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Comment on "A critical evaluation of the boron isotope-pH proxy: The accuracy of ancient ocean pH estimates" by M. Pagani, D. Lemarchand, A. Spivack and J. Gaillardet

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Abstract

Pagani et al. [Pagani M., Lemarchand D., Spivack A., and Gaillardet J. (2005). A critical evaluation of the boron isotope-pH proxy: the accuracy of ancient ocean pH estimates. *Geochim. Cosmochim. Acta* **69**(4), 953–961] use data from previous boron isotope studies to suggest that the fractionation between boric acid and borate in seawater as well as the history of $\delta^{11}B$ in seawater are poorly understood, thus limiting our ability to capture realistic ocean pH with this proxy. Although we agree with the authors that the long recognized uncertainty in the secular variation of $\delta^{11}B_{seawater}$ imposes a temporal limit on paleo-pH reconstructions, their evaluation of the $\delta^{11}B$/pH relationship in carbonates is flawed. Potential complications from vital, temperature and dissolution effects reported in that paper are based on studies that are experimentally and/or analytically poorly constrained. Using published validation studies we will demonstrate that many of the problems outlined by Pagani et al. have already been addressed, or are based on misinterpretations of previous work. Most importantly, statistical evaluation suggests empirical data are best described by a fractionation of $\sim 20‰$. Recent paleoreconstructions confirm that the boron isotope proxy can be used with confidence, if sample selection and analyses are done carefully.
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1. INTRODUCTION

The boron isotope fractionation between boric acid, $B(OH)_3$, and borate, $B(OH)_4^-$, (ε_{B3-B4}) results from differences in vibrational energy and molecular geometry of the two boron species. Paleoceanographers commonly use a fractionation factor α_{B3-B4} of ~ 1.019 (where $\varepsilon_{(B3-B4)} =$ (fractionation factor $\alpha_{(B3-B4)} - 1)*1000$), which has been determined numerically by Kakihana et al. (1977). Pagani et al. (2005) recognized that a number of boron isotope studies (e.g. Vengosh et al., 1991; Spivack et al., 1993; Spivack and You, 1997) have revealed $\delta^{11}B$ data in marine carbonates much lower than 19‰. Because 19‰ is the lowest possible boron isotopic composition of borate in seawater at pH < 7 calculated using the commonly applied fractionation factor of Kakihana et al. (1977), Pagani et al. (2005) take this as an indication that the theoretical fractionation factor of $\alpha_{(B3-B4)} \sim 1.019$ (Kakihana et al., 1977) may be too small. In addition, they argue that if boron incorporation in marine carbonates occurs in equilibrium with $\delta^{11}B_{borate}$, the inorganic precipitation experiments by Sanyal et al. (2000) should help to better constrain the fractionation factor because inorganic calcite precipitation is not affected by vital effects. The best fit that they draw through Sanyal's inorganic calcite data, suggests $\varepsilon_{(B3-B4)} = 26‰$. We will first examine the quality of the data interpreted by Pagani et al. (2005) and then evaluate the validity of their proposed fractionation factor.

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2. BORON ISOTOPE ANALYSES AND POORLY CONSTRAINED STUDIES

The challenge of boron isotope analyses is the inability to correct for mass fractionation during analysis, as well as potential isobaric interference on mass 42 ($^{12}C^{14}N^{16}O^-$ ions) through organic matter contamination, which would result in an underestimate of the original $\delta^{11}B_{calcite}$ (Hemming and Hanson, 1992). It is therefore of utmost importance that strict analytical protocol be followed for every analysis, including treatment with an oxidizing solution to remove organic matter, analysis at the same temperature, and, most importantly, sample replication.

In addition to strict data acceptance criteria, sample selection has to be made carefully. Fig. 1 demonstrates that isotopic offsets between species require monospecific sample analysis. Hönisch and Hemming (2004) have demonstrated that $\delta^{11}B$ increases with shell size in the symbiont-bearing foraminifera *Globigerinoides sacculifer*, that partial dissolution decreases $\delta^{11}B$ and that larger shells provide more reliable results. Consequently, core locations should be shallow and from low productivity areas, and foraminifera shells should be from a large and restricted size range. Partial dissolution can be monitored by shell weights and microstructural analyses of the shell surface.

