Earth and Planetary Science Letters 487 (2018) 138–150

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Boron isotope-based seasonal paleo-pH reconstruction for the Southeast Atlantic – A multispecies approach using habitat preference of planktonic foraminifera

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ARTICLE INFO

Article history:
Received 29 August 2017
Received in revised form 25 January 2018
Accepted 3 February 2018
Available online xxxx
Editor: M. Frank

Keywords:
boron isotopes
planktonic foraminifera
seasonality

ABSTRACT

The boron isotopic composition of planktonic foraminiferal shell calcite ($\delta^{11}B_{Cc}$) provides valuable information on the pH of ambient water at the time of calcification. Hence, $\delta^{11}B_{Cc}$ of fossil surface-dwelling planktonic foraminifera can be used to reconstruct ancient aqueous pCO_2 if information on a second carbonate system parameter, temperature and salinity is available. However, pH and pCO_2 of surface waters may vary seasonally, largely due to changes in temperature, DIC, and alkalinity. As also the shell fluxes of planktonic foraminifera show species-specific seasonal patterns that are linked to intra-annual changes in temperature, it is obvious that $\delta^{11}B_{Cc}$ of a certain species reflects the pH and thus pCO_2 biased towards a specific time period within a year. This is important to consider for the interpretation of fossil $\delta^{11}B_{Cc}$ records that may mirror seasonal pH signals. Here we present new Multi-Collector Inductively Coupled Mass Spectrometry (MC-ICPMS) $\delta^{11}B_{Cc}$ coretop data for the planktonic foraminifera species *Globigerina bulloides*, *Globigerinoides ruber*, *Trilobatus sacculifer* and *Orbulina universa* and compare them with $\delta^{11}B_{borate}$ derived from seasonally resolved carbonate system parameters. We show that the inferred season-adjusted $\delta^{11}B_{Cc}/\delta^{11}B_{borate}$ relationships are similar to existing calibrations and can be combined with published $\delta^{11}B_{Cc}$ field and culture data to augment paleo-pH calibrations. To test the applicability of these calibrations, we used a core drilled on the Walvis Ridge in the Southeast Atlantic spanning the last 330,000 years to reconstruct changes in surface-water pCO_2. The reconstruction based on *G. bulloides*, which reflects the austral spring season, was shown to yield values that closely resemble the Vostok ice-core data indicating that surface-water pCO_2 was close to equilibrium with the atmosphere during the cooler spring season. In contrast, pCO_2 estimated from $\delta^{11}B_{Cc}$ of *O. universa*, *T. sacculifer* and *G. ruber* that predominantly lived during the warmer seasons, exhibits up to ∼50 ppmv higher values than the Vostok ice-core data. This is probably due to the higher austral summer and fall temperatures, as shown by Mg/Ca to be on average ∼4 °C higher than during the cooler spring season, accounting for an increase in pCO_2 of ∼4% per 1 °C. Our results demonstrate that paleo-pH estimates based on $\delta^{11}B_{Cc}$ contain a significant seasonal signal reflecting the habitat preference of the recording foraminifera species.

1. Introduction

The boron isotopic composition of planktonic foraminiferal calcium carbonate ($\delta^{11}B_{Cc}$) is widely used in paleoceanography for reconstructing sea-surface pH and pCO_2 (e.g., Foster, 2008; Hönisch et al., 2009; Martínez-Botí et al., 2015). The principle behind the $\delta^{11}B_{Cc}$-pH proxy lies in the speciation of boron that mainly exists in seawater as trigonal boric acid, $B(OH)_3$, and charged tetrahedral borate ion, $B(OH)_4^-$, where only $B(OH)_4^-$ is assumed to be incorporated into the calcium carbonate lattice (e.g., Branson et al., 2015; Hemming and Hanson, 1992). As the relative proportion of $B(OH)_4^-$ to the total boron increases with increasing pH and the isotopic fractionation between the two aqueous boron species is con-

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https://doi.org/10.1016/j.epsl.2018.02.002
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stant (Klochko et al., 2006), the isotopic composition of borate ($\delta^{11}B_{borate}$) increases as well.

