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Revisiting the dependence of thermocline-dwelling foraminiferal B/Ca on temperature and $[CO_3^{2-}]$, and its application in reconstruction of the subsurface carbonate system in the tropical western Pacific since 24 ka

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Abstract

The B/Ca ratio of planktonic foraminifer shells has been used as a proxy for reconstructing past ocean carbonate chemistry. However, recent studies have revealed significant uncertainties associated with this proxy, such as whether seawater temperature or $[CO_3^{2-}]$ is the dominant control on the partition coefficient (K_D) of planktonic foraminiferal B/Ca. To address these uncertainties and thus improve our understanding of the planktonic foraminiferal B/Ca proxy, we analysed B/Ca ratios in the tests of *Neogloboquadrina dutertrei* (300–355 μm) and *Pulleniatina obliquiloculata* (355–400 μm) in surface sediment samples from the tropical western Pacific and South China Sea. The relationship between these B/Ca ratios and bottom water calcite saturation states ($\Delta[CO_3^{2-}]$) is weak, thus suggesting only a small dissolution effect on the B/Ca of the two species. The correlation coefficients (R^2) between the B/Ca ratios of *N. dutertrei* and *P. obliquiloculata* and environmental parameters (e.g., temperature, salinity, phosphate, DIC and ALK) in the tropical western Pacific and South China Sea are not high enough to justify using B/Ca ratios as a palaeoenvironmental proxy in the study areas. The significant correlation between K_D values of *N. dutertrei* and *P. obliquiloculata* and carbonate system parameters (e.g., $[CO_3^{2-}]$, DIC, ALK, pH and $[HCO_3^-]$) in the study area reflect chemical links between the K_D denominator and these variables. Based on our surface sediment calibration, an empirical relationship between the K_D of *N. dutertrei* and temperature is proposed in the tropical western Pacific. We also generated a record of B/Ca ratios in *N. dutertrei* (300–355 μm) from Core MD06-3052 in the tropical western Pacific over the past 24 ka to evaluate the application of the revised B/Ca proxy method. Based on the reconstructed empirical relationship for B/Ca and subsurface seawater ALK, we estimated subsurface seawater carbonate system parameters in the tropical western Pacific since 24 ka. In general, the estimated subsurface seawater pH and $[CO_3^{2-}]$ show an increase with time, and the record of subsurface seawater pCO_2 shows a decrease with time, in the tropical western Pacific over the past 24 ka. The consistent trends in subsurface seawater pCO_2 and opal flux during deglaciation may imply that the reported increase in subsurface water pCO_2 in the study area was promoted by enhanced upwelling in the Southern Ocean.

Key words: planktonic foraminifera, B/Ca, carbonate chemistry, tropical western Pacific, South China Sea

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1 Introduction

Reconstructing the carbonate chemistry of seawater requires an understanding of its temperature, salinity, pressure and at least two of the six carbonate system parameters: pH, $[CO_2]$, concentrations of bicarbonate ($[HCO_3^-]$) and carbonate ions ($[CO_3^{2-}]$), total alkalinity (ALK) and total dissolved carbon (DIC). Given that

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direct measurements of past carbonate system parameters are not possible, proxies such as B/Ca ratios of foraminiferal calcite have been developed and applied in this context (Yu et al., 2007, 2010; Foster, 2008; Naik et al., 2010; Foster and Sexton, 2014; Naik et al., 2015). Dissolved boron in seawater is present in two species, boric acid ($B(OH)_3$) and the borate ion ($B(OH)_4^-$), the relative proportions of which are pH-dependent (Dickson, 1990; Klochko et al., 2006). Boron is found mainly in $B(OH)_4^-$ at high pH, and $B(OH)_3$ at low pH. $B(OH)_4^-$ is thought to be the predominant form of boron incorporated into calcium carbonate, and Hemming and Hanson (1992) proposed the following balanced exchange reaction for the substitution of boron into carbonate:

$$CaCO_3 + B(OH)_4^- \longleftrightarrow Ca(HBO_3) + HCO_3^- + H_2O. \quad (1)$$

The partition coefficient, K_D, for this reaction has been defined as follows (Yu et al., 2007):

$$K_D = \frac{[B/Ca]_{CaCO_3}}{[B(OH)_4^-/HCO_3^-]_{seawater}}. \quad (2)$$

Thus, with an accurate constraint on K_D, it should be possible to estimate seawater palaeo-pH using B/Ca ratios in marine calcium carbonate (Yu et al., 2007).

Yu et al. (2007) found that K_D is strongly dependent on calcification temperature. However, later studies found that seawater $[CO_3^{2-}]$ also affects K_D (Foster, 2008). Furthermore, both negative and positive correlations between K_D and temperature have been reported in different studies (Yu et al., 2007; Foster, 2008; Tripati et al., 2009), whereas culture experiments with living planktonic foraminifera suggest that temperature has little influence on K_D (Allen et al., 2011). In addition, Allen and Hönisch (2012) demonstrated that the correlation between K_D and $[CO_3^{2-}]$ is artificial. In summary, there are major inconsistencies in the reported empirical relationships for K_D, which suggest that the factors that control K_D have yet to be identified.

Previous studies on B/Ca ratios in the shells (or "tests") of planktonic foraminifera suggest that boron incorporation is species-specific, which implies a potential influence of symbiosis and/or depth habitat on boron incorporation (Yu et al., 2007; Hendry et al., 2009; Seki et al., 2010; Allen et al., 2011; Allen and Hönisch, 2012). Other factors such as salinity (Allen et al., 2011; Henehan et al., 2015), growth and calcification rates (Ni et al., 2007; Salmon et al., 2016), $[PO_4^{3-}]$ (Henehan et al., 2015), light intensity (Babila et al., 2014) and DIC (Allen and Hönisch, 2012; Haynes et al., 2017) have also been reported as influences on the incorporation of boron into planktonic foraminifera tests. However, Holland et al. (2017), Haynes et al. (2017), and Allen et al. (2016) all suggest that it is likely that B/Ca does not depend on growth rate in cultured planktonic foraminifera. The uncertainties surrounding the fundamental kinetics of boron incorporation again show that the factors controlling planktonic foraminiferal B/Ca remain poorly constrained.

Furthermore, dissolution can significantly affect the ratios of trace elements to calcium (e.g., Mg/Ca and Sr/Ca) in foraminifer tests (Rosenthal and Boyle, 1993; Brown and Elderfield, 1996; Dekens et al., 2002; Regenberg et al., 2006; Johnstone et al., 2010). To quantify the influence of dissolution, Dekens et al. (2002) analysed Mg/Ca in the tests of the planktonic foraminifer species *Globigerinoides ruber*, *G. sacculifer*, and *Neogloboquadrina dutertrei*, and their results suggested that *N. dutertrei* is the most sensitive to dissolution and that *G. sacculifer* is the most resistant. Later, Seki et al. (2010) and Coadic et al. (2013) reported that B/Ca ratios in the tests of *G. sacculifer* can indeed be modified by dissolution, whereas the B/Ca ratios in *G. ruber* tests were not altered (Seki et al., 2010). B/Ca values in tests of *Globorotalia inflata* from the North Atlantic were also reported to be largely resistant to dissolution (Yu et al., 2007). Other studies have also suggested that dissolution effects on planktonic foraminiferal B/Ca are species-specific (Dai et al., 2016). Therefore, the effect of dissolution on B/Ca ratios of planktonic foraminifera, and thus their application in palaeoceanographic reconstructions, remains debated.

The main aim of this study was to investigate the application of the B/Ca proxy to the reconstruction of the seawater carbonate system. To ensure the veracity of the results, we firstly evaluated the effect of dissolution on B/Ca ratios of planktonic foraminifera by exploring the relationship between B/Ca ratios and seawater depth and bottom water calcite saturation states ($\Delta[CO_3^{2-}]$). We used sediment samples from the tropical western Pacific and South China Sea to explore the relationship between planktonic foraminiferal B/Ca and seawater parameters (e.g., temperature, salinity, $[PO_4^{3-}]$, DIC, ALK, pH, $[CO_3^{2-}]$, $[HCO_3^-]$ and $[B(OH)_4^-]$) in the subsurface carbonate system, and we then used these samples to investigate the controls of the seawater parameters on K_D. We focused on two planktonic foraminifera species (*N. dutertrei* and *Pulleniatina obliquiloculata*) and performed measurements on a restricted test size fraction to minimize the influence of growth rate and ontogenetic and species-specific effects on B/Ca (Ni et al., 2007; Yu et al., 2007; Allen and Hönisch, 2012; Salmon et al., 2016). Finally, using our revised empirical relationships for K_D, we undertook down-core measurements of B/Ca ratios in foraminifera tests and reconstructed the subsurface carbonate system of the tropical western Pacific over the past 24 ka.

2 Materials and methods

2.1 *Samples*

We selected 15 surface sediment samples from the tropical western Pacific and South China Sea, including two core-top samples (Fig. 1, Table 1). The core-top samples, MD06-3047B (2–3 cm) and MD06-3052 (6–8 cm), were collected using the Calypso Giant Piston Corer during the International Marine Global Change Studies Program (IMAGES) cruise "Marco Polo 2" on the R/V *Marion-Dufresne* in 2006. Surface sediment samples from the South China Sea and tropical western Pacific were collected using a box corer onboard the R/V *Science No. 1* in 2012 and R/V *Science* in 2015, respectively. From these samples, we picked tests of two planktonic species from two size fractions: *N. dutertrei* (300–355 μm) and *P. obliquiloculata* (355–400 μm). These surface sediment samples were collected from water depths between 128 and 3 556 m (Table 1), thereby providing an ideal opportunity to investigate the effects of dissolution on B/Ca ratios in the two species. In addition, by analysing *N. dutertrei* and *P. obliquiloculata* in the tropical western Pacific and South China Sea we could distinguish the effects of seawater parameters including $[CO_3^{2-}]$ and temperature on B/Ca and K_D and develop empirical relationships for B/Ca in these areas. Following this, we generated a down-core record of B/Ca ratios in *N. dutertrei* (300–355 μm) from core MD06-3052 (Fig. 1) spanning the past 24 ka (based on the age model of Qiu et al. (2014)). We then used our empirical relationships to reconstruct the palaeo-carbonate system in the subsurface waters of the tropical western Pacific over the past 24 ka.

