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Evaluation of sample pretreatment methods for boron concentration analysis☆

Wei Wei [a,b,c,*], Thomas Algeo [a,c,d,e], Lin Chen [f], Zhiquan Li [b], Cody Lazowski [b], Katherine Snihur [b], Daniel Alessi [b], Kurt Konhauser [b]

[a] State Key Laboratory of Geomicrobiology and Environmental Changes (GMEC), School of Earth Sciences, China University of Geosciences-Wuhan, Wuhan, China
[b] Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB, Canada
[c] Department of Geosciences, University of Cincinnati, Cincinnati, OH 45221, USA
[d] State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences, Wuhan 430074, China
[e] State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Chengdu University of Technology, Chengdu 610059, China
[f] Wuhan Center of China Geological Survey, Wuhan 430205, Hubei, China

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ABSTRACT

Elemental boron (B) concentrations have been shown to be useful in reconstruction of paleosalinity conditions. Accurate measurement of the B content of a sample is critical for this purpose, but B is a light and relatively volatile element, substantial amounts of which can be lost through sample preparation protocols that fail to take this property of B into consideration. Here, we evaluate the effects of four commonly used sample preparation protocols on measured B concentrations. The Conventional Acid Method uses concentrated HNO_3 and HF, but the latter acid can cause volatilization of B. A second method, the modified Conventional Acid Method, uses the same acids but with the addition of H_3PO_4 to reduce B volatility. Two further methods eliminate HF entirely: the Ammonium Digestion Method makes use of NH_4F/NH_4HF_2, and the Alkali Fusion Method fuses the sample with Na_2O_2. We tested 9 samples and 4 standards using these four pretreatment methods. Our results show that the Alkali Fusion Method consistently has the highest B yields, with an average recovery rate of ~98 %, whereas the other methods have average yields ranging from 72 % to 92 %. Owing to the potential for incomplete B recovery using these other methods (especially the Conventional Acid Method, which has the lowest recovery rate), salinity values based on those methods are likely to be underestimated. Given the dominant use of the Conventional Acid Method in older studies reporting B concentrations, paleosalinity estimates based on those studies will require re-evaluation. In the future, we recommend that all studies measuring B concentrations make use of the Alkali Fusion Method in order to achieve near-quantitative recovery, and to provide for maximum robustness and comparability of paleosalinity estimates among studies.

1. Introduction

Elemental boron (B) concentration data play an important role in paleoenvironmental studies. The boron/gallium (B/Ga) proxy for analysis of depositional salinity in ancient shale facies was developed by Wei et al. (2018) and Wei and Algeo (2020), and it has now been applied in numerous studies (e.g., Remírez and Algeo, 2020; Cheng et al., 2021, 2023; Song et al., 2021; Wei et al., 2022; Gilleaudeau et al., 2023; Liu et al., 2024, 2025; Remírez et al., 2024, 2025a, 2025b; Sun et al., 2024; Wang et al., 2024). Recently, B concentration data (in the form of the "excess boron" proxy, B_{xs}) were shown to be useful for assessment of salinity in ancient carbonate facies by Wei et al. (2025), and its application to mixed-lithology (carbonate-shale) cyclothemic successions was demonstrated by Algeo et al. (2025). It should be noted that B concentration data have long been generated in the context of B isotope studies aimed at reconstruction of ancient seawater pH (e.g., Sanyal et al., 2001; Pagani et al., 2005; Noireaux et al., 2015), in which a complete extraction of B from the sample is a precondition for accurate B isotope analysis. Moreover, B is an essential element for plants and tends to accumulate in vegetable and animal tissues, making its concentration

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* Corresponding author at: State Key Laboratory of Geomicrobiology and Environmental Changes (GMEC), School of Earth Sciences, China University of Geosciences-Wuhan, Wuhan, China.

E-mail address: weiwei910911@163.com (W. Wei).

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in soil and food of interest to biologists and nutritionists (e.g., Banuelos and Akohoue, 1994; Bakirdere et al., 2010; Roux et al., 2015). Thus, accurate measurement of B concentrations in geological and biological materials is of concern in the broad natural science research community.

