



# Direct measurement of the boron isotope fractionation factor: Reducing the uncertainty in reconstructing ocean paleo-pH



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## ARTICLE INFO

### Article history:

Received 26 September 2014

Received in revised form 3 January 2015

Accepted 6 January 2015

Available online 21 January 2015

Editor: G.M. Henderson

### Keywords:

boron isotope fractionation

paleo-pH

ocean acidity

ocean chemistry

reverse osmosis

## ABSTRACT

The boron isotopic composition of calcium carbonate skeletons is a promising proxy method for reconstructing paleo-ocean pH and atmospheric CO<sub>2</sub> from the geological record. Although the boron isotope methodology has been used extensively over the past two decades to determine ancient ocean-pH, the actual value of the boron isotope fractionation factor ( $\epsilon_B$ ) between the two main dissolved boron species, <sup>11</sup>B(OH)<sub>3</sub> and <sup>10</sup>B(OH)<sub>4</sub><sup>-</sup>, has remained uncertain. Initially,  $\epsilon_B$  values were theoretically computed from vibrational frequencies of boron species, resulting in a value of ~19‰. Later, spectrophotometric pH measurements on artificial seawater suggested a higher value of ~27‰. A few independent theoretical models also pointed to a higher  $\epsilon_B$  value. Here we provide, for the first time, an independent empirical fractionation factor ( $\epsilon_B = 26.0 \pm 1.0\text{‰}$ ; 25 °C), determined by direct measurements of B(OH)<sub>3</sub> in seawater and other solutions. Boric acid was isolated by preferential passage through a reverse osmosis membrane under controlled pH conditions. We further demonstrate that applying the Pitzer ion-interaction approach, combined with ion-pairing calculations, results in a more accurate determination of species distribution in aquatic solutions of different chemical composition, relative to the traditional two-species boron-system approach. We show that using the revised approach reduces both the error in simulating ancient atmospheric CO<sub>2</sub> (by up to 21%) and the overall uncertainty of applying boron isotopes for paleo-pH reconstruction. Combined, this revised methodology lays the foundation for a more accurate determination of ocean paleo-pH through time.

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## 1. Introduction

One of the key components of the boron isotope methodology for determining the paleo-pH of the ocean is the magnitude of the isotopic fractionation ( $\epsilon_B$ ) between B(OH)<sub>4</sub><sup>-</sup>, which is assumed to be preferentially incorporated into calcium carbonate skeletons, and B(OH)<sub>3</sub> in seawater (Vengosh et al., 1991; Hemming and Hanson, 1992; Spivack et al., 1993; Palmer et al., 1998; Pearson and Palmer, 2000; Xiao et al., 2014). Yet the value of this fractionation factor has been debated, leading to considerable uncertainty in the accuracy of attempts to reconstruct acidity variations of the ocean through time (Pagani et al., 2005; Honisch et al., 2007, 2009; Kakhana et al., 1977; Oi, 2000; Klochko et al., 2006; Liu and Tossell, 2005; Zeebe, 2005). Early paleo-pH reconstructions (Palmer et al., 1998; Pearson and Palmer, 2000) used the theoretical value  $\epsilon_B = 19.4\text{‰}$ , suggested by Kakhana et al. (1977), while later theoretical works yielded higher values, i.e. 26.0‰ (Oi, 2000),

26.7‰ (Liu and Tossell, 2005), and 26–28‰ (Rustad et al., 2010). Zeebe (2005) showed that different assumptions and calculation methods applied within the theoretical framework result in wide variations in  $\epsilon_B$  (in the range 20–50‰), although several arguments supported values in the higher range ( $\epsilon_B > 30\text{‰}$ ). The latter authors emphasized the need for an independent experimental measurement of  $\epsilon_B$  (Zeebe, 2005). A purely empirical approach, based on spectroscopic pH measurements of borate buffer solutions containing only <sup>11</sup>B or <sup>10</sup>B, yielded a value of 27.2‰ (Klochko et al., 2006), which supported the higher  $\epsilon_B$ . In a recent review  $\epsilon_B = 26.0\text{‰}$  was considered the best available value for the boron fractionation factor (Xiao et al., 2014).

