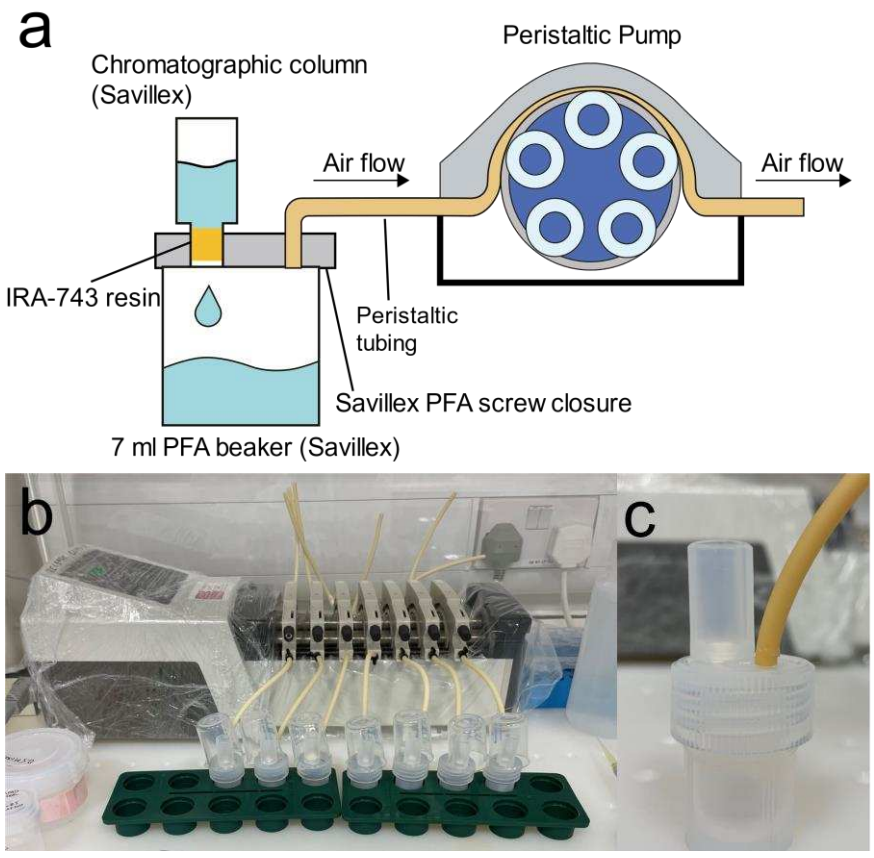

Figure 1. **a.** Schematic illustration of the peri-column system. **b.** Photo of our peri-column setup in the clean laboratory at STAiG. **c.** A close-up photo showing a chromatographic column and a peristaltic tubing fitted into the 7ml Savillex Teflon vial.

2.1.4 PFA vials and plastics

Two pre-cleaned 7ml Savillex Teflon vials per sample are required for collecting the separated boron and an extra elution 'tail'. To clean the vials, they were firstly filled with 7 M HNO_3 (reagent grade), capped, and left on a hot plate at 140 °C overnight, and then rinsed with Milli-Q water three times. Then, we used KimWipes to wipe the interior of the vials and lid with acetone to remove any organic residues, followed by triple rinsing with Milli-Q water. Next, they were placed in a Teflon jar filled with 7 M HNO_3 (reagent grade), left on a hot plate overnight, and again rinsed with Milli-Q water three times. The process was then repeated with 6 M HCl (reagent grade). One day before the column chromatography, the Teflon vials were filled with 1.5 M HNO_3 (distilled grade) and left on a hot plate overnight. They were rinsed with Milli-Q water three times and dried in a boron-free clean hood.

Samples were analysed in 2 ml pre-cleaned Eppendorf centrifuge tubes per sample, which fit directly into the CETAC ASX-100 Micro Autosampler. To prepare the centrifuge tubes, we submerged them into a plastic jar filled with 1 M HCl (distilled grade) and placed them on a hot plate at 60 °C overnight. Tubes were then rinsed with Milli-Q water three times and dried in a clean hood. Before the column chromatography, we rinsed the tubes with 1.5 M HNO_3 (distilled grade) once and Milli-Q water three times using a wash bottle.

