



Reconstructing past seawater pH from boron isotopes in carbonates

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Resum

Des de la revolució industrial, la concentració de CO₂ a l'atmosfera ha augmentat de manera molt significativa, amb el consegüent augment de l'efecte d'hivernacle, molt relacionat amb l'actual escalfament global. Per sort, la Terra disposa d'una sèrie de reservoris, sobretot els oceans, que atrapen una quantitat significativa d'aquest excés de CO₂. No obstant això, com a resultat de l'absorció marina de CO₂, les aigües s'estan acidificant progressivament i comprometran, potser de manera devastadora, el desenvolupament d'organismes marins, sobretot d'aquells que construeixen un esquelet de carbonat (coralls, musclos, cloïsses, etc.). Per entendre l'abast d'aquest problema, és molt important conèixer com ha variat el pH al llarg del temps, sobretot durant aquells períodes de què no disposem de dades instrumentals, les quals es limiten a la darrera dècada. Amb aquesta finalitat, disposem d'un indicador indirecte o *proxy*, la composició isotòpica de bor en carbonats fòssils biogènics, que ens permet reconstruir la variació del pH marí al llarg del temps. En aquesta revisió expliquem els fonaments d'aquest *proxy*, mostrem els calibratges que s'han fet fins al moment, comentem breument els requeriments analítics per a la mesura dels isòtops de bor i exposem els resultats que s'han obtingut fins ara.

Paraules clau: isòtops de bor, acidificació oceànica, pH marí, paleoceanografia, coralls

Abstract

Since the Industrial Revolution, the CO₂ concentration in the atmosphere has increased substantially, enhancing the greenhouse effect, which is very much related to current global warming. Fortunately, the Earth has a series of reservoirs, especially its oceans, which trap a significant amount of the excess CO₂. This marine absorption of CO₂, however, results in progressive acidification of the oceans, which has detrimental and possibly devastating effects for marine organisms, particularly those that construct a skeleton of calcium carbonate (corals, mussels, clams, etc.). To understand the magnitude of this problem, it is crucial to know how seawater pH has oscillated in the past, particularly during those periods of time that are not covered by instrumental measurements, which are restricted to the last decade. For this purpose, the isotopic composition of boron in fossil biogenic carbonates provides a geochemical indicator, or proxy, which allows reconstruction of the past variations in seawater pH. In this review, we explain the theoretical grounds of this proxy, show the empirical calibrations carried out so far, briefly comment on some aspects of boron-isotope analysis, and list the results of paleo-pH reconstructions published so far.

Keywords: boron isotopes, ocean acidification, seawater pH, paleoceanography, corals

One of the major environmental challenges currently facing our society is the impact of increased atmospheric CO₂ due to the combustion of fossil fuels. It has been nearly five decades since the late Prof. David Keeling started the "Keeling curve", a highly cited time-series of atmospheric CO₂ from unpolluted air at Mauna Loa Observatory (located at an elevation of ~3,300m on the Hawaiian Island of Maui). These measurements became the first clear demonstration that CO₂ emitted from human ac-

tivities indeed accumulated in the atmosphere, and showed that the atmospheric CO₂ concentration rose from 316 parts per million by volume (ppmv) of dry air in 1959 to 377 ppmv in 2004 [1].

Analyses of air bubbles trapped in ice cores provided further evidence that the atmosphere was achieving levels of atmospheric CO₂ that were unprecedented for many years, centuries, millennia, and even hundreds of millennia. An early study demonstrated that CO₂ had never been as high as during the last two centuries [2] and subsequent research clearly evidenced that current levels were unprecedented for the last 420,000 years [3]. Very recently, new drilling efforts have culminated with a record of atmospheric CO₂ contained in more than 3 km of ice and covering the last 650,000 years [4]. This

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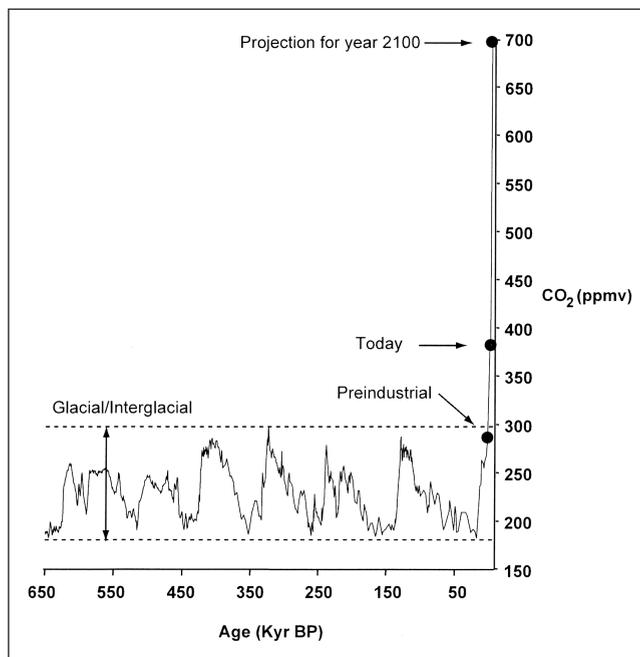


Figure 1. Variability of atmospheric CO_2 concentration during the last 650,000 years as inferred from the composition of air bubbles trapped in Antarctic ice cores [3,4]. The abrupt increase in CO_2 since the Industrial Revolution, due to the burning of fossil fuels, is evidenced by measurements in ice cores at Siple Station [2] and direct atmospheric measurements at Mauna Loa [1]. Projections of atmospheric CO_2 for the year 2001 correspond to mid-range scenarios from the Intergovernmental Panel on Climate Change (IPCC), such as the IS92a scenario from the second IPCC report [60] and the A1B from the third IPCC report [61].

last study has documented that during this enormous stretch of time CO_2 levels have never been as high as they currently are.

