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Boron isotope calibration of large benthic foraminifera species using LA-MC-ICP-MS

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Constraining Earth's climate sensitivity using past climate reconstructions is one of the key contributions of palaeoclimate data to preparing for ongoing anthropogenic climate change. Precisely determining atmospheric CO_2 concentrations during past key warm intervals such as the early-middle Paleogene is an ideal target in this respect. Of the available palaeo-CO_2 proxies, the boron isotopic composition of marine carbonates is a key method of producing quantitative pH/CO_2 reconstructions, yet data are lacking, or available at low resolution for parts of the Eocene.

The boron isotope pH proxy generally relies on empirical calibrations to relate the measured boron isotopic composition of the foraminifera to the boron isotopic composition of the aqueous borate ion in the paleo-ocean. Empirical calibration of planktonic foraminifera has shown that species or group-specific vital effects are present, with the implication that the application of the proxy to lineages with only indirect descendants is associated with some uncertainty.

To address this, we present an empirical calibration for an under-utilised group that was very abundant during the Paleogene, the shallow-dwelling large benthic nummulitid foraminifera (LBF, specifically *Operculina ammonoides*). An advantage of this group is that *Operculina* has a lineage extending back to the early Paleogene, and is closely related to the widespread Eocene *Nummulites*. Our calibration is based on measurements of samples grown under a range of carbonate chemistries in laboratory culture, spanning a pH range of ~7.6 to 8.4. We use LA-MC-ICPMS as analytical technique for which LBFs are particularly well-suited and demonstrate that samples can be characterized to a precision of up to 0.3‰ (typically <0.5‰, 2SE, n = 20-50) when using 10^{13} Ω resistors and a 40 µm laser spot. This combination of using a so far underutilized biomineral archive, a robust calibration and spatially-resolved δ^{11}B-measurements paves the way towards an improved palaeo-pH/pCO_2 reconstruction for the Paleogene, with implications for understanding Earth's climate sensitivity during past warm intervals.