The freshly drilled lids of the 7 mL Savillex Teflon vials were first smoothed with sandpaper and intensely rinsed with Milli-Q water until no visible residue remained attached. The surface and holes were then physically cleaned using acetone on a lab wipe. Subsequently, the lids were cleaned following the same procedure as the centrifuge tubes. The used 1 M HCl (distilled grade) solution was discarded. After that, the lids underwent additional cleaning via the aforementioned 7 M HNO_3 (reagent grade) and 6 M HCl (reagent grade) bath procedure that is used for the Teflon vials. They were then rinsed with 1.5 M HNO_3 (distilled grade) applied via wash bottle, followed by triple Milli-Q water rinses.

Because the duration of the peri-column procedure is short and drilled lids do not make direct contact with reagents or samples, stringent cleaning between uses, as done for the Teflon vials used to catch eluates, is not essential for lids. After each use with the peri-column, the lids should be wiped with acetone and Milli-Q water and stored in cleaned plastic bag. Before the next usage, the lids were cleaned following the aforementioned centrifuge tube cleaning procedure.

2.2 Gravity column chromatography for boron purification

The columns were firstly cleaned by multiple rinse of 0.5 M HNO_3 and Milli-Q water to remove any potential residues of boron and matrix elements. Subsequently, the sample-buffer mixtures were slowly pipetted dropwise into the columns to allow the boron within the solution to be better captured by the boron-specific resin and to avoid disturbance of the resin bed. The maximum volume pipetted in during sample loading is 200 µl; any larger sample-buffer volumes were loaded in multiple applications. To wash out the matrix elements, the columns underwent eleven rinses with 150 µl of Milli-Q water. This was followed by carefully pipetting 100 µl of 0.5 M HNO_3 through the columns to elute the boron bound to the resin. To ensure complete

boron recovery, and sufficient volume for MC-ICPMS analysis, 600 µl of 0.5 M HNO_3 was used, meaning this step is repeated 6 times. The actual volume of eluant acid can be adjusted depending on the carbonate sample size, mass spectrometry method, and resin performance varying across different labs by checking the column calibration. To confirm the complete recovery of all the boron from the resin, an additional 100 µl of 0.5 M HNO_3 was passed through the column and collected, known as the "tail".

2.3 Operating procedures for the peri-column

The overall procedure for the peri-column follows a similar structure to the gravity approach, including column pre-wash, sample loading, matrix wash, elution, and column re-wash steps. However, it has been optimised to produce faster and more consistent results. Table 2 provides a detailed protocol. Once the reagent was pipetted into the peri-column, the peristaltic pump was activated with a pump speed of 85 revolutions per minute (RPM) to accelerate the flow. It is advised to maintain the pump speed below 85 RPM to prevent frit tilting and the associated resin leakage. The flow rate of peri-column is approximately 100 µl /s. The peristaltic pump should not be used to increase the flow rate during sample loading, as rapid flow can lead to incomplete boron capture by the resin and unwanted fractionation (Section 3.1).

To remove matrix elements in the sample, we performed 7 rinses using 500 µl of Milli-Q water, which is a reduced rinse number compared to gravity column method (11 steps with 150 µl). Following the completion of matrix wash, pre-cleaned 7ml Savillex Teflon vials were screwed onto the system to collect the eluted samples. A volume of 600 µl 0.5 M HNO_3 is sufficient to achieve over 99% boron recovery using the peri-column method. Similarly, another set of pre-cleaned 7ml Savillex Teflon vials was connected to the peri-column to collect the tail elution. After the tail elution was completed, the Teflon vials used for column wash were reconnected peri-column to clean and condition the resin for storage.

Table 2. Protocols of the boron separation using the peri-column approach described in this study.

Step	Purpose	Reagent	Pump speed (RPM)	Collection/Discard
1	Resin pre-clean	2 × 2000 µL 0.5M HNO_3	85	Discard
2	Condition	2 × 2000 µL Milli-Q water	85	Discard
3	Load sample	$NH_4CH_3CO_2$ - sample mixture	0	Discard
4	Matrix wash	7 × 500 µL Milli-Q water	85	Discard
5	Boron elution	5 or 6 × 100 µL 0.5M HNO_3	85	Collect
6	Tail elution	100 µL 0.5M HNO_3	85	Collect
7	Resin post-clean	2 × 2000 µL 0.5M HNO_3	85	Discard
8	Condition	2 × 2000 µL Milli-Q water	85	Discard

2.4 Mass spectrometry

Purified samples were transferred from 7ml Savillex Teflon vials into pre-cleaned 2 ml Eppendorf centrifuge tubes prior to analysis. 10 µl splits of each purified sample were extracted into another batch of 2 ml Eppendorf centrifuge tubes and diluted with 140 µl 0.5 M HNO_3. These samples were analysed for concentrations of B ([B]) and Na ([Na]), Mg ([Mg]), and Ca

([Ca]) to assess the effectiveness of matrix wash and boron recovery. This was done before conducting the $\delta^{11}B$ analysis by peak hopping on the MC-ICPMS.

