

Development of B/Ca in planktonic foraminifera as a proxy for seawater pH

Tali Babila

babila@marine.rutgers.edu

Rutgers University Institute of Marine and Coastal Science 71 Dudley Road New Brunswick, NJ 08901



ABSTRACT:

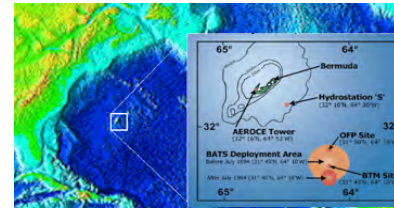
An increasing body of evidence suggests that calcification rates of marine organisms may decrease because of lowering surface ocean pH due to the recent anthropogenic increase of atmospheric carbon dioxide emissions. The development of the new geochemical proxy in the field of paleoceanography, Boron/Calcium (B/Ca) ratios in planktonic foraminifera may be used to reconstruct seawater pH. The reliability of this new proxy depends, however, on the knowledge of the pH and temperature effects on boron incorporation into foraminiferal tests. Recent studies based on down core records have suggested that B/Ca ratios in planktonic foraminifera shells may potentially be used as a proxy for surface seawater pH. I propose to validate these preliminary results by conducting a sediment trap based calibration using surface dwelling planktonic foraminifera collected seasonally over the over the past 25 years. This study will focus on two mixed layer spinose-species *Globigerinoides ruber* and *G. sacculifer* which record surface conditions (where the pH change will be at maximum) and therefore may potentially be used to reconstruct atmospheric pCO₂. Using the B/Ca-temperature relationship and Mg/Ca measurements on the same samples, as an independent proxy of temperature³ will allow the temperature effect on B/Ca to be removed and thus determine pH.

Test Site: Bermuda Oceanic Flux Program (OFF)



Since 1978, the Oceanic Flux Program (OFFP) has continuously measured particle fluxes in the deep Sargasso Sea. The OFF site is located 75 km SE of Bermuda (32°05'N 64°15'W), in the western part of the North Atlantic gyre, offering bimonthly (1978-1989) to biweekly (1989-present) sample resolution

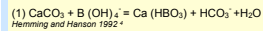
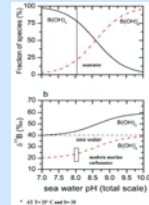
Continuous hydrographic data of SSTs, salinity, DIC, alkalinity and pCO₂ are available from the Bermuda Atlantic Time-Series Study (BATS) from 1984 to present.



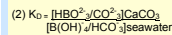
Objectives:

- Use the Bermuda sediment trap time-series to calibrate the temperature dependence of B/Ca into the tests of planktonic foraminifera collected over three year intervals
- Test whether samples over the 25 year time interval record the surface water pH decrease of ~0.04 observed in the instrumental record.

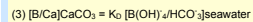
Background on B/Ca



Based on (1) we can define the partition coefficient (K_p) in CaCO_3 :



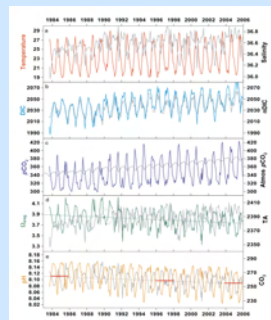
And the measured ratio in foraminiferal calcite is:



Boron isotopic values for modern marine carbonates are within the isotopic range of borate suggesting that borate is the boron species incorporated into biogenic carbonates

Dissolved boron in seawater exists as $\text{B}(\text{OH})_3$, boric acid and $\text{B}(\text{OH})_4^-$, borate and their relative abundance is highly pH dependent. Boron incorporation into calcite is theorized to be borate because the isotopic composition of bulk marine carbonates falls within the range of borate⁴. The partition coefficient K_p determines the boron fractionation between $\text{B}/\text{Ca}_{\text{shell}}$ and $\text{B}/\text{Ca}_{\text{seawater}}$. Reconstructing $[\text{B}/\text{Ca}]_{\text{seawater}}$ provides in principle a method to estimate pH assuming that K_p is constant. Preliminary studies have suggested that K_p is strongly species dependent and therefore related to calcification temperature⁵. There is a need to resolve a possible temperature effect on B/Ca and any additional environmental factors such as salinity that may affect seawater-calcite fractionation.

Why a Sediment-Trap based Calibration?



