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# Paleoceanography and Paleoclimatology®








## RESEARCH ARTICLE

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## Perspectives for Best Practices in Boron-Based CO<sub>2</sub> Reconstruction

### Special Collection:

Advances and Best Practices in Boron-based paleo-CO<sub>2</sub> reconstruction

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### Key Points:

- Boron isotopes are an important marine paleoclimate proxy to reconstruct past ocean pH and atmospheric carbon dioxide in geological time
- Sources of uncertainty of past CO<sub>2</sub> estimation shifts from primarily modern oceanography to seawater chemistry and biology beyond 20 Myrs
- Encouragement of collaborative and inclusive future efforts to strengthen the boron isotope community

### Supporting Information:

Supporting Information may be found in the online version of this article.

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**Abstract** Since atmospheric carbon dioxide (CO<sub>2</sub>) is a key driver of global temperatures over geological time, determining past CO<sub>2</sub> and fluxes among Earth's carbon reservoirs is critical in resolving drivers and feedbacks within Earth's climate system. Such CO<sub>2</sub> reconstructions are challenging prior to ice core records of the last 800 kyrs, and yet it is beyond this time where the most promising analogs for our warmer, higher CO<sub>2</sub> future lie. Amongst proxies for past CO<sub>2</sub> reconstruction, boron isotopes ( $\delta^{11}\text{B}$ , primarily measured in foraminiferal carbonate) have become one of the most well-established, having demonstrated their ability to replicate atmospheric CO<sub>2</sub> during periods where ice core estimates are available for comparison. Although analytical reproducibility across laboratories has greatly improved in recent years, the approaches taken to derive CO<sub>2</sub> estimates from these boron isotope measurements remain variable. For example, there are significant inconsistencies in how seawater temperature, boron isotope, and elemental composition are estimated, in how a second carbonate system parameter is used to constrain the carbonate system, in how ecophysiological imprints on proxy signals are accounted for, and in how uncertainties are quantified and propagated. The need to better harmonize practices in the community motivated a series of virtual workshops and a PAGES-supported meeting, and ultimately this AGU Special Collection “Advances and Best Practices in Boron-based Paleo-CO<sub>2</sub> Reconstruction.” In this synthesis article, we briefly summarize the history of approaches to address these issues, current limitations and strengths of the proxy, and highlight some important points to consider when applying the boron isotope proxy.

## 1. Introduction

The use of boron isotope ratios in marine carbonates was first proposed to reconstruct the pH and therefore CO<sub>2</sub> of natural systems in the 1990s (Figure 1, Hemming & Hanson, 1992; Spivack et al., 1993). Due to its behavior being analogous to the carbonate system in seawater, boron isotope ratios have a real quantified link to the carbon cycle, and over their development, many advancements in both theory and method have been made. Nowhere is this more evident than in the recent CenCO<sub>2</sub>PIP compilation of community-vetted Cenozoic CO<sub>2</sub> proxy records (Hönisch et al., 2023), which leans heavily on the boron isotope proxy (805 out of 1,579 data points). Beyond the reach of ice core records of CO<sub>2</sub> (~800 kyrs BP, the boron isotope-CO<sub>2</sub> proxy, as applied to marine carbonates, has yielded some of the most continuous, reproducible and precise CO<sub>2</sub> records, comparing favorably to other marine and terrestrial CO<sub>2</sub> proxies. Confidence in the accuracy of these records has led to a greater presence for paleo-CO<sub>2</sub> proxies in the latest IPCC report (IPCC & WG1, 2021), bolstered by demonstrable consistency between the ice core and boron isotope CO<sub>2</sub> records (Chalk et al., 2017; de la Vega, Chalk, et al., 2020; Hönisch & Hemming, 2005), and by interlaboratory comparison efforts that show good agreement for analysis of carbonate standards independent of cleaning protocols (Gutjahr et al., 2021; Stewart et al., 2021). However, while confidence in the robustness of the proxy as a whole appears justified, on a more detailed level, there are significant differences in how the proxy is being applied across the paleoceanographic community. This in effect introduces discord in long term CO<sub>2</sub> records, and runs the risk of undermining the progress that has been made in the boron isotope proxy community over the past decades. Two recent compilation efforts have attempted to reduce this discord within Cenozoic records, taking quite different approaches to do so. Rae et al. (2021) compiles a subset of records viewed as most reliable, harmonizing some of the secondary inputs which are required to generate the final CO<sub>2</sub> records from boron isotope ratios (e.g., the isotopic composition of boron in seawater). In contrast,

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Hönisch et al. (2023) opts to compile all boron isotope-derived CO<sub>2</sub> records that meet a prescribed quality control standard, without substantially altering any of the accessory inputs that were assumed when calculating these CO<sub>2</sub> records in the primary publications. The advantage of the former approach is that any noise stemming from the ancillary inputs of CO<sub>2</sub> calculations, and inconsistent calculation methodology, was minimized. A disadvantage, however, is that it is not always appropriate to assume the same range of for example, second carbonate system parameters for all sites at all times in the Cenozoic, as to do so may ignore justifiable differences in Earth system parameters, and in addition any incorrect assumption could either alter the magnitude of CO<sub>2</sub> signal reconstructed, such as muting the potential variability, or cause a systematic inaccuracy in the whole record. In the case of the CenCO<sub>2</sub>PIP approach, the temporal flexibility in which secondary input parameters are permitted to change between study time intervals may better reflect the reality of a planet that is constantly evolving, and total uncertainty. On the other hand, it can result in situations where included studies that are adjacent in time are built on mutually incompatible secondary assumptions, such as those investigated in Köhler (2023), who uses boron isotope data in conjunction with a fully constrained carbonate system model to assess consistency between emission scenarios and δ<sup>11</sup>B-pH data.

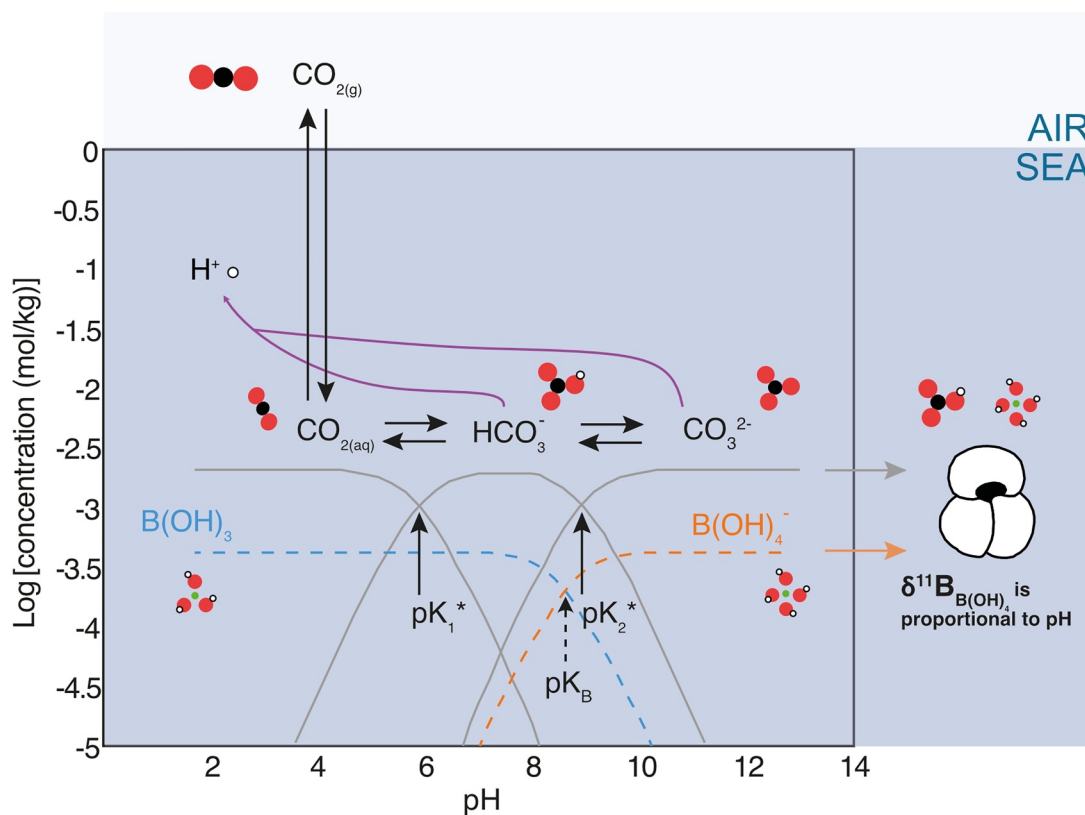
Building on community-based initiatives like p-CO<sub>2</sub>.org and CenCO<sub>2</sub>PIP, in 2021 a series of online consensus-building workshops were begun, continuing to an in-person PAGES-funded workshop in 2022 at the International Conference of Paleoceanography in Bergen (Anagnostou et al., 2023). The aim of these workshops was that by fostering exchange of ideas and best practices amongst the boron isotope community, whether that be in analytical techniques, calculation routines, or in the choice of accessory inputs that are needed for the calculation of CO<sub>2</sub> from boron isotope ratios, scatter on boron-based CO<sub>2</sub> records could be reduced not through post-hoc imposition of a common set of assumptions, but by community led convergence on more consistent ways of analyzing data. This special collection of papers showcases some of the ongoing advances in boron isotope-based CO<sub>2</sub> reconstruction that were discussed during, or informed by, these meetings, as well as some additional manuscripts which are highly relevant to the field. In doing so it builds a picture of the state of the art, and the prospective areas where advances can still be made. In this synthesis article, we briefly summarize the history, practicalities, limitations and strengths of the proxy, and highlight some important points to consider when applying the boron isotope-CO<sub>2</sub> proxy, in light of some of the recent advances published in this special collection and elsewhere.

## 2. Methodological Advances

### 2.1. Background

In almost all major advances in paleoceanography, including the development of paleotemperature proxy science in the mid 20th century, the development of new theoretical concepts and paradigms has been intrinsically linked to the establishment of new analytical methods and capabilities (e.g., Emiliani, 1966). Boron isotope-based CO<sub>2</sub> reconstruction is no exception to this legacy approach in the paleoceanographic community. Advances in technology and methodology do more than merely reduce the uncertainty on a given data point, they can open up new geological archives and areas for study. Reduction in sample size requirements offers benefits beyond the obvious of requiring fewer picked foraminifera from sediment samples: it also greatly increases the feasibility of calibration and hypothesis testing through tow and culturing studies and sedimentological studies from carbonate poor regions.

Analysis of boron isotopes in marine microfossils has developed substantially, fostering the exponential growth of application studies from the starting point of the proxy in the early 1990s to the present day (Figure 2). Boron isotope analysis presents a unique combination of challenges: low ionization potential, volatility and general low abundance in sample material. Several comprehensive reviews of the development of analytical protocols already exist (e.g., Marschall and Foster (2018)), and to avoid unnecessary replication we briefly summarize here and in Table 1. Through much of the early development of the boron isotope-pH proxy, the key analytical frontier was the establishment of reproducibility, interoperability and consistency between laboratories just as it is in the establishment of the clumped isotope paleotemperature proxy (e.g., Bernasconi et al. (2018)). Early analyses relied heavily on thermal ionization mass spectrometry, firstly positive-TIMS (P-TIMS) and later by negative-TIMS (N-TIMS). While P-TIMS displayed promising levels of reproducibility during the early establishment of the proxy, the application of the method to paleoceanographic questions was (and is still today) typically limited by sample size requirements. The relatively much smaller sample size requirements associated with N-TIMS opened up a range of applications, and facilitated some pioneering work in the boron isotope field (e.g.,

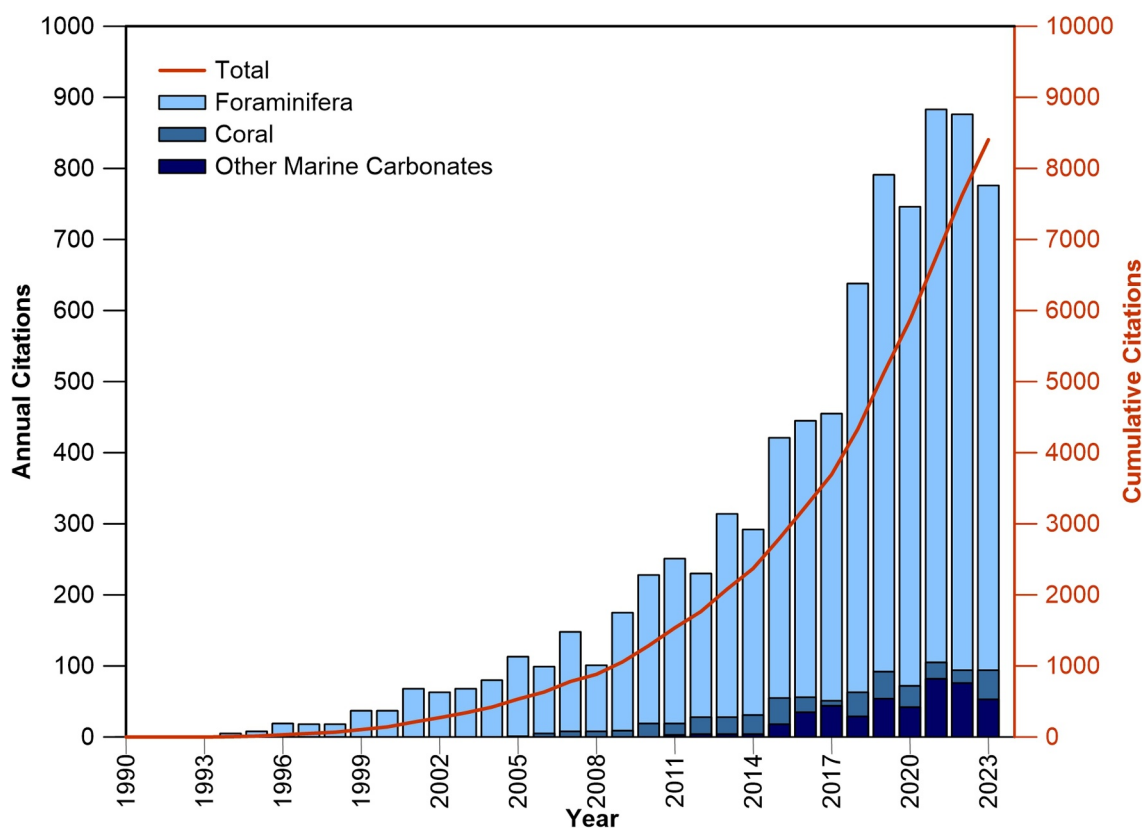


**Figure 1.** Carbonate and boron system Bjerrum plot, a graphical representation of the equilibrium reactions in the two groups. Here shown with a theoretical Dissolved Inorganic Carbon of 2,100  $\mu\text{mol kg}^{-1}$ , salinity of 35 psu, and at a temperature of 25  $^{\circ}\text{C}$ . Concentrations of the various chemical species are shown in the gray (carbonate), blue and orange (boron) lines in log mol/kg. As  $\text{CO}_2$  dissolves in sea water, it impacts the pH dependent equilibrium reactions of the carbonate and boron systems releasing  $\text{H}^+$  ions ( $10^{-\text{pH}}$ , ~acidity). At high pH relatively more carbonate ion and borate ion are available for inclusion into carbonate minerals, this also impacts the  $\delta^{11}\text{B}$  of borate incorporated. Modified from Zeebe and Wolf-Gladrow (2001). Carbon, oxygen, hydrogen and boron are indicated by black, red, white, and green atoms respectively, dissociation constants are shown using pK notation.