One problem encountered in boron concentration research is that a number of different sample pretreatment protocols are in use, depending on the laboratory conducting the analysis and the type of study being undertaken. When B is analyzed by ICP-MS as part of a larger suite of elements, conventional acid methods making use of a mixture of HF and HNO_3 are widely used to achieve complete sample digestion, but this approach almost invariably results in partial loss of B due to volatilization. Specifically, HF tends to cause significant volatilization of B to boron trifluoride (BF_3) (Liu et al., 2019), and some degree of acid volatilization is associated with HNO_3, $HClO_4$, and H_2SO_4 as well (Ishikawa and Nakamura, 1990; Nakamura et al., 1992; Katagiri et al., 2006; Misra et al., 2014). In paleosalinity research, B loss from a sample can lead to incorrect salinity facies interpretations, e.g., a marine sample might be inferred to have come from a brackish environment—an obviously undesirable outcome.

Various means of limiting B loss due to volatilization during sample preparation have been proposed. The closed-system microwave digestion method was designed to accelerate the digestion process by subjecting acidized samples to higher temperatures and pressures, but subsequent open-vessel drying can still lead to nonnegligible B loss as in conventional acid methods (Topper and Kotuby-Amacher, 1990; Araújo et al., 2002; Dai et al., 2014). For this reason, it is necessary to analyze an aliquot of each sample separately for B, making use of an optimized pretreatment protocol to limit or completely avoid B loss due to volatilization. In this context, various methods of sample digestion (Banuelos and Akohoue, 1994; Evans and Krähenbühl, 1994; Sah and Brown, 1997; Nyomora et al., 1997; Dai et al., 2014) and B measurement (Cai et al., 2023; Tan et al., 2023; Zhang et al., 2024) have been proposed. Notably, the B isotope community has developed the alkali fusion method (Cai et al., 2023) as well as the cation exchange method using a boron-specific resin to concentrate and purify sample B (Aggarwal and You, 2017; Zhang et al., 2024). These methods are reported to quantitatively extract B from a sample, yielding $\delta^{11}B$ measurements accurate to within 0.25 ‰ and 0.32 ‰, respectively. However, they involve special equipment and greater time and resource investment than is commonly expended in elemental studies.

With regard to studies utilizing B concentration data for paleosalinity research, several sample pretreatment protocols have been developed. The Wuhan Center laboratory (Wuhan Center of China Geological Survey, Wuhan 430205, Hubei, China) has modified the conventional acid method by addition of H_3PO_4 during sample digestion to suppress volatilization of B through its precipitation as BPO_4 (Thomas, 2008; Dai et al., 2014; Liu et al., 2024). Another method uses the alkaline agent NH_4F_2 to digest siliciclastic material, thereby avoiding production of the volatile H_3PO_4 compound (Zhang et al., 2012a; Magaldi et al., 2019; Liu et al., 2023). Lastly, samples can be fused at high temperatures with Na_2O_2 or NaOH as a flux agent, which also avoids use of acids prone to B volatilization (Gélinas et al., 1998; Cai et al., 2023; Lei et al., 2024). However, the relative efficacy of these various pretreatment protocols in suppressing or eliminating B loss remains unknown.

Here, we undertake a comparative study of four sample pretreatment protocols to assess their relative effectiveness in reducing B loss during sample preparation and, thus, at recovering the most robust paleosalinity signal possible. To test these pretreatment methods, we assembled a set of nine samples including black shales, gray shales, and marls, and we chose four standards with different B contents for analysis. We then pretreated each sample or standard using (1) the Conventional Acid Method (CAM; using a mixture of HF and HNO_3); (2) the modified Conventional Acid Method (CAM-P; with addition of H_3PO_4 to minimize B volatilization); (3) the Ammonium Digestion Method (ADM; using NH_4F/NH_4HF_2); and (4) the Alkali Fusion Method (AFM; based on fusion of the sample with Na_2O_2). All analytical work was undertaken in the Geobiology Laboratory of the University of Alberta (Department of Earth and Atmospheric Sciences, Earth Sciences Building, Edmonton, Alberta, T6G 2E3, Canada). The results of this study provide insights into the efficacy of different pretreatment protocols and how best to minimize boron loss due to volatilization in B concentration analysis.