Boron isotope analysis was performed on a Thermo Fisher Neptune Plus MC-ICPMS at STAiG using sample-standard bracketing (Foster, 2008; Foster et al., 2013; Rae et al., 2018; Rae et al., 2011). Prior to analysis, purified samples, blanks, and standards were spiked with concentrated HF to yield a solution of 0.5 M HNO_3-0.3 M HF. This spiking aimed at minimising boron evaporation, reducing background, facilitating boron wash out, and shortening the bracketing time (Misra et al., 2014; Rae et al., 2018; Zeebe & Rae, 2020). The same batch of distilled 0.5 M HNO_3 was used for sample elution, dilution of the bracketing standard NIST SRM 951, and preparation of instrumental blanks. This ensured accurate background correction via on-peak zeroing and consistent instrumental matrix effects. To monitor the accuracy and consistency of the analytical sequence, multiple measurements of Ca-free boric acid standards ERM-AE121 (Vogl et al., 2010) and BIGD (Foster et al., 2013) were taken and produced identical results. The propagated analytical error for $\delta^{11}B$ analysis for these 7.5ng boron samples, which yielded 12.5 ppb analytical solutions, was estimated over multiple analyses of 7.5-15ng boron at STAiG. This long term standard deviation (2σ) was <0.21 ‰ (Trudgill, 2023).

The matrix element and boron concentrations during the Milli-Q matrix removal steps were analysed on an Agilent 8900 QQQ-ICP-MS (QQQ) at STAiG, spiking the Milli-Q washes with concentrated HNO_3 to give a solution of 0.5 M HNO_3. The typical reproducibility for Ca, Mg, Na, Sr, Al, Mn and B was better than 3% 2RSD (relative standard deviation). Note that this trace element analysis was only performed to verify the reliability of the two column methods and is not part of the procedure for routine $\delta^{11}B$ analysis.

2.5 Pump speed test

To explore the shortest duration for the total procedure for a reliable peri-column method, we tested the fastest peristaltic pump speed at which reliable $\delta^{11}B$ values can be produced. Because both incomplete boron capture during sample loading and incomplete boron collection during elution can result in isotopic fractionation, testing accelerated flow rates in both stages is required to verify reproducibility. 90 RPM is the maximum speed for our peristaltic pump. We first tested $\delta^{11}B$ values of standard 8301f using the peristaltic pump at 90 RPM throughout all column chromatography steps. A second test turned off the pump, during sample loading only, but otherwise maintained 90 RPM.

High pump speeds might destabilise the frit in the column, thereby shortening the lifetime of the peri-column system. Observation of the position and flatness of the frit in the column is recommended after each use. If signs of frit instability are observed, the pump speed should be reduced until frit movement ceases. The optimal pump on/off sequence identified previously will then be re-examined to verify the suitability of this new pump speed.

3 Results and discussion

3.1 Pump speed

The total duration of the peri-column method was determined by the speed setting of the peristaltic pump. Our objective was to find the highest pump speed that would produce consistently good results. After testing multiple speeds, we discovered that continuously using the maximum pump speed of 90 RPM caused instability of the frit, leading to resin leakage from

the column. We therefore slowed down the peristaltic pump speed to 85 RPM as a compromise between procedural duration and frit stability.

Our additional tests show no fractionation for the accelerated elution step. However, using the peristaltic pump during the loading stage of the standard 8301f resulted in low and variable $\delta^{11}B$ values of 13.86 ± 0.91 ‰ (2 standard deviation (SD), n = 14) (Figure 4a), which is significantly offset from the certified values (Stewart et al., 2021) and STAiG long-term mean $\delta^{11}B$ value (14.61 ± 0.21 ‰, 2SD; between 2019-2023) (Trudgill, 2023). We attribute this to the incomplete boron capture in the resin caused by excessive pump speed during the sample loading stage. This is consistent with variable loss of isotopically-heavy boric acid during loading, with the fast transit speed preventing re-speciation to the borate form that absorbs to the resin (Lemarchand et al., 2002). To combat this, we suggest utilising gravity loading instead of peristaltic pump acceleration during the sample loading stage. At the optimal setting of gravity speed during loading, and 85 RPM during the remainder of the protocol, the purification protocol can be completed in 1.5 hours for 12 samples. This is 4.5-10.5 hours faster than the traditional approach.

