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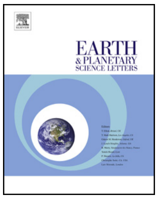

Calcification and growth processes in planktonic foraminifera complicate the use of B/Ca and U/Ca as carbonate chemistry proxies

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ABSTRACT

Although boron and uranium to calcium ratios (B/Ca, U/Ca) in planktonic foraminifera have recently received much attention as potential proxies for ocean carbonate chemistry, the extent of a carbonate chemistry control on these ratios remains contentious. Here, we use bi-weekly sediment trap samples collected from the subtropical North Atlantic in combination with measured oceanographic data from the same location to evaluate the dominant oceanographic controls on B/Ca and U/Ca in three depth-stratified species of planktonic foraminifera. We also test the control of biological, growth-related, processes on planktonic foraminiferal B and U incorporation by using foraminifer test area density ($\mu g/\mu m^2$) (a monitor of test thickness) and test size from the same samples. B/Ca and U/Ca show little or no significant correlation with carbonate system parameters both within this study and in comparison with other published works. We provide the first evidence for a strong positive relationship between area density (test thickness) and B/Ca, and reveal that this is consistent in all species studied, suggesting a likely role for calcification in controlling boron partitioning into foraminiferal calcite. This finding is consistent with previous observations of less efficient discrimination against trace element 'impurities' (such as B), at higher calcification rates. We observe little or no dependency of B/Ca on test size. In marked contrast, we find that U/Ca displays a strong species-specific dependency on test size in all species, but no relationship with test thickness, implicating some other biological control (possibly related to growth), rather than a calcification control, on U incorporation into foraminiferal calcite. Our results caution against the use of B/Ca and U/Ca in planktonic foraminifera as reliable proxies for the ocean carbonate system and recommend that future work should concentrate on improving the mechanistic understanding of how planktonic foraminifer calcification and growth rates regulate boron and uranium incorporation into the test.

1. Introduction

B/Ca and U/Ca of planktonic foraminiferal calcite have previously been suggested to reflect the carbonate chemistry of seawater (Russell et al., 2004; Allen et al., 2011, 2012) and could potentially be used to reconstruct past ocean carbonate chemistry changes (Yu et al., 2007; Foster, 2008). Documenting past seawater carbonate chemistry changes is important in defining the processes that drive Earth's climate system and carbon cycle, and how these will respond to future anthropogenic climate change. Theoretically, boron exists in seawater as two species, boric acid [$B(OH_3)$] and borate ion [$B(OH)_4^-$], the proportions of which are pH dependent, (see equilibrium equation (1) below).

$$B(OH_3) + H_2O \longleftrightarrow B(OH)_4^- + H^+ \qquad (1)$$

Because $B(OH)_4^-$ is a charged ion, it is thought that this is the only species which substitutes for CO_3^{2-} in calcite (Hemming and Hanson, 1992; Sanyal et al., 2000), and this has been supported by recent studies (Rae et al., 2011; Branson et al., 2015). Increasing pH therefore leads to greater incorporation of B in the $CaCO_3$ lattice due to increasing abundance of aqueous borate, (see equilibrium equation (2) below).

$$\begin{aligned} &CaCO_{3\ solid} + B(OH)^-_{4\ aqueous} \\ &\quad \rightarrow Ca(HBO_3)_{solid} + HCO^-_{3\ aqueous} + H_2O \qquad (2) \end{aligned}$$

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This leads to an exchange distribution coefficient (K_D) (Yu et al., 2007), (see equilibrium equation (3) below).

$$K_D = [B/Ca]_{solid}/\left[B(OH)_4^-/HCO_3^-\right]_{seawater} \tag{3}$$

However, a variety of evidence also exists arguing against a primary carbonate control on B/Ca ratios including: (1) The lack of correlation of B/Ca and pH-dependent boron isotope composition (Foster, 2008) and measured carbonate system parameters (Babila et al., 2014), (2) Higher B/Ca in upwelling regions despite lower pH conditions (Naik and Naidu, 2014), (3) Species-specific sensitivities of B/Ca to carbonate chemistry (Allen and Hönisch, 2012), (4) Size-dependent B incorporation into foraminiferal calcite (Yu et al., 2007; Babila et al., 2014; Henehan et al., 2015), (5) Discrepancies between culture and open-ocean studies of the sensitivity of B/Ca to $[CO_3^{2-}]$ (Yu et al., 2007; Allen and Hönisch, 2012). Additionally, a number of other environmental variables have been reported to influence B concentrations in foraminiferal calcite including, temperature (Hathorne et al., 2009; Naik and Naidu, 2014), salinity (Allen et al., 2011, 2012; Henehan et al., 2015), light intensity (Babila et al., 2014), and $[PO_4^{3-}]$ (Henehan et al., 2015).

As with boron, uranium incorporation into planktonic foraminifera is also theoretically controlled by $[CO_3^{2-}]$ because it exists in seawater as a series of carbonate complexes and is likely incorporated into calcite as either $UO_2(CO_3)_2^{2-}$ and/or $UO_2(CO_3)_3^{4-}$ (Yu et al., 2008 and references therein). Therefore, the decreasing abundance of $UO_2(CO_3)_2^{2-}$ with greater $[CO_3^{2-}]$ should also be reflected by decreasing foraminiferal U/Ca (Russell et al., 2004). Yet, like boron, a number of other variables in addition to the carbonate system have been suggested to also influence U incorporation, including calcification temperature (Russell et al., 1996; Yu et al., 2008), growth rate (Ni et al., 2007), and species-specific differences (Yu et al., 2008).