2. Materials

Samples of several lithologies containing a wide range of boron concentrations were selected for testing in this study (Table 1). The black shale lithology is represented by Sample GX-84 from the Lower Triassic Daye Formation in South China (Lei et al., 2017; Wu et al., 2022); Sample Dupont-79.5 from the Upper Devonian Chattanooga Formation in Tennessee, USA (Over et al., 2019; Song et al., 2021), and Sample LJC-SJT-30 from the middle Cambrian Shuijintuo Formation in South China (Zhang et al., 2018; Shen et al., 2020). The gray shale lithology is represented by samples Chanute-321.5 and Chanute-326, which accumulated as nearshore shales in a broad epicontinental sea of Midcontinent North America during the Late Pennsylvanian (Heckel, 2013; Algeo et al., 2025). The marl lithology is represented by samples MM-117 from the Upper Ordovician Bull Fork Formation in eastern Kentucky (Brett et al., 2018; Liu et al., 2024) and ONNY-31, ONNY-32, and ONNY-33 from the Upper Ordovician Acton Scott Formation in Wales (Hannigan and Brookfield, 2013). Prior to analysis, all samples were ground with an agate mortar and pestle to a particle size of finer than 200 mesh (< 70 μm).

To track B recovery rates, we also analyzed four standards with established B concentrations, i.e., the Chinese national standards GSR-1 (24 ± 3 ppm; Xie et al., 1989; Guo et al., 2023), GSR-5 (154 ± 11 ppm; Xie et al., 1989), and GSR-6 (16 ± 4 ppm; Xie et al., 1989), and the internal laboratory standard STSD-3 (82 ppm ± 4; Lynch, 1990) (Table 1). GSR-5, which is a certified reference material representing a typical shale composition, and GSR-6, which is a carbonaceous shale with high carbonate content, were analyzed using all four pretreatment methods. The other two standards, GSR-1 (granite) and STSD-3 (fine-grained stream sediment), were analyzed using a subset of pretreatment protocols: GSR-1 by CAM and ADM, and STSD-3 by CAM.

3. Pretreatment protocols

3.1. *Conventional acid method*

The Conventional Acid Method (CAM) is the most commonly used pretreatment protocol for elemental analysis of shale and mudstone samples owing to its efficacy in dissolving siliciclastic material (Zhang et al., 2012b; Levi et al., 2018; Zhang and Hu, 2019). In detail, this procedure entails weighing about 50 mg of powdered sample into a Teflon bomb, moistening with a few drops of ultrapure water, followed by addition of 1 mL concentrated HNO_3 and 1 mL HF. The sealed bomb is heated at 190 °C in an oven for >48 h; after cooling, the bomb is opened and evaporated at 115 °C to incipient dryness for 2–3 h, followed by addition of 1 mL HNO_3 and evaporation again to incipient dryness. The resultant salt is redissolved by adding 3 mL of 30 % HNO_3 and resealed and heated in the bomb at 190 °C for >12 h. Finally, the concentrated solution is transferred to a polyethylene bottle and diluted to ~100 g (corresponding to a dilution factor of ~1:2000) using a 2 % HNO_3 solution prior to ICP-MS analysis. (Note: the acids and other reagents used in the present study were ultrapure laboratory-grade chemicals supplied by Thermo Scientific Chemicals.)

3.2. *Conventional acid method with H_3PO_4*

The Conventional Acid Method with H_3PO_4 (CAM-P) is identical to CAM except for the addition of 1 mL of H_3PO_4 to the samples prior to mixing with HF. The purpose of adding phosphoric acid is to reduce formation of the volatile compound BF_3 in the solution by precipitation

Table 1
Study samples.

Sample ID	Formation	Stage (Period)	Age (Ma)	Location	Lithology	References
GX-84	Daye	Induan (Lower Triassic)	250	Ganxi, China	Black shale	Lei et al. (2017); Wu et al. (2022)
Dupont 79.5	Chattanooga	Famennian (Upper Devon)	365	Western Tennessee	Black shale	Over et al. (2019); Song et al. (2021)
LJC-SJT-30	Shuijintuo	Stage 3 (middle Cambrian)	520	Hubei, China	Black shale	Zhang et al. (2018); Shen et al. (2020)
Chanute-321.5	Chanute	Missourian (Upper Penn)	305	Eastern Kansas	Gray shale	Heckel (2013); Algeo et al. (2025)
Chanute-326	Chanute	Missourian (Upper Penn)	305	Eastern Kansas	Gray shale	Heckel (2013); Algeo et al. (2025)
MM-117	Bull Fork	Katian (Upper Ordov)	450	Eastern Kentucky	Marl	Brett et al. (2018); Liu et al. (2024)
ONNY-31	Acton Scott	Caradoc (lower Up Ordov)	450	Onny Valley, Wales	Marl	Hannigan and Brookfield (2013)
ONNY-32	Acton Scott	Caradoc (lower Up Ordov)	450	Onny Valley, Wales	Marl	Hannigan and Brookfield (2013)
ONNY-33	Acton Scott	Caradoc (lower Up Ordov)	450	Onny Valley, Wales	Marl	Hannigan and Brookfield (2013)

of boron as BPO_4 (Hlaváček and Hlaváčková, 1989; Song et al., 2014).

