



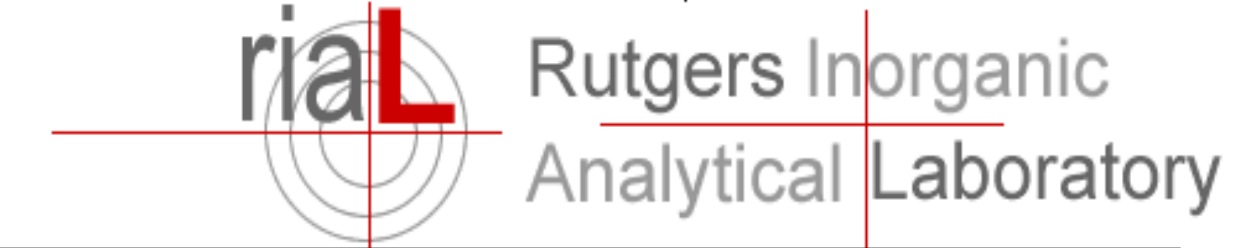
# Development of B/Ca as a seawater pH proxy using sediment trap time series

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## (1) ABSTRACT

Boron/Calcium (B/Ca) ratios in planktonic foraminifera have been suggested as a potential proxy to reconstruct seawater pH (Yu et al. 2007) and, with another parameter of the carbonate system, atmospheric carbon dioxide. However, in addition to pH the calcification temperature has a strong influence on the incorporation of boron into foraminiferal tests. To assess the various influences of these parameters we have measured B/Ca, as well as Mg/Ca and oxygen isotopes as independent temperature proxies, in *Globigerinoides ruber* white from the Bermuda Oceanic Flux Program (OFP) sediment traps through several seasonal cycles. Initial results indicate a significant covariation between B/Ca and calcification temperature. We compare our data with results available from previously published down-core calibration studies and with new sediment trap data from South China Sea which were collected through the South East Asian Time-series Study (SEATS). All these studies combined indicate that temperature is the dominant control with pH being a secondary influence. Thus, determining the temperature dependence of B/Ca is critical for accurate pH reconstruction. We are currently using both sediment traps to assess whether the long-term decrease in surface water pH driven by anthropogenic ocean acidification is recorded in foraminiferal B/Ca. These records will be used to estimate the relative contributions of temperature and pH.

## (2) OBJECTIVES

•Use the OFP and South China Sea sediment trap time-series to determine the B/Ca-temperature relationship by using Mg/Ca as an independent proxy for calcification temperature

