

Geochemistry, Geophysics, Geosystems®

RESEARCH ARTICLE

10.1029/2024GC011845

Special Collection:

Advances and Best Practices in Boron-based paleo-CO₂ reconstruction

Key Points:

- New protocol for $\delta^{11}\text{B}$ analysis of biocarbonates successfully applied to low [B] *Globigerina bulloides* bulk samples in limited quantity
- Major increase in $\delta^{11}\text{B}$ precision and accuracy thanks to a pioneering strategy of transient signal analysis for reduced volumes (80 μL , $n = 3$)
- Homogeneous $\delta^{11}\text{B}$ signatures across three size fractions of *Globigerina bulloides* samples indicate no ontogenetic effect on their $\delta^{11}\text{B}$

Correspondence to:

M. Paulhac Buisson,
buisson@cerege.fr

Citation:

Paulhac Buisson, M., Louvat, P., Karancz, S., Tian, R., Raitzsch, M., Bijma, J., & Rollion-Bard, C. (2025). Determination of $\delta^{11}\text{B}$ in planktonic foraminifera at the ng level: Application to the ontogenetic variability in *Globigerina bulloides*. *Geochemistry, Geophysics, Geosystems*, 26, e2024GC011845. <https://doi.org/10.1029/2024GC011845>

Received 6 SEP 2024

Accepted 22 SEP 2025

Author Contributions:

Conceptualization: Matthieu Paulhac Buisson, Pascale Louvat, Markus Raitzsch, Jelle Bijma, Claire Rollion-Bard

Formal analysis: Matthieu Paulhac Buisson, Pascale Louvat, Szabina Karancz, Ruchen Tian, Markus Raitzsch

Funding acquisition: Pascale Louvat, Jelle Bijma, Claire Rollion-Bard

© 2025 The Author(s). Geochemistry, Geophysics, Geosystems published by Wiley Periodicals LLC on behalf of American Geophysical Union. This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs License](#), which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

Determination of $\delta^{11}\text{B}$ in Planktonic Foraminifera at the ng Level: Application to the Ontogenetic Variability in *Globigerina bulloides*

Matthieu Paulhac Buisson^{1,2} , Pascale Louvat^{1,3}, Szabina Karancz^{4,5} , Ruchen Tian^{4,6} , Markus Raitzsch^{4,7}, Jelle Bijma^{4,6} , and Claire Rollion-Bard⁸

¹Université Paris Cité, Institut de physique du globe de Paris, CNRS, Paris, France, ²Aix-Marseille Université, CNRS, IRD, INRAE, CEREGE, Aix-en-Provence, France, ³Université de Pau et des Pays de l'Adour, IPREM, CNRS-UMR 5254, Pau, France, ⁴Alfred-Wegener-Institut, Helmholtz-Zentrum für Polar- und Meeresforschung, Bremerhaven, Germany, ⁵NIOZ-Royal Netherlands Institute for Sea Research, Texel, The Netherlands, ⁶Jacobs University, Bremen, Germany, ⁷MARUM - Centre for Marine Environmental Sciences, University of Bremen, Bremen, Germany, ⁸Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, UMR 8212, CEA-CNRS-UVSQ, Gif-sur-Yvette, France

Abstract The boron isotope ratio ($\delta^{11}\text{B}$) of planktonic foraminifera is a robust proxy for determining oceanic pH and inferring atmospheric $p\text{CO}_2$ during the Cenozoic. However, measuring $\delta^{11}\text{B}$ in these small and low [B] samples (3–16 ppm) is challenging, as a precision below 0.8‰ (2SD) is required, equivalent to ~ 0.1 pH units, which reflects the scale of anthropogenic acidification or glacial/interglacial alternations. Moreover, uncertainties in paleoclimate reconstructions from biocarbonates are due to biomineralization processes, requiring species-specific calibrations of the pH- $\delta^{11}\text{B}$ relationship to account for the so-called “vital effect.” While such calibrations exist for many species, the influence of foraminiferal size on $\delta^{11}\text{B}$ remains poorly studied. We measured $\delta^{11}\text{B}$ of *Globigerina bulloides* (80–190 tests, 3–5 ppm [B]), for three different size fractions (250–315, 315–400, and >400 μm), collected from the upper part of a core from the Chilean Margin. We validated a novel analytical method combining microdistillation for B purification and micro-direct injection (μ -dDIHEN) to the Multi-Collector Inductively Coupled Plasma Mass Spectrometer for accurate and precise (0.1–0.5‰, 2SD) $\delta^{11}\text{B}$ analysis of the smallest samples (only 1–2 ng B in solution). This approach injects only 10 μL of solution, producing short injection peaks that minimize blank effects through transient signal processing, thereby improving paleo-pH reconstructions from small-sized foraminifera. Our results show no size-dependent variations in $\delta^{11}\text{B}$ of symbiont-barren *G. bulloides*, confirming that its microenvironment is primarily influenced by respiration and calcification. This contrasts with symbiont-bearing species, where $\delta^{11}\text{B}$ varies with symbiont density due to photosynthetic activity.

Plain Language Summary The boron isotope ratio ($^{11}\text{B}/^{10}\text{B}$) in biocarbonates, CaCO_3 minerals produced by certain groups of marine organisms, reflects the seawater pH in which they formed, allowing for the reconstruction of atmospheric CO_2 level, closely linked to ocean pH, over the last 65 million years. Such reconstructions rely on pristine and single-species calcitic shells of planktonic foraminifera, unicellular eukaryotic microorganisms living in the ocean subsurface. However, B isotope ratio ($\delta^{11}\text{B}$) analysis is challenging, especially for these tiny, boron-poor samples, and requires advanced protocols to minimize uncertainties, crucial for precise paleoclimatic reconstitutions. Additionally, seawater pH calculations from boron isotope ratios in these biocarbonates account for slight changes within the microenvironment pH induced by the species-dependent mechanisms of shell formation. Our study focused on *Globigerina bulloides*, the planktonic foraminifera species with the lowest boron concentration, to test whether their boron isotope ratios are size-dependent. We developed, tested, and validated breakthrough $\delta^{11}\text{B}$ measurements with only half the sample mass typically needed, while maintaining or even improving accuracy and precision. Our findings show no size effect on the boron isotope ratio of the symbiont-barren *G. bulloides*, unlike some other species for which the microenvironment pH gradually increases with symbiotic algae density through photosynthetic CO_2 consumption.

1. Introduction

The boron isotope ratio of marine biogenic carbonates is usually used to infer the pH of seawater for paleo-oceanographic reconstructions (e.g., Alves et al., 2024; Foster, 2008; Hemming & Hanson, 1992; Henehan

Investigation: Matthieu Paulhac Buisson, Pascale Louvat, Szabina Karancz, Ruchen Tian, Markus Raitzsch

Methodology: Matthieu Paulhac Buisson, Pascale Louvat

Project administration:

Matthieu Paulhac Buisson, Pascale Louvat, Markus Raitzsch, Jelle Bijma, Claire Rollion-Bard

Resources: Pascale Louvat, Markus Raitzsch, Jelle Bijma, Claire Rollion-Bard

Supervision: Pascale Louvat, Markus Raitzsch, Jelle Bijma, Claire Rollion-Bard

Validation: Matthieu Paulhac Buisson, Pascale Louvat, Claire Rollion-Bard

Visualization: Matthieu Paulhac Buisson

Writing – original draft:

Matthieu Paulhac Buisson

Writing – review & editing:

Matthieu Paulhac Buisson, Pascale Louvat, Szabina Karancz, Ruchen Tian, Claire Rollion-Bard

et al., 2013, 2016; Pearson & Palmer, 2000; Rae et al., 2011; Raitzsch et al., 2018; Sanyal et al., 1996, 2001; Tarique et al., 2023; Vengosh et al., 1991). The basis of the $\delta^{11}\text{B}$ -pH proxy relies on the constant equilibrium fractionation of $27.2 \pm 0.6\text{‰}$ (Klochko et al., 2006; Nir et al., 2015) between the two dissolved boron species: the trigonal weak acid $\text{B}(\text{OH})_3$ and its conjugated base, the tetrahedral borate anion $\text{B}(\text{OH})_4^-$ (Dickson, 1990; Roy et al., 1993). As the dissociation constant of this acid/base couple (pK_B of 8.60, at 25°C, atmospheric pressure, 35 psu; Dickson, 1990) is close to the oceanic pH (~ 8.1), small fluctuations in seawater pH lead to significant variations in the relative abundances of boric acid and borate anion. Conversely, the total boron content and the isotopic composition of the ocean remain invariant, displaying a modern concentration of 4.68 ± 0.01 ppm and a $\delta^{11}\text{B}_\text{sw}$ value of $39.61 \pm 0.20\text{‰}$ (Foster et al., 2010; Lee et al., 2010). Given that borate ions are preferentially incorporated as a substitute of the carbonate ion into the calcium carbonate lattice of many marine biogenic carbonates (Balan et al., 2016; Branson et al., 2015; Cusack et al., 2015; Hemming & Hanson, 1992; Noireaux et al., 2015; Rollion-Bard et al., 2011; Sen et al., 1994; Vengosh et al., 1991), the pH of the fluid from which the carbonate has precipitated can therefore be deduced by mass balance (with known oceanic B concentration and $\delta^{11}\text{B}_\text{sw}$) from the measured $\delta^{11}\text{B}$ of the carbonate (Hemming & Hanson, 1992). Another advantage of using this proxy is that boron has a long residence time in the ocean, estimated at 14 Myr (Lemarchand, Gaillardet, Lewin, & Allègre, 2002). “Vital effects,” that is, the observed differences between the inorganic elemental and isotopic compositions of a carbonate precipitated from seawater and the compositions of biogenic carbonates (Urey et al., 1951), must nevertheless be accounted for. Calcification processes in foraminifera heavily rely on the modification of the seawater composition at the site of calcification to favor carbonate precipitation (e.g., de Nooijer et al., 2014; Erez, 2003; Nehrke et al., 2013). This change has an impact on the concentrations of Ca^{2+} and CO_3^{2-} at the calcification site, either taken up directly from seawater and/or by a selective removal of the other ions except Ca^{2+} and CO_3^{2-} , a strong pH gradient and/or a transmembrane ion transport (Bentov et al., 2009; de Nooijer et al., 2014; Erez, 2003; Rollion-Bard & Erez, 2010; Toyofuku et al., 2017). Species-specific calibrations of the $\delta^{11}\text{B}_\text{borate}$ (i.e., pH)- $\delta^{11}\text{B}_\text{carbonate}$ relationship, necessary to take these “vital effects” into account, are based on either sediment coretop samples, foraminifera cultures, or water column sampling (e.g., Foster, 2008; Guillermic et al., 2020; Henahan et al., 2013; Martínez-Botí, Marino, et al., 2015; Rae et al., 2011; Raitzsch et al., 2018). The deviation of the $\delta^{11}\text{B}_\text{carbonate}$ to $\delta^{11}\text{B}_\text{borate}$ relationships from the 1:1 line signifies the different physiological mechanisms that create the calcifying fluid with a pH different from that of seawater (Chalk & Rollion-Bard, 2025; de Nooijer et al., 2009; Erez, 2003; Jørgensen et al., 1985; Rae, 2018; Rollion-Bard & Erez, 2010; Toyofuku et al., 2017). The calcifying fluid pH is mainly modified by Ca/proton pumps, and then altered by symbiont photosynthesis, when present, and by respiration and calcification (de Nooijer et al., 2014; Erez, 2003; Henahan et al., 2013, 2016; Hönisch et al., 2003; Nehrke et al., 2013; Toyofuku et al., 2017; Zeebe et al., 2003). Ontogenetic variations also influence $\delta^{11}\text{B}$ in the symbiont-bearing planktonic foraminifera *Globigerinoides ruber* and *Trilobatus sacculifer*, with $\delta^{11}\text{B}$ increasing with shell size due to a higher symbiont density (Henahan et al., 2013, 2016; Hönisch et al., 2021; Hönisch & Hemming, 2004). As a result, the size fraction of these species must be uniform and homogenized across paleoclimatic and paleoceanographic studies to ensure comparability. In contrast, this size effect on $\delta^{11}\text{B}$ in other species of planktonic foraminifera remains poorly studied.

Measuring $\delta^{11}\text{B}$ of foraminifera is also challenging due to their small size and low boron concentration. Moreover, the species-specific approach, essential to obtain high fidelity records of paleo-pH, restricts sample size availability. The analysis of cultured samples, which is a critical requirement for the application of this proxy, also requires high precision on tiny masses of CaCO_3 , while only small and fragmented specimens are often preserved during key climatic intervals. The range of B concentration reported in the literature for planktonic foraminifera is 40–60 $\mu\text{mol/mol}$ for *Globigerina bulloides* and 80–120 $\mu\text{mol/mol}$ for *G. ruber*, which implies that approximately 400 specimens and 100 specimens, respectively, need to be collected for one bulk sample ($\sim 2\text{--}20$ ng B; Rae, 2018). Benthic foraminifera have an elevated boron concentration (100–250 $\mu\text{mol/mol}$), and given that they are generally heavier, 2–20 individual tests can provide sufficient material for the analysis. However, the application of benthic foraminifera is generally limited by their low absolute abundance in sediments (Rae et al., 2011; Raitzsch et al., 2011, 2020). The necessity to clean foraminifera samples of organic matter, clays and oxide contaminants, which interfere with elemental and isotopic analysis, leads to an additional loss of more than 30% of the sample mass through its partial dissolution (Barker et al., 2003). This fraction can be even higher if a reductive cleaning step is operated after the oxidative cleaning to ensure oxide removal (Pang et al., 2020; Yu et al., 2007). The reduction in sample mass during shell cleaning procedures must therefore be accounted for during sample preparation to ensure reliable $\delta^{11}\text{B}$ measurements and also the determination of major, minor, and

trace element concentrations. In particular, the Mg/Ca ratio is used to estimate seawater temperature, which in turn allows for more accurate determination of the boric acid dissociation constant, a parameter primarily dependent on temperature and, to a lesser extent, on salinity and pressure (e.g., Gutjahr et al., 2017; Hennehan et al., 2019; Martínez-Botí, Foster, et al., 2015; Raitzsch et al., 2018). The pH variations observed for ocean acidification during the Anthropocene or during glacial/interglacial transitions are about 0.1–0.15 pH units (Caldeira & Wickett, 2003; Hönsch & Hemming, 2005; Orr et al., 2005; Sanyal et al., 1995), whereas pH oscillated only between 7.5 and 8.2 over the last 300 Myr (Hönsch et al., 2012). Therefore, the precision required on the $\delta^{11}\text{B}$ measurements must be better than $\pm 0.8\text{‰}$, corresponding to ~ 0.1 pH units. They are particularly challenging for such small-sized samples with low B concentrations, necessitating rigorous control of chemistry blanks during boron extraction and mass spectrometry measurements. This is especially critical given the inherent difficulties in purifying and analyzing boron on ICP-MS, including its volatility in an acid medium, stickiness, large instrumental mass fractionation, and poor ionization (Foster, 2008; Louvat et al., 2011, 2014; McCulloch et al., 2014; Rehkämper et al., 2001).

In this study, we investigated the ontogenetic variability of $\delta^{11}\text{B}$ within the planktonic foraminifera species *G. bulloides*, originating from the top of a marine sediment core and sieved at different sizes. First, this application allowed us to test and validate the analytical protocol developed at the Institut de physique du globe de Paris (IPGP) to precisely and accurately measure $\delta^{11}\text{B}$ of small amounts of marine biogenic carbonates at low B concentration (Buisson et al., 2021; Louvat et al., 2019). Second, we successfully implemented for the first time in carbonate solutions with low boron content a new approach consisting of small volume injection loops and the generation of transient signals on MC-ICP-MS.

2. Material and Methods

2.1. Analytical Background

Bulk $\delta^{11}\text{B}$ analysis of carbonate samples with MC-ICP-MS (Multi-Collector Inductively Coupled Plasma Mass Spectrometer) has been developed since the early 2000s, and its use has become widespread in laboratories (Foster, 2008; Foster et al., 2018; Lécuyer et al., 2002; Louvat et al., 2011; McCulloch et al., 2014; Rae et al., 2011). These analyses are preceded by the dissolution of the samples and extraction of the boron, typically performed using ion exchange chromatography (Hemming & Hanson, 1994; Kiss, 1988; Lemarchand, Gaillardet, Göpel, & Manhès, 2002; Paris et al., 2010). MC-ICP-MS has gradually supplanted the Thermal Ionization Mass Spectrometer (Positive TIMS, Gaillardet & Allègre, 1995; Ishikawa & Nagaishi, 2011; Wei et al., 2009, and Negative TIMS, Clarkson et al., 2015; Foster et al., 2006, 2013; Hemming & Hanson, 1992, 1994; Hönsch et al., 2004; Vengosh et al., 1989) thanks to higher ionization yields, a more stable mass bias and higher analysis throughput. Subsequently, analytical improvements over the last decade in MC-ICP-MS have allowed the precise measurement of $\delta^{11}\text{B}$ in small carbonates samples with low B concentration thanks to strategies preventing the memory effect of boron in ICP-MS, such as different introduction systems, rinse solution or addition of gaseous ammonia (Chanakya & Misra, 2022; Foster et al., 2013; Foster, 2008; Louvat et al., 2014; Misra, Owen et al., 2014; Rae et al., 2011; Raitzsch et al., 2018; Trudgill et al., 2024; Figure 1).