3.3. Ammonium digestion method

The Ammonium Digestion Method (ADM) eliminates the acid HF, thus precluding formation of the volatile compound BF_3 (Zhang et al., 2012a). In detail, this procedure entails sequential weighing of 200 mg of NH_4HF_2 powder and 50 mg of sample powder (<74 μm) into a 7-mL screw-top PFA vial (Savillex, Eden Prairie, MN, USA). The vial is then capped and heated at 230 °C in an electric oven for 3 h (an electric oven provides more uniform heating than a hotplate). After cooling, 2 mL of HNO_3 is added, and the vial is capped and placed on a hotplate at 160 °C. After 1 h, the vial is opened and evaporated to near dryness at 160 °C on a hotplate, and the final residue is then dissolved in 1 mL of HNO_3, 1 mL of MQ water, and 1 mL of 1 $\mu g\ g^{-1}$ In internal standard solution. The vial is then recapped and heated at 120 °C for 6 h to obtain a clear solution, and the final solution is transferred to a polyethylene bottle and gravimetrically diluted with 2 % (*v*/*v*) HNO_3 to a total mass of 100 g. A reagent blank solution is simultaneously prepared for each group in the same way. The digestion parameters, including digestion temperature and time, amount of NH_4HF_2, and sample mass, can be adjusted to optimize the NH_4HF_2 – open-vessel acid digestion procedure through analyses of trace elements in GSP-2 (Zhang et al., 2012a).

3.4. Alkali fusion method

The Alkali Fusion Method (AFM) was originally developed for analysis of volatile elements such as iodine (I) (Musashi et al., 1990; Gélinas et al., 1998; Shimizu et al., 2006). Given the relative volatility of B, this method may also serve to prevent or limit B loss during sample digestion. The original version of the AFM procedure used NaOH as a reagent, fusing the sample at a high flux/rock ratio (8:1) and a high fusion temperature (up to 900 °C) (Musashi et al., 1990; Tonarini et al., 1997). However, a high boron background in the NaOH reagent combined with a high flux/rock ratio can potentially influence measurements of boron concentrations and isotopic compositions in samples. Therefore, Cai et al. (2023) replaced NaOH (B concentrations up to ~2.9 ppm) with Na_2O_2 (B concentrations of 0.054 ppm), which has a lower boron background, and adopted a lower flux/rock ratio (3:1), minimizing the influence of the reagent on sample B measurements. Cai et al. (2023) also recommended a lower reaction temperature (710 °C), increasing the safety of the procedure.

Our pretreatment protocol follows that of Cai et al. (2023): ~3 g of solid Na_2O_2 are dissolved into 20 mL of deionized water, and a known volume of the reagent solution is then placed in a clean silver crucible and weighed. About 100 mg of sample powder are weighed and added to the reagent solution, and the crucible is then agitated so that the sample powder is evenly distributed around its bottom. After thorough mixing, the sample-flux mixture is heated on a hotplate at 90 °C for ~2 h to drive off excess water; the sample-flux mixture is dried to a paste, and the crucible is covered and heated in a furnace at 710 °C for 10 min. After fusion, the crucible is allowed to cool to room temperature. The resulting hydroxide is gently warmed with 2–3 mL of deionized water on a hotplate at ~50–60 °C to facilitate loosening and subsequent transfer into a centrifuge tube. The samples are then dissolved using 1 mL of 6-M HCl and diluted with HNO_3 to a final volume of 100 mL. The solutions are thoroughly mixed to ensure homogeneity before analysis by ICP-MS.

In order to limit systematic bias as much as possible, all samples were analyzed by the same operator on the same ICP-MS instrument. Nonetheless, we are aware of the possibility of inadvertent errors linked to incomplete sample digestion, sample contamination, spill of digestion residue, or incomplete transfer of residue during transitions in the pretreatment process.

4. Results

The analytical results for samples and standards are given in Tables 2 and 3, respectively. Recovery rates are shown in Fig. 1. Relative to the published B concentrations of the standards, measured B concentrations were generally lower. An exception was analysis of GSR-1 by ADM and GSR-6 by AFM, which yielded B concentrations slightly higher than the reported values. The average recovery rates of the four pretreatment methods are 72 % for CAM, 75 % for CAM-P, 92 % for ADM, and 98 % for AFM (Fig. 2).

