

The B/Ca and Cd/Ca of a subsurface-dwelling foraminifera *Pulleniatina obliquiloculata* in the tropical Indo-Pacific Ocean: implications for the subsurface carbonate chemistry estimation

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Abstract

Pulleniatina obliquiloculata shells from 16 core-top samples from the tropical Indo-Pacific Oceans are analyzed for the ratios of boron and cadmium to calcium (B/Ca and Cd/Ca). The B/Ca ratios show a very weak positive relationship with $[B(OH)_4^-]$ and the dissolved carbonate species at the apparent calcification depth of *P. obliquiloculata*. The boron partition coefficients (K_D) between *P. obliquiloculata* B/Ca and seawater $[B(OH)_4^-]/[HCO_3^-]$ distribute around 1.1×10^{-3} – 1.3×10^{-3} with a mean value of $(1.19 \pm 0.12) \times 10^{-3}$, and are significantly related to the nutrient concentration, especially phosphate. The lack of any clear correlation between the *P. obliquiloculata* B/Ca and seawater carbonate chemical parameters suggests that the physiochemical controls on boron incorporation are masked by the complexity of natural seawater condition. But the significant dependence of K_D on nutrient may likely be explained by a nutrient related growth-rate effect. Cd/Ca of *P. obliquiloculata* shows significant correlation with seawater phosphate concentration, and its partition coefficients (D_{Cd}) are significantly related to temperature. A first-principle methodology of *P. obliquiloculata* B/Ca is applied, with the aid of Cd/Ca as a phosphate proxy and a constraint on K_D , to estimating sea water carbonate chemistry (e.g., pH). The results are fairly promising and allow us to propose the possibility to apply the combination of B/Ca and Cd/Ca proxies (and also Mg/Ca and $\delta^{18}O$ for estimating temperature and salinity) for the paleo-reconstruction of seawater carbonate chemistry.

Key words: *Pulleniatina obliquiloculata*, B/Ca, Cd/Ca, paleo-pH estimation

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1 Introduction

The ratio of boron to calcium contents (B/Ca) in foraminiferal shells may be used to reconstruct seawater carbon chemistry because of the theoretical pH-dependency of boron content in carbonate. When dissolved in sea water, boron exists as tetrahedrally-coordinating $B(OH)_4^-$ and trigonally-coordinating $B(OH)_3$, and their relative abundances are pH-dependent due to the reaction: $B(OH)_3 + H_2O = B(OH)_4^- + H^+$, i.e., $[B(OH)_4^-]/[B(OH)_3]$ concentration) increases with increasing pH. Since the primary species of dissolve $B(OH)_3$ boron incorporated into carbonate is believed to be $B(OH)_4^-$ (Vengosh et al., 1991; Hemming and Hanson, 1992), the relative content of boron in carbonate is supposed to increase with pH at constant total dissolved boron (B_T) (Sanyal et al., 2000; He et al., 2013). Assessments of the relationship between solid carbonate B/Ca and the liquid inorganic carbon chemistry has been performed on inorganic calcite (e.g., Sanyal et al., 2000; Uchikawa et al., 2015) and several planktonic

foraminifera species from core-top sediment (e.g., Foster, 2008; Yu et al., 2013; Dai et al., 2016; Quintana Krupinski et al., 2017), sediment traps (e.g., Hendry et al., 2009; Babila et al., 2014; Salmon et al., 2016) and culture experiments (e.g., Allen et al., 2011, 2012, 2016; Henehan et al., 2015; Haynes et al., 2017; Howes et al., 2017). But, regarding the B/Ca ratio, it is still under fierce debate about the fundamental kinetic of boron incorporation, the correlation of B/Ca with sea-water physiochemical parameters, and the practical application of B/Ca proxy.

Owing to different molecular geometries and vibrational frequencies, $B(OH)_3$ is more enriched in ^{11}B than $B(OH)_4^-$ by a constant $\delta^{11}B$ offset of 27.2‰ at equilibrium (Klochko et al., 2006). Since the $\delta^{11}B$ of B_T in modern seawater is at 39.6‰ (Foster et al., 2010), the $\delta^{11}B$ of $B(OH)_3$ and $B(OH)_4^-$ are pH dependent. Based on the close agreement between $\delta^{11}B$ values of either biogenic or synthetic $CaCO_3$ and the $B(OH)_4^-$ of seawater or other experimental solutions (Vengosh et al., 1991; Hemming and Hanson,

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1992; Sanyal et al., 1996, 2000, 2001; Henehan et al., 2013), as well as the positive correlation of the boron content in synthetic CaCO_3 with the solution pH and B_T (Hemming et al., 1995; Sanyal et al., 2000; He et al., 2013) (raising B_T at constant pH increases both $[\text{B}(\text{OH})_4^-]$ and $[\text{B}(\text{OH})_3]$, while raising pH at constant B_T increases $[\text{B}(\text{OH})_4^-]$ but decreases $[\text{B}(\text{OH})_3]$), it was suggested that $\text{B}(\text{OH})_4^-$ should be the major species of boron to be incorporated into CaCO_3 lattice: $\text{CaCO}_3 + \text{B}(\text{OH})_4^- \rightarrow \text{Ca}(\text{HBO}_3) + \text{HCO}_3^- + \text{H}_2\text{O}$. The fluid-solid B distribution coefficient “ K_D ” may be expressed as: $K_D = [\text{HBO}_3^{2-}/\text{CO}_3^{2-}]_{\text{solid}} / [\text{B}(\text{OH})_4^-/\text{HCO}_3^-]_{\text{fluid}}$ (Hemming and Hanson, 1992), and simplified later as $K_D = [\text{B}/\text{Ca}]_{\text{solid}} / [\text{B}(\text{OH})_4^-/\text{HCO}_3^-]_{\text{fluid}}$ based on the stoichiometric approximation of $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ in carbonate (Yu et al., 2007).

However, such a mode of B incorporation requires a tetrahedral to trigonal coordination change from $\text{B}(\text{OH})_4^-$ to HBO_3^{2-} , and is controversial because both trigonal and tetrahedral forms of boron were reported to exist in calcite and aragonite (Sen et al., 1994; Klochko et al., 2009) and B may also reside in non-lattice (defect) sites in calcite (Ruiz-Agudo et al., 2012). Moreover, the B abundance in calcite increases with calcite growth rates (Gabitov et al., 2014; Uchikawa et al., 2015). The kinetic enrichment of B at a higher calcification rate could be explained by a “growth entrapment model” which posits the boron incorporation as a competition between the calcite growth rate and the diffusivity of B within the outermost regions of the growing crystals (Watson, 2004; Gabitov et al., 2014), or a “surface kinetic model” which views the boron incorporation as a competition between the calcite precipitation rate and the molecular exchange on the solid-fluid interface through dissolution-reprecipitation cycles (DePaolo, 2011). Uchikawa et al. (2015) suggest that there is a potential threshold of calcification rate, below which the primary pathway of B incorporation is via $\text{B}(\text{OH})_4^-$, and conversely above which incorporation of $\text{B}(\text{OH})_3$ is kinetically enhanced.

Practically, the B/Ca ratio in planktonic foraminiferal calcite was applied to estimate seawater pH via calculation of seawater $[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]$ on the basis of that the partitioning coefficient K_D and at least one more carbonate chemistry parameter (e.g., alkalinity) could be independently constrained or estimated (Yu et al., 2007; Tripathi et al., 2009). However, the temperature effect on K_D was found either positive (Wara et al., 2003; Yu et al., 2007; Tripathi et al., 2009) or negative (Foster, 2008). For cultured planktonic foraminifera, little influence of temperature variations on K_D could be found (Sanyal et al., 1996; Allen et al., 2011, 2012). Factors other than temperature were noted to influence K_D , including seawater $[\text{CO}_3^{2-}]$ (Foster, 2008), foraminifer growth rate (Ni et al., 2007), as well as pH, B_T and salinity (Sanyal et al., 1996; Allen et al., 2011, 2012). In addition, besides $[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]$, the ratio of borate to dissolved inorganic carbon (DIC) $[\text{B}(\text{OH})_4^-/\text{DIC}]$ could be a controlling parameter for B/Ca due to the potential incorporation of CO_3^{2-} ion into calcite (Allen and Hönisch, 2012; Allen et al., 2012). While, in practical terms the difference between using $[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]$ and $[\text{B}(\text{OH})_4^-/\text{DIC}]$ is negligible as DIC is composed mainly of HCO_3^- under typical seawater conditions.