Many of the studies cited by Pagani et al. (2005) violate these strict criteria. For instance, Spivack et al. (1993) and Spivack and You (1997) analyzed mixed species or bulk sediments without cleaning for organic matter contamination, and the results are thus potentially compromised by isobaric interference, dissolution and species effects. In addition, Spivack and You (1997) separated the carbonate and silicate phase 30 min after dissolution in HCl. This procedure likely results in boron being leached from clay particles and out of the silicate phases which might modify the $\delta^{11}B_{calcite}$ (typically towards lighter values). In contrast, Vengosh et al. (1991) restricted their analyses to single species and cleaned for organic matter, but their study shows a much larger analytical uncertainty and $\delta^{11}B$ range (i.e. 14.2–32.2‰) than measured in any other study to date (~19–26‰, various studies). Comparison of modern *G. sacculifer* samples from the equatorial Atlantic and Gulf of Eilat additionally reveals poor consistency between the Vengosh et al. (1991) data. The 5‰ difference between the two samples would imply a ~0.4–0.5 units difference in surface seawater pH, which is unreasonable given the small range in modern tropical seawater pH. These issues raise the question whether some of the samples might have been altered diagenetically and/or how sound the analytical procedure was at the time of this early study.

3. INORGANIC CALCITE PRECIPITATION AND THE FRACTIONATION FACTOR

In summary, many of the early studies were analytically and experimentally poorly constrained and their results should not be relied upon to make fundamental changes in our current understanding of the boron isotope proxy. However, the empirical calibration curves generated by Sanyal et al. (1996, 2000, 2001) fulfill all criteria for high-
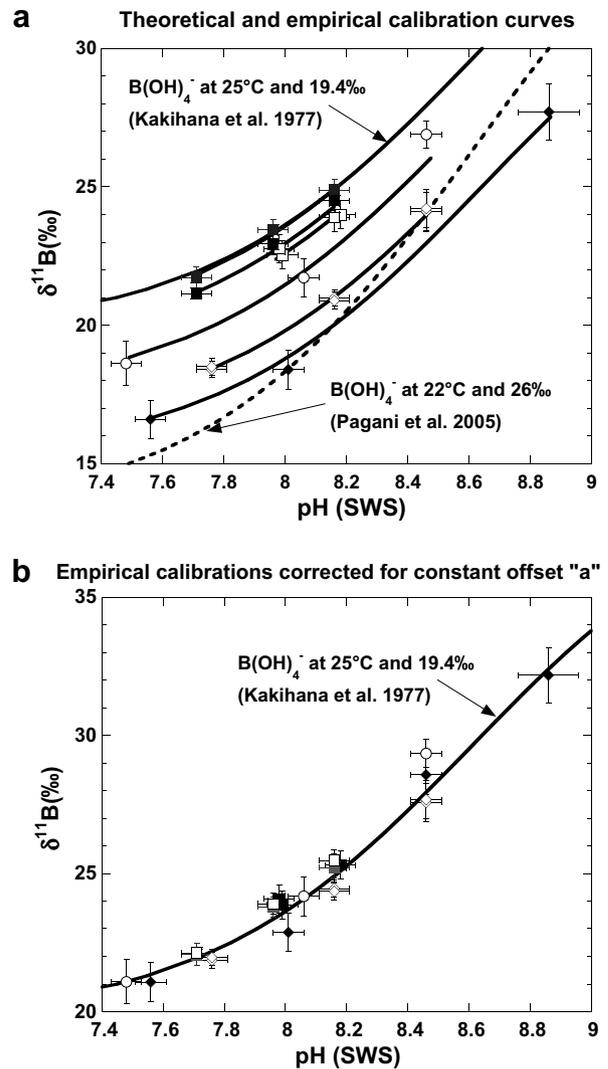
a   Theoretical and empirical calibration curves

b   Empirical calibrations corrected for constant offset "a"