Palmer et al. (1998); Pearson and Palmer (2000); Sanyal et al. (1995)). However, N-TIMS has problems associated with strong within-run instrumental fractionation and interference from minor isotopologues (such as  $^{10}\text{B}^{17}\text{O}^{16}\text{O}$  complexes interfering with  $^{11}\text{B}^{16}\text{O}_2$ , and organic molecule breakdown to  $^{12}\text{C}^{14}\text{N}^{16}\text{O}$  which interferes with  $^{10}\text{B}^{16}\text{O}_2$ ), and in the early 2000s it was apparent that large inconsistencies existed between laboratories (Gonfiantini et al., 2003; Hönisch et al., 2003). A major advance came with the development of MC-ICPMS mass spectrometers, and their application to boron isotope geochemistry (Foster, 2008), and although offsets between the two techniques become apparent, the data are comparable (e.g., Farmer et al., 2016; Foster et al., 2013). Provided problems associated with sample wash-out and complete matrix separation are dealt with, plasma mass spectrometry presents a variety of advantages over P/N-TIMS, with higher sample throughput, and an ability to better quantify instrumental mass fractionation through sample standard bracketing. Partly as a result of these analytical improvements, interlaboratory comparability has improved greatly in recent years (Gutjahr et al., 2021), allowing greater comparability of published data sets, and with it advances in our understanding of the ways by which the proxy works (e.g., Raitzsch et al. (2018)), and how  $\text{CO}_2$  varied in the past. In this promising analytical landscape, the methodological frontiers of the boron isotope proxy have become more concerned with processing efficiency, miniaturization, blank elimination, and spatial resolution.

## 2.2. Matrix Separation

One realm in which there have been a number of recent developments (some published within this special collection) is in the efficient separation of sample B from carbonate matrix prior to analysis (a necessary prerequisite for solution MC-ICPMS analysis). Traditionally, this has been achieved by column chemistry, building on methods by Lemarchand, Gaillardet, Göpel, and Manhès (2002), and leveraging the boron-specific anion



**Figure 2.** Citation report of publications spanning 1970–2023 of past boron isotope reconstructions of atmospheric carbon dioxide and ocean pH/carbonate chemistry. A total of 109 papers are published (8,403 total citations) and include paleo-reconstructions based on planktonic foraminifera in pale blue ( $n = 74$ ), coral in light blue ( $n = 28$ ) and other marine carbonates in dark blue ( $n = 7$ ). The interest is growing over time as techniques and precision improve to more than 800 citations per year. Yearly citation data included herein are derived from Clarivate™ (Web of Science™). © Clarivate 2023. All rights reserved.

exchange Amberlite IRA-743 resin (Kiss, 1988). By this method, the sample is buffered and passed through gravity columns, where the resin efficiently strips the borate ion out of the solution, and the remaining boron rapidly re-equilibrates, producing more borate ion until all of the boron is bonded in the column. Most boron-based  $\text{CO}_2$  reconstructions to date have been generated from such manual gravity columns (e.g., Anagnostou et al., 2020; Anderson et al., 2024; Chalk et al., 2017; Foster, 2008), as they have been shown to produce reliable and repeatable data. However, the procedure to purify samples is lengthy, depending on the design and age of the columns, and involves constant supervision. The process of custom-making and calibrating columns is time consuming and labour intensive, meaning only specialized laboratories can perform the separation. Column performance is reduced after many uses, and particularly following exposure to matrices with high organic content, requiring refitting and recalibration (de la Vega, Foster, et al., 2020). These columns must be small to ensure the minimum collection acid is used, because boron is volatile and there is no possibility to dry samples down to concentrate them. Finally, in part because of this volatility, columns are susceptible to fall-in blank contamination during the procedure (e.g., de la Vega, Foster, et al., 2020; Kubota et al., 2021; Trudgill et al., 2024; Xu et al., 2024), and must remain covered as much as possible during chemistry—and yet, if columns are designed to drip quickly to minimize handling time, they may be too fast for the kinetics of boron re-equilibration in the resin bed, and therefore fractionate  $\delta^{11}\text{B}$  of the samples. All these issues have motivated researchers to devise alternative methods of boron purification.

Microsublimation as a method for boron purification was first proposed and developed by Gaillardet et al. (2001), and involves heating samples and allowing the pure evaporated boric acid to accumulate in the top of a conical beaker. Since its development, the method has been applied to a variety of environmental materials (Lemarchand, Gaillardet, Göpel, & Manhès, 2002; Y.-H. Liu et al., 2018), including corals (Anagnostou et al., 2012; Y. W. Liu et al., 2013; Rodríguez-Díaz et al., 2024; Wang et al., 2010) and foraminifera (Misra et al., 2014; Rodríguez-Díaz

**Table 1**  
A Summary of the Principal Methods Used to Measure Boron Isotopes for the Purposes of CO<sub>2</sub> Reconstruction Alongside Their Strengths and Weaknesses, \* Denotes This Special Collection

Principle analytical method	Purification method	Key reference(s)	Strengths	Weaknesses	Other
MC-ICPMS	Column chemistry	(Foster et al., 2008; Kiss, 1988)	Small samples, reproducible, validated.	Blank, specialized lab required, care to avoid matrix overloading.	Has provided the bulk of published $\delta^{11}\text{B-CO}_2$ data
	Microsublimation	(Gaillardet et al., 2001; Lemarchand, Gaillardet, Lewin & Allegre, 2002; Misra et al., 2014; Wang et al., 2010)	Reduced sample handling, low blank.	Not easily reproducible, temperature control is crucial, possible matrix effects	
	PrepFAST	de la Vega, Foster, et al. (2020)	Rapid, no/little human intervention required.	Reproducibility can be impacted by machine and sample cleaning.	Relatively large investment required for machine.
	Pumped columns "Peri-columns"	Xu et al. (2024)	Rapid, low blank.	All samples must be treated identically, speed of pump must be carefully calibrated.	Specialized equipment required
	"Batch" purification	Trudgill et al. (2024)	Limits blank issues, can take place at a leisurely pace.	Manually intensive, can be difficult to achieve full boron yield.	
	Direct injection	(Buisson et al., 2021; Louvat et al., 2011, 2014) Paulhac Buisson et al. (2025)	Samples down to 1 ng with 0.5% precision.	Stability difficult to achieve, small samples require transient signals to be used.	d-DIHEN system required for mass spectrometer.
LA-MC-ICPMS	n/a only cleaning	(Babila et al., 2022; Fietzke et al., 2010; Sadekov et al., 2019; Standish et al., 2019)	No clean lab required, high spatial fidelity. High sensitivity.	Low precision, necessity for correction, expensive equipment, boron concentration low as not separated.	Potentially has a different selection of applications, for example, coral calcification etc.
N-TIMS	n/a only cleaning Matrix removed in some methods.	(Hemming et al., 2008; Hemming & Hanson, 1992; Y. W. Liu et al., 2013)	High sensitivity.	Reproducibility, ionization % difficult to know for certain.	P-TIMS largely replaced.

Note. Other analytical methods are available (e.g., NanoSIMS, Marschall and Montealeone, 2015) but are not commonly used for  $\delta^{11}\text{B-CO}_2$  reconstruction.

et al., 2024). A major advantage of microsublimation is the low boron blank ( $<20$  pg) associated with it, since the sample remains closed at all times, as well as the considerably greater ease and speed of operation. Possible hazards with the method stem from the large isotope fractionation associated with evaporation, meaning that even very small (and thus hard to quantify) losses of B through escape of volatiles, or retention in the solid phase, can have a significant influence on overall results. With careful handling, the long-term reproducibility can be better than  $0.3\text{‰}$  (2sd, Wang et al., 2010; Y.-H. Liu et al., 2018), although it is notable that studies that use this technique consistently report slightly poorer reproducibility for carbonate standards than the  $\sim 0.2\text{‰}$  routinely achievable with gravity columns.

Other matrix separation routines retain the use of anion exchange resin, but aim to reduce blank contamination from the operator, and increase sample throughput. The prepFAST-MC method, for instance, includes a sealed  $25\ \mu\text{L}$  column of Amberlite IRA743 resin, mimicking the traditional gravity column chemistry approach, but samples are processed with an automated set of pumps, without the need for manual loading and extraction of B. This significantly reduces hands-on time and need for expert training as well as reducing blank by reducing operator handling contamination risks. de la Vega, Foster, et al. (2020) developed the method and demonstrated its efficacy for coral and seawater matrices, and boric acid solutions, with up to  $25\ \text{ng}$  B load, and  $60\ \text{min}$  per sample processing time. They demonstrated efficient matrix washout, with comparable  $\delta^{11}\text{B}$  accuracy and precision to the gravity column purification method, and low B procedural blank ( $<60\ \text{pg}$  B). However, while the authors found the system can be adapted for other matrices, such as foraminifera, it requires regular maintenance and screening to prevent blank build up and preserve data quality.

Another new development to boron purification is provided in this special collection by Xu et al. (2024), who present pumped ion-exchange gravity columns (“peri-columns”) designed to greatly speed up the process of boron separation, reducing sample processing time up to eight-fold ( $1.5\ \text{hr}$  for 12 columns). This is achieved by using a peristaltic pump system to create a negative pressure gradient in a Teflon beaker below the column and encourage solutions to pass through. Since the solution never passes through the pump or vacuum tubing, low blanks ( $<30\ \text{pg}$  B) were obtained over a range of boron matrices. Components are commercially available and no liquid is retained on the column after each addition, which holds promise in improving levels of accuracy and reproducibility, provided sample loading and pump speed is well calibrated.

A final alternative to gravity columns is the so-called “batch method” presented in this special collection by Trudgill et al. (2024). In this method, solutions are pipetted in and out of  $1.5\ \text{ml}$  centrifuge tubes filled with pre-cleaned resin, and the ion exchange reaction happens in a sealed environment, with adequate time for boron re-equilibration to occur in the pore space. This presents several advantages over the “traditional” column chemistry, namely that total procedural blanks can be kept low even in sub-optimal laboratory environments, helping to improve consistency between samples and session, however, it is manually intensive, requiring a lot of pipetting. It is also more time efficient as the processing can be done at the user's pace, and up to 24 batch tubes can be processed in the same time as a column set (typically 10–20 columns). Provided matrices stay within defined parameters of ionic strength and acid:sample:buffer ratio, the method promises good reproducibility across a range of sample sizes and matrix types.

While it is possible that traditional gravity columns may remain the “gold standard” in the short term, methodological advances such as those included in this special collection demonstrate the ingenuity of the community, and the breadth of options available to boron isotope geochemists moving forward. The ability to choose from a range of analytical strategies according to one's laboratory infrastructure and sample type improves accessibility of the proxy, while a diversity of methodologies reduces the risk that a method-specific structural bias pervades the entire community.

### 2.3. Sample Miniaturization and Spatial Resolution

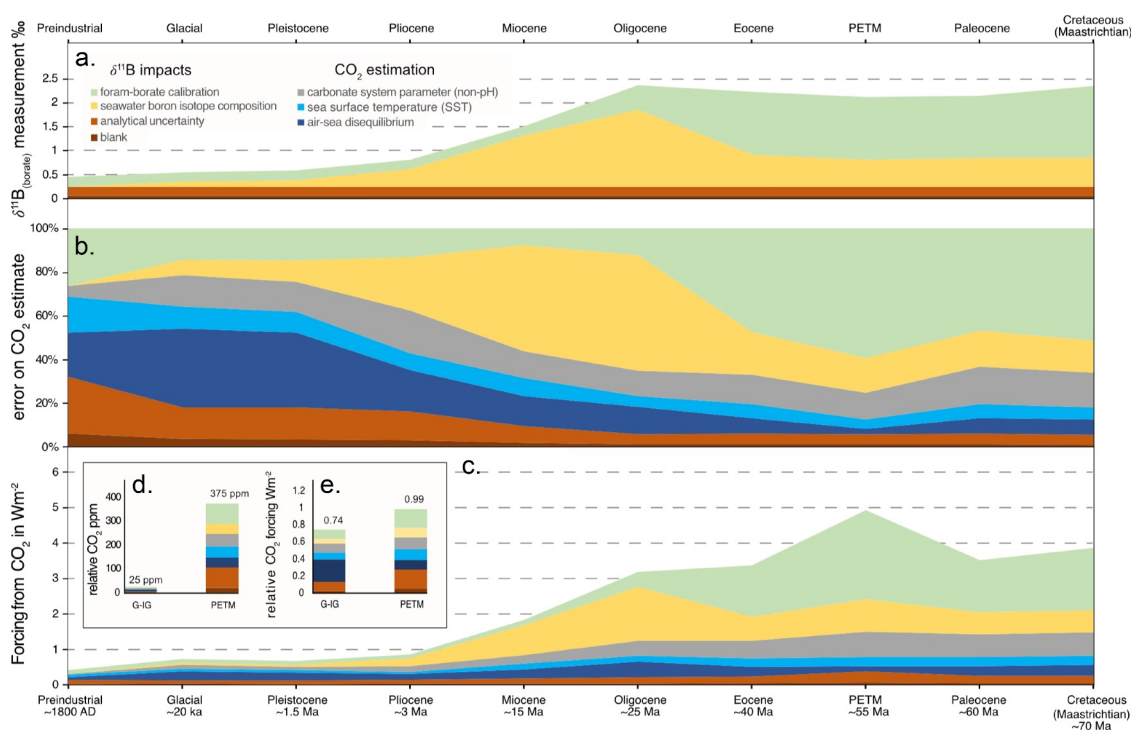
Long-standing open questions surrounding how the boron isotope-pH proxy works, and carbon cycle dynamics during rapid perturbations and transient climate events, would benefit greatly from reductions in the sample size required for analysis. Foraminiferal culture calibrations over a broader range of temperatures, light levels and seawater chemistries are a more feasible prospect if a few individuals (or a few individual chambers) are needed per datapoint, as opposed to, e.g., more than a hundred specimens (e.g., Henehan et al., 2013) or boron addition which changes the buffering capacity of culture media (Howes et al., 2017). Similarly, the temporal resolution at which we can study ocean pH change during an event is greatly improved if enough foraminifera

