[Paleoceanography]

Supporting Information for

The evolution of deep ocean chemistry in the Eastern Equatorial Pacific over the last deglaciation

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Introduction

This supporting information provides additional details on the LA-ICPMS analyses performed in this study as well as all the new data displayed in the article.

LA-ICPMS analytical details

Spatially-resolved B/Ca analysis by depth-profiling in *Cibicides wuellerstorfi* were performed using the RESOlution M-50 prototype 193 nm ArF laser ablation system coupled to an Agilent 7500ce quadrupole ICPMS at Royal Holloway University of London, UK [*Müller et al.*, 2009]. This analytical set-up utilizes a 193 nm ArF laser and two-volume Laurin ablation cell, which results in improved ablation characteristics compared to 213 nm systems (for instance, it ensures controlled ablation of carbonates, *Müller and Fietzke* [2016]), and a 99% washout time of <2 s maximizing spatial resolution [*Müller et al.*, 2009]. National Institute of Standards and Technology (NIST) SRM 610 and 612 glasses were used as external standards for calibration using the concentration data from *Jochum et al.*, [2011] and ^{43}Ca was used as internal standard. Data accuracy was assessed over the course of 15 months (in 3 periods of time) by calibrating 18 analyses of the MPI-DING komatiite glasses GOR132 and GOR128 [*Jochum et al.*, 2006] (treated as unknowns) to both NIST standard glasses. The accuracy for most element/Ca ratios is better than 5% [*Evans et al.*, 2015], and GOR128 standardised using either NIST glass results in B/Ca accuracy <3% and precision <10%. Nylon6 tubing (characteristically lower in volatiles such as sulphur) was used for these analyses to connect the LA system to the ICPMS since it was found to result in a greatly improved ^{11}B instrumental background conditions; the analyses presented here are characterised by signal/noise ratios of 50-100. A Nylon6-squid signal smoothing device was also included since it is necessary to avoid spectral skew when using repetition rates lower than 5 Hz (as it is the case for foraminifer analysis) [*Eggins et al.*, 1998; *Müller et al.*, 2009; *Evans and Müller*, 2013] and maintains smooth signals despite the low laser repetition rates.

Between three and six *C. wuellerstorfi* specimens from each of the 15 downcore samples selected from sediment core ODP1240 (Table S2) and two to nine specimens from nine core-top samples (Table S1) were picked from the >212 μm size fraction. *C. wuellerstorfi* chambers are typically narrow and this species has a low B concentration (~20 ppm). These factors necessitated the use of a 96 μm spot size for ablation, which is larger than individual chambers. Thus, two to three depth profiles were performed per shell in this species, from the oldest part to the youngest part of each individual. Before ablation, *C. wuellerstorfi* individuals were rinsed in milliQ water (without ultrasonication) and secured on double-sided adhesive tape mounted onto glass slides. All analyses were performed at a laser repetition rate of 2 Hz, and at a laser fluence on sample of ~4 J/cm^2. The following dwell times (with a primary focus on ^{11}B) were used: ^{11}B (50 ms), ^{24}Mg (30 ms), ^{25}Mg (30 ms), ^{27}Al (10 ms), ^{43}Ca (20 ms), ^{55}Mn (10 ms), ^{88}Sr (5 ms), ^{89}Y (10 ms), ^{138}Ba (5 ms) and ^{238}U (10 m), resulting in an overall ~200 ms sweep time that facilitated four complete readings per second. The analyses were carried out in a Helium atmosphere (850 ml/min), to which Argon was added downstream of the ablation cell as carrier gas (~450 ml/min), ahead of the squid signal smoothing device. An additional diatomic gas, H_2 (8.5 ml/min flow), was also added downstream of the ablation cell as it resulted in improved sensitivity for the elements of interest. *C. wuellerstorfi* samples were ablated for a maximum of 200 s with delays of 30 s between measurements for backgrounds, while NIST610/612 were ablated after ~ 6-8 samples for a duration of 120 s with delays of 40 s between measurements.

