

RESPONSE TO REFEREE #2

This work aims at proposing a new approach to determine the B isotopic composition of the oceans over the past 25 Ma. This is one of the three pillars of the atmospheric pCO₂ reconstruction over geological timescales from B isotopes in marine carbonates. The two other pillars are the pH dependence of the B isotopic fractionation and the change of seawater alkalinity. Even if the few δ¹¹B_{sw} reconstructions published so far all point to a slow increase during the last tens of Ma, they are all based on models and assumptions that are sometimes difficult to ascertain. In that, any effort to provide new and independent approach is the most welcome for the scientific community. Since it is definitely a tricky task, any effort of developing new approaches has therefore to be acknowledged.

We thank the referee for the positive view on our new approach to reconstruct δ¹¹B_{sw}, and we also appreciate the constructive criticism on the way that we describe and discuss prior results. In response to the concerns raised here and by the other referee we have modified the tone of the manuscript with regard to prior work and we emphasize the progress towards a consensus on past seawater boron isotope change that is supported by different approaches, including our own.

The past δ¹¹B_{sw} modeled in this study is based on new B isotopic data on paired planktic and benthic foraminifera. Two scenarios have been tested to derive δ¹¹B_{sw}: the first one assumes a constant pH gradient along the seawater depth-profile and the second one uses δ¹³C data to model possible variation of the seawater pH depth-profile. Even claimed to be a new approach by the authors, using paired foraminifera living at different depths in the water column was first introduced by Pearson and Palmer (1999).

In the revised manuscript we will make it clear the approach we are using is an extension of that first introduced by Pearson and Palmer (1999). The

novelty of our approach, however, is in (a) combining measurements on planktic and deep ocean benthic foraminifera, and (b) correcting for change in the surface/bottom water pH gradient using $\delta^{13}\text{C}$ (as mentioned below).

The originality of the present work is the attempt to anchor this approach with other data ($\delta^{13}\text{C}$) and climate model. Finally, the present work ends with a model of evolution of the marine $\delta^{11}\text{B}_{\text{sw}}$ very close and consistent with the previous work, which is already fine, but the large scatter of data (Fig 9) makes possible any $\delta^{11}\text{B}_{\text{sw}}$ value between +42‰ and +32‰. After data smoothing (which statistical meaning being questionable from a so small database), the authors end with a narrow range of possible values which spreading approaches the uncertainty of previous approaches (see fig. 10). This is then a bit disappointing and this is could be easily corrected if the paper starts with a more upfront position and objective of their work in comparison to previous ones. This starts in the abstract: one of the most discussed issue of using B isotopes in carbonates to reconstruct past seawater pH is first the actual relationship between the B isotopic fractionation and the pH. So far, many works have provided “calibration curve” using different foraminifera species, and they all come with differences attributed to “biological effect”. Another point is the B speciation in carbonates and the actual process of B incorporation. I personally think that most of the published $\delta^{11}\text{B}_{\text{sw}}$ are actually consistent and what we need now is a more accurate model that will narrow the range of possible values. The present work also needs to acknowledge that the approach based on paired foraminifera living at different depths in the water column was first proposed by Pearson and Palmer in 1999! Later, sensitivity tests carried by Pagani et al. (2004) showed that this approach is rather inaccurate.

In the revised manuscript we will make it clear the approach we are using is an extension of that first introduced by Pearson and Palmer (1999). The inaccuracies pointed out in Pagani et al., (2005) mainly refer to the difficult of assigning a depth habitat to individual foraminiferal species, species-dependent isotope effects, the analytical uncertainty of the carbonate. In our

study, by focusing on the surface to deep gradient we avoid the difficulty of defining calcification depths for multiple species. The analytical uncertainty and species-specific isotope effect are both better understood and accounted for in this work.

In Fig. 1 is presented a simplified B cycle in the ocean but, presented as it is, there is a large imbalance between inputs and outputs: the B inputs by precipitation is one order of magnitude higher than the sum of all the others. Then, either this input flux is balanced by output by sea salts or evaporation of gaseous B and then this loop is that fast that it must be taken into account, or atmospheric B derives from a continental source and a huge output flux is missing. One possibility is that the atmospheric B content (certainly in gaseous form and not sea salts) derives from anthropic activities, which are irrelevant for reconstructions on geological timescales. Whatever the explanation is, the B marine cycle like presented in fig. 1 at least useless if not wrong. I would therefore strongly suggest to revise this figure and the corresponding text, in particular lines 66-71 where the atmospheric fluxes are discussed.

