**Biogeosciences
Discussions**

Interactive comment on "Abrupt sea surface pH change at the end of the Younger Dryas in the central sub-equatorial Pacific inferred from boron isotope abundance in corals (*Porites*)" *by* E. Douville et al.

E. Douville et al.

Eric.Douville@lsce.ipsl.fr

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Overall we greatly acknowledge the constructive and very helpful review given by reviewer 2. We have carefully revised according to his suggestions as outlined in detail below anf in the supplement pdf document.

Anonymous Referee #2

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In this manuscript the authors present both a regional scale investigation into how well

the d11B-pH proxy in corals matches modern seawater and show how this proxy in corals can be used to reconstruct seawater pH in the past. They present a temporal record from the Central Pacific that indicates that during the Younger Dryas this region became a significant source of CO_2 to the atmosphere, which is an exciting conclusion. The data appear sound and confirm the veracity of previously published coral data by NTIMS and PTIMS. Similarly, although not an ideal comparison and by no means an exact replicate, the data presented also broadly confirm the accuracy of theforaminiferal NTIMS study of Pearson and Palmer (2003) from the western Equatorial Pacific. I therefore feel this manuscript represents a significant advance and should be published. I have a few comments however that need to be addressed before acceptance. I will discuss these in order of appearance rather than significance:

1. I found the discussion on p.1964 of the hydrological setting rather confusing, and this confusion was not helped by the diagram associated with this section (Figure 2). Is there a way to make this clearer? Also it was not obvious which points relate to the El Nino year of 1994 on this figure. Line 10 on this page is "..on the seawater scale, as reported on the modern pH scale, .." what is the "modern pH scale"?

The revised version of the manuscript is now modified taking care to well precise the scale of pH used (seawater or total hydrogen ion pH scales). We also replaced the term "modern pH scale" by "as present day pH" both in the Figure and text. We further slightly simplified Figure 2 in order to clearer present the El Nino event of 1994 in this Figure.

2. My main concern with this study is that coral samples represent a snap shot of time. On p1965 line 25 it is stated that "Each of these samples represents more than one year." On p.1974 it is stated that "In corals, the sampling represents one or a few years of growth: : :". This is not a problem if there was little inter annual variability in pH in this region. The fact is however that every recent coral record from the Pacific, including some of this authors (e.g. Douville et al., 2009 – "Our results further reveal that seawater pH changes in the Fiji area are strongly affected by regional processes such as

the South Pacific Convergence Zone (SPCZ) tightly linked the Pacific Decadal Oscillation (PDO)" – see http://adsabs.harvard.edu/abs/2009AGUFMGC24A..04D), indicates significant interannual pH variations. This is also consistent with direct measurements of seawater which show, as the authors discuss, significant variation associated with ENSO cycles (e.g. Feely et al., 1999). The authors need to be more explicit about how many years they are sampling for their records and discuss what biases this may introduce. I agree that this is not going to affect their conclusions and the recognition of the YD spike in pH but I feel this needs to be discussed so as to better compare later work with this study.

The end of the sentence "Each of these samples represents more than one year" was modified to "… represents one or two years".

And we added in the text (3.2. Chemical Preparation):

"The most important here is to carefully collect a piece of coral integrating both low and high density bands in order to smooth out the effect of seasonal pH changes and to keep always the same sampling strategy."

In contrast, to study and measure interdecadal changes of pH, one needs to keep the sampling close to one or two years. We have chosen this sampling strategy both in this study and for the Fiji study cited above. In this case we obtained very reproducible and coherent results.

3. When neutralising the dissolved coral to pH 8-9 were any precipitates formed? Also how was the resin cleaned? Was the matrix of each sample, after column separation, examined in order to identify those samples where column chemistry may have not been effective? A bit more detailed needed.

