Earth and Planetary Science Letters 414 (2015) 1–5

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

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

Oded Nir[a], Avner Vengosh[b,*], Jennifer S. Harkness[b], Gary S. Dwyer[b], Ori Lahav[a]

[a] Faculty of Civil and Environmental Engineering, Technion, Haifa, 32000, Israel
[b] Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, NC 27708, United States

ARTICLE INFO

Article history:
Received 26 September 2014
Received in revised form 3 January 2015
Accepted 6 January 2015
Available online xxxx
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_2 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 (ε_B) between the two main dissolved boron species, $^{11}B(OH)_3$ and $^{10}B(OH)_4^-$, has remained uncertain. Initially, ε_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 ε_B value. Here we provide, for the first time, an independent empirical fractionation factor ($\varepsilon_B = 26.0 \pm 1.0‰; 25\,°C$), determined by direct measurements of $B(OH)_3$ 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_2 (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.

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 (ε_B) between $B(OH)_4^-$, which is assumed to be preferentially incorporated into calcium carbonate skeletons, and $B(OH)_3$ 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, Kakihana 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 $\varepsilon_B = 19.4‰$, suggested by Kakihana 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 ε_B (in the range 20–50‰), although several arguments supported values in the higher range ($\varepsilon_B > 30‰$). The latter authors emphasized the need for an independent experimental measurement of ε_B (Zeebe, 2005). A purely empirical approach, based on spectroscopic pH measurements of borate buffer solutions containing only ^{11}B or ^{10}B, yielded a value of 27.2‰ (Klochko et al., 2006), which supported the higher ε_B. In a recent review $\varepsilon_B = 26.0‰$ 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 ε_B. The methodology is based on preferential passage of $B(OH)_3$ through reverse osmosis (RO) membranes along with the rejection of the charged $B(OH)_4^-$ and associated ion-pairs. The isotopic measurement of RO permeates, comprised almost entirely of the uncharged $B(OH)_3$, 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

---

[*] Corresponding author.
E-mail address: vengosh@duke.edu (A. Vengosh).

http://dx.doi.org/10.1016/j.epsl.2015.01.006
0012-821X/© 2015 Elsevier B.V. All rights reserved.

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 ($\delta^{11}B$) composition of the total boron system (B_T, $\delta^{11}B_T$), boric acid (B_3, $\delta^{11}B_3$), borate (B_4, $\delta^{11}B_4$; including borate ion-pairs), $\alpha_B(10^{-3}\varepsilon_B + 1)$, and ε_B (the fractionation factor between boron species):

$$\delta^{11}B_4 = \frac{\delta^{11}B_T \cdot B_T - \varepsilon_B B_3}{B_4 + \alpha_B B_3} \tag{1}$$

$$\delta^{11}B_3 = \delta^{11}B_4 \cdot \alpha_B + \varepsilon_B \tag{2}$$

Substituting Eq. (1) into Eq. (2), eliminating α_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:

$$\delta^{11}B_3 = \varepsilon_B\left[1 - B_3/B_T + 10^{-3}\left(\delta^{11}B_T - \delta^{11}B_3 \cdot B_3/B_T\right)\right] + \delta^{11}B_T \tag{3}$$

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., $B(OH)_3$, CO_2, H^+ and 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 $\delta^{11}B$ 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 ($^{11}B/^{10}B = 4.0051 \pm 0.0023$; $n = 63$) 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 CNO^- (mass 42) interference, based on negligible signal at proxy mass 26 (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 (ε_B) value. Hence, using a solution with known B_T and $\delta^{11}B_T$ and assuming that the measured $\delta^{11}B$ of the permeate exclusively reflects the $\delta^{11}B_3$ in the feed (i.e., only $B(OH)_3$ passes through the RO membrane), a plot of $\delta^{11}B$ (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 ε_B is the slope and $\delta^{11}B_T$ 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 ε_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 ($pK_b^* = 8.597$ @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 Ca^{2+} and 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 Ca^{2+} and 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