can be picked for analysis from 0.5 cm of core thickness, rather than >3 cm. Thus, other promising methodological advances in the field surround the reduction in sample size required for a mass spectrometer analysis. A major step in sample size requirement is the roll-out of high resistivity  $10^{13} \Omega$  (and before  $10^{12} \Omega$ ) amplifiers for MC-ICPMS devices, meaning Johnson-Nyquist noise on Faraday cups becomes proportionally reduced for small sample signals. A further methodological advance is provided in this special collection by Paulhac Buisson et al. (2025), building on the earlier work by Louvat et al. (2014), whereby rather than being nebulized into a spray chamber (where most sample B is lost), analyte solutions are directly injected into the plasma. Using transient signals (to allow for extra small volumes) the demountable-Direct Injection High Efficiency Nebulizer method can measure samples containing less than 1 ng B (compared to a typical 15–20 ng), and in addition results in improved washout time. To date, plasma instability arising from the method has limited its application within the field of past  $\text{CO}_2$  reconstruction, but Paulhac Buisson et al. (2025) demonstrate the considerable potential of the method through their work determining  $\delta^{11}\text{B}$  size effects in foraminifera of low B concentrations.

Another area of methodological advance is in situ boron isotope analysis, which includes measurements of single foraminifera shells and enhanced spatial-resolution of marine carbonates (e.g., corals and foraminifera) via laser ablation MC-ICPMS. A critical advance in this has been the recognition of interference from scattered ions (such as  $\text{Ca}^{4+}$ ) on  $^{10}\text{B}$  signals which biases  $\delta^{11}\text{B}$  toward light values (Evans et al., 2021; Sadekov et al., 2019; Standish et al., 2019), although this phenomenon does not appear to be present in all instrumentation and analytical methods (Fietzke & Anagnostou, 2023; Steinhöfel et al., 2023). To correct the contribution of the interference involves monitoring a mass range proximal to  $^{10}\text{B}$ , and analyzing a range of known carbonate standards of differing B/Ca, applying a post-hoc correction to sample values according to the ratio of  $^{11}\text{B}$  to interference in each sample (Coenen et al., 2024; Evans et al., 2021; Sadekov et al., 2019; Standish et al., 2019). Although the analysis of small transient signals, and the multiplicative uncertainty propagating through matrix correction means that individual foraminifera laser  $\delta^{11}\text{B}$  measurements are associated with larger analytical uncertainties compared to solution methods, the technique may still yield useful insights in sample-limited studies. The ability to resolve intra-shell chamber-to-chamber variability and individual vs. population  $\delta^{11}\text{B}$  values may provide insights on ontogeny, biomineralization and ecological contributions to foraminiferal “vital effects” (see below). To date, published analyses of single planktic foraminifera reveal a large degree of inter-individual variability that are significantly too large to be consistent with seasonal or depth-related differences, or modeled vital effects (Mayk et al., 2020).

### 3. Boron Isotope Calibrations and Vital Effects

It has been shown that the  $\delta^{11}\text{B}$  of planktic foraminifera, while changing with pH broadly as predicted by the theoretical basis of the proxy (Hemming & Hanson, 1992; Vengosh et al., 1991), is not equal to seawater borate  $\delta^{11}\text{B}$  (e.g., Henehan et al., 2016; Raitzsch et al., 2018; Sanyal et al., 2001). Such offsets have been attributed to modifications of the pH within the immediate microenvironment of foraminifera shells through photosynthesis ( $\text{CO}_2$  uptake), respiration ( $\text{CO}_2$  release) and calcification ( $\text{CO}_2$  release), collectively known as “vital effects” (Hönisch et al., 2003; Zeebe et al., 2003), and can be accounted for in extant species through the use of species-specific pH calibrations (e.g., Henehan et al., 2016 and references therein). Prior to ~20 Myr, however, there are few or no extant species available, which means beyond this time the contribution of uncertainty from vital effects to  $\text{CO}_2$  reconstructions becomes substantially larger (see Figure 3). For extinct foraminifera, an accurate evaluation of foraminifera vital effects remains a challenge, and introduces uncertainty that is difficult to quantify. In the literature this uncertainty has been dealt with a number of ways. For example, analogies with modern ecophysiology can be drawn from independent O and C isotope analysis and relative positions within multi-species depth profiles (Anagnostou et al., 2016; Babila et al., 2018; Henehan et al., 2020). It has also been suggested that size-fraction differences in  $\delta^{11}\text{B}$  may be indicative of symbiosis, with increasing  $\delta^{11}\text{B}$  with size potentially indicative of symbiosis and non-symbiotic species showing no such increase, or a decrease (Henehan et al., 2016). In addition, determination of offsets in  $\delta^{11}\text{B}$  across species can be used to inform the choice of species calibration (Anagnostou et al., 2020; Harper et al., 2020; Henehan et al., 2019, 2020). In this special collection, Anderson et al. (2024) measure offsets between species to imbricate known vital effects from extant foraminifera through Oligocene ancestors, adding sequentially more extinct species through time. Although perhaps not feasible for the Cretaceous, where turnover of species is geologically instantaneous and almost complete, this approach has great potential for improving our  $\text{CO}_2$  estimates in the Cenozoic, and has resulted in a significant improvement of our



**Figure 3.** Contribution of uncertainties in  $\text{CO}_2$  calculations over the past ~70 million years. (top, a) The total contribution to uncertainty on the reconstruction of borate (excluding chemistry calculation inputs) by age, from left to right the Preindustrial, Last Glacial Maximum, Middle Pleistocene, Pliocene, Miocene, Oligocene, Eocene, Paleocene-Eocene Thermal Maximum (PETM), Paleocene and Late Cretaceous. The major component is analytical and foraminifera calibration for the recent, and calibration and sea water composition for the pre-Pliocene. (middle, b) The relative contribution of each error to calculated  $\text{CO}_2$  values, the importance of analytical uncertainty, temperature, and disequilibrium is highest in the Plio-Pleistocene but less important than seawater chemistry and foraminifera calibrations in the Miocene and Paleocene. (bottom, c) The contribution of each uncertainty in radiative forcing from  $\text{CO}_2$  in absolute terms. Inset (left, d): relative uncertainty across glacial-interglacial cycles (left bars) and PETM onset in (right bars) relative  $\text{CO}_2$  and (right, e) relative forcing. Despite the much larger absolute (c) and relative errors (d) during the PETM, the impact of the uncertainty on forcing is much lower at high  $\text{CO}_2$  due to the logarithmic nature of  $\text{CO}_2$  forcing on climate (e).

understanding of Oligocene  $\text{CO}_2$ . Improvements in interlaboratory agreement (Gutjahr et al., 2021; Stewart et al., 2021) assist in deriving and constraining vital effect corrections via improved accuracy, even between different studies, although caution must still be taken when re-interpreting older published calibrations (see Henehan et al., 2016). Finally, it is also worth noting that the adjustment of modern calibrations to account for past seawater  $\delta^{11}\text{B}$  has significantly reduced the absolute magnitude of vital effect corrections implied for extinct foraminifera (Greenop et al., 2019), and that uncertainty stemming from vital effect corrections can also be significantly reduced by reconstructing relative changes in seawater pH/atmospheric  $\text{CO}_2$  through time (Figure 3).

Despite the available strategies to parameterize vital effects in extinct planktonic foraminifera, a full mechanistic understanding of their origin must ultimately remain a goal for the community. Aside from symbiont activity, species-specific differences in pH modification of seawater vacuolization have also been proposed as potential avenues for exploration for species-specific vital effects (de Nooijer et al., 2014; Hönisch et al., 2021). The potential for intra-shell measurements of  $\delta^{11}\text{B}$  by laser ablation, and now the ability to achieve planktic foraminiferal reproduction in vitro (Davis et al., 2020; Meilland et al., 2023), mean we are at an exciting juncture in understanding vital effects.

#### 4. Impacts of Foraminiferal Preservation and Sample Impurity on Boron Isotope Ratios

The boron concentration and isotope composition of foraminifera can be altered by dissolution and diagenesis post mortem, in the water column and during sediment burial. Most  $\delta^{11}\text{B}$ -based  $\text{CO}_2$  records are generated from core sites above the paleo-carbonate compensation depth (CCD) located in the tropical to mid-latitudes, where  $\text{CO}_2$  concentrations in the surface ocean are more likely to be in equilibrium with the atmosphere (Figure 3b).

Core sites selected for minimal CO<sub>2</sub> disequilibrium are however not necessarily the locations with the best preservation of calcium carbonate sediments. Supplemental information such as temperature ( $\delta^{18}\text{O}$ , Mg/Ca) required for CO<sub>2</sub> reconstruction is known to be highly susceptible to diagenetic alteration, specifically in tropical sites with large surface to deep ocean temperature gradients. While unknown temperature adds additional uncertainty to climate sensitivity calculations, relative uncertainty in temperature proxies only minimally contributes to calculated CO<sub>2</sub> uncertainty and even less to radiative forcing calculation (Hain et al., 2018, & Figure 3 light blue bands).

Several strategies are used to evaluate the potential impacts on foraminiferal  $\delta^{11}\text{B}$  signatures from varying quality of preservation. Visually, foraminiferal specimens with glassy shell texture are the qualitative benchmark for optimal preservation compared with poorly preserved specimens with opaque frosty shell texture (Pearson et al., 2001; Sexton et al., 2006). These are typically found in continental shelf sites such as ODP 174AX located in the Mid-Atlantic US coastal plain and Tanzania, where low porosity clay-rich sediments mean any alteration occurs in a relatively closed system and results in minimal change in isotopic composition (Anagnostou et al., 2016; Babila et al., 2022; Badger et al., 2013; Pearson et al., 2009). This is in contrast to pelagic, high-porosity, predominantly calcium carbonate sands, such as ODP Site 865 located on Allison Guyot, where recrystallization occurs in a completely or partially open system at oversaturated calcium carbonate conditions, possibly resulting in isotopic re-equilibration and/or carbonate overgrowth (Kozdon et al., 2013). Besides visual appearance, more detailed imaging techniques such as electron microscope and X-ray micro-tomography can provide quantitative information on shell thickness and porosity, and qualitative information on phase transformations or crystal reordering.

Geochemical metrics such as Sr/Ca are also used to monitor the degree of potential diagenetic alteration (Kozdon et al., 2013), because Sr is released into pore fluids during calcite dissolution and excluded during inorganic calcite (re)precipitation. Further, electron microprobe analyses have been used to identify elemental banding as an indication of elemental preservation even in recrystallized foraminifera, offering the opportunity to utilize diagenetically altered archives for reconstructions when specific conditions are met (Staudigel et al., 2022). To date there have only been a few studies that have assessed the effect of dissolution and diagenesis on foraminifera boron isotopes. Some evidence does point to a potential effect of dissolution on  $\delta^{11}\text{B}$ , which appears to be strongly species-specific (Hönisch & Hemming, 2004; Ni et al., 2007; Seki et al., 2010). Furthermore, dissolution may affect other trace and minor element concentrations in some planktonic foraminifera species that are used in calculating pH and CO<sub>2</sub>. For example, Mg/Ca derived sea surface temperatures (SSTs) are commonly used in the estimation of dissociation constants necessary for  $\delta^{11}\text{B}$ -CO<sub>2</sub> calculation. Global compilation assessment on the impact of dissolution on Mg/Ca shows a similar pattern of Mg loss (e.g., lower SSTs) below a critical threshold value for bottom water saturation state (Regenberg et al., 2014). In the case that bottom water saturation state ( $\Delta\text{CO}_3^{2-}$ ) values are uncertain, the potential dissolution bias on planktonic foraminifera Mg/Ca values is unaccounted for, and the lower calculated SSTs would result in lower  $\delta^{11}\text{B}_{\text{borate}}$  estimates and hence introduce an additional source of systematic uncertainty on CO<sub>2</sub> reconstruction. In the case of recrystallization, Edgar et al. (2015) examined inter-species differences in two time-equivalent samples—one well-preserved, glassy, from Tanzania and one poorly-preserved, frosty, from ODP 865. Although Sr/Ca and B/Ca ratios were lower in the recrystallized foraminifera, there was negligible difference in their absolute  $\delta^{11}\text{B}$ , or in the  $\delta^{11}\text{B}$  offset between specimens (Edgar et al., 2015). This muted impact of diagenetic recrystallization on foraminiferal  $\delta^{11}\text{B}$  records is encouraging for CO<sub>2</sub> reconstruction, and indeed is supported by the consistency of CO<sub>2</sub> estimates in recent compilations (Hönisch et al., 2023; Rae et al., 2021) although caution is warranted, as diagenesis is heterogeneous in space and time, and the apparent absence of effects in these cases does not preclude their occurrence elsewhere.

