



Core-top calibration of B/Ca in Pacific Ocean *Neogloboquadrina incompta* and *Globigerina bulloides* as a surface water carbonate system proxy



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ABSTRACT

Practical methods for reconstructing past ocean carbonate chemistry are needed to study past periods of ocean acidification and improve understanding of the marine carbonate system's role in the global climate cycles. Planktic foraminiferal B/Ca may fill this role, but requires better understanding and improved proxy calibrations. We used Pacific Ocean core-top sediments to generate new calibrations of the B/Ca proxy for past carbonate system parameters in two upwelling/subpolar species of asymbiotic planktic foraminifera (*Globigerina bulloides* and *Neogloboquadrina incompta*). Both species show significant positive correlation of B/Ca with calcite saturation (Ω_{calcite}) and carbonate ion concentration ($[\text{CO}_3^{2-}]$) across a broad range of environmental conditions. This suggests a calcification rate control on B/Ca incorporation (as Ω_{calcite} regulates calcification rate), in agreement with recent inorganic calcite studies. This is also consistent with a surface entrapment model of trace element incorporation into CaCO_3 . In neither species is B/Ca significantly correlated with pH, suggesting that pH does not directly regulate boron incorporation, and that calculation of pH directly from foraminiferal B/Ca is not suitable. Correlations between B/Ca and $[\text{B}(\text{OH})_4^-]$, $[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]$, and $[\text{B}(\text{OH})_4^-]/\text{DIC}$ are weaker than with Ω_{calcite} . Boron partition coefficients ($K_D = [\text{B}/\text{Ca}]_{\text{solid}}/[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]_{\text{seawater}}$) show little or no correlation with $[\text{CO}_3^{2-}]$ or temperature and vary widely, providing no support for application of K_D to calculate carbonate system parameters from B/Ca. We also discuss potential effects of depth-related dissolution, temperature, and salinity on B/Ca. These empirical calibrations linking foraminiferal calcite B/Ca with Ω_{calcite} provide a strong tool for reconstructing the past ocean carbonate system and improve our understanding of the proxy's geochemical basis.

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1. Introduction

The global ocean acts as a major reservoir for atmospheric CO_2 and thus plays a fundamental role in the climate system. Uptake of atmospheric CO_2 by the oceans both in the past and today results in lower ocean pH and calcium carbonate saturation (Ω_{calcite} and $\Omega_{\text{aragonite}}$), impacting many marine organisms that are sensitive to fluctuations in these carbonate system parameters (Doney et al., 2009). In light of accelerating anthropogenic CO_2 emissions and ocean acidification, there is a need for proxies that can be used to

reconstruct past ocean carbonate chemistry and provide data sets for climate model testing. Constraining the marine carbonate system requires quantitative knowledge of at least two of the six marine carbonate system parameters (pH, $[\text{CO}_3^{2-}]$, $[\text{HCO}_3^-]$, $[\text{CO}_{2\text{aq}}]$, total alkalinity (TA), dissolved inorganic carbon (DIC), Zeebe and Wolf-Gladrow, 2005) as well as temperature, salinity, and pressure, and allows insight into ocean–atmosphere carbon exchange, and in areas where surface waters and the atmosphere are equilibrated, could allow reconstruction of past atmospheric $p\text{CO}_2$.

While proxies for some carbonate system parameters have been developed and applied (e.g. boron isotope ($\delta^{11}\text{B}$) in CaCO_3 for seawater pH reconstruction), carbonate system proxies that can be applied at moderate or high resolution in down-core studies are needed. The ratio of boron to calcium (B/Ca) in planktic foraminiferal calcite has been suggested as a proxy for one of several related seawater variables: either carbonate ion concentration

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($[\text{CO}_3^{2-}]$, Foster, 2008; Hendry et al., 2009), the ratio of seawater borate to bicarbonate ($[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]$, Palmer et al., 2010; Tripathi et al., 2009; Yu et al., 2007b), or the ratio of borate to dissolved inorganic carbon ($[\text{B}(\text{OH})_4^-]/[\text{DIC}]$, Allen and Hönisch, 2012; Allen et al., 2012) (the latter two may serve as proxies for pH if total aqueous boron and DIC are known).

The relationship between B/Ca and $[\text{CO}_3^{2-}]$ is consistent with studies reporting a strong calcification rate control over B/Ca in inorganic calcite (Gabitov et al., 2014; Kaczmarek et al., 2016; Ruiz-Agudo et al., 2012; Uchikawa et al., 2015); some foraminiferal calcite data also suggest calcification rate control over B/Ca (Henehan et al., 2015; Naik and Naidu, 2014; Penman et al., 2014). Calcification rate is regulated by Ω_{calcite} (Zeebe and Wolf-Gladrow, 2005; $\Omega_{\text{calcite}} = ([\text{CO}_3^{2-}] * [\text{Ca}^{2+}]_{\text{in situ}}) / K_{\text{sp}}$, where K_{sp} is $([\text{CO}_3^{2-}] * [\text{Ca}^{2+}])_{\text{saturation}}$); since $[\text{Ca}^{2+}]$ varies only slightly in the global ocean, variability in $[\text{CO}_3^{2-}]_{\text{in situ}}/[\text{CO}_3^{2-}]_{\text{saturation}}$ is the dominant control over Ω and calcification rate. Reconstructed Ω_{calcite} , pH or $[\text{CO}_3^{2-}]$ can be combined with another carbonate system variable and data on temperature, pressure, salinity and total P and Si content to reconstruct the entire carbonate system. An important analytical advantage of B/Ca over $\delta^{11}\text{B}$ as a carbonate-system proxy is its smaller sample size requirements and simpler sample preparation and analysis, which can be performed concurrently with analysis of other elemental ratios such as Mg/Ca (widely used for paleo-temperature reconstruction) and U/Ca and Li/Ca (other elements which may reflect the carbonate system), allowing higher-resolution records to be produced.

The development and application of boron-based carbonate system proxies (B/Ca and $\delta^{11}\text{B}$) is based on the pH control over the relative abundance of the two dissolved aqueous boron species in seawater (borate $\text{B}(\text{OH})_4^-$ and boric acid $\text{B}(\text{OH})_3$), of which $\text{B}(\text{OH})_4^-$ dominates at higher pH (Hemming and Hanson, 1992). Because the boron isotope ($\delta^{11}\text{B}$) composition of calcite agrees with the seawater $\text{B}(\text{OH})_4^-$ $\delta^{11}\text{B}$ composition, Hemming and Hanson (1992) suggested that the tetrahedral $\text{B}(\text{OH})_4^-$ is adsorbed onto calcite surfaces and then dehydroxylated to form BO_3^{3-} during calcite formation, ultimately substituting for CO_3^{2-} in the calcite lattice. The calcite B concentration and $\delta^{11}\text{B}$ ultimately depends on the $\text{B}(\text{OH})_4^-$ concentration in seawater (a function of pH), and potentially also on other factors. An equilibrium reaction and partition coefficient (K_{D}) for boron incorporation were proposed by Hemming and Hanson (1992):



$$K_{\text{D}} = [\text{HBO}_3^{2-}/\text{CO}_3^{2-}]_{\text{solid}}/[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]_{\text{seawater}} \quad (2)$$

This expression for K_{D} was later simplified, based on the stoichiometry of calcite $[\text{CO}_3^{2-}] \approx [\text{Ca}^{2+}]$ (Yu et al., 2007b):

$$K_{\text{D}} = [\text{B}/\text{Ca}]_{\text{solid}}/[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]_{\text{seawater}} \quad (3)$$

Initial core-top calibrations of the B/Ca proxy in planktic foraminifera applied the theoretical partition coefficient (K_{D} ; equation (3)) to calculate pH or $[\text{CO}_3^{2-}]$, and found a strong relationship of K_{D} with temperature (Foster, 2008; Yu et al., 2007b) (but with opposite sign), and sometimes with $[\text{CO}_3^{2-}]$ (Foster, 2008) or growth rate (Ni et al., 2007). However, lack of consensus about how to apply K_{D} , strong covariance of carbonate system parameters with one another and with temperature, and an incomplete understanding of the role of individual ion species on boron incorporation created uncertainty regarding application of K_{D} with this proxy (Allen and Hönisch, 2012; Seki et al., 2010). Further, some of the K_{D} -based carbonate system reconstructions (Foster, 2008; Tripathi et al., 2009; Yu et al., 2007b) yielded results for some species that were later shown to be effectively independent of the measured variations in B/Ca (Allen and Hönisch, 2012; Seki et al., 2010). Subsequent calibration of the B/Ca proxy in cultured planktic foraminifera has

shown strong direct relationships between B/Ca and carbonate system parameters (Allen et al., 2012, 2011). Accordingly, some researchers recommend that calibrations of this proxy test and develop empirical calibrations of the B/Ca proxy directly with environmental parameters, rather than using K_{D} (Allen et al., 2012; Allen and Hönisch, 2012), like with other trace element proxies (e.g. Mg/Ca). We follow this approach, and discuss mechanistic explanations for our results.

While laboratory culture studies have begun to establish B/Ca calibrations for photosymbiont-bearing tropical or subtropical species of planktic foraminifera (Allen et al., 2012, 2011), little B/Ca calibration work has been done in species common in nutrient-rich upwelling zones and mid- and high-latitude areas. In addition, B/Ca has been under-studied in asymbiotic species, whose carbonate chemistry is not affected by symbiont photosynthesis and thus may be easier to interpret.

In this study, we present Pacific core-top calibrations of B/Ca in two asymbiotic species common in subpolar, temperate, and upwelling zones, *Neogloboquadrina incompta* (also known as *Neogloboquadrina pachyderma* (dextral)) and *Globigerina bulloides*, and investigate controls on boron incorporation in these species in Pacific Ocean samples. Because of the wide geographical distributions and range of habitats of this study's samples (Fig. 1), we assign calcification depths appropriate for each sample based on its Mg/Ca or $\delta^{18}\text{O}$ temperature or literature data, and then assign water column carbonate chemistry data (based on the sample-specific calcification depth) for establishing a B/Ca calibration. Robust calibrations for *N. incompta* and *G. bulloides* will allow quantitative reconstructions of ocean carbonate chemistry in new regions, allowing us to study past ocean acidification events and interactions between seawater carbonate chemistry and climate.

