

# New pH evidence for changes in intermediate South East Pacific carbon storage during the last deglaciation

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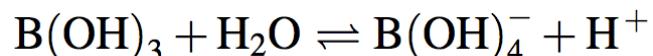
ÉCOLE DOCTORALE  
**Sciences mécaniques et  
énergétiques, matériaux  
et géosciences (SMEAG)**

## **Study purpose:**

Creation of a high resolution pH record for the last deglaciation in the intermediate South East Pacific (1.5 km deep) using the «  $\delta^{11}\text{B}$ -pH » proxy described in Rae et al. 2011.

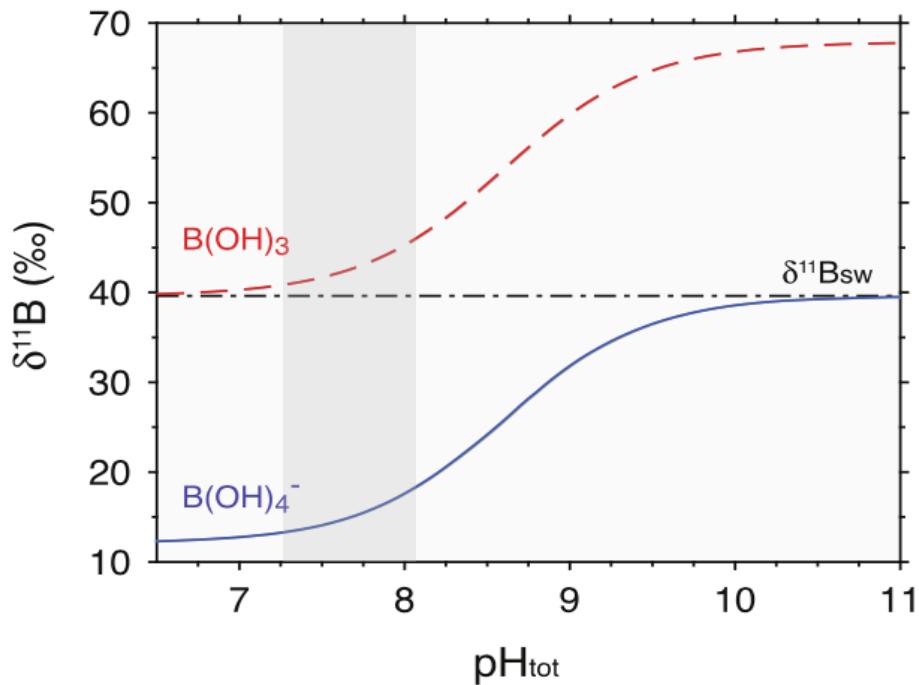
## Carbonate $\delta^{11}\text{B}$ -pH proxy

- Boron is stored in ocean as an Acid-Base couple (*Dickson A.G. 1990*) with a  $pK_B$  very close to typical ocean pH, causing the equilibrium to be very sensitive to any pH variations.