The last upgrades on MC-ICP-MS have reached their apogee with a precision of 0.2‰ (2SD) for carbonate samples containing only 2.5–3 ng of boron, thanks to the $10^{13}\ \Omega$ resistors as amplifiers linked to Faraday cups (Lloyd et al., 2018; Trudgill et al., 2024; Figure 1). They improve the signal/noise ratio by a factor of 10 and therefore enable the measurements of smaller low-current ion beams (Lloyd et al., 2018). Furthermore, the fast and low-blank batch method for B purification, combined with a low-flow nebulizer ($\sim 35\ \mu\text{L}\cdot\text{min}^{-1}$) and the addition of HF to facilitate the washout, allowed $\delta^{11}\text{B}$ analysis on a low volume of sample with small B concentrations (500 μL , 2.5–10 ng, Trudgill et al., 2024). IPGP reported precisions of 0.1‰ on plasma MC-ICP-MS for pure boric acid solutions and samples with boron mass higher than 20 ng and 0.2‰ for ~ 20 ng B in carbonate samples (Louvat et al., 2014; Figure 1), using an automated direct injection nebulizer allowing a higher sensitivity and shorter washout times (d-DIHEN, Louvat et al., 2011, 2014). This sample introduction system has been recently miniaturized (μ -dDIHEN, Louvat et al., 2019) to reduce the amount of solution consumed to 240 μL for triplicate $\delta^{11}\text{B}$ measurements of one sample during a standard-sample bracketing sequence (SSB). This new μ -dDIHEN device, combined with the low-blank microdistillation (or microsublimation) technique to extract boron from the carbonate matrix (Gaillardet et al., 2001; Misra, Owen et al., 2014; Raitzsch et al., 2018; Wang et al., 2010) and $10^{13}\ \Omega$ resistors as amplifiers (Lloyd et al., 2018), has been successfully tested for biogenic

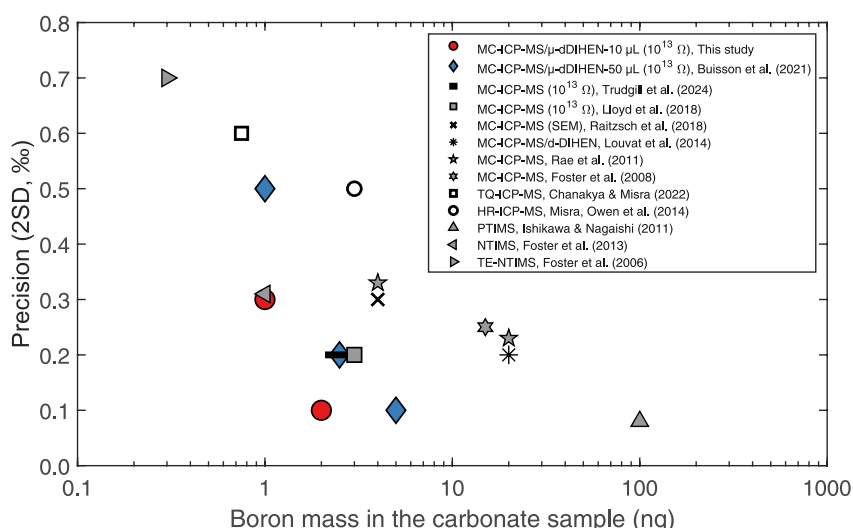


Figure 1. Precision (2SD) for one sample reported in the literature and this study versus the minimum mass of boron analyzed using a range of analytical techniques: Positive (PTIMS, Ishikawa & Nagaishi, 2011), Negative (NTIMS, Foster et al., 2013) and Total Evaporation Negative (TE-N, Foster et al., 2006) Thermal Ionization Mass Spectrometer (TIMS), High-Resolution (HR, Misra, Owen et al., 2014), Triple Quad (TQ, Chanakya & Misra, 2022) and Multi-Collector (MC, Buisson et al., 2021; Foster, 2008; Lloyd et al., 2018; Louvat et al., 2014; Rae et al., 2011; Raitzsch et al., 2018; Trudgill et al., 2024) Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Specific features of some analyses have been detailed, for the introduction system (direct injection d-DIHEN and μ -d-DIHEN, respectively, with a 10 μ L and a 50 μ L sample loop) and the ion detection (Secondary Multipliers Electrons SEM and Faraday cups with 10^{13} Ω resistors as amplifiers).

carbonate samples. It displayed a 2SD precision of 0.2‰ for 2.5 ng of boron and 0.5‰ for sample solutions containing only 1 ng (Buisson et al., 2021; Figure 1). The μ d-DIHEN introduction device enabled further reduction of the quantity of solution consumed for a triplicate analysis down to $\sim$ 80 μ L, leading to a new calculation strategy based on transient signal measurements never used so far for boron isotopes in solution (Louvat et al., 2019). This analytical approach aims to minimize the required sample amount while increasing the number of chemical analyses possible on the same sample.

2.2. Foraminifera Samples

The sample material is from the sediment core PS97/122-1 (Lamy, 2016), collected along the Chilean margin (54.10°S, 74.91°W), at a water depth of 2,558 m for a length of 10.77 m. ^{14}C measurements of *G. bulloides* samples performed at the Alfred-Wegener-Institut (AWI, Bremerhaven, Germany) revealed that the depths 1–2 cm, 18–19 cm, 25–26 cm, were 1450 ± 80 , 7446 ± 83 and 9276 ± 124 years old, respectively, which is pretty consistent with the preliminary estimate of the sedimentation rate at $\sim$ 3 cm/kyr for the whole Holocene. Each sample, taken every centimeter, was freeze-dried, wet sieved at 63 μ m and dried in an oven at 40°C for two to three days. For this study, we used samples from the upper part of the core, between 7 and 38 cm, placing this pool of samples in the Holocene, dry-sieved into size fractions of >400 μ m, 315–400 μ m and 250–315 μ m. Thereafter, we handpicked under an optical microscope only well-preserved shells of the shallow-dwelling planktonic foraminifera *G. bulloides* ($\sim$ 80–190 shells per sample), living in temperate to subpolar water and upwelling zones (Schiebel & Hemleben, 2017). In parallel, four *G. bulloides* samples of the size fraction 315–400 μ m (19–20, 21–22, 25–26 and 29–30 cm) were independently analyzed at the AWI for their boron isotopes following the analytical protocol described in Raitzsch et al. (2018).

2.3. Reagents, Material and Labware

The foraminifera cleaning, dissolution, boron extraction and the preparation of standards and reference materials were carried out with supra-pure chemical reagents, distilled nitric acid HNO_3 (DST1000 device, Savillex, Eden Prairie, MN, USA) and Milli-Q (MQ) water (resistivity >18 M Ω cm and Q-pod with 0.22 μ m Millipak Express filter, Millipore, Burlington, MA, USA), in an over-pressured and air-filtered clean room with boron-free H14 HEPA filters (Megacell III, AAF, Vincennes, France). All the Eppendorf vials (for foraminifera cleaning) and

0.5 mL polypropylene tubes (for $\delta^{11}\text{B}$ analysis in transient mode) were boiled in 3 N HCl in a Teflon jar at 95°C, then rinsed with MQ water and soaked in 0.5 N HNO_3 . The Savillex fin legged conical teflon vials were boiled in 3 N HNO_3 and then rinsed as described above. The polypropylene (PP) tubes for the MC-ICP-MS measurements in static mode were filled with 0.5 N HNO_3 for a few days. After the acid treatments, all the labware was rinsed with MQ water and dried at room temperature. The pipette tips were washed just before use by pipetting three times 0.5 N HNO_3 and then MQ water.

2.4. Foraminifera Cleaning

The picked foraminifera were cleaned following a protocol adapted from Barker et al. (2003) and Rae et al. (2011). They were initially gently cracked between two clean glass slides under a binocular to open the foraminifera test chambers. The shell fragments were then transferred to 500 μL Eppendorf vials with MQ water. The samples were rinsed and ultrasonicated 6–8 times with MQ water until no clay residue was visible. The organic matter was then oxidized with 0.1 N NaH_4OH buffered-1% H_2O_2 in a hot water bath at 80°C. They were immediately rinsed three times with MQ water and transferred to 1.5 mL Eppendorf vials for leaching with 0.0005 N HNO_3 to remove any adsorbed contaminants. They were finally rinsed again with MQ water and gradually (drop by drop) dissolved with 0.5 N HNO_3 for a final ~ 100 –200 μL solution and ultimately stocked in a Teflon vial.

The reductive cleaning step with ammonia-ammonium acetate buffer, citric acid and hydrazine for ferromanganese oxy-hydroxides removal is delicate as it decreases the Mg/Ca ratio of the foraminifera through partial dissolution (Barker et al., 2003; Pang et al., 2020; Yu et al., 2007) without impacting the B/Ca ratio and $\delta^{11}\text{B}$ value (Misra, Greaves et al., 2014; Misra, Owen et al., 2014; Yu et al., 2007). In the context of paleo-pH reconstructions, because we generally need the Mg/Ca ratio to deduce the seawater temperature and then calculate the acid boric/borate dissociation constant, we have chosen to omit the reductive cleaning. To check the efficiency of the cleaning protocol, Al/Ca and Mn/Ca ratios have been measured with a Quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-QMS, Agilent 7900) at IPGP, following a protocol adapted from Yu et al. (2005). A small aliquot of the solution samples (few μL) was diluted in 5 mL of HNO_3 0.5 N. The final solution was then introduced into the plasma spray of the ICP-MS with a μ -nebulizer, and the addition of He in a collision cell allowed for the reduction of polyatomic interferences.

2.5. Boron Isotope Analysis in Static Mode

The whole protocol for boron purification and isotope ratio measurement is fully described in Louvat et al. (2019) and Buisson et al. (2021). Briefly, boron was separated from the carbonate matrix by microdistillation (Buisson et al., 2021; Gaillardet et al., 2001; Misra, Owen et al., 2014; Raitzsch et al., 2018; Wang et al., 2010). A 50 μL droplet of the dissolved carbonate sample was loaded on the cap of a pre-cleaned 5 mL Savillex Teflon fin legged conical vial. The vial was rapidly and tightly closed, then coated in an aluminum foil entirely except for the upper tip, and placed (still upside down) on a hotplate for 24 hr at 95°C (see Figure 1 in Buisson et al., 2021). Vials were then carefully removed from the hot plate, flipped and allowed to cool for 15 min. The distillate (recovered in the vial bottom) was finally diluted with 450 μL of MQ water for a final HNO_3 concentration at 0.05 N, the chosen medium for $\delta^{11}\text{B}$ analysis (Louvato et al., 2011, 2014). The 0.5 mL final solution was transferred to 5 mL polypropylene tubes for immediate analysis.

The $\delta^{11}\text{B}$ measurements were carried out at low mass resolution ($m/\Delta m = 400$) on a MC-ICP-MS Neptune (ThermoScientific, MA, USA) at IPGP. The instrument was customized for small signals, combining Jet sampler and X skimmer cones, and two $10^{13} \Omega$ resistors as amplifiers for Faraday cups H3 (^{11}B signal) and L3 (^{10}B signal). The solutions were introduced into the plasma with a fully automated direct injection nebulizer (d-DIHEN, Analab, Strasbourg, France; Louvat et al., 2011, 2014) in flow injection analysis mode, and supplied by a gas displacement pump (GDP, ESI, USA), the whole system constituting the μ -dDIHEN set-up (Louvato et al., 2019). Briefly, a 50 μL sample loop of the FAST valve (ESI, USA) is filled with the sample, standard or reference material solution and then driven to the nebulizer with a 0.05 N HNO_3 carrier solution from the GDP, pushed by an argon pressure regulated with a micro-mass-flowmeter (El Flow, Bronkhorst, France). In the present study, the GDP liquid flow rate was set at 25–30 $\mu\text{L min}^{-1}$ in order to achieve a stable signal plateau lasting ~ 100 s for each injection peak, allowing measurement of the $^{11}\text{B}/^{10}\text{B}$ ratio in 12 cycles of 8 s (Louvato et al., 2019). Prior to the $\delta^{11}\text{B}$ analysis, B concentration was measured to match within $\pm 5\%$ the concentrations of the sample, standard and

reference material solutions. For each sample, the average boron isotope ratio and its associated repeatability (2SD) were calculated from five $\delta^{11}\text{B}$ values (background corrected) obtained after three successive sample-standard bracketing measurements (Buisson et al., 2021; Louvat et al., 2014), consuming in total only 240 μL of solution. Boron isotope ratios are reported as $\delta^{11}\text{B}$ in ‰, relative to the boric acid international standard reference NIST SRM 951 (USA; Catanzaro et al., 1970):

$$\delta^{11}\text{B} = \left(\frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample or reference material}}}{(^{11}\text{B}/^{10}\text{B})_{\text{NIST SRM 951}}} - 1 \right) \times 1000. \quad (1)$$

Purified sample solutions contained between ~ 1.6 ppb (0.8 ng) and ~ 6.9 ppb (3.45 ng) of boron, corresponding to ^{11}B signals between ~ 20 and ~ 100 mV. The procedural blank was 12 ± 4 pg (1SD, $n = 4$), representing $\sim 1.5\%$ of the B content for the less concentrated sample. The boric acid reference material ERM-AE121 (BAM, Germany; Vogl & Rosner, 2011) was systematically measured at the same concentration as the samples (1.6–6.9 ppb) to check the quality of the $\delta^{11}\text{B}$ measurements, while the carbonate reference material MVS-1 (GEOMAR, Kiel, Germany, Jurikova et al., 2019) was purified together with the *G. bulloides* samples to additionally validate the $\delta^{11}\text{B}$ determinations on a carbonate matrix.

2.6. Boron Isotope Analysis in Transient Mode

As the B concentrations of the foraminifera samples were very low after microdistillation extraction (between 1.6 and 6.9 ppb), we attempted an alternative measurement strategy to increase the concentration by reducing the sample volume consumption and consequently improving the signal/noise ratio. We used a smaller injection loop of 10 μL instead of 50 μL and measured in transient signal mode, in place of static mode (Louvat et al., 2019). After validation of this approach for the two reference materials ERM-AE121 (Vogl & Rosner, 2011) and MVS-1 (Jurikova et al., 2019), some of the samples were re-measured in this mode.

With such a small volume, the injection peaks do not last long enough for continuous stable signal measurements; the ^{11}B and ^{10}B signals are transient, and consequently, the whole peaks were measured in 180 cycles of 1 s, including baseline signals before and after the B peak (Figures 2a–2c). For each injection of a sample, standard or reference material, the $^{11}\text{B}/^{10}\text{B}$ ratio was calculated from the slope of a linear regression (using the fit linear regression model, fitlm in MATLAB, Figures 2d and 2e) based on 180 measurements of ^{11}B and ^{10}B signals, described by the equation:

$$^{11}\text{B} = (a \pm u_a) ^{10}\text{B} + (b \pm u_b), \quad (2)$$

with a the slope of the linear regression representing the $^{11}\text{B}/^{10}\text{B}$ ratio, u_a the uncertainty of the slope corresponding to the internal precision of the $^{11}\text{B}/^{10}\text{B}$ ratio, b the intercept of the regression and u_b the uncertainty of the intercept (Epov et al., 2010; Fietzke et al., 2008). Unlike the static analysis mode, transient analysis did not require any blank correction. Given that the on-peak zero baseline (0.05 N HNO_3 carrier solution, before and after the transient peak) is included in the linear regression (Figures 2d and 2e), the slope (i.e., the $^{11}\text{B}/^{10}\text{B}$ ratio) is then defined by a linear function weighted between the background and the maximum intensity. The linear regression method was proven to be more efficient for accurate and reproducible isotope ratio determination than the peak apex, peak area integration or point by point methods (Epov et al., 2010; Guéguen et al., 2015; Rodríguez-González et al., 2012).