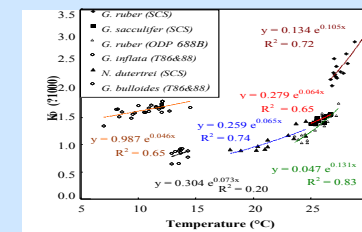
Seasonal and long-term (1983-2006) changes in surface water chemistry at Bermuda Hydration Station S Bates 2007²

Large annual cycle in surface water pCO₂ of about 100µatm, which is predominantly driven by the 8-10°C seasonal change in SST

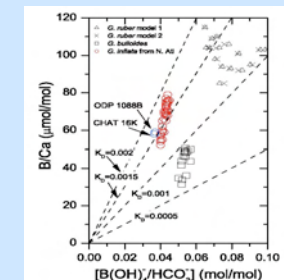
Surface water pH changes seasonally by ~0.115 with the lowest values during the warm (SST=27°C), high pCO₂ summer months. Atmospheric pCO₂ increased by ~40µatm between 1983-2006 causing a decrease of ~0.04 in surface water pH.

	1983-2006	1983-2006
Temp.	8-10°C	+0.37°C
Salinity	0.1	+0.19
ΔDIC	~30	+19.1 µmol/kg
ΔALK	~30	+1.4 µmol/kg
pCO ₂	90-100µatm	+7.3 µatm
pH	0.115	-0.037
$\text{B}/\text{Ca}_{\text{shell}}/\text{HCO}_3^-$	0.003	-0.005
K_p	0.001-0.002 (20-29°C)	0.002 (25°C)
B/Ca	~50 µmol/mol	10 µmol/mol

Preliminary Core top Calibrations



Core-top calibration of the dependence of boron partition coefficient (K_p) on temperature for several planktonic foraminiferal species. Temperature estimates for the South China Sea (SCS) are derived from Mg/Ca based SSTs.



Foraminiferal B/Ca vs. seawater $[\text{B}(\text{OH})_3]/[\text{HCO}_3^-]$. The dashed lines mark the linear relationships with constant K_p . Note that foraminiferal B/Ca data do not fall on any of these lines therefore K_p is not constant and may depend on temperature. Figure from Yu et al. 2007²

Methodological Challenges:

- Limitation on small sample size due to the rigorous cleaning procedure required for analysis
- Measurements of B/Ca ratios difficulties include high B blanks and a B memory effect from the ICP-MS introduction system



Remaining Questions:

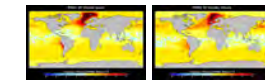
- (1) What boron species is incorporated into foraminiferal calcite?
- (2) Is boron incorporation controlled by pH or CO₂?
- (3) What is the temperature effect on KD?

Future Research Goals:

- Development of a micro-FAST flow injection sample introduction system coupled with HR-ICP-MS for the analysis of sub 100µL volumes.
- Analysis of planktonic shell weight variability using sediment trap time-series to quantify dissolution from anthropogenic ocean acidification in addition to validating B/Ca as a pH proxy
- Utilizing the geologic record for paleo-analogs for future ocean acidification conditions to study the long term effects of decreased pH on calcification

Possible Geological Applications

The *Mid-Pliocene warm period* (~4-5 Ma), when global temperatures particularly at the high latitudes are believed to have been significantly warmer than today and atmospheric pCO₂ was arguably similar to the present day level of ~380 ppmV.



USGS Pliocene Research, Interpretation, and Synoptic Mapping (PRISM)

The Pliocene-Eocene Thermal Maximum (PETM ~55Ma) as a paleo analog for future ocean acidification conditions. It is estimated that the ~100µatm increase in anthropogenic pCO₂ has led to a decrease of about 0.15 units (Galeira and Wickett 2005). If this trend continues, the lowering of oceanic pH, may result in reduced calcification rates.

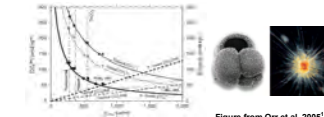


Figure from Orr et al. 2005¹

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References:

- ¹Orr, J. C., and others (2005) Anthropogenic ocean acidification over the twenty first century and its impact on calcifying organisms. *Science*, 310, 979-985.
- ²Yu, J., G. H. Hemming, & J. G. Meade. (2007) B/Ca in planktonic foraminifera: a proxy for surface seawater pH. *Geochimica et Cosmochimica Acta*, 71, 1025-1035.
- ³Wickett, B. J., and G. W. K. Moore. (2002) Estimating the temperature dependence of Mg/Ca and Sr/Ca in foraminifera. *Marine Chemistry*, 76, 169-180.
- ⁴Hemming, G. G., and H. E. Hesse. (1992) Boron isotopic composition and incorporation in modern marine carbonates. *Geochimica et Cosmochimica Acta*, 56, 107-115.
- ⁵Yu, J., G. H. Hemming, & J. G. Meade. (2007) B/Ca in planktonic foraminifera: a proxy for surface seawater pH. *Geochimica et Cosmochimica Acta*, 71, 1025-1035.