

100 million years of ocean pH and atmospheric CO₂ – novel reconstructions of seawater chemistry

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In partnership with **Durham University**

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Key Words

1. Climate Change, Carbon Cycle, CO₂, Geochemistry

Overview

During the last 60 Million years, Earth witnessed a number of fundamental changes in climate (Zachos 2001). CO₂ is implicated in many of the long term trends, Milankovitch rhythms, and abrupt events that characterise Cenozoic climate change, but despite recent progress, absolute CO₂ levels remain poorly constrained (Figure 1). This in turn limits our understanding of processes ranging from the sensitivity of major ice sheets to CO₂ forcing, to the range of ocean acidities that marine life can tolerate.

This project will provide new constraints on pH and CO₂ change during key intervals of the last 100 Million years using the boron isotope composition ($\delta^{11}\text{B}$) of foraminifera (Foster & Rae 2016; Rae 2018). This novel proxy has been successfully applied to constrain changes in CO₂ on these timescales, but estimates of absolute CO₂ levels remain limited by a lack of constraints on the boron isotope composition of seawater, around which the $\delta^{11}\text{B}$ -pH proxy hinges (Figure 2). A major goal of this project is thus to create new estimates of $\delta^{11}\text{B}$ of seawater ($\delta^{11}\text{B}_{\text{SW}}$). This will be achieved using 3 complimentary approaches. Firstly, if pH can be constrained, measurements of $\delta^{11}\text{B}$ in carbonates will be chiefly a function of $\delta^{11}\text{B}_{\text{SW}}$. We will exploit this by making carbonate $\delta^{11}\text{B}$ measurements across well-constrained oceanic pH gradients and in environments where pH reaches known limits. Secondly we will investigate novel archives of seawater chemistry, such as evaporites, that have $\delta^{11}\text{B}$ close to that of seawater. Using a multi-tracer approach we will constrain the influence of seawater vs secondary

processes on $\delta^{11}\text{B}$ in these archives. Thirdly, we will use a variety of modelling approaches to constrain changes in seawater chemistry, taking advantage of complementary isotopic records including lithium and sulphur.

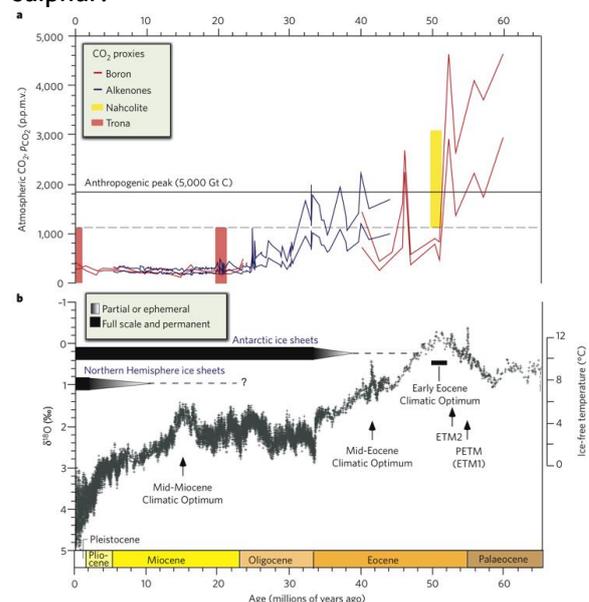


Fig 1: CO₂ and climate change over the last 60 Myr (Zachos et al. 2008). Despite recent additions to the CO₂ record, uncertainties remain in absolute CO₂ values. The key barrier to better CO₂ estimates is constraints on the evolution of $\delta^{11}\text{B}$ of seawater.

Our new constraints on $\delta^{11}\text{B}_{\text{SW}}$ will allow us to provide new estimates of absolute pH and CO₂ values using both new and published $\delta^{11}\text{B}$ records from carbonates.

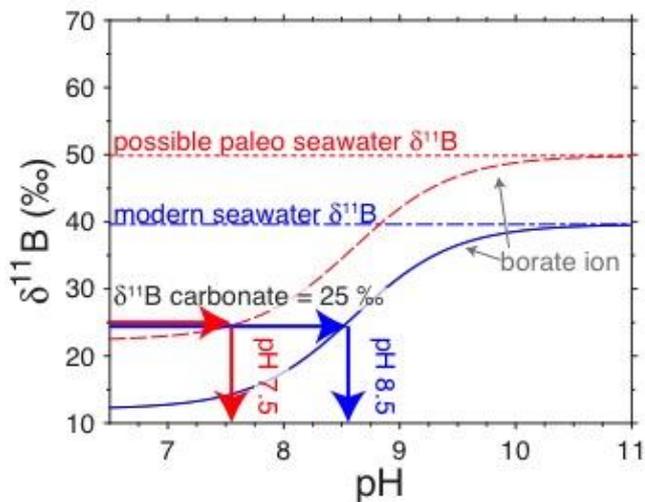


Fig 2: The boron isotope composition of borate ion is a function of $\delta^{11}\text{B}_{\text{SW}}$ and pH. Borate ion is incorporated into marine carbonates, so if $\delta^{11}\text{B}_{\text{SW}}$ is known, pH (and CO_2) can be reconstructed from measurements of carbonate $\delta^{11}\text{B}$. However on timescales of >5 Myr $\delta^{11}\text{B}_{\text{SW}}$ may change, leading to different absolute pH and CO_2 estimates. In the illustration shown above, a 10 ‰ difference in $\delta^{11}\text{B}_{\text{SW}}$ leads to a whole pH unit difference in pH reconstructed from the same $\delta^{11}\text{B}$ measurement, and gives pCO_2 values of ~ 1800 ppm vs ~ 100 ppm.

Methodology

Marine carbonate samples are made available through ongoing collaborations and from the IODP. These will be analysed for boron isotopes in the St Andrews Isotope Geochemistry (STAiG) labs, following techniques established by Foster (2008) and Rae et al. (2011), and recently developed to improve precision on small samples.

New fieldwork will be undertaken to collect evaporite samples from key sections across Europe.

Analyses of evaporite samples from the field will be complemented by laboratory precipitation experiments.

Modelling of the isotopic evolution of seawater will be carried out in collaboration with Ed Tipper's group at the University of Cambridge.

The project is designed to be flexible, with the opportunity to focus on approaches, time intervals, and techniques of particular interest to the student.

Timeline

Year 1: Fieldwork, experimental set-up, sediment core sampling, training in clean laboratory methods and mass spectrometry, initial measurements, literature review

Year 2: Complete experiments and fieldwork, generate boron isotope records from carbonate and evaporite archives, training in numerical techniques.

Years 3 and 4: Finalize data sets, apply numerical techniques, prepare written manuscripts and write thesis.

Training & Skills

The student will gain specific training in mass spectrometry, clean lab chemistry, experimental geochemistry, and fieldwork, as well as broader education in geochemistry, oceanography, and climate science. Over the course of the PhD the student will gain transferable skills such as scientific writing, statistics and data analysis, and problem-solving, as well as time management and working towards a long-term goal.

References & Further Reading

- Foster (2008), *EPSL*, 271, 254-266.
 Foster & Rae (2016), *AnnRev*, 44, (207-237)
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 Rae et al. (2011), *EPSL*, 302, 403-413.
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