As for the static mode, an $^{11}\text{B}/^{10}\text{B}$ ratio was determined for each B injection, and we performed quick sample-standard bracketing measurements in triplicate for each sample or reference material following Louvat et al. (2014). Multiple analyses of the reference solution ERM-AE121 were also regularly performed to ensure the quality of the $\delta^{11}\text{B}$ measurements in transient mode. Validation of the transient mode was also done with several aliquots of 5 μL (2.5 ng B) and 10 μL (5 ng B) of the reference material MVS-1 stock solution (500 ppb; Jurikova et al., 2019) diluted with 45 and 40 μL of HNO_3 0.5 N to mimic the B amount of the foraminifera samples on the beaker cap. MVS-1 aliquots were microdistilled and then diluted with 100 and 150 μL of 0.5 N HNO_3 , respectively, for a final B concentration of ~ 16.7 and ~ 25 ppb. From the same foraminifera solutions (after cleaning and dissolution), we repeated the microdistillation protocol with 50 μL of the carbonate solution, but only 150 μL of 0.5 N HNO_3 was added. This is why all the solutions of standards, reference materials, samples,

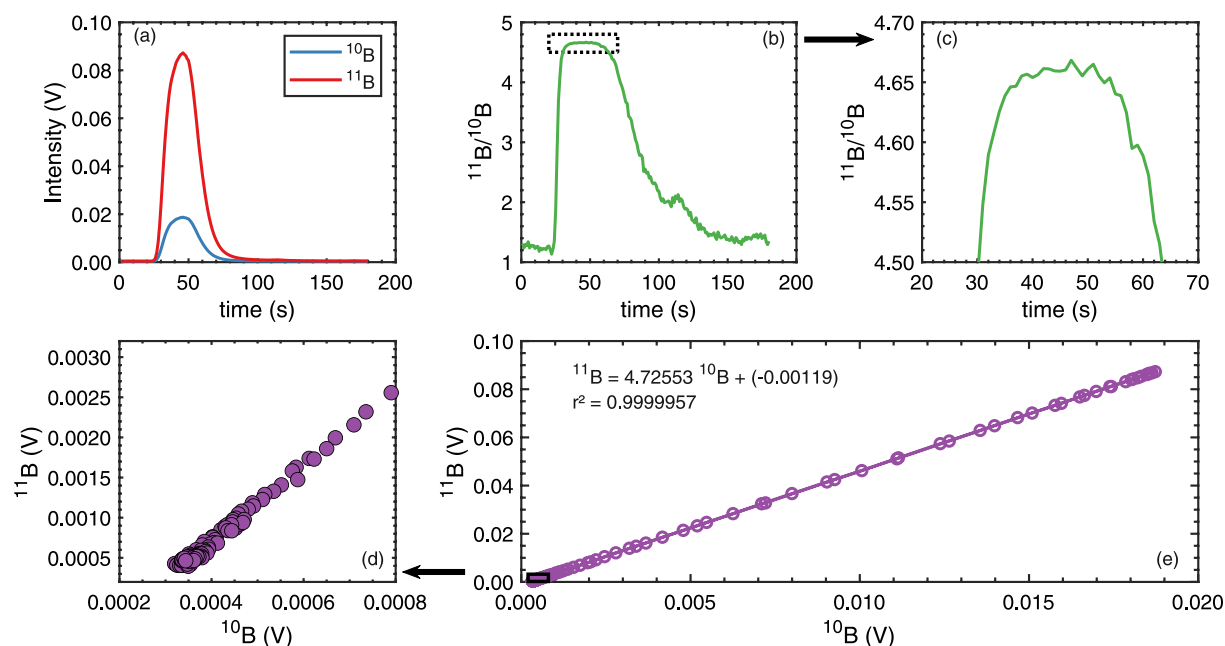


Figure 2. Example of an injection peak with a 10 μL sample loop, a sample uptake rate at 25 $\mu\text{L}\cdot\text{min}^{-1}$ and a B concentration of 5 ppb for the *G. bulloides* sample at the depth 23–24 cm and the fraction 250–315 μm . (a) Signal (in V) of the ^{10}B and ^{11}B masses during the measurement, including background before and after the transient signal. (b) Evolution of the $^{11}\text{B}/^{10}\text{B}$ ratio during the 180 s measurement. (c) Zoom on the peak apex reached during the $^{11}\text{B}/^{10}\text{B}$ ratio measurement. (d) Zoom on the start of the linear regression between ^{11}B (V) and ^{10}B (V), comprising the background measurement points. (e) Linear regression between the ^{11}B and the ^{10}B signals (V) from the 180 measurements to determine the $^{11}\text{B}/^{10}\text{B}$ ratio.

and the carrier solution were prepared in 0.5 N HNO_3 medium instead of 0.05 N HNO_3 to prevent matrix effects (Louvât et al., 2011). With the transient method, the triplicated measurement (10 μL sample loop) consumes only 80 μL , that is, $\sim 27 \mu\text{L}$ per injection, instead of 240 μL for static mode (50 μL sample loop; Louvat et al., 2019). This protocol allowed a significant increase in the B concentration of the sample solutions, reaching between 5 ppb (1 ng) and 25 ppb (5 ng), and in the ^{11}B signal intensity, ranging from 70 to 350 mV.

3. Results and Discussion

In the rest of this article, we chose to consider all foraminifera samples as markers of unique environmental conditions, the Holocene being perceived as a relatively stable climatic period compared to the Pleistocene and its interglacial/glacial oscillations (Indermühle et al., 1999; Kaufman & Broadman, 2023; Monnin, 2001; Monnin et al., 2004; Schmitt et al., 2012). Therefore, to compare our data and validate our analytical protocol, we chose to address the average of the $\delta^{11}\text{B}$ values measured along the upper part of the core.

3.1. Cleaning Efficiency

The presence of clay and Fe-Mn oxide remaining after cleaning can be evaluated by measuring Al/Ca and Mn/Ca ratios (Figure 3). The Mn/Ca ratio was very low for all the foraminifera sample solutions ($16.7 \pm 10.8 \mu\text{mol/mol}$, 2SD), lower than the limit of 30 $\mu\text{mol/mol}$ proposed by Martin and Lea (2002) for sufficient cleaning (Figure 3b). But most samples exhibited high Al/Ca ratios, above the “usual” threshold of 100 $\mu\text{mol/mol}$ (Rae et al., 2011). However, this ratio is not correlated with the measured $\delta^{11}\text{B}$ (in static mode, Figure 3a), excluding a potential impact of residual clays on the determination of $\delta^{11}\text{B}$ (e.g., Gutjahr et al., 2017; Henehan et al., 2019; Rae et al., 2011).

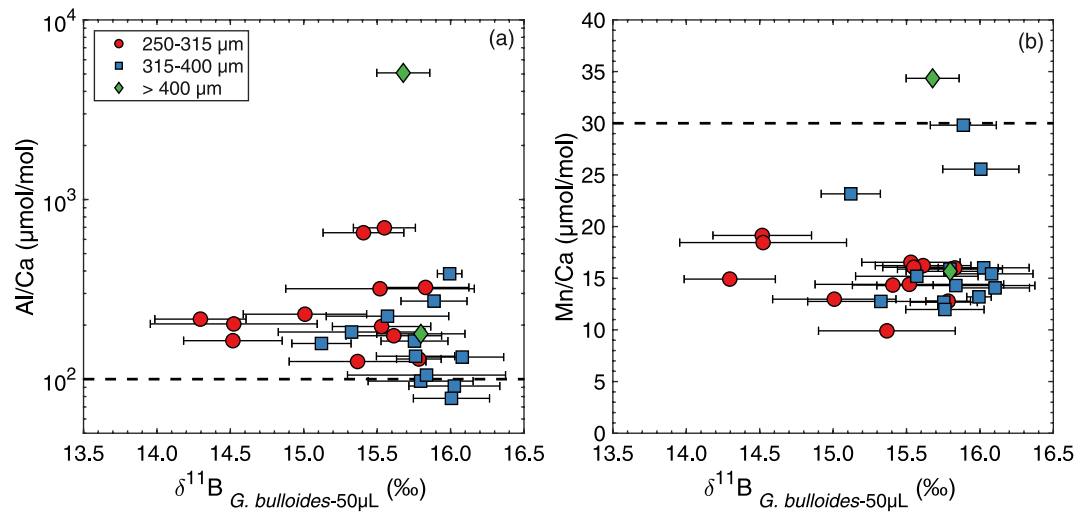


Figure 3. Crossplots between the Al/Ca ratio (a) and Mn/Ca ratio (b) against the $\delta^{11}\text{B}$ measured in static mode (50 μL loop) for the *G. bulloides* samples to check possible remaining contamination after cleaning. The dashed line for the Al/Ca ratio is the 100 $\mu\text{mol/mol}$ threshold determined by Rae et al. (2011) and the Mn/Ca threshold of 30 $\mu\text{mol/mol}$ from Martin and Lea (2002).

3.2. $\delta^{11}\text{B}$ Measurements

3.2.1. $\delta^{11}\text{B}$ Results in Static Mode

The boric acid reference material ERM-AE121 ($\delta^{11}\text{B} = +19.9 \pm 0.6\text{‰}$, Vogl & Rosner, 2011) averaged at $19.47 \pm 0.32\text{‰}$ (2SD, $n = 13$, Table 1, Figure 4) in complete agreement with the long-term IPGP value ($\delta^{11}\text{B} = 19.56 \pm 0.17\text{‰}$, 2SD, $n = 90$ for 200 ppb solutions, Buisson et al., 2021; Louvat et al., 2019). The slightly higher variability in the present study ($\pm 0.32\text{‰}$) is due to the measurements at very low concentrations, but is

Table 1

$\delta^{11}\text{B}$ Measurements Performed on the Certified Reference Solution ERM-AE121 (Vogl & Rosner, 2011) and the Carbonate Reference Material MVS-1 (Jurikova et al., 2019), Associated With the Concentration or the Amount of Boron at Which They Were Analyzed in Static Mode (50 μL Loop) or in Transient Mode (10 μL Loop)

ERM-AE121 ($19.9 \pm 0.6\text{‰}$)						MVS-1 ($15.95 \pm 0.19\text{‰}$, 2SD, $n = 46$)					
50 μL loop (static mode)			10 μL loop (transient mode)			50 μL loop (static mode)			10 μL loop (transient mode)		
[B] (ppb)	$\delta^{11}\text{B}$ (‰)	2SD (‰)	[B] (ppb)	$\delta^{11}\text{B}$ (‰)	2SD (‰)	m_{B} (ng)	$\delta^{11}\text{B}$ (‰)	2SD (‰)	m_{B} (ng)	$\delta^{11}\text{B}$ (‰)	2SD (‰)
1.6	19.28	0.18	5.4	19.61	0.21	15	16.02	0.14	2.5	15.67	0.20
1.7	19.60	0.53	8.0	19.66	0.38	20	15.93	0.26	2.5	15.77	0.22
2.5	19.35	0.22	10.0	19.55	0.53	20	15.95	0.14	2.5	15.77	0.24
2.6	19.16	0.21	10.0	19.73	0.18				2.5	15.80	0.15
2.8	19.69	0.30	17.0	19.56	0.31				2.5	15.83	0.21
3.1	19.40	0.12	20.0	19.63	0.33				2.5	15.88	0.04
3.2	19.42	0.28	25.0	19.65	0.23				2.5	15.92	0.50
3.6	19.42	0.61							2.5	15.96	0.19
4.2	19.66	0.24							5.0	15.84	0.22
5.0	19.67	0.14							5.0	15.84	0.24
5.5	19.46	0.22							5.0	15.87	0.23
6.3	19.49	0.15							5.0	15.99	0.26
6.3	19.55	0.13							5.0	16.04	0.23
									5.0	16.09	0.23
Mean	19.47	0.32	Mean	19.63	0.13	Mean	15.96	0.09	Mean	15.88	0.23

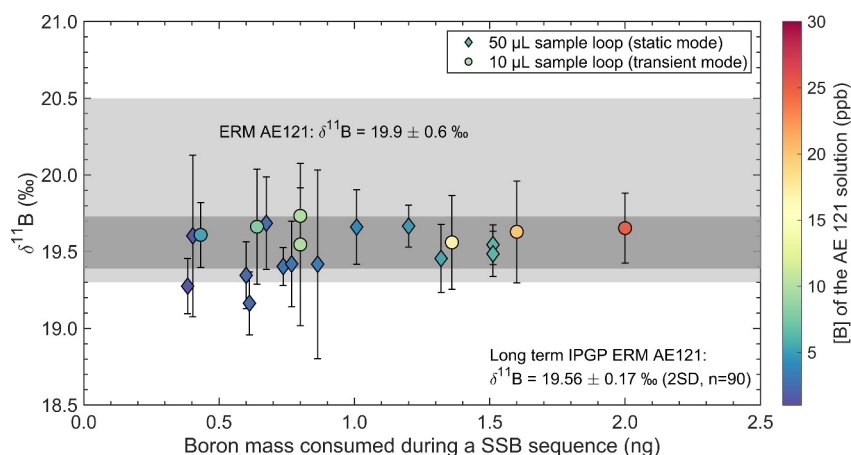


Figure 4. Reproducibility of the $\delta^{11}\text{B}$ measured at ~ 1.7 – ~ 25 ppb for the reference material ERM-AE121 according to the boron mass consumed during a standard-sample bracketing (SSB) sequence in static mode (50 μL sample loop, 240 μL of solution sampled) and in transient mode (10 μL sample loop, 80 μL of solution sampled). The light grey band corresponds to the reference value, $19.9 \pm 0.6\text{‰}$ (Vogl & Rosner, 2011), and the dark grey band corresponds to IPGP long-term reproducibility, $19.56 \pm 0.17\text{‰}$ (2SD, $n=90$; Buisson et al., 2021; Louvat et al., 2019).

similar to the reproducibility reported in Buisson et al. (2021; $\delta^{11}\text{B} = 19.55 \pm 0.34\text{‰}$, 2SD, $n = 103$) for [B] in the solution between 1 and 50 ppb. The average $\delta^{11}\text{B}$ value for the carbonate reference material MVS-1 was $15.96 \pm 0.09\text{‰}$ (2SD, $n = 3$, Table 1), in full agreement with the reference value of $15.95 \pm 0.19\text{‰}$ (2SD, $n = 46$, Jurikova et al., 2019).

Picking at least 400 individual *G. bulloides* shells per sample is usually recommended for providing enough boron to analyze (e.g., Martínez-Botí, Marino, et al., 2015). Our samples contained half as many shells (Table 2), and the measurements were therefore carried out on solutions with very low [B]. In static mode, *G. bulloides* $\delta^{11}\text{B}$ ranged between 14.30 and 15.83‰ with an average of $15.25 \pm 1.06\text{‰}$ (2SD, $n = 12$) for the 250–315 μm fraction. The two other fractions have very similar values, with an average of $15.79 \pm 0.57\text{‰}$ (2SD, $n = 13$, between 15.12 and 16.10‰) for the 315–400 μm and $15.74 \pm 0.17\text{‰}$ (2SD, $n = 2$) for the >400 μm size fraction (Table 2, Figure 5); this is in agreement within uncertainties with measurements carried out at AWI in Bremerhaven (Germany) on the same core samples ($15.89 \pm 0.32\text{‰}$, 2SD, $n = 4$, Table 2, Figure 5).