Although geochemical metrics to objectively assess the preservation and pristine composition of foraminifera do exist, often boron isotope data are published with only a limited quantity of elemental composition data (e.g., element/Ca ratios). In particular, Al/Ca ratios are a powerful tool to detect contamination from clay, which can influence  $\delta^{11}\text{B}$  by introducing isotopically-light contaminant B that is adsorbed to it. Additional element/Ca ratios that can help to indicate clay contamination include Mn/Ca, Fe/Ca, Ti/Ca, and U/Ca, although Fe and Mn contamination can also stem from ferromanganese coatings, which are typically low [B] (Axelsson et al., 2002; Yu et al., 2007). We encourage the community to accompany  $\delta^{11}\text{B}$  values with a suite of element/Ca results to help identify possible sources of contamination. In addition, methodological descriptions of sample treatment and cleaning can lack sufficient detail to assess whether observed element/Ca data are primary or a potential artifact of

too much/too little cleaning, leading to potentially important datasets being vetted from future compilations or altered data being included erroneously. Important to note is whether clay removal and oxidative cleaning steps were performed (e.g., Barker et al., 2003), if, and how, samples were also subject to additional steps such as reductive cleaning (e.g., Boyle & Keigwin, 1985). While reductive cleaning may prove helpful in some instances, it can lead to partial sample dissolution (Yu et al., 2007), which in at least some cases has led to changes in measured  $\delta^{11}\text{B}$  (e.g., Hönisch & Hemming, 2004; Ni et al., 2007), as well as trace element ratios used as accessory inputs for pH and  $\text{CO}_2$  calculations (e.g., Mg/Ca; Regenberg et al., 2014).

## 5. Accessory Inputs for Calculating Past Atmospheric Carbon Dioxide ( $\text{CO}_2$ )

### 5.1. Boron Isotope Composition of Seawater ( $\delta^{11}\text{B}_{\text{sw}}$ )

Reconstruction of pH, and by extension  $\text{CO}_2$ , requires knowledge of  $\delta^{11}\text{B}_{\text{sw}}$ . While the modern ocean  $\delta^{11}\text{B}_{\text{sw}}$  is well-characterized through direct seawater measurements (Foster et al., 2010; Lemarchand et al., 2000),  $\delta^{11}\text{B}_{\text{sw}}$  is expected to have differed in the past, varying over geological time scales of  $\sim 10$  million years (the residence time of boron in seawater) as a result of changes to major boron inputs and output fluxes (Jurikova et al., 2023; Lemarchand et al., 2000). The geological record of  $\delta^{11}\text{B}_{\text{sw}}$  has been, however, notoriously difficult to constrain because most potential seawater archives (carbonates, opal, clays) most likely preferentially incorporate the charged borate ion rather than bulk seawater boron composition (e.g., Hemming & Hanson, 1992). Halite fluid inclusions show some promise for recording  $\delta^{11}\text{B}_{\text{sw}}$ , but uncertainties remain about the extent of preservation of primary  $\delta^{11}\text{B}$  signatures in halites (Paris et al., 2010). In the absence of direct means for deriving past  $\delta^{11}\text{B}_{\text{sw}}$ , most studies reconstructing ocean pH and atmospheric  $\text{CO}_2$  from boron isotopes have relied on obtaining  $\delta^{11}\text{B}_{\text{sw}}$  by back-calculation from  $\delta^{11}\text{B}_{\text{CaCO}_3}$  by making assumptions about pH and/or the carbonate system. An approach for constraining past  $\delta^{11}\text{B}_{\text{sw}}$  exploits the presence of a vertical gradient in ocean pH, through surface to subsurface foraminiferal  $\delta^{11}\text{B}$  measurements, which is linked to gradients in carbon isotopes, Dissolved Inorganic Carbon (DIC) and apparent oxygen utilization and compare to modern oceanic pH gradients (Anagnostou et al., 2016; Foster et al., 2012; Greenop et al., 2017; Henehan et al., 2019; Palmer et al., 1998; Pearson & Palmer, 2000). Past  $\delta^{11}\text{B}_{\text{sw}}$  has also been constrained by making assumptions about long-term deep-sea pH change through time and comparing to geochemical records (Raitzsch and Hönisch, 2013), and in studies focusing on short-term carbon cycle events and mass extinctions by making assumptions about background pre-event pH underpinned by model outputs (Babila et al., 2022; Clarkson et al., 2015; Gutjahr et al., 2017; Jurikova et al., 2020). So far all of these approaches have produced valuable constraints on possible  $\delta^{11}\text{B}_{\text{sw}}$  values during various time intervals, which combined provide a more complete reconstruction of  $\delta^{11}\text{B}_{\text{sw}}$ .

In this special collection, Whiteford, Heaton, et al. (2024), present a statistically-robust  $\delta^{11}\text{B}_{\text{sw}}$  record over the Cenozoic which integrates previously published and updated  $\delta^{11}\text{B}_{\text{sw}}$  estimates. Whiteford, Heaton, et al. (2024) apply a Gaussian process technique to interpolate between the individual  $\delta^{11}\text{B}_{\text{sw}}$  estimates, generating a Cenozoic  $\delta^{11}\text{B}_{\text{sw}}$  reconstruction with rigorously propagated uncertainties. The use of the Gaussian technique also enables the authors to incorporate a mechanistic understanding of realistic  $\delta^{11}\text{B}_{\text{sw}}$  rate of change into the interpolation, thereby creating a Cenozoic  $\delta^{11}\text{B}_{\text{sw}}$  reconstruction that is grounded in our current understanding of past seawater boron budgets.

That we are still somewhat away from a full understanding of the geologic evolution of  $\delta^{11}\text{B}_{\text{sw}}$  is also made evident in Whiteford, Heaton, et al. (2024). Major data gaps limiting our understanding of  $\delta^{11}\text{B}_{\text{sw}}$  exist in particular in the Paleogene and the Miocene, where empirical constraints are either limited or inconsistent, leading to a large uncertainty bound. For example, in the Miocene, Whiteford, Heaton, et al. (2024) suggest  $\sim 1\%$  higher  $\delta^{11}\text{B}_{\text{sw}}$  than considered in recent calculations of pH and  $\text{CO}_2$  (Rae et al., 2021) implying seawater pH  $\sim 0.15$  units more acidic and leaving  $\text{CO}_2$  as much as 50% higher for a time interval considered crucial to understanding the climate system in a warmer world. To better judge what the true  $\delta^{11}\text{B}_{\text{sw}}$  was in the past, it would help to have an improved understanding of the boron cycle, and how it differed in for example, the Miocene. While Ring et al. (2025) in this special issue do not present a new, complete model for the evolving global boron cycle, they demonstrate that the canonical explanation for why  $\delta^{11}\text{B}_{\text{sw}}$  changed geologically-rapidly in the Neogene—that the adsorption flux of isotopically-light B onto clastic sediments increased with enhanced erosion (Lemarchand, Gaillardet, Göpel, & Manhès, 2002)—is almost certainly incorrect. Instead, they argue, the adsorption flux should have been broadly stable over the past 40 Myr. It is therefore clear that alongside efforts to

provide new empirical constraints on  $\delta^{11}\text{B}_{\text{sw}}$  in the geological past, there is still considerable scope to improve our current understanding of the global boron cycle, to provide a theoretical scaffold to corroborate these constraints.

## 5.2. A Second Ocean Carbonate System Parameter

Seawater pH is an important metric of the state of seawater carbonate chemistry; however two variables of the carbonate system are required in order to robustly estimate atmospheric  $\text{CO}_2$ , and quantitative proxies for other seawater carbonate chemistry parameters are lacking.

Orbital scale Plio-Pleistocene reconstructions spanning the last 5 million years commonly use a range of alkalinity informed by modern values, salinity, or sea-level to be combined with pH to calculate atmospheric  $\text{CO}_2$  (Chalk et al., 2017; Dyez et al., 2018; Henehan et al., 2013; Martínez-Botí et al., 2015). A strategy to minimize the influence of assumptions about secondary carbonate system constraints is to focus on relative pH change ( $\Delta\text{pH}$ ) instead of reconstructing absolute pH and  $\text{CO}_2$ . Based on theoretical carbonate chemistry numerical solutions both carbon and  $\text{CaCO}_3$  addition/removal and temperature effects on solubility equilibrium constants contribute a fractional change in  $\text{H}^+$  (pH) and  $\text{CO}_2$ , which results in a linear relationship between  $\Delta\text{pH}$  and climate forcing from  $\text{CO}_2$ . This formalized approach (Hain et al., 2018) therefore only requires a record of past  $\delta^{11}\text{B}_{\text{borate}}$  to reconstruct  $\text{CO}_2$  climate forcing on orbital timescales ( $< \sim 1$  Myr) and does not require independent knowledge of a seawater carbonate chemistry parameter, temperature, or  $\delta^{11}\text{B}_{\text{sw}}$ . The  $\text{CO}_2$  climate forcing calculations derived from ice core measurements and boron isotope  $\Delta\text{pH}$  estimates are consistent, providing validation of the formalism approach (Hain et al., 2018). This approach is best suited for determination of orbital  $\text{CO}_2$  climate forcing over intervals up to  $\sim 1$  million years in duration (the approximate residence time of C in the Earth system), through reconstruction of  $\Delta\text{pH}$  change and  $\Delta\text{forcing}$  from  $\text{CO}_2$  (Brown et al., 2022; de la Vega et al., 2023; Hain et al., 2018).

Prior to the Pliocene, ocean carbonate chemistry (alkalinity and DIC) likely evolved far beyond modern constraints. The carbonate system can be simulated, and carbon cycle model (GEOCARB and LOSCAR) estimates of carbonate chemistry over the last 100 million years are consistent with long term trends in boron isotope and alkenone  $\text{CO}_2$  reconstructions (Berner, 2001; Zeebe and Tyrrell, 2018). However, abrupt ( $< \sim 100$  kyr) climate perturbations such as the Paleogene hyperthermals (i.e., PETM and ETM-2), or other periods where there may have been large oceanic carbon (DIC) changes, require a different treatment for constraining the marine carbonate system (Hönisch et al., 2012; Ridgwell & Schmidt, 2010). Following, we list a number of treatment examples in the literature.

In the Miocene, Sossdian et al. (2018) use a data-driven approach to estimate surface ocean DIC by utilizing records of deep ocean pH and carbonate ion, seawater chemistry [ $\text{Ca}^{2+}$ ] and CCD reconstructions. Deep ocean carbonate ion was calculated based on CCD reconstructions (Pälike et al., 2012; Sime et al., 2007) and assuming either a constant modern [ $\text{Ca}^{2+}$ ] seawater value or [ $\text{Ca}^{2+}$ ] reconstructed from halite inclusions (Brennan et al., 2013; Horita et al., 2002). Deep-ocean benthic boron isotope pH records (Greenop et al., 2017; Raitzsch and Hönisch, 2013) and estimated carbonate ion were then combined with assumptions of oceanic carbon reservoir changes to derive surface ocean DIC. An alternative data-driven approach to reconstruct a secondary ocean carbonate chemistry parameter combines Miocene planktonic foraminiferal boron isotope pH records with B/Ca to derive surface ocean DIC (Sossdian et al., 2020). Good agreement between these two data-driven approaches (Sossdian et al., 2018, 2020), as well as with model estimates of long-term ocean carbonate chemistry (Boudreau et al., 2018; Caves et al., 2016; Longman et al., 2022; Zeebe and Tyrrell, 2018) offers support to these reconstructions of Neogene DIC, and in turn boron isotope-derived atmospheric  $\text{CO}_2$ .

Paleogene carbonate chemistry (DIC and alkalinity) history is comparatively even less understood. In the absence of independent direct estimates,  $\text{CO}_2$  reconstructions tend to be more reliant on long-term or equilibrium model runs and CCD reconstructions. One prediction of these models is that oceanic calcium carbonate saturation state ( $\Omega$ ) is stable on tectonic timescales, due the buffering effect of carbonate compensation (see e.g. Zeebe & Westbroek, 2003), together with the global carbon cycle balance of volcanic outgassing and silicate weathering. Early Paleogene surface ocean  $\Omega$  estimates are relatively constant ( $\pm 1$ ) under a range of carbon cycle modeling studies (Berner, 2001; Boudreau et al., 2018; Ridgwell and Schmidt, 2010; Zeebe and Tyrrell, 2018). However, surface ocean  $\Omega$  is tightly coupled to temperature, and so some Paleogene boron-derived  $\text{CO}_2$  records (Anagnostou et al., 2016, 2020) use spatial GENIE model output to compute site-specific  $\Omega$  values expected based on

their paleolatitude. Alternatively, boron-based ( $\delta^{11}\text{B}$  and B/Ca) reconstructions over carbon cycle perturbations are combined with long-term model DIC estimates (e.g., Zeebe and Tyrrell, 2018) and/or proxy-informed carbon cycle modeling to estimate atmospheric  $\text{CO}_2$  (Harper et al., 2020; Haynes & Hönisch, 2020; Henehan et al., 2019, 2020), or sensitivity analyses are carried out on a range of potential second carbonate system constraints (Harper et al., 2024).

A compilation of boron isotope atmospheric  $\text{CO}_2$  (Rae et al., 2021) over the past 66 million years evaluated four different second carbonate chemistry scenarios of constant alkalinity, DIC,  $\Omega$ , and CCD values, increasing uncertainty with age. It is encouraging given the range of second carbonate chemistry scenarios and varying assumptions that have been made that the broad long-term  $\text{CO}_2$  trends are robust. In this special collection, Köhler, 2023 use the carbon cycle model BICYCLE to generate a wide range of simulations of carbonate chemistries and  $\text{CO}_2$  outputs to provide a consistency check at least for more recent time intervals, enabling a better comparison of all boron isotope  $\text{CO}_2$  reconstructions and a better connection to mechanistic links of  $\text{CO}_2$  change. Emergent knowledge of Phanerozoic ocean carbonate chemistry history when combined with the available boron isotope  $\text{CO}_2$  records will support future investigation of the specific constraints most appropriate for the environmental conditions at different time intervals in Earth's past (e.g., CCD, alkalinity,  $\Omega$ , pH range).