The first empirical $\delta^{11}B_{Cc}$-pH calibrations over a broad pH range on cultured material (Sanyal et al., 1996, e.g., 2001) suggested species-specific offsets but similar sensitivities of $\delta^{11}B_{Cc}$ to pH lower than that predicted by aqueous fractionation (Klochko et al., 2006), whereas recent studies indicate that sensitivities are also species-specific (Henehan et al., 2013, 2016; Howes et al., 2017). The $\delta^{11}B_{Cc}$ offset from $\delta^{11}B_{borate}$ appears to be related to differences among the species in the degree of alteration of the microenvironment surrounding the foraminifera due to photosynthesis of their symbionts (increasing pH) and/or respiration and calcification (lowering pH) (e.g., Hönisch et al., 2003; Zeebe et al., 2003). The balance between these processes influencing the microenvironmental pH defines the offset of $\delta^{11}B_{Cc}$ from ambient seawater $\delta^{11}B_{borate}$. In addition, the sensitivity of symbiont-bearing foraminifera decreases with increasing pH, i.e. the slope of $\delta^{11}B_{Cc}$ versus pH is flatter than for $\delta^{11}B_{borate}$. A comprehensive explanation for this behaviour is still lacking, but might also be related to the symbionts, which increasingly buffer the microenvironment as pH is lowering (Henehan et al., 2016).

The most appropriate way to establish empirical $\delta^{11}B_{Cc}$-pH relationships for use on fossil material is to culture foraminifera over a broad pH range under controlled conditions. However, some culture experiments provide too little calcite to analyze and so to compensate the low B recovery, foraminifera have been often cultured under elevated B concentrations (Hönisch et al., 2003; Howes et al., 2017; Sanyal et al., 2001). The effect of elevated [B] is not well examined but may buffer the "acidifying" and "alkalizing" processes such as respiration/calcification and photosynthesis, respectively, that could lead to an altered $\delta^{11}B_{Cc}$ (Hönisch et al., 2003; Zeebe et al., 2003). Other problems that may be associated with cultured foraminifera are that they possibly represent a shock response; they may have incorrect light and temperature levels, or they are not allowed for vertical migration etc. Hence, in addition to culture experiments, it is necessary to carry out empirical $\delta^{11}B_{Cc}/\delta^{11}B_{borate}$ calibrations based on field samples where natural conditions, both in terms of seawater chemistry and physiology (e.g., food supply), regulate the expression of the boron isotopes. As planktonic foraminiferal shell fluxes may vary on an intra-annual scale (Jonkers and Kučera, 2015) and the carbonate chemistry and $\delta^{11}B_{borate}$ may vary seasonally as well (Fig. 1), we compare $\delta^{11}B_{Cc}$ of the target species with $\delta^{11}B_{borate}$ determined from carbonate system parameters, temperature and salinity from the season where foraminifera are most abundant. In earlier coretop studies, the annual means of temperature, salinity and carbonate system parameters and their uncertainties based on intra-annual variations were considered instead.

To examine the relevance of season-adjusted carbonate chemistry for $\delta^{11}B_{Cc}$, we present new $\delta^{11}B_{Cc}$ data for the planktonic foraminifera species *Globigerina bulloides*, *Globigerinoides ruber* (white), *Trilobatus sacculifer* and *Orbulina universa*. The samples were picked from surface sediments taken in the Indian Ocean, the Red Sea, but mainly in the South Atlantic (Fig. 2) since $\delta^{11}B_{Cc}$ data from this part of the Atlantic Ocean are sparse, compared to the North Atlantic and Pacific Ocean. Further, our dataset provides a relatively large gradient in temperature, salinity, and considerable seasonal variations in $\delta^{11}B_{borate}$ (Fig. S1). The $\delta^{11}B_{Cc}$ is compared with $\delta^{11}B_{borate}$ of the season with the highest shell fluxes, calculated from seasonally resolved data on carbonate system parameters, temperature and salinity. The new data are compared with existing field and culture data from the literature and combined to augment the species-specific $\delta^{11}B_{Cc}/\delta^{11}B_{borate}$ calibrations. Based on the knowledge of peak abundances among these species, we compiled a multispecies record over the last three glacial cycles to decipher seasonal differences in surface-water pH and pCO_2 from