For pH values higher than 9, one can in fact obtain white precipitates but this formation is reversible and absent at pH < 9. In addition, we systemically verify that our final pH at the end of this step is between 7 and 8. In the revised text, we have added the range

of values reflecting pH conditions at the end of this chemical step. More details are described now in the text (see again part 3.2. Chemical preparation)

4. It is encouraging that the authors don't see any difference between introduction systems (p1966) but I can't easily see the data in the table. A cross plot would be more useful here as this comparison is important. Also, if samples have been measured more than once by either technique a separate entry is needed on Table 1. Please show all data rather than means and std dev. For instance, from table 1 it appears that the key sample at 11.47 kyr from Marquesas Island has been run three times – is that the case? If so, please show all the ratios you collected. Also, where there has only been 1 measurement is the std dev the internal or external precision? Similarly, when they have been measured more than once is this the entry in the std dev column the std dev of these multiple analyses. Can the authors also make a distinction between complete procedural replicates (e.g. new dissolution of powders), repeats of the same dissolved sample (e.g. separate chemical treatments of the same dissolved powder) and repeats of the same sample solution after chemistry (repeats of the same purified sample).

In agreement with the reviewer suggestion, we added a new Figure (Figure 3 in the revised manuscript) representing a cross plot of results obtained from the two different introduction systems. This figure confirms that all results given in this study are within the external reproducibility of 0.25 ‰ As asked, we also detailed in table 1 d11B values obtained from the two different introduction systems after new sampling and chemistry. In contrast, as all others results are within the external reproducibility of 0.25 ‰ (for example: B01: 26.34‰ , B02‰$26.46\ B03:26.78\ B04:$ $26.61\ this sample was collected 4 times), we kept the average values and showed only the number of t$

See new Figure 3

5. p1967. It might be better to reference some earlier studies than Pagani et al., 2005 on line 20. How about Hemming and Hanson (1992) and Vengosh et al. (1991)?

This point was now revised in agreement also with the comment of reviewer 1!

6. p1968. Kakihana et al. (1977) suggested that the isotopic fractionation factor (alpha) between the two aqueous boron species was 1.0194 from theoretical calculations based on vibrational frequency data. It has subsequently been shown however by Rustad and Bylaska (2007) that these calculations were erroneous, and so produced values for alpha that were too low. That 1.0194 is too low is confirmed by several recent studies using a variety of techniques (e.g. Oi, 2000; Zeebe, 2005, Liu and Tossell, 2005; Rustad et al., 2010). Finally, this saga was drawn to a close with the first direct measurement of alpha in seawater by Klochko et al. (2006). There is now no getting away from it – the isotopic fractionation factor between the two boron bearing species in seawater (boric acid and borate ion) is 1.0272, not 1.0194. This section has to be rewritten to reflect this. Crucially the authors need to draw a distinction between alpha (1.0272) and the pH-d11B response that has been defined by a number of culturing studies and can be approximated by using an alpha value different to the true alpha (e.g. Hönisch et al., 2007; _1.0194). These studies have shown that the pH response recorded by a number of species over a wide pH range is shallower than 1.0272 predicts for B(OH)4- in seawater. This is telling us something useful about either how boron is incorporated into CaCO3 (Klochko et al., 2009) or about vital effects in corals. It is legitimate to use a shallower pH response than 1.0272, e.g. one approximated by the sloped defined by an alpha of 1.0194, if the culture data warrants it, but the authors need to be explicit in their reasons for doing this. Also, although Figure 1 is instructive it would be better to plot all these coral data on a d11B vs pH plot to show that 1.0194 is valid for all the data and no additional offsets are required. Or, since SST and SSS are different perhaps a plot of d11B of BOH4- using 1.0194 (or other alpha value) vs. d11B measured.

All this part was now revised in taking into account this comment. For example, we can read now:

"The first trend (alpha $\geq$ 0.980-0.981) is usually applied today for paleo-reconstructions

even though, today, the alpha value of 0.974 is considered the unique and verified isotopic fractionation factor in seawater (Klochko et al., 2006)."

We also modified the sentence in conclusion concerning validation of the model and we can read now:

"Our d11B, [B] and pH results obtained with the empirical isotopic fractionation factor close to 0.981 for modern corals agree with previous observations from laboratory calibration experiments."

