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*)

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Abstract

The "$\delta^{11}B$ - pH" technique was applied to modern and ancient corals *Porites* from the sub-equatorial Pacific areas (Tahiti and Marquesas) spanning a time interval from 0 to 20,720 calendar years to determine the amplitude of pH changes between the Last Glacial Period and the Holocene. Boron isotopes were measured by Multi-Collector - Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) with an external reproducibility of 0.25‰, allowing a precision of about ± 0.03 pH-units for pH values obtained between 8 and 8.3. The boron concentration [B] and isotopic composition of modern samples indicate that the temperature strongly controls the partition coefficient K_D for different aragonite species. Modern coral $\delta^{11}B$ values and the reconstructed sea surface pH values for different Pacific areas match the measured pH expressed on the seawater scale and confirm the calculation parameters that were previously determined by laboratory calibration exercises. Most ancient sea surface pH reconstructions near Marquesas are higher than modern values. These values range between 8.19 and 8.27 for the Holocene and reached 8.30 at the end of the last glacial period (20.7 kyr B.P.). At the end of the Younger Dryas (11.50 ± 0.1 kyr B.P.), the central sub-equatorial Pacific experienced a dramatic drop of up to 0.2 pH-units from the average pH of 8.2 before and after this short event. Using the marine carbonate algorithms, we recalculated the aqueous pCO_2 to be 440 ± 25 ppmV at around 11.5 kyr B.P. for corals at Marquesas and ~500 ppmV near Tahiti where it was assumed that pCO_2 in the atmosphere was 250 ppmV. Throughout the Holocene, the difference in pCO_2 between the ocean and the atmosphere at Marquesas (ΔpCO_2) indicates that the surface waters behave as a moderate CO_2 sink or source (-40 to 20 ppmV) during El Niño-like conditions. In contrast, during the last glacial/interglacial transition, this area was a marked source of CO_2 (21 to 92 ppmV) for the atmosphere, highlighting predominant La Niña-like conditions. Such conditions were particularly pronounced at the end of the Younger Dryas with a large amount of CO_2 released with ΔpCO_2 of +185 ± 25 ppmV. This last finding provides further evidence of the marked changes to the water mass pH and temperature properties in the equatorial Pacific at the Younger Dryas- Holocene transition and

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the strong impact of oceanic dynamic on the atmospheric CO_2 content.

Keywords: boron isotopes; corals; sea surface pH; $p$$CO_2$; Pacific Ocean; Holocene; last glacial/interglacial transition

1. Introduction

The acidity of the ocean surface is increasing because of anthropogenic emission of CO_2 into the atmosphere. This increase may have severe consequences for those organisms which build their external skeleton out of calcium carbonate ($CaCO_3$) (Orr et al., 2005). During the last 200 years, roughly fifty percent of the anthropogenic CO_2 (IPCC, 2005) contributed to the acidification of the superficial ocean by 0.1 pH-units. Models suggest that the sea surface pH could drop by ~ 0.4 units before the year 2100 if the present–day trend of carbon dioxide increase continues (Caldeira and Wickett, 2003). Today, the oceanic sources and sinks of CO_2 show a high degree of spatial and annual to inter-annual variability. For instance, the wind is strengthening, and uptake of CO_2 in the Southern Ocean is reduced (Le Quéré et al., 2007). Changes in the marine biological pump control carbon removal from the upper ocean into the deep ocean (McGillicuddy et al., 2007). Changes have taken place in the oceanic circulation (Feely et al., 1999; Inoue et al., 2001), and these changes may counteract the anthropogenic acidification of the ocean. In the past, the atmospheric pCO_2 changed by ~ 80 to 100 ppmV between glacial and interglacial periods (Hönisch and Hemming, 2005; Hönisch et al., 2009; Monnin et al., 2001; Monnin et al., 2004; Petit et al., 1999). Those variations are commonly ascribed to changes in the oceanic uptake of CO_2 because the ocean is the largest carbon reservoir in the atmosphere-hydrosphere-biosphere system. However, the CO_2 exchange and related mechanisms have not yet been fully understood and quantified (Archer et al., 2000; Kohfeld et al., 2005; Sigman and Boyle, 2000). Quantifying changes in the oceanic pCO_2 over the centennial and millennial time scales will elucidate the role of the oceanic carbon cycle and the links between the oceanic and atmospheric changes of pCO_2 and their consequences on ecosystems.

Ocean acidification and past sea surface pH or pCO_2 may be deduced from the boron isotopic composition ($\delta^{11}B$) of biogenic carbonates (Hemming and Hanson, 1992; Spivack et al., 1993). During the past decade, numerous studies evaluated the "$\delta^{11}B$ – pH" relationship using experimental studies or laboratory cultures of foraminifera and corals (Hemming et al., 1995; Hönisch et al., 2004; Reynaud et al., 2004; Sanyal et al., 1996; Sanyal et al., 2000). Only a few studies based on tropical corals focused on the past hundreds or thousands of years. These first studies investigated the western Pacific Ocean (Pelejero et al., 2005; Wei et al., 2009) and more recently the South China Sea (Liu et al., 2009). Those studies revealed pronounced sea surface pH changes by 0.2-0.3 during the Holocene. These changes were strongly controlled by climate (monsoon) or oceanographic patterns (Pacific Decadal Oscillation).

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First we describe in detail the modern "pH – Sea Surface Temperature" relationships for surface waters of the *sub*-Equatorial Pacific Ocean and the protocols used here to reconstruct the pH and $p\mathrm{CO_2}$ properties of surface waters. We also present the δ^{11}B-pH relationship and partition coefficient for boron K_D obtained from modern *Porites* collected in tropical areas of various sea surface temperatures (SSTs). Then, we use the derived relationships to investigate ancient corals recovered from drowned reefs off the Marquesas and from modern reefs near the Tahiti Islands in the central equatorial Pacific (Fig. 1) to reconstruct past pH, SST and $p\mathrm{CO_2}$ levels of these areas. These new results are compared to previous results from modern or ancient corals of the genera *Acropora* and *Porites* (Gaillardet and Allègre, 1995) and from planktonic foraminifera (Palmer and Pearson, 2003). The deduced changes in the sea surface pH and SST are evaluated against oceanographic patterns, and the estimated oceanic $p\mathrm{CO_2}$ values are compared to atmospheric values measured in Antarctic ice cores (Monnin et al., 2001; Monnin et al., 2004).

2. Hydrological setting of the central tropical Pacific Ocean: "pH – SST" relationships

The pH and SST data show that in the modern equatorial Pacific, the sea surface pH and SST between 5°S and 20°S are highly negatively correlated (Fig. 2, data from http://www.nodc.noaa.gov/OC5/ SELECT/dbsearch/dbsearch.html) (Lefèvre et al., 1994). This correlation is especially strong between 80°W and 170°W because of the cold and $\mathrm{CO_2}$-rich waters coming from the major deep water upwelling along the eastern coasts of the sub-

Equatorial Pacific Ocean. In the eastern Pacific, the nutrient-rich surface waters are characterised by low pH and cool SST (Fig. 2a). The pH ranges from ~ 7.98 to about 8.01-8.06, as reported as present day pH (Fig. 2a), and the SST varies from 20.4°C to 23.1°C. At latitudes between 15°S and 20°S, the pH increases slightly by about 0.05 pH-units, and the SST increases by 3°C from 80°W to 170°W. This increase is more than 0.07 pH-units between 5°S and 10°S (Fig. 2b). In the western Pacific, high pH values of 8.22 ± 0.03 and warm SSTs are observed during the boreal summer. During the boreal winter, the pH drops by 0.1 pH-unit. The SSTs are uniformly around 29.5°C between 5°S and 15°S and lower by about 4°C between 15°S and 20°S. In the central Pacific between 130°W and 150°W and at latitudes higher than 15°S, warm surface waters with a SST of 28.6°C and a pH of ~8.22 were observed during 1994, an El Niño year. These waters show pH-SST properties similar to those of the western Pacific surface waters (Fig. 2).

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Most present day pH values for Marquesas and Tahiti (5-17°S) between 130°W and 150°W range from 8.10 to 8.15 (Fig. 2). This east-west pH-SSTs pattern corresponds to the well-known seasonal variation of the zonal distribution of water masses along the equator. This pattern is modified by changes in the wind strength. During El Niño years, westward water transport through the South Equatorial Current SEC decreases in the central Pacific because of eastward transport of warmer water from the western Pacific (Taft and Kessler, 1991). The sea surface pH increases under these conditions. When strong easterlies return, the westward SEC flow increases, and the equatorial thermocline shoals and favours contribution of more CO_2-rich waters. Consequently, during La Niña-like conditions, acidic cold waters are advected from the east toward the central Pacific (Taft and Kessler, 1991).