Recently, several planktonic foraminifera culture studies have been conducted to investigate direct linkages of B/Ca with seawater properties and shown that B/Ca can be positively correlated to pH, $[\text{B}(\text{OH})_4^-/\text{HCO}_3^-]$ and $[\text{B}(\text{OH})_4^-/\text{DIC}]$, and potentially negatively correlated to DIC (Allen et al., 2011, 2012; Henehan et al., 2015; Haynes et al., 2017; Howes et al., 2017). However, these relationships are usually lost or largely weakened in plank-

ton tows or sedimentary samples (e.g., Haynes et al., 2017; Quintana Krupinski et al., 2017). On the basis of foraminifera samples from plankton tows, sediment traps and core-top sediments, it is found that phosphate concentration $[\text{PO}_4^{4-}]$ strongly affects the B/Ca of *Globigerinoides ruber* (Henehan et al., 2015), test thickness correlates well with the B/Ca of several spinose planktonic foraminifera (*Orbulina universa*, *G. ruber* pink and *Globorotalia truncatulinoides*) (Salmon et al., 2016), and seawater calcite saturation (Ω_{calcite}) significantly determines the B/Ca of *G. bulloides* and *Neogloboquadrina incompta* (Quintana Krupinski et al., 2017). These observations may imply a growth rate control on the B/Ca of planktonic foraminifera. When applying the laboratory-based empirical calibrations of the B/Ca proxy directly with carbonate system parameters for marine sedimentary samples, several difficulties may be met: (1) many physiochemical parameters co-vary in seawater, (2) other environmental factors may mask the relationships found in laboratory; and (3) the chemistry of the calcification pool may deviate from the ambient seawater due to species-specific biological processes (i.e., vital effect).

Therefore, although cultured foraminifera and synthesized carbonate experiments can provide empirical evidences about the physiochemical controls on B/Ca, measurements on the field samples are also important for the practical usage of this proxy for sediment-based paleo-reconstructions. By far, several studies have been performed for photosymbiont-bearing and mixed-layer dwelling species of planktonic foraminifera (Allen et al., 2011, 2012; Babila et al., 2014; Henehan et al., 2015; Haynes et al., 2017; Howes et al., 2017). But the B/Ca calibration work has been under-studied for asymbiotic and subsurface dwelling species (Yu et al., 2013; Quintana Krupinski et al., 2017), whose carbonate chemistry is supposed to be simpler due to the lack of symbiont photosynthesis. The subsurface dwelling planktonic foraminifera carry key information about the water beneath the mixed-layer, and thus would help to better understand the ocean-atmosphere interaction in terms of upper-water vertical carbon exchange.

In this study, we focus on *P. obliquiloculata*, a subsurface dwelling planktonic foraminifer that has been deployed for reconstructions of the thermocline condition in low-latitude oceans (Prell and Damuth, 1978; Kennett et al., 1985; Jian et al., 2000; Xu et al., 2008). B/Ca of *P. obliquiloculata* was proved to be barely affected by post-depositional dissolution effect (Dai et al., 2016). We analyze the B/Ca and Cd/Ca ratios of *P. obliquiloculata* taken from 16 core-top samples from the tropical western Pacific, Indian and Atlantic Oceans. Our results may provide practical constraints for the paleoceanographic application of B/Ca and Cd/Ca proxies to reconstruct subsurface water carbonate chemistry and nutrient concentration.

2 Methods

2.1 Materials

The core-top samples were collected from the sediment core repository of LSCE (Laboratoire des Sciences du Climat et de l'Environnement/IPSL) and two Chinese cruises (Table 1). These cores were retrieved from sub-basins or sea-mounts above the calcium compensation depth (water depth less than 3 000 m) (Table 1). The samples range over the tropical western Pacific and Indian Oceans (Fig. 1, with one tropical North Atlantic sample), where modern seawater properties in the water column, including alkalinity and total CO_2 , are determined (Table 1). All these core-top samples are younger than 2 ka, based on AMS ^{14}C

Table 1. Core-top *P. obliquiloculata* results and related seawater parameters

Site	Location	WD/m	<i>P. obliquiloculata</i> results										Seawater parameters					
			PoCD/m	$\delta^{18}\text{O}/\text{PDB}\%$	MSW/ μg	(B/Ca)/ $\mu\text{mol}\cdot\text{mol}^{-1}$	(Mg/Ca)/ $\text{mmol}\cdot\text{mol}^{-1}$	(Cd/Ca)/ $\mu\text{mol}\cdot\text{mol}^{-1}$	T/°C	S	[SiO ₄ ⁴⁻]/ $\mu\text{mol}\cdot\text{kg}^{-1}$	[PO ₄ ³⁻]/ $\mu\text{mol}\cdot\text{kg}^{-1}$	[NO ₃ ⁻]/ $\mu\text{mol}\cdot\text{kg}^{-1}$	ALK/ $\mu\text{mol}\cdot\text{kg}^{-1}$	TCO ₂ / $\mu\text{mol}\cdot\text{kg}^{-1}$			
1 ERDC-92-BX	2.2°S, 157.0°E	1 598	125	-1.39	48.1	56.33±2.10	2.79±0.16	0.0353±0.0048	27.20	35.39	3.56	0.63	6.98	2 309.2	2 051.4			
2 MD00-2358	12.3°S, 112.7°E	2 520	75–100	-0.51	31.8	56.30±1.28	1.91±0.12	0.0581±0.0034	23.55	34.63	9.91	0.48	5.14	2 280.2	2 008.1			
3 MD00-2359G	9.2°S, 114.7°E	2 775	50	-1.48	38.5	60.07±2.75	2.30±0.05	0.0318±0.0020	26.06	34.52	7.79	0.22	1.70	2 276.5	1 963.1			
4 MD77-176	14.5°N, 93.1°E	1 375	30–50	-2.54	25.6	54.25±0.64	2.42±0.11	0.0394±0.0035	27.48	32.86	3.43	0.13	0.15	2 277.1	1 946.0			
5 MD77-191	77.5°N, 6.7°E	1 254	30–50	-1.9	28.7	61.63±2.25	2.42±0.04	0.0250±0.0038	27.50	34.91	4.59	0.47	3.36	2 311.2	2 010.9			
6 MD79-255 CP	19.0°S, 37.5°E	1 226	50	-0.71	36.1	62.75	1.86	0.0134	24.87	34.25	3.19	0.29	0.86	2 307.8	1 998.7			
7 MD79-257	20.4°S, 36.3°E	1 262	50	-1.03	32.6	61.89	2.06	0.0115	24.66	34.16	3.15	0.32	0.97	2 310.8	2 000.5			
8 MD98-2165	9.7°S, 118.3°E	2 100	75	-1.82	22.9	63.22	2.14	0.0384	24.48	34.47	12.60	0.70	8.81	2 282.3	1 995.6			
9 MD98-2188	14.8°N, 123.5°E	730	75	-1.38	25.3	65.41±1.74	2.77±0.16	0.0109±0.0021	26.71	34.17	6.09	0.16	0.96	2 278.0	1 954.1			
10 MD10-3336	2.3°N, 126.2°E	1 485	75	-1.38	17.2	60.63±1.26	2.11±0.09	0.0375±0.0190	26.66	34.57	4.41	0.41	3.33	2 278.1	1 983.7			
11 MD10-3340	0.5°S, 128.7°E	1 094	50–75	-2.07	20.8	61.75±0.62	3.04±0.17	0.0145±0.0029	27.88	34.39	2.36	0.46	2.71	2 270.6	1 960.2			
12 WNP-1	15.1°N, 123.8°E	2 400	100	-1.22	26.9	48.78±0.03	2.43±0.11		25.50	34.40	8.13	0.21	2.33	2 284.7	1 971.9			
13 WNP-2	15.2°N, 122.7°E	2 410	75		20.6	57.67	2.30	0.0153	26.57	34.16	10.11	0.13	1.35	2 278.4	1 960.3			
14 WNP-3	17.6°N, 122.7°E	2 701	75	-1.21	16.9	55.52±0.30	2.09±0.02	0.0176±0.0006	25.41	34.13	7.28	0.23	0.65	2 277.9	1 966.6			
15 KX21-2	1.4°S, 158.0°E	1 588	100	-1.57	64.02	64.02	2.78	0.0329	26.59	34.86	2.67	0.48	4.41	2 301.9	2 024.2			
16 INMD-48-BX-1	29.8°N, 316.8°E	2 836	50	0.05	46.9	65.94±2.11	2.10±0.15	0.0069±0.0031	23.30	34.82	0.90	0.03	0.10	2 412.6	2 075.3			