Here, we utilise bi-weekly samples from a sediment trap time series from the subtropical North Atlantic (Salmon et al., 2015) to address the unresolved and potentially conflicting issues with these proxies. Sediment trap time series provide a unique opportunity to evaluate controls on the geochemical composition of planktonic foraminifera within their natural habitat where multiple variables influence their calcification simultaneously. This contrasts with laboratory methods, which although have been instrumental in ground-truthing relationships between geochemical proxies and environmental variables, typically isolate only single variables to determine their influence on foraminiferal calcite. The bi-weekly sampling resolution provided by the sediment traps is also advantageous because it captures the lifecycles of most planktonic foraminiferal species, which typically follow the monthly lunar cycle (Jonkers and Kučera, 2015), with evidence of an annual cycle for encrusted *Globorotalia truncatulinoides* (Hemleben et al., 1985; McKenna and Prell, 2004). We measured B/Ca and U/Ca ratios, test calcification (thickness) and growth parameters (size) of three planktonic foraminifer species from bi-weekly sediment trap samples spanning four years (1998–2000 and 2008–2010), from the Sargasso Sea (Fig. 1a). These data were coupled with in-situ oceanographic data (temperature, salinity, chlorophyll and carbonate system parameters) from the Bermuda Atlantic Time Series (BATS) in the same locality to evaluate the controls on uranium and boron incorporation into planktonic foraminifera (Fig. 1b–c).

2. Materials and methods

We use bi-weekly sediment trap samples selected from the Ocean Flux Programme time series in the Sargasso Sea (31°50′N, 64°10′W) together with the concurrent oceanographic data from the nearby BATS site (31°40′N, 64°10′W). We utilise samples collected from two equivalent 2.5-yr intervals (1998–2000 and 2008–2010) at 1500 m water depth to capture seasonal variations in the test parameters and geochemical composition of three species of foraminifera (*Globigerinoides ruber* (pink), *Orbulina universa* and *Globorotalia truncatulinoides*, non-encrusted (nc) and encrusted (c)), each living at different depths in the water column. Test weights and sizes were measured individually in order to calculate test area density (μg/μm^2) of each sample (details in section 2.3).

Tests used for geochemical analysis ranged in size (shown in Table 2), but on average were *G. ruber* (p) = 366 μm, *O. universa* = 720 μm, *G. truncatulinoides* (nc) = 492 μm, *G. truncatulinoides* (c) = 709 μm. *G. truncatulinoides* reproduce in the surface waters, as evidenced from plankton tows (Hemleben et al., 1985) before sinking to depth and adding a secondary calcite crust which approximately doubles the weight of the test (McKenna and Prell, 2004). Figure A.1 provides guidance for conversion of digitally measured test size to traditional sieve sizes. We used the right-coiling variety of *G. truncatulinoides* in this study which all belong to the same genetic group (Type II) (Ujiié et al., 2010), as this is the dominant genotype present at our Sargasso Sea study site. Likewise, we analyse the more abundant thinner shelled Sargasso genotype of *O. universa*, which is morphologically distinct under high magnification, from the thicker-walled Caribbean genotype (Morard et al., 2009). By selecting species from a wide range of water depth habitats (approximately 0–400 m), we are able to compare oceanographic data with species' geochemical compositions across larger environmental gradients; e.g. from 0–400 m at this site, temperature ranges up to ~10 °C (Fig. 1b) and $[CO_3^{2-}]$ by ~50–60 μmol/kg (Fig. 1c), with a minimal change in salinity (~0.2).

After being measured, planktonic foraminifera tests were gently cracked to open and subjected to chemical cleaning involving an extended oxidation step to remove any excess organic matter present in sediment trap material (50% H_2O_2 in 0.2M NaOH) (Anand et al., 2003), followed by a weak acid leach, prior to final dissolution (Barker et al., 2003). B/Ca and U/Ca analyses were carried out on a Thermo® Element XR Inductively-Coupled Plasma Mass Spectrometer (HR-ICP-MS), at the Godwin Laboratory at Cambridge University. Long-term precision on standard runs of B/Ca (and Mg/Ca used for calcification temperatures calculations) is <1.0% (2σ). External precision is <4.0% (2σ) for B/Ca and U/Ca, and <1.0% (2σ) for Mg/Ca using Cambridge consistency standards (Misra et al., 2014). B, Mg blank levels were <2% and U was <5% of typical [B], [Mg] and [U] in foraminifera samples. An in-house standard was used to correct for drift over the run.

2.1. Calcification temperature and depth calculations

Calcification temperatures were determined from analysing the $\delta^{18}O_{calcite}$ in the same aliquot of sample used for trace element analyses. Stable isotope analyses were performed on a Finnigan GasBench and Delta^{plus} Advantage stable isotope mass spectrometer at the Open University (long term standard reproducibility is ±0.084‰ for $\delta^{18}O$ and ±0.061‰ for $\delta^{13}C$) and are reported relative to Vienna Pee Dee Belemnite (V-PDB). Temperature and salinity data from different depth habitats were taken from the Bermuda Atlantic Time Series (BATS) to calculate the $\delta^{18}O$ of calcite in equilibrium with seawater ($\delta^{18}O_{sw}$). The $\delta^{18}O_{sw}$ at Bermuda was calculated using the 0–50 m $\delta^{18}O_{sw}$-salinity relationship for the tropical–subtropical Atlantic available through the NASA seawater database (Arbuszewski et al., 2010; Schmidt et al., 1999). Calcification temperatures were then calculated using $\delta^{18}O_{calcite}$ and calculated $\delta^{18}O_{sw}$ where available. For *G. ruber* (p) and *G. truncatulinoides*, we use the rearrangement of the palaeotemperature equation of O'Neil et al. (1969) and Shackleton (1974) and for *O. universa*, we used the low-light palaeotemperature equation of Bemis et al. (1998). For samples where no stable isotope data