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3. Materials and Methods

3.1. Geographical setting and regional modern SST

The "$\delta^{11}B$ – pH" indicator was applied to modern *Porites* collected from New Caledonia (2001-2004), Moorea (1950) and Ishigaki Islands (Fig. 1). The New Caledonia

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sample used in this paper comes from outside the lagoon on the upper part of the barrier reef slope. This site is called Fausse passe d'Uitoé. The SST was measured at this site every month since 2000 and had a mean value of 24.4 ± 1.9°C (Table 1). The coral skeleton spans the period from 2001-2004. *Porites* from Ishigaki Island is the coral reference material JCp-1 prepared by the Geological Survey of Japan (Inoue et al., 2004). The regional SST over the last two decades in this area is close to 26.1 ± 2.1°C. The average SST of a sample from Moorea (MOO 3A-1-02) was 27.1 ± 0.5°C (Boiseau, 1998). Another modern sample is COM3 from the Red Sea. This sample grew at annually averaged SST of 22.5 ± 1.5°C (Gertman and Brenner, 2004; Heiss et al., 1999). According to modern observations (http://www.nodc.noaa.gov) (Henin, 1999), the Marquesas area has a mean annual SST of 28 ± 1°C. The ancient *Porites* studied here were collected from submerged reefs off the Marquesas and Tahiti Islands in the Equatorial Pacific. Coral ages, which span from 20.72 ± 0.20 kyr B.P. to 0.25 ± 0.03 kyr B.P., were obtained by mass spectrometric U-Th dating (Paterne et al., 2004; Cabioch et al., 2008).

3.2. Chemical preparation

The mean annual growth bands of *Porites* are about 10 mm in our samples. About 400 mg of the coral skeleton were cut along the growth axis systematically. Each of these samples represents one or two years. 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. The coral fragments were crushed in an agate mortar, and the resulting carbonate powder was washed three times with ultra-pure water in an ultrasound bath (Gaillardet and Allègre, 1995). Then, the powder was dissolved in diluted ultrapure Merck's acid 1N HNO_3 before chemical purification. The solutions were purified on the anion exchange resin Amberlite IRA 743 using the batch method developed by Lécuyer et al. (2002). In 50ml polypropylene corning centrifuge tubes, the solutions were neutralised to a pH of 7-8. Resin, previously cleaned using 4N HNO_3, was added in sufficient quantity (500 mg) to extract 100 % of the boron from solution for each standard and sample.

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The tubes, until 25 including samples and standards, were shaken for more than four hours before the resin was rinsed three times with MQ water. Then, the boron was eluted by three successive volumes of 5ml of 0.1N HNO_3. Extraction yields of close to 100% and accurate purification (level of residual Ca and major cations) were verified for each standard or sample by Inductively Coupled Plasma – Quadrupole Mass Spectrometry (ICP-QMS). Finally, the boron concentration was adjusted to 200 ppb in 2% nitric acid for MC-ICPMS analyses.

3.3. Boron isotope measurements

The boron isotope composition was determined with double-focusing sector-field multi-collector inductively coupled plasma mass spectrometers (MC-ICPMS Neptune of ThermoFisher Scientific) both in the Advanced Mass Spectrometry Laboratory of Thermo Fisher Scientific in Bremen (Germany) and at the Institut de Physique du Globe in Paris (France). Common introduction in Bremen was by a quartz double-pass spray chamber, and in Paris we used a direct injection high efficiency nebuliser (d-DIHEN). Mass drift of the $^{11}B/^{10}B$ ratio with time was systemically controlled by standard-sample bracketing. Most of the $\delta^{11}B$ values presented here were determined using the direct injection technique, which allows a strong reduction of the analytical blank contributions. Those contributions were lower than 0.5 ‰ for each isotope with a rinse time of three minutes or less (Louvat et al., *in press*). Comparison of repeated analyses for four different samples (DW1281c_78a1; DW1261_68a1; DW1281_75a2; MOO 3A-1-02) using direct injection (d-DIHEN) and conventional introduction yields excellent agreement within the analytical uncertainty given here (Figure 3, Table 1). The reproducibility and accuracy of the $^{11}B/^{10}B$ ratios were calculated from repeated analyses of the boric acid standard NBS-951 and the North Atlantic Seawater Standard NASS-II. The measured external reproducibility of 0.25‰ (2σ) is similar to the reproducibility that was recently published for MC-ICPMS analyses of Neptune (Foster, 2008; Louvat et al., *in press*). A mean $\delta^{11}B$ of 39.9 ‰ (n=20, 2σ) was measured for NASS-II. This value is also within the external precision values of 39.7 - 40.2‰ previously published for thermal ionization mass

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spectrometry (TIMS) or MC-ICPMS measurements (Gaillardet and Allègre, 1995; Hemming and Hanson, 1992; Hönisch et al., 2004; Wei et al., 2009; Louvat et al., *in press*). The external reproducibility of 0.25‰ (2 σ) represents our analytical precision for each of the analyzed samples. The boron isotopic composition of seawater ($\delta^{11}B_{SW}$) used for pH calculations was 39.9 ‰. Boron concentrations were measured with a precision of ± 3% (2σ) by ICP-QMS (ThermoFisher X-series) at Laboratoire des Sciences du Climat et de l'Environnement (LSCE) in Gif-sur-Yvette (France).

3.4. pH and *p*CO$_2$ calculations for seawater

The sea surface paleo-pH can be reliably reconstructed by measuring the boron isotopes in tropical corals. Two previous calibration exercises using laboratory-cultured corals (*Acropora* and *Porites*) demonstrate the validity of the technique and provide empirical calculation parameters (Hönisch et al., 2004; Reynaud et al., 2004). These pH calculations are based on isotopic fractionation by the coral of two boron species: borate ions $B(OH)_4^-$ and boric acid $B(OH)_3$. The relative proportions of these species and their isotopic composition in seawater are pH-dependent (Hemming and Hanson, 1992; Vengosh et al., 1991). Thus borate ions $B(OH)_4^-$ dissolved in seawater would be preferentially incorporated into the carbonate skeleton by substitution of bicarbonate ions (Hemming and Hanson, 1992). Consequently, the relationship (Eq. 1) between pH and $\delta^{11}B$ is as follows:

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$$pH_{SW} = pK_B - \log\left(\frac{\delta^{11}B_{SW} - \delta^{11}B_{carbonate}}{\alpha^{-1}\delta^{11}B_{carbonate} - \delta^{11}B_{SW} + 1000(\alpha^{-1} - 1)}\right) \qquad (1)$$

where pK_B is the equilibrium constant between the boric acid $B(OH)_3$ and the borate ions $B(OH)_4^-$ in seawater (Dickson, 1990). $\delta^{11}B_{carbonate}$ ($\delta^{11}B$) is the isotopic composition of boron measured here in *Porites*. $\delta^{11}B_{SW}$ is the isotopic composition of boron measured for seawater. And the value α (α_{4-3}) is the isotopic fractionation factor between the two boron bearing

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species in seawater (boric acid and borate ion) for the following equilibrium (R1):

$$^{11}B(OH)_3 + {}^{10}B(OH)_4^- \xleftrightarrow{\alpha_{4-3}} {}^{10}B(OH)_3 + {}^{11}B(OH)_4^- \qquad \text{(R1)}$$

Factors such as temperature, salinity, light, food (Hönisch et al., 2004), and especially the coefficient α determine the uncertainties associated with calculating the pH (Pagani et al., 2005). Until recently, α was the subject of numerous empirical or theoretical studies with the goal of precisely determining its value. The following two major trends appear from these studies: (1) $\alpha \geq 0.980$-0.981 (Gaillardet and Allègre, 1995; Hemming et al., 1995; Hönisch et al., 2004; Hönisch et al., 2007; Kakihana et al., 1977; Palmer and Pearson, 2003; Sanchez-Valle et al., 2005; Sanyal et al., 1996; Sanyal et al., 2000; Xiao et al., 2006) and (2) $\alpha \leq 0.974$-0.976 (Foster et al., 2008; Klochko et al., 2006; Lécuyer et al., 2002; Pagani et al., 2005; Zeebe, 2005). The first trend ($\alpha \geq 0.980$-0.981) is usually applied today for paleo-reconstructions, even though, today, the α value of 0.974 is considered the unique and verified isotopic fractionation factor in seawater (Klochko et al., 2006). The calculated sea surface pH from our δ^{11}B data (described below) would range from 8.4 to 8.6 with this theoretical value. These values are 0.3 to 0.4 pH-units higher than the expected present day pH. To reconstruct pH values that are more compatible with the seawater or total hydrogen ion pH scales, we use a value of the coefficient α of 0.981 (Kakihana et al., 1977). This value was empirically determined by calibration for both coral genera *Acropora* and *Porites* (Hönisch et al., 2004; Reynaud et al., 2004). These laboratory experiments reveal also a systematic 0.6 δ^{11}B offset between these two coral types over the pH range from 7.7 to 8.2. These δ^{11}B offset may result in a systematic pH offset between the two genera of corals. This offset was taken into account by adding 0.6 δ-units to the δ^{11}B values of each ancient *Acropora* sample from Tahiti for comparison with our *Porites* δ^{11}B values (Gaillardet and Allègre, 1995).