$$K_B = \frac{[\text{B(OH)}_4^-][\text{H}^+]}{[\text{B(OH)}_3]}$$

$$pK_B \approx 8.6.$$

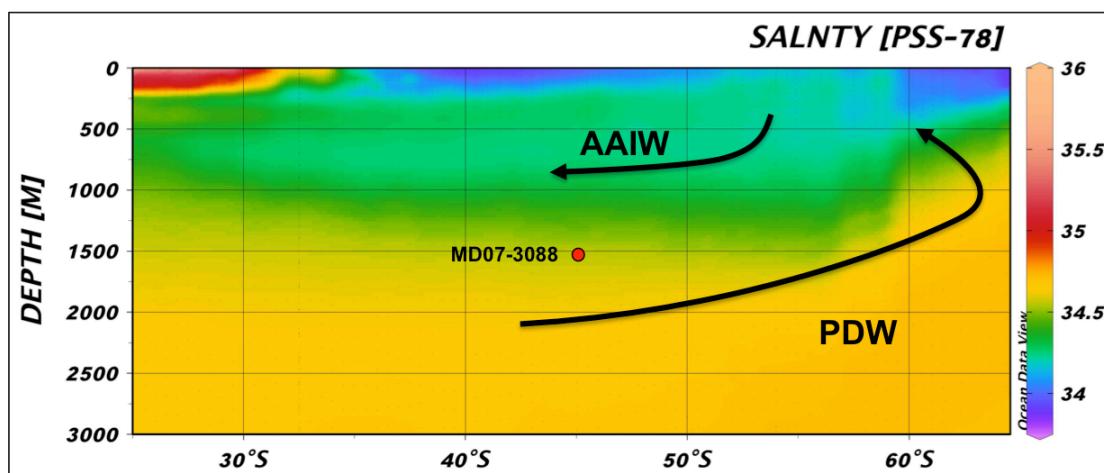
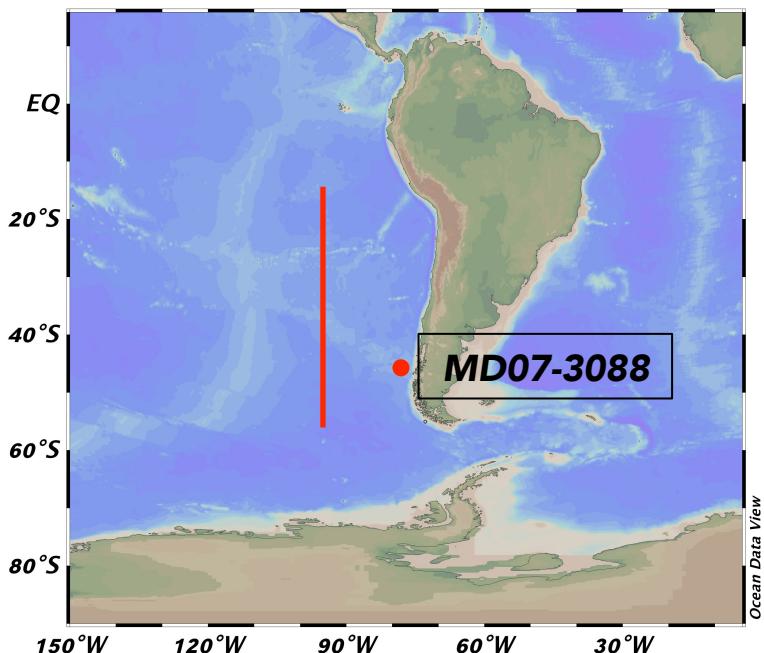


- The boron isotopic composition of epifaunal benthic foraminiferas record the boron isotope composition of borate ion  $[\text{B(OH)}_4^-]$  in seawater (*Vengosh et al. 1991 ; Hemming and Hanson 1992*).  $\delta^{11}\text{B}_{\text{borate ion}}$  being a function of seawater pH (blue line),  $\delta^{11}\text{B}_{\text{carbonate}}$  can be used for seawater pH reconstruction (*Rae et al. 2011*).

$$pH = pK_B^* - \log\left(-\frac{\delta^{11}\text{B}_{\text{sw}} - \delta^{11}\text{B}_{\text{CaCO}_3}}{\delta^{11}\text{B}_{\text{sw}} - \alpha_B * \delta^{11}\text{B}_{\text{CaCO}_3} - (\alpha_B - 1) * 1000}\right)$$

- $\delta^{11}\text{B}_{\text{sw}} = 39.61\text{‰}$  (*Foster G.L. 2010*)
- $\alpha_B = 27.2\text{‰}$  (*Klochko et al. 2006*)