LA-ICPMS data reduction

Data reduction, broadly based on *Longerich et al.* [1996], was carried out by using a custom Excel template, which allows data to be "despiked" (to remove outliers), standardised using NIST glasses, checked for possible machine drift, and normalised to ^{43}Ca. Several steps to exclude any possible contaminant phases from the data were also applied. Step 1: Surface contamination of the shells was monitored and discarded if present. Step 2: the segment of the analysis suitable for integration was isolated, i.e. the part of the ablation profile characterised by a steady element intensity decrease. Accidental analysis of a material other than the foraminifer shell, such as the tape or the glass slide underlying the foraminifera, is easily identifiable from a sudden decrease in the ^{43}Ca count rate and by very noisy element signals. The decrease in intensity through the course of the analysis is a standard feature of laser-ablation depth profiling, which occurs as washout of the ablated material becomes less efficient as the crater depth increases, and because craters are typically cone-shaped [*Eggins et al.*, 1998] so that less material is removed as the analysis progresses. The use of an internal standard (^{43}Ca) demonstrably accurately corrects for this. Step 3: Elevated Al/Ca indicates incomplete removal of clay particles [*Boyle*, 1983; *Bolton et al.*, 2011; *Marr et al.*, 2011] and therefore portions of the profiles with Al/Ca ratios higher than 500 µmol/mol were discarded, even when this restriction results in the omission of an entire profile from the sample mean. Intra-spot B/Ca variability of the *C. wuellerstorfi* analysed here was between 12-13%, representing much lower variability than previous reported LA-ICPMS measurements in this species (~40% of intra-chamber variability; *Raitzsch et al.*, [2011]). The final suitable profile segments selected for integration were then averaged by spot, by specimen and finally by sediment interval for subsequent palaeo-reconstructions. All spots with B/Ca that were higher than the interval average plus 2SD (defined as outliers, *Evans and Müller* [2013]) were removed (~4%), in order to screen for potential contaminant phases that might exclusively bias B/Ca estimates.

Tables

Table S1. Seawater chemistry data for the B/Ca-$\Delta[CO_3^{2-}]$ core-top calibration. $[CO_3^{2-}]$ and Ω_C were estimated by using CO2SYS [*Lewis et al.*, 1998; *Pierrot et al.*, 2006] with seawater data from: *GLODAPv2 (HA-stC: 58GS20090528 transect; station 290; 1,970 m; HA-stE: 77DN20020420 transect; station 9; 640 m); **CATARINA cruise data; ***BD3 cruise data (1989); ****GLODAP data (WOCE A17 transect data; station 23075B; 3,935 m).

Table S2. B/Ca in *C. wuellerstorfi* from core ODP1240 analysed by LA-ICPMS, along with derived $\Delta[CO_3^{2-}]$ and $[CO_3^{2-}]$ downcore. $[CO_3^{2-}]$ was estimated by $\Delta[CO_3^{2-}]+[CO_3^{2-}]_{sat\text{-}mod}$, where $\Delta[CO_3^{2-}]=(B/Ca-177.1)/1.14$ [*Yu and Elderfield*, 2007] and $[CO_3^{2-}]_{sat\text{-}mod}= [CO_3^{2-}]_{mod}/\Omega_{C\ mod}$. Modern seawater parameters were calculated using ALK and TCO_2 data from GLODAP data set (P19C transect): $[CO_3^{2-}]_{mod}$ = 67.6 µmol/kg and $\Omega_{C\ mod}$ = 0.9 µmol/kg.

Table S3. $\delta^{13}C$ in *C. wuellerstorfi* from core ODP1240 analysed at the University of Cambridge and Universitat de Barcelona.

Table S4. U/Ca in the coating of *Neogloboquadrina dutertrei* from core ODP1240.