Three 250–315 μm samples have $\delta^{11}\text{B}$ values lower than the other samples from the same upper part of the core (stars in Table 2, purple box in Figure 5) and all of them had the lowest B concentrations measured in sample solutions (1.6–1.7 ppb, i.e., 0.80–0.85 ng B). Furthermore, one 250–315 μm sample at 2.5 ppb and one 315–400 μm sample with the lowest concentration for this fraction (2.6 ppb) show in the same way lower $\delta^{11}\text{B}$ values than the rest of the sample pools (stars in Table 2, purple box in Figure 5). The latter is, in addition, 1‰ lower than the $\delta^{11}\text{B}$ value of AWI at the same depth (25–26 cm, Table 2). They clearly appear as outliers, being lower or equivalent to the median – 1.5*IQR (interquartile range, i.e., 15.10‰) for the whole data set. This is in line with our previous observations that the protocol coupling the μ -dDIHEN setup and the microdistillation has a threshold at 1–2 ppb (0.5–1.0 ng B) where the measurement quality starts to worsen (Buisson et al., 2021). This phenomenon is mainly due to very low signal intensities (leading to poorer measurement statistics) and a greater influence of boron memory effect, contamination during the dilution steps and/or residual matrix effects, all contributing to lower $\delta^{11}\text{B}$ values. Procedural blanks are notably enriched in ^{10}B (Louvat et al., 2014). It is, however, noteworthy that some other $\delta^{11}\text{B}$ values around 2.3–2.5 ppb for the 250–315 μm fraction agree, in contrast, with measurements performed at higher concentrations (Table 2, Figure 5). Impacts of a poor cleaning can be ruled out as low $\delta^{11}\text{B}$ values do not translate into systematic high Al/Ca and Mn/Ca ratios (Figure 3). As there were no analytical issues, this difference in $\delta^{11}\text{B}$ values for samples measured at this very low level of [B] could be due to a slight contamination through the instrumental B memory effect or B evaporation from the opened vials (Buisson et al., 2021). The >400 μm and 315–400 μm fractions globally gathered more material than the 250–315 μm fractions (with probably less loss during cleaning, Table 2) and consequently were less concerned by these aforementioned effects (concentrations after microdistillation: 2.6–6.9 ppb for >400 μm and 315–400 μm and 1.6–4.2 ppb for 250–315 μm). These preliminary results shed light on the validity of the

Table 2

$\delta^{11}\text{B}$ Results Obtained in Static (50 μL) and Transient (10 μL) Mode for Three Different Size Fractions at IGP for *G. bulloides* Samples From the Upper Part of the Core PS97/122-1

<i>G. bulloides</i> samples			50 μL loop (static mode)			10 μL loop (transient mode)			AWI measurements		Al/Ca ($\mu\text{mol/mol}$)	Mn/Ca ($\mu\text{mol/mol}$)
Depth (cm)	Fraction (μm)	Tests	[B] (ppb)	$\delta^{11}\text{B}$ (‰)	2SD (‰)	[B] (ppb)	$\delta^{11}\text{B}$ (‰)	2SD (‰)	$\delta^{11}\text{B}$ (‰)	2SD (‰)		
15–16	250–315	150	3.1	15.37	0.47	11.7	15.68	0.33			125	10
17–18	250–315	150	1.6	14.52*	0.34						164	19
19–20	250–315	150	2.5	14.52*	0.57	10.7	15.63	0.36			203	18
21–22	250–315	150	3.6	15.41	0.28						653	14
23–24	250–315	150	1.7	15.01*	0.42	5.4	15.76	0.32			230	13
25–26†	250–315	150	1.6	14.30*	0.31	6.6	16.10	0.52			216	15
27–28	250–315	150	2.4	15.52	0.64	10.9	15.92	0.17			319	14
29–30	250–315	150	3.5	15.78	0.15	11.3	15.62	0.30			129	13
31–32	250–315	150	2.3	15.53	0.33						196	17
33–34	250–315	150	2.5	15.61	0.33	7.7	15.56	0.23			174	16
35–36	250–315	150	3.0	15.55	0.21						696	16
37–38	250–315	150	4.2	15.83	0.30	12.1	15.31	0.46			324	16
7–8	315–400	190	6.8	16.01	0.26	23.7	15.92	0.18			78	26
11–12	315–400	190	6.7	15.89	0.22	22.8	16.15	0.16			272	30
15–16	315–400	185	6.7	15.99	0.08	23.2	15.40	0.15			386	13
17–18	315–400	120	5.5	15.80	0.36	27.1	15.76	0.16			98	16
19–20	315–400	190	4.5	15.84	0.54	18.4	15.46	0.19	15.91	0.25	105	14
21–22	315–400	150	5.0	15.57	0.42	18.0	15.54	0.16	15.67	0.25	224	15
23–24	315–400	190	3.1	15.75	0.23	10.0	16.10	0.46			163	13
25–26†	315–400	150	2.6	15.12*	0.20	10.5	16.09	0.28	16.06	0.46	158	23
27–28	315–400	190	2.8	15.76	0.27	11.1	16.24	0.11			134	12
29–30	315–400	150	3.8	15.33	0.50	18.7	15.86	0.29	15.92	0.25	183	13
31–32	315–400	190	4.6	16.10	0.23	26.5	16.24	0.27			43	14
33–34	315–400	150	6.4	16.03	0.31	21.7	16.12	0.21			92	16
35–36	315–400	190				27.2	16.15	0.34			351	15
37–38	315–400	180	6.9	16.08	0.28	24.0	16.09	0.22			133	15
7–8	>400	100	6.0	15.68	0.18	20.1	15.68	0.19			5071	34
11–12	>400	80	6.4	15.80	0.30	24.1	15.57	0.19			179	16

Note. The number of shells picked per sample, B concentration after microdistillation, Al/Ca and Mn/Ca ratios to check the potential contaminations and $\delta^{11}\text{B}$ values for four exactly same depths determined at AWI following the protocol of Raitzsch et al. (2018) are also displayed. The dagger indicates the age of the 25–26 cm sample, 9276 ± 124 years, from ^{14}C measurements (the 18–19 cm sample, not measured here, exhibit an age of 7446 ± 83 years) whereas the stars symbolized discarded $\delta^{11}\text{B}$ values in the discussion part (see main text).

analytical protocol developed in Buisson et al. (2021) to measure boron isotopes in low [B] planktonic foraminifera samples. Nevertheless, for future studies using this method, we advise to measure samples with at least 3 ppb after the cleaning and microdistillation steps, corresponding to 1.5 ng B.

3.2.2. $\delta^{11}\text{B}$ Results in Transient Mode

In transient mode, the multiple analyses of the reference solution ERM-AE121 (Vogl & Rosner, 2011) and of the carbonate reference material MVS-1 (Jurikova et al., 2019), at low B concentrations (5–25 ppb) and B masses (2.5–5 ng) respectively to imitate the concentration range of the foraminifera solution samples, yielded $\delta^{11}\text{B}$ average values of $19.63 \pm 0.13\text{‰}$ (2SD, $n = 7$, Table 1, Figure 4) and $15.88 \pm 0.23\text{‰}$ (2SD, $n = 14$, Table 1, Figure 6), in full agreement with their reference values ($19.9 \pm 0.6\text{‰}$ and $15.95 \pm 0.19\text{‰}$, 2SD, $n = 46$).

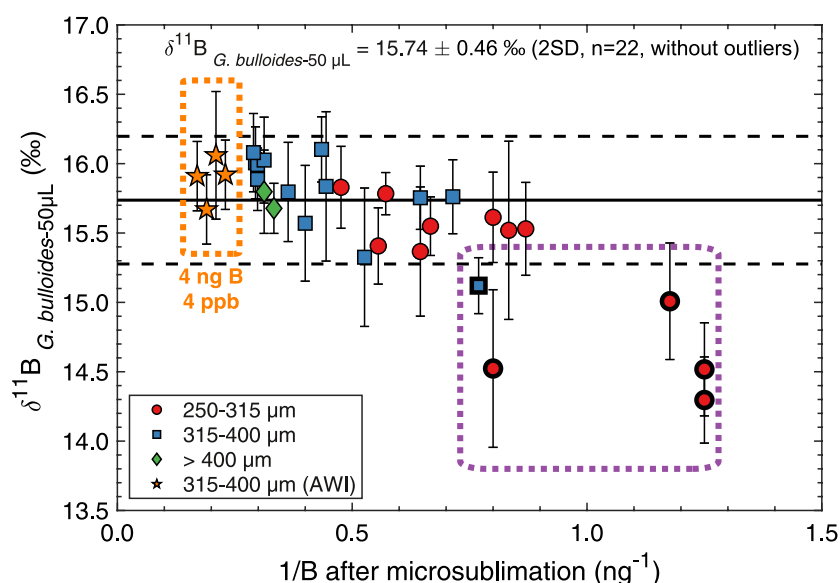


Figure 5. $\delta^{11}\text{B}$ of the *G. bulloides* samples measured in static mode (50 μL loop) plotted against $1/B$ (in ng^{-1}) after the microdistillation purification (Table 2). The solid and dotted black lines correspond to the mean and reproducibility, $15.74 \pm 0.46\text{‰}$ (2SD, $n = 22$), obtained from the three size fractions combined and without the five outlier values (see main text), surrounded by the dotted purple rectangle and with an accentuated black outline. Results of four samples from the same upper part of the core at the 315–400 μm size fraction (Table 2) measured in the AWI laboratory are also shown, following the analytical protocol described in Raitzsch et al. (2018). All measured at a concentration of 4 ppb, they are arbitrarily placed in the dotted orange rectangle.

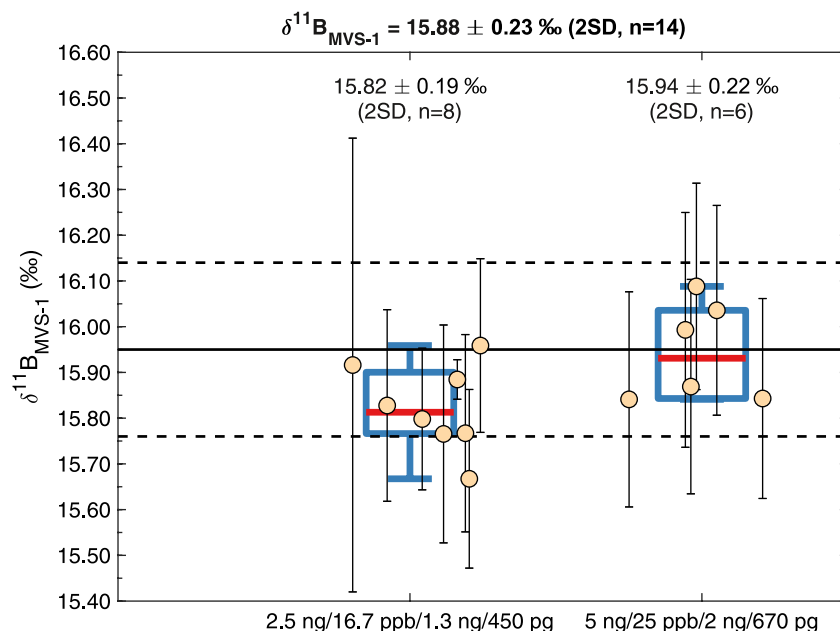


Figure 6. Reproducibility of $\delta^{11}\text{B}$ analyses ($15.88 \pm 0.23\text{‰}$, 2SD, $n = 14$) achieved in transient mode (10 μL loop) on the carbonate reference material MVS-1 (Jurikova et al., 2019) compared to the reference value of $15.95 \pm 0.19\text{‰}$ (2SD, $n = 46$) represented by the dashed and solid black lines. The statistical parameters are expressed as box plots in blue, with the median in red. 2.5 (left box plot) and 5 ng (right box plot) of boron were loaded on the cap of the beaker for the microdistillation separation, for, respectively, a final solution of 16.7 ppb (final volume of 150 μL) and 25 ppb (final volume of 200 μL), a total boron consumption during a SSB of 1.3 and 2 ng and a boron mass consumed per injection of 450 and 670 pg.

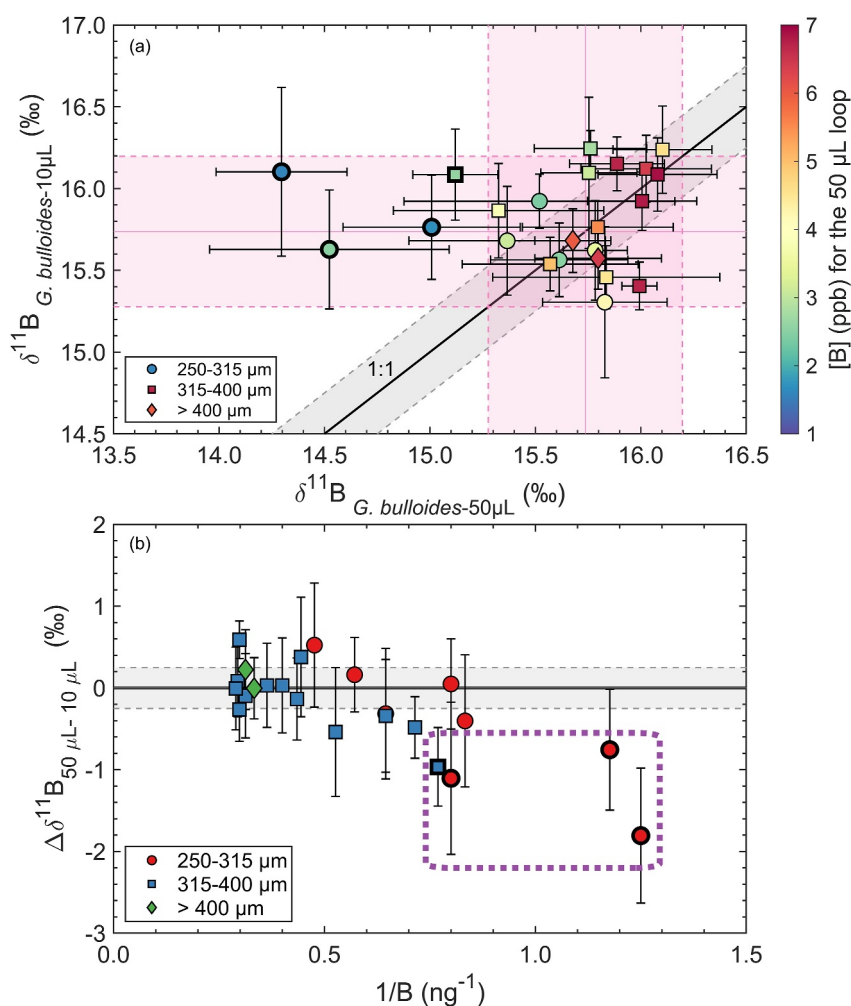


Figure 7. (a) Crossplot between the $\delta^{11}\text{B}$ of *G. bulloides* measured in static mode with a 50 μL sample loop and the $\delta^{11}\text{B}$ measured in transient mode with a 10 μL sample loop. The color code provides the B concentration at which the samples have been measured for the static mode (Table 2). The dark grey band represents the 0.25‰ envelope around the 1:1 line, whereas the pink bands define our measurements envelope from the static mode without the outliers (Table 2, $15.74 \pm 0.46\text{‰}$, 2SD, $n = 22$). (b) Difference between $\delta^{11}\text{B}$ measurements of *G. bulloides* in static and transient mode against $1/B$ (in ng^{-1}) after the microdistillation purification (Table 2) for the three size fractions. The grey band corresponds to a 0.25‰ envelope centered on the zero black line. The outliers (stars in Table 2) are highlighted with the darker outlines in panels (a) and (b), and the dotted purple rectangle in panel (b).

Especially, $\delta^{11}\text{B}$ values of MVS-1 aliquots displayed excellent individual 2SD repeatability, between 0.04 and 0.26‰ (with one exception at 0.50‰, Table 1, Figure 6), for only 1.3 and 2 ng B consumed during a triplicate SSB analysis, that is, 450 and 670 pg per injection, respectively. This transient method led to a threefold reduction in the total volume consumed, a threefold increase in the sample solutions [B], and a decrease in memory effect due to the smaller volumes injected. These results emphasize that the matrix acidity (0.05 or 0.5 N) and the $10^{13}\Omega$ resistors as amplifiers (much slower than the $10^{11}\Omega$ resistors) did not alter the analysis quality in the transient mode.

The average $\delta^{11}\text{B}$ of the foraminifera samples measured in transient mode was $15.94 \pm 0.58\text{‰}$ (2SD, $n = 14$, between 15.40 and 16.24‰) for the 315–400 μm fractions and $15.63 \pm 0.15\text{‰}$ (2SD, $n = 2$) for the 400–315 μm fractions, analytically indistinguishable from the static mode values (Table 2, Figure 7). Compared to the static mode, $\delta^{11}\text{B}$ reproducibility for the 125–250 μm fraction was improved. Four of the five samples with low [B] that were outliers in the static mode were measured in the average range with the transient mode ($15.70 \pm 0.48\text{‰}$, 2SD, $n = 8$), in good agreement with the other sample size fractions (Table 2, Figure 7a). Moreover, these measurements with transient signals allow us to attest the accuracy of the $\delta^{11}\text{B}$ values at 2.4 and 2.5 ppb

(250–315 μm fraction, 29–30 and 33–34 cm), called into question in static mode (Table 2, Figures 5 and 7). By extension, the $\delta^{11}\text{B}$ value at 2.3 ppb (250–315 μm fraction, 31–32 cm, Table 2) is then considered accurate, although no other measurements have been able to confirm this, as it is very close to the $\delta^{11}\text{B}$ values obtained at the same concentration and validated with the transient mode. Altogether, the transient $\delta^{11}\text{B}$ measurement approach (with the 10 μL sample loop of the $\mu\text{-dDIHEN}$) shows an excellent agreement with the traditional method (e.g., AWI measurements) and the static mode (above 3 ppb), but additionally offers the possibility to measure samples with very low B concentrations at higher precision and accuracy (Figure 7) thanks to the threefold reduction in required sample volume and therefore a threefold increase in boron concentration. In the end, considering the lowest concentrations measured in transient mode (5.4–6.6 ppb, 1.1–1.3 ng B in 200 μL), this analytical development corresponds to a very low level of boron analyzed of 400 pg (80 μL for a sample standard bracketing in triplicate, i.e., ~ 125 pg of boron per injection), for 2SD reproducibilities reaching 0.32 and 0.52‰ (2SD, Table 2, Figure 1). This method, therefore, provides data for samples with low B content, with the added advantage of not requiring background correction.