Note: WD represents water depth, Alk alkalinity, PoCD predicted *P. obliquiloculata* calcification depth, PDB Pee Dee Belemnite standard, MSW mean shell weight. Temperature and salinity data from SODA2.1.6 (Carton and Giese, 2010), nutrient data from WOA09 (Garcia et al., 2010). Alkalinity and total CO₂ (TCO₂) data from GLODAP (Key et al., 2004) (anthropogenic CO₂ eliminated, Sabine et al., 2004).

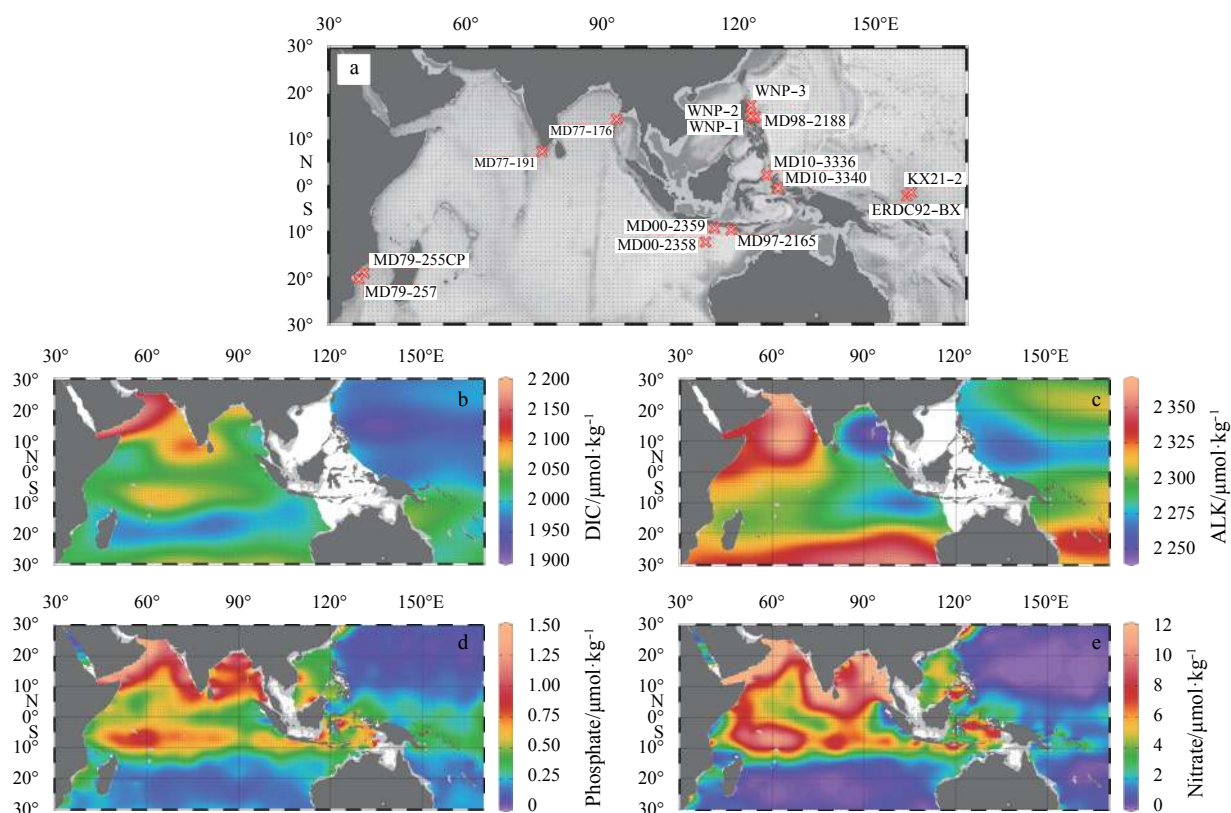


Fig. 1. Site locations (a), spatial distributions of total CO₂ (b, DIC) and alkalinity (c, ALK) (GLODAP), and the annual mean phosphate (d) and nitrate (e) (WOA09), at 75 m water depth over the tropical Indian and western Pacific Oceans.

dates and $\delta^{18}\text{O}$ stratigraphy.

2.2 Laboratory analyses

More than 24 clean and intact *P. obliquiloculata* tests were picked from the 350–450 μm size fraction of each sample. The specimens were weighted by a Sartorius microbalance scale and then gently cracked, and the fragments were well mixed. One third (>0.15 mg) of the fragments were cleaned by ultrapure water (18.2 M Ω) and methanol in ultrasonic bath, and analyzed on a MAT252/253 for $\delta^{18}\text{O}$. The $\delta^{18}\text{O}$ analyses were monitored by China National Standard GBW04405, and converted to PDB standard via NBS19. The analytical error of $\delta^{18}\text{O}$ is 0.07‰ (1σ) by replicate measurements on GBW04405 (Cheng et al., 2005).

The other two thirds (>0.3 mg) were cleaned following the “Cd-cleaning” protocol (Martin and Lea, 2002; Rosenthal et al., 2004). After cleaning, we inspected all samples under a microscope and removed all shell fragments attaching possible contamination (e.g., dark minerals, brownish clusters). All sample handling following crushing was done in a laminar flow fume hood in the air-cleaned laboratory, and samples were kept closed in vials to avoid possible contamination from the air. All the plasticwares used for the pretreatment processes were pre-washed by ultrapure water and 10 mol/L nitric acid (optima grade), to remove all possible contaminations.

The elemental ratios were analyzed on a Thermo-X7 ICP-MS following a method revised from Yu et al. (2005). Samples were fully dissolved on the day of measurement by 300 μL of 0.075 mol/L nitric acid (optima grade), then 50 μL of the solutions were mixed with 50 μL 0.075 mol/L nitric acid and then measured for a first-run to acquire the calcium concentration. For the final measurement, the [Ca] of all samples were diluted to 100×10^{-6} , or 60×10^{-6}

if the concentrations were low, and the total volume of the samples is kept larger than 350 μL to ensure at least five runs for each sample. The calibration equations of the element to calcium ratios were established by a matrix of standards with varying [Ca] of 60×10^{-6} and 100×10^{-6} for each element. Between every three samples, one consistency standard is inserted to monitor and correct the drifting and mass bias effects. The mean relative uncertainties of *P. obliquiloculata* B/Ca, Mg/Ca and Cd/Ca are 2.3%, 4.4% and 18.7% (2σ), respectively, indicated by 11 replicate samples. The relatively large uncertainty in Cd/Ca results relates to the low cadmium content in foraminifera shells, and perhaps to the remnant contamination due to diagenetic oxides.

