

THE BORON ISOTOPE PROXY: A LITERATURE REVIEW

Hana Jurikova

GEOMAR Helmholtz Centre for Ocean Research Kiel

Introduction

The global biogeochemical cycling of carbon is fundamental for life on Earth and therefore of critical importance to science. The ocean plays a key role in the carbon cycling as the largest active CO₂ reservoir. Moreover, exchange between the surface ocean and the atmosphere means that fluxes in pCO₂ of the ocean and the atmosphere are coupled and therefore one can provide information on the other. The critical chemical parameter is pH, since the ocean pH and pCO₂ are directly related. Dissolution of aqueous CO₂ in seawater increases the hydrogen ion (H⁺) concentration in the ocean and thus decreases ocean pH and vice-versa, as follows:



If we are able to reconstruct the past ocean pH along Earth's geological record, we could gain insights into carbon cycle perturbations during key periods of evolutionary history, extend our understanding on the changing ocean chemistry and the controls on atmospheric chemistry and provide new constrains on the fluctuations of the global carbon cycle and natural pCO₂ levels (a review on our current understanding of ocean acidification history is available in Hönisch et al. 2012).

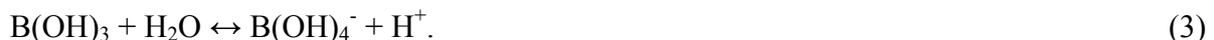
Boron isotopes and its application as a pH proxy

Historically, our knowledge of ancient seawater pH has been limited to model predictions. However, over the last couple decades the boron isotope composition of marine calcium carbonate has emerged as a new promising paleo-pH proxy (Vengosh et al. 1991, Hemming & Hanson 1992, Spivack et al. 1993, Sanyal et al. 2000, Pagani et al. 2005, Hemming & Hönisch 2007).

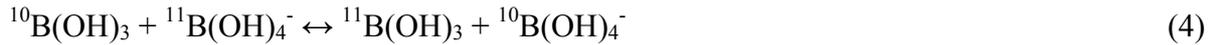
Boron has two isotopes, ¹⁰B and ¹¹B (approximately 20% and 80% of total B, respectively), and the ¹¹B/¹⁰B variations are expressed in the standard delta notations in per mille (‰) relative to the reference material NIST SRM 951 boric acid (Catanzaro et al. 1970) as follows:

$$\delta^{11}\text{B} (\text{‰}) = [(\text{}^{11}\text{B}/\text{}^{10}\text{B}_{\text{sample}})/(\text{}^{11}\text{B}/\text{}^{10}\text{B}_{\text{standard}})-1] \times 1000 \quad (2)$$

The principle of the δ¹¹B proxy is based on the speciation of boron in seawater. Boron is present in seawater almost exclusively as trigonal boric acid [B(OH)₃] and tetrahedral borate ion [B(OH)₄⁻]. The relative proportion of boron species is pH dependent as defined by the following equilibrium:



Because of the differences in coordination and the subsequent B-O bond vibrational frequencies, an isotopic fractionation exists between the two species. Thus, as the distribution of boric acid and borate ion change with pH, so does their isotopic composition. The associated isotopic fractionation may be described as:



where the equilibrium constant $^{11-10}\text{K}_\text{B}$ (also termed as α_{4-3} or α_B in literature) is defined as:

$$^{11-10}\text{K}_\text{B} = \frac{[^{11}\text{B}(\text{OH})_3] \times [^{10}\text{B}(\text{OH})_4^-]}{[^{10}\text{B}(\text{OH})_3] \times [^{11}\text{B}(\text{OH})_4^-]} \quad (5)$$

Given a value for $^{11-10}\text{K}_\text{B}$ the isotopic composition of both boron species in seawater varies predictably with pH. Kakihana et al. (1977) first determined empirically the fractionation factor to be 1.008 (0.501 mol/l) to 1.016 (0.010 mol/l) at 25°C, inversely dependent on the boric acid concentration of the external solution. Although the magnitude of the factor has been a subject of debate throughout the years, recent reports point to a value close to 1.030 (in seawater at 25°C), which has been supported by theoretical studies (Zeebe 2005) as well as experimentally derived (1.0272±0.0006 in seawater at 25°C, Klochko et al. 2006) and currently appears to be the preferred fractionation factor. Providing $^{11-10}\text{K}_\text{B}$ and pK_B^* , the dissociation constant for boric acid at in situ temperature, salinity and pressure (commonly calculated according Dickson 1990), pH can be calculated from the $\delta^{11}\text{B}$ values of either boron species, e.g. borate ion:

$$\text{pH} = \text{pK}_\text{B}^* - \log \left(- \frac{\delta^{11}\text{B}_\text{sw} - \delta^{11}\text{B}_\text{borate}}{\delta^{11}\text{B}_\text{sw} - (^{11-10}\text{K}_\text{B} \times \delta^{11}\text{B}_\text{borate}) - 10^3(^{11-10}\text{K}_\text{B} - 1)} \right) \quad (6)$$

where $\delta^{11}\text{B}_\text{sw}$ is the isotopic composition of seawater (39.61‰, Foster et al. 2010) which is consistent due to the long oceanic residence time of boron, approximately 14 to 20 million years (Taylor & McLennan 1985, Spivack & Edmond 1987). For studies investigating the geological past it is critical to first constrain the boron isotopic composition of ancient oceans before the model can be applied (Pagani et al. 2005, Joachimski et al. 2005). This exercise is not trivial and is one key source of uncertainty in early Cenozoic and older pH reconstructions (Raitzsch & Hönisch 2013).

Boron in carbonates

First efforts were predominantly oriented toward boron investigations in clay minerals. Spivack et al. (1987) have shown that approximately 90% of bulk boron in clays is not in isotopic equilibrium with seawater and hence not indicative of their depositional environments, making these unsuitable candidates for paleoenvironmental reconstructions. A new promising candidate became carbonate-forming skeletal components of marine organisms, which depend on seawater as main boron source.

Early studies using biogenic carbonates and experiments with inorganically precipitated carbonates showed that only aqueous borate ion is being preferentially incorporated into the calcium carbonate structure (Hemming & Hanson 1992, Hemming et al. 1995, Sanyal et al. 2000). If only borate ions are incorporated into carbonate structures and this occurs without isotopic fractionation, marine carbonates should record the pH of seawater from which they were formed. However, the $\delta^{11}\text{B}$ measurements of modern marine calcifiers show a trend to higher values compared to the $\delta^{11}\text{B}$ of borate in seawater and are commonly attributed to species-specific vital effects such as photosynthesis or proton-cation exchange reactions (Hönisch et al. 2003, Rollion-Bard & Erez 2010). Nonetheless a relationship does exist between the $\delta^{11}\text{B}$ of carbonate skeleton and seawater pH, as demonstrated by culture

experiments on foraminifera and corals, providing species-specific calibrations can be made (Trotter et al. 2001, Hönisch et al. 2004, Anagnostou et al. 2012, Henehan et al. 2013). Recent experiments on synthetic calcite and aragonite point to a much more complex mechanism of boron incorporation than previously thought. Noireaux et al. (2015) observed both tetrahedral BO_4 as well as trigonal BO_3 in the precipitated calcite, with its $\delta^{11}\text{B}$ higher than that of aqueous borate and less sensitive to solution pH variations compared to aragonite. Additionally, they suggested a coordination change from BO_4 to BO_3 upon boron incorporation in the solid, as the fraction of BO_3 measured in the calcite was higher than that inferred from $\delta^{11}\text{B}$.

Hemming & Hanson (1992) proposed the following mechanisms for the substitution of boron into carbonate, which also has implications for boron concentration in carbonates, which often increases with decreasing pH:



The partition coefficient K_D for the B(OH)_4^- species substitution into carbonates can be expressed as:

$$K_D = \frac{[\text{B/Ca}]_{\text{CaCO}_3}}{[\text{B(OH)}_4^-/\text{HCO}_3^-]_{\text{sw}}} \quad (8)$$

This term predicts that the $[\text{B(OH)}_4^-/\text{HCO}_3^-]_{\text{sw}}$ (and therefore the B/Ca ratio) is proportional to pH and with increasing pH the B(OH)_4^- concentration will increase as the HCO_3^- decreases (see Yu et al. 2007). Providing that we could quantify the K_D in Eq. (8) or if it is constant, it may be possible to constrain paleo-pH values merely based on boron concentrations in calcium carbonate. Several studies assessed the reliability of B/Ca in foraminifera but report variable B/Ca ratios in individual species, with increasing test size (Ni et al. 2007) as well as calcification temperatures (Yu et al. 2007). Application of the B/Ca ratios therefore remains a challenge and to date could not be established as a quantitative pH proxy (Allen & Hönisch 2012, Uchikawa et al. 2015, Henehan et al. 2015).

