

Eocene $p\text{CO}_2$ estimates based on $\delta^{11}\text{B}$ of larger benthic foraminifera measured by LA-MC-ICPMS

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Constraining Earth's climate sensitivity using past climate reconstructions is one of the key contributions palaeoclimate research can make to inform us about ongoing anthropogenic climate change. Obtaining reliable estimates of atmospheric CO_2 during past warm intervals such as the early Eocene is thus a prime objective. Of the available palaeo- CO_2 proxies beyond direct ice core measurements, the boron isotopic composition of marine calcifying organisms is one of the most robust method of producing quantitative $\text{pH}/p\text{CO}_2$ reconstructions. However, data are lacking, or available at low resolution only for parts of the Eocene.

We use our recently-established empirical boron isotope calibration (Coenen et al. in prep.) of the extant shallow-dwelling large benthic foraminifera (LBF) *Operculina ammonoides* to reconstruct $\text{pH}/p\text{CO}_2$ in the early-middle Eocene. The advantage of this extant family is that it extends back to the early Paleogene, with *O. ammonoides* being closely related to the abundant and widespread Eocene Nummulites. This calibration, using both cultured and field-collected LBF, overall shows a low sensitivity to pH compared to other calibrations. However, using a diffusion-reaction model, we demonstrate that the larger than natural diffuse boundary layer present during the culturing process can explain the shallower slope of the boron isotope calibration. On the other hand, field-collected specimens appear

to be more pH sensitive, hinting to the robustness of *Operculina ammonoides* as a boron isotope proxy carrier.

This calibration allows the conversion of the measured boron isotopic composition of carefully-screened fossil LBFs from the Paris and Hampshire basins into a seawater pH estimate, which in turn can be converted into estimated early and mid-Eocene atmospheric $p\text{CO}_2$.

Sample preservation was assessed by SEM to diagnose possible recrystallisation and LA-ICPMS to evaluate chemical preservation. For instance, lowering of the normally high Mg/Ca and Sr/Ca , characteristic of the large benthic foraminifera, was associated with diagenetic recrystallisation. The selected pristine samples were then analysed using LA-MC-ICPMS to determine their boron isotopic composition and reconstruct past $\text{pH}/p\text{CO}_2$. Our initial dataset agrees well with previously published records and strengthens the notion that some intervals within the early Eocene were characterised by $p\text{CO}_2 > 1500$.