If the current concentrations of CO_2 in the atmosphere are put into context with those of the past, as determined by instrumental and ice-core records, a worrisome global picture emerges. Furthermore, the likely projections that atmospheric CO_2 will achieve by the end of century are certainly cause for alarm (Fig. 1). We humans are subjecting the Earth to a serious perturbation, with harmful consequences on a planetary scale.

So far, most of the research on the possible consequences of this unprecedented injection of CO_2 into the atmosphere has focused on global warming and climate-related effects. This important endeavor has overshadowed, however, another yet more direct consequence of the rise in atmospheric CO_2 , a consequence with possibly devastating effects for marine ecosystems: the progressive acidification of the oceans.

Part of the excess of atmospheric CO_2 is being absorbed by the oceans, thus minimizing the greenhouse effect of CO_2 . According to Sabine et al. [5], without this oceanic uptake, atmospheric CO_2 today would be about 55 ppm higher than it is. Even though this oceanic uptake is "climatically advantageous" for us, it comes at a price. As CO_2 dissolves in seawater, it takes part in a range of chemical reactions that result in a rise in the concentration of bicarbonate ions and protons (H^+) and thus in an increase in seawater acidity. Basic mass-balance calculations indicate that global oceans in the year 2000 should have already acidified by 0.1 pH units relative to prein-

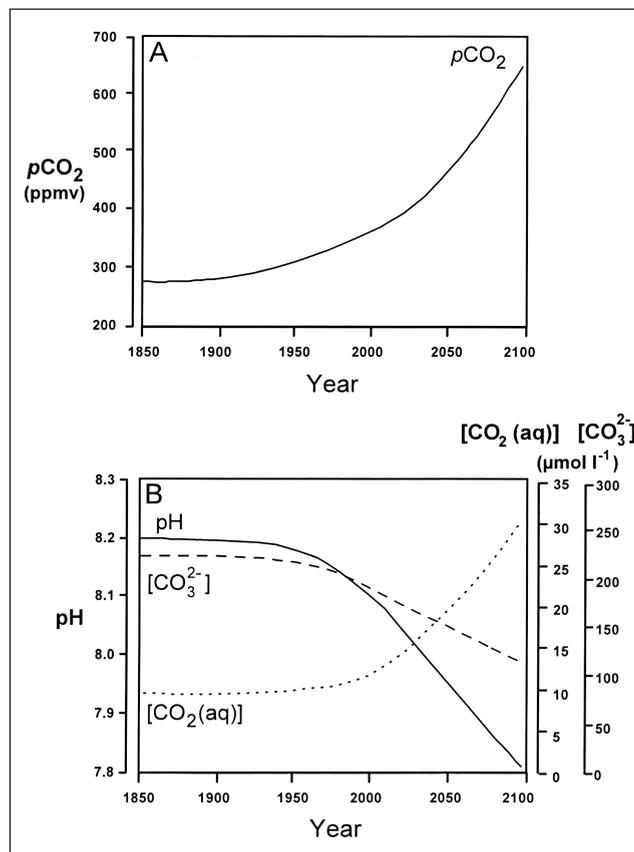


Figure 2. (A) History of atmospheric CO_2 concentration since the year 1850 and projections until the year 2100, according to a IS92a scenario of the IPCC 2nd report [60], approximated by a linear increase of CO_2 emissions from 6.3 GtC yr^{-1} to 20 GtC yr^{-1} in the year 2100 [7]. (B) Estimated evolution of pH, $[\text{CO}_2(\text{aq})]$ and $[\text{CO}_3^{2-}]$ in the surface global oceans based on the CO_2 trend in (A) (redrawn from [7]).

dustrial times (Fig. 2) [6,7,8]. Predictions point towards acidification in the order of 0.3–0.5 pH units by 2100 (Fig. 2B) and of nearly 0.8 pH units by 2300 [8], a scenario for which there is no obvious precedent over the previous hundreds of millions of years [9].

This change in seawater chemistry towards more corrosive conditions has the potential to affect marine ecosystems in many ways. It will make calcification in calcifying organisms more difficult (basically because of the associated decrease in carbonate ion concentration, Fig. 2B), alter the chemistry of nutrients and toxins, perhaps change the physiology and reproduction of larger animals, and affect the exchange of gases between the oceans and atmosphere, interacting with global Earth systems and climate-related feedbacks. Despite this potential threat in multiple directions, which has recently been reviewed and reported upon by the Royal Society [10], there is still little research quantifying the real impacts of ocean acidification.

To better understand the magnitude of the environmental problem of ocean acidification, it is very important to know the ranges of pH variability at different time scales. This knowledge is crucial to establish the levels of pH tolerance for marine organisms and to improve our understanding of the role and mechanisms of the oceans in absorbing atmospheric CO_2 . Because instrumental records of seawater pH exceeding a single

decade are not yet available, past variations of pH need to be reconstructed using proxies in suitable archives.

Several proxies have been developed to reconstruct past changes in atmospheric CO₂, which are particularly useful for ages predating those that can be studied by means of ice cores ([11] and references therein). Carbonate δ¹³C in certain pedogenic minerals is one such proxy. Some of these minerals are formed from either biologically or atmospherically derived soil CO₂. Since these two components differ in their δ¹³C signature, the concentration of atmospheric CO₂ can be estimated after making a few assumptions (i.e. [12]). This method is particularly reliable for relatively old periods, particularly the pre-Tertiary, with high levels of CO₂.