2. Methods

2.1. Samples

Elemental and isotopic analyses were conducted on two species of planktic, asymbiotic foraminifera from Pacific Ocean core-top samples (Fig. 1) representing a range of carbonate chemistry and temperature conditions. *G. bulloides* is often found in a near-surface to mixed layer habitat, and *N. incompta* is commonly found close to the thermocline, but sometimes nearer to the surface (absolute depth ranges for both species vary by region) (Field, 2004; Sautter and Thunell, 1991a). *N. incompta* from 31 sites and *G. bulloides* from 37 sites were analyzed (Table S1, S2).

Core-top samples came from a combination of different surface-preserving core types, including multicores, box-cores, gravity and piston cores, and push cores obtained by ROV (Remotely Operated Vehicle), and were collected from water depths between 250 m and 3900 m (Table S1, S2; Fig. 2). All samples were from the upper 9 cm of the sediment, and most (54 of the 68) were from the upper 5 cm, indicating that the samples most likely represent late Holocene sediments. Samples were confirmed to be of Holocene age either by previous age determination by other investigators or verified using the $\delta^{18}\text{O}$ values of *N. incompta* and *G. bulloides* (Table S1, S2).

2.2. Sample preparation

For each core-top sample, ~ 80 *N. incompta* tests in the 125–250 μm size fraction or ~ 40 *G. bulloides* tests in the 250–355 μm size fraction (seven samples were from a wider size range due to limited abundance, but only three of these were used in the calibration, and do not represent outliers in the data; Table S1) were picked for a total weight of ~ 200 –350 μg per sample. Mean weight per shell of pooled shells in each sample was determined

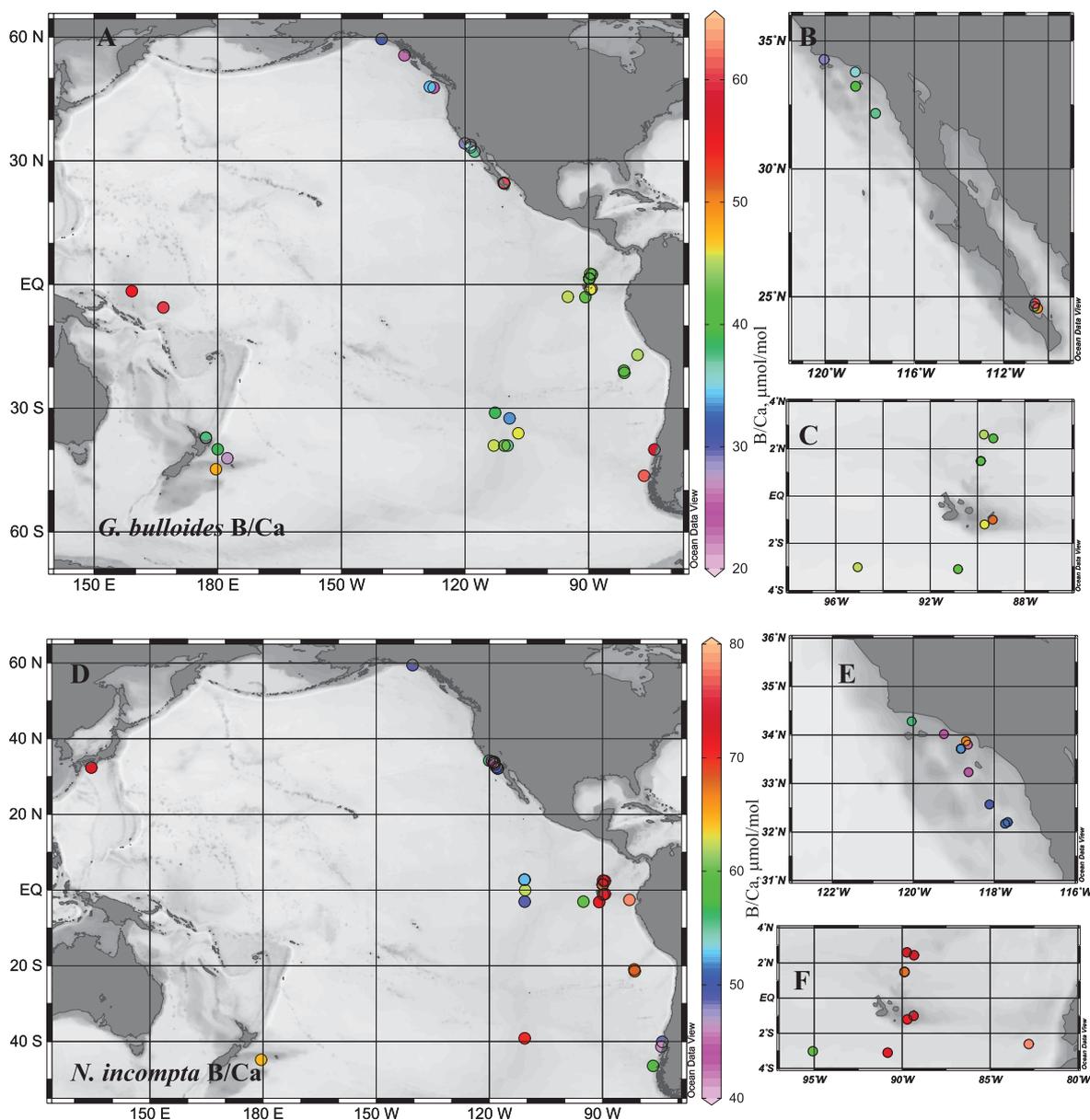


Fig. 1. Maps showing the location of core-top samples and B/Ca results. Maps A, B, C show *G. bulloides* locations and B/Ca values (see color bar for scale, which differs from *N. incompta* scale); inset B shows Southern California and Gulf of California samples, and inset C shows Galapagos samples. Maps D, E, F show *N. incompta* locations and B/Ca values (note that the color bar scale differs from *G. bulloides*); inset E shows Southern California samples, and inset F shows Galapagos samples. Created using Ocean Data View software. (For interpretation of color in this figure, the reader is referred to the web version of this article.)

using a Sartorius Microbalance scale. The samples were crushed and cleaned following the methods of [Martin and Lea \(2002\)](#) (revised from [Boyle and Keigwin, 1985](#)). Sample cleaning consisted of multiple ultrasonication steps in boron-clean MilliQ water and methanol, a reductive and oxidative step, and additional rinses with boron-clean MilliQ water. A reductive cleaning step was included because it has been shown that this step is important for removal of Mg associated with remnant organic matter and adsorbed phases ([Bian and Martin, 2010](#)). These methods have been shown by [Yu et al. \(2007a\)](#) to yield results equivalent to those without the reductive step ([Barker et al., 2003](#)), though the reductive step results in some preferential Mg loss (about 15%, which can be corrected for following [Regenberg et al., 2006](#) and [Rosenthal et al., 2004](#) – not corrected here). All sample handling following crushing was done in a laminar flow fume hood, and samples were kept closed whenever possible to avoid boron contamination from air filters.

2.3. Elemental analysis

All analyses (^{11}B , ^{24}Mg , ^{43}Ca , ^{238}U , ^{27}Al , ^{55}Mn and ^{56}Fe) were conducted concurrently by Inductively Coupled Mass Spectrometer (ICP-MS, Finnigan Element XR) at UCSF using the procedure described in [Brown et al. \(2011\)](#) based on established techniques ([Al-Ammar et al., 2000](#); [Rosenthal et al., 1999](#)). The cleaned tests were transferred to acid-cleaned plasticware on the day of analysis and dissolved in 400 μL of 0.075 HNO_3 (Optima grade). A small number of early analytical runs were free-aspirated using a Teflon spray-chamber, but the vast majority of analyses used a peristaltic pump and a cyclonic quartz spray chamber. These results were comparable, but the latter pumping technique had a more stable calcium signal. Ammonia gas injected into the spray chamber at 5 mL/min reduced the memory effects common in boron analysis. Instrument boron blanks were reduced using washout and uptake times of 30 s and 40 s, respectively.