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To estimate the oceanic pCO_2 from the $\delta^{11}B$-pH values of the corals, we followed the procedure described by Hönisch and Hemming (2005). This procedure is based on the determination of two of the four parameters of the marine carbonate equilibrium (pCO_2, ΣCO_2, alkalinity and pH) in addition to Sea Surface Salinity (SSS) and SST. Using the National Oceanic and Atmospheric Administration (NOAA) data for modern water masses in the sub-Equatorial Pacific Ocean, we obtain a linear correlation between the total alkalinity (A_k) and the SSS of [$A_k = 0.0688*SSS – 0.0484$; $R^2 = 0.974$; n = 233].

We hypothesise that the present-day "A_k – SSS" relationship was also valid in the past. Past salinities can be estimated from sea-level changes through the past (Bard et al., 1996). For example, a reduction of -60m occurred during the Younger Dryas (YD) over a mean oceanic depth of 3,800m. This estimate takes into account the modern salinity near Tahiti and the Marquesas Islands of 35.6 ± 1 practical salinity units (psu) as a reference (Delcroix et al., 1996). From this calculation, the salinity in the past was about 36.2 psu in the central Pacific and about 34.8 psu in the eastern Pacific during the YD (Table 1). We consider today's mean seasonal salinity variability of ± 1 psu (Delcroix et al., 1996) in the calculation. The oceanic pCO_2 calculation was performed from pH and total alkalinity values listed in Table 1 using the guide to best practices for ocean CO_2 measurements by Dickson et al. (2007) with K_1 and K_2 from Lueker et al. (2000), K_W from (Millero, 1995), K_0 from Weiss (1974) and pH values on the total hydrogen ion pH scale close to the seawater one.

4. Results and discussion

To verify the reliability of pH reconstruction from boron isotopes in corals, we first analyzed the $\delta^{11}B$ and pH data for modern *Porites* samples collected from various areas and compared our results with the present day pH measured in the Pacific. Those areas cover a range of SST values and allow us to further elucidate the influence of the temperature on the incorporation of boron and its isotopic composition in corals. For each area, the measured or previously published values of $\delta^{11}B$ and [B] in *Porites* are evaluated against a theoretical curve

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that illustrates the preferential incorporation of borate ions in corals by substituting for the bicarbonate ions (Hemming and Hanson, 1992). This approach allows us to determine the various values of the partition coefficient K_D and to establish a link between the SST and this K_D. Similar exercises were done for the ancient corals from Marquesas and Tahiti to obtain information about the past SST. Finally, the changes in the pH and the pCO_2 as a function of time will be discussed in the central sub-equatorial Pacific by using the results of the "δ^{11}B – pH" calculation for both *Porites* near Marquesas (this study) and *Acropora* near Tahiti (Gaillardet and Allègre, 1995). This analysis takes into account the observed SST data.

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4.1. Reconstruction of the pH and SST from δ^{11}B and [B] data in modern Porites

4.1.1. pH deduced from δ^{11}B in modern Porites

The mean δ^{11}B values measured in modern *Porites* (Table 1) were about 25.8 ± 0.2 ‰ (n=6) for Moorea (1950AD), 24.8 ± 0.3 ‰ (n=8) for New Caledonia (2001-2004AD) and 24.5 ± 0.2 ‰ (n=17) for the Ishigaki Island (JCp-1). These values are similar to the modern value of 24.8 ‰ published for the Fanning Island (Hemming et al., 1998) and higher than the values of 23.6 ‰ and 23 ‰ found for the Red Sea (Gaillardet and Allègre, 1995) and Flinders Reef (~1990AD) along the Great Barrier Reef (Pelejero et al., 2005), respectively. According to the regional SST and SSS of 35 psu, the deduced sea surface pH was 7.98 for the Red Sea, 8.05 for the Ishigaki area, 8.07 for Fanning Island, 8.07 ± 0.3 for New Caledonia and 8.13 and 8.18 for Moorea in 1991AD and 1950AD, respectively. The δ^{11}B value for Moorea was higher by + 0.5 ‰ than the previous measurement in 1991 (Gaillardet and Allègre, 1995). This change corresponds to the pH change of 0.05 pH-unit. These values from modern *Porites* off the Moorea match the pH values measured in this area (Fig. 2). The inter-decadal variability linked, for example, to the Pacific Decadal Oscillation (PDO), could explain the difference observed in the western Pacific (Pelejero et al., 2005), but this δ^{11}B change could also reflect the consequences of surface water acidification during the industrial era given our own recent

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description of the last century at Fiji (Douville et al., 2009). Finally, the pH values deduced from the modern *Porites* for various areas of the Pacific Ocean match well with the present day pH map (Fig. 1) that was calculated on the seawater scale. These results corroborate the analyses that were based on empirical α values and previous lab calibrations on the tropical coral *Porites* (Hönisch et al., 2004; Reynaud et al., 2004).

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4.1.2. SST and the partition constant K_D for aragonite corals

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All of the $\delta^{11}B$ values versus [B] obtained here (Table 1) for modern *Porites* from Moorea, Ishigaki and New Caledonia Islands in the Pacific Ocean were compared to available published values for Moorea, Fanning Island and the Red Sea (Gaillardet and Allègre, 1995; Hemming et al., 1998) and plotted (Fig. 4a) to verify the model of a unique incorporation of boron (as borate ions) into the corals by substitution of bicarbonates ions (Hemming and Hanson, 1992; Sanyal et al., 2000; Yu and Elderfield, 2007; Foster, 2008). This model suggests that the [B] (or B/Ca) in corals increases together with the $\delta^{11}B$ and is controlled by the borate/bicarbonate abundance ratio in seawater according to the following relationship (Eq. 2):

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$$[B/Ca]_{corals} = K_D * [B(OH)_4^- / HCO_3^-]_{seawater} \qquad (2)$$

where K_D is the partition coefficient for boron. For various pH conditions, the theoretical $\delta^{11}B$ or $[B(OH)_4^- / HCO_3^-]$ ratios for seawater and the [B] for corals can be calculated and plotted by setting a K_D value. This model curve can be directly compared and fitted to points that correspond to the $\delta^{11}B$ and the [B] values measured in corals for each studied area. Model curves were generated with empirical values of α = 0.981 (Kakihana et al., 1977), $\delta^{11}B_{SW}$ = 39.9 ‰ (this work) and pK_B = 8.56 (Dickson, 1990) at 28°C and 35 psu. Figure 4a does not validate the model for a one and unique partition coefficient K_D but shows scattered points that represent various values of the partition coefficient K_D ranging between 0.0068

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(Moorea) and 0.0125 (Red Sea). In contrast, a similar graph for ancient corals shows values better validating the model with average K_D values of 0.0057 and 0.0068 for the Marquesas and Tahiti samples, respectively (Fig. 4b). The highest values are observed for the corals that grew at the end the Younger Dryas with values up to 0.0095 (Tahiti).

To evaluate the potential effect of the SST on this coefficient, the borate/bicarbonate molar ratios for seawater $[B(OH)_4^-/HCO_3^-]_{seawater}$ were first re-calculated from the measured $\delta^{11}B$-pH values using the regional SST and then compared to the measured boron/calcium molar ratios ($[B/Ca]_{coral}$) for all of the corals studied here (Fig. 5). This graph shows that the regional SST strongly controls the partition coefficient K_D, which is 0.0057 or less for the highest temperature (in the Marquesas area or Fanning Island during the winter season and the influence of warm and high pH waters, see below) and 0.0125 for the lowest SST (close to 22.5°C in the Red Sea). The K_D values are plotted versus the SST for modern *Porites* in Figure 6a. This figure shows a strong linear relationship with a regression coefficient (R^2) of 0.99. This linear dependence confirms that the boron in corals is more easily incorporated in aragonite at low temperatures, as previously observed in *Porites* (Fallon et al., 2003).

To test whether this linear temperature dependence of K_D applies (i) to ancient corals near Marquesas and (ii) to a wider temperature range that affects cold-water corals such as *Lophelia pertusa*, we extrapolated the regression towards SSTs of 28-29°C and temperatures of 5.5 to 11°C (Fig. 6b). This low temperature range covers the North Atlantic intermediate waters, which today have pH values approximately 7.95±0.05. For pH 7.95, the K_D deduced from boron concentrations in *Lophelia pertusa* (Douville et al., 2007) at local temperature agrees with the established regression (Fig. 6b). The average K_D of ancient Marquesas corals was 0.0057 (Fig. 4b). This value fits the linear temperature dependence described above well with deviations of no more than ±1°C at 28°C (Fig. 5). These reconstructed temperatures match the mean SST observed today near Marquesas. However, the lowest SSTs are estimated at the end of the Younger Dryas (YD) or during the glacial period, and higher SSTs are suggested by Figure 5 for the Marquesas corals that are about 9 and 14-15 kyr B.P. old, respectively.