### 5.3. Ocean Temperature

Seawater temperature values are needed to calculate the dissociation/equilibrium constants of the carbonate and borate systems, and thus uncertainty in paleotemperature estimates contributes to the total uncertainty in seawater pH and atmospheric boron-based  $\text{CO}_2$  reconstructions. A full summary of available marine proxies for seawater temperature is presented elsewhere (Hollis et al., 2019). Instead here we will focus on foraminiferal Mg/Ca ratios, which are a common proxy for paleotemperature estimates, since most boron isotope laboratories will measure this routinely while screening for clay contamination and the estimates will then come from exactly the same sample material as  $\delta^{11}\text{B}$  values. One of the key complications of the foraminiferal Mg/Ca-temperature proxy, however, is the influence of non-thermal effects on Mg/Ca, such as seawater Mg/Ca, pH and DIC (e.g., Allen et al., 2016; Evans et al., 2016; Gray & Evans, 2019; Holland et al., 2020; Morley et al., 2024; Russell et al., 2004). This poses a particular computational challenge for boron isotope reconstruction, and necessitates an iterative approach, such as MgCaRB (<https://github.com/dbjevans/MgCaRB>; unless using Bayesian methods, e.g. Harper et al., 2024). In this special collection, Haynes et al. (2023) investigate this carbonate system imprint on the Mg/Ca-temperature proxy further, and challenge existing literature with a set of culture experiments at different pH, [DIC], [Ca], [Mg], and temperature. Some of the most common foraminifera species used for Mg/Ca (and  $\delta^{11}\text{B}$ ) measurements were grown, and the results show that Mg/Ca is less sensitive to pH at lower seawater Mg/Ca values typical of the early Cenozoic. It is also shown that, even in modern conditions, not all species of foraminifera display a dependency of Mg/Ca on pH/DIC, raising questions about the mechanisms behind these apparent effects. The authors further suggest new calibrations for the Mg/Ca proxy and argue against multi-species transfer functions because of the starkly different responses to pH observed between modern species. This result challenges the blanket use of a pH correction on the Mg/Ca temperature proxy with extinct species of foraminifera. Although there are examples where a pH-correction on Mg/Ca temperatures can improve consistency with other proxies (Henehan et al., 2019, 2020), Haynes et al. (2023) clearly demonstrate this should not be treated as the default. Multi-proxy approaches, more dedicated culturing experiments, and cross-species comparisons, ideally using well preserved foraminifera, will be a step forward for the utility of these corrections.

### 5.4. Computational Methods

Although the primary obstacles to directly compare boron-based paleo- $\text{CO}_2$  reconstructions lie in the different assumptions and decisions made in constraining the aforementioned accessory inputs, inconsistencies between studies may also stem from differences in how resultant calculations are carried out. Just as analytical techniques have advanced significantly in the past decade, the sophistication of methods used to calculate  $\text{CO}_2$  has increased significantly from the simple pen and paper or spreadsheet-based calculations of early work. For  $\text{CO}_2$  reconstructions in the more recent geological past, where bulk seawater chemistry can be assumed to be the same as or close to the modern day, the community has a wide range of carbonate system calculator packages at their disposal (e.g., Gattuso et al., 2019; Humphreys et al., 2022; Robbins et al., 2010; van Heuven et al., 2011; Zeebe & Wolf-Gladrow, 2001). These can often be integrated into scripts and routines to automate and speed up carbonate system calculations, improving repeatability and traceability of calculations, but potentially introducing small

**Table 2**  
A Selection of Showing Several (Not Necessarily Realistic) Test Cases for Calculation of pH and pCO<sub>2</sub> Targets

	“Pleistocene type”				“Eocene type”			
	5	2,000	5	2,000	2,000	5	5	
Depth (m)	5	2,000	5	2,000	2,000	5	5	
Temperature (°C)	15	15	25	15	15	25	25	
Salinity	33	35	35	35	35	35	35	
δ <sup>11</sup> B <sub>borate</sub> (‰)	22	14	18	14	14	18	18	
δ <sup>11</sup> B <sub>sw</sub> (‰)	39.61	39.61	39.61	38	39.61	38	39.61	
[Ca] (mmol/kg)	10	10	10	30	30	30	30	
[Mg] (mmol/kg)	53	53	53	35	35	35	35	
[SO <sub>4</sub> <sup>-</sup> ] (mmol/kg)	29	29	29	29	29	29	29	
Alkalinity (μmol/kg)	2,300	2,300	2,300	2,300	2,300	2,300	2,300	
pH target	8.470	7.494	8.037	7.765	7.477	8.156	8.020	
pCO <sub>2</sub> target (μatm)	118	1,320	406	667	1,371	283	420	

*Note.* The inputs from the table above, when calculated in line with best practice should give the target values in the bottom two rows. Note these calculations use the cross-platform package Kgen (Whiteford, Branson, & Mayk, 2024) to generate equilibrium constants, and calculate pH from δ<sup>11</sup>B using their isotopic ratio, rather than delta notation. Use of the more traditional formula in delta notation will result in discrepancies of ~0.009 pH.

differences in CO<sub>2</sub> calculations arising from inconsistencies in these packages (Orr et al., 2015). Furthermore, studies sometimes differ in their choice of carbonate system K constants (e.g., Lueker et al., 2000 vs. Millero et al., 2002) or boron-chlorinity relationship (Uppstrom, 1974 vs. Lee et al., 2010) within these packages, which hinders comparability.

Beyond the timescales of modern-like bulk seawater chemistry, scope for inconsistencies in calculation methods is even greater. This is because while in modern seawater equilibrium constants can be computed for a given temperature, salinity and pressure, when going further back in time variable concentrations of Mg and Ca (to name but two) in seawater can also influence equilibrium constants via changes in ion-pairing behavior (Hain et al., 2015; Zeebe & Tyrrell, 2019). Although there has been some debate as to how this effect should be parameterized (Hain et al., 2018; Zeebe & Tyrrell, 2018, 2019), the need to account for it is clear. Comprehensive Pitzer ion-interaction models (such as the pitzer.dat database included with PHREEQC; Parkhurst and Appelo, 2013) are currently considered the most accurate way to derive equilibrium constants in differential seawater chemistries, and demonstrably agree well with empirical derivations (Henehan et al., 2022). However, these platforms were not designed with a paleoceanographic community in mind, and integrating these into practical carbonate system calculation pipelines can be challenging, requiring a high degree of coding literacy and/or computing power. Partly as a result of this, the pitzer-based MyAMI model (Hain et al., 2015) was published with a look-up table which fit the results of simulations to polynomials according to

seawater [Mg] and [Ca]. While computationally efficient and easy to implement into existing scripts, this look-up table contained unfortunate inaccuracies (see Whiteford, Branson, & Mayk, 2024) that have fed into several published CO<sub>2</sub> records (e.g., Henehan et al., 2019; Henehan et al., 2020). A regenerated look-up table has since been integrated within the carbonate calculation package seacarb (Raitzsch et al., 2021) which can be extracted or used within the framework of the R package to allow the user to account for changing seawater Mg and Ca concentrations.

Another area in which significant advances have been made over the last decade is in the statistical methods used to propagate uncertainties in boron-based CO<sub>2</sub> estimates. While early studies tended to rely on quadratic additions of the uncertainty associated with each accessory input, in particular for deeper time applications where uncertainties in accessory inputs may come into play at multiple points in the calculation process (e.g., seawater [Ca], which affects equilibrium constants, Mg/Ca temperatures and Ω as a second carbonate system parameter), Monte Carlo simulation-based approaches are increasingly preferred (e.g., de la Vega et al., 2023; Martinez-Boti et al., 2015). Although such methods of uncertainty propagation are relatively simple to implement, the need to optimize computational efficiency and to tailor calculation routines to unique challenges associated with different time periods and data sets has led many researchers to devise their own scripts. Inevitably, in such cases discrepancies in scripts can arise. The contribution of Whiteford, Branson, and Mayk (2024), “Kgen” in this issue helps to resolve one source of potential inconsistency, by providing a method of reliably and consistently calculating equilibrium constants that can be implemented in Monte Carlo scripts, whether written in Python, Matlab, or R. To add to this, here we provide a reference table of test values that can be used to benchmark and compare the consistency of scripts (Table 2). We suggest that when publishing CO<sub>2</sub> records calculated using new scripts, authors a) wherever possible use Kgen to ensure consistency (or provide a version of their data set that does, if specific other formulation is desired), and b) provide the results that their script returns for these test values. Furthermore, if using Monte Carlo uncertainty propagation, authors should state clearly not only which uncertainties are accounted for, but should also make clear the nature of the probability distributions assumed for each input parameter uncertainty. We note also, that nascent application of Bayesian approaches to calculating boron-based CO<sub>2</sub> estimates (Harper et al., 2024), if and when applied more widely, may well warrant an analogous set of recommendations in future for this method.

## 6. Emergent Boron Isotope Ocean pH and Carbon Dioxide (CO<sub>2</sub>) Proxy Archives

As is evident from the advances made in all aspects of boron-based CO<sub>2</sub> reconstruction discussed above, the proxy is developing rapidly. Where, then, do the next frontiers in boron isotope proxy applications lie? For one, to date the majority of boron isotope-derived CO<sub>2</sub> reconstructions have been obtained from deep-sea sediment cores. However, critical temporal gaps in pH and CO<sub>2</sub> records exist for past carbon perturbations (PETM and Paleogene hyperthermals), as a result of widespread chemical erosion of carbonate sediments and global ocean acidification (Babila et al., 2018; Hönisch et al., 2012). For climate reconstructions of such events, continental shelf sites are desirable because of their high sedimentation rates and improved foraminifera preservation (i.e., located above CCD) compared to deep-sea cores. Potentially useful for studies relying on coastal/continental shelf sediments, Hong et al. (2024) developed a sequential leaching technique to separate carbonate phase of mixed carbonate-silicate limestones. This provides an avenue to generate reliable  $\delta^{11}\text{B}$  measurements from heterogeneous bulk carbonates. Such sites, however, can often be affected by enhanced seasonal pH variability and potential meteoric diagenesis (Stewart et al., 2015) complicating interpretation of boron isotopes in shallow environments. Also in this special collection, Hardage et al. (2025) provide such a case, investigating boron isotope variability in modern coastal benthic foraminifera species *Ammonia parkinsoniana*. The authors find a  $\delta^{11}\text{B}$ -pH sensitivity for *A. parkinsoniana* consistent with cosmopolitan benthic foraminifera, which is promising. However, in the marginal setting of this study, groundwater flow likely altered regional  $\delta^{11}\text{B}_{\text{sw}}$  values contributing to scatter in the *A. parkinsoniana* boron isotope-pH relationship (Hardage et al., 2025).

Analytical innovations also allow for data to be generated from new archives. Coupling of MC-ICPMS with laser ablation represents a major methodological advancement compared to traditional solution methods that requires milligrams of carbonate sample, thereby offering opportunities to obtain unprecedented “snapshots” of past ocean pH based on boron isotope analysis of a single foraminifera shell, or populations of single shells (Coenen et al., 2024; Mayk et al., 2020; Raitzsch et al., 2021; Standish et al., 2019) (Table 1). As an example of the power of these approaches, first such single-shell boron isotope paleo-record uncovered a hidden precursor carbon pulse—with total emissions similar to those of anthropogenic sources—that drove ocean warming and acidification prior to the PETM (Babila et al., 2022).

Outside of calcite archives, in this special collection Donald et al. (2024) present the first down-core application of the boron isotope proxy to diatom silica, after its relationship with environmental pH and thus CO<sub>2</sub> had previously been established in culture (Donald et al., 2020). The ability to generate pH records from diatoms represents a breakthrough, notably in areas of the ocean where carbonate accumulation may be low or preservation challenging, such as in the high latitude Pacific and Southern Oceans. Donald et al. (2024)'s new data from the North Pacific show a CO<sub>2</sub> decline associated with the intensification of Northern Hemisphere Glaciation, in agreement with comparable data derived from foraminifera (Martínez-Botí et al., 2015). Sedimentologically, this period is also marked by a collapse of opal production in the region, implying a major climatic shift, but one that neither impacts the  $\delta^{11}\text{B}_{\text{diatom}}$  nor the  $[\text{B}]_{\text{diatom}}$ , instilling confidence that the proxy is insensitive to opal production rates.

Finally, while CO<sub>2</sub> over the Cenozoic is increasingly well understood, further back into Earth's past, reconstructions of CO<sub>2</sub> are limited to a few studies, as preservation and fossil material availability becomes increasingly limited, and uncertainty in parameters such as  $\delta^{11}\text{B}_{\text{sw}}$  become even larger. Emerging boron isotope methods (e.g., low number/single shell LA-MC-ICPMS analyses) and sample substrates such as for example, biogenic silica, or non-foraminifera carbonates may well play a significant role in expanding ocean pH and atmospheric CO<sub>2</sub> reconstructions deeper into the Phanerozoic Era; some such as brachiopods are already emerging (Jurikova et al., 2020; Legett et al., 2020; Müller et al., 2020). Alongside this, improvements in our understanding of the controls on seawater  $\delta^{11}\text{B}$  (Ring et al., 2025), and how to quantify uncertainty in this parameter deeper in Earth history (Jurikova et al., 2025; Whiteford, Heaton, et al., 2024) will permit greater confidence in our understanding of the geological evolution of atmospheric CO<sub>2</sub> deeper in Earth's climate history.

## 7. Conclusion and Future Community Outlook

Boron-derived estimates of seawater pH and atmospheric CO<sub>2</sub> have come a long way since their conceptualization, but remain short of the spatial and temporal coverage of other more established proxies (e.g., oxygen isotopes, carbon isotopes, Mg/Ca). Despite the plethora of recent studies (Figure 2), limited orbitally-resolved  $\delta^{11}\text{B}$ -CO<sub>2</sub> data exists, and none prior to the Pliocene. Multi-million-year gaps remain in the continuous record of for example, the Paleogene (Hönisch et al., 2023). In addition, most Cretaceous-Cenozoic boron derived CO<sub>2</sub>

reconstructions are single-site records, mostly within the tropics/subtropics, leaving these susceptible to uncertainty stemming from their ocean environment, preservation quality and/or regional oceanography. Particular intervals of interest due to lack of data are the Early Pleistocene, the Middle to Late Miocene, Oligocene, Paleocene and Cretaceous. The maturity of the boron isotope-pH proxy is such that such issues can now be addressed, not least thanks to a number of advancements highlighted in this special issue. Moving forward, we propose a number of suggestions to the community:

1. The generation and integration of more multiproxy records of CO<sub>2</sub> (e.g., Hönisch et al., 2023), carbonate system (e.g., B/Ca, CCD, %CaCO<sub>3</sub>), and seawater temperature (Mg/Ca, clumped isotopes, organic biomarkers). Combination of such multiproxy records requires careful harmonization of age models (e.g., de Vleeschouwer et al., 2020; Westerhold et al., 2020, an active field of research currently).
2. Further studies focusing on understanding the origin of vital effects and quantifying vital effects in extinct species.
3. Generation of new constraints on  $\delta^{11}\text{B}_{\text{sw}}$  from different proxy archives, focusing on periods where few estimates exist (e.g., Paleogene and Cretaceous), and where such estimates are highly uncertain (Miocene).
4. Focused studies on the impact of preservation on data validity, and strategies to reliably identify diagenetic issues, including recording of metadata in  $\delta^{11}\text{B}$  publications (e.g., Mg/Ca, Mn/Ca, Fe/Ca, Ti/Ca, Al/Ca, Na/Ca, Sr/Ca, i.e. the full set of element/Ca measured).
5. Use of community-tested scripts for data processing to ensure consistent results wherever applicable.