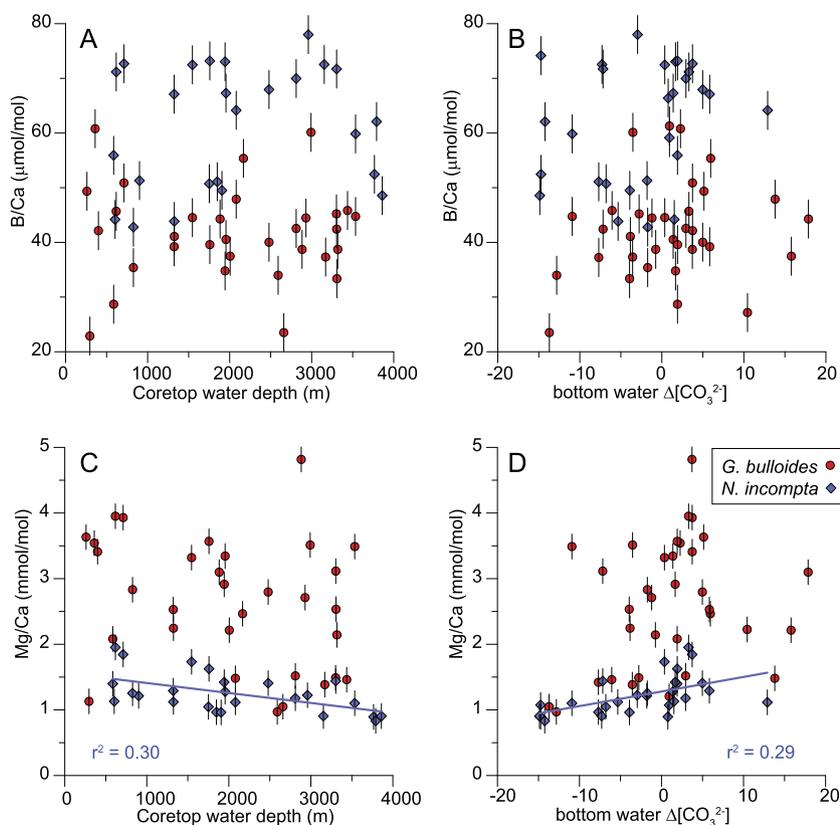


Fig. 2. Core-top B/Ca versus sediment-water interface depth (here referred to as core-top water depth) (A) and bottom water $\Delta[\text{CO}_3^{2-}]$ (B), and core-top Mg/Ca versus core-top water depth (C) and bottom water $\Delta[\text{CO}_3^{2-}]$ (D). *N. incompta* (blue diamonds) and *G. bulloides* (red circles); r^2 is shown where a significant correlation is found ($p < 0.01$), with text color indicating species. B/Ca and Mg/Ca error bars reflect one standard deviation of the solid foraminiferal standard (see methods), which represents a more conservative error than the liquid consistency standard. In panels B and D, samples with $\Delta[\text{CO}_3^{2-}]$ values greater than 20 $\mu\text{mol/kg}$ have been omitted due to a non-linear relationship between the higher and lower $\Delta[\text{CO}_3^{2-}]$ values (samples with high $\Delta[\text{CO}_3^{2-}]$ are not from undersaturated conditions, and so are not susceptible to dissolution effects on trace elements). B/Ca is uncorrelated with sample water depth and $\Delta[\text{CO}_3^{2-}]$ for both species (A and B), implying that in these species, B/Ca is not affected by depth-related dissolution. For *G. bulloides*, a lack of correlation of Mg/Ca with water depth and $\Delta[\text{CO}_3^{2-}]$ suggests that this species does not experience depth-related Mg/Ca dissolution. However, *N. incompta* Mg/Ca is significantly ($p = 0.004$) correlated with sample water depth (C) and $\Delta[\text{CO}_3^{2-}]$ (D), and appears to be affected by depth-related dissolution based on calculated temperatures. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In-run blanks for all elements of interest were measured on the same 0.075 N nitric acid solution used for sample dissolution. To monitor intra-run variability, a liquid consistency standard (B/Ca = 60.14 $\mu\text{mol/mol}$, [Ca] = 100 ppm) and a solid foraminiferal consistency standard (composed of crushed and mixed *Pullenia obliquiculata* (>500 μm) from core-top PLDS-77BX; B/Ca = 51.5 $\mu\text{mol/mol}$) were used. To account for possible matrix effects due to varying [Ca] and Element/Calcium (El/Ca) in the samples, we used a set of five liquid calibration standards of varying El/Ca diluted to four calcium concentrations ranging from 20–150 ppm to generate calibration equations for each element before each day's analysis. However, matrix effects (differing [Ca] for the same El/Ca) were small (calibration equations for different [Ca] with the same El/Ca were not significantly different), and so element daily calibrations combined El/Ca results at differing [Ca] into a single calibration equation. We corrected for drift and mass bias using the liquid consistency standard. When foraminiferal abundance permitted, we performed duplicate analyses of foraminifera by splitting crushed samples before cleaning (56% of *N. incompta* samples, 43% of *G. bulloides* samples). The boron blank during analysis was $\sim 9\%$ of the liquid consistency standard B value (blanks for all other elements were lower) and was subtracted from the signal; the blank remained relatively stable during a typical run. Replicate analysis of the solid foraminiferal consistency standard yielded reproducibility of $\pm 7\%$ (3.5 $\mu\text{mol/mol}$; 1σ) for B/Ca and $\pm 9\%$ (0.19 mmol/mol; 1σ) for Mg/Ca between runs; this standard is used to confirm long-term stability of the liquid standards and to pro-

vide the most conservative error bars on the foraminiferal El/Ca data. The between-run reproducibility (based on measurement of the liquid consistency standard and blanks after every 5 samples; $n = 139$) was $\pm 1.2\%$ (1σ) for B/Ca and $\pm 0.3\%$ for Mg/Ca, and the in-run reproducibility was $\pm 1.3\%$ (1σ) for B/Ca and $\pm 0.4\%$ for Mg/Ca.

2.4. Stable isotopes

Carbon and oxygen stable isotope ratios were measured for all core-top samples of both species in the same size fractions used for elemental analysis. Depending on shell weight, 4–18 tests were pooled per sample, and replicate analyses were conducted for approximately half the samples. Samples were analyzed at UCSC using an IRMS (MAT-256) with a Kiel auto-carbonate device, or, for 14 samples, using a Prism model IRMS with a dual inlet carbonate device. Analytical precision based on replicate measurements of the in-house carbonate standard Carrara Marble and NBS-19 included with each analytical run was $\pm 0.06\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.03\text{‰}$ for $\delta^{13}\text{C}$ (1σ).

2.5. Hydrographic data

Hydrographic data for most core-top sites were obtained from the 2009 World Ocean Atlas (WOA09; water column temperature, salinity, and nutrient concentrations ([PO_4^{3-}] and [SiO_3]), http://www.nodc.noaa.gov/OC5/WOA09/pr_woa09.html), and DIC (also

known as TCO₂), total alkalinity (ALK) and anthropogenic CO₂ were obtained from the Global Ocean Data Analysis Project (GLODAP, version 1.1; Key, 2004). Gridded output was produced using Ocean Data View's 3D interpolation tool (Schlitzer, 2006) (Table S1, S2). For the coastal areas, we selected non-gridded hydrographic data that is more geographically precise due to the greater spatial variability of hydrographic conditions and because these areas are more heavily represented in our dataset. Data sources for coastal sample areas in Southern California and Washington State are the North American Carbon Program (2007 data; Feely et al., 2008) and the Pacific Marine Environmental Lab (PMEL) West Coast Carbon Cruise (2011 data; Patsavas et al., 2015), and data for one Canadian coastal sample are from the 2010 Canadian Coastal Carbon Cruise (British Columbia, D. Ianson, pers. comm.) (Table S1, S2).

After correcting DIC for anthropogenic CO₂ contribution (Sabine et al., 2004), we used the hydrographic data to calculate pre-industrial carbonate system parameters (pH, [CO₃²⁻], HCO₃⁻, DIC, B(OH)₄⁻, and other derivative parameters; Table S1 and S2) using the program CO₂sys.xls version 2.1 (Pelletier et al., 2007), with K1 and K2 from Lueker et al., 2000, K_B and K_{H5O4} from Dickson (1990), total B from Lee et al. (2010), and pH on the total scale. At each sample location, we determined bottom water $\Delta[\text{CO}_3^{2-}]$ ($\Delta[\text{CO}_3^{2-}] = [\text{CO}_3^{2-}]_{\text{in-situ}} - [\text{CO}_3^{2-}]_{\text{saturation}}$) to evaluate potential post-depositional effects on shell chemistry using gridded data from the WOA09 hydrographic and the GLODAP 1.1 carbonate chemistry datasets.

2.6. Calcification depths

One of the largest sources of uncertainty in relating foraminiferal shell chemistry to water column conditions derives from the selection of calcification depths and the corresponding temperature, salinity, and carbonate system parameters. Vertical gradients in hydrographic parameters (including carbonate chemistry) are often steep, such that selection of a depth some tens of meters shallower or deeper results in significantly different calcification conditions. As this study uses samples from diverse geographic and oceanographic conditions, we assigned a specific calcification depth for each sample area and species.

Calcification depths were generally assigned based on temperatures reconstructed from Mg/Ca for *G. bulloides* and from $\delta^{18}\text{O}$ for *N. incompta* (Table S1, S2). We matched the proxy-derived calcification temperature to the local temperature profile from hydrographic data to select calcification depth and depth-specific hydrographic parameters. For *G. bulloides*, we applied the species-specific Mg/Ca temperature calibration of Mashiotto et al. (1999); these calculated temperatures were generally within 1 °C of those calculated from other region-specific *G. bulloides* Mg/Ca-temperature calibrations (Marr et al., 2011; McConnell and Thunell, 2005).

Although we measured Mg/Ca in *N. incompta*, existing calibration relationships for *N. incompta* (von Langen et al., 2005) and *N. pachyderma* (sinistral) (Elderfield and Ganssen, 2000; Nürnberg et al., 1996) resulted in calcification depths that were much deeper than described for this species. Depth-related partial dissolution in low bottom water $\Delta[\text{CO}_3^{2-}]$ may have lowered the Mg/Ca values of some *N. incompta* samples in this dataset (see discussion, Section 4.7). Indeed, *N. incompta* Mg/Ca shows a significant ($p < 0.01$) decreasing trend with bottom water depth (Fig. 2C). Though techniques exist for correcting Mg/Ca for depth-related dissolution (Mekik et al., 2007; Regenberg et al., 2006), the required species-specific calibrations are not available for *N. incompta*.

Therefore, for *N. incompta*, we used $\delta^{18}\text{O}$ temperatures to select calcification depths ($\delta^{18}\text{O}$ is uncorrelated with core-top depth); when $\delta^{18}\text{O}$ -based calcification temperatures were compared with local hydrographic profiles, they generally yielded water temperatures in agreement with regionally-determined calcification depths

estimated from plankton tow and sediment trap studies. We used a *N. incompta*-specific $\delta^{18}\text{O}$ -temperature calibration (von Langen et al., 2000, as in Bemis et al., 2002), and to select local water $\delta^{18}\text{O}$, we used the global sea surface $\delta^{18}\text{O}$ database (Schmidt et al., 1999) (subtracting 0.04‰ from surface water values to account for *N. incompta*'s subsurface calcification), or for Southern California core-tops, we applied the local salinity- $\delta^{18}\text{O}$ relationship of Bemis et al. (2002) to calculate water $\delta^{18}\text{O}$ at a typical calcification depth (Sautter and Thunell, 1991b). *N. incompta* $\delta^{18}\text{O}$ -based calcification temperatures ranged between 7°–18 °C for samples outside the equatorial zone, and 13°–21 °C for the eastern equatorial Pacific (3°N to 3°S).