Fig. 1. (a) Empirical $\delta^{11}B$/pH relationships in marine carbonates. From top down symbols indicate *Porites cylindrica* (grey squares), Acopora nobilis (black squares), *Acropora* sp. (open squares), *G. sacculifer* (open circles), inorganic calcite (open diamonds), and *O. universa* (black diamonds). pH data were recalculated for the seawater scale where necessary. Empirical calibration fits were calculated according to Eq. (1), using the respective experimental temperature and salinity settings summarized in Table 1. The dashed line indicates the shape of the borate curve if the fractionation was 26‰ at 22 °C. Note that all empirical curves are parallel to each other but show constant offsets at all pH values when $\varepsilon_{(B3–B4)} \sim 20‰$ (Kakihana et al., 1977). Relative offsets are more variable with pH when $\varepsilon_{(B3–B4)} = 26‰$ (Pagani et al., 2005), see also Table 1 for the respective root-mean square errors. (b) After correction for their respective constant offset "a" all empirical data fall onto the theoretical borate curve.

quality analyses and are consistent with coretop data from various ocean regions (Sanyal et al., 1995; Sanyal and Bijma, 1999) but $\delta^{11}B$ data at the lowest experimental pH values still exceed the 19‰ limit (Fig. 1). To solve this problem, Pagani et al. (2005) suggest a larger fractionation of $\varepsilon_{(B3–B4)} = 26‰$, which they suggest as the best fit through

the synthetic calcite data by Sanyal et al. (2000). Fig. 1 shows all empirical calibration data and the dashed line indicates the shape of the borate curve if the fractionation was 26‰ (as suggested by Pagani) at 22 °C, the temperature at which Sanyal et al. (2000) performed their experiments. The synthetic calcite data do not match the 26‰ curve as well as in Pagani's original publication. This is because all calibration experiments were performed in natural or artificial seawater but the experimental seawater pH was measured on the (freshwater) NBS scale. Because Dickson (1990) determined pK_B in artificial seawater on the total pH scale, the empirical data need to be corrected for the difference between pH scales. The CO2SYS program by Lewis and Wallace (1998) allows a simple estimate for the difference between the pH scales under the experimental salinities and temperatures. By subtracting 0.14 from pH on the NBS-scale, pH on the seawater scale can be calculated. This moves the data to the left along the pH axis. Pagani's best fit curve would thus need to be corrected towards a smaller fractionation factor in order to pass through the data, approximately 1.024. However, because Pagani et al. (2005) cited Oi (2000), who suggested a fractionation factor of 1.025, and because more recent studies consistently suggest a fractionation >27‰, we will restrict our discussion to Pagani's originally suggested 26‰ curve for comparison with the empirical data (Fig. 1a). Relative to this steeper borate curve, all empirical δ^{11}B/pH relationships, including the synthetic calcite curve by Sanyal et al. (2000), would have varying offsets at different pH. We demonstrate this statistically, by calculating the least-squares fits for the empirical δ^{11}B/pH relationships with the general equation

$$pH = pK_B - \log(-(\delta^{11}B_{sw} - \delta^{11}B_c - a)/(\delta^{11}B_{sw} - \alpha_{(B3-B4)}$$
$$* (\delta^{11}B_c + a) - \varepsilon_{(B3-B4)})) \qquad (1)$$

where $\delta^{11}B_{sw} = 39.5‰$, $\delta^{11}B_c$ is the isotopic composition of the measured carbonate, $\alpha_{(B3-B4)}$ is the fractionation factor, $\varepsilon_{(B3-B4)}$ the fractionation, pK_B is a function of temperature and salinity (Dickson, 1990) and 'a' is the constant offset between the theoretical borate curve and empirical calibration data for a specific sample type. The necessity for a constant offset from the theoretical borate curve was inferred by estimating the confidence intervals, at 95%, for each empirical data set, which confirmed that, in each case, the value of the offset was significantly different from zero (Emery and Thompson, 1997). Relative to a fractionation of ~20‰ (Case 1), the root-mean square errors, e_{rms}, of all empirical data sets are larger when a fractionation of 26‰ is applied (Case 2, Table 1). The e_{rms} would be even larger if a fractionation >26‰ was applied.