We decided to keep the Figure 1 showing a map of present day pH for the Pacific and the relative good and qualitative coherence between such pH (on the seawater scale) and pH calculated from boron isotopes for various recent tropical corals.

In contrast, we have decided not to plot our calculated pH in comparison to local measured pH because we are lacking enough accurate pH, SSS and SST data for all the areas and regarding the time covered by the coral samples.

7. For the estimates of pH and pCO2 the authors need estimates of SSS, SST and total alkalinity appropriate for each age examined as these parameters can influence the calculations. Perhaps these could come from nearby deep ocean sites or from the corals themselves (e.g. Sr/Ca?).

Sr/Ca values are not available for all the samples so we decided to keep SST of 28°C and 27°C as described in the text for Marquesas and ERDC and Tahiti. We also discuss in the text that 3°C have a relatively small impact on the pH calculation and can not in any case explain the low pH or high pCO2 observed at the end of the Younger Dryas. In fact, possible temperature effects cannot impact on the conclusions on this work. In contrast, we calculated now in the revised manuscript both pH, pCO2 and DpCO2 considering SSS and AT estimated for the past. These last values are now included in Table 1.

8. p1969. The authors should use the dissociation constants and pH scale recom-

mended by Dickson (2007 - Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean CO2 measurements. PICES Special Publication 3, 191 pp.).

We would like to thank the reviewer for this particular important remark. This recommendation was applied and is now described in the text. New values are listed in Table 1.

9. p1971. I'm confused by line 13-15: "[B]..increases together with d11B and is controlled by: : :" in figure 3a [B] decreases as d11B increases. Contrary to what is said here this observation is not reconcilable with the model of Hemming and Hanson (1992) of how boron is incorporated into CaCO3. Please explain.

We admit that this paragraph was not very clear. So, we revised the text distinguishing results obtained for modern samples (Fig 4a) coming from various SST areas and results obtained for ancient corals coming from the same areas (Tahiti – Marquesas, Fig.4b) with relative stable temperatures. In this last case, values tend to confirm and validate the model of Hemming and Hanson (1992). One of the interests of this paper is to show a to strong effect of temperature on the B geochemistry in corals and that such models can be validated only for stable SST.

10. p1972. line 20. I'm not sure so much space should be given to discussing unpublished data – they could be incorporated in this manuscript or the discussion of L. pertusa data of Douville et al. (2007) should be removed.

We decided here to keep the paragraph about deep sea coral because such data (boron concentrations) are very useful to illustrate the role of temperature on B concentrations in various aragonite forming corals and consequently on the partition coefficient KD : Lower temperature induce higher boron and KD values and vice versa. The range of boron concentrations measured for deep-sea corals and used here to establish KD values are now given in the caption of Figure 6.

C1409

11. p1973. line 3. Can Hemming et al. (1998) data from Fanning Island be plotted directly on Figure 5?

To add values for Fanning Island on Figure 6 now like for the other sites, we need d11B values of corals representing the mean of at least one year. Here, we feel that averaging the published d11B values based on a seasonal timescale does not correspond to the same sampling strategy and may induce a significantly different annual trend and KD.

12. p1973. Section 4.2. Is it possible to do some sort of cross plot for the new coral data and the foram data of Palmer and Pearson (2003)?

It would be very nice to compare both areas and archives (central Pacific and Western pacific) and its relationship of Ocean atmosphere regarding CO2. However this exercise appears here not opportune because of the fact that each dot for ERDC foraminifera integrates roughly about 1000 years while each coral value represents only one year of growth. To make seriously this cross plot, we need similar resolution and ages for both areas and archives.

13. p1975. Line 2. Another abstract is referenced here.

Yes, last December this paper was presented at the AGU fall Meeting and is as such published as abstract and hopefully it will be submitted soon!