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Similar trends are observed for the old corals near Tahiti. These corals have a mean K_D of 0.0068 (SST # 27°C) and a pronounced and unique SST decrease of 2.5°C around 11.5 kyr B.P. ago. Another example of the influence of the SST on the partition coefficient K_D is from the seasonal data published at Fanning Island (Fig. 4a and 5). The seasonal SSTs in the Fanning Islands vary by 3°C. The highest temperatures are close to 28°C and correspond to surface waters of high pH recorded by the high density bands of the modern *Porites* (http://www.nodc.noaa.gov; Hemming et al., 1998; Hönisch et al., 2004). This amplitude of seasonal SST changes matches the temperature (24.5°C - 27.5°C) described in Figure 5. Thus, at Fanning Islands the highest SST of about 27.5°C corresponds to a low K_D close to ~0.006 (Fig. 5), and points close to a high K_D of ~0.0095 corresponding to 24.5°C.

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4.2. Variations of "δ^{11}B- pH" as a function of time

In fossil *Porites* from Marquesas (Table 1), the δ^{11}B values vary from 26.0 to 26.6‰ during the Holocene, drastically fall to 24.7‰ at the end of the Younger Dryas, and then rise again to values between 25.6 and 26.4‰ during the beginning of the Younger Dryas and Bölling Allerød. The highest value (27.1 ‰) was observed during the last glacial period (20.7 kyr B.P.). During the Holocene, all of the deduced values for the sea surface pH from Marquesas and Tahiti are similar at 8.23 ± 0.04 (Table 1, Fig. 7). These values are equivalent to modern pH (~8.15) (Fig. 2a) when accounting for the model prediction for anthropogenic acidification on the order of 0.07 pH-units (Sabine et al., 2004). At the end of the YD at ~11.5 kyr B.P., uniformly low pH values (~7.99-8.06) are observed close to both islands (Fig. 7). These low pH values are preceded by high pH values (8.14 to 8.30) during the Bölling Allerød and the last glacial/interglacial transition (Fig. 7). From foraminifera in the "western" Pacific (ERDC-92), pH reconstruction using the δ^{11}B method yields ~8.23, ~8.13, and ~8.20 for the early, middle, and late Holocene. During the YD, pH-values were ~8.16, and during the Bölling Allerød, they were between 8.1 and 8.2. During the last glacial period, the highest pH values are estimated at ~8.3 (Palmer and Pearson, 2003). The central equatorial Pacific

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experienced larger pH changes (0.2 pH-units) than the western Pacific (~0.1 pH-units) during the transition between the YD and the Holocene. This difference may be attributed to the temporal resolution obtained using corals and foraminifera. In corals, the sampling represents one or two years of growth, while the 1cm-thick samples in the western Pacific deep-sea sediment core ERDC-92, due to because the low sedimentation rate of 1.4 cm/kyr (Palmer and Pearson, 2003), include numerous foraminifera covering several hundred years. Bioturbation probably smoothed the amplitude of the pH variations.

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Variations of the sea surface pH are related to changes in surface water pCO_2, which is controlled by the CO_2 uptake from surface water through ocean-atmosphere CO_2 gas exchange. This gas exchange is modulated by the temperature, wind intensity, photosynthesis, lateral or vertical advection and mixing of different water masses. During the YD, the SSTs were slightly lower than the modern SSTs by ~1°C to ~3°C in the eastern Pacific (Kienast et al., 2006; Koutavas et al., 2002). These values were either similar (Palmer and Pearson, 2003) or lower by 3°C to 4.5°C in the western part of the Pacific (Beck et al., 1997; Corrège et al., 2004; Gagan et al., 2004) and lower by 1.5°C in the central part at Tahiti (Asami et al., 2009). If the SST dropped by ~3°C (25°C), the calculated pH would be about 8.07 rather than 8.04 because of the temperature dependence of pK_B (Dickson, 1990). As previously observed and especially for Tahiti (Fig. 5), a change in the SST of ± 1-3°C has a minimal effect on the calculation of the pH.

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This temperature effect cannot account for the calculated change of ~ 0.2 pH-units observed at the transition between the YD and the Holocene. Estimates of the pH from *Porites* collected on the Flinders reef system in the southwestern Pacific reveal inter-decadal changes of ~0.3 pH-units over the past 300 years (Pelejero et al., 2005). These changes were attributed to local effects caused by the large lagoon platform structure of the Flinders reef, the water pCO_2 build-up through coral calcification and the renewal rate of lagoon water by the South Equatorial current pulsed by the PDO (Pelejero et al., 2005). In the central equatorial Pacific, the impact of these local effects cannot be completely excluded. However, the probability of detecting the extreme changes of 0.2 pH-units from corals collected in the two distant islands Tahiti and Marquesas is low given that the samples only provide information for a few years in the Holocene, which began around 11,5 kyr B.P. ago. A recent sea surface pH-$\delta^{11}B$ study at the Fiji Islands showed a slight pH change because of the PDO (Douville et al., 2009). In addition, all ancient corals during the Holocene and until the last glacial period show relatively stable pH values close to 8.19-8.23, and 15 years of recent observations indicate a stable ΔpCO_2 in this area (see below, Fig. 8). These observations indicate major and rapid changes in the Pacific oceanic patterns during the transition between the YD and Holocene.

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The estimated pH drop near Tahiti and Marquesas at the end of the YD could be accounted for by an intensified upwelling and westward advection of cooler eastern water masses to the central Pacific. These eastern water masses are characterised today by low pH and also low SST, especially for latitudes between 15°S and 20°S (Tahiti's latitudes, Fig. 2a). Sustained La Niña-like conditions operated at the end of the YD. That interpretation is supported by the presence of a strong east-west SST gradient in the equatorial Pacific around 11,500 years ago (Koutavas et al., 2006). The pH change from 8.04 to 8.23 at the YD-Holocene transition in the Marquesas area indicates a rapid change to more frequent El Niño-like climatic conditions in the equatorial south Pacific. Such changes are also observed in the east-west Pacific SST reconstruction (Koutavas et al., 2006).

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4.3. Estimates of the atmosphere-ocean ΔpCO_2

In the central sub-equatorial Pacific (Tahiti and Marquesas), ten Holocene values of pCO_2 have a mean average of about ~ 250 ± 30 ppmV for a pH of 8.23 ±0.04 (SSS: 35.6; SST: 28°C) (Table 1). At the end of the YD, the pCO_2 estimated for a pH of 8.04 was ~ 440 ppmV (SSS: 36.2; SST: 28°C) or ~450 ppmV (SSS: 34.8; SST: 25°C) when considering an intensified westward advection of the eastern Pacific water masses of low salinity and temperature. According to the past atmospheric pCO_2 from EPICA Dome C ice cores from Antarctica (Monnin et al., 2001; Monnin et al., 2004), the ocean-atmosphere ΔpCO_2 differences were

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between - 53 and + 20 ppmV during the Holocene, between 21 and + 91 ppmV before the YD with five pronounced positive values during the last deglaciation and + 185 ± 25 ppmV at the end of the YD ($pCO_{2\ atm}$ = 250 ppmV). From similar calculations, the ΔpCO_2 (~ -15 ppmV) for the two modern corals (1950AD, 1991AD) from Tahiti (Fig. 7) are close to equilibrium as recently published by Takahashi et al., (2009) for this area. This trend is also in agreement with modern ΔpCO_2 measurements (Fig. 8), which are either close to zero or slightly positive (Dandonneau, 1995; Feely et al., 2002; Feely et al., 1999; Goyet et al., 2009; Goyet and Peltzer, 1997).

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Since the early Holocene until today, sea surface waters in the central sub-equatorial Pacific have mainly served as a moderate sink or source of CO_2 for the atmosphere in the vicinity of both Tahiti and the Marquesas Islands (Fig. 7 and 8). Our slight negative or positive ΔpCO_2 values agree with previous suggestions that more frequent El Niño-like oceanographic conditions occurred during the Holocene (Gagan et al., 2004; Koutavas et al., 2006). In contrast, the sub-equatorial sea surface waters in the central Pacific were a more pronounced source of CO_2 to the atmosphere during the last glacial/interglacial transition. This source of CO_2 strongly intensified around 11.5 kyr B.P. at the end of the YD and quickly reversed during the transition between the YD and the Holocene.

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Such feature is connected first to the rapid rise of the atmospheric pCO_2 of ~ 15-20 ppmV (Fig. 7). This rise was observed quasi-synchronously in the EPICA Dome C ice core (EDC) (Monnin et al., 2001; Monnin et al., 2004) by using refined chronology (Marchitto et al., 2007). Once the chronology of TLD and EDC ice cores is adjusted, this rise is also accompanied by a rapid increase of the atmospheric $\delta^{13}CO_2$ values. This connection was observed in the Taylor Dome ice core (TLD) in Antarctica (Smith et al., 1999) and more recently also in EPICA Dome C (Lourantou et al., *in press*). Marchitto et *al.* (2007) showed that the ^{14}C ages of the intermediate waters in the Eastern Pacific decreased rapidly during YD-Holocene transition. These authors suggest that the aging of the intermediate waters was caused by northward penetration of the Antarctic Intermediate Water (AAIW) that was greater than the

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penetration occurring today (Marchitto et al., 2007), and the AAIW had old ^{14}C ages and depleted δ^{13}C values. The high $\Delta p\mathrm{CO}_2$ at the end of the YD, that was deduced from the δ^{11}B-pH indicator provides further evidence of the marked changes in the properties of the water masses in the equatorial Pacific and demonstrates the impact of these changes on the atmospheric CO_2 content.