2.3 Main apparent calcification depth of *P. obliquiloculata*

The main calcification depth of *P. obliquiloculata* was believed to situate mainly in the seasonal thermocline (e.g., Xu et al., 2006 and references therein). However, recent tropical Indo-Pacific core-top study and plankton tow observations reveal that the calcification depth of *P. obliquiloculata* may fluctuate between 30 and 150 m. Therefore, in this study, we calculated the inorganic carbonate $\delta^{18}\text{O}$ by seawater temperature and salinity (McCrea, 1950), where the salinity was converted to seawater $\delta^{18}\text{O}$ using the region-specific equations of LeGrande and Schmidt, (2011). Then we compared the measured shell $\delta^{18}\text{O}$ of *P. obliquiloculata* with the predicted inorganic carbonate $\delta^{18}\text{O}$. Consequently, we can define the main apparent calcification depth of *P. obliquiloculata* as the depth where minimal differences between the shell and inorganic carbonate $\delta^{18}\text{O}$ are found (Dang et al., 2018). Accordingly, for the following seawater carbonate system calculations and related discussions, we will always deal with the related seawater parameters at the defined ap-

parent calcification depths (Table 1).

2.4 Seawater CO₂ chemistry calculation

For each site, the seawater temperature and salinity (from SODA2.1.6) (Carton and Giese, 2010), and the concentrations of nutrients (from WOA09) (Garcia et al., 2010) are retrieved from the most nearby grid point (1°×1° grids). Seawater alkalinity and DIC are taken from the most nearby GLODAP grids (Key et al., 2004). The other parameters of seawater CO₂ system are calculated by CO2Sys V2.1 (Lewis and Wallace, 1998) (the physiochemical constants for the calculations are selected based on the default settings of the program and the units of parameters used in this study). The uncertainties of temperature, salinity, nutrients, alkalinity and total CO₂ are given by the respective datasets. The 2σ error of seawater [B(OH)₄⁻], [HCO₃⁻], [CO₃²⁻] are estimated by Monte Carlo simulations, using 3 000 random sub-samples.

3 Results and discussion

3.1 *P. obliquiloculata* B/Ca and the carbonate system parameters

The B/Ca of our core-top *P. obliquiloculata* samples range between 49 and 66 μmol/mol (Table 1). The *P. obliquiloculata* B/Ca values of this study are comparable to the observations on other subsurface foraminifer species (Henehan et al., 2016), e.g., *N. dutertrei* from tropical eastern Pacific and Atlantic core-tops

(B/Ca=48–62 μmol/mol) (Foster, 2008), and *N. pachyderma* (sinistral) from North Atlantic core-tops (B/Ca=56–67 μmol/mol) (Yu et al., 2013) and a sub-Antarctic sediment trap (B/Ca=45–77 μmol/mol) (Hendry et al., 2009). However, *P. obliquiloculata* B/Ca results from the tropical Indo-Pacific in this study are slightly lower than those from the Ontong-Java Plateau and Mauritius-Mascarene Seas (62–74 μmol/mol) (Dai et al., 2016), which were performed on smaller *P. obliquiloculata* tests (300–355 μm).

We plotted the *P. obliquiloculata* B/Ca against parameters of the seawater carbonate system at the defined main apparent calcification depth, including pH, [CO₂] (aqueous CO₂), Ω_{calcite}, [B(OH)₄⁻], and the dissolved inorganic carbon species and their ratios to [B(OH)₄⁻] (Fig. 2). By and large, B/Ca variation is insensitive to all these carbonate system parameters, while the highest correlation coefficients are found in B/Ca-DIC (r²=0.110) and B/Ca-[HCO₃⁻] (r²=0.060) and may suggest positive relationships between the respective parameters, although the correlations may not be that significant. (Fig. 2). A significant positive relationship between B/Ca and [B(OH)₄⁻] (or B_T) has been revealed by previous studies of synthesized calcite (e.g., Uchikawa et al., 2015), cultured foraminifera (e.g., Allen et al., 2011, 2012; Haynes et al., 2017; Howes et al., 2017) and surface-sediment foraminifera (e.g., Quintana Krupinski et al., 2017), suggesting the

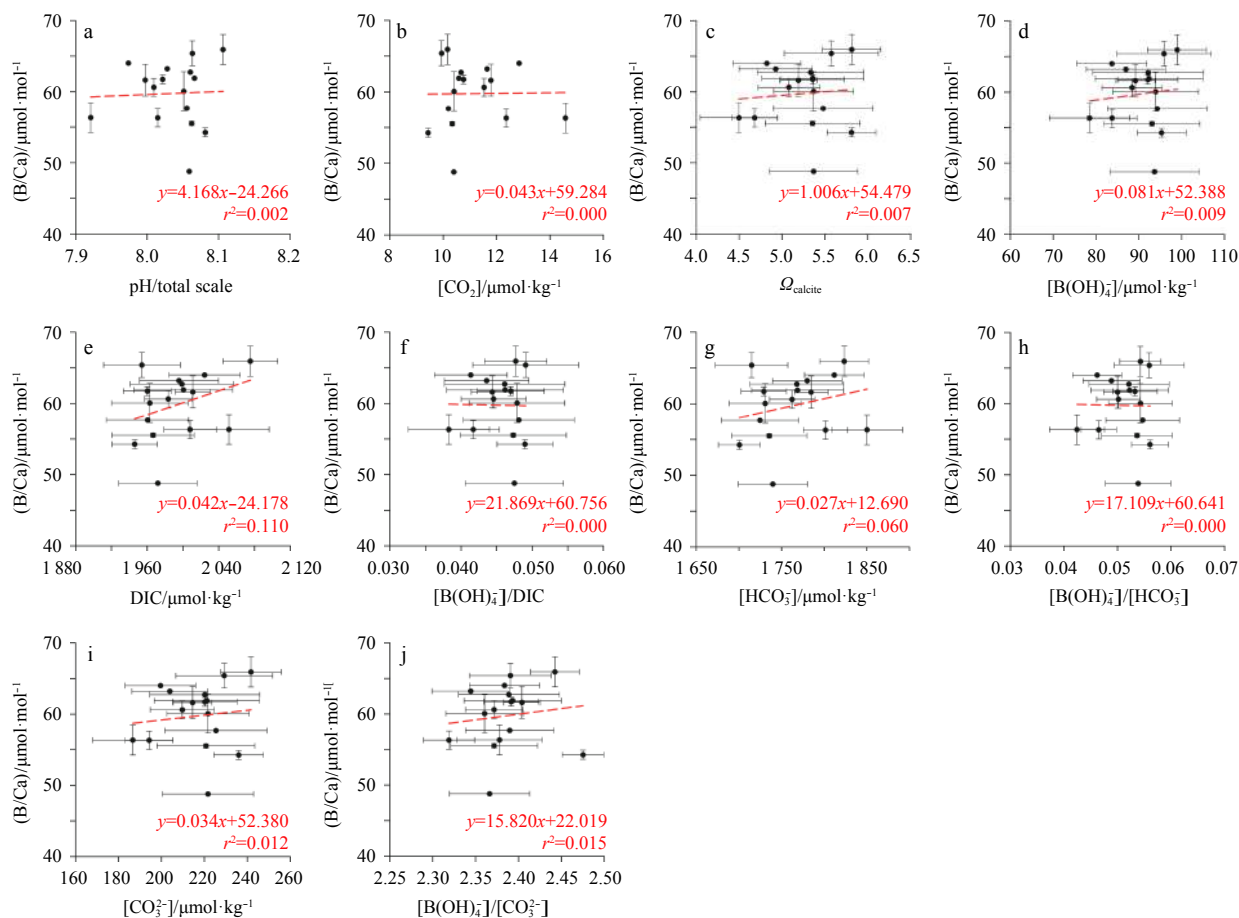


Fig. 2. Plots of *Pulleniatina obliquiloculata* B/Ca vs. pH (a), [CO₂] (b), Ω_{calcite} (c), [B(OH)₄⁻] (d), DIC and [B(OH)₄⁻]/DIC (e and f), [HCO₃⁻] and [B(OH)₄⁻]/[HCO₃⁻] (g and h), and [CO₃²⁻] and [B(OH)₄⁻]/[CO₃²⁻] (i and j). Error bars indicate the measurement uncertainty of B/Ca (2σ) and the standard deviations of seawater carbonate system parameters derived from ocean atlas datasets of nearby grids by a Monte Carlo simulation (N=3 000). The red dashed lines denote the least-squares linear regressions.

dominant influence of the dissolved B concentration on boron incorporation into calcite. However, such an effect is not clear in our results, possibly due to the complication of natural seawater environment. More importantly, it is suggested that some other factors may play a stronger role in the boron incorporation of *P. obliquiloculata* in the tropical Indo-Pacific.