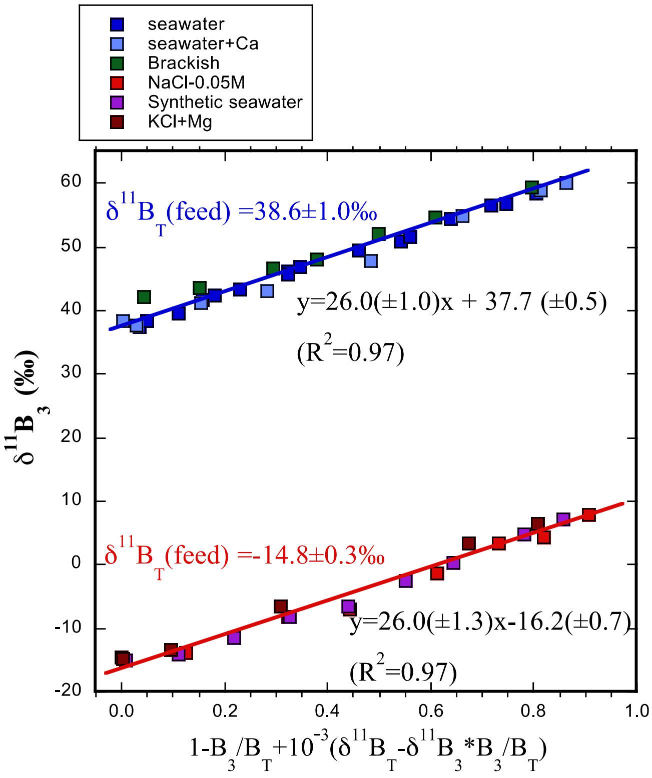

Fig. 1. Boron isotope ratios of boric acid ($\delta^{11}B_3$) versus the fraction of aquatic boron species, determined by mass-balance calculations (Eq. (3)). The slopes of the linear correlations, which were obtained from transport of seawater and synthetic solutions at varying feed pH through reverse osmosis membrane, determine the fractionation factor of the isotopic exchange between boron species. The least-squares linear regression coefficients and their associated 95% confidence intervals were determined using all measurements. The upper trend-line ($n = 92$) represents results of Mediterranean seawater (seawater and seawater + Ca) and coastal brackish groundwater. The bottom trend-line ($n = 55$) represents results of synthetic ionic solutions, to which a boron solution was added. The average feed $\delta^{11}B$ values for the natural ($n = 6$) and synthetic ($n = 2$) feed solutions are also presented.

$\delta^{11}B$ proxy. Furthermore, the seawater pH scale (pH_T), in which pK_B^* was developed, is directly related to the concentrations of hydronium ions only for modern-ocean sulfate concentration. Since relative sulfate concentrations varied significantly over geological time (Holt et al., 2014), the modern seawater pH scale, and hence pK_B^*, cannot be used for paleo-pH studies.

Instead, we propose using a general thermodynamics-based aqueous model, which covers the whole range of ionic compositions known to exist in the ancient and modern oceans. Currently, the best available model for determining aqueous-species speciation in a general fashion relies on a combination of the Pitzer ion-interaction approach and ion-pairs formation (Harvie et al., 1984). Within this model, the total B concentration in seawater is represented by four species, rather than two: $B(OH)_4^-$, $MgB(OH)_4^+$, $CaB(OH)_4^+$, and $B(OH)_3$ (Felmy and Weare, 1986). Other species, such as $B_3O_3(OH)_4^-$ and $B_4O_5(OH)_4^{-2}$, also form but are negligible at typical seawater B concentrations. Applying this model, using the software PHREEQC (Parkhurst and Appelo, 2013) to the paleo-pH proxy is shown here to increase both the accuracy and general utility of the methodology.

The boron fractionation factor was computed from the linear regression slope (Eq. (3)), illustrated in Fig. 1. RO separation of seawater and coastal brackish groundwater (upper trend line in Fig. 1), yielded $\varepsilon_B = 26.0‰ \pm 1.0$, which is consistent with theoretical values (Klochko et al., 2006; Liu and Tossell, 2005; Zeebe, 2005). This directly measured ε_B value is significantly higher than the previously estimated value of 19.4‰ (Kakihana et al., 1977) and slightly lower than the previously reported empirical value (27.2‰ ± 0.6) (Klochko et al., 2006). A practically identical ε_B value was obtained from applying the method for solutions with different ionic composition and $\delta^{11}B$ (lower line in Fig. 1). The consistency in ε_B values among the different solutions with different isotopic ratios implies no compositional effect on the fractionation factor, confirming the validity of the new methodology and the empirical value.