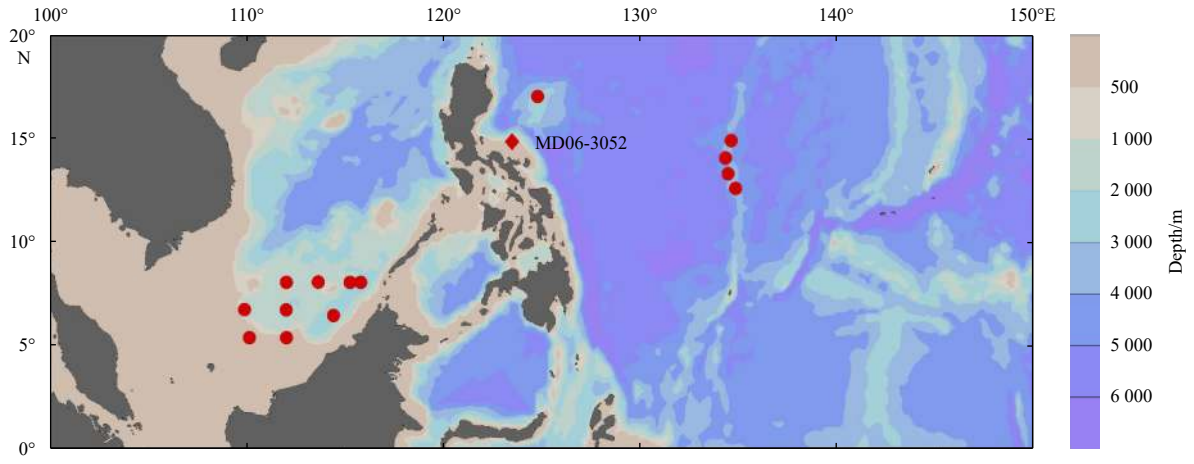

Fig. 1. Locations of surface sediment (red circles) and core sediment (red diamond) samples. The base map was drawn using the ODV (Ocean Data View; http://odv.awi.de) software package.

2.2 *B/Ca measurements*

In this study, 0.3–0.6 mg of foraminifera tests from surface sediment samples were picked for B/Ca analysis. Foraminiferal B/Ca ratios were measured in the State Key Laboratory of Marine Geology, Tongji University. Prior to analysis, the foraminifer tests were gently cracked to open the individual chambers. Clays were removed using methanol. Metal oxides were then removed through a reduction step involving a hydrazine/ammonium citrate solution, and organic material was removed via oxidization using a buffered H_2O_2 solution. Samples were leached with a 0.001 mol/L HNO_3 solution and dissolved in 0.15 mol/L HNO_3 (Lea et al., 2000; Martin and Lea, 2002). B/Ca and Mg/Ca ratios were determined on an inductively coupled plasma mass spectrometry (ICP–MS) following the method of Yu et al. (2005). All samples were measured at 100×10^{-6}[Ca] to avoid potential matrix effect on B/Ca ratios. A standard sample was analysed after every three unknowns to determine the accuracy of the results and to correct for measurement bias such as long-term drift. Based on replicate measurements of the in-house consistency standard, the long-term precision (2σ) was 1.4% for B/Ca and 2.2% for Mg/Ca. Mn/Ca and Al/Ca were also measured to examine the efficiency of the removal steps for Mn-oxyhydroxide coatings and clay. Neither ratio showed a correlation with B/Ca or Mg/Ca ratios, indicating the effectiveness of the cleaning methodology.

2.3 *Hydrological data calculations*

Previous studies have shown that *N. dutertrei* and *P. obliquiloculata* are most abundant in respective water depths of 50–100 m (within the deep chlorophyll maximum; DCM) and 100–200 m in the Western Pacific Warm Pool (Rippert et al., 2016). This is in line with the findings in other ocean basins that *N. dutertrei* inhabits water depths close to the DCM (Ravelo and Fairbanks, 1992; Dekens et al., 2002; Schmuker and Schiebel, 2002; Sadekov et al., 2013) and *P. obliquiloculata* lives in the thermocline (Ravelo and Fairbanks, 1992; Mohtadi et al., 2009; Rincón-Martínez et al., 2011). Thus, modern hydrographic parameters, including temperature (T), $[CO_3^{2-}]$, and $[B(OH)_4^-/HCO_3^-]$ were estimated at depths of 50–100 and 100–200 m for *N. dutertrei* and *P. obliquiloculata*, respectively (Table 1).

Hydrographic data from the vicinity of the study sites were obtained from Ocean Data View (http://odv.awi.de). Modern seawater temperature, salinity, and pressure (or water depth) data were collected from the World Ocean Atlas (WOA 13) database for the tropical western Pacific and South China Sea. DIC, ALK, nutrient levels (PO_4 and SiO_3), and anthropogenic CO_2 data were collected from the Global Ocean Data Analysis Project (GLODAP) (Key et al., 2004) for the tropical western Pacific as well as Global Alkalinity and Total Dissolved Carbon Estimates (Global Alkalinity & TCO_2) (Goyet et al., 2000) for the South China Sea. Temperature, salinity, DIC, ALK and nutrient levels at the study sites were then obtained for water depths of 50, 75, 100, 125, 150, 175 and 200 m by applying the inverse distance weighting method of Henehan et al. (2013) to the hydrographic data of the adjacent sites. Specifically, we calculated the hydrological parameters of the study sites using the following equations (Fig. 2):

$$L_m = \sqrt{(x_m - x_0)^2 + (y_m - y_0)^2} \quad (m = 1, 2, 3, 4), \tag{3}$$

$$L_{\text{total}} = \sum_{m=1}^{4} (1/L_m) \quad (m = 1, 2, 3, 4), \tag{4}$$

$$P_0 = \sum_{m=1}^{4} P_m[(1/L_m)/L_{\text{total}}] \quad (m = 1, 2, 3, 4), \tag{5}$$

where P_0 denotes the hydrological parameters of the study site and P_m (m = 1, 2, 3, 4) denotes the hydrological parameters of the hydrographic data site near the study sites. Furthermore, the $[CO_3^{2-}]$, $[HCO_3^-]$ and $[B(OH)_4^-]$ data from different water depths at the study sites were calculated using CO_2sys.xls (Pelletier et al., 2007). In accordance with previous studies (Yu et al., 2007; Foster, 2008), we selected the carbonic acid dissociation constants (K_1 and K_2) from Mehrbach et al. (1973) as refitted by Dickson and Millero (1987), K_{SO_4} from Dickson (1990), total boron ($[B]_{tot}$) from Uppström (1974), and the total pH scale. Finally, seawater parameters (temperature, salinity, $[PO_4^{3-}]$, DIC, ALK, pH, $[CO_3^{2-}]$, $[HCO_3^-]$, $[B(OH)_4^-]$, $[B(OH)_4^-]$/DIC, $[B(OH)_4^-]/[CO_3^{2-}]$ and $[B(OH)_4^-]/[HCO_3^-]$) values from water depths of 50–100 m (for *N. dutertrei*) and 100–200 m (for *P. obliquiloculata*) at the study sites were obtained by calculating the average values of hydrographic data from different water depths at the study sites; K_D

Table 1. B/Ca ratios of *N. dutertrei* and *P. obliquiloculata* from surface sediment samples*

Core ID	North latitude/(°)	East longitude/(°)	Water depth/m	*N. dutertrei*					*P. obliquiloculata*				
				T/°C	$[CO_3^{2-}]$/ μmol·kg^{-1}	$([B(OH)_4^-/HCO_3^-])$/ mol·mol^{-1}	(B/Ca)/ μmol·kg^{-1}	$K_D/10^{-3}$	T/°C	$[CO_3^{2-}]$/ μmol·kg^{-1}	$([B(OH)_4^-/HCO_3^-])$/ mol·mol^{-1}	(B/Ca)/ μmol·kg^{-1}	$K_D/10^{-3}$
Tropical western Pacific													
3001	14.866 9	134.627 5	3 364	27.51	276.40	0.073 77	69.93	0.948 0	23.56	244.27	0.062 43	61.76	0.989 3
3046	14.028 5	134.338 7	3 407	27.65	275.38	0.073 34	64.79	0.883 3	23.40	237.95	0.060 32	60.49	1.002 9
3091	13.267 6	134.474 3	2 632	27.69	273.35	0.072 59	69.52	0.957 7	23.05	230.61	0.057 95	65.59	1.131 8
3138	12.552 9	134.850 2	3 556	27.67	271.85	0.072 07	66.25	0.919 2	22.80	226.30	0.056 57	63.01	1.113 7
MD06-3047B	17.007 3	124.798 8	2 510	26.48	254.59	0.0657 4	65.85	1.001 6	22.73	224.03	0.056 17	57.26	1.019 4
MD06–3052	14.810 0	123.490 0	732	26.85	248.45	0.063 13	62.35	0.987 6	22.35	211.37	0.052 12	57.65	1.106 2
South China Sea													
C02A09	8.006 7	112.035 2	1 694	23.82	113.28	0.028 18	52.60	1.866 6	17.78	95.66	0.022 47	52.90	2.353 6
C02A15	8.013 1	113.649 0	1 825	24.05	107.78	0.026 84	56.84	2.117 6	17.83	92.59	0.021 70	52.88	2.437 3
C02A21	8.005 9	115.263 5	2 240	24.25	105.47	0.026 28	53.78	2.046 3	17.91	89.75	0.020 99	54.71	2.606 8
C02A23	8.000 6	115.801 2	2 551	24.42	104.88	0.026 12	55.73	2.133 8	18.00	87.45	0.020 41	54.95	2.692 1
C02F01	6.682 1	109.897 9	1 398	23.72	118.73	0.029 68	53.60	1.806 0				54.39	
C02F09	6.678 9	112.024 0	1 957	23.85	113.35	0.028 36	49.65	1.750 7	17.88	98.12	0.023 22	49.87	2.147 7
C02G18	6.400 4	114.423 6	2 139	24.03	108.58	0.027 35	54.39	1.988 7	17.84			53.99	
C02K02	5.331 3	110.150 1	148.1	23.65	118.34	0.029 71	54.89	1.847 8				53.91	
C02K09	5.330 4	112.034 7	128	23.82	114.25	0.028 70	53.13	1.851 1				55.94	