3.2 Matrix element removal and boron recovery

Effective removal of matrix elements, such as Mg, Ca, and Na, is crucial in boron column chemistry to prevent impact of matrix effects and isobaric interferences in subsequent analysis on the MC-ICPMS (Foster et al., 2013; Foster et al., 2018; Gutjahr et al., 2021; Stewart et al., 2021). Therefore, any purification method aimed at analysing $\delta^{11}B$ must demonstrate effective removal of other matrix elements. Here we conduct a step-by-step examination of matrix elements in the wash with 8301f, using an aliquot with 7.5 ng B, 200 μg Ca, 318 ng Mg, and 351 ng Na. A persistent decrease in the concentration of each matrix element through each Milli-Q rinse is clearly observed (Figure 2c). Key matrix elements from the artificial foraminiferal $CaCO_3$ standard (e.g. Ca, Sr) fall to values indistinguishable from the instrumental background. Other elements including Mg, Na, Al and Mn stay slightly above background at the final wash but are lower than 1 ppb.

We evaluated the efficacy of matrix element removal for both the standard gravity method and the peri-column approach by analysing the [Na], [Mg], and [Ca] in the purified samples. We use reference materials 8301c, 8301f, and STAiG-F1 with 7.5 ng of boron in each loaded aliquot. Throughout our analyses, the concentrations of [Na], [Mg], and [Ca] in the purified samples were all below 0.1% of the amount loaded onto columns (Figure 2a and b). This indicates that both methods demonstrated similar and effective matrix element removal, consistent with the literature (Chen et al., 2016; de la Vega et al., 2020; Foster, 2008; Guerrot et al., 2011).

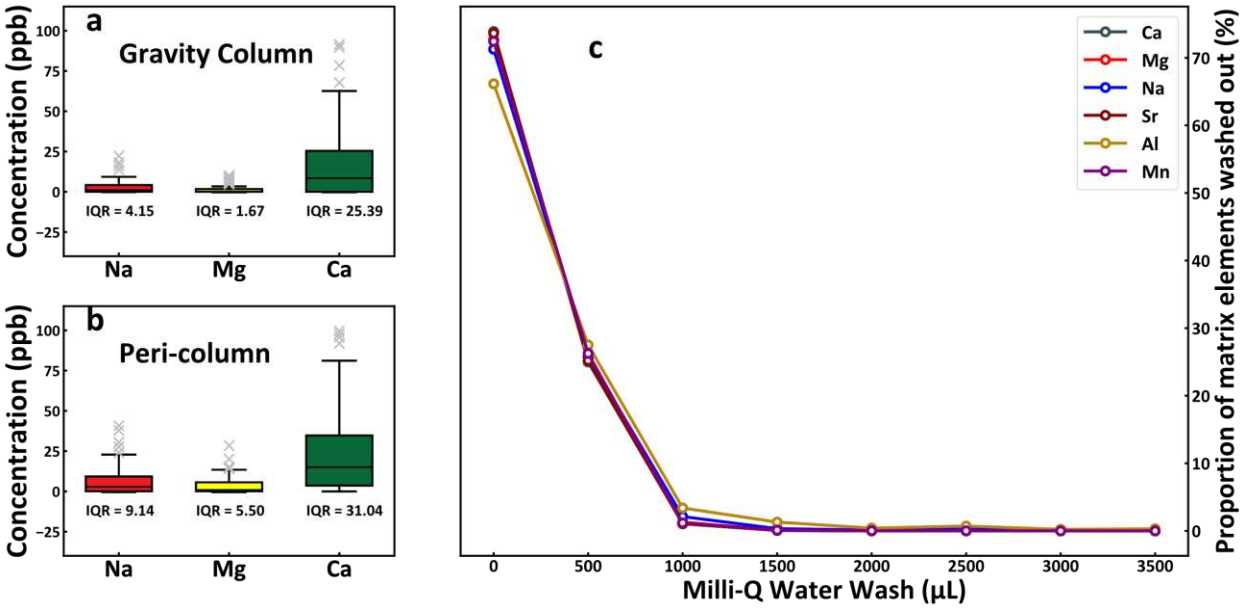

Figure 2. Box and whisker plot for the concentrations of matrix elements Na, Mg, and Ca in the aliquot of the final sample by gravity approach (**a**) and peri-column approach (**b**). Interquartile Ranges (IQR) are indicated blow each boxplot. Outliers are grey cross markers. **c**. Proportions of matrix elements washed out from each Milli-Q water rinse step using peri-column.