The measured $\delta^{11}B$ in the feed seawater and artificial solutions were 0.9‰ to 1.4‰ higher than the $\delta^{11}B_T$ value predicted by the regression intercepts for both types of experiments. This offset is probably due to systematic errors in both pH measurements (affecting boron speciation) and isotopic measurements. Systematic errors, however, have no effect on the slope, thus the uncertainty associated with the measured ε_B probably relates to the analytical precision of $\delta^{11}B$ measurements (see further discussion in Supporting Information).

The consistency in the ε_B values obtained in this study for different solutions and different pH calibration procedures confirms the validity and generality of the employed speciation model. This generality is notably lacking in previous $\delta^{11}B$ pH-proxy studies. To demonstrate the effect of different water chemistry conditions on the reconstructed pH, we plotted $\delta^{11}B_4$ (assumed to reflect $\delta^{11}B$ measured in $CaCO_3$) as function of pH for two different oceanic compositions that presumably existed in different geological times. The obtained curves (Fig. 2) were compared to the modern ocean composition. The Pitzer model was used for determining the boric acid to total boron ratio (B_3/B_T) required for the $\delta^{11}B_4$ calculation. We show that the pH–$\delta^{11}B_4$ curves are indeed affected by changes in seawater chemistry in different geological times (Fig. 2). The theoretical pH of Mid-Cretaceous ocean was ~0.14‰ lower than that of the mid-Neogene ocean for a given $\delta^{11}B_4$ value. This deviation is a result of higher Ca^{2+} and Mg^{2+} concentrations in the Middle Cretaceous seawater compared to the Middle Neogene ocean, as inferred from halite fluid inclusions (Holt et al., 2014). As mentioned, both Ca^{2+} and Mg^{2+} affect boron species distribution by interacting with the borate anion. However, since the $CaB(OH)_4^+$ ion-pair is more stable (has a larger stability constant), it has a more pronounced effect on boron speciation. This explains the deviation (approximately 0.07 pH units) between the curves representing modern seawater, seawater characterized by higher Mg^{2+} and lower Ca^{2+} ("Aragonite Sea"), and seawater characterized by higher Ca^{2+} and lower Mg^{2+} ("Calcite Sea" in the Mid-Cretaceous ocean). These pH changes infer different atmospheric CO_2; a deviation of 0.1 pH unit translates into a difference of 27% (at pH ~ 7.0) and 33% (at pH ~ 8.0) in the $CO_{2(aq)}$ concentrations determined by the $\delta^{11}B$ proxy (Fig. 2), and thereby also in the simulated $CO_{2(g)}$.

By establishing an independent and direct measurement of the boron isotope fractionation factor we confirmed recent theoretical and experimental high estimations of ε_B (26‰ to 27.2‰) (Klochko et al., 2006; Liu and Tossell, 2005; Zeebe, 2005; Rustad et al., 2010), resolving the literature dispute (Pagani et al., 2005; Hönisch et al., 2007) on the interpretation of $\delta^{11}B$ data from carbonate skeletons over the geological time. While the relatively high $\delta^{11}B$ of aragonite corals corresponds to an apparent boron-species fractionation magnitude of $\varepsilon_B \sim 20‰$ (Hönisch et al., 2007), the boron isotopic ratios of calcitic benthic foraminifera are consistent with $\varepsilon_B \sim 26–27‰$ (Hönisch et al., 2008; Rae et al., 2011), whereas calcitic planktonic foraminifera reflect intermediate values (Sanyal et al., 1996; Henehan et al., 2013). The only available inorganic calcite precipitation experiment (Sanyal et al., 2000) showed dependency of $\delta^{11}B$ in calcite with pH that follows trend-wise, but is not identical to ε_B of ~25–27‰.

In addition to the application of the paleo-pH reconstruction of the ocean, the direct determination of the magnitude of the boron isotope fractionation factor between aqueous boron species has nu-