Note: * Also shown are modern seawater temperatures, $[CO_3^{2-}]$, $[B(OH)_4^-/HCO_3^-]$, measured B/Ca, and calculated K_D. $[CO_3^{2-}]$ and $[B(OH)_4^-/HCO_3^-]$ were estimated CO_2sys.xls (Pelletier et al., 2007) using the GLODAP (Key et al., 2004), Global Alkalinity & TCO_2 (Goyet et al., 2000), and WOA 13 datasets for 50–100 m water depth for *N. dutertrei* and 100–200 m for *P. obliquiloculata*.

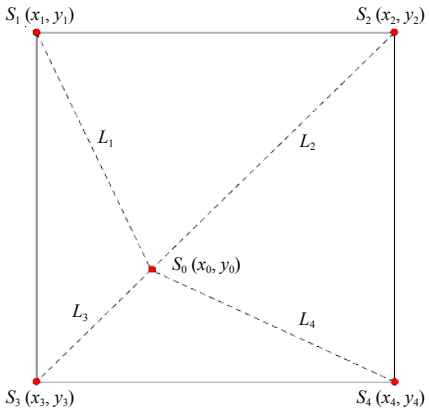

Fig. 2. Schematic diagram showing the hydrological parameter calculations for the study sites. S_0 represents the study site; S_1–S_4 represent hydrographic sites near the study sites; (x, y) represents longitude and latitude, respectively; and L_1–L_4 indicate the distance between the study site and the hydrographic site.

values were then calculated for the planktonic foraminifera using Eq. (2) (Table 1).

In addition, we also estimated bottom water $\Delta[CO_3^{2-}]$ of the study sites using data from the nearby GLODAP sites (Key et al., 2004) for the tropical western Pacific as well as Global Alkalinity & TCO_2 sites (Goyet et al., 2000) for the South China Sea. Assuming constant $[Ca^{2+}]$ in seawater, $\Delta[CO_3^{2-}]$ is defined as: $\Delta[CO_3^{2-}] = [CO_3^{2-}] - [CO_3^{2-}]/\Omega$ (Ω denotes calcite saturation states) (Yu and Elderfield, 2007). Bottom water $[CO_3^{2-}]$ and Ω were calculated using CO_2sys.xls (Pelletier et al., 2007). In this calculation, we used the same constants as for calculating the other seawater parameters.

3 Results

In the tropical western Pacific, $[CO_3^{2-}]$ values in the habitat depths of *N. dutertrei* and *P. obliquiloculata* lie within the ranges 250–280 and 210–245 μmol/kg, respectively. In contrast, in the South China Sea, $[CO_3^{2-}]$ values in the habitat depths of *N. dutertrei* and *P. obliquiloculata* lie within the ranges 105–120 and 85–100 μmol/kg, respectively. Unfortunately, the water depths at the hydrographic sites near some of the study areas in the South China Sea were shallower than 100 m. As a result, the relevant data for *P. obliquiloculata* (whose habitat depth is 100–200 m) could not be calculated (Table 1). Therefore, we reconstruct the correlation of B/Ca and K_D only with some seawater parameters at these sites. On the whole, in the study area, $[CO_3^{2-}]$ values show a clear gradient along the horizontal section and the depth transects, thereby enabling a reconstruction of the empirical relationships for K_D (Fig. 3).

B/Ca ratios in the tests of *N. dutertrei* and *P. obliquiloculata* from all depths in the two study areas agree within analytical uncertainty (Table 1, Fig. 4). In the tropical western Pacific, B/Ca ra-

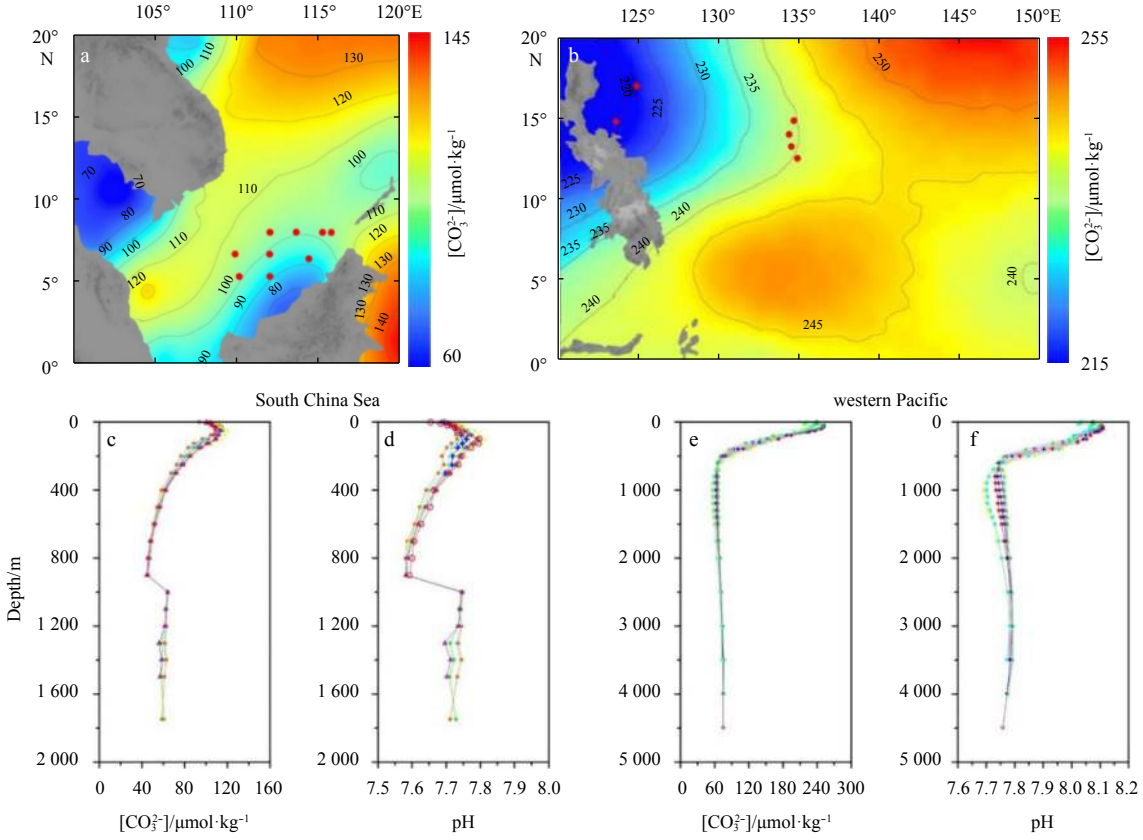

Fig. 3. Carbonate system in the study areas, as inferred from surface sediment data. $[CO_3^{2-}]$ in surface waters is shown for the South China Sea (a) and the tropical western Pacific (b). Depth profiles of $[CO_3^{2-}]$ and pH are shown for the South China Sea (c, d) and the tropical western Pacific (e, f). $[CO_3^{2-}]$ and pH were estimated with CO_2sys.xls (Pelletier et al., 2007) using the Global Alkalinity & TCO_2 (Goyet et al., 2000), GLODAP (Key et al., 2004), and WOA13 datasets.

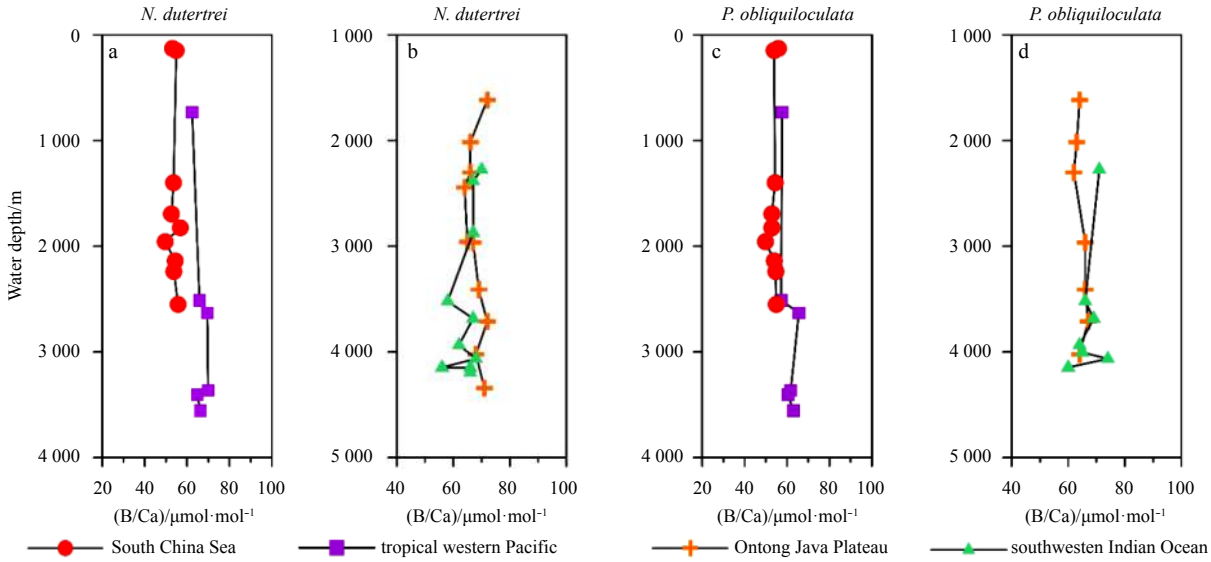

Fig. 4. Four depth transects of B/Ca values in *N. dutertrei* and *P. obliquiloculata*. Data in (a) and (c) are from this study; data in (b) and (d) are from Dai et al. (2016).