Stomatal density of leaf surfaces is another suitable proxy for reconstructing atmospheric CO₂. Stomata are small openings or pores in leaves that allow transport of CO₂ and O₂ through the leaf surface, facilitating photosynthesis. In addition, water is lost through stomata during transpiration. The density of the stomata is clearly dependent on the atmospheric levels of CO₂ (i.e. [13]), so that this parameter can be reconstructed from analyses of fossil leaves (i.e. [14]).

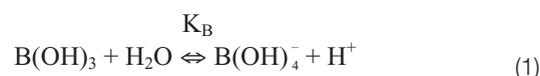
The δ¹³C of the organic remains of phytoplankton found in deep-sea sediments can also be used to estimate the partial pressure of CO₂ in seawater (pCO₂). The method is particularly reliable when specific biomarkers such as long-chain alkenones (specific to certain Haptophyta algae), are used for the δ¹³C determinations [15,16]. This proxy is based on the fact that, for many marine algae, the fractionation of carbon isotopes during marine photosynthetic carbon fixation is largely a function of the concentration of aqueous CO₂ in the growth medium. Cellular growth rate and cell geometry also need to be taken into account (e.g. [17,18]).

The methods mentioned so far provide reconstructions of atmospheric CO₂ concentration and/or oceanic pCO₂, these variables can be used to derive ocean pH if other parameters of the

carbonate system in seawater are taken into account. Over the last decades, however, another proxy has been developed that directly provides paleodata on seawater pH. This proxy is the boron isotopic composition of biogenic carbonates, and we will discuss it more in detail in the following sections.

Theoretical background

Boron in nature has two stable isotopes, ¹⁰B and ¹¹B, with the heavier isotope being more abundant (80.18%) than the lighter one (19.82%). Inorganic boron in seawater occurs in two forms, boric acid [B(OH)₃] and borate [B(OH)₄⁻]. Their relative abundances are a function of pH, with borate more abundant in more basic waters and boric acid more abundant as water becomes more acidic (Fig. 3A). The pH dependence is described by the following acid-base reaction:



which has a pK_B of 8.6 in seawater at T = 25°C and S = 35, according to Dickson [19], and where K_B is the dissociation constant:

$$K_B = \frac{[\text{B(OH)}_4^-] \times [\text{H}^+]}{[\text{B(OH)}_3]} \quad (2)$$

Most importantly, there is isotope fractionation between the two boron species due to differences in the vibrational frequencies associated with each molecular coordination and geometry. In other words, the isotope-exchange reaction:

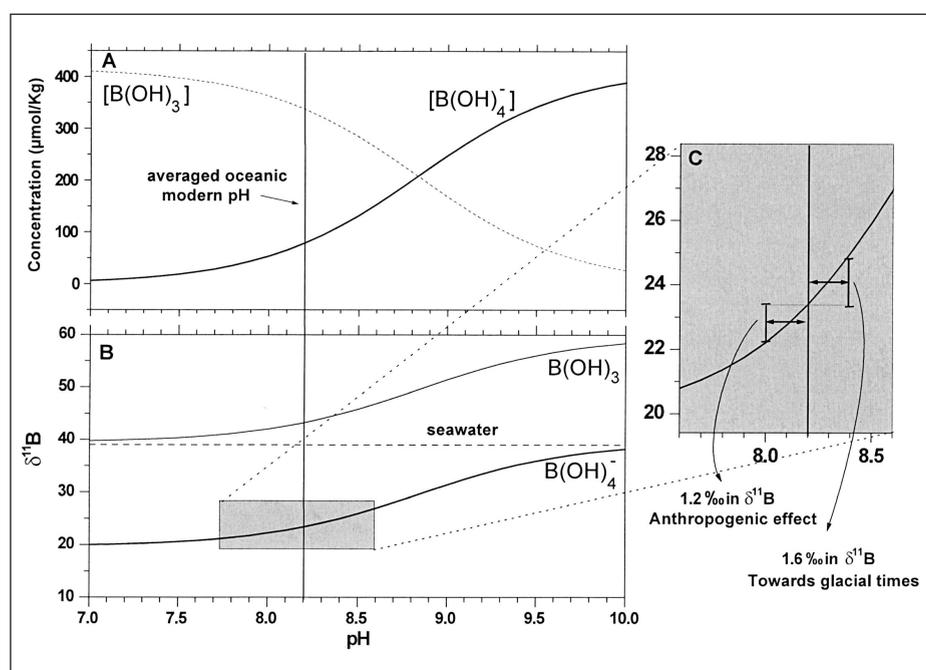
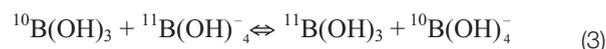


Figure 3. (A) Concentration of dissolved boron species as a function of pH. (B) Boron isotopic composition of B(OH)₃ and B(OH)₄⁻ as a function of pH. (C) Close-up of the area of interest for translation of δ¹¹B values into pH and theoretical variations in δ¹¹B associated with change in pH of 0.2 units towards low pH (e.g. anthropogenic effect) and towards high pH (e.g. glacial times when atmospheric CO₂ concentrations were lower than preindustrial times).

has an isotopic equilibrium constant defined by:

$${}^{11-10}K_B = \frac{[{}^{11}\text{B}(\text{OH})_3] \times [{}^{10}\text{B}(\text{OH})_4]}{[{}^{10}\text{B}(\text{OH})_3] \times [{}^{11}\text{B}(\text{OH})_4]} \quad (4)$$

that is greater than unity, which means that boric acid is always enriched in ${}^{11}\text{B}$ relative to borate.