The very weak B/Ca-DIC relationship and the positive B/Ca-[B(OH)₄⁻] relationship contrast with the findings from the planktonic foraminifera culture experiments in which B/Ca decreases with increasing dissolved inorganic carbon (DIC and/or [HCO₃⁻]) (Allen et al., 2012; Haynes et al., 2017). The negative effect of DIC on planktonic foraminifera B/Ca was interpreted as that borate and carbon species compete for the inclusion of boron in the calcite lattice (Howes et al., 2017). But, in the inorganic carbonate experiments, B/Ca of synthesized calcite increases with increasing [DIC] (Uchikawa et al., 2015). Additionally, B/Ca of Pacific core-top *N. incompta* and *G. bulloides* are

also positively related to [DIC] (and Ω_{calcite}) (Quintana Krupinski et al., 2017). The positive effect of DIC on calcite B/Ca was explained by a kinetic effect of the calcite growth rate, which is positively related to DIC and Ω_{calcite} (Uchikawa et al., 2015). Hence, it is implied that potentially the growth rate effect exerts a strong influence on the boron incorporation of *P. obliquiloculata*.

3.2 *P. obliquiloculata* B/Ca and the other related variables

The *P. obliquiloculata* B/Ca was further compared with properties of the shells (mean shell weight, Mg/Ca, Cd/Ca) and parameters of the seawater at the main apparent calcification depth (temperature, salinity, alkalinity and the nutrient concentrations) (Fig. 3). Again, the correlations between B/Ca and these variables are very weak, except for the salinity and the alkalinity which includes some outlying low-salinity and high-alkalinity sites (Figs 3e and f).

The B/Ca ratios of these core-top *P. obliquiloculata* samples

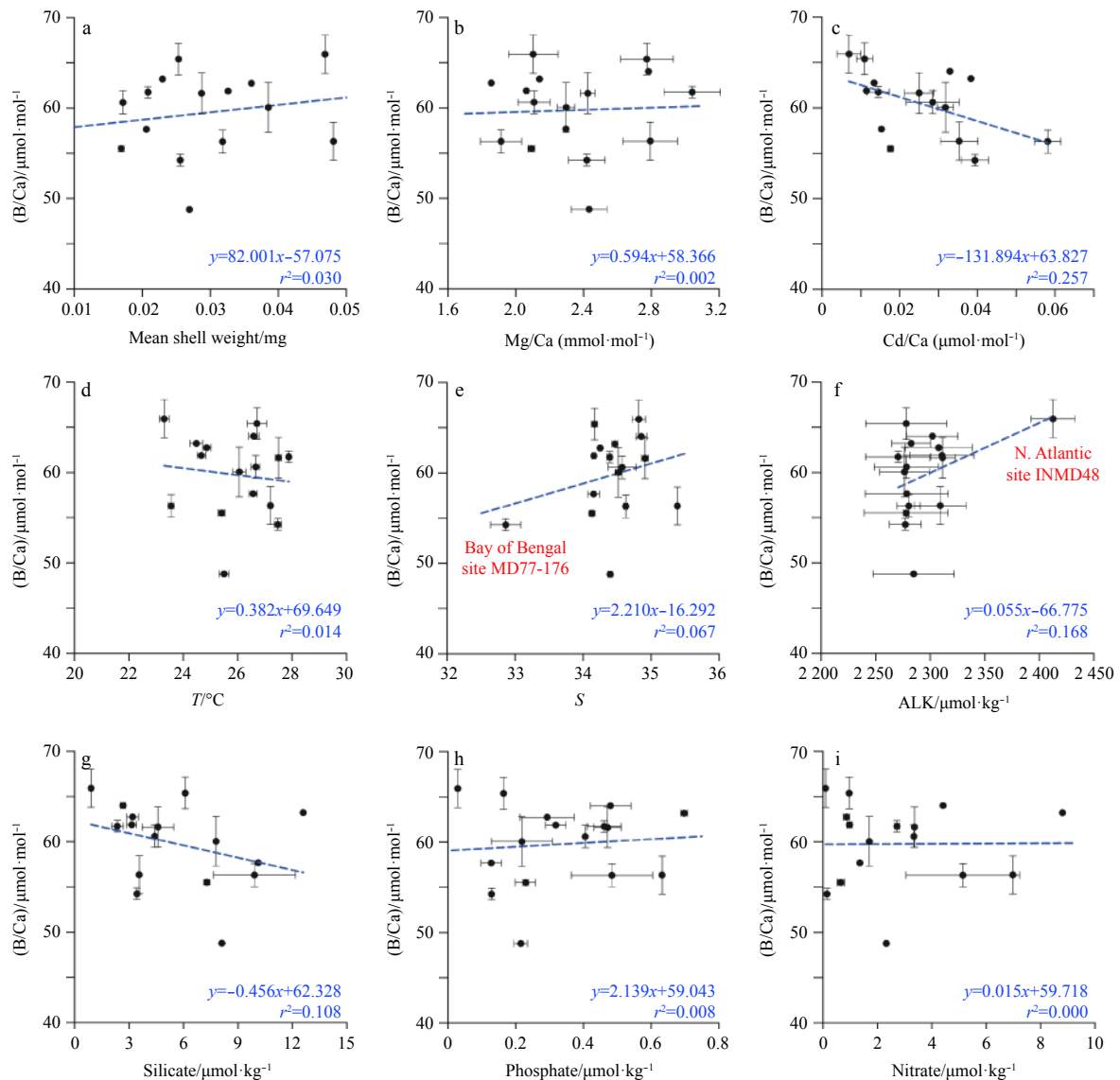


Fig. 3. Plots of *Pulleniatina obliquiloculata* B/Ca vs. mean shell weight (a), Mg/Ca (b), Cd/Ca (c), temperature and salinity (d and e, from SODA2.1.6), total alkalinity (f, from GLODAP), and nutrient concentrations of silicate (g), phosphate (h) and nitrate (i) (from WOA09). The error bars indicate the measurement uncertainty of B/Ca, Mg/Ca and Cd/Ca (2σ) and the standard errors of seawater parameters given by the corresponding data sets. Blue dashed lines denote the least-squares linear regressions.

show a very weak positive relationship with the mean shell weight (Fig. 3a). The *P. obliquiloculata* B/Ca results of Dai et al. (2016) show positive correlations with the shell weight for the Mauritius-Mascarene Sea samples, but negative correlations for those from the Ontong-Java Plateau. So, a rightful correlation between B/Ca and the shell weight is yet to be determined by the limited results.

3.3 *P. obliquiloculata* Cd/Ca and phosphate concentration

On the basis of the preferential incorporation of cadmium (Cd) relative to phosphate (P) during particle formation in the surface ocean and the vertical and latitudinal correlations of the distributions of Cd/P and P, Cd/Ca ratios in foraminifer shells can serve as an indicator of seawater phosphate concentration (Boyle, 1981; Rickaby and Elderfield, 1999; Elderfield and Rickaby, 2000). Our *P. obliquiloculata* Cd/Ca results demonstrate a strong exponential correlation to seawater phosphate concentration ($r^2=0.741$, three outliers excluded, Fig. 4a). The three outlying sites are from seasonal upwelling (MD00-2358, MD00-2359) and permanent upwelling (MD77-176) regions (Figs 1d and e). Their Cd/Ca ratios are abnormally high with respect to the atlas phosphate data (Fig. 4a). The apparent mismatch between Cd/Ca and seawater phosphate of these three sites may be primarily caused by the inappropriate selection of seawater phosphate data caused by factors like seasonal and long-term fluctuation in local upwelling, variations in the habitat depth of *P. obliquiloculata*, etc. Additional uncertainties in Cd/Ca measurements (contamination on specimens, etc.) may also be a problem.