Accurate $\delta^{11}B$ analysis requires complete boron collection to prevent isotopic fractionation. [B] evolution curves for the peri-column approach indicates good boron recovery for 8301f with a 7.5 ng boron sample size (Figure 3). Boron in the most of wash steps was indistinguishable from background, so there is no major boron loss in the wash steps. Subsequent tails after 600 µl of 0.5 M HNO_3 elution contained less than 20 pg boron (<0.3% of the sample) (Figure 3), indicating complete elution of boron from the resin during the previous elution steps.

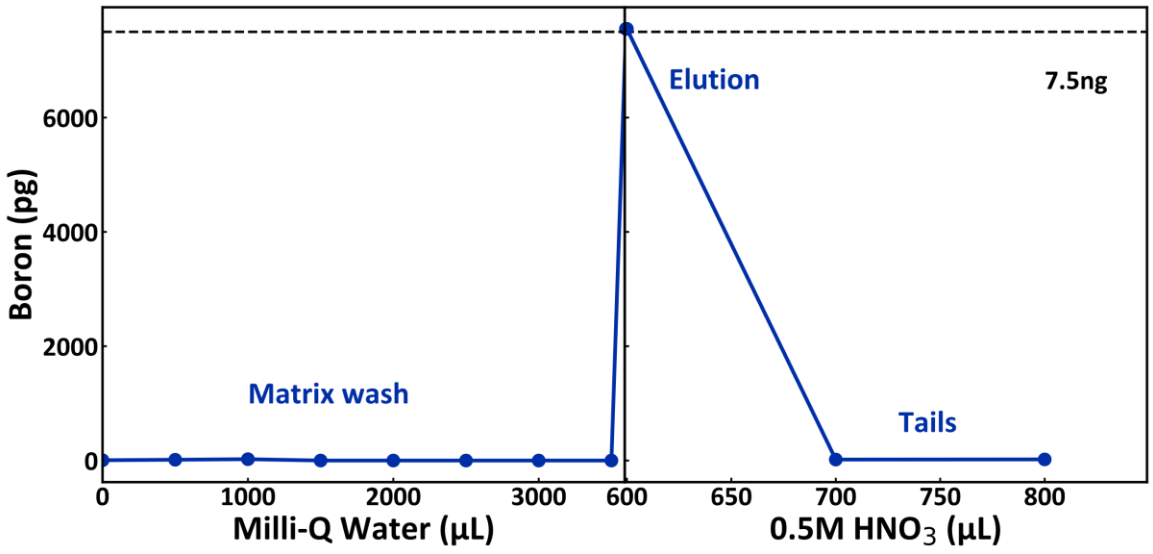

Figure 3. Boron evolution curve through matrix wash and elution from a 15ppb 8301f standard (7.5ng boron). The dashed line indicates 7.5 ng boron, the loaded mass.

3.3 Reproducibly and accuracy of $\delta^{11}B$ values from the peri-column chromatography

The mean $\delta^{11}B$ and 2SD for peri-column analyses of standards was 14.57 ± 0.26 ‰ (2SD) (n = 31) for 8301f, 24.19 ± 0.33 ‰ (2SD) (n = 10) for 8301c, 16.20 ± 0.26 ‰ (2SD) (n = 13) for STAiG-F1, and 39.52 ± 0.32 ‰ (2SD) (n = 10) for seawater (Figure 4). These results align with those generated using traditional gravity method with the same set of columns (Figure 4a and b) and fall within the range of the respective certified values (Stewart et al., 2021; Trudgill, 2023). Cross plots of $\delta^{11}B_{8301f}$ and $\delta^{11}B_{8301c}$ produced by the same Savillex columns via the traditional gravity method and peri-column approach show a negligible offset 0.06 ± 0.32 ‰ (2SD) (n = 10) for 8301f and -0.09 ± 0.19 ‰ (2SD) (n = 5) for 8301c (Figure 5a and b).

We note the hint of some subtle correlation, which may suggest minor systematic differences between columns, perhaps due to subtleties in frit positioning and geometry that influence the flow path through the resin or due to the resin itself, but any such effect is small. All in all, the evidence reviewed here supports that the peri-column method produces accurate and reproducible $\delta^{11}B$ data for foraminifera, coral, and seawater matrices, with no significant fractionation introduced.