3.3. Comparison With $\delta^{11}\text{B}$ From Other *G. bulloides* Calibrations

We echo that the pool of samples studied here reflects a relatively stable climatic period in the Holocene, and the relative stability has more or less lasted throughout the Holocene ($\pm 1^\circ\text{C}$ for the global surface temperature, 260–280 ppm for $p\text{CO}_2$; Kaufman & Broadman, 2023; Liu et al., 2014). Consequently, there was no significant change in carbonate chemistry and temperature during the studied interval of time. However, a part of the measured variability in our samples could likely be due to bioturbation, difference in the calcification depth or natural variability (e.g., Lamy et al., 2010; Moreno et al., 2010), with probable seasonal changes in hydrographic parameters associated with foraminiferal fluxes throughout the studied time period (Guillermic et al., 2020; Raitzsch et al., 2018). On the other hand, the observed $\delta^{11}\text{B}$ discrepancy in this paper is small, and its association with uncertainties for such low B-concentrated samples perfectly reflects the classical reproducibilities, standard deviations and divergences between laboratories (Foster et al., 2013; Gutjahr et al., 2021).

To compare our data with the existing *G. bulloides* calibrations, we calculated the $\delta^{11}\text{B}$ value of the seawater borate at the sampling location conditions with the following relationship (Foster & Rae, 2016):

$$\delta^{11}\text{B}_{\text{Borate}} = \frac{\delta^{11}\text{B}_{\text{sw}} + (\delta^{11}\text{B}_{\text{sw}} - \epsilon_B) * 10^{pK_B^* - \text{pH}}}{1 + \alpha_B * 10^{pK_B^* - \text{pH}}} \quad (3)$$

We first determined pH at the sampling site. Total modern alkalinity and atmospheric CO_2 are the two parameters of the oceanic carbonate system used to resolve the other parameters (Zeebe & Wolf-Gladrow, 2001). The total alkalinity (TA, 2270 ± 8 $\mu\text{mol/kg}$, 2SD) was obtained from the nearest available location to PS97/122-1 in the GLODAPv2.2023 data set (Lauvset et al., 2024) through Ocean Data View (ODT, Schlitzer, 2015). The estimate of $p\text{CO}_2$ during the Holocene comes from Antarctic ice cores (Köhler et al., 2017), set at 270 ± 10 ppm (2SD) with an annual mean disequilibrium at the core site of $\sim +6$ ppm (Takahashi et al., 2009). These data were then combined with the annual temperature ($7.29 \pm 2.16^\circ\text{C}$, 2SD), annual salinity (33.84 ± 0.21 psu, 2SD) from the World Ocean Atlas 2023 (WOA23, Reagan et al., 2024) and pressure (0 bar, *G. bulloides* living mainly above the thermocline in the first 60 m of depths, Schiebel & Hemleben, 2017), parameters also needed to establish the thermodynamic constants for the oceanic carbon and boron systems.

This allowed us to calculate the pH using the CO2SYSv3 program for MATLAB (8.180 ± 0.014 , total scale; Sharp et al., 2023), with the dissociation constants for the carbonate system from Lueker et al. (2000). The dissociation constant of boric acid, pK_B^* , was derived from the equation of Dickson (1990), whereas the boron isotope fractionation factor between boric acid and borate anion (α_B) is taken as 1.0272 ± 0.0006 (Klochko et al., 2006), ϵ_B as $(\alpha_B - 1) * 1000$ and the constant $\delta^{11}\text{B}_{\text{sw}}$ of seawater as 39.61 ± 0.20 ‰ (2SD, Foster et al., 2010). The final calculated $\delta^{11}\text{B}_{\text{Borate}}$ is 17.10 ± 0.35 ‰ (2SD), obtained with 1000 Monte-Carlo simulations.

For each size fraction, all $\delta^{11}\text{B}$ measurements (static and transient modes, and the four AWI data) were averaged, except for the values of the outliers defined above (Table 3). The 250–315 μm fraction exhibits a value of 15.64 ± 0.37 ‰ (2SD, $n = 11$), the 315–400 μm 15.93 ± 0.38 ‰ (2SD, $n = 14$) and the >400 μm 15.68 ± 0.44 ‰ (2SD, $n = 2$). These $\delta^{11}\text{B}$ values fit in the linear regression of the species-specific $\delta^{11}\text{B}_{\text{Borate}} - \delta^{11}\text{B}_{G.\text{bulloides}}$ calibration

Table 3

Average $\delta^{11}\text{B}$ per Depth for the Three Different Size Fractions 250–315, 315–400 and >400 μm of *G. bulloides* Samples From the Upper Part of the Core PS97/122-1, Compiling the $\delta^{11}\text{B}$ Results From the Static and Transient Mode Measurement Method Achieved at IPGP and From the AWI Laboratory, Without the Outliers Marked by Stars in Table 2

<i>G. bulloides</i> sample	250–315 μm fraction		315–400 μm fraction		>400 μm fraction	
Depth (cm)	$\delta^{11}\text{B}$ (‰)	U (‰)	$\delta^{11}\text{B}$ (‰)	U (‰)	$\delta^{11}\text{B}$ (‰)	U (‰)
7–8			15.96	0.32	15.68	0.27
11–12			16.02	0.28	15.69	0.35
15–16	15.52	0.57	15.70	0.17		
17–18			15.78	0.39		
19–20	15.63	0.36	15.73	0.62		
21–22	15.41	0.28	15.59	0.51		
23–24	15.76	0.32	15.92	0.52		
25–26	16.10	0.52	16.07	0.54		
27–28	15.72	0.66	16.00	0.29		
29–30	15.70	0.34	15.70	0.63		
31–32	15.53	0.33	16.17	0.36		
33–34	15.59	0.40	16.07	0.37		
35–36	15.55	0.21	16.15	0.34		
37–38	15.57	0.55	16.08	0.36		
Mean	15.64	0.37	15.93	0.38	15.68	0.44

Note. The final uncertainties have been calculated as $U = \sqrt{2SD_{\text{Static}}^2 + 2SD_{\text{Transient}}^2 + 2SD_{\text{AWI}}^2}$ for each depth as well as for the >400 μm size fraction average, whereas for the 250–315 μm and 315–400 μm size fraction average the 2 standard deviation was calculated.

(Figure 8, Martínez-Botí, Marino, et al., 2015; Raitzsch et al., 2018), with ~ 2.5 – ~ 4.5 times fewer shells than the study of Martínez-Botí, Marino, et al. (2015, 450–600 vs. 150–190 shells, Table 2). This further validates our analytical protocol to measure $\delta^{11}\text{B}$ of foraminifera samples at very low B concentration.

3.4. Biomineralization Impact and Ontogenetic Variability for $\delta^{11}\text{B}$ in *G. bulloides*

As well as validating our measurement method for low [B] foraminifera samples, this series of *G. bulloides* samples allows us to investigate potential biomineralization and size effects on the $\delta^{11}\text{B}$ values for this foraminifera species. The $\delta^{11}\text{B}$ average for the 250–315 μm fraction ($15.64 \pm 0.37\text{‰}$, Table 3) is within errors identical to the value for the 315–400 μm fraction ($15.93 \pm 0.38\text{‰}$, Table 3). Furthermore, we can also observe this lack of size effect individually at each depth of the upper part of the core, showing that the $\delta^{11}\text{B}$ difference within uncertainties is negligible with the same maximum discrepancy of ~ 0.25 – 0.30‰ (Figure 9). This range also perfectly reflects the classical reproducibility's standard deviation and divergences between laboratories (Foster et al., 2013; Gutjahr et al., 2021). Moreover, no clear trend emerges with depth (Figure 9b), with an average of $15.79 \pm 0.45\text{‰}$ for the whole pool of samples. Nevertheless, only two foraminifera samples from the >400 μm fraction were measured, limiting a firm conclusion on the absence of size effect for foraminifera between 250 and >400 μm .

Size effects for geochemical proxies such as $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{11}\text{B}$, B/Ca, Mg/Ca or Sr/Ca have been widely documented for planktonic foraminifera, illustrating the complexity of biomineralization processes (Friedrich et al., 2012; Henehan et al., 2013; Hönisch & Hemming, 2004; Kroon & Darling, 1995; Ni et al., 2007; Osborne et al., 2020; Peeters et al., 2002). Specifically, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Mg/Ca offsets between size fractions for *G. bulloides* are caused by combined environmental and metabolic conditions such as depth habitat, vertical migration, seasonality or ontogeny (and without the influence of symbionts). These conditions thus play a role in temperature, $\delta^{13}\text{C}_{\text{DIC}}$, carbonate chemistry of seawater, precipitation rate or metabolism reactions (metabolic CO_2 , food source) during calcification processes (e.g., Friedrich et al., 2012; Jonkers et al., 2013; Kroon & Darling, 1995; Peeters et al., 2002; Spero & Lea, 1996).

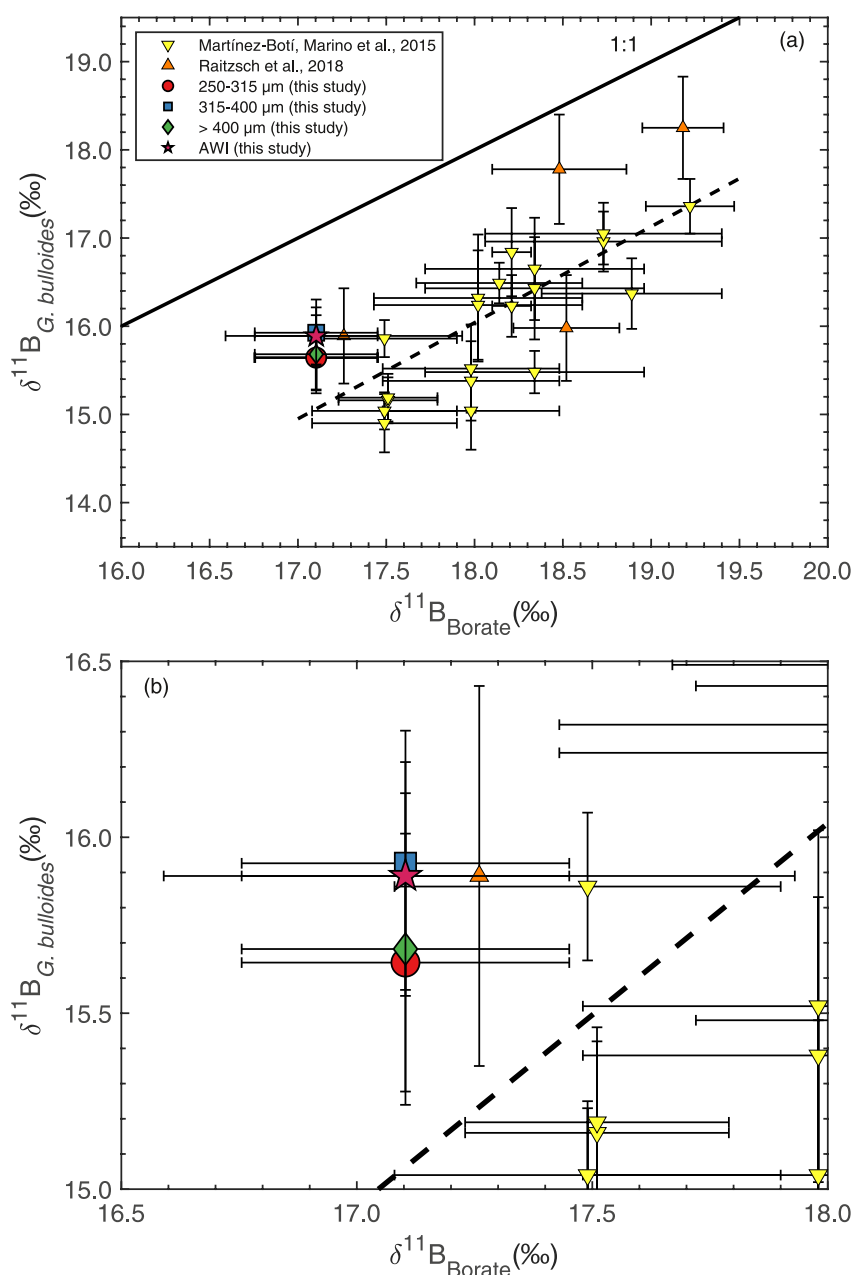


Figure 8. Comparison of the $\delta^{11}\text{B}$ measured in *G. bulloides* planktonic foraminifera against the $\delta^{11}\text{B}$ of the borate in the ambient seawater, calculated from the carbonate chemistry of the sampling location, with in panel (a) the global compilation and (b) a zoom on our *G. bulloides* measurements. The mean of the different fraction sizes is reported with their associated $\delta^{11}\text{B}_{\text{borate}}$, as well as the mean value measured at the AWI (see text for more details). The literature data come from Martínez-Botí, Marino, et al. (2015; yellow inverted triangles, 250–300 μm , 300–355 μm and 355–400 μm) and Raitzsch et al. (2018; orange triangles, 315–355 μm). The black dashed line corresponds to the calibration proposed for this species, $\delta^{11}\text{B}_{\text{G. bulloides}} = 1.09 (\pm 0.65) \cdot \delta^{11}\text{B}_{\text{borate}} - 3.58 (\pm 11.77)$ from Raitzsch et al. (2018) and the black line, the 1:1 line.

For boron isotopic compositions, the slight deviation, positive or negative, between the $\delta^{11}\text{B}$ of the seawater $\text{B}(\text{OH})_4^-$ and the $\delta^{11}\text{B}$ of planktonic foraminifera samples highlights that the incorporation of the tetrahedral borate anion is not the sole mechanism governing $\delta^{11}\text{B}$ during the species-specific biomineralization (with different slope/intercept combinations for calibrations; Foster, 2008; Guillermic et al., 2020; Hennehan et al., 2013, 2016; Martínez-Botí, Marino, et al., 2015; Raitzsch et al., 2018; Sanyal et al., 2001). The uniqueness of the tetrahedral coordination has been challenged from the start with multiple pieces of evidence of some trigonal coordination in calcite (Branson et al., 2015; Noireaux et al., 2015; Rollion-Bard et al., 2011; Sen et al., 1994;

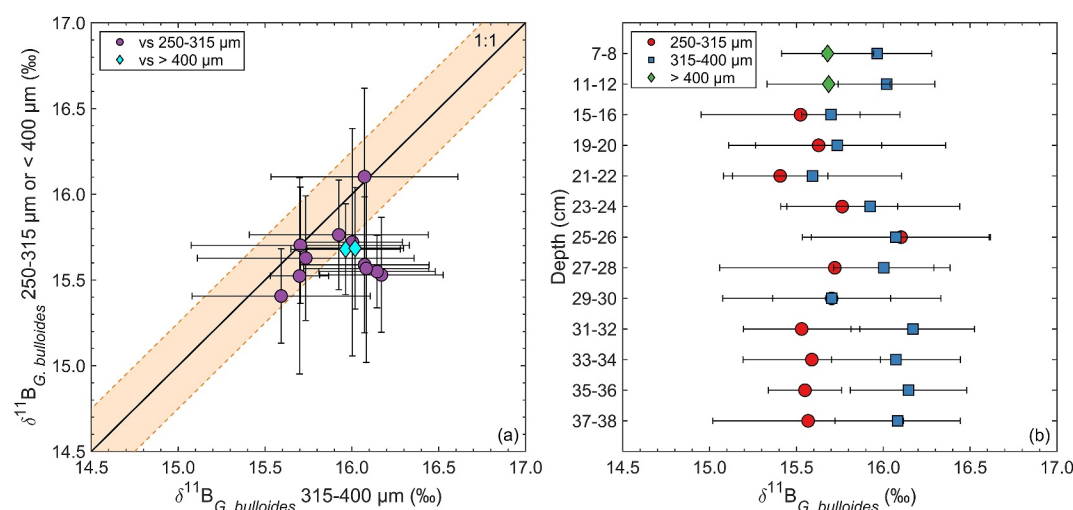


Figure 9. (a) Crossplot between the averaged *G. bulloides* $\delta^{11}\text{B}$ values (Table 3) of the size fraction 315–400 μm and the size fraction 250–315 μm (purple circle) or >400 μm (turquoise diamond). The orange band characterizes the 0.25‰ envelope around the 1:1 line. (b) Averaged *G. bulloides* $\delta^{11}\text{B}$ for the three size fractions 250–315, 315–400 and >400 μm according to the depth at which they were sampled in the core PS97/122-1.

