

## ***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.***

**Anonymous Referee #2**

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In this manuscript the authors present both a regional scale investigation into how well the  $\delta^{11}\text{B}$ -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  $\text{CO}_2$  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 the

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foraminiferal 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 Niño 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”?

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.

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

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been effective? A bit more detailed needed.

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).

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)?

6. p1968. Kakhana 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  $\alpha$

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(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;  $\sim$ 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  $CaCO_3$  (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  $BOH_4^-$  using 1.0194 (or other  $\alpha$  value) vs. d11B measured.

7. For the estimates of pH and  $pCO_2$  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?).

8. p1969. The authors should use the dissociation constants and pH scale recommended by Dickson (2007 - Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean  $CO_2$  measurements. PICES Special Publication 3, 191 pp.).

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  $CaCO_3$ . Please explain.

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.

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pertusa data of Douville et al. (2007) should be removed.

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

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)?

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

14. p1975. Holocene pCO<sub>2</sub> 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).

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

16. How well dated is the core ERDC-92? Could the fact that Palmer and Pearson (2003) see a pCO<sub>2</sub> 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.

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.

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?

Some very minor comments:

P1962. line 18-19. I don't think Hönisch and Hemming (2005) is an appropriate references to show that the pCO<sub>2</sub> varied on glacial-interglacial timescales. It is far better to

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reference the ice core measurements of the EPICA group.

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

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

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