We acknowledge that our understanding of the modern boron cycle requires further work and the view we present is overly simplified. In the revised figure and text we will refer to what is presented here as the fluxes of B that are important on geological timescales following Lemarchand et al. (2002). We will also emphasize in the text, caption and figure itself that the view we present includes a large imbalance of inputs and outputs that will need to be addressed in future work.

There is one thing that we can take for sure is the very long B residence time in the oceans. This is held by the very high B concentration in seawater (about 500 times more concentrated than river waters). Therefore, whatever the model or indirect determination of the $\delta^{11}\text{B}_{\text{sw}}$, large and rapid variation of $\delta^{11}\text{B}_{\text{sw}}$ like those mentioned line 86 are unrealistic as long as we do not identify a huge B flux, missed so far, that may have affected the B cycle over

geological time scales.

We fully agree with this comment, and indeed this the fundamental rational behind our approach of smoothing. However, in the context of this comment, while changes mentioned in the study of Simon et al., (2006) (line 86) are highly unlikely, these authors illustrate the potential uncertainty involved in modeling the boron cycle with our current understanding of changes in oceanic crust alteration through time.

A map of the sampling location would be appreciated

We add a map to the revised manuscript.

In equation (1), I think that epsilon(biological effect) would be appropriate and add in the text a discussion about the different calibration curves

A description of how the calibration curves were constructed will be added to the text.

section 2.2 is a succession of hypothesis and calculation made from a series of embedded models, which is certainly the best way to make estimation with our present knowledge, but a discussion of the possible errors propagated is critical here in a much more detailed and argued way than proposed in section 2.5. In particular, from what data is derived the estimation of ± 0.05 pH of the error made on the $\delta^{13}\text{C}$ -pH relationship (line 381)?

Also in response to the other referee's comments, we add a data table and additional description on this point to the updated manuscript. The uncertainty of the $\delta^{13}\text{C}$ -pH relationship is estimated from the model sensitivities and ensemble simulation spread. The uncertainty in $\delta^{11}\text{B}$ is described further down the section (lines 385-392). The $\pm 2^\circ\text{C}$ uncertainty in temperature is a reflection of the uncertainty in the Mg/Ca measurement and the relationship between $\text{Mg}/\text{Ca}_{\text{foraminifera}}$ and temperature. No record of salinity exists through time. Consequently, we apply a ± 2 psu unit uncertainty which we think we be sufficient to cover any potential variations. The uncertainty in [Mg] and [Ca] are derived from Horita et al., (2002).

It is difficult to follow the section 3.2. The important information is finally given in the last 5 lines of this section. Please shorten and clarify.

This section will be reworded and clarified in the revised manuscript.

This is a bit frustrating to see $\delta^{11}\text{Bsw}$ values and discussion of them only in the last 2 pages (lines 484-537). I would strongly suggest to shorten some of the previous parts and strengthen this last one.

While we acknowledge further discussion of the $\delta^{11}\text{Bsw}$ values would certainly be of interest to the boron isotope community, we hesitate to expand this section as reviewer 1 suggests it is premature to do so. However, in the revised manuscript we endeavor to cut down the sections outlining our methodology and justification of approach.

One important point is the validation of the model and the statistical treatment made on the models $\delta^{11}\text{Bsw}$ values. At first sight, fig. 9. looks far from being convincing: a large scatter of the data, which looks like not providing strong new constraints and a significant restriction of the possible data by smoothing the small dataset?

As outlined by the reviewer, boron has a long residence time in the ocean and therefore rapid variations in $\delta^{11}\text{Bsw}$ are unrealistic. We use this to justify our smoothing and provide an extra constraint on our record. This is necessary because our uncertainties in each $\delta^{11}\text{Bsw}$ reconstruction are large as a consequence of our approach where we fully propagating the uncertainties in all parameters involved. In order to strengthen the justification for our approach in the revised manuscript we will explore a number of other scenarios (e.g. binning the data, using an algorithm to smooth, and assume a spline fit) and then focus the subsequent discussion on what aspects of the evolution of $\delta^{11}\text{Bsw}$ are consistent across these scenarios and hence robust to the nature of our chosen smoothing (e.g. that $\delta^{11}\text{Bsw}$ is around xx permil

lighter than modern in the middle Miocene, and much of the change in ratio occurred during the interval xx to xx Ma).