To better constrain the *P. obliquiloculata* Cd/Ca proxy, we calculated seawater [Cd] from seawater phosphate using the relationship defined by Elderfield and Rickaby (2000), $Cd_{sw} = Cd^t / [\alpha \times (P^t/P - 1) + 1]$, where $Cd^t = 1.2$ nmol/kg, $P^t = 3.3$ $\mu\text{mol/kg}$, and $\alpha = 2$. Assuming the seawater Ca concentration to be 0.01 mol/kg (0.412 g/kg), the Cd partition coefficient for *P. obliquiloculata* is estimated as $D_{Cd} = (Cd/Ca)_{\text{foram}} / (Cd/Ca)_{sw}$. The relation between D_{Cd} of *P. obliquiloculata* and temperature is shown in Fig. 4b. The positive exponential correlation observed in this study is consistent with the results of *N. pachyderma* by Rickaby

and Elderfield (1999) and Yu et al. (2013), while there is a constant temperature offset of 23°C between our study and those on *N. pachyderma* (Fig. 4b).

3.4 *P. obliquiloculata* K_D and potential influencing factors

The partitioning coefficient K_D of *P. obliquiloculata* B/Ca is calculated as the ratio between B/Ca and seawater $[B(OH)_4^-] / [HCO_3^-]$ (Fig. 5a). The *P. obliquiloculata* $K_D \times 10^3$ values of this study distribute between 0.9 and 1.4, and centralize around 1.1–1.3 with an average of 1.19 ± 0.12 (2σ) (Fig. 5b). The rather loose correlation between *P. obliquiloculata* B/Ca and $[B(OH)_4^-] / [HCO_3^-]_{\text{seawater}}$ is similar to the observation for *G. ruber* and *N. dutertrei* (Foster, 2008), but different from the tight relations (i.e., K_D is nearly a constant) of *G. bulloides*, *N. incompta* (Quintana Krupinski et al., 2017), *N. pachyderma* (Yu et al., 2013) and *T. sacculifer* (Foster, 2008).

The estimated K_D for *P. obliquiloculata* in this study shows a weak correlation with shell weight ($r^2=0.159$, significance $F=0.4$) (Fig. 6a), but scatters widely versus temperature (Fig. 6b). *P. obliquiloculata* K_D are negatively correlated with seawater $[CO_3^{2-}]$ at its calcification depth to some degree ($r^2=0.37$, not shown), similar to the observations on some other planktonic foraminifers (Yu et al., 2007; Foster, 2008; Allen et al., 2011). The sensitivity (slope of linear fitting) of *P. obliquiloculata* K_D to $[CO_3^{2-}]$ is -0.00526 , in consistency with the results of *N. dutertrei* (-0.0043) but different from those of *G. ruber* (-0.00842) and *T. sacculifer* (-0.00255) (Foster, 2008).

Interestingly, significant positive correlations are observed between *P. obliquiloculata* K_D and the salinity (Fig. 6c) as well as seawater phosphate and nitrate concentrations at its calcification depths (Figs 6e and f), suggesting that B incorporation might be enhanced when the salinity and the nutrients increase. The influence of salinity may be explained via the B_p effect (Uchikawa et al., 2015), as total dissolved boron is tightly linked to salinity (Uppström, 1974; Lee et al., 2010). The correlation is slightly more significant between K_D and phosphate ($r^2=0.438$) than between K_D and nitrate ($r^2=0.357$). Hence, it is implied that the nutrient level within the calcification environment of *P. obliquiloculata* may exert influence on the boron incorporation

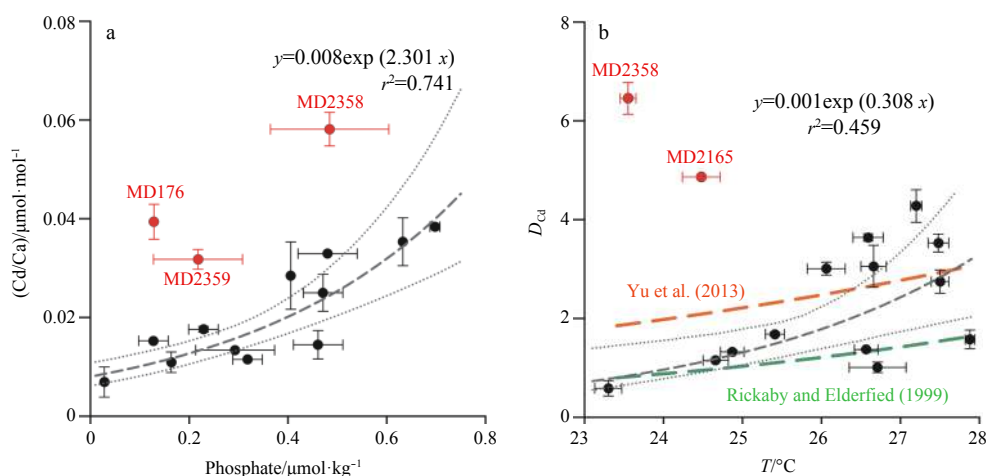


Fig. 4. *Pulleniatina. obliquiloculata* Cd/Ca vs. seawater phosphate concentration (a) and D_{Cd} vs. temperature (b). The error bars indicate measurement uncertainty of Cd/Ca (2σ), propagated error of D_{Cd} (2σ), and the standard errors of phosphate and temperature given by the data sets. The gray dashed lines and the dotted lines denote the least-squares linear regression and 95% confidence levels, respectively. The D_{Cd} - T relations modified from Rickaby and Elderfield (1999) and Yu et al. (2013) yield: $D_{Cd} = 0.75 \exp [0.16 \times (T - 23)]$ and $D_{Cd} = 1.77 \exp [0.112 \times (T - 23)]$, respectively.

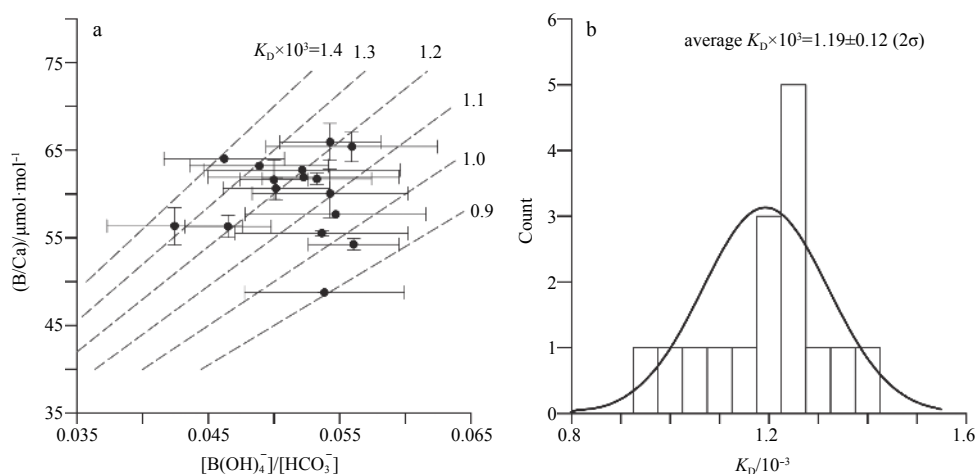


Fig. 5. B/Ca vs. seawater $[B(OH)_4^-]/[HCO_3^-]$ (a) and K_D distribution (b). The error bars indicate the measurement uncertainty of B/Ca (2σ) and the standard deviation of $[B(OH)_4^-]/[HCO_3^-]$ derived from ocean atlas data sets of nearby grids by a Monte Carlo simulation ($N=3\ 000$).

process of this species.