tios are 62–70 and 57–66 μmol/mol in *N. dutertrei* and *P. obliquiloculata*, respectively. The fact that B/Ca ratios are higher in *N. dutertrei* than in *P. obliquiloculata* at sites in the tropical western Pacific suggests species-specific influences (Allen and Hönisch, 2012). However, in the South China Sea, B/Ca ratios are 49–57 and 49–56 μmol/mol in *N. dutertrei* and *P. obliquiloculata*, respectively (Table 1, Fig. 4). The fact that B/Ca ratios in the two species are so similar at the South China Sea sites suggests that species-specific influences are negligible in this area. To understand the reasons for this difference, further investigation is needed.

Bottom water $\Delta[CO_3^{2-}]$ values at the study sites extend over a large range in the tropical western Pacific and South China Sea (Table 2). Specifically, in the tropical western Pacific, $\Delta[CO_3^{2-}]$ values range from –9.80 to 14.29 μmol/kg in water depths of 732–3 556 m; and in the South China Sea, $\Delta[CO_3^{2-}]$ values range from –35.40 to 61.04 μmol/kg in water depths of 148.1–2 551 m. The large range in $\Delta[CO_3^{2-}]$ values make the study sites ideal to investigate dissolution effects on B/Ca.

4 Discussion

4.1 *Dissolution effects on planktonic foraminiferal B/Ca*

Processes relating to the dissolution of foraminifer tests are complex, as a combination of factors may be involved. Examples of such factors include: (1) organic matter degradation, which facilitates the acidification of pore waters (Emerson and Bender, 1981; Archer et al., 1989); (2) the saturation state of bottom water relative to calcium carbonate (Broecker et al., 2001; Marchitto et al., 2005; Regenberg et al., 2006); and (3) the sensitivity of the tests of foraminifer species to dissolution (Berger, 1968; Dekens et al., 2002). Dissolution effects on B/Ca of different planktonic foraminifer species have been reported previously (e.g., Wara et al., 2003; Seki et al., 2010; Coadic et al., 2013). Some studies have

Table 2. Bottom water $\Delta[CO_3^{2-}]$ values for the study sites in the tropical western Pacific and South China Sea

Core ID	North latitude/(°)	East longitude/(°)	Water depth/m	$[CO_3^{2-}]$/μmol·kg^{-1}	Ω	$\Delta[CO_3^{2-}]$ /μmol·kg^{-1}
Tropical western Pacific						
3001	14.866 9	134.627 5	3 364	74.65	0.908 4	–7.53
3046	14.028 5	134.338 7	3 407	75.02	0.905 3	–7.85
3091	13.267 6	134.474 3	2 632	70.82	0.995 3	–0.34
3138	12.552 9	134.850 2	3 556	75.50	0.885 1	–9.80
MD06-3047B	17.007 3	124.798 8	2 510	69.45	1.000 0	0.00
MD06-3052	14.810 0	123.490 0	732	62.50	1.296 5	14.29
South China Sea						
C02A09	8.006 7	112.035 2	1 694	60.51	1.029 1	1.71
C02A15	8.013 1	113.649 0	1 825	59.97	0.996 3	–0.22
C02A21	8.005 9	115.263 5	2 240	53.38	0.813 4	–12.20
C02A23	8.000 6	115.801 2	2 551	54.86	0.786 0	–14.90
C02F01	6.682 1	109.897 9	1 398	36.66	0.662 1	–18.70
C02F09	6.678 9	112.024 0	1 957	50.49	0.813 7	–11.60
C02G18	6.400 4	114.423 6	2 139	28.96	0.450 1	–35.40
C02K02	5.331 3	110.150 1	148.1	103.83	2.426 9	61.04
C02K09	5.330 4	112.034 7	128	108.42	2.548 5	65.88

suggested that B/Ca ratios of *G. inflata* and *G. sacculifer* are not altered by dissolution, whereas they are altered in other species such as *G. ruber* (e.g., Yu et al., 2007; Seki et al., 2010). B/Ca ratios in the tests of *G. ruber*, *G. sacculifer*, *N. dutertrei*, and *P. obliquiloculata* from three depth transects (Caribbean Sea, southwestern Indian Ocean, and Ontong Java Plateau) suggest species-specific dissolution effects (Dai et al., 2016). Specifically, the data indicate that B/Ca ratios in *G. ruber* and *G. sacculifer* decrease with increasing water depth as a response to dissolution. In contrast, B/Ca ratios in *N. dutertrei* and *P. obliquiloculata* remain invariant along depth transects (Dai et al., 2016).

In the tropical western Pacific and South China Sea, B/Ca ratios of *N. dutertrei* and *P. obliquiloculata* in the surface sediment samples show negligible change (within analytical uncertainty) from the shallowest to deepest station (Figs 4a and c). This is consistent with a previous study in the Ontong Java Plateau and southwestern Indian Ocean (Figs 4b and d) (Dai et al., 2016). The fact that there is little change in B/Ca ratios with increasing water depth suggests that dissolution has little effect on B/Ca ratios of *N. dutertrei* and *P. obliquiloculata*. In order to further verify this conclusion, we examined the correlations between B/Ca ratios of *N. dutertrei* and *P. obliquiloculata* and bottom water $\Delta[CO_3^{2-}]$ in the study area (Fig. 5). In the tropical western Pacific, B/Ca values of *N. dutertrei* and *P. obliquiloculata* are weakly correlated with $\Delta[CO_3^{2-}]$ (R^2 = 0.304 and 0.250, respectively) (Fig. 5, purple symbols). In the South China Sea, B/Ca values of *N. dutertrei* and *P. obliquiloculata* are not correlated with $\Delta[CO_3^{2-}]$ (R^2 = 0.001 and 0.090, respectively) (Fig. 5, red symbols). Poor correlations between B/Ca ratios and $\Delta[CO_3^{2-}]$ in the study areas also indicate that dissolution had little effect on B/Ca ratios in both species. Given that the dissolution effect on B/Ca ratios of *N. dutertrei* and *P. obliquiloculata* is not significant, we consider that the B/Ca values of these species are mainly affected by upper ocean environmental parameters.

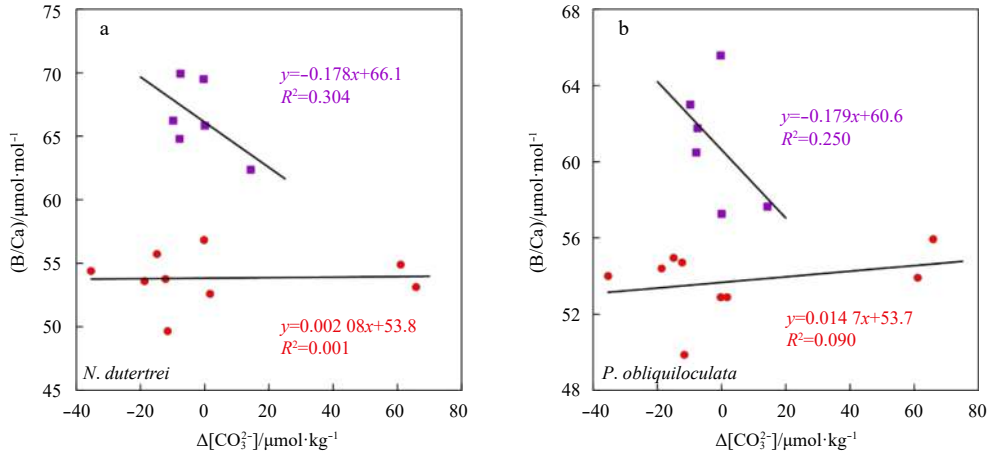

Fig. 5. Plots of B/Ca ratios versus bottom water $\Delta[CO_3^{2-}]$ for *N. dutertrei* (a) and *P. obliquiloculata* (b). The purple and red symbols represent the study sites from the tropical western Pacific and South China Sea, respectively.

4.2 *B/Ca calibration and empirical relationships*

Different methods and a variety of foraminifer species have been used for B/Ca calibrations in recent years (Yu et al., 2007; Foster, 2008; Tripati et al., 2009). If the K_D in Eq. (2) can be quantified and used in combination with the B/Ca ratios of marine calcium carbonate, it should be possible to estimate the parameters of the seawater carbonate system. However, recent studies have suggested that B/Ca ratios are directly correlated with factors such as salinity, $[PO_4^{3-}]$ and DIC (Allen and Hönisch, 2012; Henehan et al., 2015; Haynes et al., 2017). Thus, we examined the environmental controls (specifically temperature, salinity, phosphate, DIC, ALK, pH, $[CO_3^{2-}]$, $[HCO_3^-]$, $[B(OH)_4^-]$, $[B(OH)_4^-]$/DIC, $[B(OH)_4^-]/[CO_3^{2-}]$, and $[B(OH)_4^-]/[HCO_3^-]$) on boron concentrations (Figs 6 and 7) and K_D values (Figs 8 and 9) of *N. dutertrei* and *P. obliquiloculata*.