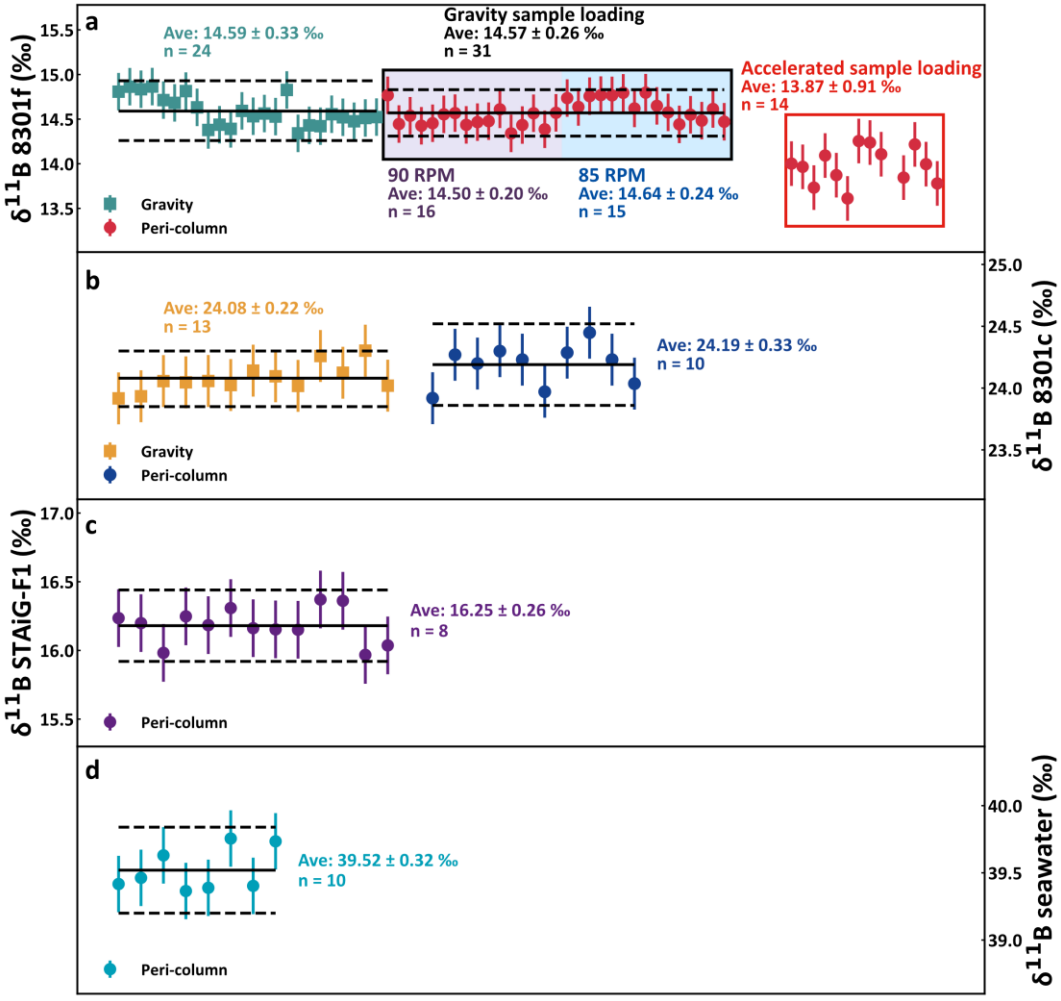

Figure 4. $\delta^{11}B$ values for 7.5 ng boron from reference materials 8301f (**a**), 8301c (**b**), STAiG-F1 (**c**), and seawater (**d**) processed on gravity columns and peri-columns. Solid line shows the average value and dashed line shows the 2SD. For panel **a**, results for 8301f by standard peri-

column approach are framed in black and shaded in violet and blue respectively for pump speed with 90 rpm and 85 rpm. The results for undertaking accelerated sample loading are framed in red.

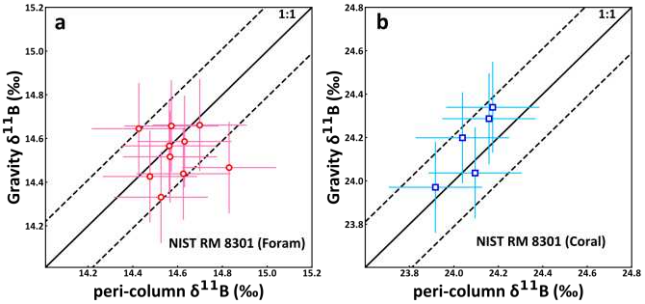

Figure 5 a, b. Cross-plots of δ^{11}B of 8301f and 8301c prepared by the same column but different boron separation approaches (traditional gravity method versus this peri-column method). 1:1 ratio line is shown by the solid line and long-term analytical reproducibility (0.21 ‰, 2σ) is shown by the dashed lines.

