Boron in $\text{CaCO}_3$ as a record of past seawater carbonate chemistry

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Boron incorporated in marine biogenic carbonates records the pH of seawater during precipitation. From reconstructing atmospheric $\text{CO}_2$ beyond ice-core records to deciphering the ocean’s role in storing and releasing carbon, boron is proving to be a vital tool in paleoclimate research.

Around a third of anthropogenic $\text{CO}_2$ released to date has been taken up by the ocean. Its future capacity to sequester carbon, however, given potentially dynamic biogeochemical feedbacks, is unclear. Studies of the geological past provide numerous examples of how the ocean regulates and moderates atmospheric $\text{CO}_2$ levels. To learn from these, however, we need effective recorders of the ocean’s carbonate system. Boron (B)-based proxies — namely B/Ca ratios and the boron isotope ($\delta^{11}\text{B}$)-pH proxy applied to marine carbonate archives — are among the most promising tools for reconstructing past ocean carbonate chemistry and atmospheric $\text{CO}_2$.

Here we briefly summarize some of the progress, problems, and prospects in the field.

**Chemical basis of boron (B) proxies**

In short, B-based proxies rely on the predictable pH-dependent speciation of dissolved B in seawater, between borate ion (B(OH)$_4^-$, prevalent at higher pH) and boric acid (B(OH)$_3^-$, prevalent at lower pH), as shown in Figure 1. The B/Ca proxy works on the assumption that the more of the charged borate ion there is in solution (due to higher pH and lower $\text{CO}_2$), the more B will be incorporated into the skeletal $\text{CaCO}_3$ of marine calcifiers. The $\delta^{11}\text{B}$-pH proxy instead leverages the constant isotope fractionation associated with borate ion and boric acid speciation. This fractionation results in a predictable relationship between the $\delta^{11}\text{B}$ of borate (the species incorporated into biogenic $\text{CaCO}_3$) and pH. This foundation in aqueous chemistry has contributed to the considerable success of B-based proxies to date.

**The B/Ca proxy**

The B/Ca proxy is attractive in that the analytical method is simpler, and it requires less sample material than the $\delta^{11}\text{B}$-pH proxy. However, the outlook for this proxy is, at present, mixed. In planktic foraminifera, a host of environmental controls are now known to influence how much of the borate present in solution at any given pH is ultimately incorporated into calcite. These include salinity, ambient phosphorous concentration, light levels, and calcification rate (e.g. Allen and Hönisch 2012; Babila et al. 2014; Henehan et al. 2015; Salmon et al. 2016). Clearly, this complicates the use of B/Ca in planktic foraminifera as a straightforward pH proxy. Indeed, high-profile early applications of the proxy to reconstruct surface-ocean pH and hence atmospheric $\text{CO}_2$ (Tripati et al. 2009) have since been shown to have been driven by secondary parameters involved in calculation, rather than the measured B/Ca data itself (Allen and Hönisch 2012). On the other hand, in deep-sea benthic foraminifera strong empirical relationships are observed between B/Ca and bottom-water carbonate saturation ($\Delta[\text{CO}_2^{\text{aq}}]$; Yu and Elderfield 2007). This has been valuable in tracking the migration of $\text{CO}_2$-rich deep-water bodies, and for the most part these reconstructions have been consistent with independent observations (e.g. $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, deep-sea coral $\delta^{11}\text{B}$). Collinearity between salinity, phosphorus, and $\Delta[\text{CO}_2^{\text{aq}}]$ within benthic foraminiferal B/Ca calibration datasets (Henehan 2013), however, means some of the non-carbonate system controls seen in planktic foraminifera could still play a role.

On a more positive note, for all of its documented competing controls, in many geological records B/Ca does appear to behave like a pH proxy. For instance, at the Paleocene-Eocene Thermal Maximum, B/Ca declines in tandem with excursions in $\delta^{11}\text{B}$ (Penman et al. 2014), suggesting that in some settings planktic foraminiferal B/Ca ratios can be at least qualitatively informative. It is thus premature at this point to discount the proxy entirely.