Uchikawa et al., 2015). As ^{11}B -enriched boric acid incorporation seems unlikely, with $\delta^{11}\text{B}_{\text{calcite}}$ values that should be much higher than those observed, this trigonal form must instead result from a re-coordination of the tetrahedral borate (Balan et al., 2016; Hemming et al., 1995; Klochko et al., 2009; Rae, 2018). For *G. bulloides* species, as well as for some other planktonic foraminifera, $\delta^{11}\text{B}$ is lower than the seawater $\delta^{11}\text{B}_{\text{borate}}$ that should have been incorporated (Guillermic et al., 2020; Henehan et al., 2016; Martínez-Botí, Marino, et al., 2015; Raitzsch et al., 2018; Yu et al., 2013). Some kinetic isotopic effects (Pagani et al., 2005) can be ruled out as the equilibration time for boron isotopes between $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ is 3–4 times faster than the growth rate of marine biogenic carbonates (Zeebe et al., 2001). The difference between the seawater $\delta^{11}\text{B}_{\text{borate}}$ and the $\delta^{11}\text{B}_{\text{calcite}}$ value for planktonic foraminifera would then arise from manipulating the calcifying fluid before the calcite precipitation. Indeed, it has been observed that many foraminifera increase the pH of the calcifying fluid isolated from seawater to promote the CaCO_3 precipitation. A pH elevation of up to 9 was observed from direct pH measurements or deduced from the $\delta^{11}\text{B}_{\text{calcite}}$ of some foraminifera species (Bentov et al., 2009; de Nooijer et al., 2009; Erez, 2003; Jørgensen et al., 1985; Nehrke et al., 2013; Rollion-Bard & Erez, 2010). However, this significant rise of pH does not necessarily result in a high $\delta^{11}\text{B}_{\text{calcite}}$, as this latter stays close to the seawater $\delta^{11}\text{B}_{\text{borate}}$ (Figure 8; e.g., Henehan et al., 2013, 2016; Raitzsch et al., 2018). Furthermore, an increase in the pH of the calcifying fluid cannot explain the lower $\delta^{11}\text{B}_{\text{calcite}}$ values than the seawater $\delta^{11}\text{B}_{\text{borate}}$ in *G. bulloides* (Figure 8).

The most plausible cause for lower $\delta^{11}\text{B}$ values in *G. bulloides* would then rely on modifications of the foraminiferal microenvironment, a region (diffusive boundary layer) where nutrients, oxygen and dissolved carbon species are transported by diffusion with strong gradients (Köhler-Rink & Köhl, 2000, 2005; Rink et al., 1998). Short equilibrium time and diffusion of the dissolved carbon species make this layer around the foraminifera very sensitive to physiological processes (Hönisch et al., 2003, 2021; Zeebe et al., 1999, 2003), like symbiont photosynthesis ($\text{CO}_2 + \text{H}_2\text{O} = \text{CH}_2\text{O} + \text{O}_2$), respiration ($\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$) and calcification ($\text{Ca}^{2+} + 2\text{HCO}_3^- = \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ or $\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3$). According to the predominant symbiont and biological process, the effect on the local pH and foraminifera $\delta^{11}\text{B}$ can be both ways. Symbiont-bearing species such as *G. ruber* and *T. sacculifer* thus exhibit a microenvironment slightly basified (0.1–0.3 pH unit) compared to surrounding seawater due to the photosynthetic activities of the symbiotic dinoflagellate, raising consequently the $\delta^{11}\text{B}_{\text{calcite}}$ of the precipitated shell (Foster, 2008; Guillermic et al., 2020; Henehan et al., 2013, 2016; Raitzsch et al., 2018). Conversely, for symbiont-barren foraminifera such as *Neoglobobulimina papyroderma*, *Neoglobobulimina dutertrei* or *G. bulloides*, the microenvironment pH decreases due to calcification and respiration, leading to a $\delta^{11}\text{B}_{\text{calcite}}$ lower than the seawater $\delta^{11}\text{B}_{\text{borate}}$ (Figure 8, Guillermic et al., 2020; Martínez-Botí, Marino, et al., 2015; Raitzsch et al., 2018; Yu et al., 2013).

Size effects have been reported for *G. ruber* and *T. sacculifer*, $\delta^{11}\text{B}_{\text{calcite}}$ increasing with the size in conjunction with the increasing density of symbionts around larger shells (Henehan et al., 2013, 2016; Hönisch et al., 2021; Hönisch & Hemming, 2004). For *G. bulloides*, the lack of symbionts and the absence of this physiological influence (Henehan et al., 2013, 2016; Martínez-Botí, Marino, et al., 2015) mean no relationship between $\delta^{11}\text{B}$ and the size of foraminifera shells, consistent with our observations in this study. Interestingly, the same observations apply for the B/Ca ratio, with higher B/Ca in larger size fractions for *G. ruber* (Babila et al., 2014), but no difference for *G. bulloides* (Osborne et al., 2020). This finding supports the reliability of $\delta^{11}\text{B}$ measurements across a range of ontogenetic stages, enhancing the utility of small-sized specimens in paleo-pH reconstructions.

4. Conclusion

The protocol for the determination of $\delta^{11}\text{B}$ on marine biogenic carbonates with low B concentrations, coupling the μ -dDIHEN setup for the direct injection of small volumes of samples into the MC-ICP-MS and the boron purification by microdistillation (Buisson et al., 2021), was applied here to foraminifera samples of *G. bulloides* from the upper 7–38 cm of a sediment core sampled on the Chilean margin. This species has the lowest B concentration among planktonic foraminifera. In this study, only half (~100–200) of the usual number of foraminifera was picked for three different shell sizes to address the ontogenetic $\delta^{11}\text{B}$ variations. The MC-ICP-MS measurements in transient mode, with a 10 μL sample injection loop, yielded repeatable $\delta^{11}\text{B}$ data, comparable to the conventional measurements performed in another laboratory (AWI) and in static mode (50 μL loop) for sample solutions with $[\text{B}] > 3$ ppb. This again assesses the validity of these transient signal analyses for very low sample volumes. Below 3 ppb, $\delta^{11}\text{B}$ measurements in static mode are, however, impacted by higher relative blank contribution. Measurements in transient signal mode, with a threefold lowering of the injected sample volume and consequently a threefold increase of solution sample $[\text{B}]$, allowed for even more accurate $\delta^{11}\text{B}$ values compared to the static mode below this 3 ppb threshold (1.5 ng B), with down to 400 pg of boron per injection (5 ppb solution, ~1 ng B) for 2SD reproducibilities reaching 0.3‰. This is the lowest amount of boron ever analyzed for such precision on bulk carbonate samples with MC-ICP-MS. The $\delta^{11}\text{B}$ values of the *G. bulloides* foraminifera samples from this study matched with the known $\delta^{11}\text{B}_{\text{Borate}}\text{--}\delta^{11}\text{B}_{G.\text{bulloides}}$ calibrations (Martínez-Botí, Marino, et al., 2015; Raitzsch et al., 2018), validating our $\delta^{11}\text{B}$ measurements on low-B containing samples. The three size fractions (250–315 μm , 315–400 μm and >400 μm) of the symbiont-barren *G. bulloides* showed no significant variations of $\delta^{11}\text{B}$. This lack of variation, directly linked to the microenvironment pH of *G. bulloides*, is explained by the absence of symbionts for these species.

The precise and accurate triplicated $\delta^{11}\text{B}$ determination in transient mode with only 1 ng of B and 80 μL of sample solution paves the way towards smaller samples and widens possible geochemical applications. This protocol could, for example, be helpful to improve knowledge on biomineralization processes of larger organisms such as corals, brachiopods, or mollusks by subsampling different parts of their structures without the significant uncertainties of *in situ* analysis (SIMS, LA-MC-ICP-MS) or to study inter-shell variability for benthic foraminifera by analyzing only one individual. Being able to multiply and/or diversify analyses for samples as small as planktonic foraminifera finally offers the opportunity to bring more constraints on the paleoclimatic and paleoceanographic reconstructions. But the transient signal method can also be adapted to other low-boron archives such as mollusks or diatom frustules, broadening the applicability of high-resolution $\delta^{11}\text{B}$ analysis across paleoclimate archives.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

All data generated for this study are published in this manuscript (Tables 1 and 2) and available in Paulhac Buisson et al., 2025.

References

- Alves, A., Paulhac Buisson, M., Louvat, P., Rollion-Bard, C., Bassinot, F., Gray, W. R., et al. (2024). Sea surface acidification events in the Andaman Sea associated with the last Toba volcanic activity. *Global and Planetary Change*, 237, 104460. <https://doi.org/10.1016/j.gloplacha.2024.104460>

Acknowledgments

We want to thank Beate Müller (AWI) and William R. Gray (LSCE, Université Paris Saclay) for their valuable help and comments for learning and developing the foraminifera cleaning protocol at IPGP, and Pierre Burckel and Barthélémy Julien (IPGP) for their analytical support. Annachiara Bartolini (CR2P, Sorbonne Université) and Guillaume Paris (CRPG, Université de Lorraine) are thanked for their helpful comments on the manuscript. We finally acknowledge Gesine Mollenhauer and Hendrik Grotheer (AWI) for the radiocarbon analysis. Sambuddha Misra and two anonymous reviewers are thanked for their insightful, thorough and helpful comments on our manuscript. This work was supported by the French National Research Agency (ANR) through the Franco-German project B2SeaCarb (ANR-16-CE92-0010). Parts of this work were supported by the IPGP multidisciplinary program PARI and by the Paris-IdF Region SESAME Grant 12015908.

- Babila, T. L., Rosenthal, Y., & Conte, M. H. (2014). Evaluation of the biogeochemical controls on B/Ca of *Globigerinoides ruber* white from the Oceanic Flux Program, Bermuda. *Earth and Planetary Science Letters*, 404, 67–76. <https://doi.org/10.1016/j.epsl.2014.05.053>
- Balan, E., Pietrucci, F., Gervais, C., Blanchard, M., Schott, J., & Gaillardet, J. (2016). First-principles study of boron speciation in calcite and aragonite. *Geochimica et Cosmochimica Acta*, 193, 119–131. <https://doi.org/10.1016/j.gca.2016.07.026>
- Barker, S., Greaves, M., & Elderfield, H. (2003). A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. *Geochemistry, Geophysics, Geosystems*, 4(9). <https://doi.org/10.1029/2003GC000559>
- Bentov, S., Brownlee, C., & Erez, J. (2009). The role of seawater endocytosis in the biomineralization process in calcareous foraminifera. *Proceedings of the National Academy of Sciences*, 106(51), 21500–21504. <https://doi.org/10.1073/pnas.0906636106>
- Branson, O., Kaczmarek, K., Redfern, S. A. T., Misra, S., Langer, G., Tyliczszak, T., et al. (2015). The coordination and distribution of B in foraminiferal calcite. *Earth and Planetary Science Letters*, 416, 67–72. <https://doi.org/10.1016/j.epsl.2015.02.006>
- Buisson, M., Louvat, P., Thaler, C., & Rollion-Bard, C. (2021). High precision MC-ICP-MS measurements of $^{11}\text{B}/^{10}\text{B}$ ratios from ng amounts of boron in carbonate samples using microsublimation and direct injection (μ -DIHEN). *Journal of Analytical Atomic Spectrometry*, 36(10), 2116–2131. <https://doi.org/10.1039/D1JA00109D>
- Caldeira, K., & Wickett, M. E. (2003). Anthropogenic carbon and ocean pH: Oceanography. *Nature*, 425(6956), 365. <https://doi.org/10.1038/425365a>
- Catanzaro, E. J., Champion, C. E., Garner, E. L., Marinenko, G., Sappenfield, K. M., & Shields, W. R. (1970). Standard reference materials: Boric acid; isotopic, and assay standard reference materials. *US National Bureau Standards Special Publication*, 260, 17–70.
- Chalk, T. B., & Rollion-Bard, C. (2025). Boron proxies: From calcification site pH to Cenozoic pCO_2 . *Elements*, 21(2), 98–104. <https://doi.org/10.2138/gselements.21.2.98>
- Chanakya, I. V. S., & Misra, S. (2022). Accurate and precise determination of the boron isotope ratio by QQQ-ICP-MS: Application to natural waters and carbonates. *Journal of Analytical Atomic Spectrometry*, 37(6), 1327–1339. <https://doi.org/10.1039/D2JA00051B>
- Clarkson, M. O., Kasemann, S. A., Wood, R. A., Lenton, T. M., Daines, S. J., Richoz, S., et al. (2015). Ocean acidification and the Permo-Triassic mass extinction. *Science*, 348(6231), 229–232. <https://doi.org/10.1126/science.aaa0193>
- Cusack, M., Kamenos, N. A., Rollion-Bard, C., & Tricot, G. (2015). Red coralline algae assessed as marine pH proxies using ^{11}B MAS NMR. *Scientific Reports*, 5(1), 8175. <https://doi.org/10.1038/srep08175>
- de Nooijer, L. J., Spero, H. J., Erez, J., Bijma, J., & Reichart, G. J. (2014). Biomineralization in perforate foraminifera. *Earth-Science Reviews*, 135, 48–58. <https://doi.org/10.1016/j.earscirev.2014.03.013>
- de Nooijer, L. J., Toyofuku, T., & Kitazato, H. (2009). Foraminifera promote calcification by elevating their intracellular pH. *Proceedings of the National Academy of Sciences*, 106(36), 15374–15378. <https://doi.org/10.1073/pnas.0904306106>
- Dickson, A. G. (1990). Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep-Sea Research, Part A: Oceanographic Research Papers*, 37(5), 755–766. [https://doi.org/10.1016/0198-0149\(90\)90004-F](https://doi.org/10.1016/0198-0149(90)90004-F)
- Epov, V. N., Beraïl, S., Jimenez-Moreno, M., Perrot, V., Pecheyran, C., Amouroux, D., & Donard, O. F. X. (2010). Approach to measure isotopic ratios in species using Multicollector-ICPMS coupled with chromatography. *Analytical Chemistry*, 82(13), 5652–5662. <https://doi.org/10.1021/ac100648f>
- Erez, J. (2003). The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies. *Reviews in Mineralogy and Geochemistry*, 54(1), 115–149. <https://doi.org/10.2113/0540115>
- Fietzke, J., Liebetrau, V., Günther, D., Gürs, K., Hametner, K., Zumholz, K., et al. (2008). An alternative data acquisition and evaluation strategy for improved isotope ratio precision using LA-MC-ICP-MS applied to stable and radiogenic strontium isotopes in carbonates. *Journal of Analytical Atomic Spectrometry*, 23(7), 955. <https://doi.org/10.1039/b717706b>
- Foster, G. L. (2008). Seawater pH, pCO_2 and $[\text{CO}_3^{2-}]$ variations in the Caribbean Sea over the last 130 kyr: A boron isotope and B/Ca study of planktic foraminifera. *Earth and Planetary Science Letters*, 271(1–4), 254–266. <https://doi.org/10.1016/j.epsl.2008.04.015>
- Foster, G. L., Hönisch, B., Paris, G., Dwyer, G. S., Rae, J. W. B., Elliott, T., et al. (2013). Interlaboratory comparison of boron isotope analyses of boric acid, seawater and marine CaCO_3 by MC-ICPMS and NTIMS. *Chemical Geology*, 358, 1–14. <https://doi.org/10.1016/j.chemgeo.2013.08.027>
- Foster, G. L., Marschall, H. R., & Palmer, M. R. (2018). Boron isotope analysis of geological materials. In H. Marschall & G. L. Foster (Eds.), *Boron isotopes* (pp. 13–31). Springer International Publishing. https://doi.org/10.1007/978-3-319-64666-4_2
- Foster, G. L., Ni, Y., Haley, B., & Elliott, T. (2006). Accurate and precise isotopic measurement of sub-nanogram sized samples of foraminiferal hosted boron by total evaporation NTIMS. *Chemical Geology*, 230(1–2), 161–174. <https://doi.org/10.1016/j.chemgeo.2005.12.006>
- Foster, G. L., Pogge von Strandmann, P. a. E., & Rae, J. W. B. (2010). Boron and magnesium isotopic composition of seawater. *Geochemistry, Geophysics, Geosystems*, 11(8). <https://doi.org/10.1029/2010GC003201>
- Foster, G. L., & Rae, J. W. B. (2016). Reconstructing ocean pH with boron isotopes in foraminifera. *Annual Review of Earth and Planetary Sciences*, 44(1), 207–237. <https://doi.org/10.1146/annurev-earth-060115-012226>
- Friedrich, O., Schiebel, R., Wilson, P. A., Weldeab, S., Beer, C. J., Cooper, M. J., & Fiebig, J. (2012). Influence of test size, water depth, and ecology on Mg/Ca, Sr/Ca, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in nine modern species of planktic foraminifers. *Earth and Planetary Science Letters*, 319–320, 133–145. <https://doi.org/10.1016/j.epsl.2011.12.002>
- Gaillardet, J., & Allègre, C. J. (1995). Boron isotopic compositions of corals: Seawater or diagenesis record? *Earth and Planetary Science Letters*, 136(3–4), 665–676. [https://doi.org/10.1016/0012-821X\(95\)00180-K](https://doi.org/10.1016/0012-821X(95)00180-K)
- Gaillardet, J., Lemarchand, D., Göpel, C., & Manhès, G. (2001). Evaporation and sublimation of boric acid: Application for boron purification from organic rich solutions. *Geostandards and Geoanalytical Research*, 25(1), 67–75. <https://doi.org/10.1111/j.1751-908X.2001.tb00788.x>
- Guéguen, F., Isnard, H., Nonell, A., Vio, L., Vercoeur, T., & Chartier, F. (2015). Neodymium isotope ratio measurements by LC-MC-ICPMS for nuclear applications: Investigation of isotopic fractionation and mass bias correction. *Journal of Analytical Atomic Spectrometry*, 30(2), 443–452. <https://doi.org/10.1039/C4JA00361F>
- Guillermic, M., Misra, S., Eagle, R., Villa, A., Chang, F., & Tripathi, A. (2020). Seawater pH reconstruction using boron isotopes in multiple planktonic foraminifera species with different depth habitats and their potential to constrain pH and pCO_2 gradients. *Biogeosciences*, 17(13), 3487–3510. <https://doi.org/10.5194/bg-17-3487-2020>
- Gutjahr, M., Bordier, L., Douville, E., Farmer, J., Foster, G. L., Hathorne, E. C., et al. (2021). Sub-Permil interlaboratory consistency for solution-based Boron Isotope analyses on marine carbonates. *Geostandards and Geoanalytical Research*, 45(1), 59–75. <https://doi.org/10.1111/ggr.12364>
- Gutjahr, M., Ridgwell, A., Sexton, P. F., Anagnostou, E., Pearson, P. N., Pälke, H., et al. (2017). Very large release of mostly volcanic carbon during the Palaeocene-Eocene Thermal Maximum. *Nature*, 548(7669), 573–577. <https://doi.org/10.1038/nature23646>
- Hemming, N. G., & Hanson, G. N. (1992). Boron isotopic composition and concentration in modern marine carbonates. *Geochimica et Cosmochimica Acta*, 56(1), 537–543. [https://doi.org/10.1016/0016-7037\(92\)90151-8](https://doi.org/10.1016/0016-7037(92)90151-8)