However, in a small number of samples ($n = 6$ for *N. incompta*, $n = 8$ for *G. bulloides*), both Mg/Ca and $\delta^{18}\text{O}$ calcification temperatures ($\pm 2^\circ\text{C}$) provided depths well outside of the range of species- and region-specific literature values for calcification depth. In those cases, we applied literature-based, region- and species-based calcification depths (these previous studies determined calcification depths using plankton tows and sediment traps, and some of these studies used Mg/Ca or $\delta^{18}\text{O}$ to determine calcification depth; Table S1, S2), which compared well with nearby geochemically-derived calcification depths. The calcification depths we used (whether from Mg/Ca, $\delta^{18}\text{O}$, or selected from the literature) agree with those determined for the appropriate regions in Pacific Ocean studies (Bolton and Marr, 2013; Field, 2004; Marr et al., 2011; McConnell and Thunell, 2005; Pak and Kennett, 2002; Reynolds and Thunell, 1985; Sautter and Thunell, 1991a; Ujiie and Ujiie, 2000).

2.7. Data treatment

We evaluated the relationship between B/Ca and calcification depth water parameters using the Pearson correlation coefficient of B/Ca with each parameter, a Student's t-test, and a bivariate least squares regression (generated using PAST software; Hammer et al., 2001). We also evaluated the correlation of calcification depth water parameters with each other (Table S3) and of trace element data with each other (Table S4; generated using PAST software; Hammer et al., 2001). Parameters evaluated at calcification depth are temperature, salinity, [PO₄³⁻], alkalinity, DIC, pH, [CO₃²⁻], B(OH)₄⁻, Ω_{calcite} , and the ratio of B(OH)₄⁻ to HCO₃⁻, DIC, and [CO₃²⁻], as well as bottom water $\Delta[\text{CO}_3^{2-}]$.

3. Results

3.1. Sample selection and trace element data quality assessment

Twenty-seven *G. bulloides* and twenty-four *N. incompta* samples were used for the core-top calibration based on the availability of water column carbonate chemistry data, sample age, and the quality of the El/Ca data (i.e. uncontaminated as determined by deviation of samples' U, Mn, Fe or Al values from other samples in the same region). B/Ca data show little or no significant correlation with the other elements measured, and Mg/Ca in *G. bulloides* is not significantly correlated with any other element (Table S4). Five additional *G. bulloides* samples that belong to a distinct morphotype of *G. bulloides* (referred to as "encrusted *G. bulloides*" due to an outer calcite crust) and had suitable water data were also used here. We present two calibrations for *G. bulloides*: one for only the non-encrusted *G. bulloides* (Section 4.4), and one including both encrusted (5) and non-encrusted (27) *G. bulloides* (Section 4.6). All foraminiferal geochemical data collected for this study are shown in Tables S1 and S2.

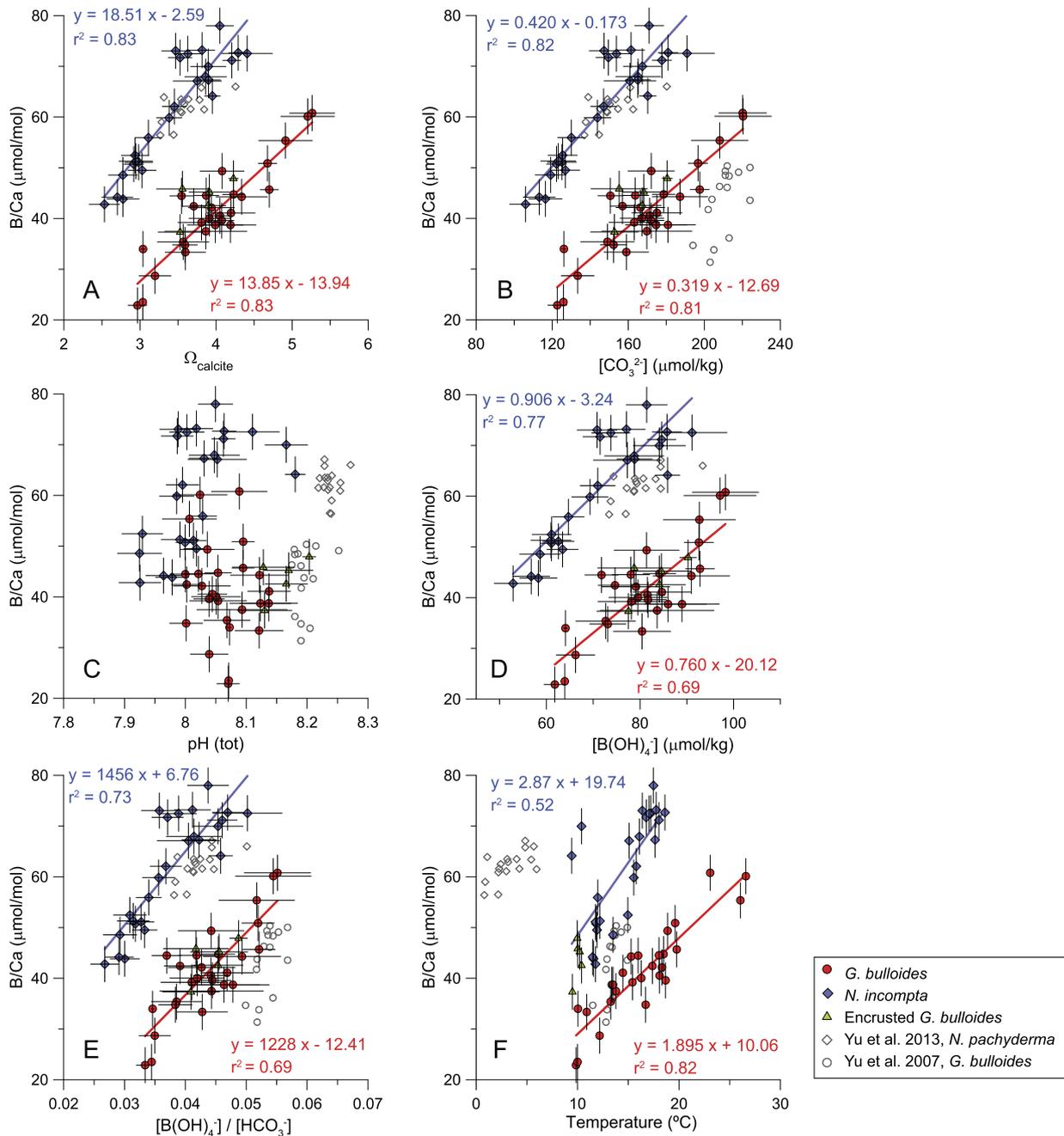


Fig. 3. Variation of B/Ca with environmental parameters at the assigned calcification depth in two species of core-top planktic foraminifera (*N. incompta* and *G. bulloides*) from across the Pacific. *N. incompta* data generated in this study are shown in blue diamonds with error bars, *G. bulloides* data generated in this study are shown in red circles with error bars. The encrusted morphotype of *G. bulloides* is shown in green triangles, and is not shown in this figure's regressions, but is included in the regressions in Section 4.6. North Atlantic *N. pachyderma* (sinestral) data from Yu et al. (2013) are shown in empty gray diamonds, and North Atlantic *G. bulloides* data from Yu et al. (2013) are shown in empty gray circles. In each panel, a bivariate least squares regression of B/Ca to the water parameter is shown for each species if the parameters are significantly correlated ($p < 0.001$); see also Table S3 for further r^2 and p values. B/Ca error bars reflect one standard deviation of the solid foraminiferal standard (± 3.5 μmol/mol; see methods), which represents a more conservative error than the liquid consistency standard, and horizontal error bars reflect spatial errors of GLODAP or coastal data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. Core-top B/Ca

The samples used in this study span a broad range of hydrographic conditions, including temperature (~ 9 – 27°C), salinity (~ 31.5 – 35.5), pH (~ 7.9 – 8.2), Ω_{calcite} (2.5–5.5), and $[\text{CO}_3^{2-}]$ (106–220 μmol/kg).

