Supplementary material

Assessment of paleo-ocean pH records from boron isotope ratio in the Pacific and Atlantic ocean corals: Role of anthropogenic CO_2 forcing and oceanographic factors to pH variability

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S1. Reconstruction of Theoretical pH records using CO2SYS

Carbonate system comprises of six variables i.e. pH, CO_2, $[CO_3^{2-}]$, $[HCO_3^-]$, total alkalinity (TA) and dissolved inorganic carbon (DIC) (Dickson et al., 2007; Millero, 2006; Zeebe and Wolf-Gladrow, 2001). Given any two known variables (e.g. TA and pCO_2) along with physical parameters i.e. sea surface temperature (SST), and salinity (SSS), we can theoretically calculate any of the other variables. Theoretical pH was calculated using carbonate system variables into Matlab based CO2SYS program (Van Heuven et al., 2011). Therefore, theoretical pH represents pH variation only due to changes in SST, SSS, TA and pCO_2. Past SST, SSS and TA were reconstructed based on the proxy records of Sr/Ca, Mg/Ca and $\delta^{18}O$ using the empirical relations (equations) provided in Table S1. The past atmospheric CO_2 data was taken from Law Dome Ice core (Etheridge et al., 1996) and instrumental records from the Mauna Loa observatory in Pacific (www.esrl.noaa.gov/gmd/ccgg/trends/). For theoretical pH calculation, dissociation constants of carbonic acid, K_1 and K_2 are taken from Mehrbach et al. (1973) and Dickson and Millero (1987), boric acid, K_B (Dickson, 1990) and water, K_W (DOE, 1994) and total boron concentration, B_T (Lee et al., 2010).

S2: Uncertainty associated with theoretical pH reconstruction

Theoretical pH was reconstructed using the reconstructed parameters (i.e. SST, SSS and TA) in Matlab based CO2SYS program. These reconstructed parameters are associated with uncertainties that derived from analytical uncertainties of the proxies and calibration methods. Hence, while calculating the theoretical pH, these errors will be propagated to the uncertainty associated with theoretical pH. Further, the dissociations constants used in theoretical pH estimation are depended on temperature and salinity and therefore the uncertainty associated with the carbonate system variables which finally propagate to theoretical pH estimation. A constant error of 0.5°C in SST and 0.2 psu in salinity were used in the calculations which includes analytical uncertainty and calibration equation (Gagan et al., 2012; Goodkin et al., 2005; Iijima et al., 2005; Morimoto et al., 2002; Yu et al., 2005). TA was calculated using SST and SSS records (Lee et al., 2006) with an uncertainty of 8.6 µmol/Kg. Another carbonate system parameter used for theoretical pH calculation is pCO_2. Although we have used pCO_2 record from ice core but the pCO_2 in coral reef environment is not in equilibrium with atmosphere due to reef calcification, photosynthesis or flushing of reef environment. Therefore, we accounted this offset in the pCO_2 of atmosphere and reef environment in the theoretical calculations. Spatial annual mean ΔpCO_2 ($pCO_{2\ seawater}$ – $pCO_{2\ atmosphere}$) is well documented by Takahashi et al. (2014) (Fig. S2). Fig. S2 shows that all the sites in this study have ΔpCO_2 less than ±10 µatm. Hence, a constant error of 10 µatm was used in error propagation into theoretical pH calculation. Finally, uncertainty in the theoretical pH was estimated using Monte Carlo error propogation method with 10,000-iteration (Wagener et al., 2001), which is represented as error envelop (Fig. 3).

S3: Error Sensitivity analysis:

In order to understand the error in which of the reconstructed parameters (SST, SSS, TA and pCO_2) is most sensitive to the error in theoretical pH, error sensitivity analysis was performed. Results of the error sensitivity are shown in Fig. S2.

