

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

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The boron isotopic composition of planktonic foraminiferal shell calcite ($\delta^{11}\text{B}_{\text{cc}}$) is a reliable tracer for seawater pH. Hence, under the assumption that surface-water $p\text{CO}_2$ is in equilibrium with the atmosphere, $\delta^{11}\text{B}_{\text{cc}}$ of fossil surface-dwelling planktonic foraminifera can be used to reconstruct ancient atmospheric $p\text{CO}_2$. However, pH and $p\text{CO}_2$ of surface waters may vary seasonally, largely due to changes in temperature, DIC, and alkalinity. As shell fluxes of planktonic foraminifera show species-specific seasonal patterns, linked to intra-annual changes in temperature, it is obvious that $\delta^{11}\text{B}_{\text{cc}}$ of a certain species reflects the pH and thus $p\text{CO}_2$ biased towards a specific time period within a year. This is important to consider for $\delta^{11}\text{B}$ coretop calibrations and for the interpretation of fossil $\delta^{11}\text{B}_{\text{cc}}$ records that mirror seasonal pH signals. Here we present $\delta^{11}\text{B}_{\text{cc}}$ coretop data for the planktonic foraminifera *Globigerina bulloides*, *Globigerinoides ruber*, *Trilobatus sacculifer* and *Orbulina universa* and compare them with $\delta^{11}\text{B}_{\text{borate}}$ derived from seasonally resolved carbonate system parameters.

To test the applicability of the season-adjusted 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 $p\text{CO}_2$. The reconstruction based on *G. bulloides*, reflecting the austral spring season, yields values closely following the Vostok ice-core data, indicating that surface-water $p\text{CO}_2$ was close to equilibrium with the atmosphere during the cooler spring season. In contrast, $p\text{CO}_2$ estimated from $\delta^{11}\text{B}_{\text{cc}}$ of *O. universa*, *T. sacculifer* and *G. ruber* that predominantly lived during the warmer seasons, exhibits up to ~58 ppmv higher values than the Vostok ice-core data, with larger deviations during interglacials than during glacials.

This is probably due to the higher austral fall temperatures, as shown by Mg/Ca to be on average 4.3 °C higher than during the cooler spring season, accounting for an increase in $p\text{CO}_2$ of 4 % per 1 °C. Our results show that paleo-pH estimates based on $\delta^{11}\text{B}_{\text{cc}}$ contain a significant seasonal signal reflecting the habitat preference of the recording foraminifera species.

Keywords: carbon cycle, ocean carbonate chemistry, atmospheric $p\text{CO}_2$, boron isotopes, seasonality, foraminifera