Here we present a new empirical approach for direct measurement of  $\epsilon_B$ . The methodology is based on preferential passage of B(OH)<sub>3</sub> through reverse osmosis (RO) membranes along with the rejection of the charged B(OH)<sub>4</sub><sup>-</sup> and associated ion-pairs. The isotopic measurement of RO permeates, comprised almost entirely of the uncharged B(OH)<sub>3</sub>, provides a unique setting for direct measurement of the isotopic ratios of individual boron species (Kloppmann et al., 2008). Under controlled pH, RO separation of a solution of known bulk boron isotopic composition

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permits accurate assessment of the isotopic fractionation between the two main aqueous boron species. We derived a mathematical expression to enable accurate determination of the fractionation factor by a least-square linear regression. The expression was derived from a mass balance (Zeebe and Wolf-Gladrow, 2001) of the dissolved (B) and isotopic ( $\delta^{11}\text{B}$ ) composition of the total boron system ( $B_T$ ,  $\delta^{11}\text{B}_T$ ), boric acid ( $B_3$ ,  $\delta^{11}\text{B}_3$ ), borate ( $B_4$ ,  $\delta^{11}\text{B}_4$ ; including borate ion-pairs),  $\alpha_B(10^{-3}\varepsilon_B + 1)$ , and  $\varepsilon_B$  (the fractionation factor between boron species):

$$\delta^{11}\text{B}_4 = \frac{\delta^{11}\text{B}_T \cdot B_T - \varepsilon_B B_3}{B_4 + \alpha_B B_3} \quad (1)$$

$$\delta^{11}\text{B}_3 = \delta^{11}\text{B}_4 \cdot \alpha_B + \varepsilon_B \quad (2)$$

Substituting Eq. (1) into Eq. (2), eliminating  $\alpha_B$  and  $B_4$  by using the relations  $\alpha_B = 10^{-3}\varepsilon_B + 1$  and  $B_4/B_T = 1 - B_3/B_T$ , respectively, and rearranging yields the following expression:

$$\delta^{11}\text{B}_3 = \varepsilon_B [1 - B_3/B_T + 10^{-3}(\delta^{11}\text{B}_T - \delta^{11}\text{B}_3 \cdot B_3/B_T)] + \delta^{11}\text{B}_T \quad (3)$$

Based on this framework, we conducted a series of experiments in which seawater, brackish groundwater and boron-spiked artificial solutions were passed through a reverse osmosis (RO) membrane under controlled pressure and pH. This experimental design provides a unique opportunity to isolate and exclusively measure the isotopic ratio of boric acid and thus determine the boron isotope fractionation factor between boron species.

## 2. Materials and methods

Reverse osmosis experiments were carried out using a membrane filtration pilot-scale unit, supporting one SW30HRLE-4040 Dow filmtec® membrane module (diameter = 4" and length = 40"). In the filtration experiments, the examined solution was pumped from a feed tank (containing ~100 l of solution) to a high-pressure, positive-displacement pump (Hydra-Cell, D/G-10-X), using a centrifugal booster pump (Pedrolo, 2-4CR). The pressurized feed water was pumped through a membrane element installed in a Bell, ORL4-E-1000 pressure vessel. The working pressure was controlled by a valve at the brine outlet, while the feed flow-rate (cross-flow velocity) was independently adjusted using a frequency converter to control the pump. Both parameters were continuously recorded by digital meters connected to a computer, while the permeate flow rate was determined manually by accurately measuring the change of permeate volume with time. In order to minimize concentration–polarization effects, the feed flow-rate was adjusted to the maximum value obtainable by the high-pressure pump (32 l/min). In order to minimize pH variations resulting from the concentration of the feed during a given experiment and the permeation of acid-base species (e.g.,  $\text{B}(\text{OH})_3$ ,  $\text{CO}_2$ ,  $\text{H}^+$  and  $\text{OH}^-$ ) (Nir et al., 2014), the feed pressure was adjusted to maintain a minimal permeate stream of ~1 l/min, i.e. ~3% of the feed flow rate (e.g., for seawater, the adjusted pressure was 29–31 bars). An estimation of the error resulting from these effects is provided in the supporting information file. The pH of the feed was adjusted in the different experiments by either strong acid or strong base (HCl/KOH) and the procedure was repeated for pH values in the range 7.0 to 9.5. The reported pH values are the average value between the feed and the brine streams; however the difference was always <0.03 pH units, indicative of stable operation. For each measured pH value, B speciation in the seawater feed was determined using the Pitzer approach, as implemented in the computer program PHREEQC (Parkhurst and Appelo, 2013). Accurate pH measurements in concentrated solutions (ionic strength >0.4 M) were performed by the method described by Nir et al.