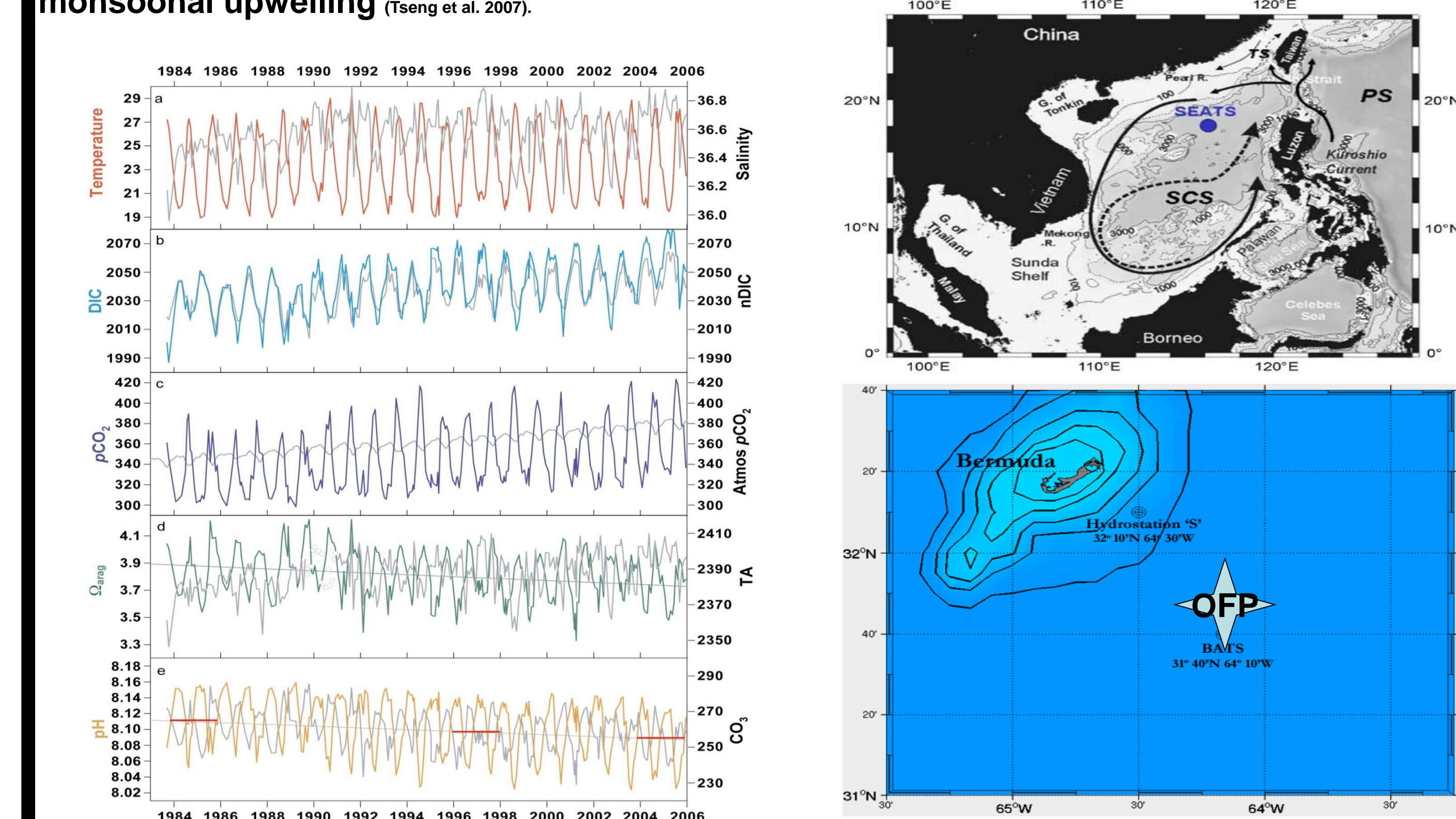
•Test whether B/Ca can be used to record the decrease in pH observed from recent surface ocean acidification