The residence time of boron in seawater has been estimated around 14 millions of years [20,21]; thus, the concentration and the isotopic composition of boron in seawater can be considered constant for shorter time scales, with values of 4.5 parts per million and +39.6‰, respectively, where the isotopic composition of boron ($\delta^{11}\text{B}$) is defined as:

$$\delta^{11}\text{B} = \left(\frac{{}^{11}\text{B}/{}^{10}\text{B}_{\text{sample}}}{{}^{11}\text{B}/{}^{10}\text{B}_{\text{standard}}} - 1 \right) \times 1000 \quad (5)$$

using boric acid NBS SRM 951 as the standard.

As discussed in the following section, the choice of ${}^{11-10}K_B$ constant has been the subject of considerable debate; but if one of the most frequently used options is adopted, the theoretically calculated ${}^{11-10}K_B = 1.0194$ from Kakhana [22] provides a constant isotopic enrichment (ϵ_B) of 19.4‰ of ${}^{11}\text{B}$ in boric acid in relation to borate. This is:

$$\epsilon_B = \left(\frac{{}^{11}\text{B}/{}^{10}\text{B}_{\text{boric}}}{{}^{11}\text{B}/{}^{10}\text{B}_{\text{borate}}} - 1 \right) \times 1000 = ({}^{11-10}K_B - 1) \times 1000 \quad (6)$$

Since, as we have seen, the concentrations of borate and boric acid in seawater depend on pH (Fig. 3A), the isotopic composition of each boron species is also a function of pH (Fig. 3B). Furthermore, as has long been suggested [23,24], calcifying organisms incorporate only borate into their skeleton; thus, the boron isotopic composition in this phase will be determined by the boron isotopic composition of borate in seawater, which, in turn, is a function of seawater pH (Fig. 3C).

From Eqs. (2) and (4), the following general equation to translate carbonate $\delta^{11}\text{B}$ into reconstructed seawater pH can be derived:

$$\text{pH} = \text{p}K_B - \log \left(\frac{-(\delta^{11}\text{B}_{\text{sw}} - \delta^{11}\text{B}_c)}{\delta^{11}\text{B}_{\text{sw}} - {}^{11-10}K_B \times \delta^{11}\text{B}_c - \epsilon_B} \right) \quad (7)$$

where $\delta^{11}\text{B}_{\text{sw}}$ is the isotopic composition of seawater (39.6‰), $\delta^{11}\text{B}_c$ is the isotopic composition of the biogenic carbonate remain, and, adopting Kakhana [22], ${}^{11-10}K_B = 1.0194$ and $\epsilon_B = 19.4$.

Empirical calibrations

So far, we have discussed the theoretical grounds behind the $\delta^{11}\text{B}$ paleo-pH proxy. Nonetheless, in order to be confident regarding its applicability, empirical calibrations are needed. So far, the $\delta^{11}\text{B}$ paleo-pH proxy has been calibrated with selected species of foraminifera and corals that were grown in aquaria under selected conditions of seawater pH. Figure 4 summarizes the results of these calibrations, including data from two experiments on precipitation of inorganic calcite [25]. Sanyal et al. [26] were the first to perform an experiment of this kind, for which they selected the foraminifer *Orbulina universa*, grown at three pH levels. As can be seen in Fig. 4, there is a clear dependence of pH on the foraminifera calcite $\delta^{11}\text{B}$, following a curve parallel to that of theoretical borate albeit with a significant offset. Later, Sanyal et al. [27] carried out a similar exercise with the foraminifer *Globigerinoides sacculifer* and also found a relationship between pH and $\delta^{11}\text{B}$, but with a significant offset from the theoretical curve, although smaller than for *O. universa*. Some experiments on the precipitation of inorganic calcite were also done and significant offsets to the borate $\delta^{11}\text{B}$ curve were observed [25]. More recently, two studies explored the applicability of this paleo-pH proxy in corals [28,29]; the calibrations were established with *Acropora nobilis*, *Porites cylindrica*, and *Acropora* sp. As can be seen in the compilation of data displayed in Fig. 4, data from corals better approached the theoretical curve of $\delta^{11}\text{B}$ in seawater borate and demonstrated very similar relationships with only small offsets. In particular, the data for *P. cylindrica* matched perfectly with the theoretical curve.

These results show convincingly that there is a strong pH dependence of the boron isotopic composition of biogenic carbonate, and the calibrations can be used to reconstruct pH from the boron isotopic composition of carbonate remains, at least for the cultured foraminifera and coral species that have