In the tropical western Pacific, in addition to correlations with temperature (R^2=0.235) and $[B(OH)_4^-]/[CO_3^{2-}]$ (R^2=0.066), B/Ca ratios of *N. dutertrei* from surface sediment samples are significantly correlated with salinity, phosphate, DIC, ALK, pH, $[CO_3^{2-}]$, $[HCO_3^-]$, $[B(OH)_4^-]$, $[B(OH)_4^-]$/DIC and $[B(OH)_4^-]/[HCO_3^-]$ (Fig. 6; purple symbols). However, in the South China Sea, B/Ca ratios of *N. dutertrei* are not correlated with these environmental parameters (Fig. 6 red symbols). The correlation between B/Ca values of *N. dutertrei* and environmental parameters is significant in the tropical western Pacific and insignificant in the South China Sea (Fig. 6), which suggests that B/Ca values of *N. dutertrei* cannot be used to directly reconstruct environmental parameters in the study area.

In the tropical western Pacific, in addition to strong correlations with ALK (R^2=0.643) and $[B(OH)_4^-]/[CO_3^{2-}]$ (R^2=0.454), B/Ca ratios of *P. obliquiloculata* from surface sediment samples do not co-vary with other environmental parameters (Fig. 7; purple symbols). In contrast, in the South China Sea, in addition to correlations with temperature (R^2=0.142), DIC (R^2=0.239) and ALK (R^2=0.011), B/Ca ratios of *P. obliquiloculata* from surface sediment samples are significantly correlated with other environmental parameters (Fig. 7; purple symbols). In summary, from all the investigated relationships between B/Ca ratios of *P. obliquiloculata* and environmental parameters, the correlation between B/Ca ratios and $[B(OH)_4^-]/[CO_3^{2-}]$ is the only one that is significant in the tropical western Pacific and South China Sea (R^2=0.454 and 0.447, respectively) (Fig. 7k). Previous studies have suggested that B/Ca ratios of planktonic foraminiferal or inorganic calcite are controlled by related carbonate system variables such as DIC (Allen and Hönisch, 2012; Haynes et al., 2017). The strong correlation between B/Ca ratios of *P. obliquiloculata*

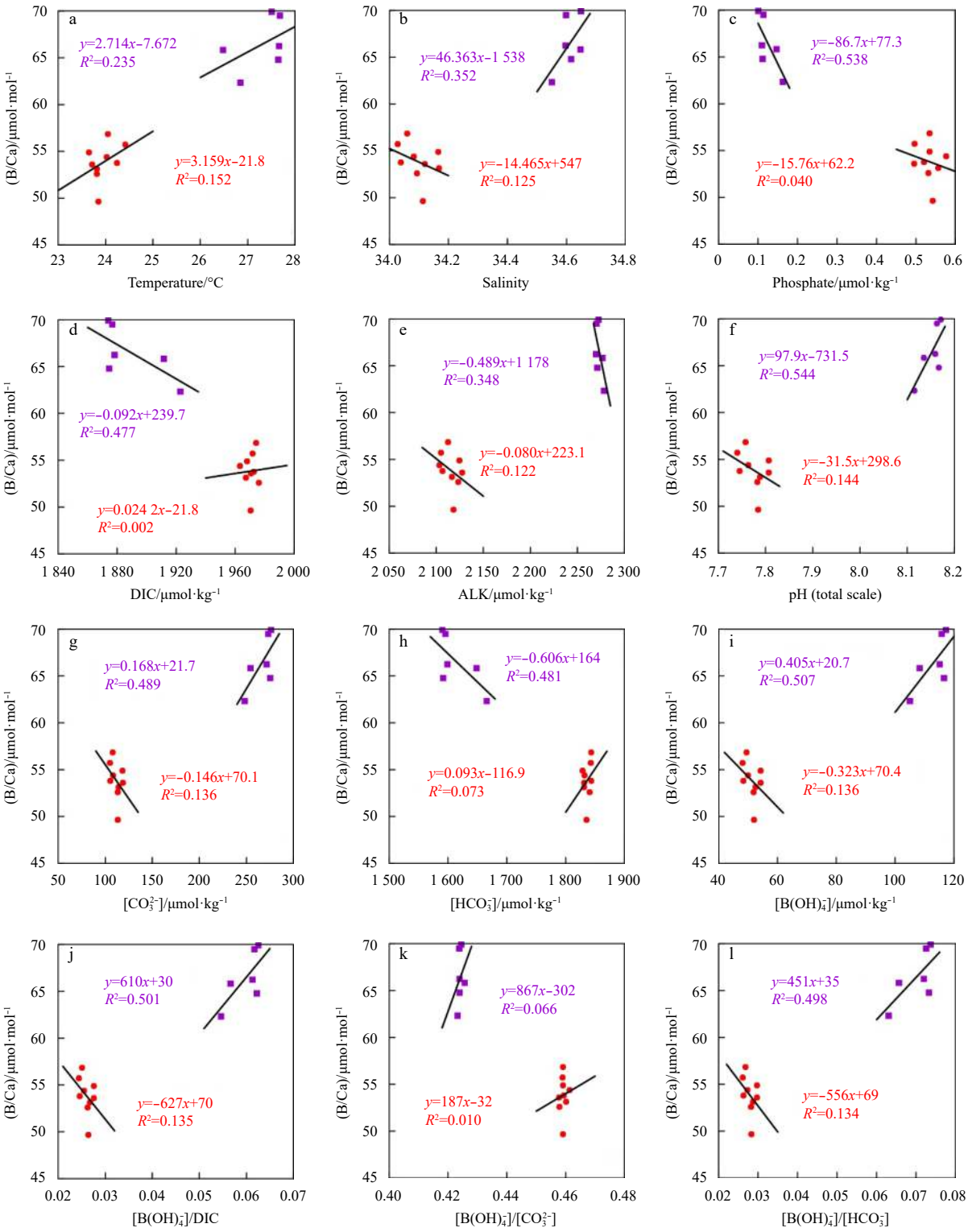

Fig. 6. Variations in B/Ca ratios of *N. dutertrei* versus various environmental parameters at assigned depths in the tropical western Pacific (purple symbols) and South China Sea (red symbols).

and $[B(OH)_4^-]/[CO_3^{2-}]$ was thus surprising, and the controls of this environmental parameter on B/Ca ratios will be explored in future research.

Given that the relationship between B/Ca ratios of *N. dutertrei* and environmental parameters is not significant, and B/Ca ratios in this species are unsuitable as a palaeoenvironmental proxy, we investigated the empirical relationships between K_D and environmental parameters (Figs 8 and 9). K_D values of *N. dutertrei* are significantly correlated with temperature, ALK, pH, $[CO_3^{2-}]$, $[HCO_3^-]$, $[B(OH)_4^-]$, $[B(OH)_4^-]$/DIC, and $[B(OH)_4^-]/[HCO_3^-]$ in the tropical western Pacific and South China Sea (Fig. 8). K_D values of *P. obliquiloculata* are significantly correlated with

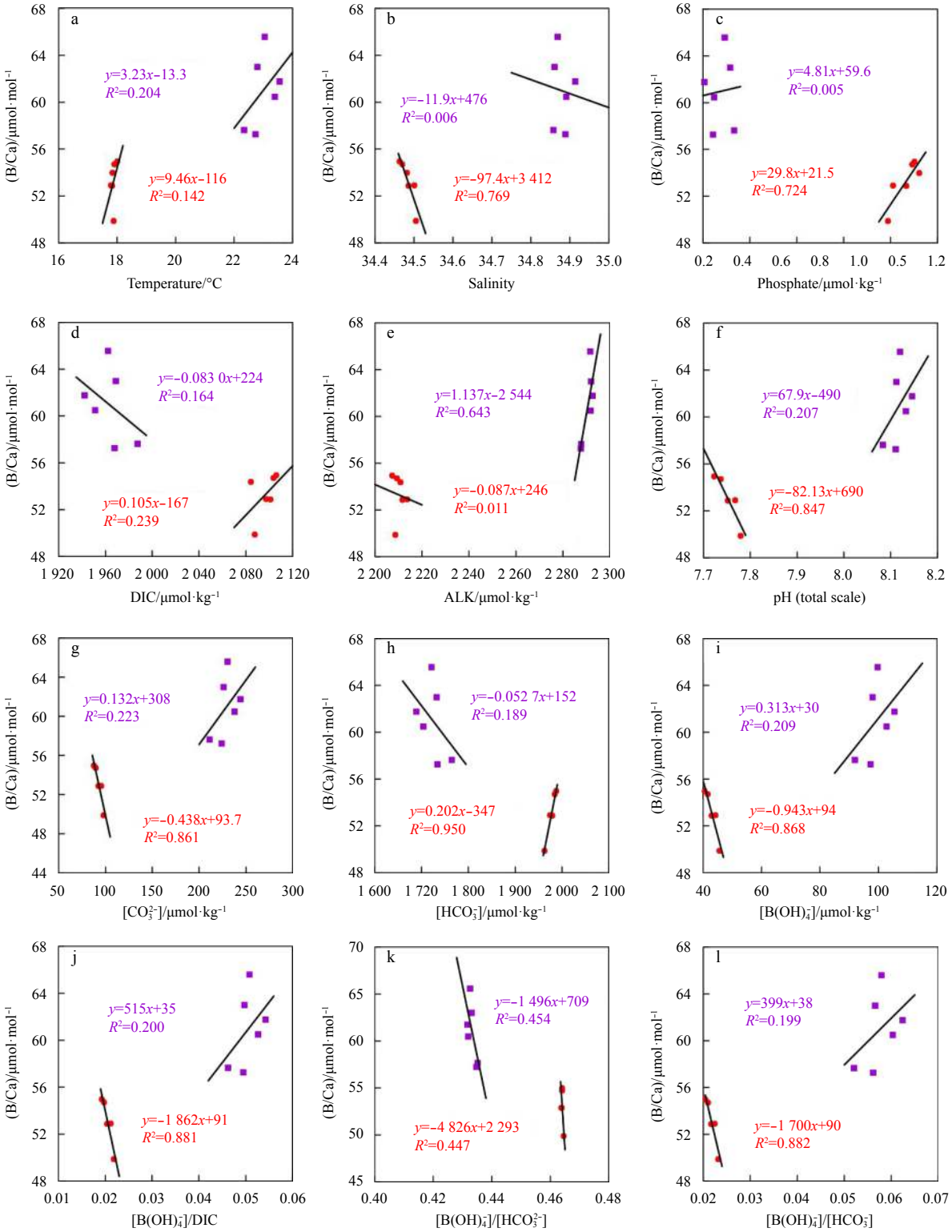

Fig. 7. Variations in B/Ca ratios of *P. obliquiloculata* with environmental parameters at assigned depths in the tropical western Pacific (purple symbols) and South China Sea (red symbols).