## (3) WHY A SEDIMENT TRAP BASED CALIBRATION?

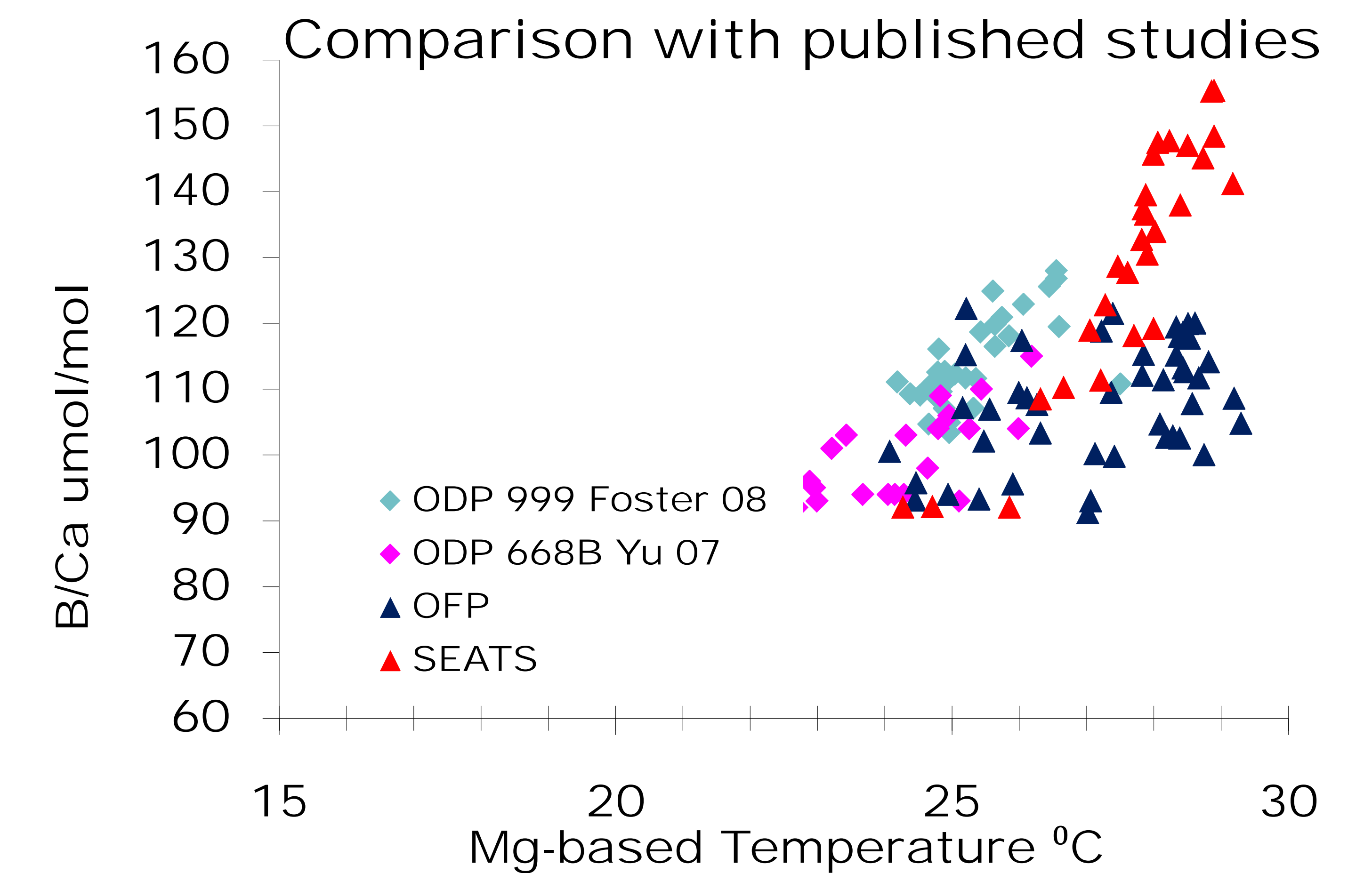