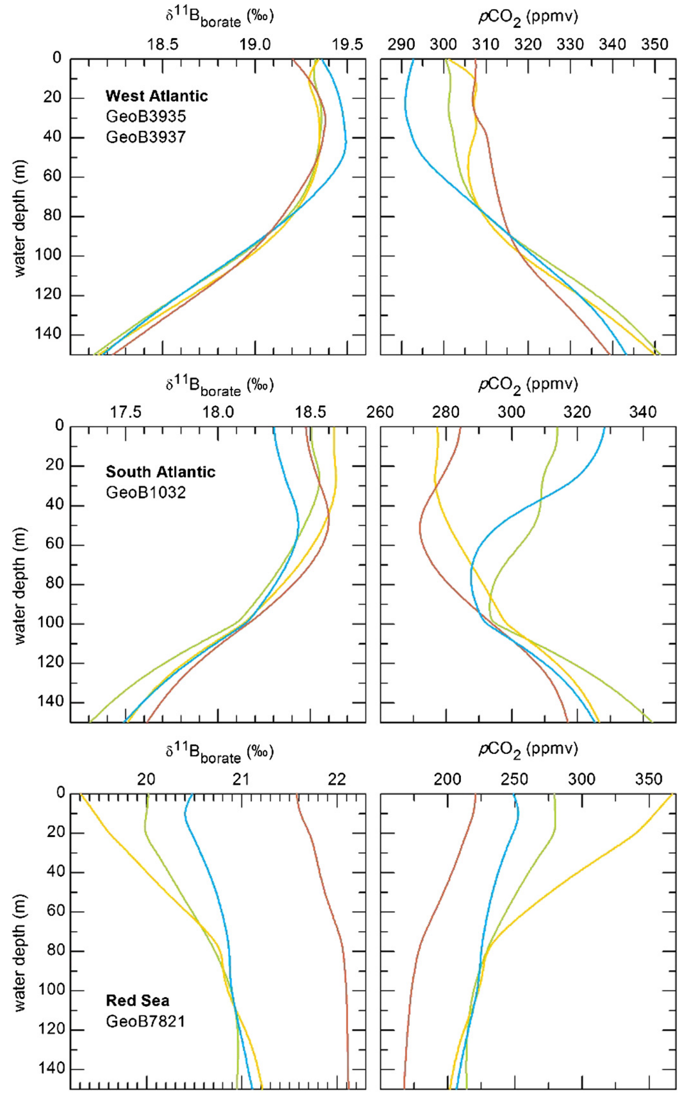

Fig. 1. Examples of seasonal variations of $\delta^{11}B_{borate}$ and pCO_2 versus water depth. The green line represents the boreal spring season (March–May), the yellow line the summer season (June–August), the brown line the fall season (September–November), and the blue line the winter season (December–February). The seasonal profiles of all sites used in this study are compiled in Fig. S1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

a sediment core drilled on the Walvis Ridge in the South Atlantic Angola Basin.

2. Material and methods

2.1. Sediment samples

To compare seasonally resolved $\delta^{11}B_{Cc}/\delta^{11}B_{borate}$ relationships with existing calibrations, we chose *G. bulloides*, *G. ruber* white (sensu stricto), *T. sacculifer* and *O. universa* as for those species the most comprehensive datasets are available (Foster, 2008; Henehan et al., 2013, 2016; Howes et al., 2017; Martínez-Botí et al., 2015; Sanyal et al., 1996, 2001). For that, we selected surface sediments (0–1 cm) from 16 multi- or boxcores mainly taken in the South Atlantic as well as a few from the Indian Ocean and the Red Sea (Fig. 2, Table 1) to cover a large spectrum of intra-annual $\delta^{11}B_{borate}$ changes (Fig. S1) and temperature, where the latter is probably the most important determinant of shell fluxes (Jonkers and Kučera, 2015). The sediments were freeze-dried and washed over