Pagani et al. (2005) recognized the poor match between the experimental data and the δ^{11}B/pH fit and argued that variable offsets relative to the theoretical curve reflect on our inability to correct for vital effects. Given how poorly a larger fractionation factor describes the measured inorganic data (which are by definition not affected by vital effects), this is in fact a fundamental argument against a larger fractionation factor.

In addition to the statistical evaluations mentioned above, we also calculated the best fits for each empirical data set, simultaneously optimizing for ε and a (Case 3, Table 1). With the exception of *Acropora* sp. (Reynaud et al., 2004), which was grown under only two pH

Table 1

Experimental seawater conditions, corresponding pK_B (according to Dickson (1990)) and $\varepsilon_{(B3-B4)}$ values (according to Kakihana et al., 1977—Case 1, Pagani et al., 2005—Case 2 and best fit—Case 3) for the empirical calibration data shown in Fig. 1

Species	Temperature (°C)	Salinity (‰)	pK_B	$\varepsilon_{(B3-B4)}$	a	e_{rms}
Case 1: calculate offset a at ε ≈ 19‰						
Borate	25.0	34.8	8.60	19.4		
G. sacculifer	27.0	36.4	8.57	19.3	2.46	1.06
O. universa	22.0	33.7	8.64	19.5	4.47	1.20
Acropora sp.	25.0/28.0	38.0	8.58/8.55	19.3	1.32	0.84
Acropora nobilis	27.0	36.4	8.57	19.3	0.97	0.43
Porites cyclindrica	27.0	36.4	8.57	19.3	0.34	0.64
Synthetic calcite	22.0	34.0	8.64	19.5	3.46	0.72
Case 2: calculate offset a at ε = 26‰						
G. sacculifer	27.0	36.4	8.57	26.0	−3.01	1.41
O. universa	22.0	33.7	8.64	26.0	−0.85	3.08
Acropora sp.	25.0/28.0	38.0	8.58/8.55	26.0	−3.70	1.17
Acropora nobilis	27.0	36.4	8.57	26.0	−4.71	1.19
Porites cyclindrica	27.0	36.4	8.57	26.0	−5.08	1.10
Synthetic calcite	22.0	34.0	8.64	26.0	−1.80	2.45
Case 3: calculate best fit for offset a and ε						
G. sacculifer	27.0	36.4	8.57	21.4	0.80	0.76
O. universa	22.0	33.7	8.64	20.5	3.62	1.12
Acropora sp.	25.0/28.0	38.0	8.58/8.55	15.9	3.85	0.71
Acropora nobilis	27.0	36.4	8.57	21.6	−1.00	0.64
Porites cyclindrica	27.0	36.4	8.57	20.4	−0.55	0.67
Synthetic calcite	22.0	34.0	8.64	19.7	3.31	0.77

The respective δ^{11}B/pH relationships were fitted using Eq. (1). a denotes the empirical offset from the respective borate curve (see also Fig. 1a) and e_{rms} is the root-mean square error of the respective least-squares fit.

conditions, all other data sets are best described by a fractionation close to 20‰. Except for the *G. sacculifer* data set (Sanyal et al., 2001), for which a slightly larger ε of 21.4‰ was calculated, the RMS errors of these best fits are not much different from the errors calculated for the Kakihana curve. Experimental evidence from six different calibration studies (corals, synthetic calcite and foraminifers) thus demonstrates they all share a similar slope with the theoretical borate curve by Kakihana et al. (1977). We demonstrate this graphically by correcting the empirical calibration data for their respective offset, so that they fall onto the theoretical borate curve (Fig. 1b). Although some deviation from the theoretical curve is expected from analytical uncertainty and differences in the experimental temperature and salinity conditions (Table 1), the match with the curve is compelling. The proposed larger fractionation factor of Pagani et al. (2005) would require a much more complicated explanation for the observed data. In contrast, the relative offsets between different curves can be explained by vital effects through physiological processes such as symbiont photosynthesis, respiration and calcification (Zeebe et al., 2003; Hönisch et al., 2003, 2004), as well as possibly matrix and/or experimental artifacts. Although physiological effects are significant, the parallelism between the empirical calibration curves demonstrates the constancy of these effects over a wide range of seawater pH.