5. Conclusions

The pH variations of the sea surface waters in the equatorial Pacific were determined from the isotopic composition of boron in the ancient corals *Porites* from reefs at Tahiti and Marquesas by MC-ICPMS analyses with an analytical uncertainty of ±0.025 pH-units. Our δ^{11}B, [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. Modern aragonite *Porites* were sampled from different geographical areas characterized by local SSTs ranging between 22.5°C and 27°C. The results reveal that the temperature strongly controls both the partition constant K_D and the incorporation of boron in various aragonite coral species. Boron is incorporated more in the aragonite skeleton at lower SST conditions. The δ^{11}B-pH values were close to ~8.23 during the Holocene in the surface waters of both Marquesas and the Tahiti Islands. This result is in agreement with the modern or pre-anthropogenic values. The δ^{11}B-pH values ranged from 8.14 to 8.30 during the last deglaciation, and the highest value measured was at 20.7 kyr B.P.

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An abrupt pH drop to ~8.04 was observed at the end of the Younger Dryas around 11.5 kyr B.P. The deduced $p\mathrm{CO}_2$ values were relatively equilibrated with the atmosphere during the Holocene and the last deglaciation, but during this event, the $p\mathrm{CO}_2$ increased to up to ~440 ppmV near both Tahiti and the Marquesas islands. The sea surface waters in the central equatorial Pacific (Tahiti, Marquesas) were a moderate sink or source of CO_2 to the atmosphere during the Holocene as present day. They were a more important source during the last

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glacial/interglacial transition, and they were a major source at the end of the YD with a $\Delta p\mathrm{CO}_2$ of at least +185 ppmV. This last finding provides further evidence of the marked changes to the properties of the water masses in the equatorial Pacific (Marchitto et al., 2007) and demonstrates the impact of these changes on the atmospheric CO_2 content. These results highlight the great potential of the "δ^{11}B-pH" methodology to precisely reconstruct past oceanic fluxes of CO_2 to the atmosphere from well-dated sea surface corals such as *Porites* and *Acropora*.

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Table caption

Table 1 **-** Isotopic composition of boron δ^{11}B (‰) and boron concentrations measured for coral and seawater samples. The $\Delta p\mathrm{CO}_2$ calculation is detailed in the text. The previously published δ^{11}B data for corals includes (*a*) (Gaillardet and Allègre, 1995); (*b*) (Hemming et al., 1998); and (*c*) (Pelejero et al., 2005). The ^{230}Th/U ages of the corals from Tahiti and Marquesas are from (Bard et al., 1996; Cabioch et al., 2008; Paterne et al., 2004). (*) ^{230}Th/U age of the sample Ta-3 is the former date published by (Gaillardet and Allègre, 1995). SST sources: (http://www.nodc.noaa.gov; (Boiseau, 1998; Gertman and Brenner, 2004; Heiss et al., 1999; Henin and Cresswell, 2005).

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Figure captions

Figure 1 – Geographical locations of the study sites, including Moorea (close to Tahiti), Marquesas, Ishigaki, New Caledonia and the Fanning Islands. The location of the ERDC-92 box core (Palmer and Pearson, 2003) is also shown. The sea surface pH from modern corals are plotted on a seawater scale pH map modified from (Pelejero et al., 2005). The δ^{11}B data of corals: (*a*) (Gaillardet and Allègre, 1995); (*b*) (Hemming et al., 1998); (*c*) (Pelejero et al., 2005); the foraminifera δ^{11}B data: (*d*) (Palmer and Pearson, 2003).

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Figure 2 – **a)** The modern sea surface pH in the sub-Equatorial Pacific Ocean as function of the geographical location. 0.07 pH-units are added to the present day pH on the pre-industrial era pH scale (see text). The month (*values in parenthesis*) of the water sampling and the averaged SSTs are also indicated. **b)** Sea surface pH in the sub-Equatorial Pacific Ocean plotted against SST between 150°E and 80°W. Similar pH-SST correlations were observed for surface waters between 80°W and 170°W at three different ranges of latitude (sources from http://www.nodc.noaa.gov/OC5/SELECT/dbsearch/dbsearch.html; measurement years: 1980-1998; depths: 0-50 m).

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Figure 3 – Comparison of MC-ICPMS analyses using direct injection (d-DIHEN) and conventional introduction for *Porites* referenced DW1281c_78a1, DW1261_68a1, DW1281_75a2 and MOO3A-1-02. δ^{11}B results show an excellent agreement of the two introduction technique within the external reproducibility considered here of ± 0.25 ‰. Error bars is the standard deviation calculated from the "n" measurements for each sample (Table 1)

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Figure 4 – The δ^{11}B values plotted against the boron concentrations **a)** for modern *Porites* from various geographical areas and **b)** for ancient *Porites* and *Acropora* near Marquesas and

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the Tahiti Islands. The theoretical curves for different partition coefficient K_D values were calculated assuming T = 28°C; S = 35 ‰; α = 0.981; and $\delta^{11}B_{SW}$ = 39.9 ‰. Seawater values used were $[B]_{seawater}$ = 416 µM and TCO_2 = 2 mM.

***Figure* 5 -** B/Ca molar ratio in coral plotted against the borate/bicarbonate molar ratio in seawater. Theoretical curves for different partition coefficient K_D values were calculated assuming T = 28°C; S = 35 ‰; α = 0.981; and $\delta^{11}B_{SW}$ = 39.9 ‰. Regional SSTs was used to calculate the borate/bicarbonate ratios for each of the corals. The temperature strongly influences the partition coefficient K_D. *Porites* near Marquesas showed a K_D of ~0.0057. The seawater values used to calibrate the partition coefficient were $[B]_{seawater}$ = 416 µM and TCO_2 = 2 mM.

***Figure* 6 –** Linear correlation between the mean regional SST and the partition coefficient K_D obtained from modern *Porites* samples collected from various SST areas. This regression shows the influence of the temperature on K_D and is valid for various aragonite species. The tropical corals are *Porites, Acropora*, and the cold sea coral is *Lophelia pertusa*. The expected area for cold sea corals (6-11°C) was determined from pH 7.95 and from the high boron concentrations (78-100 ppm) measured in North Atlantic *Lophelia pertusa* samples collected between 40°N and 70°N (Douville et al., 2007).

***Figure* 7 -** Comparison of the sub-Equatorial Pacific $\delta^{11}B$-pH of marine biogenic carbonates over the last 21,000 cal. yr. Sources are (*a*) this study; (*b*) Gaillardet and Allègre (1995); and (*c*) Palmer and Pearson (2003). Filled black diamond: modern Moorea-Tahiti *Porites* value published by Gaillardet and Allègre (1995). The calculation parameters for the pH are α = 0.981; $\delta^{11}B_{SW}$ = 39.9 ‰; S = 35 ‰; and T = 27°C for Tahiti (Moorea) and T = 28°C for the Marquesas Islands and for ERDC-92. Deduced ΔpCO_2 values (Table 1, see text) and

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Mis en forme : Police :(Par défaut) Times New Roman atmospheric pCO_2 data (Monnin et al., 2001; Monnin et al., 2004) are also plotted to illustrate the synchronization between the abrupt changes to the sea surface pH and ΔpCO_2 in the central sub-Equatorial Pacific and the atmospheric CO_2 increase of 15-20 ppmV at the end of the YD event.

***Figure* 8** – The relative stability of modern ΔpCO_2 values close to equilibrium in the Tahiti – Marquesas area between 1992AD and 2004AD ((Dandonneau, 1995; Feely et al., 2002; Feely et al., 1999; Goyet et al., 2009; Goyet and Peltzer, 1997).