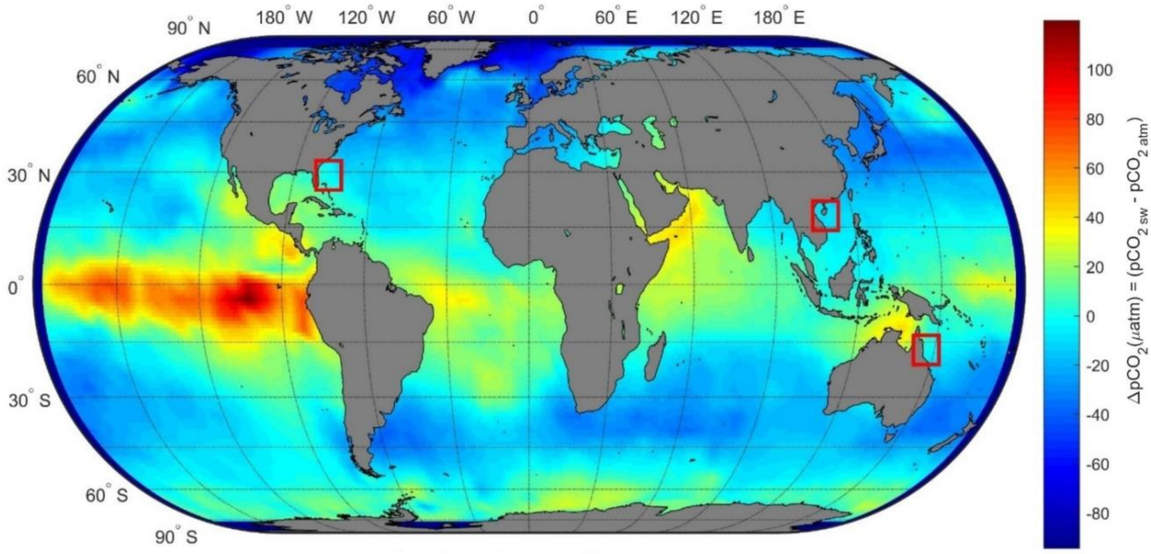

Figure S1: Surface plot of annual mean ΔpCO_2 (µatm) = ($pCO_{2\ seawater}$ – $pCO_{2\ atmosphere}$) record from Takahashi et al. (2014). Squares represents the locations from where theoretical pH was reconstructed.