Core-top *N. incompta* B/Ca values (Fig. 3, S1, Table S1, S3) are significantly correlated ($p < 0.001$) with calcification depth-specific Ω_{calcite} ($r^2 = 0.83$), $[\text{CO}_3^{2-}]$ ($r^2 = 0.82$), $[\text{B}(\text{OH})_4^-]$ ($r^2 =$

0.77), $[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]$ ($r^2 = 0.73$), $[\text{B}(\text{OH})_4^-/\text{DIC}]$ ($r^2 = 0.73$), salinity ($r^2 = 0.55$), and temperature ($r^2 = 0.52$). Core-top *G. bulloides* B/Ca values (Fig. 3, S1, Table S2, S3) are significantly correlated ($p < 0.001$) with calcification depth-specific Ω_{calcite} ($r^2 = 0.83$), $[\text{CO}_3^{2-}]$ ($r^2 = 0.81$), $[\text{B}(\text{OH})_4^-]$ ($r^2 = 0.69$), $[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]$ ($r^2 = 0.69$), $[\text{B}(\text{OH})_4^-/\text{DIC}]$ ($r^2 = 0.67$), salinity ($r^2 = 0.50$), and temperature ($r^2 = 0.82$). Many of these variables are autocorrelated, as discussed below. In neither species is B/Ca correlated with DIC or PO_4^{3-} . In some regions, correlations between B/Ca and pH

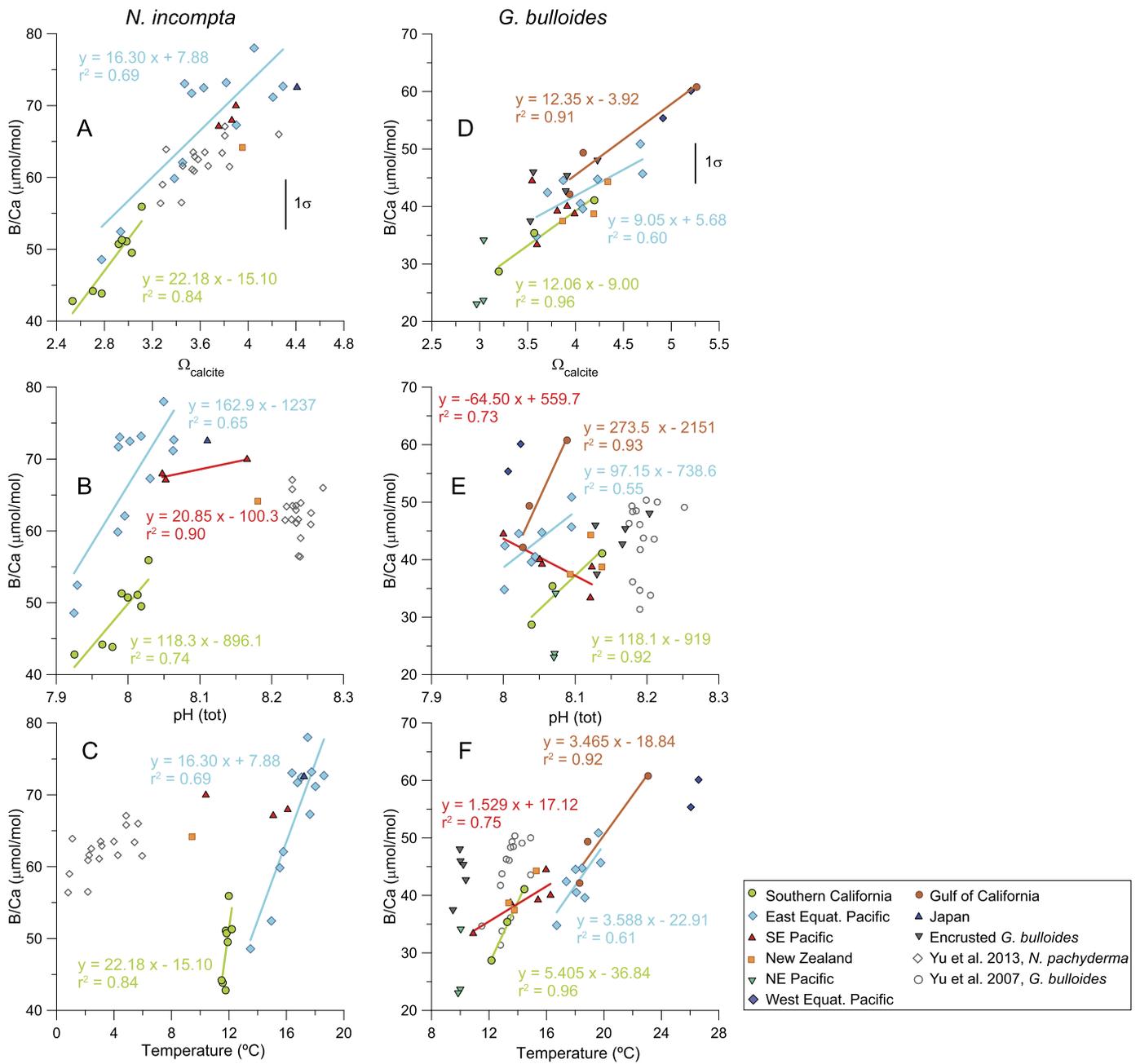


Fig. 4. Regional geographic variation of B/Ca in *N. incompta* (left panels) and *G. bulloides* (right panels) with environmental parameters at calcification depth. Regressions are shown for regions only when the correlations are significant ($p < 0.01$) (e.g. Southern California, Eastern Equatorial Pacific, Gulf of California, and in some cases, Southeast Pacific). Note that symbol types and colors differ from those in other figures. North Atlantic data are shown in empty gray symbols for comparison (Yu et al., 2007, 2013). Floating error bars shown in panels A and D reflect one B/Ca standard deviation of the solid foraminiferal standard ($\pm 3.5 \mu\text{mol/mol}$), which represents a more conservative error than the liquid consistency standard, and apply to panels B–F as well. (For interpretation of color in this figure, the reader is referred to the web version of this article.)

and temperature can be observed, but with very different, region-specific slopes (Fig. 4B, C, E, F), while regional correlations of B/Ca with Ω_{calcite} have similar slopes (Fig. 4A, D).

Though we measured U/Ca, and past studies show it may also have a relationship with carbonate chemistry (Russell et al., 2004), this relationship is inconsistent in both species studied (Table S4) and does not agree with previous studies, likely because U/Ca is more susceptible to redox-related post-depositional alteration than many other commonly measured trace elements (Morford and Emerson, 1999). Therefore, we do not treat the U/Ca data in this study.

We find large intraspecies differences in B/Ca values; *N. incompta* B/Ca values range from 43–78 $\mu\text{mol/mol}$, and *G. bulloides*

B/Ca values range from 23–61 $\mu\text{mol/mol}$. In regressions of B/Ca and Ω_{calcite} , *N. incompta* has a steeper slope and higher B/Ca values than *G. bulloides* (Fig. 3A), showing that *N. incompta* has a higher carbonate chemistry sensitivity than *G. bulloides*. Such sensitivity and interspecies differences are also seen in other planktic foraminifera species (Allen et al., 2012; Foster, 2008; Yu et al., 2007b).

Calculated K_D values (Equation (3)) range between 1.4 to 2.0 for *N. incompta* (mean = $1.7 \pm 0.2(1\sigma)$), and 0.7 to 1.2 for *G. bulloides* (mean $1.0 \pm 0.1(1\sigma)$; Fig. 5, Table S1, S2). K_D is uncorrelated (*N. incompta*) or weakly correlated with temperature (*G. bulloides*, $r^2 = 0.48$), and is not significantly correlated with $[\text{CO}_3^{2-}]$ in either species. Neither bottom water depth nor bottom water

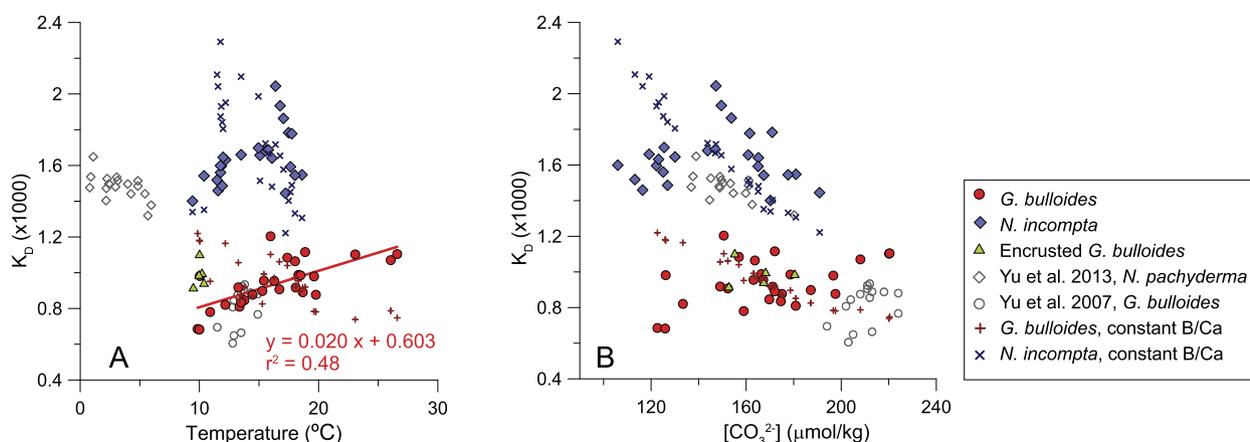


Fig. 5. Relationship of K_D (equation (3)) with temperature (A) and $[\text{CO}_3^{2-}]$ (B) for *N. incompta* (blue diamonds) and *G. bulloides* (red circles). Encrusted *G. bulloides* are shown in green triangles, but excluded from K_D calculations. North Atlantic data are shown in empty gray symbols for comparison (Yu et al., 2007, 2013). The correlations of K_D with temperature and $[\text{CO}_3^{2-}]$ are not significant ($p < 0.01$) except in the case of the *G. bulloides* K_D -temperature relationship (Table S3), and all are weaker than those of the B/Ca relationships with temperature and $[\text{CO}_3^{2-}]$. To illustrate the direct influence of B/Ca on this study's carbonate system calibrations, we show an artificial K_D relationship generated using average values of B/Ca for each species (41 $\mu\text{mol/mol}$ for *N. incompta*, 61 $\mu\text{mol/mol}$ for *G. bulloides*); blue Xs show *N. incompta* artificial K_D with constant B/Ca, and red crosses show *G. bulloides* artificial K_D with constant B/Ca. The artificial K_D relationships are different from those obtained using the individual measured B/Ca data, indicating that B/Ca does have a significant influence on these calibrations, unlike in some previous studies. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$\Delta[\text{CO}_3^{2-}]$ are correlated with B/Ca in either species (Fig. 2A, B), indicating that B/Ca in these samples is not affected by depth-related dissolution.