Henehan et al. (2015) had found a similar positive correlation between B/Ca of *G. ruber* and the phosphate concentration, hence they argued that the influence of phosphate on boron incorporation possibly function via: (1) some other hydrographic factors like productivity-related food supply and hence foraminifera growth rate; and/or (2) the kinetic influence of phosphate on crystallographic processes like the promotion effect of phosphate ions on amorphous calcium carbonate formation and/or paired substitution of PO_4^{3-} and $B(OH)_4^-$ for two CO_3^{2-} (Section 4.2 of Henehan et al. (2015) for further discussion and references). Essentially, in terms of the kinetic of carbonate precipitation, phosphate and phosphorous compounds are known to retard $CaCO_3$ precipitation (e.g., Mucci, 1986), but the boron incorporation into calcite is known to be enhanced with increasing precipitation rate (Gabitov et al., 2014; Uchikawa et al., 2015). Hence, it is difficult to explain the positive effect of phosphate on K_D by any simple kinetic influence of phosphate on the calcite formation.

It is noticeable that the *G. ruber* B/Ca of Henehan et al. (2015) only correlates with phosphate concentration, but not any other nutrients like nitrate or silicate. While, in the case of our study, the K_D of *P. obliquiloculata* is significantly correlated with both phosphate and nitrate, but not silicate (Figs 6e and f). So, it is highly likely that K_D of *P. obliquiloculata* is positively linked to the nutrient necessary for calcareous organisms. With higher nutrient, the food supply for *P. obliquiloculata*, a symbiont-barren foraminifer, should increase, and hence results in higher growth rate and enhanced boron incorporation (Gabitov et al., 2014; Uchikawa et al., 2015). Such a conjecture may find support from the positive correlation between K_D and the mean shell weight (Fig. 6a), which should be primarily related to the shell development rather than bottom dissolution, since our *P. obliquiloculata* samples are all taken above the lysocline.

Therefore, our results may provide the first clues that suggest a positive correlation between boron incorporation and calcification rate for *P. obliquiloculata*. The aforementioned relation between B/Ca values and dissolved inorganic carbon species may consistently indicate the role played by the calcification rate. In the natural marine environment, the nutrient may be an important limiting factor for the boron incorporation of *P. ob-*

liquiloculata. Therefore, practically, we may apply nutrient level as an independent variable relating to the calcification rate to supplement the estimation using *P. obliquiloculata* B/Ca proxy to deal with the subsurface seawater carbonate system.

3.5 Estimating seawater pH by the combination of *P. obliquiloculata* B/Ca and Cd/Ca

If K_D could be constrained by a relative independent variable, e.g., temperature (Wara et al., 2003; Yu et al., 2007; Tripathi et al., 2009), seawater carbonate chemical parameters like pH can be reconstructed by B/Ca-estimated $[B(OH)_4^-]/[HCO_3^-]$, with the aid of estimations of at least one more related parameters like alkalinity or $[CO_3^{2-}]$. For the paleo-reconstruction using planktonic foraminifera proxies, temperature and salinity could be calibrated by Mg/Ca and $\delta^{18}O$ (see references in Tripathi et al., 2009). The alkalinity could then be estimated by salinity based on the overall linear relationship between them (Lee et al., 2006; Foster, 2008; Jiang et al., 2014). Hence the seawater CO_2 system may be resolved by the combination of B/Ca, Mg/Ca and $\delta^{18}O$ of planktonic foraminifera (Yu et al., 2007, 2013; Foster 2008; Tripathi et al., 2009).

However, this approach was questioned because of the uncertainty of the temperature effect on K_D (Yu et al., 2007, 2013; Foster 2008; Allen et al., 2011, 2012) and the extra factors besides temperature that may influence boron incorporation and K_D (Henehan et al., 2015; Haynes et al., 2017; Howes et al., 2017; Quintana Krupinski et al., 2017). In the case of this study, the K_D of *P. obliquiloculata* is apparently not affected by temperature, but significantly related to the seawater nutrient level. Therefore, we would like to examine a potential methodology based on the phosphate dependency of *P. obliquiloculata* K_D for calculating seawater carbonate parameters.

We calculated the seawater pH for the study sites, using the modern atlas data of temperature and salinity from SODA2.1.6 (Carton and Giese, 2010), $[PO_4^{3-}]$ from WOA09 (Garcia et al., 2010) and ALK from GLODAP (Key et al., 2004). The pH values are calculated based on the estimated $[B(OH)_4^-]/[HCO_3^-]$ as well as temperature, salinity, alkalinity and pressure at the defined calcification depth, following the approach described by Tripathi et al. (2009). The calculated pH results are shown against the

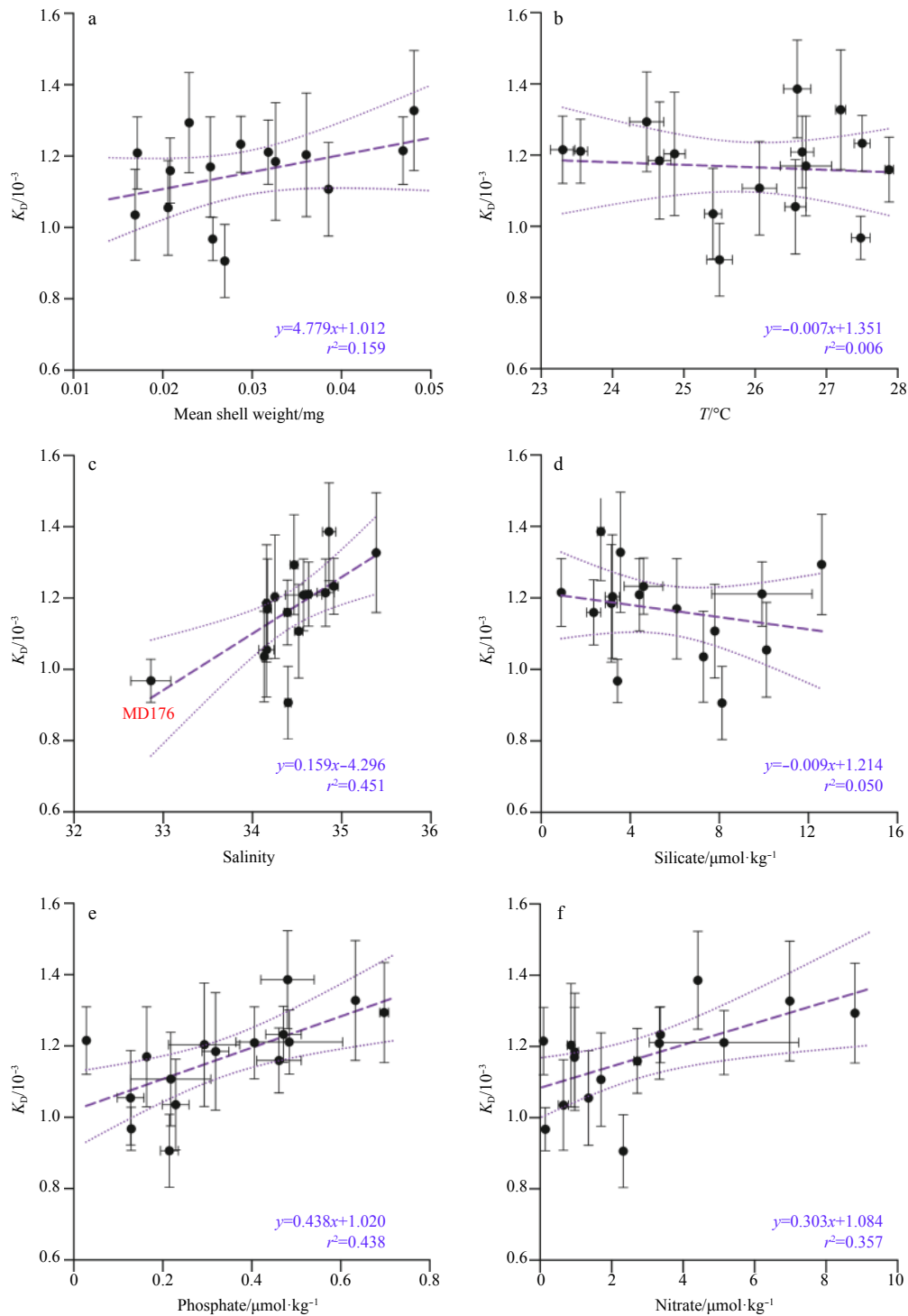


Fig. 6. Plots of *P. obliquiloculata* K_D versus mean shell weight (a), temperature (b), salinity (c), and nutrient concentrations of silicate (d), phosphate (e) and nitrate (f). The error bars are as in Fig. 3. The purple dashed lines and the dotted lines denote the least-squares linear regressions and 95% confidence interval, respectively.