To evaluate the relative efficacies of the four pretreatment methods, we determined for each sample the ratio of B concentrations from the CAM, CAM=P, and ADM analyses to that of AFM, which generally yielded the highest recovery rates (average 98 %, or near-quantitative recovery; Table 4). The average ratios are 0.68 for CAM/AFM, 0.93 for CAM-P/AFM, and 0.93 for ADM/AFM. Thus, substantial losses of B occurred during pretreatments by the CAM (~32 % on average), the CAM-P (~7 %), and the ADM (~7 %). This comparison serves to demonstrate that the Alkali Fusion Method (AFM) is superior to the other pretreatment methods tested in terms of minimizing B loss due to volatilization.

The analytical precision and accuracy of all four methods were evaluated by duplicate analyses of samples and standards (Table 1). Average relative standard deviations are 10.6 % for GSR-5 (CAM-P), 12.9 % for GSR-6 (CAM-P), 9.92 % for STSD-3 (CAM), 4.09 ± 0.74 % for Chanute-321.5 (all four methods), and 6.95 ± 4.26 % for ONN-33 (all four methods).

5. Discussion

5.1. Assessment of pretreatment protocols

Boron can be lost in the form of volatile boron trifluoride (BF_3) or as boric acid ($B(OH)_3$) under low-pH conditions, especially when samples are reacted with strong acids at high temperatures and pressures during the pretreatment procedure (Nyomora et al., 1997; Okina et al., 2018). Two of the most important factors affecting B recovery rates are the temperature during the digestion procedure and the exposure time of the unsealed vessel in the fume hood during drying (Shao et al., 2012; Rietig et al., 2021). After dissolution in conventional acids (CAM), samples are typically dried at comparatively high temperatures (ca. 115 °C) for prolonged intervals (up to 3 h). This procedure involves digestion by HF,

Table 2
Boron (B) concentrations of standards using four pretreatment methods.

Standard	Lithology	CAM	CAM-P	NDM	AFM	Reported value	Source
GSR-6 (GBW07108)	Limestone	10	10, 12	13	17	16 ± 4	Xie et al. (1989)
GSR-5 (GBW07107)	Shale	117	117, 136	133	139	154 ± 11	Xie et al. (1989)
GSR-1 (GBW07103)	Granite	19	–	26	–	24 ± 3	Xie et al. (1989); Guo et al. (2023)
STSD-3	Silty mudstone	53, 61	–	–	–	82 ± 4	Lynch (1990)

Note: all values in parts per million (ppm). CAM: Conventional Acid Method; CAM-P: Conventional Acid Method with H_3PO_4; ADM: Ammonium Digestion Method; AFM: Alkali Fusion Method.

Table 3
Boron (B) concentrations of samples using four pretreatment methods.

Sample ID	CAM	CAM-P	ADM	AFM
Chanute-321.5	97	135	131	153
Chanute-321.5	103	128	122	146
Chanute-326	124	147	138	149
Dupont 79.5	88	119	124	127
LJC-STJ-30	79	103	90	115
GX-84	23	42	46	44
ONNY-31	18	17	18	24
ONNY-32	12	15	13	14
ONNY-33	38	49	47	51
ONNY-33	34	41	45	48
MM-117	2	6.5	8	6

Note: all values in parts per million (ppm). CAM: Conventional Acid Method; CAM-P: Conventional Acid Method with H_3PO_4; ADM: Ammonium Digestion Method; AFM: Alkali Fusion Method.

which is used in order to completely dissolve silicate minerals. The CAM-P protocol has the same deficiencies although B loss is reduced by the addition of phosphoric acid, which inhibits volatilization of B by decreasing the pH of the solution and catalyzing formation of the nonvolatile B-bearing complex BPO_4. Given the much higher recovery rates of CAM-P (average 92 %) compared to CAM (average 68 %), it is clear that the addition of H_3PO_4 is useful even if it is not 100 % effective at preventing B loss (Shao et al., 2012; Dai et al., 2014). Our results suggest that partial volatilization of BF_3 prior to complete sequestration of boron in nonvolatile B-bearing complexes is the cause of the ~8 % loss of B associated with the CAM-P pretreatment protocol.