3.4. Total procedural blanks

We assessed TPBs for both protocols by examining Milli-Q Water, 0.5 M HNO_3, and 1.2 M $NH_4CH_3CO_2$ mixture with the same volume as our samples, through both the traditional gravity column and peri-column (Figure 6). TPBs obtained from the gravity method is 44 ± 70 pg of boron (n = 52). These values were comparable to the reported TPBs using the gravity column method by other research groups in the boron community (Dai et al., 2022; de la Vega et al., 2020; Douville et al., 2010; Foster, 2008; Henehan et al., 2013; Jurikova et al., 2020; Jurikova et al., 2019; Jurikova et al., 2023; Louvat et al., 2011; McCulloch et al., 2014; Rae et al., 2011; Shankle et al., 2021; Stewart et al., 2021) (Figure 6). In contrast, the peri-column yields TPBs of 11 ± 16 pg of boron (n = 33), which are less variable and smaller in size. These results are similar to those reported by de la Vega (2020) using prepFAST-MC (de la Vega et al., 2020) and substantially smaller than the previously designed peri-column method where solutions are in contact with the peristaltic pump tubing (Wei et al., 2014).

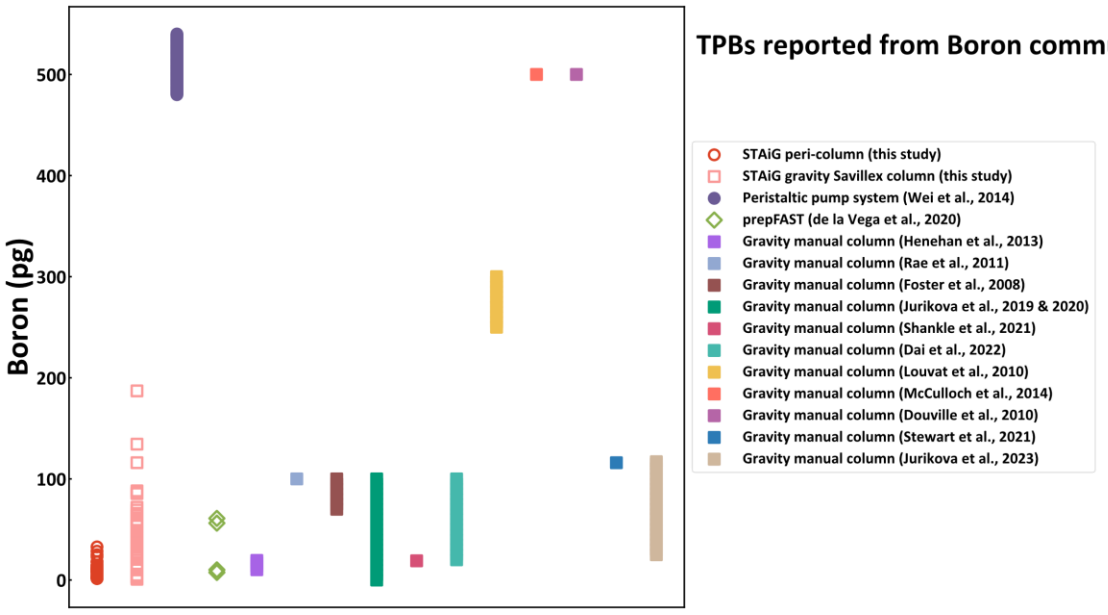

Figure 6. TPBs from peri-column (this study) in comparison to TPBs obtained from the newly published automatic prepFAST method at University of Southampton (de la Vega et al., 2020), old peristaltic pump system approach at Nanjing University (Wei et al., 2014), as well as the traditional gravity column method at University of St Andrews (this study), University of Southampton (Henehan et al., 2013), University of Bristol (Foster, 2008; Rae et al., 2011), GEOMAR (Jurikova et al., 2020; Jurikova et al., 2019), Yale University (Shankle et al., 2021), The Australian National University (Dai et al., 2022), Université Paris-Diderot (Louvat et al., 2011), The University of Western Australia (McCulloch et al., 2014), LSCE/IPSL (Douville et al., 2010), National Institute of Standards and Technology (Stewart et al., 2021), and GFZ – Helmholtz Centre Potsdam (Jurikova et al., 2023).