4. Discussion

4.1. Hydrographic context – decoupled variables

Previous studies of planktic foraminiferal and inorganic calcite have proposed that B/Ca in calcite is controlled by one of several related carbonate system variables: either pH, $[\text{CO}_3^{2-}]$, $[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]$, $[\text{B}(\text{OH})_4^-]/[\text{DIC}]$, or calcification rate (which can be indicated by Ω_{calcite}), and potentially temperature and/or salinity as well (see introduction). Some of these potential controlling variables are highly correlated with one another in our study (i.e. Ω_{calcite} , $[\text{CO}_3^{2-}]$, $[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]$, and $[\text{B}(\text{OH})_4^-]/[\text{DIC}]$), making their potential effects on B/Ca harder to distinguish based purely on this study's empirical results. However, others are uncorrelated (e.g. pH, temperature, and salinity; Table S3A, B) from other carbonate system variables (e.g. those listed above), unlike commonly seen in typical ocean conditions or prior studies (as discussed below). The partial decoupling of carbonate system variables, temperature and salinity in this cross-Pacific dataset allows us to begin to separate the effects of these normally tightly-correlated parameters on planktic foraminiferal B/Ca.

When our hydrographic and carbonate system data across the entire Pacific basin are combined, correlation between many parameters is weak or insignificant. For example, at *N. incompta* core-top sites, temperature and pH are uncorrelated ($r^2 = 0.00$), and Ω_{calcite} is not strongly correlated with temperature or pH ($r^2 = 0.39$, $r^2 = 0.56$, respectively); at *G. bulloides* sites, temperature and pH are not significantly correlated ($r^2 = 0.17$), and Ω_{calcite} is uncorrelated with pH ($r^2 = 0.01$), though Ω_{calcite} is correlated with temperature ($r^2 = 0.75$) (Table S3A, B). This frequent lack of correlation of hydrographic parameters contrasts with some previous B/Ca core-top calibration studies (Foster, 2008; Yu et al., 2013, 2007), where strong correlation ($r^2 \geq 0.7$) of temperature and $[\text{CO}_3^{2-}]$ is common (*G. bulloides*, *N. pachyderma*, *G. ruber*, *G. sacculifer*), and very strong correlation of pH and $[\text{CO}_3^{2-}]$ is seen in some cases ($r^2 > 0.95$; *G. sacculifer*, *N. dutertrei*), making it difficult to distinguish the effects of pH, temperature, and Ω_{calcite} (or $[\text{CO}_3^{2-}]$) on B/Ca.

These initially surprising relationships result from the diverse range of hydrographic settings in this study (e.g. coastal and equatorial upwelling areas, high-latitude coastal sites, open-ocean and oligotrophic settings). Although hydrographic parameters tend to co-vary within some Pacific regions (Fig. S2), each region's relationships are unique, resulting in lack of correlation of these parameters when combined. In addition, our study uses some samples from coastal upwelling regions, where the relationships between carbonate system and other hydrographic parameters differ from those in the open ocean, contributing further to the lack of correlation in the combined dataset. Some carbonate system parameters in this study are highly correlated (Ω_{calcite} , $[\text{CO}_3^{2-}]$, $[\text{B}(\text{OH})_4^-]$, $[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]$, and $[\text{B}(\text{OH})_4^-]/[\text{DIC}]$), so it is not possible to independently evaluate their potential effects on B/Ca with our data alone. However, other hydrographic parameters (pH, temperature, and Ω_{calcite}) are not inter-correlated across the whole Pacific dataset, allowing us to investigate the relationships between these parameters and B/Ca.

4.2. Controls on B/Ca

4.2.1. Carbonate system and calcification rate

In the Pacific Ocean core-top samples used in this study, B/Ca in *N. incompta* and *G. bulloides* is significantly positively correlated with calcification depth Ω_{calcite} , $[\text{CO}_3^{2-}]$, $[\text{B}(\text{OH})_4^-]$, $[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]$, and $[\text{B}(\text{OH})_4^-]/[\text{DIC}]$ (in order of decreasing r^2 ; Fig. 3); these parameters are highly correlated with one another (Table S3). The correlation of B/Ca with Ω_{calcite} is seen in a variety of regions (e.g. the upwelling-influenced Southern California, the Eastern Equatorial Pacific, and the Gulf of California; Fig. 4), suggesting a common control for both species, and that these relationships are robust across a wide range of Pacific Ocean hydrographic settings. The strong empirical correlation of B/Ca with carbonate system parameters can be used to reconstruct the carbonate system in the geologic past.

The relationships between Ω_{calcite} (and $[\text{CO}_3^{2-}]$, which co-varies with Ω_{calcite}) and B/Ca are similarly strong (Fig. 3). Recent studies provide both experimental (Gabitov et al., 2014; Kaczmarek et al., 2016; Ruiz-Agudo et al., 2012; Uchikawa et al., 2015) and theoretical (Watson, 2004) evidence for the regulation of B/Ca by calcification rate (which can be expressed using Ω_{calcite}). Since $[\text{Ca}^{2+}]$ is quasi-conservative, Ω_{calcite} can be approximated as

$\Omega_{\text{calcite}} \approx [\text{CO}_3^{2-}]_{\text{measured}}/[\text{CO}_3^{2-}]_{\text{saturation}}$ (Sarmiento and Gruber, 2006), and Ω_{calcite} can be used to calculate $[\text{CO}_3^{2-}]$ (or vice versa) on timescales $< \sim 1$ Ma (the residence time of $[\text{Ca}^{2+}]$ in seawater).

Previous core-top calibration studies of B/Ca in various species of planktic foraminifera have focused more on linking B/Ca to $[\text{CO}_3^{2-}]$ than to Ω_{calcite} , so we compare our $[\text{CO}_3^{2-}]$ results to those studies. The absolute B/Ca values measured for *N. incompta* and *G. bulloides* in this study agree with the B/Ca ranges reported by previous studies of these species in the North Atlantic (Yu et al., 2013, 2007b) (Fig. 3) and Antarctica (Hendry et al., 2009) using core-top sediments and sediment traps. The reported correlation of B/Ca with $[\text{CO}_3^{2-}]$ however has generally been weak except in the case of *Globorotalia inflata* (Allen and Hönisch, 2012; Yu et al., 2007b). This often weak correlation of B/Ca with $[\text{CO}_3^{2-}]$ reported in the published studies may be explained in part by their narrow range in $[\text{CO}_3^{2-}]$ (e.g. ~ 40 $\mu\text{mol/kg}$ in Yu et al., 2007, 2013 compared with ~ 85 (*N. incompta*) or 100 $\mu\text{mol/kg}$ (*G. bulloides*) in this study). The assignment of a constant calcification depth (e.g. 50 m) in these published studies instead of the use of varying, temperature-proxy-based calcification depths (as in this study) may have obscured the foraminiferal calcification conditions, and therefore also partially explain their often weak correlation of B/Ca with $[\text{CO}_3^{2-}]$.

Our study finds weaker relationships between B/Ca and $[\text{B}(\text{OH})_4^-]$, $[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]$ and $[\text{B}(\text{OH})_4^-]/\text{DIC}$ than with Ω_{calcite} (Fig. 3, Table S3). These parameters are related by chemical equilibria to Ω_{calcite} and so are highly correlated with Ω_{calcite} ($r^2 \geq 0.9$; Table S3), so it is possible that the relationship of these variables to B/Ca could reflect their correlation with Ω_{calcite} more than a primary influence on B/Ca.

In neither species is B/Ca significantly correlated with pH ($p < 0.001$; Fig. 3), nor is pH correlated with other carbonate system or $[\text{B}(\text{OH})_4^-]$ -related parameters for *G. bulloides* (though they are correlated in *N. incompta*; Table S3). The lack of correlation between B/Ca and pH in this study and other studies of core-top planktic foraminifera (Foster, 2008; Yu et al., 2013, 2007b) and in inorganic calcite (Uchikawa et al., 2015) strongly suggests that although pH controls the speciation of boron between borate and boric acid, other factors control the amount of boron incorporated into planktic foraminifera and inorganic calcite.

In contrast to our findings, a study of B/Ca in cultured planktic foraminifera hypothesized that Ω_{calcite} variations do not affect B/Ca (Allen et al., 2012). While Allen et al. (2012) had two pairs of samples that evaluated changes in Ω_{calcite} independently of pH (samples 4 & 5, and 8 & 9, which both had varying Ω_{calcite} , and constant (samples 4 & 5) pH or somewhat stable pH (samples 8 & 9)), the two sample pairs showed different effects. Samples 8 & 9 were intended to evaluate Ω_{calcite} changes independently of pH (pH, however, differed by 0.14 units between the two samples, and other carbonate system variables differed dramatically) and showed quite low B/Ca values occurring with dramatically elevated Ω_{calcite} (and vice versa; Ω_{calcite} 2.2 and 11.6, with measured B/Ca of 144 and 72.3 $\mu\text{mol/mol}$, respectively). Conversely, samples 4&5 showed an opposite effect: pH was constant between these two samples (though Ω_{calcite} between the two samples differed less than between samples 8&9, and some variations in temperature and salinity were present), and samples 4&5 showed higher B/Ca occurring with higher Ω_{calcite} (and vice versa; Ω_{calcite} 5.4 and 4.5, with measured B/Ca of 92.9 and 84.3 $\mu\text{mol/mol}$, respectively). These conflicting results (which could be in part due to the unusual water chemistry conditions, designed to vary some parameters more independently) left unresolved the question of how Ω_{calcite} affects planktic foraminiferal B/Ca. Our study, which shows a consistent, strong correlation between B/Ca and Ω_{calcite} but not pH (Fig. 3), can add some clarity by strongly suggesting that pH is

not a controlling variable on B/Ca, but rather Ω_{calcite} or one of its correlated variables.