temperature, salinity, phosphate, DIC, pH, $[CO_3^{2-}]$, $[HCO_3^-]$, $[B(OH)_4^-]$, $[B(OH)_4^-]$/DIC and $[B(OH)_4^-]/[HCO_3^-]$ in the tropical western Pacific and South China Sea (Fig. 9).

In this study, we found that K_D values for *N. dutertrei* and *P. obliquiloculata* are negatively correlated with temperature in the tropical western Pacific (Figs 8a and 9a), which is consistent with the results of Foster (2008). However, our results also show that K_D values for *N. dutertrei* and *P.obliquiloculata* are positively correlated with temperature in the South China Sea. Similarly, the analysis of *Globorotalia inflata* from core-top and down-core samples in the Atlantic (Yu et al., 2007), and *G. ruber* and *G. sacculifer* from down-core material in the Pacific (Tripati et al., 2009)

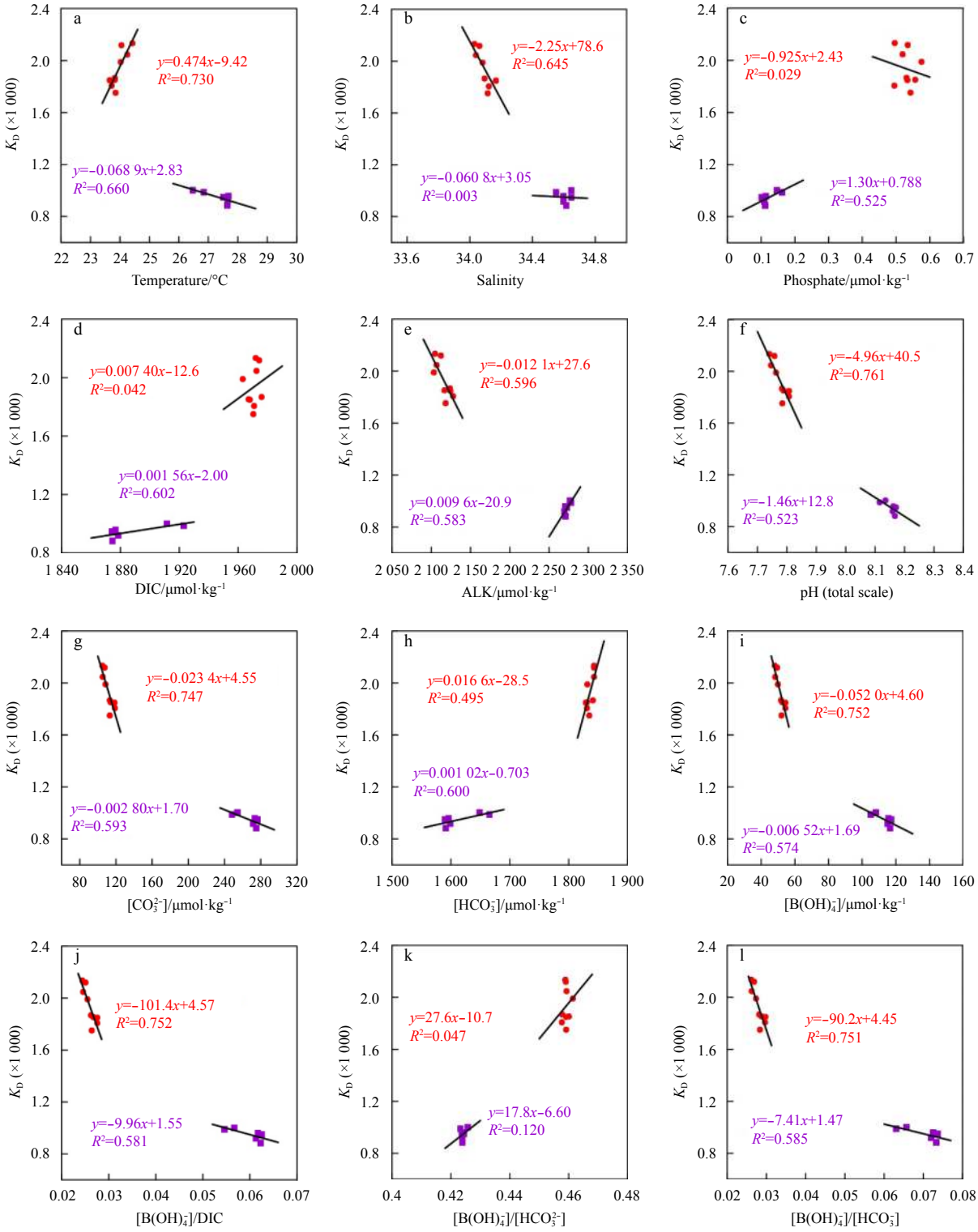

Fig. 8. K_D values of *N. dutertrei* versus environmental parameters at assigned depths in the tropical western Pacific (purple symbols) and South China Sea (red symbols).

revealed an exponential positive relationship between K_D and temperature. Despite the opposing relationships, the data show that K_D and temperature are significantly related, perhaps indicating that temperature can strongly affect K_D. Foster (2008) suggested that temperature is not the only factor controlling the incorporation of boron into calcite, and that $[CO_3^{2-}]$ in seawater is the dominant environmental control on K_D values of planktonic foraminiferal B/Ca. In our study, we also found a significant negative linear correlation between K_D values for B/Ca and $[CO_3^{2-}]$ in seawater in both the tropical western Pacific and South China Sea. In addition, significant relationships between K_D values for B/Ca and other environmental parameters (e.g., pH, $[CO_3^{2-}]$,

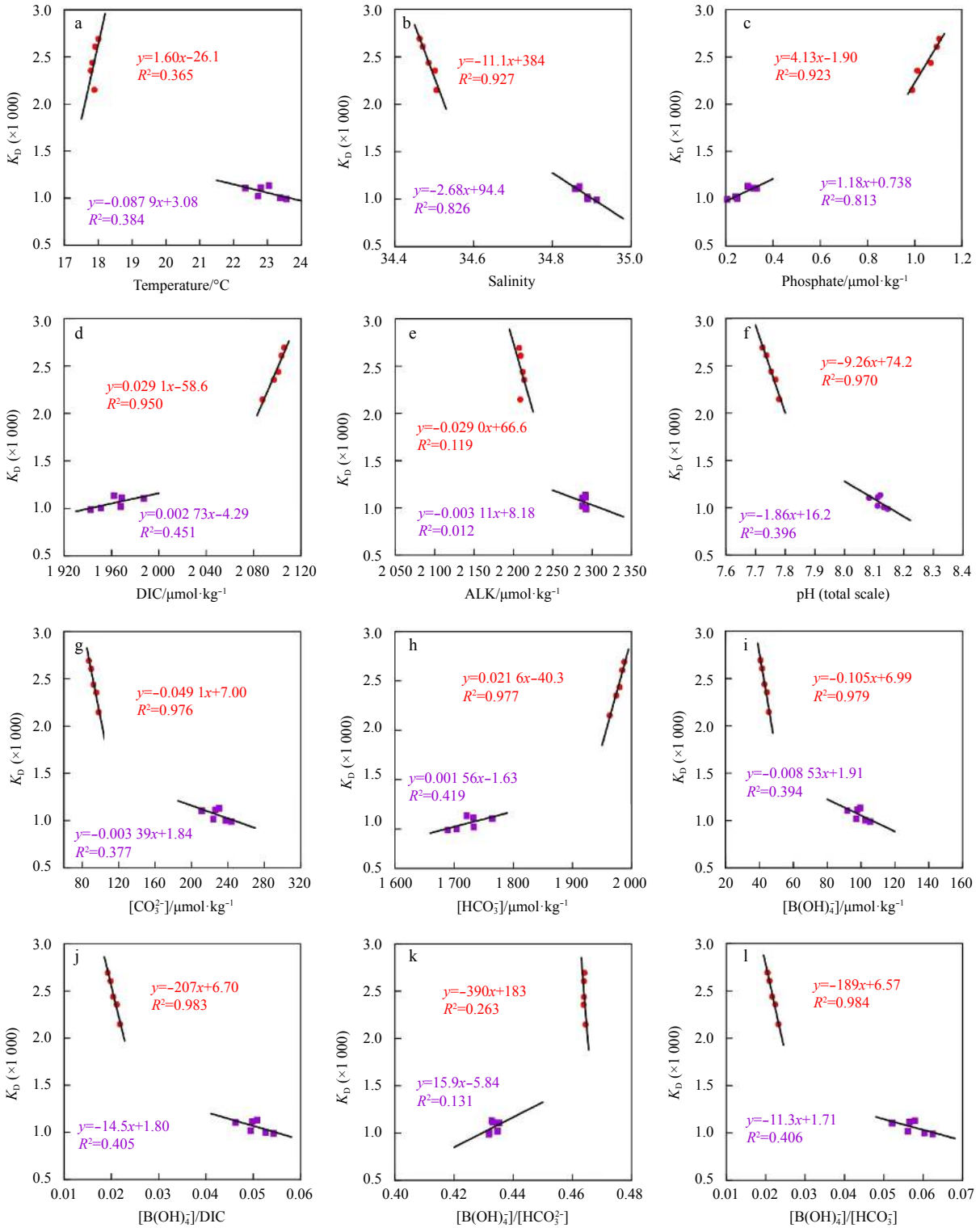

Fig. 9. K_D values of *P. obliquiloculata* versus environmental parameters at assigned depths in the tropical western Pacific (purple symbols) and South China Sea (red symbols).