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***Table 1* - Douville et al. (2010 - submitted)**

Samples, mean SST	^{230}Th/U age cal.	Boron (ppm)	LSCE number	$\delta^{11}B_{measured}$ (‰)	Std Dev. (2 σ, n)	Salinity (*Sea level*) psu	A_k µM	pH (± 0.03)	*p* C0$_2$ (ppmV)	Δ*p* CO$_2$ (ppmV)
Marquesas Islands, 28 ± 1.0°C										
Nuku Hiva DR6(1)	250 ± 30	40.0	B33^{di}	26.2	± 0.2 (2)	35.6	2401	8.21	**264**	**-16**
DW1281c _78a1	3 230 ± 30	63.2	B01, 02, 03, 04	26.5	± 0.2 (6)	35.6	2401	8.25	**238**	**-36**
			B20^{di}	26.8	± 0.3 (1)	35.6	2401	8.27	**221**	**-53**
DW1261_68a1	3 260 ± 30	60.0	B15, 16	26.3	± 0.2 (3)	35.6	2401	8.22	**260**	**-14**
			B18di	26.1	± 0.2 (4)	35.6	2401	8.21	**269**	**-5**
Eiao DR16(3)	8 990 ± 130	37.4	B31^{di}	26.0	± 0.3 (2)	35.9 (*-30m*)	2420	8.19	**281**	**20**
Eiao DR16(5)	9 110 ± 130	53.4	B32^{di}	26.3	± 0.5 (2)	35.9 (*-30m*)	2420	8.22	**259**	**-5**
Eiao DR12(1)	9 590 ± 180	43.5	B30^{di}	26.2	± 0.2 (3)	35.9 (*-30m*)	2420	8.21	**270**	**6**
DW1281 _75a2	11,470 ± 90	45.3	B13, 14	24.8	± 0.2 (4)	36.2 (*-60m*)	2440	8.06	**420**	**164**
			B19di	24.5	± 0.2 (2)	36.2 (*-60m*)	2440	8.02	**464**	**209**
Hiva Oa DR10(2)	12,420 ± 100	51.9	B27^{di}	26.2	± 0.2 (3)	36.2 (*-65m*)	2443	8.21	**273**	**34**
Eiao DR11bis(4)	13,410 ± 190	n. d.	B53^{di}	25.6	± 0.3 (1)	36.3 (*-75m*)	2449	8.14	**330**	**92**
Eiao DR8(1)	14,560 ± 180	42.1	B29^{di}	26.1	± 0.2 (2)	36.5 (*-90m*)	2459	8.19	**284**	**49**
Hiva Oa DR14bis(1)	15,450 ± 150	40.0	B28^{di}	26.1	± 0.3 (3)	36.6 (*-105m*)	2469	8.20	**281**	**57**
Hiva Oa DR8bis(1)	15,460 ± 110	43.8	B26^{di}	26.4	± 0.2 (2)	36.6 (*-105m*)	2469	8.23	**256**	**33**
Hiva Oa DR5	20,720 ± 200	63.6	B25^{di}	27.1	± 0.3 (3)	36.8 (*-125m*)	2482	8.30	**209**	**21**
Moorea-Tahiti Islands, 27.1 ± 0.5°C										
Porites:										
COM2 [a]	1991(AD)	51.0		25.3	± 0.2 (3)	35.6	2401	8.13	**340**	**-15**
MOO 3A-1-02	1950 (AD)	51.9	B11, 12	25.8	± 0.2 (3)	35.6	2401	8.18	**294**	**-16**
			B17^{di}	25.8	± 0.2 (3)	35.6	2401	8.18	**292**	**-18**
Ta P8-348	12,910 ± 30	n. d.	B56^{di}	25.9	± 0.3 (3)	36.3 (*-75m*)	2449	8.19	**287**	**53**
Ta P8-353	13,335 ± 30	n. d.	B57^{di}	26.6	± 0.2 (3)	36.3 (*-75m*)	2449	8.26	**231**	**-7**
Acropora [a] *:*										
Ta-1	8 520 ± 40	50.0		25.7	± 0.3 (2)	35.9 (*-30m*)	2420	8.23	**251**	**-10**
Ta-2	9 260 ± 50	49.0		25.4	± 0.2 (3)	35.9 (*-30m*)	2420	8.21	**273**	**12**
Ta-3	9 850 *	51.0		25.6	± 0.2 (2)	35.9 (*-30m*)	2420	8.22	**259**	**-4**
Ta-4	10,250 ± 40	52.0		25.9	± 0.3 (1)	36.0 (*-40m*)	2427	8.25	**237**	**-30**
Ta-5	10,575 ± 50	41.0		24.6	± 0.3 (1)	36.0 (*-45m*)	2430	8.11	**357**	**91**
Ta-6	10,850 ± 50	50.0		26.6	± 0.2 (2)	36.1 (*-50m)*	2433	8.32	**196**	**-69**
Ta-7	11,000 ± 40	50.0		25.3	± 0.2 (2)	36.1 (*-50m)*	2433	8.19	**290**	**26**
Ta-8	11,280 ± 30	41.0		24.4	± 0.2 (3)	36.1 (*-55m)*	2436	8.09	**387**	**123**
Ta-9	11,495 ± 30	41.0		23.6	± 0.2 (3)	36.2 (*-60m*)	2440	7.99	**508**	**254**
Ishigaki Island, 26.1 ± 2.1°C										
Porites JCp-1 (standard)	modern	47.7	*9 samplings*	24.5	± 0.1 (15)	35		8.06		
New Caledonia, 24.4 ± 1.9°C										
NC_a	2001-2002 (AD)	55.0	B84^{di}, 85^{di}	24.3	± 0.2 (2)	35		8.04		
NC_b	2002-2003 (AD)	54.6	B86^{di}, 87^{di}	24.5	± 0.6 (2)	35		8.06		
NC_c	2003-2004 (AD)	54.4	B89^{di}, 90^{di}, 91^{di}, 92^{di}	24.8	± 0.5 (4)	35		8.10		
Red Sea [a], 22.5 ± 2.0°C										
COM3	1970-80 (AD)	57.0		23.7	± 0.5 (2)	35		7.98		
Fanning Island [b], 25-28°C										
Porites Lobata	mean	50.5		24.8	-	35		8.07		
	Two year range	46.1 - 53.9	*Seasonal microsampling*	23.9 - 26.2	-	35		7.96-8.23		
Flinders Reef [c]										
FLO2A	1990s (AD)	-		23		35		~ 7.9		
	1950s (AD)	-		24.5		35		~ 8.1		
	1700 - 2000 (AD)	-		23.0 - 25.0		35		7.9 - 8.1		