This hypothesis is supported by Marshall et al. (2013) and Osborne et al. (2016), who found a pronounced effect of $[\text{CO}_3^{2-}]$ on calcification efficiency in planktic foraminifera, and other investigators have hypothesized a calcification rate control on B/Ca based on down-core B/Ca data in foraminiferal calcite (Henehan et al., 2015; Naik and Naidu, 2014; Penman et al., 2014). Experimental studies have demonstrated that calcification rate is the primary control on the concentration of boron in inorganic calcite (Gabitov et al., 2014; Kaczmarek et al., 2016; Ruiz-Agudo et al., 2012; Uchikawa et al., 2015), and discuss a mechanistic explanation for higher B/Ca values with faster calcification. These studies invoke a surface/growth entrapment model (SEMO; Watson, 2004) or a surface kinetic model (DePaolo, 2011), in which faster crystal growth (i.e. calcification rate) results in more boron being trapped in newly formed calcite surfaces because less time is available for boron to escape via diffusion or re-dissolution. The SEMO has been used to explain the incorporation of both B and Sr into calcite (Kaczmarek et al., 2016; Tang et al., 2008), and so may represent an important step toward a unified model for the incorporation of minor and trace elements into calcite.

4.2.2. Temperature and salinity effects on B/Ca

Our study finds a positive relationship between B/Ca and temperature ($r^2 = 0.82$ for *G. bulloides*, $r^2 = 0.52$ for *N. incompta*; Fig. 3F and Table S3). However, a large portion of this relationship is likely spurious, particularly for *G. bulloides*, since temperature and Ω_{calcite} are correlated at our study sites ($r^2 = 0.75$ for *G. bulloides*, $r^2 = 0.39$ for *N. incompta*). No significant temperature effect was observed in cultured *Globigerinoides ruber*, *Globigerinoides sacculifer*, and *Orbulina universa* (Allen et al., 2012). Inorganic calcite precipitation experiments independently exploring temperature effects on B/Ca are contradictory. Mavromatis et al. (2015) found no significant B/Ca difference between calcite precipitated at 5° and 25°C when other variables were stable, whereas Kaczmarek et al. (2016) observed decreasing B/Ca from 12°C to 32°C at constant calcification rate. This suggests that if a positive temperature effect on B/Ca exists (as posited by some earlier studies on planktic foraminifera, Foster, 2008; Yu et al., 2007b), it is weak, and may be overprinted by the dominant effect of calcification rate (reflected by Ω_{calcite}).

Weak correlations of B/Ca with salinity are of only slightly larger magnitude than the correlations between salinity and carbonate chemistry variables; Table S3), and suggest that salinity may have only a weak effect on B/Ca, as also shown in three species of cultured planktic foraminifera (Allen et al., 2012). B/Ca is uncorrelated with $[\text{PO}_4^{3-}]$ in our study, unlike in Henehan et al., 2015, likely due to the absence of photosymbionts in these species and their effects on carbonate chemistry.

4.3. Insights from geographic region sample groups

By dividing the results into several Pacific geographic regions, we see that some water variables are much more tightly correlated in these regions than in the overall dataset (e.g. $[\text{CO}_3^{2-}]$ and pH; Fig. S2). This allows us to evaluate which variables have a relationship with B/Ca that may be simply an artifact of the regional relationship of water parameters.

While B/Ca and pH are correlated in several regions (Fig. 4B, E), no significant correlation between B/Ca and pH is seen in the cross-Pacific dataset (Fig. 3). The B/Ca-pH regression lines in some regions differ dramatically (Fig. 4B, E), whereas the relationship of B/Ca with Ω_{calcite} is similar across various regions (Fig. 4A, D). This implies that these regional B/Ca-pH correlations are an artifact of the regional correlation of many carbonate system parameters and

environmental parameters with one another (Fig. S2). The consistently strong B/Ca– Ω_{calcite} relationship, both regionally and across the Pacific, supports a mechanistic relationship between B/Ca and Ω_{calcite} .

4.4. B/Ca calibration

Based on the strong empirical relationship between B/Ca and Ω_{calcite} that is present both regionally and across the Pacific, we report linear regressions of core-top B/Ca with Ω_{calcite} for *N. incompta*:

$$\text{B/Ca} = \Omega_{\text{calcite}} * 18.51(\pm 1.75) - 2.59(\pm 6.13) \quad (4)$$

and *G. bulloides*:

$$\text{B/Ca} = \Omega_{\text{calcite}} * 13.85(\pm 1.25) - 13.94(\pm 5.02) \quad (5)$$

where B/Ca is in $\mu\text{mol/mol}$, Ω_{calcite} is unitless, and the \pm term represents the errors in each constant. This Ω_{calcite} calibration and the following $[\text{CO}_3^{2-}]$ calibration exclude the five encrusted *G. bulloides* samples; alternate calibration equations which include the encrusted *G. bulloides* are provided in section 4.6.

For comparison with other studies, and because Ω_{calcite} and $[\text{CO}_3^{2-}]$ vary in tandem and will provide equivalent results in studies with near-surface foraminifera and stable seawater $[\text{Ca}_2^+]$ (e.g. the past 1 Ma), we also report linear fits of core-top data with $[\text{CO}_3^{2-}]$ for *N. incompta*:

$$\text{B/Ca} = [\text{CO}_3^{2-}] * 0.420(\pm 0.041) - 0.173(\pm 6.05) \quad (6)$$

and *G. bulloides*:

$$\text{B/Ca} = [\text{CO}_3^{2-}] * 0.319(\pm 0.031) - 12.69(\pm 5.29) \quad (7)$$

where B/Ca is in $\mu\text{mol/mol}$ and $[\text{CO}_3^{2-}]$ is in $\mu\text{mol/kg}$; alternate calibration equations which include the encrusted *G. bulloides* are provided in section 4.6.

A B/Ca study using cultured tropical planktic foraminifera (Allen et al., 2012) generated B/Ca– $\text{B}(\text{OH})_4^-/\text{DIC}$ calibration relationships based on theoretical assumptions. Equations relating B/Ca to $\text{B}(\text{OH})_4^-/\text{DIC}$ in the species *G. ruber*, *G. sacculifer* and *O. universa* (Allen et al., 2012) show slopes that are much shallower than those for *N. incompta* and *G. bulloides* in this study (see Fig. S1 and caption for regressions), indicating a higher carbonate system sensitivity of *N. incompta* and *G. bulloides* than the cultured tropical species. B/Ca values in this study's asymbiotic subpolar/upwelling species (range: ~ 20 – $80 \mu\text{mol/mol}$) are much lower than in the symbiont-bearing tropical species cultured in Allen et al. (2012) (range: 80 – $220 \mu\text{mol/mol}$), which is consistent with faster calcification by tropical, symbiont-bearing foraminifera in high Ω_{calcite} , warm waters. According to the SEMO, rapid calcification would allow less time for diffusion of boron out of the calcite surface layer than in slower-calcifying subpolar/upwelling foraminifera. Hence the relation between B/Ca and $\text{B}(\text{OH})_4^-/\text{DIC}$ in our study and in published records is likely also related to calcification rates.

4.5. The role of the partition coefficient K_D

K_D values in our study (Fig. 5) are comparable to those reported for North Atlantic *N. pachyderma* and *G. bulloides* (Yu et al., 2013, 2007b) and are within the range of other planktic species studied (Foster, 2008). However, we see large variations of K_D for both species, and we find no correlation of K_D with $[\text{CO}_3^{2-}]$ (Fig. 5). K_D is uncorrelated with temperature in *N. incompta*, and weakly correlated with temperature in *G. bulloides*, which agrees with a lack of temperature dependence of K_D in culture studies (Allen et al., 2012, 2011).

Some studies have generated calibrations of a constant boron partition coefficient (K_D ; Equation (3)) for inorganic calcite (Sanyal et al., 2000) and foraminiferal calcite (Yu et al., 2013) to calculate carbonate system parameters. However, recent inorganic calcite experiments find large variations in boron partition coefficients (Mavromatis et al., 2015), and studies of cultured and core-top planktic foraminifera have found that K_D varies widely between and within species (Foster, 2008; Yu et al., 2013, 2007b), likely due to non-equilibrium calcification conditions. This indicates that use of a constant K_D is not appropriate.

Alternatively, some studies of the planktic foraminifera B/Ca carbonate system proxy have generated calibrations of a variable K_D (with and without temperature dependence for K_D). However, carbonate system reconstructions based on K_D are sometimes spurious (Foster, 2008; Tripathi et al., 2009), likely due to the covariance of K_D , temperature, and carbonate parameters (Allen and Hönisch, 2012). Application of K_D to B/Ca carbonate system calibrations has been shown (e.g. by Allen and Hönisch, 2012; Seki et al., 2010) to lead to a muted signal of B/Ca in proxy reconstructions (Tripathi et al., 2009; Yu et al., 2007b), and we conclude such applications should be avoided.

We also performed a test proposed by Allen and Hönisch (2012) in which an average of the sample populations' B/Ca values is used to generate an "artificial K_D " value (by dividing average B/Ca for each species by $[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]$). If the true and "artificial" K_D relationships with environmental parameters (e.g. $[\text{CO}_3^{2-}]$ and temperature) were alike, this would indicate that the K_D calibration is independent of B/Ca variations and is driven by the denominator of K_D ($[\text{B}(\text{OH})_4^-]/\text{HCO}_3^-$) or another parameter. However, the true and "artificial" K_D relationships in this dataset are not alike for $[\text{CO}_3^{2-}]$ or temperature (Fig. 5), and so we conclude that our correlations are not driven by the K_D denominator or temperature, but rather by the variation of B/Ca with other carbonate system parameters, specifically calcification rate (indicated by Ω_{calcite}).

