CASE STUDY 30752

Boron isotopes in foraminifera

Climate change research at the University of Southampton

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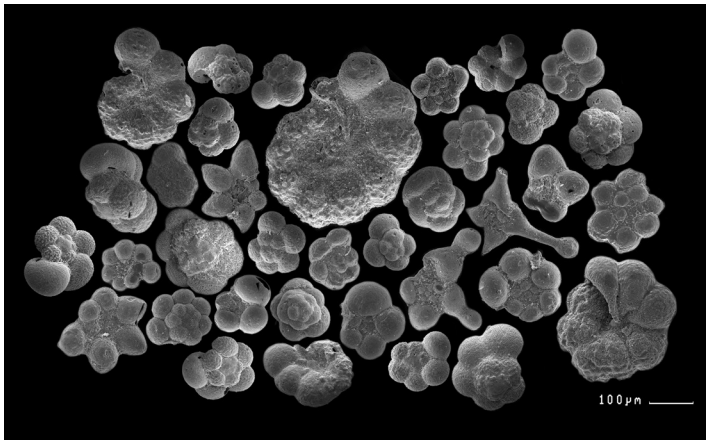
Objective

The concentration of carbon dioxide in the atmosphere plays a key role in determining the state of the Earth's climate. This is true over geological time (thousands to millions of years), as well over the last 150 years ago when humanity has been emitting this potent greenhouse gas to the atmosphere in vast quantities, increasing its concentration from around 280 ppm (typical of normal interglacial levels) to 410 ppm (last observed 3 Ma ago; de la Vega et al., 2020), trapping more heat and causing the global mean surface temperature to increase by around 1 °C. To understand exactly what is in store for the Earth in the years to come as we continue to increase atmospheric CO_2, we can turn to the rich archive of altered climate states that make up the geological record. Studying these past climates has a key role to play in determining the sensitivity of the Earth's climate to CO_2 change—a vital metric in determining the magnitude of future warmth (e.g. Martinez-Boti et al. 2015; Anagnostou et al. 2016). Ice cores from Antarctica trap small bubbles of ancient atmosphere allowing a very high fidelity record of atmospheric CO_2 to be constructed for the last 800 thousand years (Bereiter et al. 2015). While this is incredibly useful, at no time in these ice core records was atmospheric CO_2 above 300 ppm. If we want to study how Earth behaves in past warm, high CO_2 (higher or equal to the modern 410 ppm) climate states we have to look beyond the last 800 thousand years and use more indirect methods to reconstruct atmospheric CO_2. One method that holds much promise in this regard is the boron isotope pH proxy.



Introduction

The sediments that blanket the seafloor of much of the world's oceans slowly accumulate over millions of years and consist, in large part, of many thousands of < 1 mm sized shells of organisms called foraminifera (Figure 1). Foraminifera are zooplankton that inhabit the upper water column living for around a month and during this time they precipitate shells made of calcite, when the foraminifera dies these sink through the water column and settle on the seafloor. The chemical and isotopic composition of these shells record a variety of aspects of the environment when they were alive and so the shells are akin to tiny time capsules of the environment many thousands to millions of years ago.

Boron has two isotopes—boron-10 and boron-11—that occur in nature in around a 4:1 ratio of 11 to 10. The boron isotopic composition of the foraminifera's calcite shell is predominantly determined by the pH of the seawater when it was alive, this is because of the nature of boron speciation in seawater and the way in which boron is incorporated into the growing shell (for more detail see Foster and Rae, 2016). pH (the $-\log_{10}$ of [H+]) is a useful variable as it tracks the CO_2 content of the ocean and, as recent trends in surface ocean acidification confirm, this in turn reflects the CO_2 content of the atmosphere (Foster and Rae, 2016). Each foraminifera however only contains around 0.1 ng of B and samples of deep-sea mud are limited in size, number and locations due to the difficulties and expense associated with sampling the deep ocean with drill ships such as those of the Integrated Ocean Discovery Program (IODP; www.iodp.org; Figure 1). Typical sample sizes are therefore around 10 ng of B. The precisions required on the measured $^{11}B/^{10}B$ ratio are better than ± 0.5 parts per thousand (‰), making the accurate and precise measurement of foraminiferal hosted boron a significant analytical challenge.

