Use of the Boron partition coefficient ‘\(K_D\)’ and B/Ca from planktonic foraminifera in the estimation of past seawater pCO\(_2\)

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Abstract

We assess the usefulness of the empirical boron partition coefficient, \(K_D\) and B/Ca measured from planktonic foraminifera in estimation of pCO\(_2\) using three different relationships between \(K_D\) and temperature derived from various studies. Two sediment cores spanning the last 22 kyr were utilised, one from the intense CO\(_2\) source region of the Western Arabian Sea (WAS) and another from the Eastern Arabian Sea (EAS). The sea-air difference in pCO\(_2\) at these sites shows results contrary to the present day scenario. Moreover the reconstructions using the three \(K_D\) relationships lead to assorted results which suggests that the \(K_D\) approach may not be suitable in paleo-pCO\(_2\) reconstructions.

Keywords: boron, foraminifera, Arabian Sea, pCO\(_2\), partition coefficient

INTRODUCTION

Boron exists in seawater as borate (B(OH)\(_4\)) or boric acid (B(OH)\(_3\)) depending upon seawater pH, with a greater abundance of B(OH)\(_3\) at lower pH and B(OH)\(_4\) at higher pH. Since dissolved B(OH)\(_4\) is considered to be the species incorporated into foraminiferal calcite, B/Ca should increase with greater abundance of borate. Boron incorporation in foraminifera shells will thus be greater if the seawater is more alkaline. Therefore, foraminiferal B/Ca, is thought to be a potential proxy for pH and pCO\(_2\) (Yu et al., 2007; Tripati et al., 2009). Yu et al., 2007, used B/Ca ratios and the empirical boron partition coefficient, \(K_D\) (= \([\text{B/Ca}_{\text{CaCO}}] / [\text{B(OH)}_{\text{i}}][\text{HCO}_3]_{\text{seawater}}\)) to estimate seawater borate/bicarbonate ratios ([B(OH)\(_4\)]/[HCO\(_3\)]) and reproduce two glacial–interglacial cycles of pCO\(_2\). In the modern seawater, \([\text{B(OH)}_{\text{i}}][\text{HCO}_3]_{\text{seawater}}\) is proportional to pH as the concentration of B(OH)\(_4\) increases and HCO\(_3\) decreases with increasing seawater pH. If we measure B/Ca from foraminifera and \(K_D\) is estimated from temperature (core-top \(K_D\) variability is attributed to the influence of temperature on boron partitioning) (Yu et al., 2007), we can calculate \([\text{B(OH)}_{\text{i}}][\text{HCO}_3]_{\text{seawater}}\)
seawater and hence pH and pCO₂. Tripati et al., 2009 have used B/Ca ratios in the planktonic foraminifera, *Globigerinoides ruber* and *Globigerinoides sacculifer* from the western tropical Pacific to reveal that during the Middle Miocene, atmospheric pCO₂ may have been similar to modern levels. However, a recent study from the upwelling region of the Arabian Sea shows that B/Ca is not related to salinity, pH or DIC but boron incorporation in planktonic foraminifera maybe size-related (Naik and Naidu, 2014). It was also observed that the calibrations using $K_D$ can sometimes be driven by the relationship between $[\text{B(OH)}_4^-]/[\text{HCO}_3^-]$ and seawater parameters and not by B/Ca (Allen and Hönsch, 2012). In this study we test the effectiveness of $K_D$ in estimation of pCO₂ using different $K_D$ relationships, applied to two sediment cores from the Arabian Sea.

### Samples and Methods

The Western Arabian Sea core (ODP Site 723A; 18°03’N and 57°37’E; wd = 808 m) and the Eastern Arabian Sea core (AAS9/21; 14°30’N and 72°39’E; wd = 1807 m) are from above lysocline depths (Fig. 1). Both these cores cover the last ~22kyr period. The details of the Age Model, B/Ca, Mg/Ca and δ¹⁸O measurements and data are described in Naik and Naidu, 2014. CO₂ system calculations were performed using a Microsoft Excel-based programme (CO₂sys_v2.1) (Lewis and Wallace, 1998). The input parameters for this programme were salinity, temperature, alkalinity, total CO₂ and nutrients, and the constants used were as follows: pK*B and KHSO₄ are from Dickson, 1990, the relationship between total B in seawater and chlorinity from Lee et al., 2010 and K1 & K2 carbonate disassociation constants from Lueker et al., 2000. pH calculations were done on the 'total scale'. pCO₂ calculations were done using different $K_D$ equations; 1. constant $K_D$ ($K_D = 0.0015$) (Yu et al., 2007); 2. temperature sensitive $K_D$ for *G.ruber* from Yu et al., 2007 ($K_D = 0.047 \times \text{EXP} (0.131 \times \text{Mg/Ca-SST})$); and 3. temperature sensitive $K_D$ for *G.ruber* from Tripati et al., 2009 ($K_D = 0.211 \times \text{EXP} (0.064 \times \text{Mg/Ca-SST})$).