14. p1975. Holocene pCO2 values appear low for this region (and correspondingly pH appears high) for instance sea-air differences of -67 ppm are not found anywhere in the subtropics today (Takahashi et al., 2009). This may indicate an offset is needed to get pH derived from d11B to match true seawater pH (see comment #6).

Yes that could be the case. We also agree with the fact that a alpha value of 1.0194 used here for pH calculation is today not totally constrained to provide pH with an accuracy of +/- 0.03 pH-unit ($\sim$ +/-25 ppmV for pCO2). In fact, with the new pH, pCO2 and ïĄĎpCO2 calculations (see our comments 7 and 8), the low value of -67 ppm at

C1410

3230 kyr B.P. ago is now reduced to a mean value of about - 45 ppm. This value is clearly the lowest values during the Holocene and is now more compatible with (Takahashi et al., 2009) data. This low value can be also the result of an effect of the temperature (underestimated if SSTs is higher due to warm pool contribution) during this period.

In addition, the revised DpCO2 values (-15 ppm instead of -45 ppm) for Tahiti samples in both 1991 and 1950 are close to the equilibrium and now match well values today measured (figure 7 and see the reference suggested by the reviewer : Takahashi et al., 2009). This reference is now cited in the text.

15. Figure 5. "Cold Sea corals" does this mean corals from the Cold Sea, or do you mean deep sea corals?

Deep sea corals are now written in the Figure 6. More information is added to the figure caption.

16. How well dated is the core ERDC-92? Could the fact that Palmer and Pearson (2003) see a pCO2 spike at _15 kyr whereas the well dated corals here show a spike at 12 kyr be simply a chronological issue? This is worth checking out as the regional significance of what is documented in these corals would be strengthened if they better matched to the variations seen at ERDC-92.

We are not convinced by the fact that the difference observed between ERDC-92 pH values and our own values from corals is simply linked to a chronological issue. As we explain in the text : such data do not integrate the same period : 1 value for one year for coral and 1 value for around 1000 years for ERDC-92 forams. So, it appears to us to dangerous to develop a more pronounced comparison in this manuscript.

17. Figure 6. there is a filled black diamond at 0 kyr – what is this? In the caption of this figure sources are listed as 1, 2, 3 whereas in the figure they are a, b, c.

Filled black diamond is now described in the caption of the Figure 7 and numbers were

replaced by letters like for all the figures.

18. Table 1. It seems a lot of the data tabulated is "Graphically estimated from Gaillardet and Allegre, 1995". Firstly, what does this mean? And secondly, since Gaillardet is an author on the paper can't he supply the data?

U-Th ages described here for Tahiti samples are not the data published by Gaillardet and Allegre (1995) but values revised in Bard et al. (1996). Unfortunately, U-Th age for the sample called Ta-3 was not given by these last authors but only the 14C age. So we have considered here the preliminary age given by Gaillardet and Allegre (1995). This is now detailed in the Table caption.

Some very minor comments:

P1962. line 18-19. I don't think Hönisch and Hemming (2005) is an appropriate references to show that the. It is far better to reference the ice core measurements of the EPICA group.

We added "Petit et al. (1999)" as reference of the pCO2 variability on glacial-interglacial timescales

P1963. Line 6. "These first investigations investigated the: : :." Replace "investigations" with "studies".

Corrected

P1963. Line13-14. "We also present the d11B-pH and partition coefficient for boron: : :" insert the word "relationship" after "d11B-pH".

Corrected

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/7/C1403/2010/bgd-7-C1403-2010-supplement.pdf

C1413

Figure 3 - **Douville et al. (2010 - submitted)**
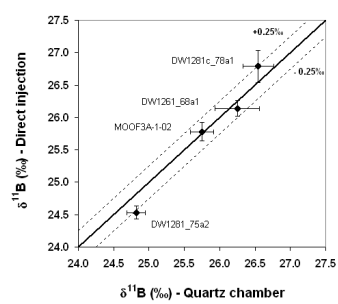

Fig. 1. Comparison of MC-ICPMS analyses using direct injection (d-DIHEN) and conventional introduction for Porites

C1414