Instrumentation

Multicollector Inductively Coupled Plasma Mass Spectrometers (MC-ICP-MS) have revolutionized the measurement of stable isotopes (Halliday et al. 1998), because although the mass bias is large (e.g. 16% at B) it is stable over sufficiently long-time intervals to allow accurate mass bias correction via sample-standard bracketing approaches. The advantage of the Thermo Scientific™ Neptune™ MC-ICP-MS is that it has a relatively high sensitivity for boron (20 V/ppm in wet plasma mode) and good mass bias stability (< 0.2‰ drift per hour). This allows us to determine the $^{11}B/^{10}B$ of foraminiferal samples to +/- 0.2‰ (95% confidence; Foster et al. 2013).

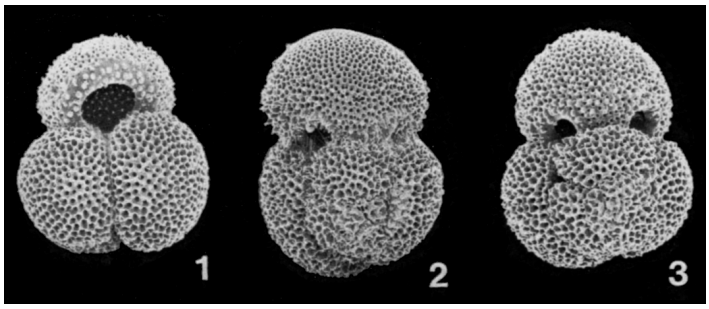


Figure 1. (top) The Joides Resolution drill ship belonging to the Integrated Discovery Program (www.iodp.org). Such ships are needed to sample the accumulations of foraminifera that blanket the seafloor. (bottom) Three images of the foraminifera Globigerinoides ruber from a core in the Central Pacific (www.microtax.org). The foraminifera is around 350 microns across.

Results

Reconstructing atmospheric CO_2 from boron isotope measurements of foraminifera is an indirect approach that needs validating before it can be readily applied to reconstructing CO_2 in the deep geological past. Figure 2 shows a comparison between CO_2 estimated by measuring the boron isotopic composition of foraminifera measured by the Neptune MC-ICP-MS vs. samples of the ancient atmosphere trapped in ice cores. The agreement is excellent confirming the suitability of the approach to reconstruct atmospheric CO_2 over the last 65 million years and more and underlines the importance of precise $^{11}B/^{10}B$ measurements.