The use of molten ammonium bifluoride salt (ADM) has recently been proposed as a digestion method for ICP-MS analysis (Zhang et al., 2012a; O'Hara et al., 2017), and it has been widely used since its development (e.g., Mariet et al., 2008). The ADM procedure entails an exposure time in the fume hood of about 0.5–1 h at a temperature of 160 °C. Although prolonged exposure at high temperatures tends to result in B loss through volatilization (as for the CAM; see above), the ADM is less prone to B loss because the sample powder has already reacted with NH_4F/NH_4HF_2 to produce a new compound, i.e., solid-phase NH_3BF_3, that effectively sequesters B. The ADM protocol has an average recovery rate of 92 %, which is also a significant improvement over the 68 % recovery rate for the CAM, although it does not match the 98 % recovery rate of the AFM. Despite HNO_3 being added to the residue for the purpose of complete sample dissolution, most B in a sample is precipitated in the form of NH_3BF_3, which prevents loss of B (in the form of BF_3) to evaporation. However, this protocol results in minor B loss

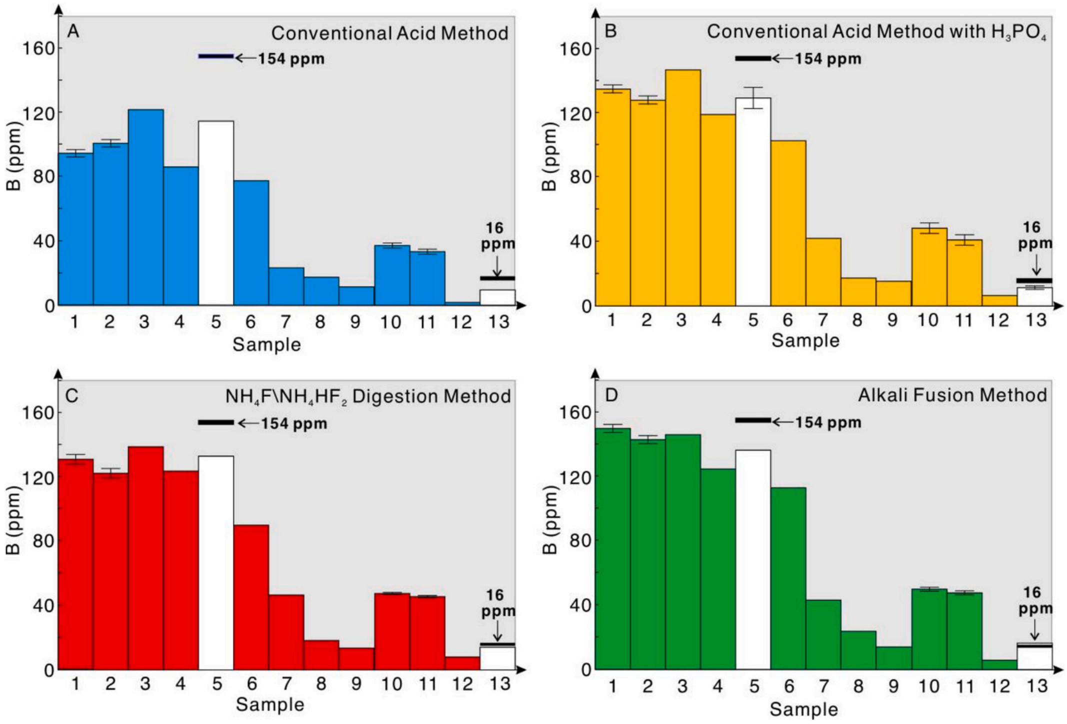

Fig. 1. Analytical results for samples treated by (A) Conventional Acid Method (CAM); (B) Conventional Acid Method with H_3PO_4 (CAM-P); (C) Ammonium Digestion Method (ADM); and (D) Alkali Fusion Method (AFM). The black bar represents the B concentration of the GSR-5 standard. 1–2: Chanute-321.5; 3: Chanute-326; 4: Dupont 79.5; 5: GSR-5; 6: LJC-STJ-30; 7: GX-84; 8: ONNY-31; 9: ONNY-32; 10–11: ONNY-33; 12: MM-117; 13: GSR-6.