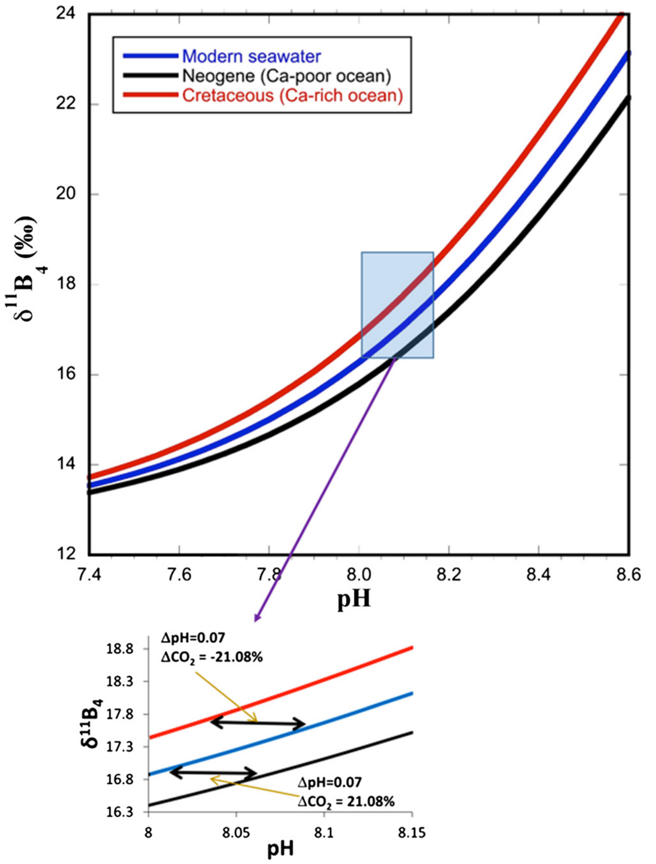

Fig. 2. $\delta^{11}B_4$ versus pH, calculated for (a) standard modern seawater ($S = 35‰$, $[Ca] = 10$ mM, $[Mg^{2+}] = 54$ mM, $SO_4^{2-} = 29$ mM; blue line); (b) seawater with higher Ca^{2+} concentration (39 mM) lower SO_4^{2-} concentration (8 mM) representing the Middle Cretaceous ocean (red line); and (c) seawater with lower concentrations of Ca^{2+} (7 mM) and Mg^{2+} (26 mM), representing the Middle Neogene ocean (black line). pH is reported in the Macinnes activity scale employed in the Pitzer implementation of PHREEQC software (~0.19 higher than the "Total" pH scale). Calculations were based on boron isotope ratio of modern seawater ($\delta^{11}B_T = 39.5‰$) and the new isotopic fractionation factor determined in this study ($\varepsilon_B = 26.0‰$). The inserted box illustrates that different reconstructed pH obtained for the three solutions in a given $\delta^{11}B_4$ infer different reconstructed CO_2 of a magnitude of ~21%.

merous geochemical and environmental implications. For example, boron isotope ratios have been used as a unique tracer to evaluate evaporation of seawater (Vengosh et al., 1992), domestic wastewater contamination and seawater intrusion (Vengosh et al., 1994), RO modification of seawater (Kloppmann et al., 2008), coal ash contamination (Ruhl et al., 2014), and the migration of hydraulic fracturing fluids in the environment (Warner et al., 2014), among many other regional groundwater studies (Vengosh, 2013). In most cases, the reactivity of dissolved boron with aquifer solids (e.g., clay minerals), particularly under saline conditions (Vengosh, 2013) causes selective uptake of ^{10}B and consequently ^{11}B enrichment in the residual solution. Given that $^{10}B(OH)_4^-$ incorporates selectively onto adsorbed sites on solids, an isotopic fractionation value of $26.0 \pm 1.0‰$ should be used in future studies assessing possible modification of boron isotopic composition from the original isotopic ratios.

In conclusion, generating independent empirical data and resolving the debate over the magnitude of the boron isotope fractionation (Pagani et al., 2005; Hönisch et al., 2007), combined with the accurate determination of boron species through the Pitzer-based ion-interaction and ion-pairing geochemical model, opens new potential for improvements in reconstruction of paleo-pH of the ocean and atmospheric CO_2 in the geological record. In particular, the new findings provide improved tools to delineate between selective and exclusive incorporation of borate species in carbonate minerals (Sanyal et al., 2000) and biological offsets (i.e. vital effects) from thermodynamic isotopic fractionation of boron species (Klochko et al., 2009).

Acknowledgements

We thank the editor, three anonymous reviewers, and Emily Klein (Duke University) for their constructive comments on the manuscript. This project was partially funded by the Israel Science Foundation (#163/14). O.N. was supported by the Rieger-JNF Fellowship for environmental studies.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2015.01.006.

References

Dickson, A.G., 1990. Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. Deep-Sea Res., A, Oceanogr. Res. Pap. 37, 755–766.