The paleoceanographic community has moved toward more collaborative efforts at understanding past climate. Initiatives like MioMEET, DeepMIP, and CenCO<sub>2</sub>PIP have brought the community together in a constructive and collegial manner. We hope that this initiative, supported by PAGES and AGU, is equally successful in advancing what is a crucial proxy for our understanding of past and future global change.

### Conflict of Interest

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

### Data Availability Statement

No new data are contained in this manuscript. Any data discussed are presented in the relevant Tables and available through the original publications discussed. Data for Figure 2 are obtained from Clarivate™ (Web of Science™) accessed in October 2024 via this link <https://www.webofscience.com/wos/woscc/citation-report/3be9eb65-0dfd-4d21-917d-39403c168597-01194f94df?page=1&sort=date-ascending> and are included as a supplementary table.

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### References

- Allen, K. A., Hönisch, B., Eggins, S. M., Haynes, L. L., Rosenthal, Y., & Yu, J. (2016). Trace element proxies for surface ocean conditions: A synthesis of culture calibrations with planktic foraminifera. *Geochimica et Cosmochimica Acta*, 193, 197–221. <https://doi.org/10.1016/j.gca.2016.08.015>
- Anagnostou, E., Babila, T. L., Chalk, T. B., Henehan, M. J., & Raitzsch, M. (2023). Boron-CO<sub>2</sub> workshop: Testing and extending the limits of the foraminiferal boron proxy for seawater pH and atmospheric CO<sub>2</sub> reconstructions. *Past Global Changes Magazine*, 31(1), 43. <https://doi.org/10.22498/pages.31.1.43>
- Anagnostou, E., Huang, K.-F., You, C.-F., Sikes, E., & Sherrell, R. (2012). Evaluation of boron isotope ratio as a pH proxy in the deep sea coral *Desmophyllum dianthus*: Evidence of physiological pH adjustment. *Earth and Planetary Science Letters*, 349, 251–260. <https://doi.org/10.1016/j.epsl.2012.07.006>
- Anagnostou, E., John, E. H., Babila, T. L., Sexton, P. F., Ridgwell, A., Lunt, D. J., et al. (2020). Proxy evidence for state-dependence of climate sensitivity in the Eocene greenhouse. *Nature Communications*, 11(1), 4436. <https://doi.org/10.1038/s41467-020-17887-x>
- Anagnostou, E., John, E. H., Edgar, K. M., Foster, G. L., Ridgwell, A., Inglis, G. N., et al. (2016). Changing atmospheric CO<sub>2</sub> concentration was the primary driver of early Cenozoic climate. *Nature*, 533(7603), 380–384. <https://doi.org/10.1038/nature17423>
- Anderson, L. B., Hönisch, B., Coxall, H. K., & Bolge, L. (2024). Atmospheric CO<sub>2</sub> estimates for the late Oligocene and early Miocene using multi-species cross-calibrations of boron isotopes. *Paleoceanography and Paleoclimatology*, 39(1), e2022PA004569. <https://doi.org/10.1029/2022pa004569>
- Axelsson, M. D., Rodushkin, I., Baxter, D. C., Ingri, J., & Öhlander, B. (2002). High spatial resolution analysis of ferromanganese concretions by LA-ICP-MS. *Geochemical Transactions*, 3, 1–8. <https://doi.org/10.1186/1467-4866-3-40>
- Babila, T. L., Penman, D. E., Hönisch, B., Kelly, D. C., Bralower, T. J., Rosenthal, Y., & Zachos, J. C. (2018). Capturing the global signature of surface ocean acidification during the Palaeocene–Eocene Thermal Maximum. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 376(2130), 20170072. <https://doi.org/10.1098/rsta.2017.0072>
- Babila, T. L., Penman, D. E., Standish, C. D., Doubrawa, M., Bralower, T. J., Robinson, M. M., et al. (2022). Surface ocean warming and acidification driven by rapid carbon release precedes Paleocene-Eocene Thermal Maximum. *Science Advances*, 8(11), eabg1025. <https://doi.org/10.1126/sciadv.abg1025>