4.6. Encrusted *G. bulloides* morphotype

Some core-top *G. bulloides* samples ($n = 8$) show distinct chemical and physical properties from the others (Fig. 3, S3, S4, Table S2), with higher $\delta^{18}\text{O}$ values (1.4‰ to 2.8‰), heavier shell weights (generally 15 – $30 \mu\text{g}$), and a narrow Mg/Ca range (1.1 – 1.5 mmol/mol , corresponding to temperatures of 7 – 10°C). These specimens are thickly-calcified with a small aperture and appear to represent a different *G. bulloides* morphotype ("encrusted *G. bulloides*") and potentially a different *G. bulloides* genotype (Darling et al., 2003). The encrusted *G. bulloides* morphotype has been found previously in the Pacific Ocean, including in Southern Californian, New Zealand, and Chilean waters (Field, 2004; Marr et al., 2011; Mohtadi et al., 2005; Osborne et al., 2016; Sautter and Thunell, 1991b), and based on its Mg/Ca and $\delta^{18}\text{O}$ signature, it appears to calcify in colder, deeper waters than most non-encrusted *G. bulloides*, as also suggested previously (Bemis et al., 2002; Sautter and Thunell, 1991b). Further background on the geochemistry and visual appearance (including Scanning Electron Microscope (SEM) images; Fig. S4) of encrusted vs. non-encrusted *G. bulloides* is provided in the supplemental information.

The B/Ca and Mg/Ca values of these encrusted *G. bulloides* are within the range of the non-encrusted *G. bulloides* (Table S2, Fig. S3), making it appropriate to include both the encrusted and non-encrusted *G. bulloides* in the B/Ca calibrations. Studies based on regions or time-periods which clearly have only non-encrusted *G. bulloides* (e.g. in the tropics and subtropics) may prefer to use calibrations that exclude the encrusted *G. bulloides* (shown in Section 4.4). However, for studies in areas or time-periods where/when both encrusted and non-encrusted *G. bulloides* occur

(e.g. areas where the proportion of the two types varies based on glacial–interglacial cycles or seasonal hydrographic changes), it is important to use calibration equations that include the encrusted *G. bulloides*. Therefore, we report linear regressions of core-top data with Ω_{calcite} and $[\text{CO}_3^{2-}]$ that combine both non-encrusted ($n = 27$) and encrusted ($n = 5$) *G. bulloides*:

$$\text{B/Ca} = \Omega_{\text{calcite}} * 13.37(\pm 1.304) - 11.31(\pm 5.215) \\ (r^2 = 0.78) \quad (8)$$

$$\text{B/Ca} = [\text{CO}_3^{2-}] * 0.313(\pm 0.031) - 11.127(\pm 5.268) \\ (r^2 = 0.77) \quad (9)$$

where B/Ca is in $\mu\text{mol/mol}$, Ω_{calcite} is unitless, and $[\text{CO}_3^{2-}]$ is in $\mu\text{mol/kg}$.

4.7. Preservation of B/Ca and Mg/Ca signals in *N. incompta* and *G. bulloides*

We find no evidence that *N. incompta* or *G. bulloides* B/Ca values are affected by post-depositional dissolution, as their B/Ca values do not correlate with $\Delta[\text{CO}_3^{2-}]$ or core-top water depth (Fig. 2A,B). A dissolution effect on B/Ca in low saturation conditions has been observed in some studies and/or some species (Coadic et al., 2013; Hönisch and Hemming, 2004; Seki et al., 2010) but is absent in other studies (Foster, 2008; Henahan et al., 2015; Wara et al., 2003). It is likely that, similar to Mg/Ca, susceptibility of B/Ca to post-depositional dissolution varies across different foraminifera species, as other work also suggests (Dai et al., 2016).

A depth-related dissolution effect on *N. incompta* Mg/Ca values is suggested by correlation of *N. incompta* Mg/Ca with water depth and $\Delta[\text{CO}_3^{2-}]$ (Fig. 2C,D), and by an average Mg/Ca temperature $7^\circ \pm 3^\circ\text{C}$ lower than the average $\delta^{18}\text{O}$ temperature using the von Langen et al. (2005) Mg/Ca calibration, or 6°C lower using the Mg/Ca calibration of Elderfield and Ganssen (2000), and 4°C for that of Nürnberg et al. (1996). This implies that carbonate system reconstructions using *N. incompta* that require reconstructed temperature need to use a different temperature proxy than Mg/Ca unless the samples are from conditions with high bottom water $\Delta[\text{CO}_3^{2-}]$ (and therefore not subject to alteration of Mg/Ca). By comparison, *G. bulloides* Mg/Ca-derived temperatures are within $<2^\circ\text{C}$ of $\delta^{18}\text{O}$ temperatures on average, and are uncorrelated with water depth or $\Delta[\text{CO}_3^{2-}]$ (Fig. 2C, D). Our results agree with those of Mekik et al. (2007), who found that Mg/Ca in *Neogloboquadrina dutertrei* from the equatorial Pacific is lower in low $\Delta[\text{CO}_3^{2-}]$ waters, but that Mg/Ca in *G. bulloides* did not vary with $\Delta[\text{CO}_3^{2-}]$.

4.8. Study limitations and suggestions for future proxy application

Empirical proxy calibrations using core-top foraminifera provide the most direct link to down-core samples, as the samples reflect the complete foraminiferal life cycle in natural marine environments and the effects of sinking in the water column and residence in the sediment, which cultured or sediment trap foraminifera cannot show, but are experienced by all down-core samples. However, core-top studies are limited by uncertainty in the growth conditions of the foraminifera, particularly because of the dearth of subsurface carbonate chemistry measurements in many regions, and because it is unclear how earlier calcification conditions compare to today. Another limitation arises from uncertainty in the depth habitat of foraminifera, which may be reasonably well constrained using temperature proxies from foraminiferal calcite, but requires high-quality local subsurface water data, and understanding of the potential seasonality of foraminiferal growth.

The spatial and temporal resolution of open-ocean hydrographic data applied in this calibration could be improved. For example,

though the GLODAP (Key, 2004) interpolated carbonate system data are the best available for many regions in this study, their spatial resolution is sometimes low, and they are often not suitable for coastal sites, so we were forced to omit eight samples from our calibrations for lack of appropriate carbonate system data. Fortunately, because of their high spatial and temporal resolution, the high-resolution regional water datasets we used for Southern California, Washington State, and British Columbia (Feely et al., 2008; Patsavas et al., 2015; D. lanson, pers. comm.) are much more appropriate; such measurements are needed for other regions. Further, calcification depths selected for some core-top samples are poorly constrained, particularly for samples in which literature-based depths were assigned when neither Mg/Ca nor $\delta^{18}\text{O}$ temperatures yielded calcification depths in agreement with prior studies. Finally, further studies constraining post-depositional effects (e.g. Mg/Ca dissolution) are needed for more species of foraminifera to better determine calcification depths.

Core-top calibration studies also experience both limitations and advantages due to their age range. The Holocene age of samples used in this study's calibrations means that the foraminifera pooled in one core-top sample may have been produced over periods from decades to thousands of years. This has the advantage that short-term seasonal or climate variations may be dampened in the B/Ca values. However, the time averaging of the pooled foraminifera in core-top samples does not exactly mirror the temporal range of the modern water data used in this study, as these measurements represent episodic, non-continuous recent water column measurements. In addition, while water data derived from GLODAP/WOA and interpolated using ODV's 3D interpolation tool are the best data available, the data's time frames averaged differ for each site, and represent a potential source of error. This results in some uncertainty about how earlier core-top calcification conditions compare to the modern measurements of water conditions.

We caution that if embarking on a down-core record from regions not thoroughly treated in this study, one should first assess the modern carbonate chemistry and modern planktic foraminiferal B/Ca from the region to confirm that the relationships found in this study apply. For example, B/Ca- Ω_{calcite} relationships are less well constrained for coastal waters near Chile, New Zealand, and the southeast Pacific; these regions require further study and data to improve applications of this proxy. However, we observed robust regional B/Ca- Ω_{calcite} relationships in Southern California, the Gulf of California, and the Eastern Equatorial Pacific; our calibrations may be applied there to reconstruct past Ω_{calcite} or $[\text{CO}_3^{2-}]$.

5. Conclusions

Core-top calibration of B/Ca in Pacific Ocean *N. incompta* and *G. bulloides* (subpolar/upwelling asymbiotic planktic foraminifera species) shows a strong significant correlation with seawater calcite saturation (Ω_{calcite}) and carbonate ion concentration ($[\text{CO}_3^{2-}]$) across diverse environmental conditions. As Ω_{calcite} is a direct regulator and indicator of calcite precipitation rate, this suggests that precipitation rate regulates the incorporation of boron into planktic foraminiferal calcite in these species. This agrees with several recent studies of inorganically-precipitated calcite which show a strong control of precipitation rate on B/Ca, and agrees with the mechanistic explanation of trace element incorporation into CaCO_3 described in the surface entrapment model (SEMO; Watson, 2004).

Though we find significant correlations of B/Ca with seawater $[\text{B}(\text{OH})_4^-]$, $[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]$, and $[\text{B}(\text{OH})_4^-/\text{DIC}]$, these are weaker than the correlation of B/Ca with Ω_{calcite} . Given the experimental and theoretical evidence for a calcification rate control over B/Ca, it is likely that the relationship between these parameters and B/Ca is due to their correlation with Ω_{calcite} . B/Ca is not signif-

icantly correlated with pH in either species, suggesting that while pH controls the speciation of boron and inorganic carbon in seawater, other factors regulate the amount of boron taken up into planktic foraminiferal carbonates; thus, planktic foraminiferal B/Ca should not be used to reconstruct pH directly. B/Ca in *N. incompta* and *G. bulloides* shows no evidence of being impacted by dissolution in low $\Delta[\text{CO}_3^{2-}]$ bottom waters.

This study finds little or no correlation of the boron partition coefficient K_D with $[\text{CO}_3^{2-}]$ or temperature. Like studies of cultured planktic foraminifera (Allen et al., 2012, 2011), our results suggest that application of a calibrated K_D (whether constant or variable) is not suitable for calculating carbonate system parameters for the Pacific Ocean using these species, or perhaps generally. Instead, our results provide the first empirical calibration directly relating B/Ca to Ω_{calcite} (or $[\text{CO}_3^{2-}]$) in core-top planktic foraminifera, which agrees with new mechanistic understanding of boron incorporation into carbonates, and can be used to reconstruct the past carbonate system to study past climate and ocean acidification events.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2017.03.007>.

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