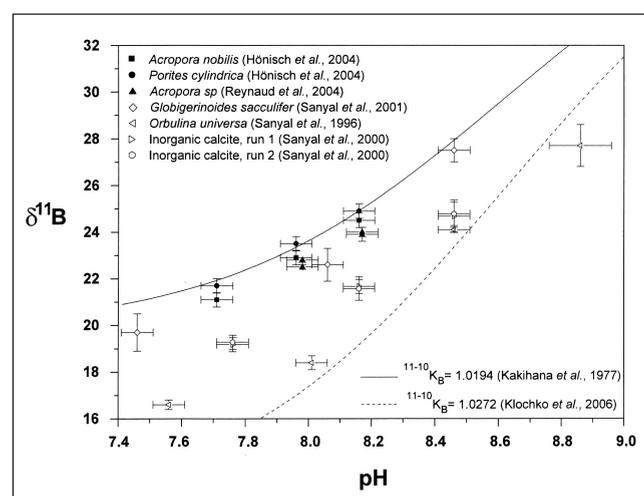


Figure 4. Empirical calibrations of the $\delta^{11}\text{B}$ vs. pH relationship in corals [28,29], foraminifera [26,27], and inorganic calcite [25]. Solid and dashed lines correspond to the theoretical $\delta^{11}\text{B}$ of $\text{B}(\text{OH})_4^-$ curves using the ${}^{11-10}K_B = 1.0194$ from [22] and the ${}^{11-10}K_B = 1.0272$ from [34], respectively. All pH data points from Sanyal et al. [25,26,27] were shifted by -0.14 pH units to account for the difference between the NBS and the seawater scales.



been calibrated so far. Obviously, an offset specific to the each species will have to be taken into account. Because this offset appears to be constant and thus pH-independent (see also [30]), an expression similar to that in Eq. (7) can be used to translate carbonate $\delta^{11}\text{B}$ into reconstructed seawater pH:

$$\text{pH} = \text{pK}_B - \log \left(\frac{-(\delta^{11}\text{B}_{\text{sw}} - \delta^{11}\text{B}_c - \phi)}{\delta^{11}\text{B}_{\text{sw}} - {}^{11-10}\text{K}_B \times (\delta^{11}\text{B}_c + \phi) - \epsilon_B} \right) \quad (8)$$

where ϕ represents each particular offset.

This offset may be related to vital effects, such as photosynthesis of symbiotic algae, respiration of the entire host-symbiont system, and/or calcification. In fact, a combination of all these parameters has been shown to strongly modulate the pH of the microenvironment associated with the foraminifera test, which has significantly different chemical characteristics from that of bulk ocean water [31]. A thorough evaluation of such vital effects in controlling the offset with the borate curve has recently been performed, demonstrating that life processes can indeed cause offsets and that these are constant over a wide pH range. [30]. This is good news for the applicability of this proxy because this study demonstrated that the existence of vital effects does not compromise the use of the proxy, provided that specific calibrations are made.

It is important to note, however, that Zeebe et al. [30] could not predict the entire magnitude of the offsets found in the foraminifera empirical calibrations, so alternatives should be considered to fully explain such deviations. One possibility is that the experimental offsets are smaller than those presented in Fig. 4, because the theoretical reference curve of $\delta^{11}\text{B}$ in borate may be different, if we consider other values of the isotopic equilibrium constant ${}^{11-10}\text{K}_B$ (4). Figure 3C shows the theoretical variation of $\delta^{11}\text{B}$ in borate (and thus in biogenic carbonate remains) with seawater pH from the value of ${}^{11-10}\text{K}_B = 1.0194$, reported by Kakihana [22]. Recently, the choice of this constant has been the subject of considerable debate. In a critical evaluation of the $\delta^{11}\text{B}$ paleo-pH proxy, Pagani et al. [32] concluded that it was more reasonable to use ${}^{11-10}\text{K}_B$ values higher than the one reported by Kakihana [22]. If this is the case, the theoretical borate curves would be steeper and slightly shifted to the right on the pH axis, so experimental data, particularly those from foraminifera experiments, would not deviate as much (Fig. 4). In a subsequent reference to this paper, however, Hönisch et al. [33] argued and demonstrated statistically that data from all empirical calibrations were best explained with the Kakihana [22] constant and by assuming a constant offset to the seawater borate $\delta^{11}\text{B}$ curve. If the empirical values had to be matched to steeper borate $\delta^{11}\text{B}$ curves, the offsets would not remain constant over the typical marine pH range, complicating any explanations of offsets based on vital effects. Regarding the choice of constants, a very recent experimental spectrophotometric study [34] reported a new estimation of ${}^{11-10}\text{K}_B = 1.0272$, which is again larger than the commonly used Kakihana [22] constant (Fig. 4).

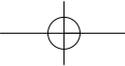
Ultimately, all these studies strongly evidence that what we really need to properly translate $\delta^{11}\text{B}$ values of biogenic remains into a record of seawater pH are consistent and species-specific calibrations. Other well-developed proxies that are frequently used in paleoceanography, such as the Sr/Ca ratio in corals for reconstructing sea surface temperatures, also display offsets that depend, not only on each coral species but on the specific area or region (e.g. [35]). Moreover, the situation is even more extreme in the applicability of yet another well-established proxy for sea surface temperatures, the U_{37}^{K} index, which is based on organic compounds (namely, long-chain alkenones) found in deep-sea sediments and synthesized by certain Haptophyta algae (see [36] for a review). So far, there is still no complete knowledge, either on the location of these compounds within the algae cell or on their function. Thus, there is no theoretical curve (analogous to the borate $\delta^{11}\text{B}$ in the case of the paleo-pH proxy) against which the experimental calibrations can be compared. However, there are calibrations, particularly an extensive one using core-tops [37], which clearly demonstrate a linear relationship of the U_{37}^{K} index with sea surface temperature, forming the basis of a now well-established method to reconstruct past sea surface temperatures using deep-sea sediments.