- Badger, M. P., Schmidt, D. N., Mackensen, A., & Pancost, R. D. (2013). High-resolution alkenone palaeobarometry indicates relatively stable pCO<sub>2</sub> during the Pliocene (3.3–2.8 Ma). *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 371(2001), 20130094. <https://doi.org/10.1098/rsta.2013.0094>
- Barker, S., Greaves, M., & Elderfield, H. (2003). A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. *Geochemistry, Geophysics, Geosystems*, 4(9), 8407. <https://doi.org/10.1029/2003gc000559>
- Bernasconi, S. M., Müller, I. A., Bergmann, K. D., Breitenbach, S. F., Fernandez, A., Hodell, D. A., et al. (2018). Reducing uncertainties in carbonate clumped isotope analysis through consistent carbonate-based standardization. *Geochemistry, Geophysics, Geosystems*, 19(9), 2895–2914. <https://doi.org/10.1029/2017gc007385>
- Berner, R. A. (2001). Modeling atmospheric O<sub>2</sub> over Phanerozoic time. *Geochimica et Cosmochimica Acta*, 65(5), 685–694. [https://doi.org/10.1016/s0016-7037\(00\)00572-x](https://doi.org/10.1016/s0016-7037(00)00572-x)
- Boudreau, B. P., Middelburg, J. J., & Luo, Y. (2018). The role of calcification in carbonate compensation. *Nature Geoscience*, 11(12), 894–900. <https://doi.org/10.1038/s41561-018-0259-5>
- Boyle, E. A., & Keigwin, L. D. (1985). Comparison of Atlantic and Pacific paleochemical records for the last 215,000 years: Changes in deep ocean circulation and chemical inventories. *Earth and Planetary Science Letters*, 76(1–2), 135–150. [https://doi.org/10.1016/0012-821x\(85\)90154-2](https://doi.org/10.1016/0012-821x(85)90154-2)
- Brennan, C., Meissner, K., Eby, M., Hillaire-Marcel, C., & Weaver, A. (2013). Impact of sea ice variability on the oxygen isotope content of seawater under glacial and interglacial conditions. *Paleoceanography and Paleoclimatology*, 28(3), 388–400. <https://doi.org/10.1002/palo.20036>
- Brown, R. M., Chalk, T. B., Crocker, A. J., Wilson, P. A., & Foster, G. L. (2022). Late Miocene cooling coupled to carbon dioxide with Pleistocene-like climate sensitivity. *Nature Geoscience*, 15(8), 664–670. <https://doi.org/10.1038/s41561-022-00982-7>
- Buisson, M., Louvat, P., Thaler, C., & Rollion-Bard, C. (2021). High precision MC-ICP-MS measurements of 11B/10B ratios from ng amounts of boron in carbonate samples using microsublimation and direct injection ( $\mu$ -dDIHEN). *Journal of Analytical Atomic Spectrometry*, 36(10), 2116–2131. <https://doi.org/10.1039/d1ja00109d>
- Caves, J. K., Jost, A. B., Lau, K. V., & Maher, K. (2016). Cenozoic carbon cycle imbalances and a variable weathering feedback. *Earth and Planetary Science Letters*, 450, 152–163. <https://doi.org/10.1016/j.epsl.2016.06.035>
- Chalk, T. B., Capron, E., Drew, M., & Panagiotopoulos, K. (2017). Interglacials of the 41 ka-world and the mid-pleistocene transition. *Past Global Changes Magazine*, 25(3), 155. <https://doi.org/10.22498/pages.25.3.155>
- Clarkson, M., Kasemann, S. A., Wood, R., Lenton, T., Daines, S., 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>
- Coenen, D., Evans, D., Jurikova, H., Dumont, M., Rae, J., & Müller, W. (2024). Determining the sources of (sub)permil-level inaccuracy during laser ablation-MC-ICPMS boron isotope measurements of carbonates. *Journal of Analytical Atomic Spectrometry*, 39(10), 2409–2420. <https://doi.org/10.1039/d4ja00154k>
- Davis, C. V., Livsey, C. M., Palmer, H. M., Hull, P. M., Thomas, E., Hill, T. M., & Benitez-Nelson, C. R. (2020). Extensive morphological variability in asexually produced planktic foraminifera. *Science Advances*, 6(28), eabb8930. <https://doi.org/10.1126/sciadv.abb8930>
- dela Vega, E., Chalk, T. B., Hain, M. P., Wilding, M. R., Casey, D., Gledhill, R., et al. (2023). Orbital CO<sub>2</sub> reconstruction using boron isotopes during the late Pleistocene, an assessment of accuracy. *Climate of the Past*, 19(12), 2493–2510. <https://doi.org/10.5194/cp-19-2493-2023>
- dela Vega, E., Chalk, T. B., Wilson, P. A., Bysani, R. P., & Foster, G. L. (2020). Atmospheric CO<sub>2</sub> during the mid-Piacenzian warm period and the M2 glaciation. *Scientific Reports*, 10(1), 11002. <https://doi.org/10.1038/s41598-020-67154-8>
- dela Vega, E., Foster, G. L., Martínez-Botí, M. A., Anagnostou, E., Field, M. P., Kim, M. H., et al. (2020). Automation of boron chromatographic purification for  $\delta^{11}\text{B}$  analysis of coral aragonite. *Rapid Communications in Mass Spectrometry*, 34(11), e8762. <https://doi.org/10.1002/rcm.8762>
- de Nooijer, L. D., Spero, H., Erez, J., Bijma, J., & Reichert, G.-J. (2014). Biomineralization in perforate foraminifera. *Earth-Science Reviews*, 135, 48–58. <https://doi.org/10.1016/j.earscirev.2014.03.013>
- de Vleeschouwer, D., Drury, A. J., Vahlenkamp, M., Rochholz, F., Liebrand, D., & Pälke, H. (2020). High-latitude biomes and rock weathering mediate climate–carbon cycle feedbacks on eccentricity timescales. *Nature Communications*, 11(1), 5013. <https://doi.org/10.1038/s41467-020-18733-w>
- Donald, H., Swann, G., Rae, J., & Foster, G. (2024). Carbon cycle and circulation change in the North Pacific Ocean at the initiation of Northern Hemisphere glaciation constrained by boron-based proxies in diatoms. *Paleoceanography and Paleoclimatology*, 39(11), e2024PA004968. <https://doi.org/10.1029/2024pa004968>
- Donald, H. K., Foster, G. L., Fröhberg, N., Swann, G. E., Poulton, A. J., Moore, C. M., & Humphreys, M. P. (2020). The pH dependency of the boron isotopic composition of diatom opal (*Thalassiosira weissflogii*). *Biogeosciences*, 17(10), 2825–2837. <https://doi.org/10.5194/bg-17-2825-2020>
- Dyez, K. A., Hönisch, B., & Schmidt, G. A. (2018). Early Pleistocene obliquity-scale pCO<sub>2</sub> variability at ~1.5 million years ago. *Paleoceanography and Paleoclimatology*, 33, 1270–1291. <https://doi.org/10.1029/2018PA003349>
- Edgar, K. M., Anagnostou, E., Pearson, P. N., & Foster, G. L. (2015). Assessing the impact of diagenesis on  $\delta^{11}\text{B}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , Sr/Ca and B/Ca values in fossil planktic foraminiferal calcite. *Geochimica et Cosmochimica Acta*, 166, 189–209. <https://doi.org/10.1016/j.gca.2015.06.018>
- Emiliani, C. (1966). Isotopic Paleotemperatures: Urey's method of paleotemperature analysis has greatly contributed to our knowledge of past climates. *Science*, 154(3751), 851–857. <https://doi.org/10.1126/science.154.3751.851>
- Evans, D., Gerdes, A., Coenen, D., Marschall, H. R., & Müller, W. (2021). Accurate correction for the matrix interference on laser ablation MC-ICPMS boron isotope measurements in CaCO<sub>3</sub> and silicate matrices. *Journal of Analytical Atomic Spectrometry*, 36(8), 1607–1617. <https://doi.org/10.1039/d1ja00073j>
- Evans, D., Wade, B. S., Henehan, M., Erez, J., & Müller, W. (2016). Revisiting carbonate chemistry controls on planktic foraminifera Mg/Ca: Implications for sea surface temperature and hydrology shifts over the Paleocene–Eocene Thermal Maximum and Eocene–Oligocene transition. *Climate of the Past*, 12(4), 819–835. <https://doi.org/10.5194/cp-12-819-2016>
- Farmer, J. R., Hönisch, B., & Uchikawa, J. (2016). Single laboratory comparison of MC-ICP-MS and N-TIMS boron isotope analyses in marine carbonates. *Chemical Geology*, 447, 173–182. <https://doi.org/10.1016/j.chemgeo.2016.11.008>
- Fietzke, J., & Anagnostou, E. (2023). Sources of inaccuracy in boron isotope measurement using LA-MC-ICP-MS. *Geostandards and Geo-analytical Research*, 47(3), 481–492. <https://doi.org/10.1111/ggr.12511>
- Fietzke, J., Heinemann, A., Taubner, I., Böhm, F., Erez, J., & Eisenhauer, A. (2010). Boron isotope ratio determination in carbonates via LA-MC-ICP-MS using soda-lime glass standards as reference material. *Journal of Analytical Atomic Spectrometry*, 25(12), 1953–1957. <https://doi.org/10.1039/c0ja00036a>
- Foster, G. L. (2008). Seawater pH, pCO<sub>2</sub> and [CO<sub>3</sub><sup>2-</sup>]<sub>3</sub> 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, 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<sub>3</sub> by MC-ICPMS and NTIMS. *Chemical Geology*, 358, 1–14. <https://doi.org/10.1016/j.chemgeo.2013.08.027>
- Foster, G. L., Lear, C. H., & Rae, J. W. B. (2012). The evolution of pCO<sub>2</sub>, ice volume and climate during the middle Miocene. *Earth and Planetary Science Letters*, 341–344, 243–254. <https://doi.org/10.1016/j.epsl.2012.06.007>
- Foster, G. L., Rae, J., & Elliott, T. (2008). Boron isotope measurements of marine carbonate using MC-ICPMS. *Geochimica et Cosmochimica Acta*, A279.
- Foster, G. L., von Strandmann, P., & Rae, J. W. B. (2010). Boron and magnesium isotopic composition of seawater. *Geochemistry, Geophysics, Geosystems*, 11(8). <https://doi.org/10.1029/2010gc003201>
- Gaillardet, J., Lemarchand, D., Göpel, C., & Manhès, G. (2001). Evaporation and sublimation of boric acid: Application for boron purification from organic rich solutions. *Geostandards Newsletter*, 25(1), 67–75. <https://doi.org/10.1111/j.1751-908x.2001.tb00788.x>
- Gattuso, J.-P., Epitalon, J.-M., Lavigne, H., & Orr, J. (2019). seacarb: Seawater carbonate chemistry. *R Package Version 3.2*, 12.
- Gonfiantini, R., Tonarini, S., Gröning, M., Adorni-Braccesi, A., Al-Ammar, A. S., Astner, M., et al. (2003). Intercomparison of boron isotope and concentration measurements. Part II: Evaluation of results. *Geostandards Newsletter*, 27(1), 41–57. <https://doi.org/10.1111/j.1751-908x.2003.tb00711.x>
- Gray, W. R., & Evans, D. (2019). Nonthermal influences on Mg/Ca in planktonic foraminifera: A review of culture studies and application to the last glacial maximum. *Paleoceanography and Paleoclimatology*, 34(3), 306–315. <https://doi.org/10.1029/2018pa003517>
- Greenop, R., Hain, M. P., Sosdian, S. M., Oliver, K. I. C., Goodwin, P., Chalk, T. B., et al. (2017). A record of Neogene seawater δ<sup>11</sup>B reconstructed from paired δ<sup>11</sup>B analyses on benthic and planktic foraminifera. *Climate of the Past*, 13(2), 149–170. <https://doi.org/10.5194/cp-13-149-2017>
- Greenop, R., Sosdian, S. M., Henehan, M. J., Wilson, P. A., Lear, C. H., & Foster, G. L. (2019). Orbital forcing, ice volume, and CO<sub>2</sub> across the Oligocene-Miocene transition. *Paleoceanography and Paleoclimatology*, 34(3), 316–328. <https://doi.org/10.1029/2018pa003420>
- 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., Pälike, 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>
- Hain, M. P., Foster, G. L., & Chalk, T. (2018). Robust constraints on past CO<sub>2</sub> climate forcing from the boron isotope proxy. *Paleoceanography and Paleoclimatology*, 33(10), 1099–1115. <https://doi.org/10.1029/2018pa003362>
- Hain, M. P., Sigman, D. M., Higgins, J. A., & Haug, G. H. (2015). The effects of secular calcium and magnesium concentration changes on the thermodynamics of seawater acid/base chemistry: Implications for Eocene and Cretaceous ocean carbon chemistry and buffering. *Global Biogeochemical Cycles*, 29(5), 517–533. <https://doi.org/10.1002/2014gb004986>
- Hardage, K., Wang, T.-H., Liu, H.-C., You, C.-F., Herrera-Silveira, J. A., Street, J. H., & Paytan, A. (2025). δ<sup>11</sup>B variability in *Ammonia parkinsoniana* and implications for paleo-pH in coastal margins. *Paleoceanography and Paleoclimatology*, 40(2), e2024PA005024. <https://doi.org/10.1029/2024pa005024>
- Harper, D., Hönisch, B., Zeebe, R., Shaffer, G., Haynes, L., Thomas, E., & Zachos, J. (2020). The magnitude of surface ocean acidification and carbon release during Eocene Thermal Maximum 2 (ETM-2) and the Paleocene-Eocene thermal maximum (PETM). *Paleoceanography and Paleoclimatology*, 35, e2019PA003699. <https://doi.org/10.1029/2019pa003699>
- Harper, D. T., Hönisch, B., Bowen, G. J., Zeebe, R. E., Haynes, L. L., Penman, D. E., & Zachos, J. C. (2024). Long- and short-term coupling of sea surface temperature and atmospheric CO<sub>2</sub> during the late Paleocene and early Eocene. *Proceedings of the National Academy of Sciences*, 121(36), e2318779121. <https://doi.org/10.1073/pnas.2318779121>
- Haynes, L. L., & Hönisch, B. (2020). The seawater carbon inventory at the Paleocene–Eocene thermal maximum. *Proceedings of the National Academy of Sciences*, 117(39), 24088–24095. <https://doi.org/10.1073/pnas.2003197117>
- Haynes, L. L., Hönisch, B., Holland, K., Eggins, S., & Rosenthal, Y. (2023). Calibrating non-thermal effects on planktic foraminiferal Mg/Ca for application across the Cenozoic. *Paleoceanography and Paleoclimatology*, 38(10), e2023PA004613. <https://doi.org/10.1029/2023pa004613>
- 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., Hönisch, B., & Bouman, C. (2008). In-run corrections for instrumental fractionation of boron isotopes by NTIMS: Filament material and loading matrix controls. *Geochimica et Cosmochimica Acta*, A365.
- Henehan, M. J., Edgar, K. M., Foster, G. L., Penman, D. E., Hull, P. M., Greenop, R., et al. (2020). Revisiting the middle Eocene climatic optimum “carbon cycle conundrum” with new estimates of atmospheric pCO<sub>2</sub> from boron isotopes. *Paleoceanography and Paleoclimatology*, 35(6), e2019PA003713. <https://doi.org/10.1029/2019pa003713>
- 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., Klein Gebbinck, C. D., Wyman, J. V. B., Hain, M. P., Rae, J. W. B., Hönisch, B., et al. (2022). No ion is an island: Multiple ions influence boron incorporation into CaCO<sub>3</sub>. *Geochimica et Cosmochimica Acta*, 318, 510–530. <https://doi.org/10.1016/j.gca.2021.12.011>
- Henehan, M. J., Rae, J. W., 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-CO<sub>2</sub> 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>
- Holland, K., Branson, O., Haynes, L. L., Hönisch, B., Allen, K. A., Russell, A. D., et al. (2020). Constraining multiple controls on planktic foraminifera Mg/Ca. *Geochimica et Cosmochimica Acta*, 273, 116–136. <https://doi.org/10.1016/j.gca.2020.01.015>
- Hollis, C. J., Dunkley Jones, T., Anagnostou, E., Bijl, P. K., Cramwinckel, M. J., Cui, Y., et al. (2019). The DeepMIP contribution to PMIP4: Methodologies for selection, compilation and analysis of latest Paleocene and early Eocene climate proxy data, incorporating version 0.1 of the DeepMIP database. *Geoscientific Model Development*, 12(7), 3149–3206. <https://doi.org/10.5194/gmd-12-3149-2019>
- Hong, W. L., Lepland, A., Crémère, A., Kirsimäe, K., Stüeken, E. E., Dumont, M., et al. (2024). A sequential leaching protocol for δ<sup>11</sup>B and trace element analyses of multi-phase carbonate rocks. *Paleoceanography and Paleoclimatology*, 39(10), e2023PA004658. <https://doi.org/10.1029/2023pa004658>
- Hönisch, B., Bijma, J., Russell, A. D., Spero, H. J., Palmer, M. R., Zeebe, R. E., & Eisenhauer, A. (2003). The influence of symbiont 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). Symbiont 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, PA4010. <https://doi.org/10.1029/2004pa001026>
- Hönisch, B., & Hemming, N. G. (2005). Surface ocean pH response to variations in pCO<sub>2</sub> 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., 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>
- Hönisch, B., Royer, D. L., Breecker, D. O., Polissar, P. J., Bowen, G. J., Henehan, M. J., et al. (2023). Toward a Cenozoic history of atmospheric CO<sub>2</sub>. *Science*, 382(6675), eadi5177. <https://doi.org/10.1126/science.adi5177>
- Horita, J., Zimmermann, H., & Holland, H. D. (2002). Chemical evolution of seawater during the Phanerozoic: Implications from the record of marine evaporites. *Geochimica et Cosmochimica Acta*, 66(21), 3733–3756. [https://doi.org/10.1016/s0016-7037\(01\)00884-5](https://doi.org/10.1016/s0016-7037(01)00884-5)
- Howes, E. L., Kaczmarek, K., Raitzsch, M., Mewes, A., Bijma, N., Horn, I., et al. (2017). Decoupled carbonate chemistry controls on the incorporation of boron into *Orbulina universa*. *Biogeosciences*, 14(2), 415–430. <https://doi.org/10.5194/bg-14-415-2017>
- Humphreys, M. P., Lewis, E. R., Sharp, J. D., & Pierrot, D. (2022). PyCO<sub>2</sub>SYS v1. 8: Marine carbonate system calculations in Python. *Geoscientific Model Development*, 15(1), 15–43. <https://doi.org/10.5194/gmd-15-15-2022>
- IPCC, & WG1. (2021). Climate change 2021: The physical science basis. In V. Masson-Delmotte, P. Zhai, A. Pirani, S. L. Connors, C. Péan, S. Berger, Contribution of working group I to the sixth assessment report of the intergovernmental panel on climate change (Vol. 2). Cambridge University Press.
- Jurikova, H., Garbelli, C., Whiteford, R., Reeves, T., Laker, G. M., Liebetrau, V., et al. (2025). Rapid rise in atmospheric CO<sub>2</sub> marked the end of the late Palaeozoic ice age. *Nature Geoscience*, 18(1), 91–97. <https://doi.org/10.1038/s41561-024-01610-2>
- Jurikova, H., Gutjahr, M., Wallmann, K., Flögel, S., Liebetrau, V., Posenato, R., et al. (2020). Permian–Triassic mass extinction pulses driven by major marine carbon cycle perturbations. *Nature Geoscience*, 13(11), 745–750. <https://doi.org/10.1038/s41561-020-00646-4>
- Jurikova, H., Ring, S. J., Henehan, M. J., Neugebauer, I., Schröder, B., Müller, D., et al. (2023). Boron geochemistry reveals the evolution of Dead Sea brines. *Earth and Planetary Science Letters*, 622, 118403. <https://doi.org/10.1016/j.epsl.2023.118403>
- 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)
- Köhler, P. (2023). Atmospheric CO<sub>2</sub> concentration based on boron isotopes versus simulations of the global carbon cycle during the Plio-Pleistocene. *Paleoceanography and Paleoclimatology*, 38(2), e2022PA004439. <https://doi.org/10.1029/2022pa004439>
- Kozdon, R., Kelly, D., Kitajima, K., Strickland, A., Fournelle, J., & Valley, J. (2013). In situ δ<sup>18</sup>O and Mg/Ca analyses of diagenetic and planktic foraminiferal calcite preserved in a deep-sea record of the Paleocene-Eocene thermal maximum. *Paleoceanography*, 28(3), 517–528. <https://doi.org/10.1002/palo.20048>
- Kubota, K., Ishikawa, T., Nagaishi, K., Kawai, T., Sagawa, T., Ikehara, M., et al. (2021). Comprehensive analysis of laboratory boron contamination for boron isotope analyses of small carbonate samples. *Chemical Geology*, 576, 120280. <https://doi.org/10.1016/j.chemgeo.2021.120280>
- 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>
- Legett, S. A., Rasbury, E. T., Grossman, E. L., Hemming, N. G., & Penman, D. E. (2020). The brachiopod δ<sup>11</sup>B record across the Carboniferous–Permian climate transition. *Paleoceanography and Paleoclimatology*, 35(10), e2019PA003838. <https://doi.org/10.1029/2019pa003838>
- 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, E., & Allegre, C. (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)
- Lemarchand, D., Gaillardet, J., Lewin, E., & Allegre, C. J. (2000). The influence of rivers on marine boron isotopes and implications for reconstructing past ocean pH. *Nature*, 408(6815), 951–954. <https://doi.org/10.1038/35050058>
- Liu, Y.-H., Huang, K.-F., & Lee, D.-C. (2018). Precise and accurate boron and lithium isotopic determinations for small sample-size geological materials by MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, 33, 846–855. <https://doi.org/10.1038/s41467-018-04463-7>
- Liu, Y. W., Aciego, S. M., Wanamaker, A. D., & Sell, B. K. (2013). A high-throughput system for boron microsublimation and isotope analysis by total evaporation thermal ionization mass spectrometry. *Rapid Communications in Mass Spectrometry*, 27(15), 1705–1714. <https://doi.org/10.1002/rcm.6619>
- Longman, J., Mills, B. J., Donnadiou, Y., & Goddérès, Y. (2022). Assessing volcanic controls on Miocene climate change. *Geophysical Research Letters*, 49(2), e2021GL096519. <https://doi.org/10.1029/2021gl096519>
- 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>
- Lueker, T. J., Dickson, A. G., & Keeling, C. D. (2000). Ocean pCO<sub>2</sub> calculated from dissolved inorganic carbon, alkalinity, and equations for K<sub>1</sub> and K<sub>2</sub>: Validation based on laboratory measurements of CO<sub>2</sub> in gas and seawater at equilibrium. *Marine Chemistry*, 70(1–3), 105–119. [https://doi.org/10.1016/s0304-4203\(00\)00022-0](https://doi.org/10.1016/s0304-4203(00)00022-0)
- Marschall, H. R., & Foster, G. L. (2018). Boron isotopes in the Earth and Planetary sciences—A short history and introduction. *Boron Isotopes: The Fifth Element*, 1–11. [https://doi.org/10.1007/978-3-319-64666-4\\_1](https://doi.org/10.1007/978-3-319-64666-4_1)
- Marschall, H. R., & Monteleone, B. D. (2015). Boron isotope analysis of silicate glass with very low boron concentrations by secondary ion mass spectrometry. *Geostandards and Geoanalytical Research*, 39(1), 31–46. <https://doi.org/10.1111/j.1751-908x.2014.00289.x>
- Martinez-Boti, 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<sub>2</sub> records. *Nature*, 518(7537), 49–54. <https://doi.org/10.1038/nature14145>
- Mayk, D., Fietzke, J., Anagnostou, E., & Paytan, A. (2020). LA-MC-ICP-MS study of boron isotopes in individual planktonic foraminifera: A novel approach to obtain seasonal variability patterns. *Chemical Geology*, 531, 119351. <https://doi.org/10.1016/j.chemgeo.2019.119351>
- Meilland, J., Ezat, M. M., Westgård, A., Manno, C., Morard, R., Siccha, M., & Kucera, M. (2023). Rare but persistent asexual reproduction explains the success of planktonic foraminifera in polar oceans. *Journal of Plankton Research*, 45(1), 15–32. <https://doi.org/10.1093/plankt/fbac069>