Figure 1 - **Douville et al. (2010 - submitted)**

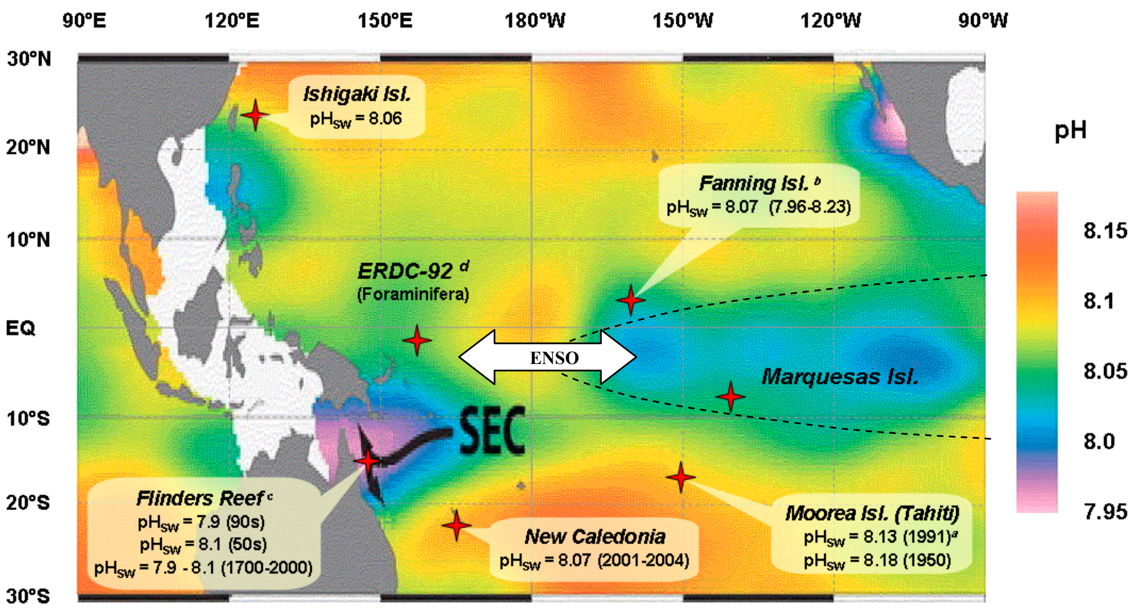


Figure 2 **- Douville et al. (2010 - submitted)**

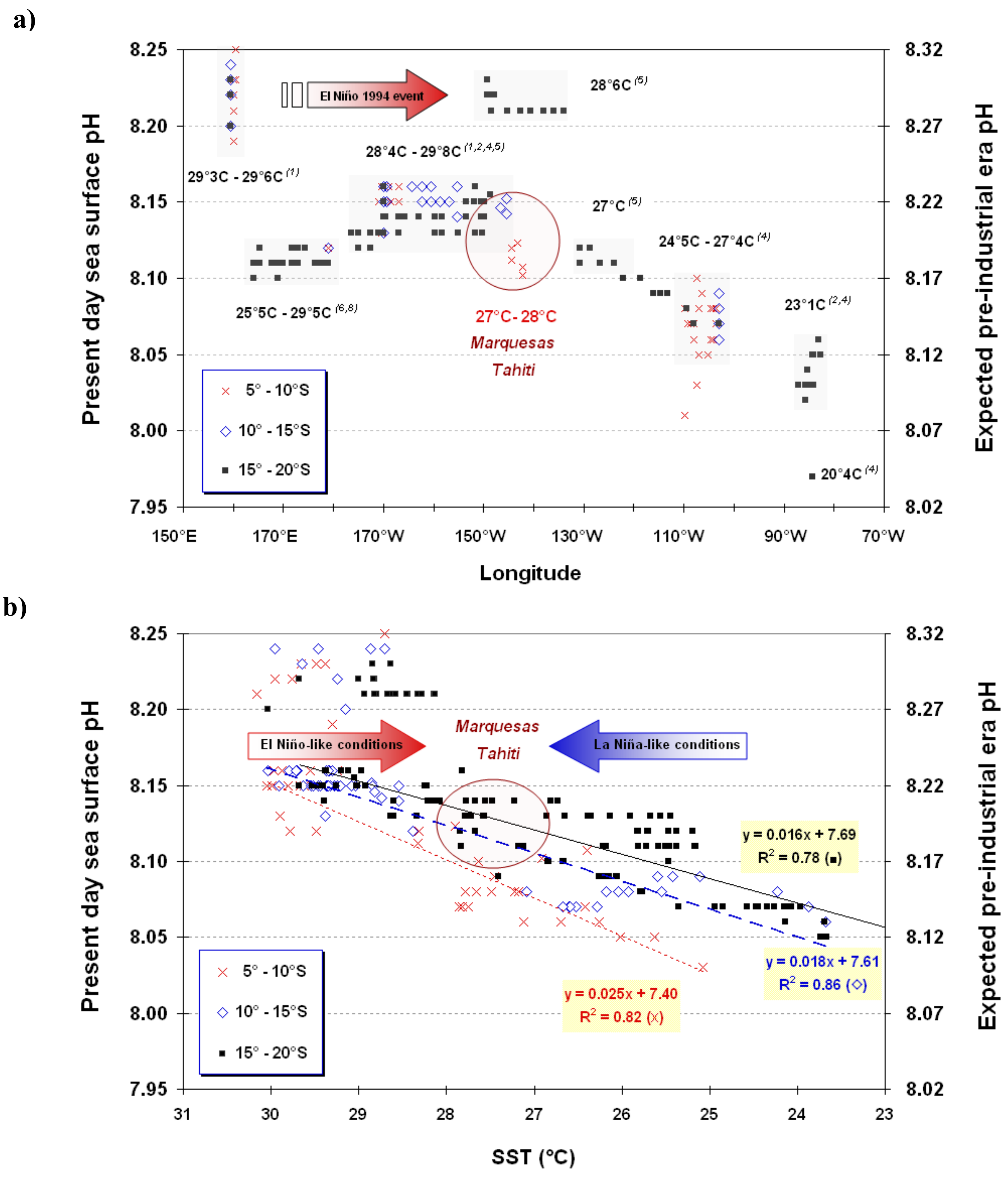
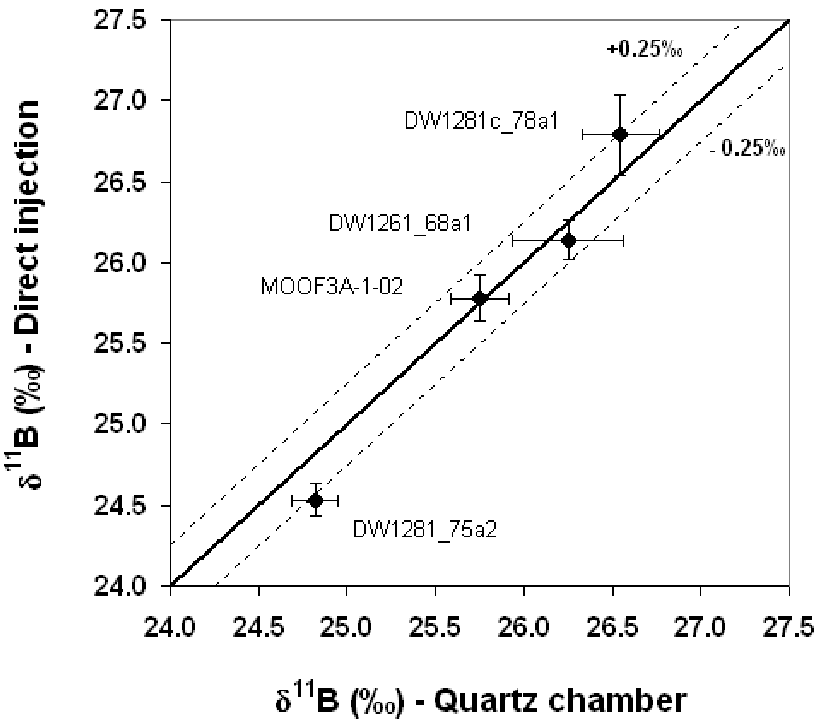


Figure 3 **- Douville et al. (2010 - submitted)**



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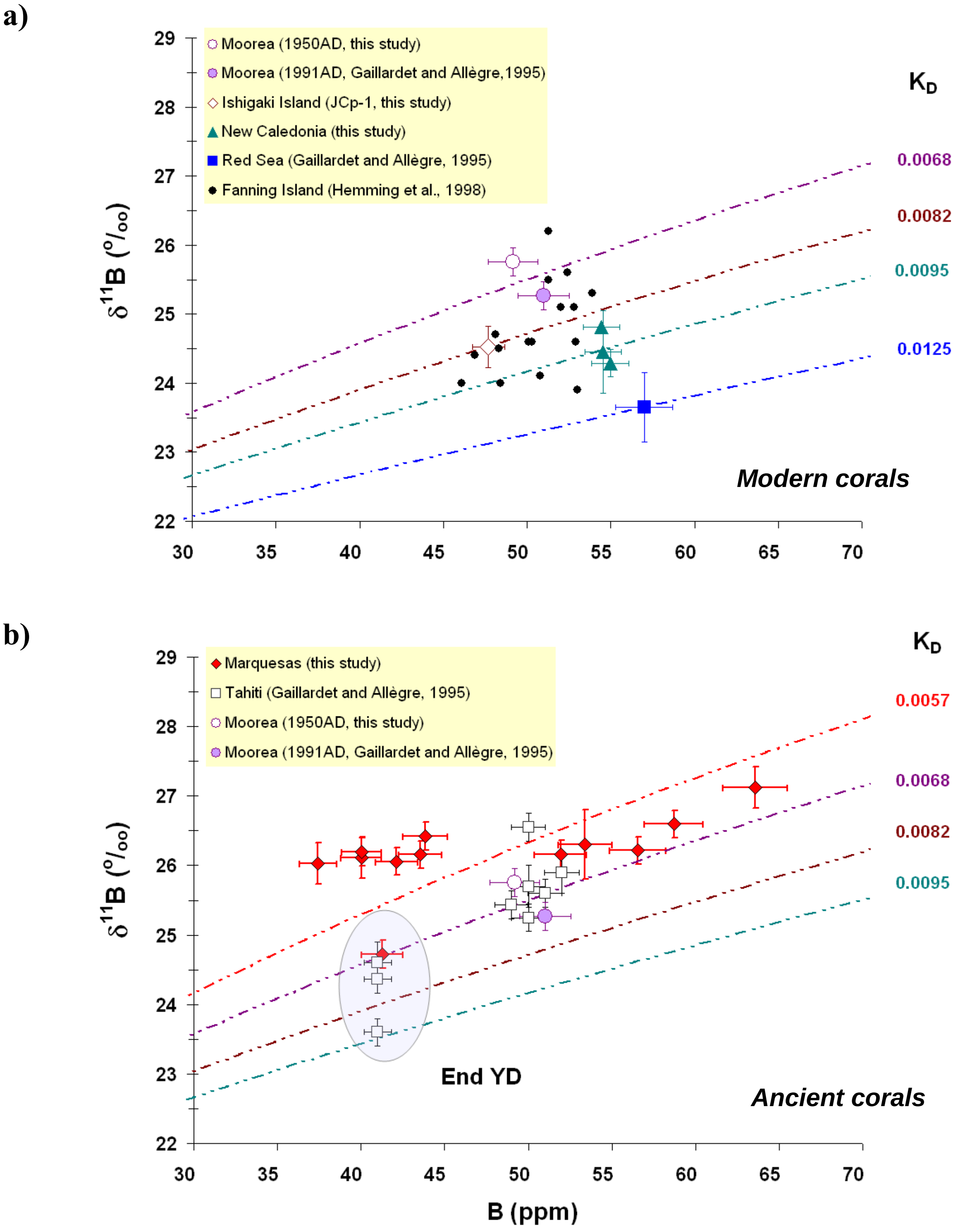