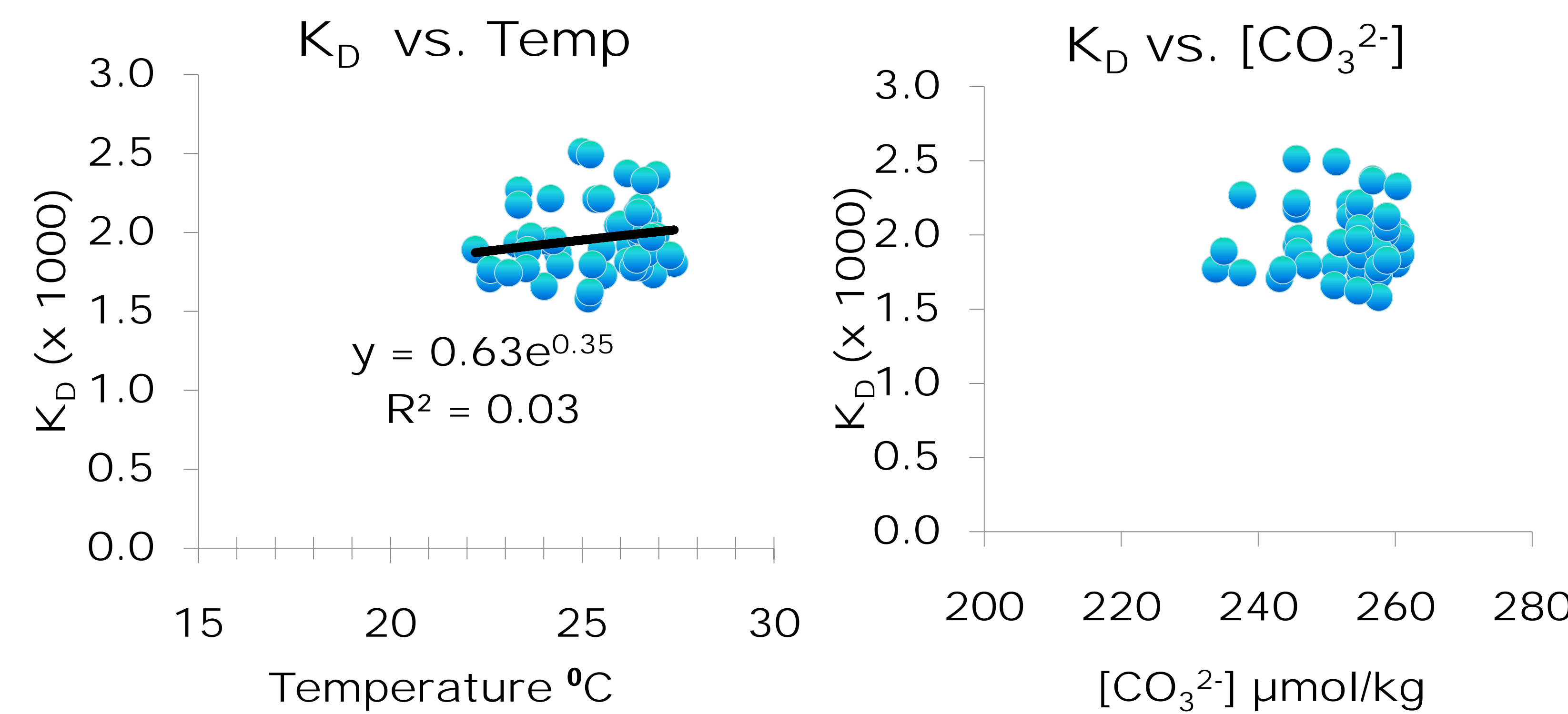
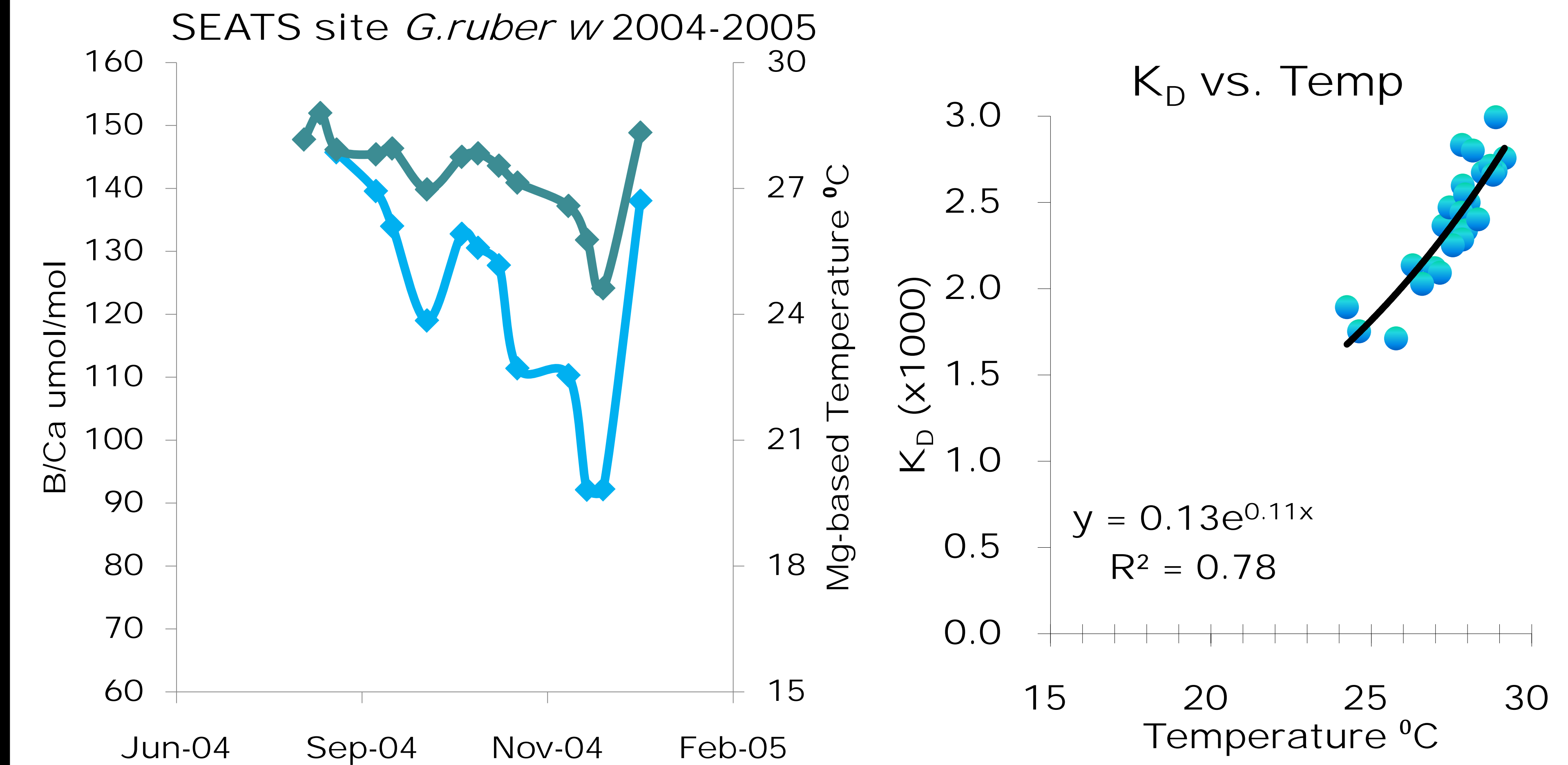
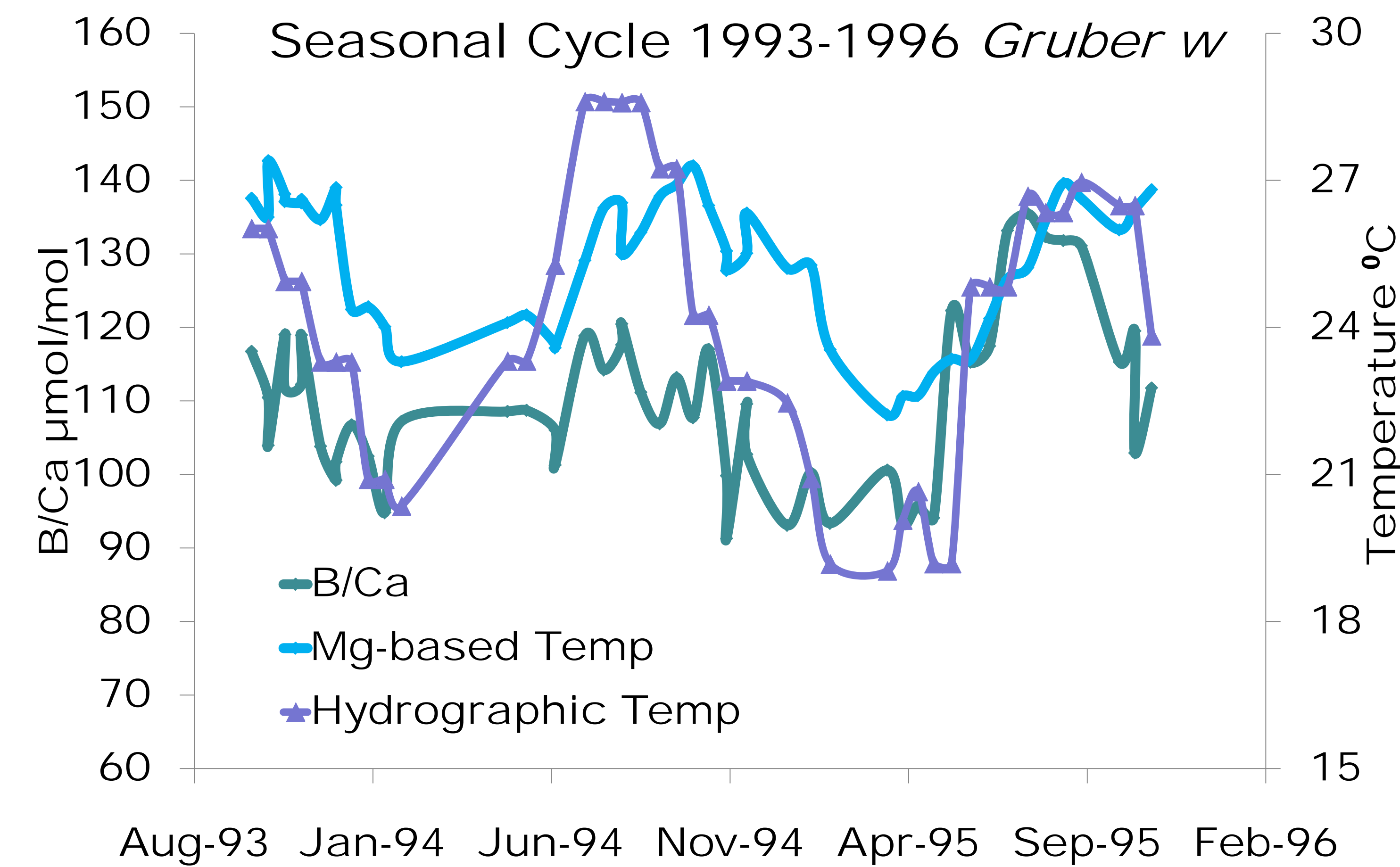
•Well preserved foraminiferal samples with biweekly resolution and contemporaneous hydrographic data that can be used to deconvolve the various influences on boron incorporation into foraminiferal tests.