modern seawater pH (GLODAP) in three groups of various K_D : (1) $K_D \times 10^3 = 1.19$ (the mean value) (Figs 7a and b); (2) K_D calibrated by Cd/Ca-derived $[\text{PO}_4^{3-}]$ (Figs 7c and d); (3) K_D estimated by WOA09 $[\text{PO}_4^{3-}]$ (Figs 7e and f). Calculations based on different ALK, from GLODAP (Key et al., 2004) (Figs 7b, d and f) or estimated by $\delta^{18}\text{O}$ -derived salinity ($\text{ALK}=43.173 \times \text{Salinity} + 798.62$, derived from the ALK and salinity data of tropical Indo-Pacific of

GLODAP, Figs 7a, c and e), are also compared. It is demonstrated that an average K_D value is clearly not applicable for the pH estimation, as the results differ largely from the observed seawater pH of GLODAP (Figs 7a and b). While, the Cd/Ca- or $[\text{PO}_4^{3-}]$ -corrected K_D may result in proper pH estimations, as indicated by the significant correlations and close relations with respect to the observed pH (Figs 7c-f). It is further implied that the

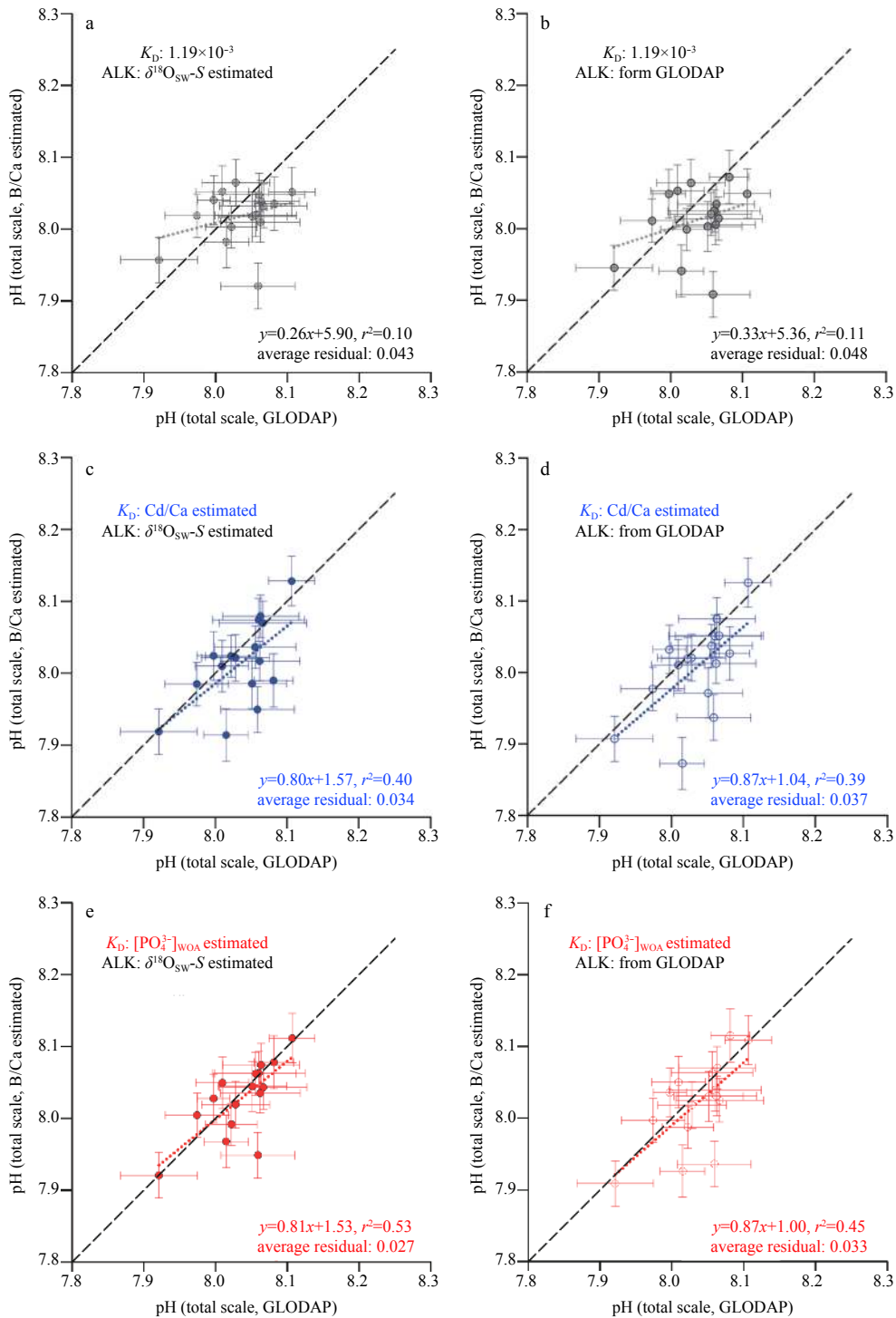


Fig. 7. Comparisons of the *Pulleniatina. obliquiloculata* B/Ca-derived pH vs. the pH of GLODAP (Key et al., 2004). The B/Ca-derived pH is calculated on the basis of various constraints of K_D and different sources of ALK: K_D is set as the mean value (1.19) (a, b) or determined by Cd/Ca-derived phosphate concentration (c, d) and the phosphate concentration from WOA09 (Garcia et al., 2010) (e, f); and ALK are estimated by $\delta^{18}O_{sw}$ -derived salinity (a, c, e) and from GLODAP (b, d, f).

uncertainties of $\delta^{18}O$ -salinity and salinity-alkalinity calibrations may introduce little influence for the pH calculation, at least for the results of this study. Therefore, we may propose that for *P. obliquiloculata* of the tropical Indo-Pacific, a combination of B/Ca and Cd/Ca (as well as Mg/Ca and $\delta^{18}O$) could serve as a rather applicable proxy method for estimating the subsurface seawater pH and the other carbonate system parameters. However, given

the limited number of samples of this study, the calibrations given in this study may need further examination before applying to paleo-reconstructions. The uncertainties of the pH calculation using B/Ca method are large (e.g., Tripathi et al., 2009). The variability of the relationship between salinity and $\delta^{18}O$ would introduce significant uncertainty into the pH calculation, especially for paleo-reconstructions.

4 Concluding remarks

In this study, we reported the B/Ca and Cd/Ca of *P. obliquiloculata* from 16 core-top samples from the tropical Indo-Pacific and attempt to examine the potential factors influencing the boron and cadmium contents of *P. obliquiloculata* shells. The Cd/Ca of *P. obliquiloculata* could be well correlated to the seawater phosphate concentration at the defined calcification depth of this species. The B/Ca of *P. obliquiloculata* shows no significant relation to the seawater carbonate chemical or other physicochemical parameters, except for some weak correlations to dissolved inorganic carbon. The K_D of *P. obliquiloculata* is apparently not affected by the temperature, but increases with increasing mean shell weight, salinity and nutrient level. The relationships between B/Ca and dissolved carbon and between K_D and nutrient may be comprehensively explained by a positive effect of the growth rate on the boron incorporation into *P. obliquiloculata* shells. On the basis of the rather tight correlations of Cd/Ca-phosphate and K_D -nutrient, we established a preliminary calibration method for estimating pH, which might be applied for paleo-reconstructions of the subsurface water carbonate system by the combination of B/Ca, Cd/Ca, Mg/Ca and $\delta^{18}O$ proxies of *P. obliquiloculata*. However, it is cautioned that the empirical calibrations given in this study are only practically robust, further in-depth investigations about the kinetic of boron incorporation and its relation to the carbonate chemistry of the calcifying fluid are needed for *P. obliquiloculata*.

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