4. COMPARISON WITH PALEO-DATA

The inadequacy of the Pagani et al. (2005) fractionation factor is further corroborated by comparison with paleo-data. Because data generated for modern *G. sacculifer* by Pearson and Palmer (2000) fall on the theoretical borate curve by Kakihana et al. (1977) and thus $\delta^{11}B_{G.\ sacc.} = \delta^{11}B_{borate}$, Pagani et al. (2005) used the larger fractionation of 26‰ to translate the Pearson and Palmer (2000) $\delta^{11}B$ data into pH values. This exercise disregards the large $\delta^{11}B$ offset between Kakihana's and Pagani's borate curve and the same offset between the *G. sacculifer* data by Pearson and Palmer (2000), and the synthetic calcite curve by Sanyal et al. (2000). As a result, the obtained pH values from Pearson and Palmer's (2000) $\delta^{11}B$ data have to be unrealistically high for modern surface seawater pH. In contrast, using the fractionation factor by Kakihana et al. (1977) yields reasonable pH data. Furthermore, Sanyal et al. (1995) estimated the glacial/interglacial pH difference in the surface ocean from boron isotopes in the planktic foraminifer *G. sacculifer* and found the result consistent with the glacial/interglacial pCO₂ difference measured in ice cores. Those studies can be taken as a confirmation for the validity of the theoretical (and empirical) fractionation factor (Kakihana et al., 1977; Sanyal et al., 2001) and they also demonstrate that the boron isotope proxy works if applied carefully.

5. TEMPERATURE AND DISSOLUTION EFFECTS

Pagani et al. (2005) refer to a study by Wara et al. (2003) which attempted to reconstruct surface ocean pH and pCO₂ over the past 5 Ma (importantly without replicate analyses). They measured $\delta^{11}B$, boron concentrations, Mg/Ca and

shell weights in the surface dwelling foraminifer *G. sacculifer*, picked from ODP site 806. Based on a poor ($r^2 = 0.30$) negative correlation between their $\delta^{11}B$ and Mg/Ca data, Wara et al. (2003) suggested that $\delta^{11}B$ is primarily controlled by growth temperature. In contrast, comparison of their data with the theoretical temperature effect on $\delta^{11}B$ (which is constrained by the respective temperature effects on the fractionation factor $\alpha_{(B3-B4)}$ and the equilibrium constant pK_B (Kakihana et al., 1977; Dickson, 1990)), with coretop $\delta^{11}B$ data from large *G. sacculifer* shells (Hönisch and Hemming, 2004) and living corals grown under two different temperatures (Reynaud et al., 2004) demonstrates that temperature exerts only a minor control on $\delta^{11}B$ (theoretically +0.13‰ per °C) relative to the dominant pH effect (∼0.8‰ per 0.1 pH unit). If the "trend" observed in the data by Wara et al. (2003) has any meaning at all, it would be most likely due to the climatological change in seawater pH: in times of higher atmospheric pCO₂, Henry's Law will drive aqueous PCO₂ towards equilibrium with the atmosphere. This will lead to a decrease in seawater pH. At the same time sea surface temperatures are higher due to stronger greenhouse forcing. Temperature and pH records may thus be covariant but not correlated. Recent paleo-pH reconstructions (e.g. Palmer and Pearson, 2003) were complemented by Mg/Ca analyses so that the theoretical temperature effect on $\delta^{11}B$ shown in Fig. 2 could be corrected.
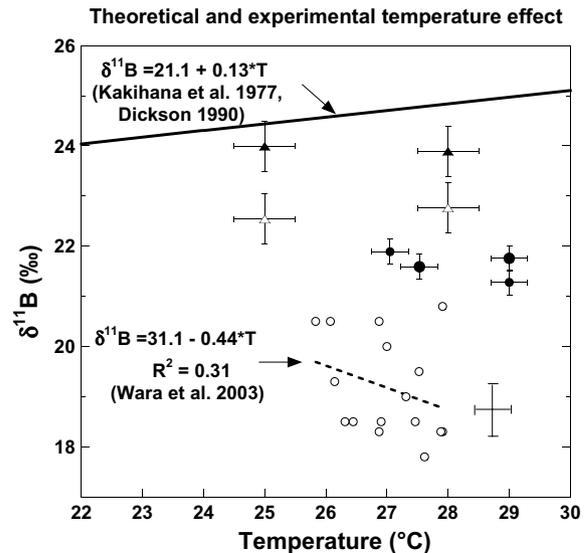