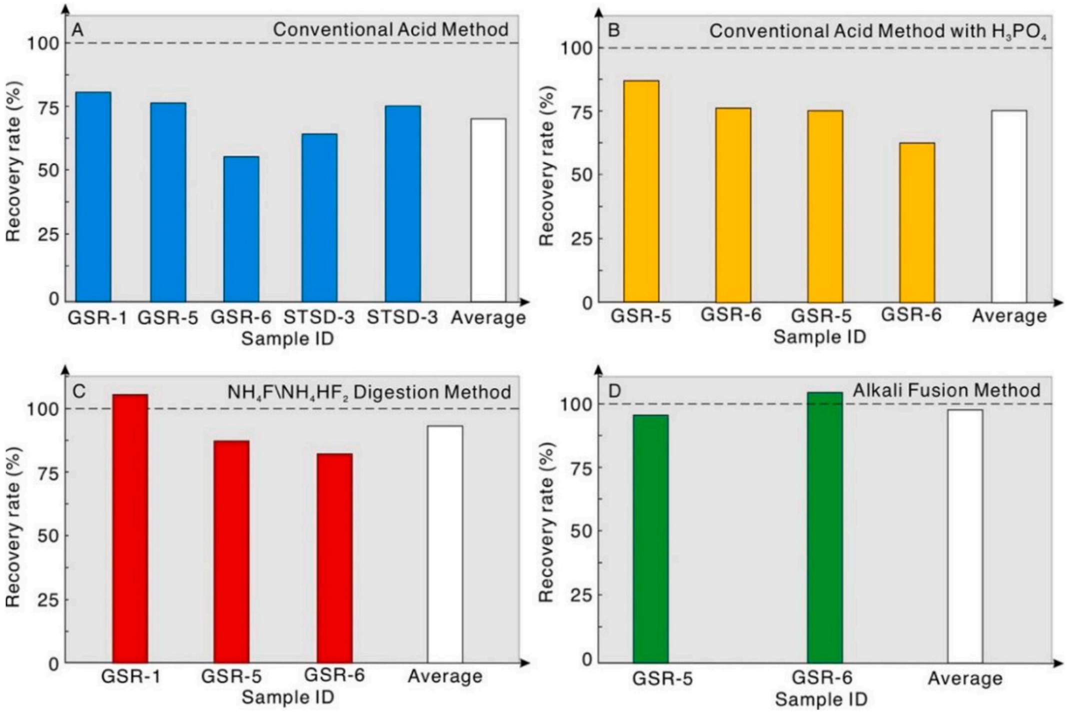

Fig. 2. Recovery rates for standards treated by (A) Conventional Acid Method (CAM); (B) Conventional Acid Method with H_3PO_4 (CAM-P); (C) Ammonium Digestion Method (ADM); and (D) Alkali Fusion Method (AFM).

Table 4
Ratio of B recovery for each pretreatment method to that of the Alkali Fusion Method by sample.

Sample ID	CAM/AFM	CAM-P/AFM	ADM/AFM
Chanute-321.5	0.63	0.88	0.86
Chanute-321.5	0.71	0.88	0.84
Chanute-326	0.83	0.98	0.93
Dupont-79.5	0.69	0.94	0.97
LJC-STJ-30	0.69	0.89	0.78
GX-84	0.52	0.95	1.04
ONNY-31	0.75	0.70	0.75
ONNY-32	0.86	1.07	0.92
ONNY-33	0.75	0.96	0.93
ONNY-33	0.71	0.86	0.94
MM-117	0.33	1.08	1.27
Average	0.68	0.93	0.93

(~8 %), probably during the drying step. Moreover, B exerts a memory effect in inductively coupled plasma-mass spectrometers, and the use of ammonia is thought to assist in washing out residual B in the analytical line (Al-Ammar et al., 1999; Cai et al., 2021). The accuracy of analytical results for the ADM may benefit from this mechanism.

The Alkali Fusion Method is the only protocol that does not involve hydrogen fluoride (HF), thus completely eliminating the risk of B loss in the form of volatile BF_3. Also, this method uses an alkaline agent and involves no evaporation step, which also protects against B loss. This method further minimizes the loss of B by adopting a relatively short exposure time (less than 2 h) and a lower temperature (90 °C) during drying. In summary, for analysis of B concentrations in sediments, the Alkali Fusion Method is clearly the optimal pretreatment procedure. This method has long proven useful for analysis of volatile elements such as fluorine and chlorine (Gélinas et al., 1998; Shimizu et al., 2006).