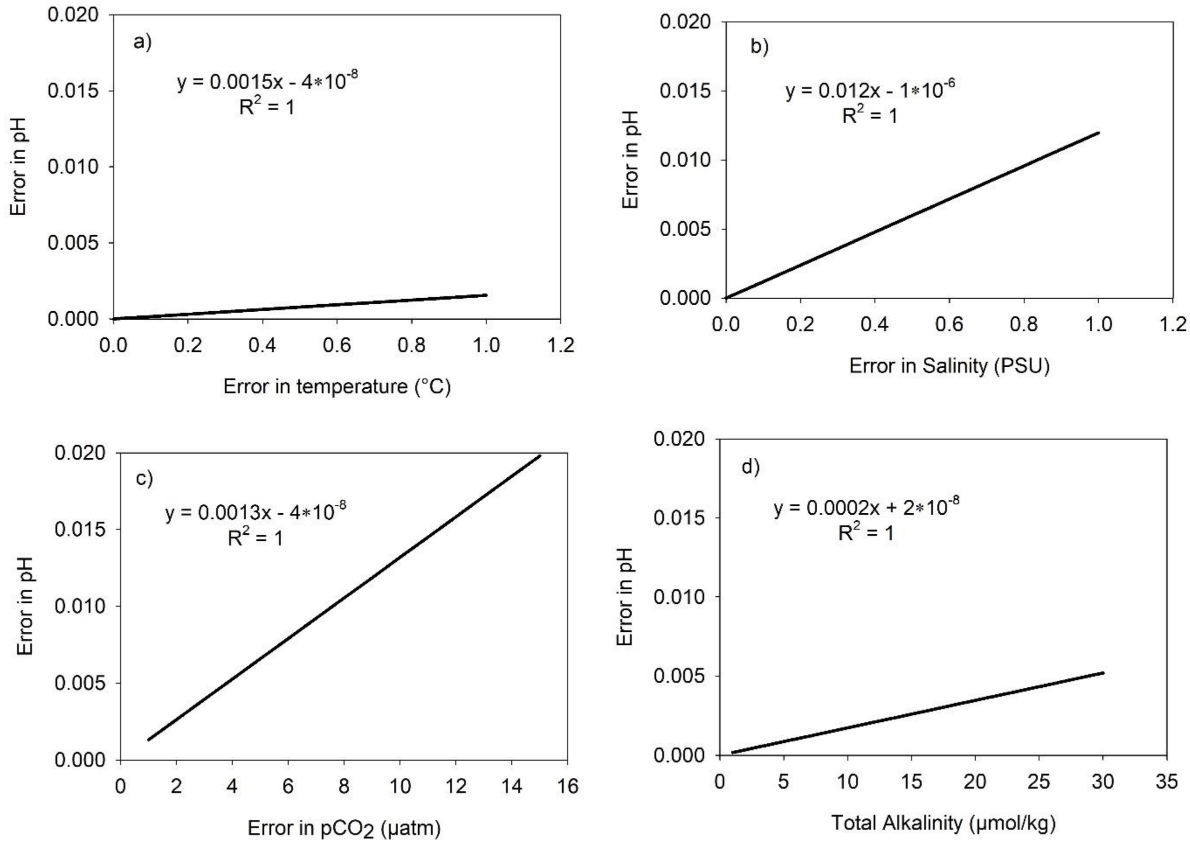

Figure S2: Error sensitivity analysis for (a) temperature (b) salinity (c) pCO_2 and (d) Total alkalinity. Slopes in theses regression equations reflect sensitivity to the error in pH.