Felmy, A.R., Weare, J.H., 1986. The prediction of borate mineral equilibria in natural waters: application to Searles lake, California. Geochim. Cosmochim. Acta 50, 2771–2783.

Foster, G.L., Hönisch, B., Paris, G., Dwyer, G.S., Rae, J.W.B., Elliott, T., Gaillardet, J., Hemming, N.G., Louvat, P., Vengosh, A., 2013. Interlaboratory comparison of boron isotope analyses of boric acid, seawater and marine $CaCO_3$ by MC-ICPMS and NTIMS. Chem. Geol. 358, 1–14.

Harvie, C.E., Møller, N., Weare, J.H., 1984. The prediction of mineral solubilities in natural waters: the Na–K–Mg–Ca–H–Cl–SO_4–OH–HCO_3–CO_3–CO_2–H_2O system to high ionic strengths at 25 °C. Geochim. Cosmochim. Acta 48, 723–751.

Hemming, N.G., Hanson, G.N., 1992. Boron isotopic composition and concentration in modern marine carbonates. Geochim. Cosmochim. Acta 56, 537–543.

Henehan, M.J., Rae, J.W.B., Foster, G.L., Erez, J., Prentice, K.C., Kucera, M., Bostock, H.C., Martínez-Botí, M.A., Milton, J.A., Wilson, P.A., Marshall, B.J., Elliott, T., 2013. Calibration of the boron isotope proxy in the planktonic foraminifera Globigerinoides Ruber for use in palaeo-CO_2 reconstruction. Earth Planet. Sci. Lett. 364, 111–122.

Holt, N.M., García-Veigas, J., Lowenstein, T.K., Giles, P.S., Williams-Stroud, S., 2014. The major-ion composition of carboniferous seawater. Geochim. Cosmochim. Acta 134, 317–334.

Hönisch, B., Hemming, N.G., Loose, B., 2007. Comment on "A critical evaluation of the boron isotope-pH proxy: the accuracy of ancient ocean pH estimates". In: Pagani, M., Lemarchand, D., Spivack, A., J., Gaillardet (Eds.), Geochim. Cosmochim. Acta 71, 1636–1641.

Hönisch, B., Bickert, T., Hemming, N.G., 2008. Modern and pleistocene boron isotope composition of the benthic foraminifer cibicidoides wuellerstorfi. Earth Planet. Sci. Lett. 272, 309–318.

Honisch, B., Hemming, N.G., Archer, D., Siddall, M., McManus, J.F., 2009. Atmospheric carbon dioxide concentration across the mid-Pleistocene transition. Science 324, 1551–1554.

Kakihana, H., Kotaka, M., Satoh, S., Nomura, M., Okamoto, M., 1977. Fundamental studies on the ion-exchange separation of boron isotopes. Bull. Chem. Soc. Jpn. 50, 158–163.

Klochko, K., Kaufman, A.J., Yao, W., Byrne, R.H., Tossell, J.A., 2006. Experimental measurement of boron isotope fractionation in seawater. Earth Planet. Sci. Lett. 248, 276–285.

Klochko, K., Cody, G.D., Tossell, J.A., Dera, P., Kaufman, A.J., 2009. Re-evaluating boron speciation in biogenic calcite and aragonite using ^{11}B MAS NMR. Geochim. Cosmochim. Acta 73, 1890–1900.

Kloppmann, W., Vengosh, A., Guerrot, K., Millot, R., Parnkaratov, I., 2008. Isotope and ion selectivity in reverse osmosis desalination: geochemical tracers for man-made freshwater. Environ. Sci. Technol. 42, 4723–4731.

Ligi, M., Bonatti, E., Cuffaro, M., Brunelli, D., 2013. Post-Mesozoic rapid increase of seawater Mg/Ca due to enhanced mantle-seawater interaction. Sci. Rep. 3, 2752.

Liu, Y., Tossell, J.A., 2005. Ab initio molecular orbital calculations for boron isotope fractionations on boric acids and borates. Geochim. Cosmochim. Acta 69, 3995–4006.

Nir, O., Marvin, E., Lahav, O., 2014. Accurate and self-consistent procedure for determining pH in seawater desalination brines and its manifestation in reverse osmosis modeling. Water Res. 64, 187–195.