3.5 $NH_4CH_3CO_2$ buffer cleaning by peri-column

The cleanliness of peri-column cleaned $NH_4CH_3CO_2$ buffer was assessed by measuring the boron amount in TPBs and evaluating the accuracy of $\delta^{11}B$ for 8301f produced with buffers of different levels of cleanliness. The loadings for TPBs consisted of 50 µl of Milli-Q, 100 µl of 0.5 M HNO_3 plus 150 µl of ~1.2 M ammonium acetate buffer. The resulting boron concentration of TPBs produced using uncleaned buffer, peri-column cleaned buffer, and peri-column double cleaned buffer were 6.5, 5.4 and 4.0 pg of boron, respectively. The $\delta^{11}B$ values for 8301f generated from the aforementioned buffers were 14.71, 14.71, and 14.52, respectively, within ± 0.21 ‰ analytical error of the long-term lab mean (Trudgill, 2023).

These results show that the peri-column method effectively produces ammonium acetate buffer of desirable cleanliness levels. Note that the boron concentration of our unclean buffer is already minimal. Nonetheless, we still strongly recommend using cleaned buffer only, as cleanliness may vary between reagent batches and labs. Our method significantly enhances lab efficiency by producing 10 ml of cleaned buffer with a single column in just 10 minutes (Table 1).

3.6 Molarity effect

The use of the peri-column method for boron separation helps minimise the molarity effect on mass spectrometry. To ensure the most accurate $\delta^{11}B$ analysis on MC-ICPMS, it is crucial to use the same nitric acid used for sample elution for the standards and blanks in the analytical sequence. It has been observed that changing the molarity of nitric acid can introduce a strong matrix effect to the measured $\delta^{11}B$ values (Chen et al., 2016), especially for small sample sizes (Trudgill, 2023). For the column method, it is difficult for gravity to force the last elution droplet to flow quickly and efficiently through the resin and frit due to the liquid tension. This is called the “last drop issue”. Therefore, the residue of Milli-Q water in the resin after the matrix wash may dilute the concentration of nitric acid for boron elution, resulting in a matrix effect on MC-ICPMS. The liquid within peri-columns is driven by a pressure gradient, resulting in a faster and more complete flow compared to gravity column. No “last drop issue” was observed for peri-columns in this study.

3.7 Consistency and lab adaption

The consistency of peri-column performance is optimised by employing manufactured Savillex microcolumns. With their thick Teflon wall (~1 mm), these sturdy columns maintain a consistent shape, including during the frit placement. Drain times for 1.5 ml volumes under

gravity alone take 6-10 minutes per column with Savillex microcolumns. This is faster and less variable than equivalent hand-made columns. Any remaining variability is not attribute to the geometry of the Savillex column but inconsistencies in frit preparation and placement by hand.

In addition, Savillex microcolumns are securely fit into the Teflon vial screw caps and vacuumed by the high-speed peristaltic pump. When vacuumed at pump speed of 85 RPM, the columns drain 1.5 ml loads within 15 seconds. The strong and consistent pressure gradient from the pump normalises any variations between the columns and related setup, for instance, lid drilling, tubing connections, etc. Nonetheless, caution is advised when setting up this method and we recommend users check the maximum flow speed for their overall set up or with notably different column designs.

The accessibility of this store-based setup should expand the application of this technique to other laboratories by reducing the expertise and training required to make and operate columns.

Further studies exploring the application of our peri-column method to other isotope systems involving chromatographic column purification would be of great interest. Our method is easily adaptable to other chromatographic procedures and labs given its flexibility, low cost, cleanliness, and ease of operation. As solutions do not pass through the peristaltic tubing, this method allows for the use of more concentrated acids, which are commonly used in other procedures, without the risk of leaching any potential contamination to the samples or damaging the pump tubing.

4 Conclusions

Our new peri-column boron purification technique enables fast, reliable, and accurate boron purification for MC-ICPMS. The $\delta^{11}B$ of foraminifera, coral, and seawater reference materials match published values and our tests confirm efficient matrix element removal and complete boron recovery. 12 samples can be processed by this method in 1.5 hours, an 8-fold reduction compared to traditional gravity columns. Due to the closed nature of this setup and the shorter air exposure time, the TPB contamination during the boron purification was consecutively reduced to ~10 pg of boron, substantially lower and more reproducible than typical gravity column protocols. Additionally, using this peri-column system can efficiently produce boron-free ammonium acetate buffer, an essential reagent for boron column chromatography. The simplicity and automation of this setup can be used by a variety of laboratories, simplifies the purification of boron, and boosts lab efficiency, and would be easily applicable to other isotopic systems.

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Open Research

Data Availability Statement: Data generated in this study is included in the manuscript. A link to the St Andrews Research Repository where the complete dataset will be available when this manuscript is accepted.

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