$[HCO_3^-]$, and $[B(OH)_4^-]$) were identified in this study (Figs 8 and 9).

A core-top calibration of B/Ca ratios in the Pacific Ocean suggests that many of these potential controlling variables are autocorrelated (Krupinski et al., 2017). Therefore, the relationship between environmental parameters was examined in this study. Based on an empirical investigation of these potential controlling variables, we found that the K_D denominator $[B(OH)_4^-]/[HCO_3^-]$ (Eq. 2) is significantly correlated with the other environmental parameters. Allen and Hönisch (2012) suggested that the significant correlation between K_D and $[CO_3^{2-}]$ reflects the chemical links between the K_D denominator $[B(OH)_4^-]/[HCO_3^-]$ and $[CO_3^{2-}]$. Thus, given that K_D is a function of $[B(OH)_4^-]/[HCO_3^-]$

(Eq. (2)) and that $[B(OH)_4^-]/[HCO_3^-]$ is correlated with the other carbonate system parameters, we consider that the correlations between K_D and these carbonate system parameters in our study (Figs 8 and 9) reflect the chemical links between the K_D denominator and these variables, implying that the correlations are artificial.

In the calculation of K_D, the parameters needed are temperature, salinity, phosphate, ALK, DIC, and B/Ca. Using temperature, salinity, phosphate, DIC, and ALK data, we can calculate $[HCO_3^-]$ and $[B(OH)_4^-]$, and then combine them with B/Ca to obtain the value of K_D from Eq. (2). Temperature, salinity, and phosphate are not part of the carbonate system, and so their correlation with the K_D values for B/Ca may be a true response to the effects of these environmental parameters on K_D. To verify this hypothesis, we replaced the values of the other environmental parameters with mean values throughout the calculation of K_D, and then explored the effect of changes in individual variables (e.g., temperature, salinity, or phosphate) on K_D values. The K_D values generated through changing a single variable are very similar (Fig. 10), indicating that temperature, salinity, and phosphate alone have little effect on the K_D values. Thus, the data show that the significant dependence of K_D on temperature (Fig. 8a), salinity (Fig. 9b), and phosphate (Fig. 9c) reported in this study is robust. In addition, in light of the lack of correlation between the K_D values of *N. dutertrei* and salinity and phosphate (Figs 8b and c), we derived an empirical relationship between K_D for B/Ca in *N. dutertrei* and temperature in the tropical western Pacific as follows (Fig. 8a):

$$K_D\ (\times 1\ 000) = -0.068\ 9 \times T + 2.83 \qquad R^2 = 0.660. \tag{6}$$

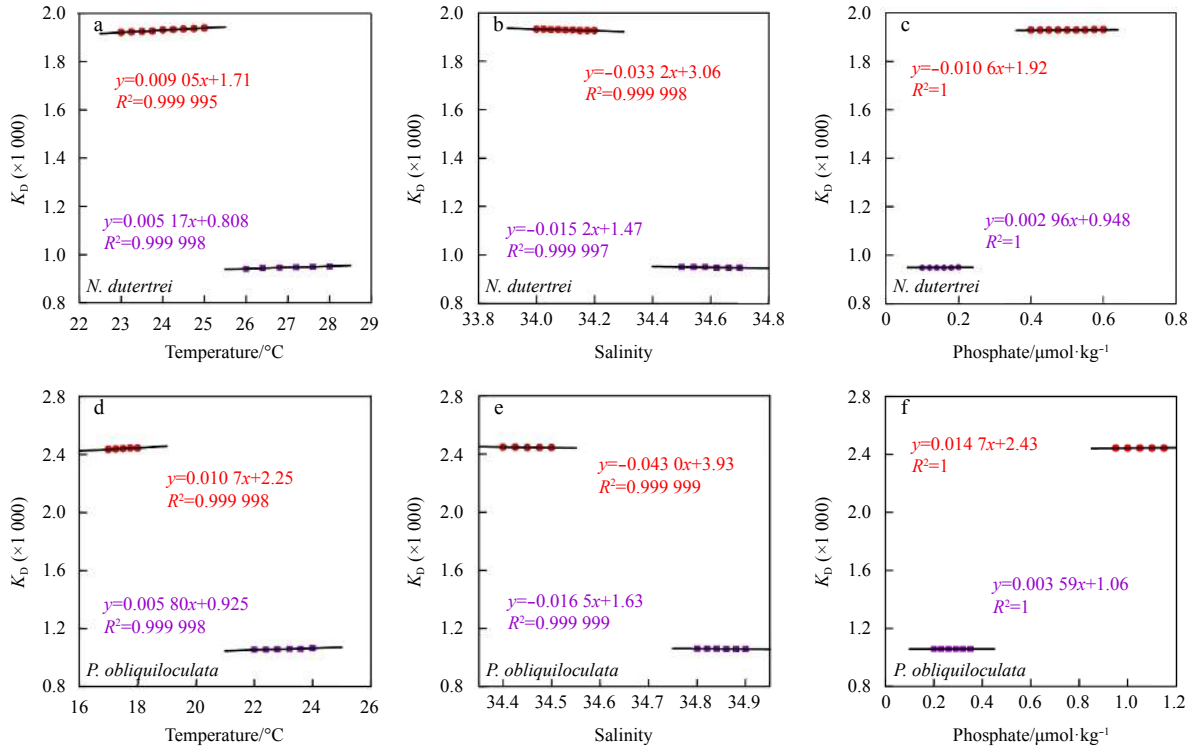

Fig. 10. Variation of K_D values of *N. dutertrei* and *P. obliquiloculata* with single variables. The purple and red symbols represent the study sites from the tropical western Pacific and South China Sea, respectively.

4.3 *Variations in the subsurface carbonate system in the tropical western Pacific over the past 24 ka*

4.3.1 *Reconstruction of subsurface seawater ALK and pH in the tropical western Pacific*

In this study, utilizing the method of Tripati et al. (2009), we used B/Ca ratios of *N. dutertrei* from core MD06-3052 to calculate subsurface seawater pH in the tropical western Pacific over the past 24 ka. The method is as follows:

(1) Based on the empirical relationship between K_D and temperature (Eq. (6)), combined with the B/Ca ratios of *N. dutertrei* from core MD06-3052 in the tropical western Pacific, $[B(OH)_4^-]/[HCO_3^-]$ of subsurface seawater was obtained from Eq. (2).

(2) ALK was reconstructed based on the local relationship between subsurface salinity and total alkalinity. The local relationship was determined using data (Olsen et al., 2016) for the region 0–20°N and 120–140°E at water depths of 50–100 m. We obtained the following equation for this area (Fig. 11):

$$\mathrm{ALK} = 67.722 \times S - 71.287 \qquad R^2 = 0.923. \tag{7}$$

(3) Local salinity was calculated using the following equation that was derived from seawater $\delta^{18}O$ and salinity data (n=70; R^2=0.914) (Schmidt et al., 1999) in the modern ocean from the area 0°–20°N and 120°–170°E at water depths of 0–100 m (Fig. 12):

$$S = (\delta^{18}O + 12.333)/0.367 \qquad R^2 = 0.914. \tag{8}$$

We derived salinity data using Mg/Ca and $\delta^{18}O$ data measured in *N. dutertrei* from core MD06-3052 (Qiu et al., unpublished data). Mg/Ca data were not available for the entire core section spanning the past 24 ka, and so we made additional

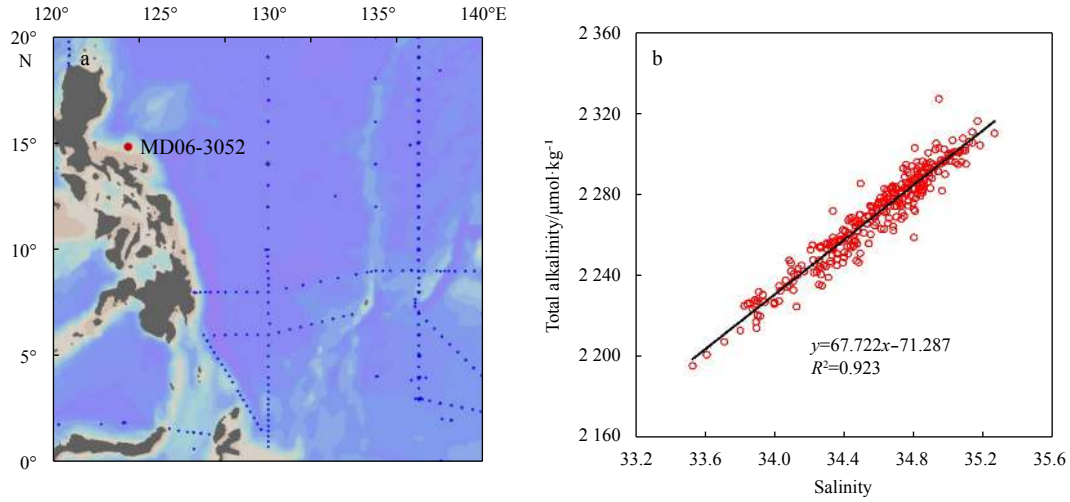

Fig. 11. Regional relationship between subsurface seawater total alkalinity and salinity. a. Locations from which data were used to reconstruct the regional relationship; the red dot represents the core MD06-3052; and b. regression equation for total alkalinity and salinity. The data are from the dataset complied by GLODAPv2 (Olsen et al., 2016). The base map was drawn using Ocean Data View (http://odv.awi.de).