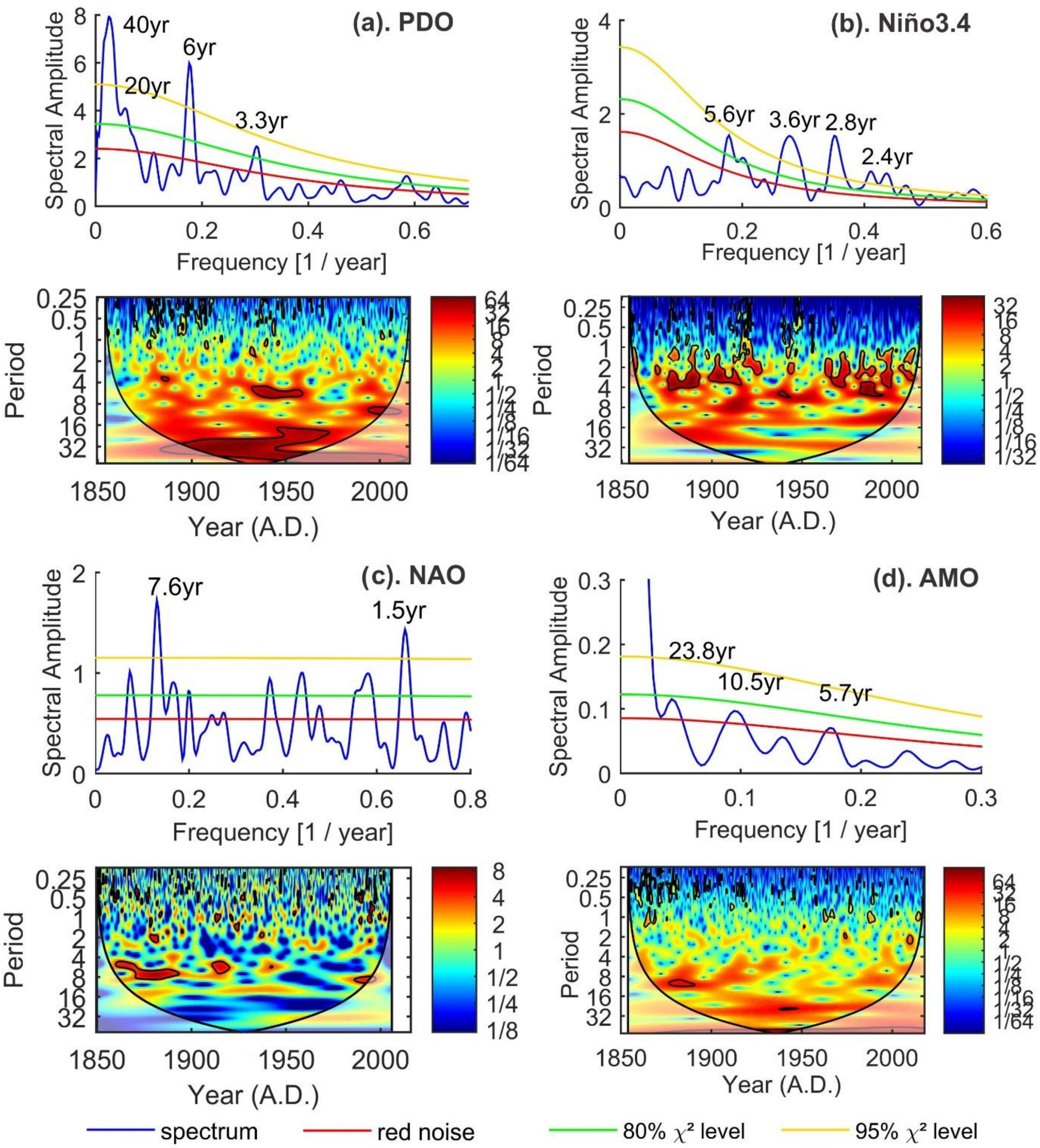

Figure S3: Spectral and wavelet analysis of climate-ocean indices:

(a) PDO (https://www.ncdc.noaa.gov/teleconnections/pdo/)

(b) ENSO (https://climexp.knmi.nl/data/iersst_nino3.4a.dat)

(c) NAO (http://www.esrl.noaa.gov/psd/gcos_wgsp/Timeseries/Data/nao.long.data) and

(d) AMO (https://climexp.knmi.nl/getindices.cgi?WMO=UKMOData/amo_hadsst&STATION).

Table S1: Equations used to calculate SST, SSS and TA.

Coral Location	**[1,2,3]Sr/Ca or Mg/Ca to SST**	**[4]SST, $\delta^{18}O_{coral}$ to $\delta^{18}O_{sw}$**	**[5]$\delta^{18}O_{sw}$ to SSS**	**[6]SSS to TA**
Great Barrier Reef (Wei et al., 2009)	[1]$Mg/Ca\ (mmol/mol)_{coral} = 0.110 \times SST\ (°C) + 1.32$	$\delta^{18}O_{sw} = 0.189 \times SST + 0.12 + \delta^{18}O_{coral}$	$\delta^{18}O_{sw} = 0.42 \times SSS - 14.3$	$TA = 2305 + 58.66 \times (SSS-35) + 2.32 \times (SSS-35)^2 - 1.41 \times (SST - 20) + 0.040 \times (SST - 20)^2$
South China Sea (Wei et al., 2015)	[2]$Sr/Ca\ (mmol/mol)_{coral} = -0.084 \times SST\ (°C) + 11.278$	$\delta^{18}O_{sw} = 0.189 \times SST + 0.12 + \delta^{18}O_{coral}$	$\delta^{18}O_{sw} = 0.42 \times SSS - 14.3$	$TA = 2305 + 58.66 \times (SSS-35) + 2.32 \times (SSS-35)^2 - 1.41 \times (SST - 20) + 0.040 \times (SST - 20)^2$
Sargasso Sea (Goodkin et al., 2015)	[3]$Sr/Ca\ (mmol/mol)_{coral} = -0.0412 \times SST\ (°C) + 10.3$	$\delta^{18}O_{sw} = 0.189 \times SST + 0.12 + \delta^{18}O_{coral}$	$\delta^{18}O_{sw} = 0.42 \times SSS - 14.3$	$TA = 2305 + 53.97\ (SSS - 35) + 2.74\ (SSS - 35)^2 - 1.16\ (SST - 20) - 0.040\ (SST - 20)^2$

[1] Yu et al. (2005); [2] Gagan et al. (2012); [3]Goodkin et al. (2005); [4] Iijima et al. (2005); [5]Morimoto et al. (2002); [6] Lee et al. (2006)

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