Analysis of boron isotopes in carbonates

The precise analysis of boron isotopes in carbonates is not a trivial task. This probably explains why, despite the huge potential of this proxy, there have been few reconstructions of paleo-pH. Several techniques have been set up to analyze boron isotopes but only a few of them are suitable for paleo-pH reconstruction purposes, because the levels of accuracy and precision required to obtain meaningful data are very high. Moreover sample availability is often an important issue, particularly in the analysis of foraminifera, where minimizing the number of fossil specimens necessary for each analysis is critical. For this reason, techniques as sensitive as possible are also crucial.

As evidenced in Fig. 3B and further detailed in Fig. 3C, the slope of the $\delta^{11}\text{B}$ vs. pH relationship is steeper towards waters of higher pH and flatter towards those of lower pH. For this reason, levels of precision to be achieved for $\delta^{11}\text{B}$ measurements should be higher in studies evaluating an anthropogenic effect (decrease in pH) than when reconstructing higher pH values, as expected, for instance, during glacial periods, when CO_2 concentrations were lower (Fig. 1). In general, precisions better than 0.5‰ and ideally $\leq 0.35\text{‰}$ (measured as $2\sigma_{\text{mean}} = 2\sigma/\sqrt{n}$) should be achieved to differentiate pH changes in the order of 0.1 units.

So far, thermal ionization mass spectrometry (TIMS) in negative mode (NTIMS) is possibly the best choice to analyze $\delta^{11}\text{B}$ in carbonates for paleo-pH reconstruction purposes. In this technique, samples are loaded onto a filament (usually made of Re, Ta, Pt, or W) that is placed in the mass spectrometer under high vacuum. Current is then passed through the filament, which then reaches high temperatures ($\sim 900^\circ\text{C}$ or over), evap-



orating the sample and ionizing it from its interaction with the hot filament surface. These ions are then accelerated, separated, and detected by the mass spectrometer. For most other applications, TIMS is operated in positive mode (PTIMS), which means that the accelerated and detected ions are positively charged. Although boron isotopes can be analyzed with excellent precision and accuracy by PTIMS, boron concentrations needed in this technique are two orders of magnitude higher than those for NTIMS.

In NTIMS, boron isotopes are analyzed as BO_2^- , so that masses of 42 and 43 (for $^{10}\text{BO}_2^-$ and $^{11}\text{BO}_2^-$, respectively) must be monitored. Details on a typical set up of boron isotopes in corals by NTIMS can be found in [38]. Briefly, samples of coral powder weighing 200–600 μg are thoroughly cleaned with H_2O_2 to remove any organic material and then rinsed several times with Milli-Q water (obtained using a specific Q-Gard boron purification pack) in an ultrasonic bath to remove salts. Samples are then dried under an infrared lamp and dissolved with excess HCl to ensure acidic conditions during loading (and hence total conversion of borate to boric acid). One μl of solution containing about 5 ng B is then loaded onto a zone-refined rhenium filament outgassed and oxidized for a minimum of 5 days. This is followed by 1 μl of B-free seawater, which helps reduce isotopic fractionation during the run, and enhances ionization. The samples are analyzed on a Finnigan Triton in negative mode. The multicollector detector of this apparatus simultaneously measures $^{10}\text{BO}_2^-$ and $^{11}\text{BO}_2^-$ in two of the Faraday cups. The filament current is raised gradually to reach an operating temperature of $970 \pm 10^\circ\text{C}$, and data are collected over a 30-min period, with ion beams of at least 400 mV for $^{11}\text{BO}_2^-$ (and normally up to 2–3 V). Sample $\delta^{11}\text{B}$ values are calculated using Eq. (5) and the $^{11}\text{B}/^{10}\text{B}$ ratio of the sample and the $^{11}\text{B}/^{10}\text{B}$ ratio of the NBS SRM 951 boric acid standard, which is analyzed in the same way as the sample.

An important aspect to be controlled during the NTIMS analysis is the isotopic fractionation during the run, which is strongly reduced with the addition of boron-free seawater to the top of the sample during filament loading. Normally, runs need to be discarded if fractionation is $> 1\%$ throughout the 30-min run.

Further details on the analysis of boron isotopes by NTIMS were given by Hemming and Hanson [39]. NTIMS can also be used running the filaments until complete exhaustion of the signal, an option that has recently been reviewed and optimized for the analysis of foraminifera [40]. This alternative (known as total evaporation NTIMS) is useful for the analysis of very small amounts of boron, as samples with as little as 300 pg of boron can be examined. When analyzing such small amounts of boron, however, special attention has to be paid to minimizing boron blanks.

Some advances have also been made in the analysis of boron isotopes by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) [41,42], which appears to be another suitable option. One advantage of MC-ICP-MS over TIMS is the high sample throughput. However, an important difficulty that must be overcome is the strong memory effect of boron, which tends to adhere to all instrument compo-

nents and accessories. The use of direct injection, thus avoiding the spray chamber, may reduce memory effects [42]. The amount of boron needed for the analyses, however, is still too large for this technique to be useful in paleoreconstructions, particularly those based on foraminifera [40], which is one of the fossils found in sediments most commonly used in paleoceanography (see the review by Mortyn and Martínez-Botí [43] in this volume).

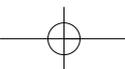
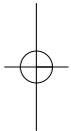
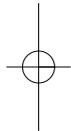
Reviews on boron isotope geochemistry and on analytical techniques for the analysis of boron isotopes have been published by Barth [44], Aggarwal and Palmer [45], Palmer and Swihart [46], Swihart [47], and You [48], and the results of an intercalibration exercise involving $\delta^{11}\text{B}$ in a variety of phases were reported by Gonfiantini et al. [49]. Recently, other analytical approaches, such as ion microprobe [50] and laser ablation multiple multiplier ICP-MS [51] have also been evaluated.