### Results and Discussion

The Arabian Sea is influenced by the south-west (SW) monsoon winds during the northern hemisphere summer and north-east (NE) monsoon winds during winter (Wyrtki 2009). The strong south-westerly monsoon winds cause offshore Ekman transport and intense seasonal upwelling along the Oman and Somalia margins and weak upwelling along some parts of the east coast of India (Wyrtki 2009). The upwelled waters are laden with high CO₂ and the western Arabian Sea (WAS) in comparison to the eastern Arabian Sea (EAS) is thus an intense CO₂ source to the atmosphere with pCO₂ values reaching ~600 µatm during the SW monsoon (Sarma, 2003).
B/Ca ratios at ODP Site 723A ranged from 124 to 179 µmol/mol and in Core AAS9/21 they ranged from 117 to 132 µmol/mol for the last 22 kyr (Naik and Naidu, 2014). By using B/Ca data, reconstructed salinity and temperature from the cores ODP723A and AAS9/21 and different $K_D$ relationships, we calculated borate/bicarbonate ratios and subsequently the pCO$_2$. At ODP Site 723A, reconstructed pCO$_2$ varies from 110 to 286 ppmv which is atypical of this region wherein present day pCO$_2$ values reach up to 700 ppmv during the South-West Monsoon and is a strong source of CO$_2$ to the atmosphere (Sarma, 2003). As seen at ODP Site 723A, though the pCO$_2$ pattern using the three $K_D$ relationships is the same, the differences in pCO$_2$ reconstructed using these equations is large, of up to 100 ppmv (Fig. 2). Lowest pCO$_2$ values are noticed between 9 to 12 kyr. However on the contrary, pCO$_2$ reconstruction using the more reliable boron isotopes in this region show highest pCO$_2$ values at 12 kyr corresponding to the Younger Dryas period, due to an increase in the Asian Summer Monsoon (ASM) (Palmer et al., 2010).

The core AAS9/21 shows an overall pCO$_2$ increase through the time period using the three $K_D$ relationships, with pCO$_2$ values ranging from 158 to 429 ppmv. In comparison to modern day values (~400 ppmv; Sarma, 2003), the core-top pCO$_2$ reconstruction using the $K_D$ relationship by Yu et al., 2007 (Fig. 2) gives a rather closer comparison. The pCO$_2$ pattern using the three relationships are similar but the difference between the reconstructions is very large of up to 178 ppmv at 2.55 kyr. Moreover the EAS is a weaker upwelling region in comparison to the WAS, but the pCO$_2$ reconstructions give a different picture showing higher pCO$_2$ in the EAS and lower in the WAS. This can be better illustrated based on the $\Delta$pCO$_2$, which is calculated as the difference in pCO$_2$ obtained from the sediment cores (pCO$_2^{sw}$) and the ice-core CO$_2$ (pCO$_2^{atm}$) record (Smith et al., 1999) over time, $\Delta$pCO$_2$ = pCO$_2^{sw}$ - pCO$_2^{atm}$ (Fig. 3). Using the three $K_D$ relationships, it was seen that ODP Site 723A was a sink of atmospheric CO$_2$ throughout the study period, with $\Delta$pCO$_2$ ranging from 12 to -152 ppmv. However as seen earlier, this site is well-known to be a strong source of CO$_2$ to the atmosphere. Results from the EAS are as well contrary to the modern day scenario. $\Delta$pCO$_2$ at AAS9/21 ranged from 167 to -81 ppmv. $\Delta$pCO$_2$ calculated using the two $K_D$ approaches, constant $K_D$ and temperature sensitive $K_D$ by Yu et al., 2007, show that Site AAS9/21 was a source of atmospheric CO$_2$ for the last 22 kyr whereas the third $K_D$ relationship by Tripati et al., 2009, depict this site as a CO$_2$ sink. Thus, the reconstructed pCO$_2$ using different $K_D$ approach give an assorted picture and are contradictory to what is known about western and the eastern Arabian Sea, in the modern times.
CONCLUSIONS

The present study illustrates the problems of the ‘$K_D$’ approach. The pCO$_2$ calculated using the three $K_D$ equations provide variable results with differences in pCO$_2$ values which are much larger compared to a glacial-interglacial CO$_2$ shift. The inconsistencies observed in estimation of pCO$_2$ thus indicate that the use of $K_D$ should be avoided until we gain significant knowledge on relative impacts of different chemical species on boron incorporation.

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REFERENCES:


**Figure legends:**

**Fig. 1:** Chlorophyll-\(a\) concentration from SeaWiFS (in mg/m\(^3\)) during the south-west monsoon period; June–September, 1998 (source: http://gdata1.sci.gsfc.nasa.gov/) with overlaid core locations. The Western Arabian Sea is seen to be more productive than the eastern counterpart.

**Fig. 2:** The top panel shows pCO\(_2\) reconstructed from ODP723A using constant \(K_D\) (squares, \(K_D = 0.0015\)); using temperature sensitive \(K_D\) for \textit{G.ruber} from Yu et al. (2007) (circles, \(K_D = 0.047 \times \exp(0.131 \times \text{Mg/Ca-SST})\)); and temperature sensitive \(K_D\) for \textit{G.ruber} from Tripati et al. (2009) (triangles, \(K_D = 0.211 \times \exp(0.064 \times \text{Mg/Ca-SST})\)). The lower panel is the same as upper panel but for AAS9/21.

**Fig. 3:** The top panel shows \(\Delta CO_2\) (difference in CO\(_2\) between sea and air; atmospheric CO\(_2\) data taken from ice-core, Smith et al., 1999) using different \(K_D\) relationships as shown in Fig. 1. The lower panel is the same as upper panel but for AAS9/21.