**The boron isotope-pH proxy**

Using boron isotopes circumvents many issues associated with B/Ca, allowing for quantitative reconstruction of pH and $\text{CO}_2$. For example, diagenetic recrystallisation of fossil $\text{CaCO}_3$ may result in loss of B (thus changing B/Ca), but the isotopic composition of the remaining B is unaffected (Edgar et al. 2015). Furthermore, factors like temperature and salinity have no competing effects on $\delta^{11}\text{B}$ outside of their well-understood quantifiable effect on aqueous B speciation (e.g. Henehan et al. 2016). Most importantly, the dominant control of seawater pH on $\delta^{11}\text{B}$ has been repeatedly...
demonstrated. For example, pH reconstructed from the δ^11B of core-top deep-sea benthic foraminifera closely matches the pH of the water in which they grew (Rae et al. 2011), indicating the sole incorporation of borate into foraminifera and supporting the chemical foundation of the proxy.

For other calcifiers, although the control of pH on δ^11B is clear, skeletal carbonate rarely records the δ^11B of ambient seawater borate (δ^11B_{borate}) exactly. Instead, their δ^11B reflects a combination of δ^11B_{borate} and a superimposed (typically species-specific) physiologically induced offset, termed a ’vital effect’. In the case of corals, this vital effect reflects the pH to which the calcifying fluid has been raised, which in turn varies with bulk seawater pH (Venn et al. 2013). In brachiopods and bivalves the situation is perhaps more complex, but their δ^11B demonstrably varies with ambient pH (e.g. Jurikova et al. 2019).

In planktic foraminifera – our primary archive of surface-water pH and atmospheric CO₂ – vital effects are also ubiquitous (unlike in deep-sea benthic foraminifera). Although we know foraminifera also raise the pH of their internal calcifying fluid (Bentov et al. 2009), thus far the most compelling explanation for species-specific deviations from δ^11B_{borate} is microenvironment alteration (e.g. Henehan et al. 2016). This framework recognizes that planktic foraminifera don’t “see” ambient seawater, but rather a layer of seawater immediately surrounding their shell that is too small for turbulent mixing. It predicts, and indeed explains why, symbiont-bearing foraminifera living in the euphotic zone record higher-than-ambient pH and δ^11B_{borate} because their photosynthetic symbionts take up CO₂ from their microenvironment. Conversely, species living below the euphotic zone, or those that don’t host symbionts, are surrounded by seawater that is richer in respired CO₂, and hence lower in pH. This also explains the lack of vital effects in deep-sea benthic foraminifera, as their slow biomineralization rates mean diffusion can keep pace with release of respired CO₂.

Although foraminiferal δ^11B clearly varies with pH and CO₂ regardless of vital effects (see e.g. data from Chalk et al. 2017 plotted in Fig. 2a), individual species differ significantly in their δ^11B-pH (or more commonly δ^11B_{borate}-δ^11B_{borate}) calibrations. If a species’ calibration is known, pH and CO₂ values can be calculated from oligotrophic ocean regions with an accuracy and precision rivaled only by ice cores (Fig. 2b; in purple). However, without a calibration, for example with extinct species, quantifying absolute pH is more challenging. For example, if one erroneously applied a calibration derived for Orbulina universa to these same Globigerinoides ruber data from Chalk et al. (2017; Fig. 2c, in orange), reconstructed CO₂ would be inaccurate. Thankfully, efforts to model and constrain vital effects in extinct species are ongoing (e.g. within the SWEET consortium; deepmip.org/sweet); these will reduce this source of uncertainty in deep-time reconstructions.

Beyond reconstructing atmospheric CO₂ (by measuring δ^11B in planktic foraminifera from regions where the atmosphere and surface ocean CO₂ are in equilibrium), the δ^11B-pH proxy can also be used to detect transient regional changes in air-sea CO₂ disequilibrium. This has elucidated the role of changing ocean carbon storage in driving glacial-interglacial CO₂ change, with CO₂ release from the deep ocean to the atmosphere now known to have played a major role in pushing the Earth out of the last ice age (e.g. Martinez-Boti et al. 2015; Rae et al. 2018).

There is considerable potential for such approaches to be applied in deeper time, for instance to investigate changes in ocean carbon storage during hyperthermal events. Ongoing analytical advances and shrinking sample size requirements mean these sorts of applications are coming into reach, potentially overhauling our understanding of how the ocean has influenced atmospheric CO₂ through geological history.

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**REFERENCES**
Babila TL et al. (2014) Earth Planet Sc Lett 404: 67–76
Penman DE et al. (2014) Paleoceanography 29: 357–369
Rae JWb et al. (2011) Earth Planet Sc Lett 302: 403–413
Salmon KH et al. (2016) Earth Planet Sc Lett 449: 372–381
Tripati AK et al. (2009) Science 326: 1394–1397

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