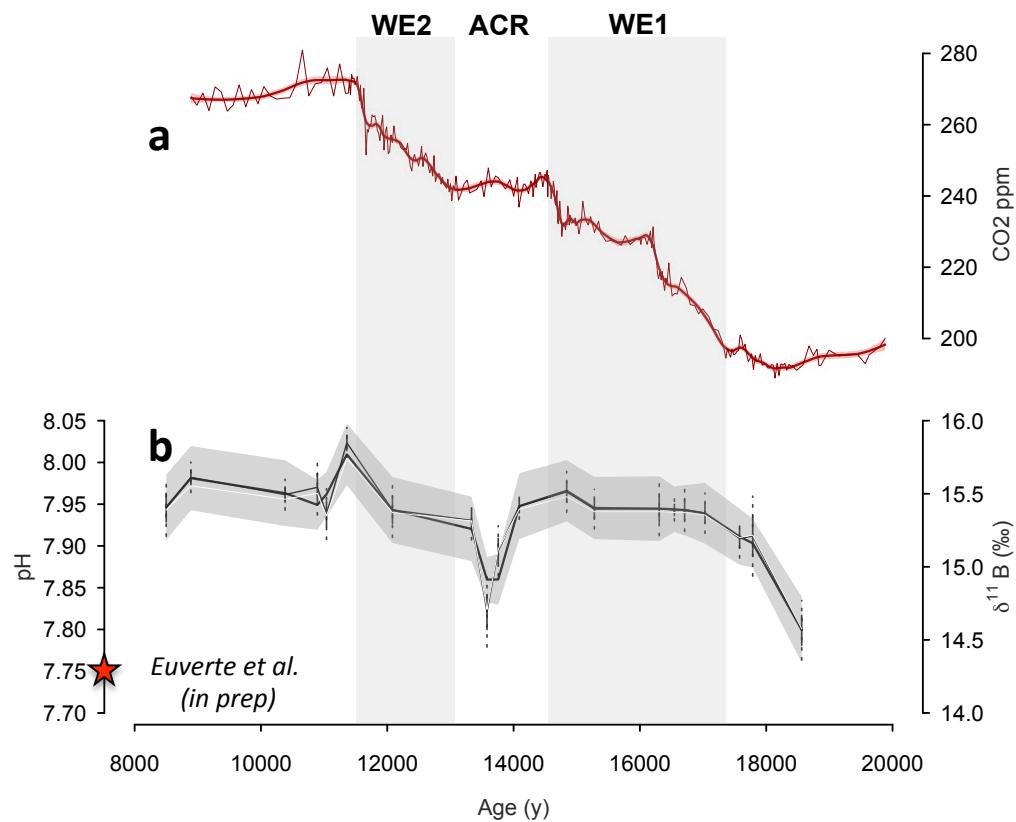
## Samples



- 46.1°S, 75.7°W
- 1536m
- 24m, 0-21 ka
- Modern temperature: 2.7°C
- Modern salinity: 34.5 psu
- Sample measured: *cibicides wuellestorfi*