•OFP-Large annual cycle in surface water pCO<sub>2</sub> of ~80µatm, which is predominantly driven by the 8-10°C seasonal change in SST. Surface water pH changes seasonally by ~0.115 with the lowest values during the warm, high pCO<sub>2</sub> summer months (Fig. bottom left Bates 2007).

•SEATS- Seasonal temperature change of 24-30 °C and pCO<sub>2</sub> of 340-400 µatm driven by winter monsoonal upwelling (Tseng et al. 2007).



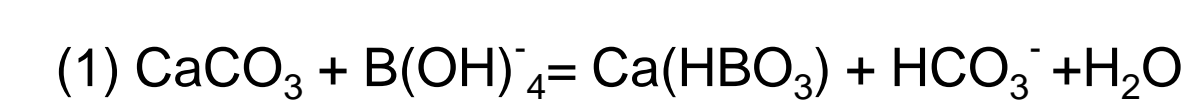
## (5) RESULTS



## (4) BACKGROUND ON BORON/CALCIUM

Boron in seawater exists predominantly as two species, borate B(OH)<sub>4</sub><sup>-</sup> and boric acid B(OH)<sub>3</sub> and their relative abundance is dependent on pH.

Evidence from boron isotopes in modern marine carbonates are within the isotopic range of borate suggesting it is the boron species incorporated into marine carbonates (Hemming & Hanson 1992)

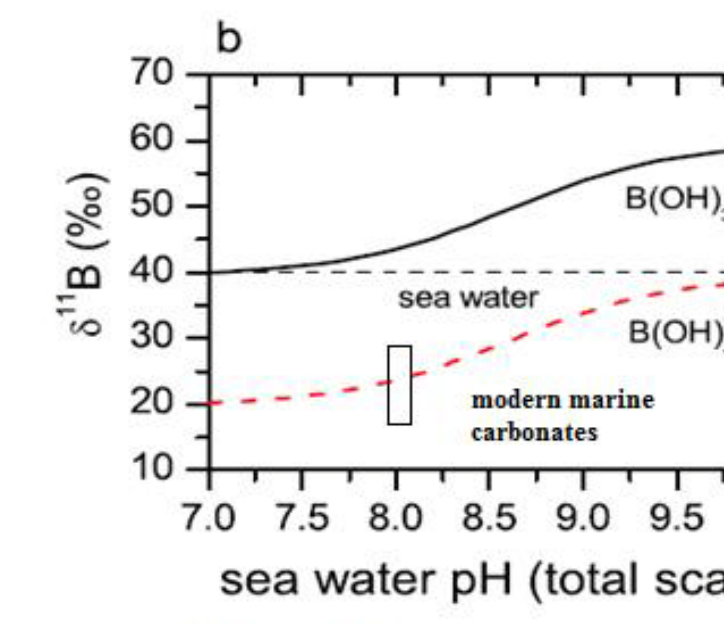
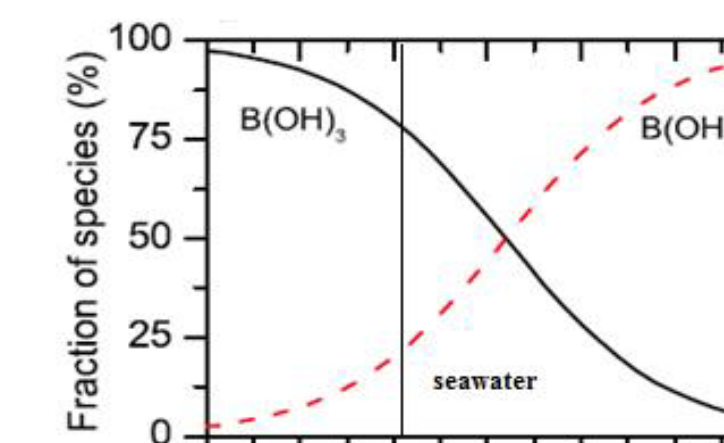


Based on (1) we can define the partition coefficient (K<sub>D</sub>) in CaCO<sub>3</sub>:

$$(2) K_D = \frac{[\text{HBO}_3^-] / [\text{CO}_3^{2-}]_{\text{CaCO}_3}}{[\text{B(OH)}_4^-] / [\text{HCO}_3^-]_{\text{seawater}}}$$

And the measured ratio in foraminiferal calcite is:

$$(3) \frac{[\text{B/Ca}]_{\text{CaCO}_3}}{[\text{CaCO}_3]} = K_D \frac{[\text{B(OH)}_4^-] / [\text{HCO}_3^-]_{\text{seawater}}}{[\text{CaCO}_3]}$$



## CONCLUSIONS:

•Both SEATS and OFP have seasonal variability of B/Ca that co-varies with calcification temperature.

•The K<sub>D</sub> to temperature relationship is minimal at OFP suggesting that regional effects are influencing boron incorporation. A stronger influence of pH may be reducing the temperature effect.

•Both SEATS and previously published calibrations suggest that calcification temperature has a dominant influence on B/Ca ratios in *Gruber w.*

•Future work of developing B/Ca as a seawater proxy is to understand the effect of dissolution on boron so that accurate pH may be reconstructed.

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