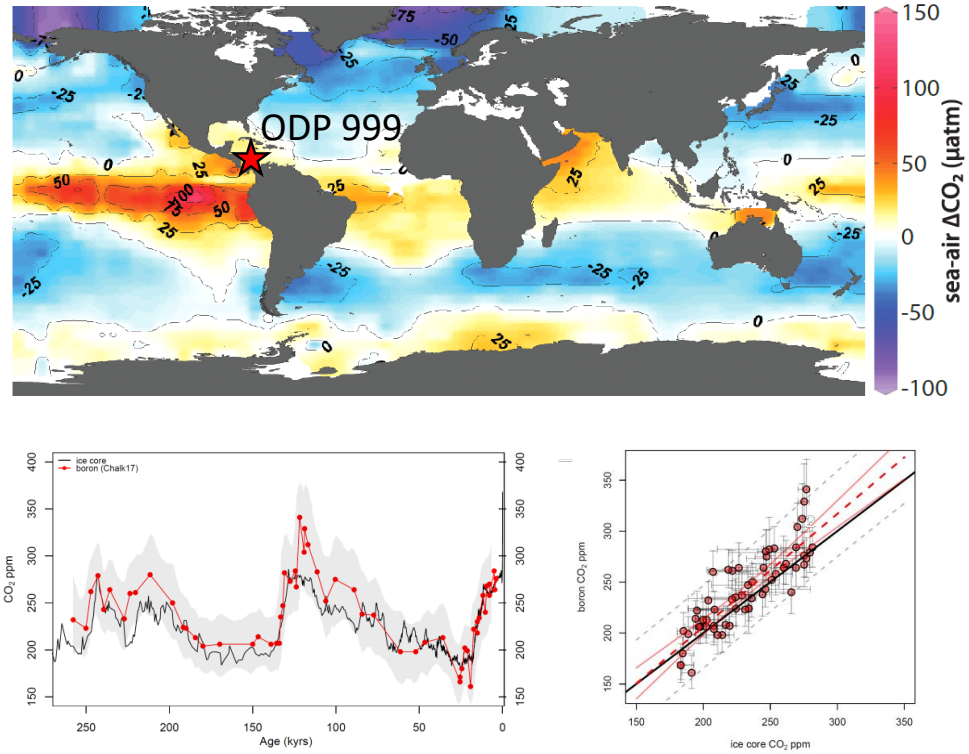


Figure 2. A comparison between ice-core based CO_2 (black) and boron isotope based (red) CO_2 data from the last 250 thousand years (grey band is the uncertainty at 95% confidence and the location of the core is shown in the map on top). Bottom right is a cross plot of ice core vs. boron-derived CO_2. The good level of agreement between the methods provides high confidence that the boron based approach can be applied to reconstruct CO_2 throughout at least the last 65 million years. The data are from Chalk et al. (2017).

Conclusion

The boron isotope pH proxy offers a powerful way to reconstruct atmospheric CO_2 in the geological past. The mass bias at boron is however large (16%), sample sizes are small and required precision is high, making the associated boron isotope measurements particularly challenging. By using the Neptune MC-ICP-MS at the University of Southampton (Figure 3) we have shown that the boron isotope pH proxy faithfully records atmospheric CO_2 variations (Figure 2). We are now working with colleagues from many other institutes around the world to use the boron isotope proxy to build up a picture of how CO_2 and climate are related in our geological past (www.p-CO2.org). This information feeds into the Intergovernmental Panel on Climate Change Sixth Assessment report (www.ipcc.ch) and therefore forms a vital part of our efforts to tackle climate change by improving our understanding of how the climate system works.

Figure 3. Elwyn de la Vega (standing) running boron isotopes on foraminifera on the Neptune MC-ICP-MS 1 in the Geochemistry Laboratory of the School of Ocean and Earth Science, University of Southampton.

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References

- Anagnostou, E., John, E.H., Edgar, K.M., Foster, G.L., Ridgwell, A., Inglis, G.N., Pancost, R.D., Lunt, D.J., Pearson, P.N., Changing atmospheric CO_2 concentration was the primary driver of early Cenozoic climate. *Nature.* **2016**, *533*, 380–384.
- Bereiter, B., Eggleson, S., Schmitt, J., Nehrbass-Ahles, C., Stocker, T.F., Fischer, H., Kipfstuhl, S., Chappellaz, J., Revision of the EPICA Dome C CO_2 record from 800 to 600 kyr before present. *Geophycial Research Letters.* **2015**, *42*, 542–549.
- Foster, G.L., Honisch, B., Paris, G., Dwyer, G.S., Rae, J.W.B., Elliott, T., Gaillardet, J., Hemming, N.G., Louvat, P., Vengosh, A., Interlaboratory comparison of boron isotope analysis of boric acid, seawater and marine $CaCO_3$ by MC-ICPMS and NTIMS. *Chem. Geol.* **2013**, *358*, 1–14.
- Foster, G.L., Rae, J.W.B., Reconstructing ocean pH with boron isotopes in foraminifera. *Annual Review of Earth and Planetary Science.* **2016**, *44.*
- Halliday, A.N., Lee, D.C., Christensen, J.N., Rehkamper, M., Yi, W., Luo, X.Z., Hall, C.M., Ballentine, C.J., Pettke, T., Stirling, C., Applications of multiple collector-ICPMS to cosmochemistry, geochemistry, and paleoceanography. *Geochimica et cosmochimica acta.* **1998**, *62*, 919–940.
- Martinez-Boti, M.A., Foster, G.L., Chalk, T.B., Rohling, E.J., Sexton, P.F., Lunt, D.J., Pancost, R.D., Badger, M.P.S., Schmidt, D., Plio-Pleistocene climate sensitivity evaluated using high-resolution CO_2 records. *Nature.* **2015**, *518*, 49–54.
- Chalk, T.B., Hain, M.P., Foster, G.L., Rohling, E.J., Sexton, P.F., Badger, M.P.S., Cherry, S.G., Hasenfratz, A.P., Haug, G.H., Jaccard, S.L., Martínez-García, A., Pälike, H., Pancost, R.D., Wilson, P.A., Causes of ice age intensification across the Mid-Pleistocene Transition. *Proceedings of the National Academy of Sciences.* **2017**, *114*, 13114–1311

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