(2014). The compositions of all feed solutions used in the study are provided in the supporting information file. The RO experiments were conducted in a full recirculation mode, i.e. the brine and permeate streams were directed back to the feed tank and the system was allowed to stabilize for at least 20 min for every RO experimental point before collecting samples. Samples from the permeate stream were analyzed for  $\delta^{11}\text{B}$  at Duke University by negative thermal ionization mass spectrometry (Vengosh et al., 1991; Foster et al., 2013), using a Triton (ThermoFisher) mass spectrometer. Prior to loading, samples were treated with peroxide to remove organic matter and CNO complexes, in a vertical laminar flow clean hood equipped with boron-free PTFE HEPA filtration. Measurement of external replicates of SRM951 standard ( $^{11}\text{B}/^{10}\text{B} = 4.0051 \pm 0.0023$ ;  $n = 63$ ) during the last 12 months yielded a precision of 0.6‰. All isotopic measurements were conducted for at least three external replicates and were systematically monitored for negligible  $\text{CNO}^-$  (mass 42) interference, based on negligible signal at proxy mass 26 ( $\text{CN}^-$ ). Total loading blank was <15 pg B as determined by isotope dilution (NIST951). Boron contents were measured by inductively coupled-mass spectrometry (ICP-MS) on a VG PlasmaQuad-3 ICP-MS at Duke University.

## 3. Results and discussion

By controlling the pH variations of the feed solutions, the ratio between the boron species in the solution (i.e., the value of the bracketed expression in Eq. (3)) and the preferential transport of boric acid through the RO membrane would vary, but not the fractionation factor ( $\varepsilon_B$ ) value. Hence, using a solution with known  $B_T$  and  $\delta^{11}\text{B}_T$  and assuming that the measured  $\delta^{11}\text{B}$  of the permeate exclusively reflects the  $\delta^{11}\text{B}_3$  in the feed (i.e., only  $\text{B}(\text{OH})_3$  passes through the RO membrane), a plot of  $\delta^{11}\text{B}$  (permeate) versus the distribution of boron species induced by the pH conditions (i.e., the bracketed expression) should result in a linear curve, for which  $\varepsilon_B$  is the slope and  $\delta^{11}\text{B}_T$  of the feed is the intercept (Fig. 1).

In order to evaluate the distribution of boron species in any type of solution, including modern and fossil seawater with apparent different chemical compositions, we present an alternative and more generic approach based on ion–interaction and ion–pairing modeling. This methodology was employed in this study for the determination of the  $B_3/B_T$  ratio appearing in Eq. (3), thus enabling  $\varepsilon_B$  to be determined for any solution composition. Subsequently, the ion interaction approach, used here for the first time in the context of the pH proxy, is shown to have significant implications for the application of the boron proxy, which is very sensitive to accurate speciation calculations. Previous studies have thus far utilized the binary (two species) representation of the boron system, in which an empirical dissociation constant ( $\text{p}K_b^* = 8.597$  @25 °C and  $S = 35$  g/kg (Dickson, 1990) has been commonly used. Given that the  $K_b^*(T, S)$  of the binary system in seawater represents a wide range of temperatures (273.15–318.15 K), pressures (from 0 to 300 bar) and salinities (0–45 g/kg), this commonly used constant can indeed be considered accurate for the modern ocean composition. However, this constant cannot be applied reliably to different aqueous phase compositions, such as the aquatic chemistry assumed to compose the ancient ocean and/or other environmental settings. For example, fluid inclusions in marine halite crystals combined with geochemical modeling for ancient ocean composition have suggested that during the Cretaceous period (~130 Ma), the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations were respectively 20–29 mmol/kg higher and 5–15 mmol/kg lower relative to modern seawater (Ligi et al., 2013; Holt et al., 2014). Variations in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  proportions in the ancient seawater would have affected specific ion interactions (e.g., ion–pairs formation), and thereby the apparent  $K_b^*$  value, rendering the binary approach inaccurate for determining paleo-pH by the

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