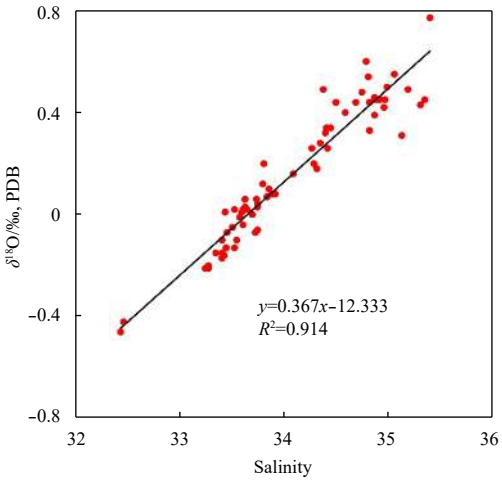

Fig. 12. Local relationship between seawater $\delta^{18}O$ and salinity (data are from Schmidt et al. (1999)).

Mg/Ca measurements.

(4) We obtained ALK estimates using Eqs (7) and (8), and foraminiferal $\delta^{18}O$ data for which the temperature signal and effect of continental ice volume had been removed (in accordance with Bemis et al. (1998) and Waelbroeck et al. (2002), respectively).

(5) Finally, the practical alkalinity is used as an approximation for total alkalinity in seawater (Zeebe and Wolf-Gladrow, 2001). The practical alkalinity is defined as:

$$[ALK] = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]. \quad (9)$$

We substituted the following Eqs (10)–(13) into Eq. (9):

$$[CO_3^{2-}] = [HCO_3^-] \times k_2/[H^+], \quad (10)$$

$$[B(OH)_4^-] = [B_{tot}] \times K_B/([H^+] + K_B), \quad (11)$$

$$[OH^-] = K_w/[H^+], \quad (12)$$

$$[HCO_3^-] = K_B \times B_{tot} \times ([H^+] + K_B) \times ([B(OH)_4^-]/[HCO_3^-])^{-1}. \quad (13)$$

One element cubic equation for $[H^+]$ can be obtained by algebraic manipulation of the resultant equation. $[H^+]$ can be acquired by solving the one element cubic equation, and then the pH value of the subsurface seawater in the tropical western Pacific was determined for the past 24 ka.

Using ALK and pH in addition to temperature and salinity, allows pCO_2 and $[CO_3^{2-}]$ of the subsurface seawater to be calculated using CO_2sys.xls (Pelletier et al., 2007) (Fig. 13). Throughout the calculation process, we selected the carbonic acid dissociation constants (K_1 and K_2) from Mehrbach et al. (1973) as refitted by Dickson and Millero (1987), K_B and K_{SO_4} from Dickson (1990), K_w from Millero (1995), total boron ($[B]_{tot}$) from Uppström (1974), and the total pH scale.

4.3.2 *Down-core record of subsurface seawater pCO_2 over the past 24 ka from core MD06-3052*

In general, the B/Ca ratios of *N. dutertrei* (Fig. 13a) and the reconstructed subsurface seawater ALK (Fig. 13b) in the tropical western Pacific shows no obvious directional change over the past 24 ka. In contrast, the estimated subsurface seawater pH (Fig. 13c) and $[CO_3^{2-}]$ (Fig. 13d) in the tropical western Pacific show an increase with time, and the record of subsurface seawater pCO_2 in the tropical western Pacific shows a decrease with time (Fig. 13e). In general, the values of subsurface seawater pH, $[CO_3^{2-}]$ and pCO_2 in MIS 2 are more stable than those in the Holocene (Fig. 13), which may indicate that the subsurface carbonate system was more active in the Holocene than in MIS 2. During the last deglacial, subsurface seawater pCO_2 values peak while subsurface seawater pH and $[CO_3^{2-}]$ lie in a minima.

It has been established that upwelling of Circumpolar Deep Water (CDW) during deglaciation releases CO_2 that was previously stored in deep water, and increases atmospheric CO_2 concentrations. This upwelling water, which contains elevated nutri-

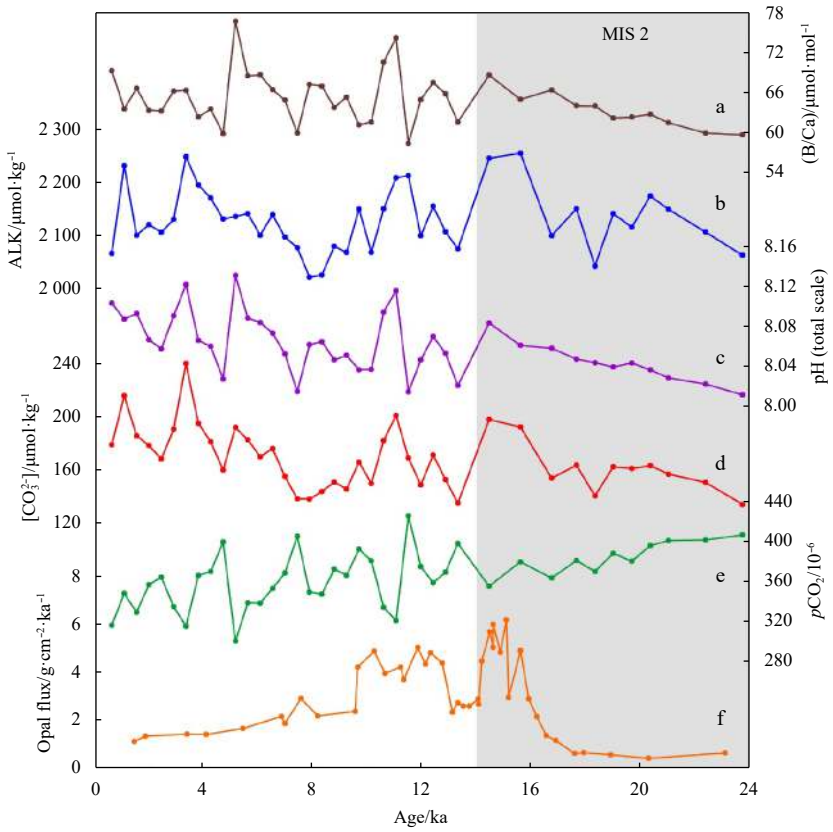

Fig. 13. Changes in the subsurface carbonate system in the tropical western Pacific over the past 24 ka. B/Ca ratios in *N. dutertrei* from core MD06-3052 (a). Calculated subsurface seawater ALK (b) and pH (c) in the tropical western Pacific. Reconstructed subsurface seawater $[CO_3^{2-}]$ (d) and pCO_2 (e) in the tropical western Pacific. Opal flux from core TN057-13PC in the Southern Ocean (Anderson et al., 2009) (f). The grey vertical bar indicates marine isotope stage 2 (MIS 2).

ent and dissolved CO_2 concentrations, and DIC with low $\delta^{13}C$ values, was also carried to low-latitude regions through the enhanced Antarctic Intermediate Water (AAIW) and Subantarctic Mode Water (SAMW) (Spero and Lea, 2002; Anderson et al., 2009). It has been suggested that opal flux, and thus upwelling, were enhanced during deglaciation in the Southern Ocean (Anderson et al., 2009) (Fig. 13f). The consistent variations in the tropical western Pacific subsurface pCO_2 during the last interval resemble the changes in the opal flux in the Southern Ocean (Figs 13e and f), and potentially imply a palaeoceanographic linkage between the two areas. Thus, we deduce that upwelling of deep water in the Southern Ocean likely imparted a chemical signature (e.g., dissolved CO_2 concentrations and DIC with low $\delta^{13}C$ values) via the AAIW and SAMW to our study area during the deglaciation.

5 Conclusions

We measured B/Ca ratios in the tests of *N. dutertrei* and *P. obliquiloculata* in surface sediment samples from the tropical western Pacific and South China Sea to investigate the effects of dissolution on B/Ca values and to re-assess the relationship between B/Ca and temperature and $[CO_3^{2-}]$ for these species. We also reconstructed the subsurface carbonate parameters in the tropical western Pacific over the past 24 ka using B/Ca ratios of *N. dutertrei* in core MD06-3052. The results of this study led to the following conclusions:

(1) Analysis of surface sediment samples indicates a negligible dissolution effect on the B/Ca ratios of *N. dutertrei* and *P. obliquiloculata* in the tropical western Pacific and South China Sea.

(2) B/Ca ratios of *N. dutertrei* and *P. obliquiloculata* in the tropical western Pacific and South China Sea cannot be used to directly reconstruct seawater parameters. The correlation between K_D values of B/Ca in the studied *N. dutertrei* and *P. obliquiloculata* and carbonate system parameters (e.g., $[CO_3^{2-}]$, DIC, ALK, pH, and $[HCO_3^-]$) are artificial. There is a robust and significant dependence of K_D values in *N. dutertrei* and *P. obliquiloculata* on temperature in the tropical western Pacific and South China Sea.

(3) The reconstructed subsurface pCO_2 record from core MD06-3052 shows a decrease over the last 24 ka. Our results serve as a preliminary attempt to apply the B/Ca ratios of subsurface dwelling planktonic foraminifera to reconstructions of subsurface seawater carbonate chemistry.

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