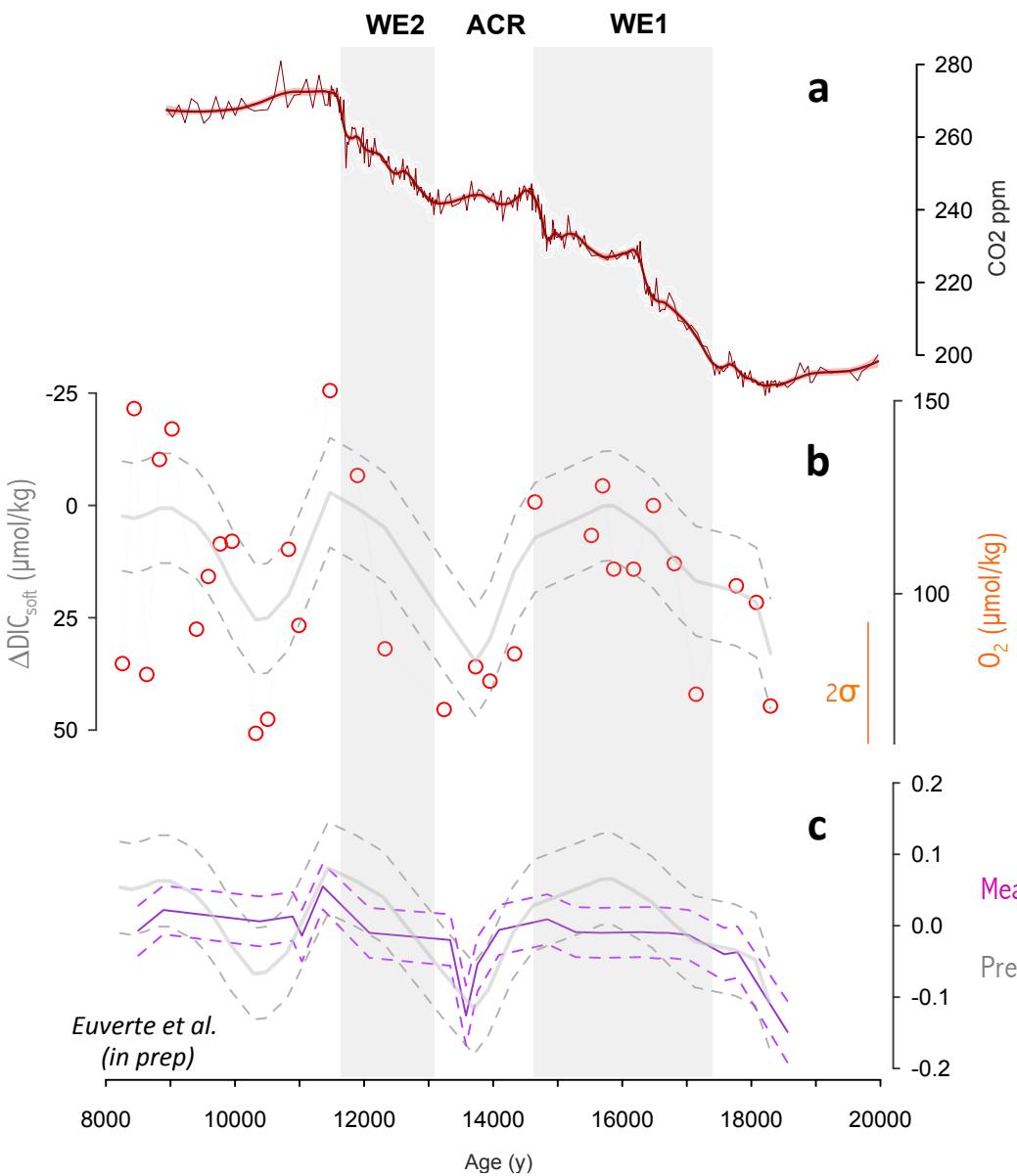
## Results



- a) WAIS divide ice core CO<sub>2</sub><sub>atm</sub>
- b) Intermediate water  $\delta^{11}\text{B}$  data from South East Pacific (This study). Red star is actual pH. Grey shaded zones marks periods of increasing CO<sub>2</sub><sub>atm</sub> (warming event 1 and 2). ACR = Antarctic Cold Reversal. Dashed lines are 2 sigma errors in  $\delta^{11}\text{B}$ .