Oi, T., 2000. Calculations of reduced partition function ratios of monomeric and dimeric boric acids and borates by the ab initio molecular orbital theory. J. Nucl. Sci. Technol. 37 (2), 166–172.

Pagani, M., Lemarchand, D., Spivack, A., Gaillardet, J., 2005. A critical evaluation of the boron isotope-pH proxy: the accuracy of ancient ocean pH estimates. Geochim. Cosmochim. Acta 69, 953–961.

Palmer, M.R., Pearson, P.N., Cobb, S.J., 1998. Reconstructing past ocean pH-depth profiles. Science 282, 1468–1471.

Parkhurst, D.L., Appelo, C.A.J., 2013. Description of input and examples for PHREEQC version 3 – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. In: U.S. Geological Survey Techniques and Methods, Book 6, Chap. A43. 497 pp. Available at http://pubs.usgs.gov/tm/06/a43/, 2013.

Pearson, P.N., Palmer, M.R., 2000. Atmospheric carbon dioxide concentrations over the past 60 million years. Nature 406, 695–699.

Rae, J.W.B., Foster, G.L., Schmidt, D.N., Elliott, T., 2011. Boron isotopes and B/Ca in benthic foraminifera: proxies for the deep ocean carbonate system. Earth Planet. Sci. Lett. 302, 403–413.

Ruhl, R.L., Dwyer, G., Hsu-Kim, H., Vengosh, A., 2014. Boron and strontium isotopic characterization of coal combustion residuals: validation of new environmental tracers. Environ. Sci. Technol. 48, 14790–14798.

Rustad, J.R., Bylaska, E.J., Jackson, V.E., Dixon, D.A., 2010. Calculation of boron-isotope fractionation between $B(OH)_3(aq)$ and $B(OH)_4^-(aq)$. Geochim. Cosmochim. Acta 74, 2843–2850.

Sanyal, A., Hemming, N.G., Broecker, W.S., Lea, D.W., Spero, H.J., Hanson, G.N., 1996. Oceanic pH control on the boron isotopic composition of foraminifera: evidence from culture experiments. Paleoceanography 11, 513–517.

Sanyal, A., Nugent, M., Reeder, R.J., Bijma, J., 2000. Seawater pH control on the boron isotopic composition of calcite: evidence from inorganic calcite precipitation experiments. Geochim. Cosmochim. Acta 64, 1551–1555.

Spivack, A.J., You, C., Smith, H.J., 1993. Foraminiferal boron isotope ratios as a proxy for surface ocean pH over the past 21 Myr. Nature 363, 149–151.

Vengosh, A., 2013. Salinization and saline environments. In: Sherwood Lollar, B. (Ed.), Environmental Geochemistry. In: Holland, H.D., Turekian, K.T. (Eds.), Treatise in Geochemistry, vol. 11. Elsevier Science, pp. 325–378.

Vengosh, A., Kolodny, Y., Starinsky, A., Chivas, A.R., McCulloch, M.T., 1991. Coprecipitation and isotopic fractionation of boron in modern biogenic carbonates. Geochim. Cosmochim. Acta 55, 2901–2910.

Vengosh, A., Starinsky, A., Kolodny, Y., Chivas, A.R., Raab, M., 1992. Boron isotope variations during fractional evaporation of sea water: new constraints on the marine vs. nonmarine debate. Geology 20, 799–802.

Vengosh, A., Heumann, K.G., Juraske, S., Kasher, R., 1994. Boron isotope application for tracing sources of contamination in groundwater. Environ. Sci. Technol. 28, 1968–1974.

Warner, N.R., Darrah, T.H., Jackson, R.B., Millot, R., Kloppmann, W., Vengosh, A., 2014. New tracers identify hydraulic fracturing fluids and accidental releases from oil and gas operations. Environ. Sci. Technol. 48, 12552–12560.

Xiao, J., Jin, Z., Xiao, Y., He, M., 2014. Controlling factors of the δ^{11}B–pH proxy and its research direction. Environ. Earth Sci. 71, 1641–1650.

Zeebe, R.E., 2005. Stable boron isotope fractionation between dissolved $B(OH)_3$ and $B(OH)_4^-$. Geochim. Cosmochim. Acta 69, 2753–2766.

Zeebe, R.E., Wolf-Gladrow, D., 2001. CO_2 in Seawater: Equilibrium, Kinetics, Isotopes. Elsevier Science.