Examples of paleo-pH reconstructions

The $\delta^{11}\text{B}$ proxy has already provided some important reconstructions of pH using foraminifera, although in most of the studies very few data points were obtained at a very low temporal resolution. A large number of these studies focused on pre-Quaternary times, although the results must be interpreted with caution, because temporal variations of $\delta^{11}\text{B}$ in seawater for these ages, considering that the residence time of boron in seawater is ~ 14 million years [20,21], are still not well-constrained. Therefore, it is not yet clear whether $\delta^{11}\text{B}$ in carbonates over these ages truly records seawater pH or instead reflects the boron-isotope composition of seawater [20,21].

Regarding studies on pre-Quaternary ages, Spivack et al. [52] focused on the last 21 million years, providing only five data points over this interval. Later, Palmer et al. [53] analyzed planktonic foraminifera at different depth habitats from five sedimentary sections covering the last 15.7 million years (Myr). Pearson and Palmer [54] focused on the middle Eocene and studied benthic and planktonic foraminifera from different depth habitats, but for only one sample dated to 43 Myr ago. More recently, Pearson and Palmer [55] studied more extensively the entire Cenozoic and provided 35 individual surface-water pH estimates distributed over the past 60 Myr. According to this study, seawater pH would have dropped to 7.4–7.6 from 60 to 52 Myr ago, and then rose gradually to reach more or less constant pH values between 8.0 and 8.2 during the last 20 Myr.

Only a few studies have focused on more recent times, particularly on the glacial to interglacial transitions, to evaluate whether the low atmospheric CO_2 concentrations typical of glacial periods coexisted with high seawater pH levels. Sanyal et al. [56], for example, compared modern vs. glacial foraminifera from the tropical Atlantic and Pacific Oceans and found that surface glacial water was 0.2 ± 0.1 pH units higher than today. Moreover, deep waters were even slightly more basic, 0.3 ± 0.1 pH units higher than today. Although for the surface oceans this change in pH seems feasible, such a change in deep-water pH would mean that the carbonate ion concen-



tration in deep waters during glacial times increased significantly, a result that is at odds with other sedimentary observations, as the same authors acknowledged [56]. A subsequent study on the eastern equatorial Pacific Ocean focused on the penultimate glacial to interglacial transition, about 130 thousand years (Kyr) ago [57]. Surprisingly, this reconstruction showed a constant surface-seawater pH before and after this transition. Regarding deep waters, however, and in agreement with previous work, the pH of glacial deep water was 0.3 units higher than during the interglacial.

More recently, two studies containing a larger number of $\delta^{11}\text{B}$ data points were published. One of them focused on the last 23 Kyr in the western equatorial Pacific Ocean [58], finding again evidences of higher pH values in glacial surface waters. This work, which provided a continuous record of pH for the entire deglaciation and Holocene, also showed a period of significantly lowered pH between 18 and 13.8 Kyr before present (BP), which was ascribed to enhanced outgassing of CO_2 from the oceans probably resulting from an oceanic configuration typical of a La Niña event. The most recent reconstruction of seawater pH from foraminifera in marine sediments was published by Hönisch and Hemming [59]. Their data, which have been replotted in Fig. 5 superimposed on the evolution of atmospheric CO_2 reconstructed from ice cores, shows convincingly that atmospheric CO_2 and surface seawater pH oscillated synchronously over glacial to interglacial transitions. Surface ocean pH was found to be on average 0.18 ± 0.03 pH units higher during glacial times than during the interglacials, thus confirming the initial results by Sanyal et al. [56].

In addition to the use of foraminifera, more recently, the method described here has proved to be successful for corals. The $\delta^{11}\text{B}$ analysis of a massive *Porites* species coral from Flinders Reef, in the Coral Sea, northeast Australia [38], allowed reconstruction of seawater pH in this reef for the last 300 years. Interestingly, instead of finding the predicted acidification that should be occurring since industrialization (Fig. 2B), the authors reported a marked ~50-year cyclicity of ~0.3 units

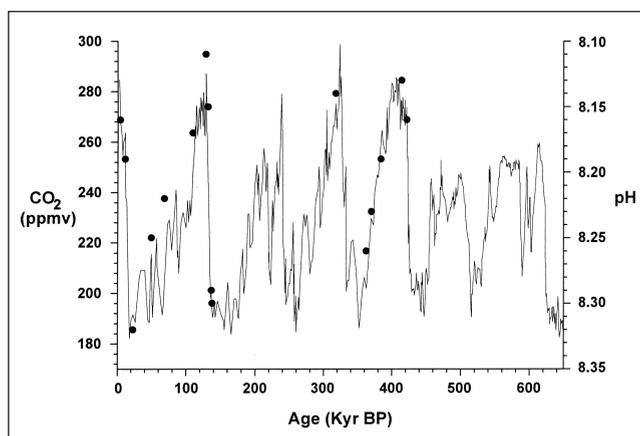


Figure 5. Record of sea surface pH (solid circles) reconstructed using $\delta^{11}\text{B}$ in planktonic foraminifera from a sediment core retrieved in the eastern equatorial Atlantic [59]. The data were superimposed onto the record of atmospheric CO_2 concentration during the last 650,000 years (solid line), as inferred from the composition of air bubbles trapped in Antarctica ice cores [3, 4].