- Hemming, N. G., & Hanson, G. N. (1994). A procedure for the isotopic analysis of boron by negative thermal ionization mass spectrometry. *Chemical Geology*, 114(1–2), 147–156. [https://doi.org/10.1016/0009-2541\(94\)90048-5](https://doi.org/10.1016/0009-2541(94)90048-5)
- Hemming, N. G., Reeder, R. J., & Hanson, G. N. (1995). Mineral-fluid partitioning and isotopic fractionation of boron in synthetic calcium carbonate. *Geochimica et Cosmochimica Acta*, 59(2), 371–379. [https://doi.org/10.1016/0016-7037\(95\)00288-B](https://doi.org/10.1016/0016-7037(95)00288-B)
- Henehan, M. J., Foster, G. L., Bostock, H. C., Greenop, R., Marshall, B. J., & Wilson, P. A. (2016). A new boron isotope-pH calibration for *Orbulina universa*, with implications for understanding and accounting for 'vital effects'. *Earth and Planetary Science Letters*, 454, 282–292. <https://doi.org/10.1016/j.epsl.2016.09.024>
- Henehan, M. J., Rae, J. W. B., Foster, G. L., Erez, J., Prentice, K. C., Kucera, M., et al. (2013). Calibration of the boron isotope proxy in the planktonic foraminifera *Globigerinoides ruber* for use in palaeo-CO₂ reconstruction. *Earth and Planetary Science Letters*, 364, 111–122. <https://doi.org/10.1016/j.epsl.2012.12.029>
- Henehan, M. J., Ridgwell, A., Thomas, E., Zhang, S., Alegret, L., Schmidt, D. N., et al. (2019). Rapid ocean acidification and protracted Earth system recovery followed the end-Cretaceous Chicxulub impact. *Proceedings of the National Academy of Sciences*, 116(45), 22500–22504. <https://doi.org/10.1073/pnas.1905989116>
- Hönisch, B., Bijma, J., Russell, A. D., Spero, H. J., Palmer, M. R., Zeebe, R. E., & Eisenhauer, A. (2003). The influence of symbiotic photosynthesis on the boron isotopic composition of foraminifera shells. *Marine Micropaleontology*, 49(1–2), 87–96. [https://doi.org/10.1016/S0377-8398\(03\)00030-6](https://doi.org/10.1016/S0377-8398(03)00030-6)
- Hönisch, B., Fish, C. R., Phelps, S. R., Haynes, L. L., Dyez, K., Holland, K., et al. (2021). Symbiotic photosynthesis and its effect on boron proxies in planktic foraminifera. *Paleoceanography and Paleoclimatology*, 36(10), e2020PA004022. <https://doi.org/10.1029/2020PA004022>
- Hönisch, B., & Hemming, N. G. (2004). Ground-truthing the boron isotope-paleo-pH proxy in planktonic foraminifera shells: Partial dissolution and shell size effects. *Paleoceanography*, 19(4). <https://doi.org/10.1029/2004PA001026>
- Hönisch, B., & Hemming, N. G. (2005). Surface ocean pH response to variations in pCO₂ through two full glacial cycles. *Earth and Planetary Science Letters*, 236(1–2), 305–314. <https://doi.org/10.1016/j.epsl.2005.04.027>
- Hönisch, B., Hemming, N. G., Grottoli, A. G., Amat, A., Hanson, G. N., & Bijma, J. (2004). Assessing scleractinian corals as recorders for paleo-pH: Empirical calibration and vital effects. *Geochimica et Cosmochimica Acta*, 68(18), 3675–3685. <https://doi.org/10.1016/j.gca.2004.03.002>
- Hönisch, B., Ridgwell, A., Schmidt, D. N., Thomas, E., Gibbs, S. J., Sluijs, A., et al. (2012). The geological record of Ocean acidification. *Science*, 335(6072), 1058–1063. <https://doi.org/10.1126/science.1208277>
- Indermühle, A., Stocker, T. F., Joos, F., Fischer, H., Smith, H. J., Wahlen, M., et al. (1999). Holocene carbon-cycle dynamics based on CO₂ trapped in ice at Taylor Dome, Antarctica. *Nature*, 398(6723), 121–126. <https://doi.org/10.1038/18158>
- Ishikawa, T., & Nagaishi, K. (2011). High-precision isotopic analysis of boron by positive thermal ionization mass spectrometry with sample preheating. *Journal of Analytical Atomic Spectrometry*, 26(2), 359–365. <https://doi.org/10.1039/c0ja00060d>
- Jonkers, L., van Heuven, S., Zahn, R., & Peeters, F. J. C. (2013). Seasonal patterns of shell flux, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of small and large *N. pachyderma* (s) and *G. bulloides* in the subpolar North Atlantic. *Paleoceanography*, 28(1), 164–174. <https://doi.org/10.1002/palo.20018>
- Jørgensen, B. B., Erez, J., Revsbech, P., & Cohen, Y. (1985). Symbiotic photosynthesis in a planktonic foraminiferan, *Globigerinoides sacculifer* (Brady), studied with microelectrodes. *Limnology & Oceanography*, 30(6), 1253–1267. <https://doi.org/10.4319/lo.1985.30.6.1253>
- Jurikova, H., Liebetrau, V., Gutjahr, M., Rollion-Bard, C., Hu, M. Y., Krause, S., et al. (2019). Boron isotope systematics of cultured brachiopods: Response to acidification, vital effects and implications for palaeo-pH reconstruction. *Geochimica et Cosmochimica Acta*, 248, 370–386. <https://doi.org/10.1016/j.gca.2019.01.015>
- Kaufman, D. S., & Broadman, E. (2023). Revisiting the Holocene global temperature conundrum. *Nature*, 614(7948), 425–435. <https://doi.org/10.1038/s41586-022-05536-w>
- Kiss, E. (1988). Ion-exchange separation and spectrophotometric determination of boron in geological materials. *Analytica Chimica Acta*, 211, 243–256. [https://doi.org/10.1016/S0003-2670\(00\)83684-3](https://doi.org/10.1016/S0003-2670(00)83684-3)
- Klochko, K., Cody, G. D., Tossell, J. A., Dera, P., & Kaufman, A. J. (2009). Re-evaluating boron speciation in biogenic calcite and aragonite using ¹¹B MAS NMR. *Geochimica et Cosmochimica Acta*, 73(7), 1890–1900. <https://doi.org/10.1016/j.gca.2009.01.002>
- Klochko, K., Kaufman, A. J., Yao, W., Byrne, R. H., & Tossell, J. A. (2006). Experimental measurement of boron isotope fractionation in seawater. *Earth and Planetary Science Letters*, 248(1–2), 276–285. <https://doi.org/10.1016/j.epsl.2006.05.034>
- Köhler, P., Nehrbass-Ahles, C., Schmitt, J., Stocker, T. F., & Fischer, H. (2017). A 156 kyr smoothed history of the atmospheric greenhouse gases CO₂, CH₄, and N₂O and their radiative forcing. *Earth System Science Data*, 9(1), 363–387. <https://doi.org/10.5194/essd-9-363-2017>
- Köhler-Rink, S., & Kühl, M. (2000). Microsensor studies of photosynthesis and respiration in larger symbiotic foraminifera. I the physico-chemical microenvironment of *Marginalipora vertebalis*, *Amphistegina lobifera* and *Amphisorus hemprichii*. *Marine Biology*, 137(3), 473–486. <https://doi.org/10.1007/s002270000335>
- Köhler-Rink, S., & Kühl, M. (2005). The chemical microenvironment of the symbiotic planktonic foraminifer *Orbulina universa*. *Marine Biology Research*, 1(1), 68–78. <https://doi.org/10.1080/17451000510019015>
- Kroon, D., & Darling, K. (1995). Size and upwelling control of the stable isotope composition of *Neogloboquadrina dutertrei* (d'Orbigny), *Globigerinoides ruber* (d'Orbigny) and *Globigerina bulloides* d'Orbigny: examples from the Panama Basin and Arabian Sea. *Journal of Foraminiferal Research*, 25(1), 39–52. <https://doi.org/10.2113/gsjfr.25.1.39>
- Lamy, F. (2016). The Expedition PS97 of the Research Vessel POLARSTERN to the Drake Passage in 2016 [Berichte zur Polar- und Meeresforschung]. https://doi.org/10.2312/BzPM_0701_2016
- Lamy, F., Kilian, R., Arz, H. W., Francois, J.-P., Kaiser, J., Prange, M., & Steinke, T. (2010). Holocene changes in the position and intensity of the southern westerly wind belt. *Nature Geoscience*, 3(10), 695–699. <https://doi.org/10.1038/ngeo959>
- Lauvset, S. K., Lange, N., Tanhua, T., Bittig, H. C., Olsen, A., Kozyr, A., et al. (2024). The annual update GLODAPv2.2023: The global interior ocean biogeochemical data product. *Earth System Science Data*, 16(4), 2047–2072. <https://doi.org/10.5194/essd-16-2047-2024>
- Lécuyer, C., Grandjean, P., Reynard, B., Albarède, F., & Telouk, P. (2002). ¹¹B/¹⁰B analysis of geological materials by ICP-MS Plasma 54: Application to the boron fractionation between brachiopod calcite and seawater. *Chemical Geology*, 186(1–2), 45–55. [https://doi.org/10.1016/S0009-2541\(01\)00425-9](https://doi.org/10.1016/S0009-2541(01)00425-9)
- Lee, K., Kim, T.-W., Byrne, R. H., Millero, F. J., Feely, R. A., & Liu, Y.-M. (2010). The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta*, 74(6), 1801–1811. <https://doi.org/10.1016/j.gca.2009.12.027>
- Lemarchand, D., Gaillardet, J., Göpel, C., & Manhès, G. (2002). An optimized procedure for boron separation and mass spectrometry analysis for river samples. *Chemical Geology*, 182(2–4), 323–334. [https://doi.org/10.1016/S0009-2541\(01\)00329-1](https://doi.org/10.1016/S0009-2541(01)00329-1)
- Lemarchand, D., Gaillardet, J., Lewin, É., & Allègre, C. J. (2002). Boron isotope systematics in large rivers: Implications for the marine boron budget and paleo-pH reconstruction over the Cenozoic. *Chemical Geology*, 190(1–4), 123–140. [https://doi.org/10.1016/S0009-2541\(02\)00114-6](https://doi.org/10.1016/S0009-2541(02)00114-6)

- Liu, Z., Zhu, J., Rosenthal, Y., Zhang, X., Otto-Bliesner, B. L., Timmermann, A., et al. (2014). The Holocene temperature conundrum. *Proceedings of the National Academy of Sciences*, 111(34), E3501–E3505. <https://doi.org/10.1073/pnas.1407229111>
- Lloyd, N. S., Sadekov, A. Y., & Misra, S. (2018). Application of 10^{13} ohm Faraday cup current amplifiers for boron isotopic analyses by solution mode and laser ablation multicollector inductively coupled plasma mass spectrometry. *Rapid Communications in Mass Spectrometry*, 32(1), 9–18. <https://doi.org/10.1002/rcm.8009>
- Louvat, P., Bouchez, J., & Paris, G. (2011). MC-ICP-MS isotope measurements with direct injection nebulisation (d-DIHEN): Optimisation and application to boron in seawater and Carbonate samples. *Geostandards and Geoanalytical Research*, 35(1), 75–88. <https://doi.org/10.1111/j.1751-908X.2010.00057.x>
- Louvat, P., Moureau, J., Paris, G., Bouchez, J., Noireaux, J., & Gaillardet, J. (2014). A fully automated direct injection nebulizer (d-DIHEN) for MC-ICP-MS isotope analysis: Application to boron isotope ratio measurements. *Journal of Analytical Atomic Spectrometry*, 29(9), 1698–1707. <https://doi.org/10.1039/C4JA00098F>
- Louvat, P., Tharaud, M., Buisson, M., Rollion-Bard, C., & Benedetti, M. F. (2019). μ -dDIHEN: A new micro-flow liquid sample introduction system for direct injection nebulization in ICP-MS. *Journal of Analytical Atomic Spectrometry*, 34(8), 1553–1563. <https://doi.org/10.1039/C9JA00146H>
- Lueker, T. J., Dickson, A. G., & Keeling, C. D. (2000). Ocean $p\text{CO}_2$ calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2: Validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium. *Marine Chemistry*, 70(1), 105–119. [https://doi.org/10.1016/S0304-4203\(00\)00022-0](https://doi.org/10.1016/S0304-4203(00)00022-0)
- Martin, P. A., & Lea, D. W. (2002). A simple evaluation of cleaning procedures on fossil benthic foraminiferal Mg/Ca. *Geochemistry, Geophysics, Geosystems*, 3(10), 1–8. <https://doi.org/10.1029/2001GC000280>
- Martínez-Botí, M. A., Foster, G. L., Chalk, T. B., Rohling, E. J., Sexton, P. F., Lunt, D. J., et al. (2015). Plio-Pleistocene climate sensitivity evaluated using high-resolution CO_2 records. *Nature*, 518(7537), 49–54. <https://doi.org/10.1038/nature14145>
- Martínez-Botí, M. A., Marino, G., Foster, G. L., Ziveri, P., Henehan, M. J., Rae, J. W. B., et al. (2015). Boron isotope evidence for oceanic carbon dioxide leakage during the last deglaciation. *Nature*, 518(7538), 219–222. <https://doi.org/10.1038/nature14155>
- McCulloch, M. T., Holcomb, M., Rankenburg, K., & Trotter, J. A. (2014). Rapid, high-precision measurements of boron isotopic compositions in marine carbonates: Boron isotopic measurements in marine carbonates. *Rapid Communications in Mass Spectrometry*, 28(24), 2704–2712. <https://doi.org/10.1002/rcm.7065>
- Misra, S., Greaves, M., Owen, R., Kerr, J., Elmore, A. C., & Elderfield, H. (2014). Determination of B/Ca of natural carbonates by HR-ICP-MS. *Geochemistry, Geophysics, Geosystems*, 15(4), 1617–1628. <https://doi.org/10.1002/2013GC005049>
- Misra, S., Owen, R., Kerr, J., Greaves, M., & Elderfield, H. (2014). Determination of $\delta^{11}\text{B}$ by HR-ICP-MS from mass limited samples: Application to natural carbonates and water samples. *Geochimica et Cosmochimica Acta*, 140, 531–552. <https://doi.org/10.1016/j.gca.2014.05.047>
- Monnin, E., Indermühle, A., Dällenbach, A., Flückiger, J., Stauffer, B., Stocker, T. F., et al. (2001). Atmospheric CO_2 Concentrations over the last glacial termination. *Science*, 291(5501), 112–114. <https://doi.org/10.1126/science.291.5501.112>
- Monnin, E., Steig, E. J., Siegenthaler, U., Kawamura, K., Schwander, J., Stauffer, B., et al. (2004). Evidence for substantial accumulation rate variability in Antarctica during the Holocene, through synchronization of CO_2 in the Taylor Dome, Dome C and DML ice cores. *Earth and Planetary Science Letters*, 224(1–2), 45–54. <https://doi.org/10.1016/j.epsl.2004.05.007>
- Moreno, P. I., Francois, J. P., Moy, C. M., & Villa-Martínez, R. (2010). Covariability of the Southern Westerlies and atmospheric CO_2 during the Holocene. *Geology*, 38(8), 727–730. <https://doi.org/10.1130/G30962.1>
- Nehrke, G., Keul, N., Langer, G., de Nooijer, L. J., Bijma, J., & Meibom, A. (2013). A new model for biomineralization and trace-element signatures of foraminifera tests. *Biogeosciences*, 10(10), 6759–6767. <https://doi.org/10.5194/bg-10-6759-2013>
- Ni, Y., Foster, G. L., Bailey, T., Elliott, T., Schmidt, D. N., Pearson, P., et al. (2007). A core top assessment of proxies for the ocean carbonate system in surface-dwelling foraminifers. *Paleoceanography*, 22(3). <https://doi.org/10.1029/2006PA001337>
- Nir, O., Vengosh, A., Harkness, J. S., Dwyer, G. S., & Lahav, O. (2015). Direct measurement of the boron isotope fractionation factor: Reducing the uncertainty in reconstructing ocean paleo-pH. *Earth and Planetary Science Letters*, 414, 1–5. <https://doi.org/10.1016/j.epsl.2015.01.006>
- Noireaux, J., Mavromatis, V., Gaillardet, J., Schott, J., Montouillout, V., Louvat, P., et al. (2015). Crystallographic control on the boron isotope paleo-pH proxy. *Earth and Planetary Science Letters*, 430, 398–407. <https://doi.org/10.1016/j.epsl.2015.07.063>
- Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., Feely, R. A., et al. (2005). Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature*, 437(7059), 681–686. <https://doi.org/10.1038/nature04095>
- Osborne, E. B., Umling, N. E., Bizimis, M., Buckley, W., Sadekov, A., Tappa, E., et al. (2020). A sediment trap evaluation of B/Ca as a carbonate system proxy in asymbiotic and nondinoflagellate hosting planktonic foraminifera. *Paleoceanography and Paleoclimatology*, 35(2), e2019PA003682. <https://doi.org/10.1029/2019PA003682>
- Pagani, M., Lemarchand, D., Spivack, A., & Gaillardet, J. (2005). A critical evaluation of the boron isotope-pH proxy: The accuracy of ancient ocean pH estimates. *Geochimica et Cosmochimica Acta*, 69(4), 953–961. <https://doi.org/10.1016/j.gca.2004.07.029>
- Pang, X., Bassinot, F., & Sepulcre, S. (2020). Cleaning method impact on the Mg/Ca of three planktonic foraminifer species: A downcore study along a depth transect. *Chemical Geology*, 549, 119690. <https://doi.org/10.1016/j.chemgeo.2020.119690>
- Paris, G., Bartolini, A., Donnadieu, Y., Beaumont, V., & Gaillardet, J. (2010). Investigating boron isotopes in a middle Jurassic micritic sequence: Primary vs. diagenetic signal. *Chemical Geology*, 275(3–4), 117–126. <https://doi.org/10.1016/j.chemgeo.2010.03.013>
- Paulhac Buisson, M., Louvat, P., Karancz, S., Tian, R., Raitzsch, M., Bijma, J., & Rollion-Bard, C. (2025). Determination of $\delta^{11}\text{B}$ in Planktonic Foraminifera at the ng Level: Application to the Ontogenetic Variability in Globigerina bulloides. [Dataset]. *Geochemistry, Geophysics, Geosystems*. <https://doi.org/10.6084/m9.figshare.26940490.v1>
- Pearson, P. N., & Palmer, M. R. (2000). Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature*, 406(6797), 695–699. <https://doi.org/10.1038/35021000>
- Peeters, F. J. C., Brummer, G.-J. A., & Ganssen, G. (2002). The effect of upwelling on the distribution and stable isotope composition of *Globigerina bulloides* and *Globigerinoides ruber* (planktic Foraminifera) in modern surface waters of the NW Arabian Sea. *Global and Planetary Change*, 34(3), 269–291. [https://doi.org/10.1016/S0921-8181\(02\)00120-0](https://doi.org/10.1016/S0921-8181(02)00120-0)
- Rae, J. W. B. (2018). Boron isotopes in foraminifera: Systematics, biomineralisation, and CO_2 reconstruction. In H. Marshall & G. Foster (Eds.), *Boron isotopes: The fifth element* (pp. 107–143). Springer International Publishing. https://doi.org/10.1007/978-3-319-64666-4_5
- Rae, J. W. B., Foster, G. L., Schmidt, D. N., & Elliott, T. (2011). Boron isotopes and B/Ca in benthic foraminifera: Proxies for the deep ocean carbonate system. *Earth and Planetary Science Letters*, 302(3–4), 403–413. <https://doi.org/10.1016/j.epsl.2010.12.034>
- Raitzsch, M., Bijma, J., Benthien, A., Richter, K.-U., Steinhofel, G., & Kučera, M. (2018). Boron isotope-based seasonal paleo-pH reconstruction for the Southeast Atlantic – A multispecies approach using habitat preference of planktonic foraminifera. *Earth and Planetary Science Letters*, 487, 138–150. <https://doi.org/10.1016/j.epsl.2018.02.002>