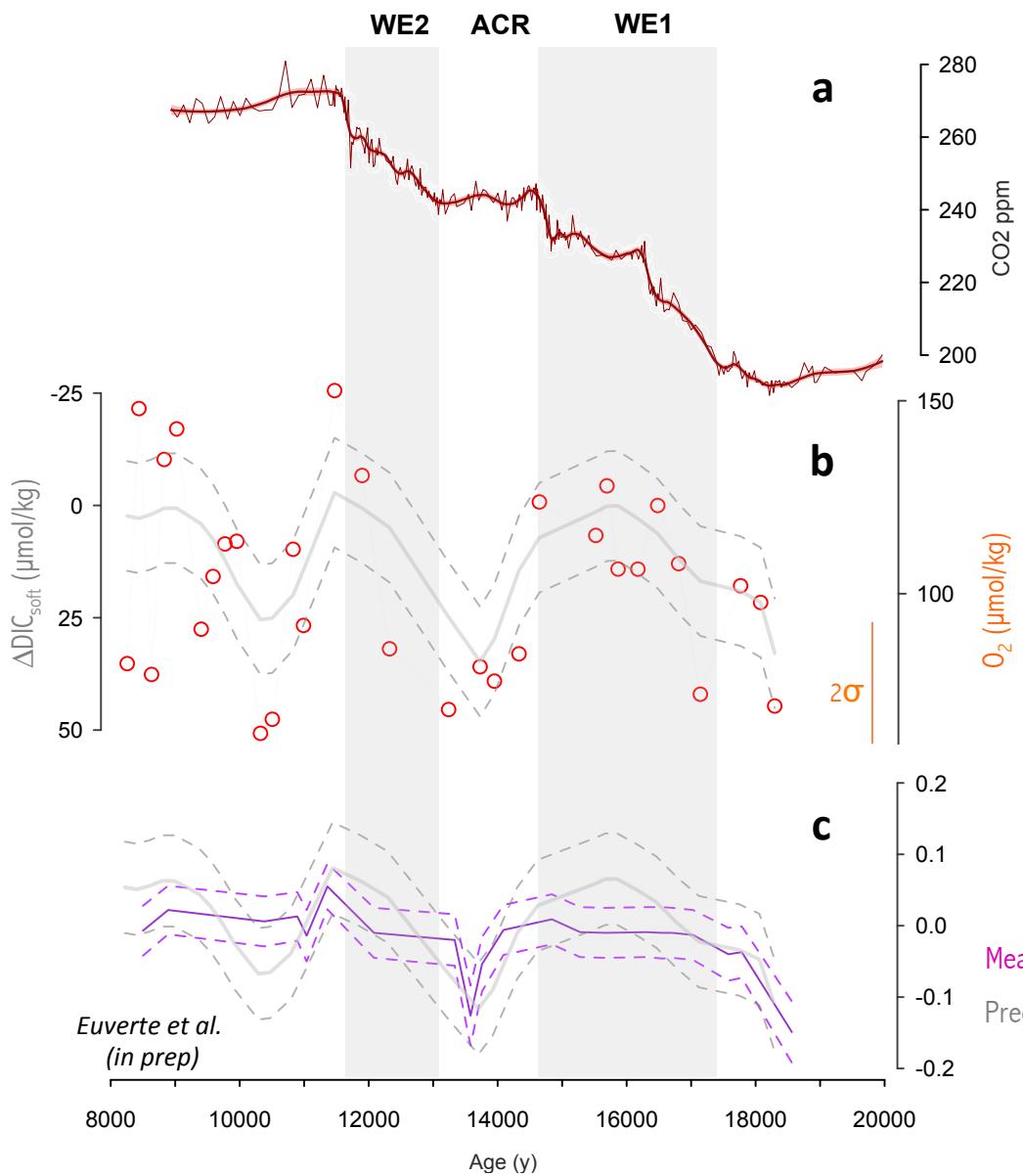
- $\Delta\delta^{11}\text{B}$  glacial-interglacial range =  $1.28 \pm 0.1\text{‰} \Leftrightarrow \text{G-IG } \Delta\text{pH} = 0.21 \pm 0.03$
- Between 18 and 8 ka,  $\delta^{11}\text{B}$  indicate rapid (<1000y) variations around a steady state ~15.5‰.
- Disparity between early holocene and modern pH could be attributed to lack of core top data.
- First increase in  $\delta^{11}\text{B}$  happening between 18.6 and 17.8 ( $\pm 0.35$ ) ka.

# Interpretations



- a) WAIS divide ice core  $\text{CO}_2_{\text{atm}}$
- b) Red circles are  $\text{O}_2$  record reconstructed using calibration from Hoogakker 2015.  $\text{O}_2$  is converted into  $\Delta\text{DIC}_{\text{soft}}$  tissues using Redfield stoichiometry (grey line).
- c) « Predicted pH » (grey line) is the calculated pH change only due to  $\Delta\text{DIC}_{\text{soft}}$  evolution. « Measured pH » (purple line) is pH data from this study.

# Interpretations



- Within 2 sigma error bars, predicted and measured  $\Delta\text{pH}$  are coincident. Therefore it seems that pH at intermediate depth is mostly driven by changes in respired  $\text{CO}_2$  storage.
- pH increase before 18ka coincides with AABW strengthening (Beny et al. 2020), sea ice retreat (Allen and Pudsey 2011) and degassing in equatorial Pacific (Martinez-Botí et al. 2015). These data are coherent with a early  $\text{CO}_2$  degassing prior to  $\text{CO}_{2\text{atm}}$  increase recorded into Antarctic ice cores.

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