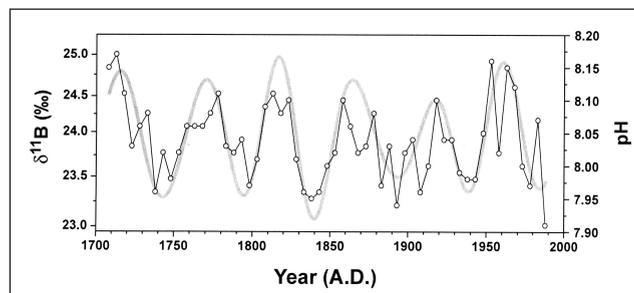


Figure 6. Record of coral $\delta^{11}\text{B}$ (left axis) as a proxy for reef water pH (right axis) for the period covering the last 300 years, based on the analysis of a *Porites* sp. coral from Flinders Reef, offshore of northeastern Australia, in the Coral Sea. The thick gray curve is the output of Gaussian filtering of coral pH at a frequency of $0.02 \pm 0.01 \text{ yr}^{-1}$, which represents the 1/50 year component of the pH variation. (Adapted from Pelejero et al. [38])

of change in marine pH (Fig. 6). The results of this study are significant for several reasons: (1) they represent the first reconstruction of pH that shows how pH has changed in the past 300 years for a specific site; (2) they show surprising interdecadal oscillations of pH of relatively large amplitude; and (3) they suggest and illustrate how natural cycles in reef-water pH could enhance or mitigate the vulnerability of corals to future ocean acidification. Moreover, they also provide insight into the natural pH ranges in which corals are adapted to live, of importance in the context of future acidification and its effects on marine ecosystems. In a sense, these results are encouraging since they show that some corals are well-adapted to changes in marine pH of at least 0.3 units. They also show that acidification at Flinders Reef might be delayed due to the presumable development of a new 50-year cycle in the next decades. However, once this cycle reaches minimum pH values, waters in Flinders Reef will very likely experience pH levels with no precedents, at least compared to the last 300 years. Once pH levels are such that the values of aragonite saturation are too low for corals to develop, reefs will grow progressively weaker and will tend to be poorly cemented, which will lend them more susceptible to erosion by wave action. One limitation of this work is that it provides a reconstruction for only one specific reef, and more work needs to be done in other reefs to be able to extrapolate results and obtain a more global oceanic picture.

Conclusion and future research needs

Understanding how ocean pH has changed in the past is crucial to fully assessing the magnitude of the environmental problem resulting from progressive acidification of the oceans. This knowledge is crucial to establish the levels of pH tolerance for marine organisms and to improve our understanding of the role and mechanisms of the oceans in absorbing atmospheric CO_2 . Since instrumental records of seawater pH exceeding a single decade are not yet available, past variations of pH need to be reconstructed using proxies in suitable archives. The isotopic composition of boron in biogenic marine carbonates is, so far, the only practical means to determine seawater pH variations back through time. Empirical calibrations show convincingly

that, at least by means of the cultured foraminifera and coral species that have been evaluated so far, it is possible to reconstruct seawater pH from boron isotopes in carbonate remains. This method should thus be fully exploited over different time scales and marine realms to obtain a more global picture of the natural variation of pH in the world's oceans and seas. Several questions concerning the applicability of the method, especially for Early Cenozoic reconstructions, should also be addressed. It is very possible, for instance, that significant variations in the boron isotopic composition of seawater occurred at these large time scales, a topic that should be evaluated thoroughly before reliable reconstructions can be obtained. In addition, because these reconstructions are based on foraminifera that are no longer extant, ways to cross-calibrate the isotopic composition of boron in these foraminifera with modern species should be investigated. For more recent times, a full evaluation of the glacial to interglacial change in deep-water pH also remains an issue, because the data obtained so far remain controversial. Finally, regarding reconstructions using corals, more work needs to be done in other reefs to corroborate whether natural cycles of pH are a common feature of these complex systems.

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About the authors

Dr. Eva Calvo (Ramón y Cajal Researcher) and Dr. Carles Pelejero (ICREA Research Professor) began working at the Institut de Ciències del Mar, CSIC, Barcelona, in early 2005, after nearly 4 years of postdoctoral work in Australia. Their research focuses on paleoclimatology, paleoceanography, and marine biogeochemistry, three scientific disciplines that they have addressed during doctoral studies at the Institute of Chemistry and Environmental Research, CSIC, Barcelona (Calvo obtained her PhD in 2001 and Pelejero in 2000), as a postdoctoral researcher (2001–2004) at the Australian National University and

Geoscience Australia in Canberra, Australia, and presently, at the Institut de Ciències del Mar, back in Barcelona. For their PhD theses, Calvo and Pelejero studied molecular biomarkers in deep-sea sediments as recorders of past climatic and environmental conditions. During their postdoctoral research, they developed new methodologies for the elemental and isotopic analysis of marine biogenic carbonates and siliceous organisms using inductively coupled plasma-mass spectrometry and thermal ionization-mass spectrometry with multiple collectors. A major success was the set-up of a complex technique to analyze the boron isotopic composition of corals in order to reconstruct past

*variations in ocean pH. Using this technique, they were able to reconstruct the oceanic pH for the last 300 years, as described in this review and originally published in *Science* in September, 2005. At the ICM, they are engaged in several lines of research, some of which involve assessment of the impact of ocean acidification. This is a continuation of the work initiated in Australia. Calvo and Pelejero, together with Dr. Rafel Simó and Dr. Marta Ribes, have recently constituted the Catalan Research Group of Marine Biogeochemistry and Global Change, with ocean acidification being one of its main research targets. The group is funded by the Generalitat de Catalunya.*