5.2. Assessment of B concentrations of standards

The B contents of the four standards used in this study were quantified decades ago using a variety of analytical methods including ICP-MS, flame atomic absorption spectrometry, colorimetry, and others (Xie et al., 1989; Lynch, 1990). Because of the vintage of this work, the pretreatment protocol used is likely to have been a conventional acid digestion method, although the original studies are not specific on this point. Despite this uncertainty, the standards analyzed using the AFM pretreatment protocol yielded 98 % of their expected values on average, i.e., near-quantitative recovery. This result not only supports the robustness of the AFM protocol but also suggests that B has not been lost in significant amounts from powdered standards that have sat on the shelf for several decades. Apart from the AFM, the other pretreatment protocols (i.e., CAM, CAM-P, and ADM) yielded B concentrations that were lower than their reported values, mostly by ~10–20 % (Table 2). These losses are in line with those exhibited by samples prepared using these pretreatment protocols (Table 3) and with the ratios of these protocols to the AFM protocol (Table 4).

5.3. Comparison with methodology of the boron isotope research community

We acknowledge that the boron isotope research community has developed sophisticated techniques to quantitatively extract B from sediment samples, including the alkali fusion and resin-based cationic exchange methods (He et al., 2015; Aggarwal and You, 2017; Sun et al., 2019; Cai et al., 2021, 2023; Zhang et al., 2024). In the improved version of the AFM developed by Cai et al. (2023), adoption of Na_2O_2 as a reagent permits a low flux/sample mass ratio (FSMR) (3:1), thus reducing background boron levels, and a relatively low fusion temperature (710 °C), thus improving lab safety. Moreover, use of relatively inexpensive silver crucibles minimizes analytical expenses. In the resin-based cationic exchange method developed by Zhang et al. (2024), a B-specific resin is used in an alkaline environment to collect and purify sample B, limiting potential effects related to elements that have a strong B adsorption capacity in high-pH solutions (i.e., Al, Fe, and rare earth elements). These techniques have been demonstrated to quantitatively recover B for robust $\delta^{11}B$ measurements.

Although the techniques used in the B isotope research community are robust, they require specialized laboratory facilities and entail greater expenditure of effort and resources than are typical in elemental studies. Given that the resin-based cationic exchange method extracts only B from samples, this method has not been widely adopted by researchers in the paleoenvironmental community because of the need for concentration data not only for B but also for other elements used as paleoenvironmental proxies, e.g., Ga, Sr, and Ba for salinity, and Mo, U, V, and Re for redox analysis. Moreover, B isotope studies are typically based on a few dozen analyses, whereas elemental studies (including those with a paleosalinity focus) often process a much larger number of samples (i.e., hundreds). Thus, our findings will be of significance in particular for paleoenvironmental researchers interested in rapidly processing large numbers of samples for B concentrations.

6. Conclusions

Of the four sample pretreatment methods tested in this study, the Alkali Fusion Method (AFM) is the only one that does not involve hydrogen fluoride (HF), the use of which has a tendency to generate a compound (BF_3) that is lost through volatilization. Moreover, the AFM protocol uses an alkaline agent and involves no evaporation, further limiting B loss during sample preparation. This method has a uniformly high recovery rate of B, up to ~98 %, whereas the other pretreatment methods have lower recovery rates ranging from 72 % to 92 %. The AFM also shows superior time and cost efficiency compared to conventional methods. We therefore recommend that the AFM pretreatment method be adopted as the standard protocol for sample preparation for B concentration analysis by ICP-MS. Following Cai et al. (2023), we further recommend adoption of a lower flux/rock ratio (3:1) to minimize the influence of background B in the reagent on sample B measurements, a short evaporation time (~2 h) to limit B loss, and a low reaction temperature (710 °C) for the sake of lab safety. Our results suggest that this approach ensures near-quantitative recovery of sample B.

CRediT authorship contribution statement

Wei Wei: Writing – original draft, Conceptualization. **Thomas Algeo:** Writing – review & editing, Conceptualization. **Lin Chen:** Writing – review & editing. **Zhiquan Li:** Methodology. **Cody Lazowski:** Methodology. **Katherine Snihur:** Methodology, Data curation. **Daniel Alessi:** Writing – review & editing, Conceptualization. **Kurt Konhauser:** Writing – review & editing, Conceptualization.

Declaration of competing interest

All authors: Wei Wei, Thomas Algeo, Lin Chen, Zhiquan Li, Cody Lazowski, Katherine Snihur, Daniel Alessi, Kurt Konhauser confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2025.122838.

Data availability

All study data are available in the Supplemental Information file.

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