Theoretical and experimental temperature effect

Fig. 2. Theoretical temperature effect on $\delta^{11}B_{borate}$, in response to change in pK_B and fractionation between 22 and 30 °C (solid line, Kakihana et al., 1977; Dickson, 1990). Cultured *Acropora* sp. grown under two pH and temperature conditions (open triangles at pH 7.98, closed triangles at pH 8.17, Reynaud et al., 2004), pristine coretop *G. sacculifer* data from Hönisch and Hemming (solid circles, 2004), and downcore data from Wara et al. (open circles, 2003). The cross indicates Wara's reported uncertainties. While coretop foraminifer and cultured coral data confirm the minor temperature control on $\delta^{11}B$ (theoretically +0.13‰ per °C) relative to the dominant pH effect (∼0.8‰ per 0.1 pH unit), the temperature effect suggested by Wara et al. (2003) is based on an extremely poor correlation which is likely due to analytical, diagenetic and/or climatological uncertainties (see text for details).

Late Pleistocene/Holocene PCO_2 and pH estimates based on this approach match ice core records and the modern data shown in Fig. 2 confirm that this is a valid approach.

The dissolution effect mentioned by Pagani et al. (2005) is based on a similarly poor ''correlation'' between the Wara et al. (2003) $\delta^{11}B$ and average shell weight data ($r^2 = 0.25$). However, a coretop study by Hönisch and Hemming (2004) confirmed that dissolution decreases $\delta^{11}B$ in planktonic foraminifers. Shells picked from deeper water follow a gradual decrease in $\delta^{11}B$ that is consistent with a decrease in shell weights and the microstructural breakdown of the shell surfaces. Data from the Ontong-Java Plateau suggest that the dissolution effect is more pronounced in smaller shells, which is consistent with a larger surface area to volume ratio. In summary, dissolution is a serious problem for boron isotope studies, but it can be minimized by selecting shallow sediment cores in low productivity areas and by restricting analyses to the largest shell size fractions.

6. CONCLUSIONS

Many boron isotope studies evaluated by Pagani et al. (2005) applied the proxy without a proper validation process. Boron isotopes are admittedly still very difficult to measure accurately, and without the essential replicate analyses necessary to evaluate data quality, it is best to not use those studies to make strong geochemical interpretations. The larger fractionation factor suggested by Pagani et al. (2005) is inconsistent with all six existing empirical calibration curves for the boron isotope proxy. The shape and inflection point of these six curves is best described by a fractionation factor of ~1.020 (similar to the theoretical factor suggested by Kakihana et al. (1977)), and species specific offsets determine the relative position of the empirical curves to each other. The uncertainties and complications that Pagani et al. (2005) suggest disappear if a fractionation of $\sim20‰$ is applied. More analytical development and more empirical validation is necessary to fully realize the potential of boron isotopes as a paleo-pH measure, but great care needs to be taken to insure we do not step backwards in this endeavor.

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