- Millero, F. J., Pierrot, D., Lee, K., Wanninkhof, R., Feely, R., Sabine, C. L., et al. (2002). Dissociation constants for carbonic acid determined from field measurements. *Deep Sea Research Part I: Oceanographic Research Papers*, 49(10), 1705–1723. [https://doi.org/10.1016/s0967-0637\(02\)00093-6](https://doi.org/10.1016/s0967-0637(02)00093-6)
- 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>
- Morley, A., de la Vega, E., Raitzsch, M., Bijma, J., Ninnemann, U., Foster, G., et al. (2024). A solution for constraining past marine Polar Amplification. *Nature Communications*, 15(1), 9002. <https://doi.org/10.1038/s41467-024-53424-w>
- Müller, T., Jurikova, H., Gutjahr, M., Tomašových, A., Schlögl, J., Liebetrau, V., et al. (2020). Ocean acidification during the early Toarcian extinction event: Evidence from boron isotopes in brachiopods. *Geology*, 48(12), 1184–1188. <https://doi.org/10.1130/g47781.1>
- 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, PA3212. <https://doi.org/10.1029/2006pa001337>
- Orr, J. C., Epitalon, J. M., & Gattuso, J. P. (2015). Comparison of ten packages that compute ocean carbonate chemistry. *Biogeosciences*, 12(5), 1483–1510. <https://doi.org/10.5194/bg-12-1483-2015>
- Pälike, H., Lyle, M. W., Nishi, H., Raffi, I., Ridgwell, A., Gamage, K., et al. (2012). A Cenozoic record of the equatorial Pacific carbonate compensation depth. *Nature*, 488(7413), 609–614. <https://doi.org/10.1038/nature11360>
- Palmer, M. R., Pearson, P. N., & Cobb, S. J. (1998). Reconstructing past ocean pH-depth profiles. *Science*, 282(5393), 1468–1471. <https://doi.org/10.1126/science.282.5393.1468>
- Paris, G., Gaillardet, J., & Louvat, P. (2010). Geological evolution of seawater boron isotopic composition recorded in evaporites. *Geology*, 38(11), 1035–1038. <https://doi.org/10.1130/g31321.1>
- Parkhurst, D. L., & Appelo, C. (2013). Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *U.S. Geological Survey Techniques and Methods*, 6, 497.
- 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>
- Pearson, P. N., Ditchfield, P. W., Singano, J., Harcourt-Brown, K. G., Nicholas, C. J., Olsson, R. K., et al. (2001). Warm tropical sea surface temperatures in the Late Cretaceous and Eocene epochs. *Nature*, 413(6855), 481–487. <https://doi.org/10.1038/35097000>
- Pearson, P. N., Foster, G. L., & Wade, B. S. (2009). Atmospheric carbon dioxide through the Eocene–Oligocene climate transition. *Nature*, 461(7267), 1110–1113. <https://doi.org/10.1038/nature08447>
- 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>
- Rae, J. W., Zhang, Y. G., Liu, X., Foster, G. L., Stoll, H. M., & Whiteford, R. D. (2021). Atmospheric  $\text{CO}_2$  over the past 66 million years from marine archives. *Annual Review of Earth and Planetary Sciences*, 49(1), 609–641. <https://doi.org/10.1146/annurev-earth-082420-063026>
- Raitzsch, M., Bijma, J., Benthien, A., Richter, K.-U., Steinhöfel, 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., Hain, M., Henehan, M., & Gattuso, J.-P. (2021). seacarb - seacarb extension for deep-time carbonate system calculations. Zenodo. <https://doi.org/10.5281/zenodo.5909811>
- Raitzsch, M., & Hönisch, B. (2013). Cenozoic boron isotope variations in benthic foraminifers. *Geology*, 41(5), 591–594. <https://doi.org/10.1130/g34031.1>
- Regenberg, M., Regenberg, A., Garbe-Schönberg, D., & Lea, D. W. (2014). Global dissolution effects on planktonic foraminiferal Mg/Ca ratios controlled by the calcite-saturation state of bottom waters. *Paleoceanography*, 29(3), 127–142. <https://doi.org/10.1002/2013pa002492>
- Ridgwell, A., & Schmidt, D. N. (2010). Past constraints on the vulnerability of marine calcifiers to massive carbon dioxide release. *Nature Geoscience*, 3, 196–200. <https://doi.org/10.1038/ngeo755>
- Ring, S. J., Henehan, M. J., Frings, P. J., Blukis, R., & von Blanckenburg, F. (2025). Late Cenozoic rise in seawater  $\delta^{11}\text{B}$  not driven by increasing boron adsorption. *Geochemistry, Geophysics, Geosystems*, 26(5), e2024GC011911. <https://doi.org/10.1029/2024gc011911>
- Robbins, L., Hansen, M., Kleypas, J., & Meylan, S. (2010). CO2calc: A user-friendly seawater carbon calculator for Windows, Mac OS X, and iOS (iPhone). *US Geological Survey*.
- Rodríguez-Díaz, C. N., Paredes, E., Pena, L. D., Cacho, I., Pelejero, C., & Calvo, E. (2024). Nanogram-scale boron isotope analysis through micro-distillation and Nu Plasma 3 MC-ICP-MS. *Talanta*, 269, 125473. <https://doi.org/10.1016/j.talanta.2023.125473>
- Russell, A. D., Hönisch, B., Spero, H. J., & Lea, D. W. (2004). Effects of seawater carbonate ion concentration and temperature on shell U, Mg, and Sr in cultured planktonic foraminifera. *Geochimica et Cosmochimica Acta*, 68(21), 4347–4361. <https://doi.org/10.1016/j.gca.2004.03.013>
- Sadekov, A., Lloyd, N. S., Misra, S., Trotter, J., D'Olivo, J., & McCulloch, M. (2019). Accurate and precise microscale measurements of boron isotope ratios in calcium carbonates using laser ablation multicollector-ICPMS. *Journal of Analytical Atomic Spectrometry*, 34(3), 550–560. <https://doi.org/10.1039/c8ja00444g>
- 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., 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>
- Seki, O., Foster, G. L., Schmidt, D. N., Mackensen, A., Kawamura, K., & Pancost, R. D. (2010). Alkenone and boron-based Pliocene  $\text{pCO}_2$  records. *Earth and Planetary Science Letters*, 292(1–2), 201–211. <https://doi.org/10.1016/j.epsl.2010.01.037>
- Sexton, P. F., Wilson, P. A., & Pearson, P. N. (2006). Microstructural and geochemical perspectives on planktic foraminiferal preservation: “Glassy” versus “Frosty”. *Geochemistry, Geophysics, Geosystems*, 7(12). <https://doi.org/10.1029/2006gc001291>
- Sime, N. G., Christina, L., Tipper, E. T., Tripathi, A., Galy, A., & Bickle, M. J. (2007). Interpreting the Ca isotope record of marine biogenic carbonates. *Geochimica et Cosmochimica Acta*, 71(16), 3979–3989. <https://doi.org/10.1016/j.gca.2007.06.009>
- Sosdian, S. M., Babila, T. L., Greenop, R., Foster, G. L., & Lear, C. H. (2020). Ocean Carbon Storage across the middle Miocene: A new interpretation for the Monterey Event. *Nature Communications*, 11(1), 134. <https://doi.org/10.1038/s41467-019-13792-0>
- Sosdian, S. M., Greenop, R., Hain, M. P., Foster, G. L., Pearson, P. N., & Lear, C. H. (2018). Constraining the evolution of Neogene ocean carbonate chemistry using the boron isotope pH proxy. *Earth and Planetary Science Letters*, 498, 362–376. <https://doi.org/10.1016/j.epsl.2018.06.017>
- Spivack, A. J., You, C.-F., & Smith, H. J. (1993). Foraminiferal boron isotope ratios as a proxy for surface ocean pH over the past 21 Myr. *Nature*, 363(6425), 149–151. <https://doi.org/10.1038/363149a0>

- Standish, C. D., Chalk, T. B., Babila, T. L., Milton, J. A., Palmer, M. R., & Foster, G. L. (2019). The effect of matrix interferences on *in situ* boron isotope analysis by laser ablation multi-collector inductively coupled plasma mass spectrometry. *Rapid Communications in Mass Spectrometry*, 33(10), 959–968. <https://doi.org/10.1002/rcm.8432>
- Staudigel, P. T., John, E. H., Buse, B., Pearson, P. N., & Lear, C. H. (2022). Apparent preservation of primary foraminiferal Mg/Ca ratios and Mg-banding in recrystallized foraminifera. *Geology*, 50(7), 760–764. <https://doi.org/10.1130/g49984.1>
- Steinhöfel, G., Beck, K. K., Benthien, A., Richter, K.-U., Schmidt-Grieb, G. M., & Bijma, J. (2023). Matrix-independent boron isotope analysis of silicate and carbonate reference materials by ultraviolet femtosecond laser ablation multi-collector inductively coupled plasma mass spectrometry with application to the cold-water coral *Desmophyllum dianthus*. *Rapid Communications in Mass Spectrometry*, 37(13), e9508. <https://doi.org/10.1002/rcm.9508>
- Stewart, J. A., Christopher, S. J., Kucklick, J. R., Bordier, L., Chalk, T. B., Dapoigny, A., et al. (2021). NIST RM 8301 boron isotopes in marine carbonate (simulated coral and foraminifera solutions): Inter-laboratory  $\delta^{11}\text{B}$  and trace element ratio value assignment. *Geostandards and Geoanalytical Research*, 45(1), 77–96. <https://doi.org/10.1111/ggr.12363>
- Stewart, J. A., Gutjahr, M., Pearce, F., Swart, P. K., & Foster, G. L. (2015). Boron during meteoric diagenesis and its potential implications for Marinoan snowball Earth  $\delta^{11}\text{B}$ -pH excursions. *Geology*, 43(7), 627–630. <https://doi.org/10.1130/g36652.1>
- 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>
- Uppström, L. R. (1974). The boron/chlorinity ratio of deep-sea water from the Pacific Ocean. *Deep-Sea Research A*, 21(2), 161–162. [https://doi.org/10.1016/0011-7471\(74\)90074-6](https://doi.org/10.1016/0011-7471(74)90074-6)
- Van Heuven, S., Pierrot, D., Rae, J., Lewis, E., & Wallace, D. (2011). MATLAB program developed for CO<sub>2</sub> system calculations, ORNL/CDIAC-105b. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy. <https://doi.org/10.3334/CDIAC/otg>
- 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)
- 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>
- Westerhold, T., Marwan, N., Drury, A. J., Liebrand, D., Agnini, C., Anagnostou, E., et al. (2020). An astronomically dated record of Earth's climate and its predictability over the last 66 million years. *Science*, 369(6509), 1383–1387. <https://doi.org/10.1126/science.aba6853>
- Whiteford, R., Branson, O., & Mayk, D. (2024). Using Kgen to generate cross-verified apparent equilibrium constants (K\*s) for Palaeoseawater carbonate chemistry. *Geochemistry, Geophysics, Geosystems*, 26, e2023GC011417. <https://doi.org/10.1029/2023GC011417>
- Whiteford, R., Heaton, T. J., Henehan, M. J., Anagnostou, E., Jurikova, H., Foster, G. L., & Rae, J. W. B. (2024). Reconstruction of Cenozoic  $\delta^{11}\text{B}_{\text{sw}}$  using a Gaussian process. *Paleoceanography and Paleoclimatology*, 39(6), e2023PA004769. <https://doi.org/10.1029/2023pa004769>
- Xu, C., Jurikova, H., Nuber, S., Steele, R. C. J., Trudgill, M., Barker, S., et al. (2024). A rapid, simple, and low-blank pumped ion-exchange column chromatography technique for boron purification from carbonate and seawater matrices. *Geochemistry, Geophysics, Geosystems*, 25(2), e2023GC011228. <https://doi.org/10.1029/2023gc011228>
- Yu, J., Elderfield, H., & Hoenisch, B. (2007). B/Ca in planktonic foraminifera as a proxy for surface seawater pH. *Paleoceanography*, 22, PA2202. <https://doi.org/10.1029/2006pa001347>
- Zeebe, R. E., & Tyrrell, T. (2018). Comment on “The effects of secular calcium and magnesium concentration changes on the thermodynamics of seawater acid/base chemistry: Implications for Eocene and Cretaceous ocean carbon chemistry and buffering” by Hain et al.(2015). *Global Biogeochemical Cycles*, 32(5), 895–897. <https://doi.org/10.1002/2017gb005786>
- Zeebe, R. E., & Tyrrell, T. (2019). History of carbonate ion concentration over the last 100 million years II: Revised calculations and new data. *Geochimica et Cosmochimica Acta*, 257, 373–392. <https://doi.org/10.1016/j.gca.2019.02.041>
- Zeebe, R. E., & Westbroek, P. (2003). A simple model for the CaCO<sub>3</sub> saturation state of the ocean: The “Strangelove,” the “Neritan,” and the “Cretan” Ocean. *Geochemistry, Geophysics, Geosystems*, 4(12), 1104. <https://doi.org/10.1029/2003gc000538>
- Zeebe, R. E., & Wolf-Gladrow, D. A. (2001). *CO<sub>2</sub> in seawater: Equilibrium, kinetics, isotopes*. Elsevier Science Limited.
- Zeebe, R. E., Wolf-Gladrow, D. A., Bijma, J., & Honisch, 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), 1043. <https://doi.org/10.1029/2003pa000881>