Up-to-date paleo-pH reconstructions

Although the theoretical foundation of the boron isotope proxy is now well established and over the past years also became well supported in an experimental framework, accurate reconstructions still pose a challenge, as a number of obstacles lie in the creation of reliable boron-based pH records. Minimizing the laboratory boron blank is crucial for high precision work and requires boron-free working conditions and materials. Understanding the $^{11}\text{B}/^{10}\text{B}$ offset between laboratories and mass spectrometric approaches (NTIMS, LA-ICP-MS, MC-ICP-MS) is fundamental for validating the method and providing intercomparable results. Likewise, species-specific calibrations and cautious choice of archives are critical for consistent paleo-reconstructions. While Cenozoic and modern ocean pH reconstructions are largely based on monospecific foraminiferal archives (occasionally brachiopods, corals and algae) older reconstructions predominantly use bulk carbonates, and therefore result incomparable. Moreover, evaluating for diagenetic alternations only adds to the challenges of providing reliable interpretations of ancient pH, especially on larger geological time scales.

First efforts to reconstruct past ocean pH by Spivack et al. (1993) demonstrated that $\delta^{11}\text{B}$ of foraminiferal tests from deep-sediment cores from late Cenozoic (the period for which $\delta^{11}\text{B}_{\text{sw}}$ is constant) shows to be a promising archive. They report low ocean pH values of 7.4 ± 0.2 21

Ma ago, which increased to present value of 8.2 ± 0.2 about 7.5 Ma ago, in agreement with suggestions that atmospheric CO₂ concentrations may have been higher 21 Ma ago. Following studies using foraminiferal archives reconstructed the ocean pH during the glacial period (Sanyal et al. 1995, Sanyal & Bijima 1999) and Miocene (Palmer et al. 1998). Pearson & Palmer (1999, 2000) extended the record to the past 60 Ma, suggesting atmospheric CO₂ >2000 ppm from 60 to 52 Ma, followed by a decline between 55 to 40 Ma ago and stabilization of CO₂ levels below 500 ppm as of early Miocene. Recent studies expanded the foraminiferal record with reconstructions from the deglacial period (Martinez-Boti et al. 2015a), glacial period (Foster & Sexton 2014), the last glacial cycle (Foster 2008, Hönisch et al. 2008) and Pliocene (Bartoli et al. 2011, Martinez-Boti et al. 2015b). The interpretation of pH and CO₂ values spanning older periods, in particular for when the $\delta^{11}\text{B}_{\text{sw}}$ is no longer constant must be however cautious, as multiple assumptions are required to fully constrain all the parameters in the model.

To reconstruct the atmospheric carbon dioxide evolution over older time spans, several studies measured $\delta^{11}\text{B}$ in various biogenic and abiogenic bulk carbonates. Kasemann et al. (2005, 2010) and Ohnemüller et al. (2014) applied the boron proxy to investigate paleoenvironmental conditions during the Marinoan snowball Earth (app. 635 Ma), while Clarkson et al. (2015) report on ocean acidification event during the Permo-Triassic Boundary (app. 252 Ma). Although measurements of carbonate formations offer us an important look into older timeframes of extreme climate and provide encouraging results for the boron pH-proxy, further studies – if possible using single carbonate species – are essential to reproduce such trends and provide robust results.

Recent reports point towards brachiopods as another potential paleo-pH recorders, following proper assessment of internal boron isotopic variability (Joachimski et al. 2005, Penman et al. 2013). Brachiopods can present an advantage in particular as Phanerozoic archives, as they are highly abundant in the geological record and their shells are composed of low-magnesium calcite, making them more resilient to alterations of primary chemical signals. While we expect brachiopod calcite to be more variable in its $\delta^{11}\text{B}$ composition, the abundance of single, in place well-preserved shells allows carbon cycle reconstructions extending into the Mesozoic and Paleozoic Era.

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