- Raitzsch, M., Hathorne, E. C., Kuhnert, H., Groeneveld, J., & Bickert, T. (2011). Modern and late Pleistocene B/Ca ratios of the benthic foraminifer *Planulina wuellerstorfi* determined with laser ablation ICP-MS. *Geology*, 39(11), 1039–1042. <https://doi.org/10.1130/G32009.1>
- Raitzsch, M., Rollion-Bard, C., Horn, I., Steinhofel, G., Benthien, A., Richter, K.-U., et al. (2020). Technical note: Single-shell $\delta^{11}\text{B}$ analysis of *Cibicides wuellerstorfi* using femtosecond laser ablation MC-ICPMS and secondary ion mass spectrometry. *Biogeosciences*, 17(21), 5365–5375. <https://doi.org/10.5194/bg-17-5365-2020>
- Reagan, J. R., Boyer, T. P., Garcia, H. E., Locarnini, R. A., Baranova, O. K., Bouchard, C., et al. (2024). *World Ocean Atlas 2023*. Dataset: NCEI Accession, 270533. NOAA National Centers for Environmental Information.
- Rehkämper, M., Schönbachler, M., & Stirling, C. H. (2001). Multiple collector ICP-MS: Introduction to instrumentation, measurement techniques and analytical capabilities. *Geostandards and Geoanalytical Research*, 25(1), 23–40. <https://doi.org/10.1111/j.1751-908X.2001.tb00785.x>
- Rink, S., Kühl, M., Bijma, J., & Spero, H. J. (1998). Microsensor studies of photosynthesis and respiration in the symbiotic foraminifer *Orbulina universa*. *Marine Biology*, 131(4), 583–595. <https://doi.org/10.1007/s002270050350>
- Rodríguez-González, P., Epov, V. N., Pecheyran, C., Amouroux, D., & Donard, O. F. X. (2012). Species-specific stable isotope analysis by the hyphenation of chromatographic techniques with MC-ICPMS. *Mass Spectrometry Reviews*, 31(4), 504–521. <https://doi.org/10.1002/mas.20352>
- Rollion-Bard, C., Blamart, D., Trebosc, J., Tricot, G., Mussi, A., & Cuif, J.-P. (2011). Boron isotopes as pH proxy: A new look at boron speciation in deep-sea corals using ^{11}B MAS NMR and EELS. *Geochimica et Cosmochimica Acta*, 75(4), 1003–1012. <https://doi.org/10.1016/j.gca.2010.11.023>
- Rollion-Bard, C., & Erez, J. (2010). Intra-shell boron isotope ratios in the symbiont-bearing benthic foraminifer *Amphistegina lobifera*: Implications for $\delta^{11}\text{B}$ vital effects and paleo-pH reconstructions. *Geochimica et Cosmochimica Acta*, 74(5), 1530–1536. <https://doi.org/10.1016/j.gca.2009.11.017>
- Roy, R. N., Roy, L. N., Lawson, M., Vogel, K. M., Porter Moore, C., Davis, W., & Millero, F. J. (1993). Thermodynamics of the dissociation of boric acid in seawater at $S = 35$ from 0 to 55°C. *Marine Chemistry*, 44(2–4), 243–248. [https://doi.org/10.1016/0304-4203\(93\)90206-4](https://doi.org/10.1016/0304-4203(93)90206-4)
- Sanyal, A., Bijma, J., Spero, H., & Lea, D. W. (2001). Empirical relationship between pH and the boron isotopic composition of *Globigerinoides sacculifer*: Implications for the boron isotope paleo-pH proxy. *Paleoceanography*, 16(5), 515–519. <https://doi.org/10.1029/2000PA000547>
- Sanyal, A., Hemming, N. G., Broecker, W. S., Lea, D. W., Spero, H. J., & Hanson, G. N. (1996). Oceanic pH control on the boron isotopic composition of foraminifera: Evidence from culture experiments. *Paleoceanography*, 11(5), 513–517. <https://doi.org/10.1029/96PA01858>
- Sanyal, A., Hemming, N. G., Hanson, G. N., & Broecker, W. S. (1995). Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. *Nature*, 373(6511), 234–236. <https://doi.org/10.1038/373234a0>
- Schiebel, R., & Hemleben, C. (2017). *Planktic foraminifera in the modern ocean*. Springer Berlin Heidelberg. <https://doi.org/10.1007/978-3-662-50297-6>
- Schlitzer, R. (2015). Data analysis and visualization with Ocean Data View. *CMOS Bulletin SCMO*, 43(1), 9–13.
- Schmitt, J., Schneider, R., Elsig, J., Leuenberger, D., Laurantou, A., Chappellaz, J., et al. (2012). Carbon isotope constraints on the deglacial CO_2 rise from ice cores. *Science*, 336(6082), 711–714. <https://doi.org/10.1126/science.1217161>
- Sen, S., Stebbins, J. F., Hemming, N. G., & Ghosh, B. (1994). Coordination environments of B impurities in calcite and aragonite polymorphs: A ^{11}B MAS NMR study. *American Mineralogist*, 79(9–10), 819–825.
- Sharp, J. D., Pierrot, D., Humphreys, M. P., Epitalon, J.-M., Orr, J. C., Lewis, E. R., & Wallace, D. W. R. (2023). *CO2SYSv3 for MATLAB*. Zenodo. <https://doi.org/10.5281/zenodo.7552554>
- Spero, H. J., & Lea, D. W. (1996). Experimental determination of stable isotope variability in *Globigerina bulloides*: Implications for paleoceanographic reconstructions. *Marine Micropaleontology*, 28(3), 231–246. [https://doi.org/10.1016/0377-8398\(96\)00003-5](https://doi.org/10.1016/0377-8398(96)00003-5)
- Takahashi, T., Sutherland, S. C., Wanninkhof, R., Sweeney, C., Feely, R. A., Chipman, D. W., et al. (2009). Climatological mean and decadal change in surface ocean $p\text{CO}_2$, and net sea–air CO_2 flux over the global oceans. *Deep Sea Research Part II: Topical Studies in Oceanography*, 56(8), 554–577. <https://doi.org/10.1016/j.dsr2.2008.12.009>
- Tarique, M., Rahaman, W., Lathika, N., Prabhat, P., Thamban, M., & Misra, S. (2023). Enhanced CO_2 degassing from the tropical Indian Ocean during cold climatic events of the last glacial cycle. *Paleoceanography and Paleoclimatology*, 38(12), e2022PA004570. <https://doi.org/10.1029/2022PA004570>
- Toyofuku, T., Matsuo, M. Y., de Nooijer, L. J., Nagai, Y., Kawada, S., Fujita, K., et al. (2017). Proton pumping accompanies calcification in foraminifera. *Nature Communications*, 8(1), 14145. <https://doi.org/10.1038/ncomms14145>
- Trudgill, M., Nuber, S., Block, H. E., Crumpton-Banks, J., Jurikova, H., Little, E., et al. (2024). A simple, low-blank batch purification method for high-precision boron isotope analysis. *Geochemistry, Geophysics, Geosystems*, 25(3), e2023GC011350. <https://doi.org/10.1029/2023GC011350>
- Uchikawa, J., Penman, D. E., Zachos, J. C., & Zeebe, R. E. (2015). Experimental evidence for kinetic effects on B/Ca in synthetic calcite: Implications for potential $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ incorporation. *Geochimica et Cosmochimica Acta*, 150, 171–191. <https://doi.org/10.1016/j.gca.2014.11.022>
- Urey, H. C., Lowenstam, H. A., Epstein, S., & McKinney, C. R. (1951). Measurement of paleotemperatures and temperatures of the Upper Cretaceous of England, Denmark, and the Southeastern United States. *GSA Bulletin*, 62(4), 399–416. [https://doi.org/10.1130/0016-7606\(1951\)62\[399:MOPATO\]2.0.CO;2](https://doi.org/10.1130/0016-7606(1951)62[399:MOPATO]2.0.CO;2)
- Vengosh, A., Chivas, A. R., & McCulloch, M. T. (1989). Direct determination of boron and chlorine isotopic compositions in geological materials by negative thermal-ionization mass spectrometry. *Chemical Geology: Isotope Geoscience section*, 79(4), 333–343. [https://doi.org/10.1016/0168-9622\(89\)90039-0](https://doi.org/10.1016/0168-9622(89)90039-0)
- Vengosh, A., Kolodny, Y., Starinsky, A., Chivas, A. R., & McCulloch, M. T. (1991). Coprecipitation and isotopic fractionation of boron in modern biogenic carbonates. *Geochimica et Cosmochimica Acta*, 55(10), 2901–2910. [https://doi.org/10.1016/0016-7037\(91\)90455-E](https://doi.org/10.1016/0016-7037(91)90455-E)
- Vogl, J., & Rosner, M. (2011). Production and certification of a unique set of isotope and Delta reference materials for boron isotope determination in geochemical, environmental and industrial materials. *Geostandards and Geoanalytical Research*, 36(2), 161–175. <https://doi.org/10.1111/j.1751-908X.2011.00136.x>
- Wang, B.-S., You, C.-F., Huang, K.-F., Wu, S.-F., Aggarwal, S. K., Chung, C.-H., & Lin, P.-Y. (2010). Direct separation of boron from Na- and Ca-rich matrices by sublimation for stable isotope measurement by MC-ICP-MS. *Talanta*, 82(4), 1378–1384. <https://doi.org/10.1016/j.talanta.2010.07.010>
- Wei, G., McCulloch, M. T., Mortimer, G., Deng, W., & Xie, L. (2009). Evidence for ocean acidification in the Great Barrier Reef of Australia. *Geochimica et Cosmochimica Acta*, 73(8), 2332–2346. <https://doi.org/10.1016/j.gca.2009.02.009>
- Yu, J., Day, J., Greaves, M., & Elderfield, H. (2005). Determination of multiple element/calcium ratios in foraminiferal calcite by quadrupole ICP-MS. *Geochemistry, Geophysics, Geosystems*, 6(8). <https://doi.org/10.1029/2005GC000964>

- Yu, J., Elderfield, H., Greaves, M., & Day, J. (2007). Preferential dissolution of benthic foraminiferal calcite during laboratory reductive cleaning. *Geochemistry, Geophysics, Geosystems*, 8(6). <https://doi.org/10.1029/2006GC001571>
- Yu, J., Thornalley, D. J. R., Rae, J. W. B., & McCave, N. I. (2013). Calibration and application of B/Ca, Cd/Ca, and $\delta^{11}\text{B}$ in *Neogloboquadrina pachyderma* (sinistral) to constrain CO_2 uptake in the subpolar North Atlantic during the last deglaciation. *Paleoceanography*, 28(2), 237–252. <https://doi.org/10.1002/palo.20024>
- Zeebe, R. E., Bijma, J., & Wolf-Gladrow, D. A. (1999). A diffusion-reaction model of carbon isotope fractionation in foraminifera. *Marine Chemistry*, 64(3), 199–227. [https://doi.org/10.1016/S0304-4203\(98\)00075-9](https://doi.org/10.1016/S0304-4203(98)00075-9)
- Zeebe, R. E., Sanyal, A., Ortiz, J. D., & Wolf-Gladrow, D. A. (2001). A theoretical study of the kinetics of the boric acid–borate equilibrium in seawater. *Marine Chemistry*, 73(2), 113–124. [https://doi.org/10.1016/S0304-4203\(00\)00100-6](https://doi.org/10.1016/S0304-4203(00)00100-6)
- Zeebe, R. E., & Wolf-Gladrow, D. (2001). *CO₂ in seawater: Equilibrium, kinetics, isotopes* (Vol. 65, p. 346). Elsevier Oceanography Book Series. Retrieved from <https://www.elsevier.com/books/co2-in-seawater-equilibrium-kinetics-isotopes/zeebe/978-0-444-50946-8>
- Zeebe, R. E., Wolf-Gladrow, D. A., Bijma, J., & Hönisch, B. (2003). Vital effects in foraminifera do not compromise the use of $\delta^{11}\text{B}$ as a paleo-pH indicator: Evidence from modeling. *Paleoceanography*, 18(2). <https://doi.org/10.1029/2003PA000881>