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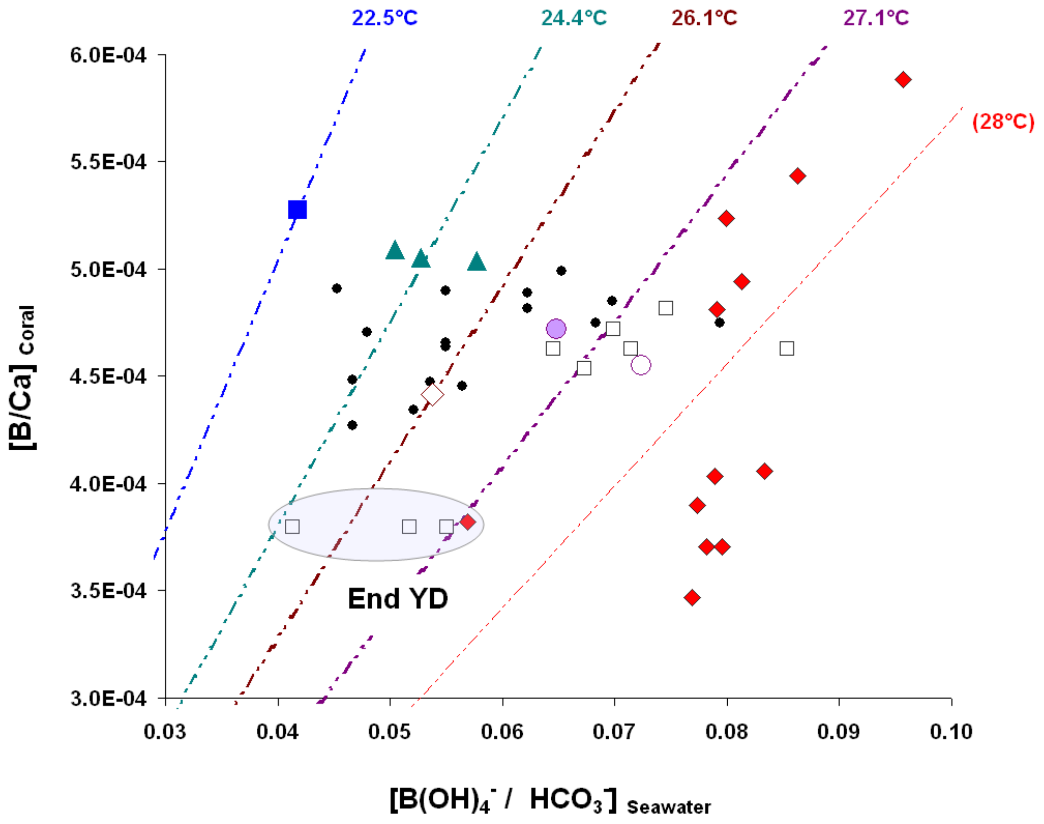

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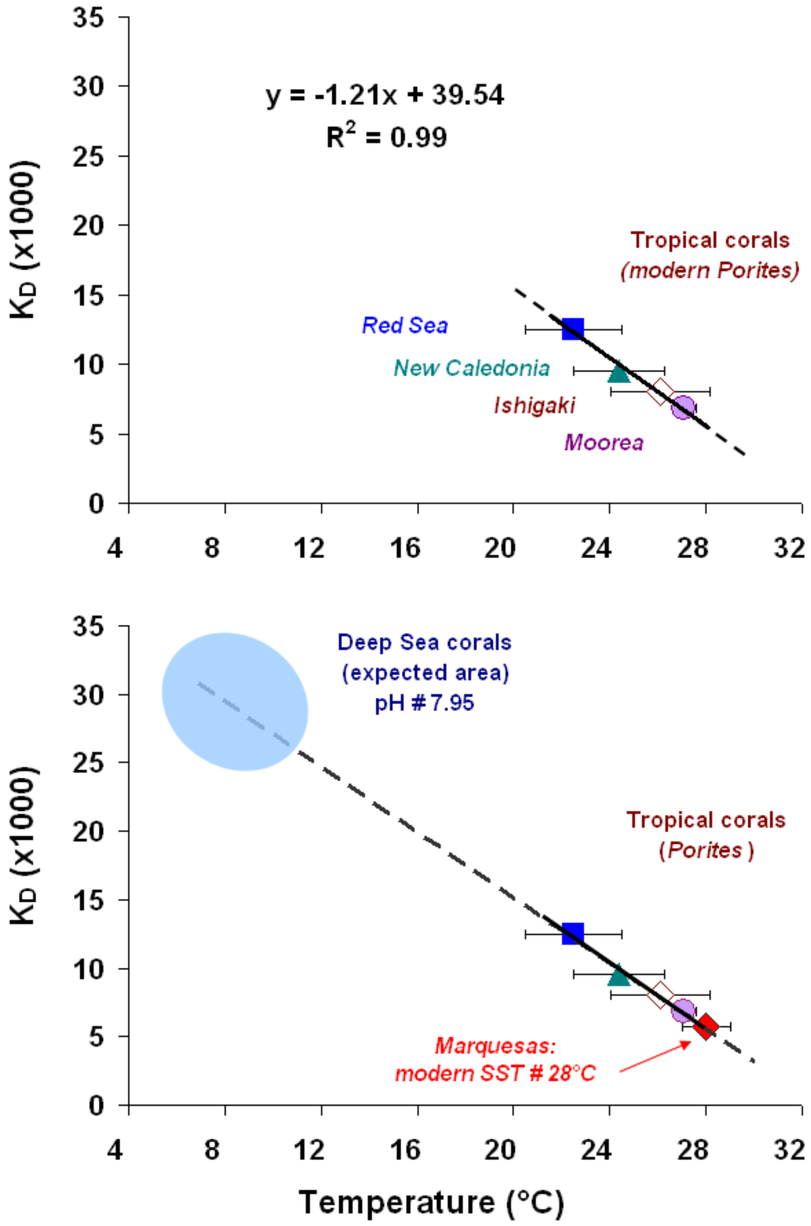

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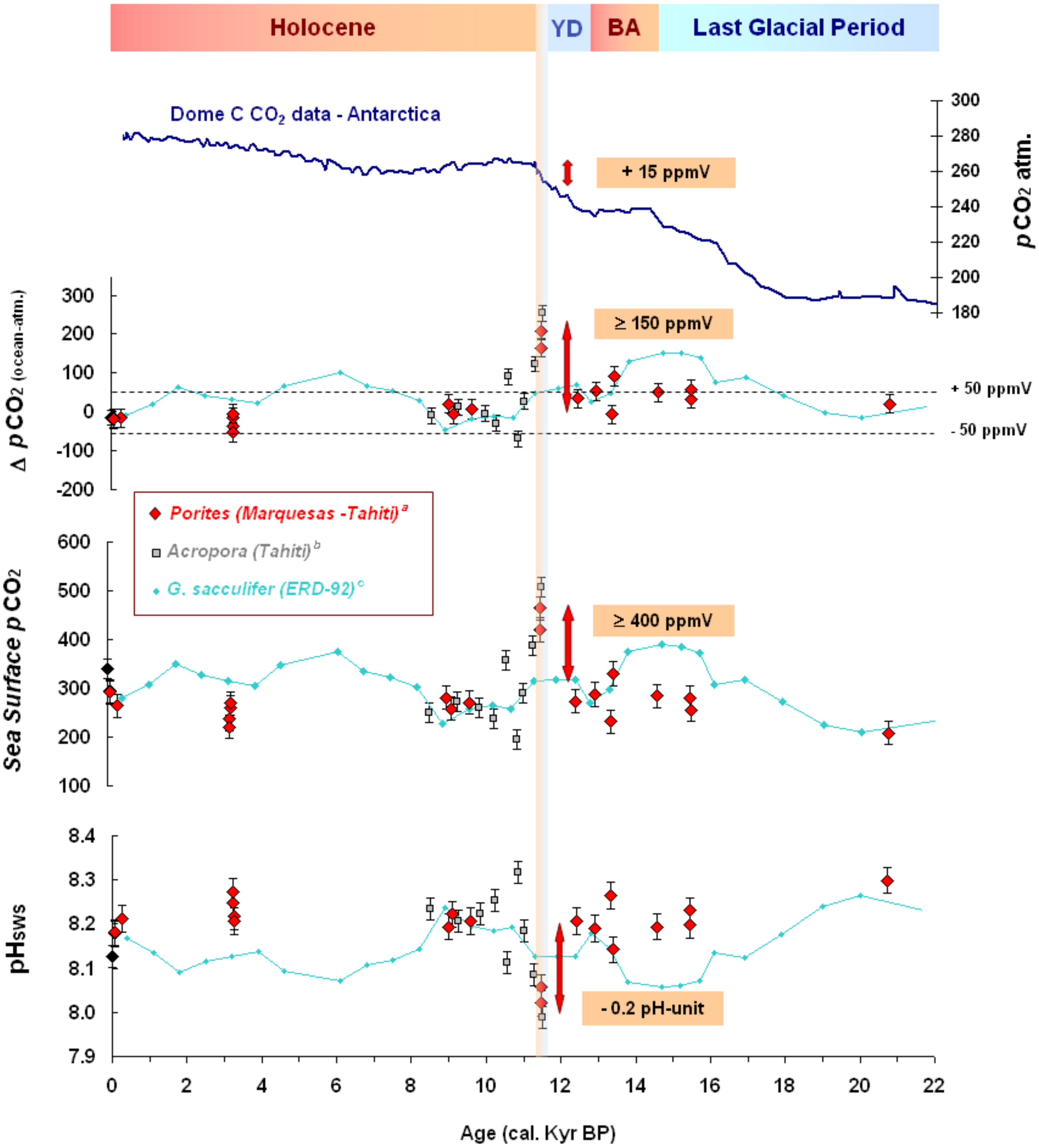
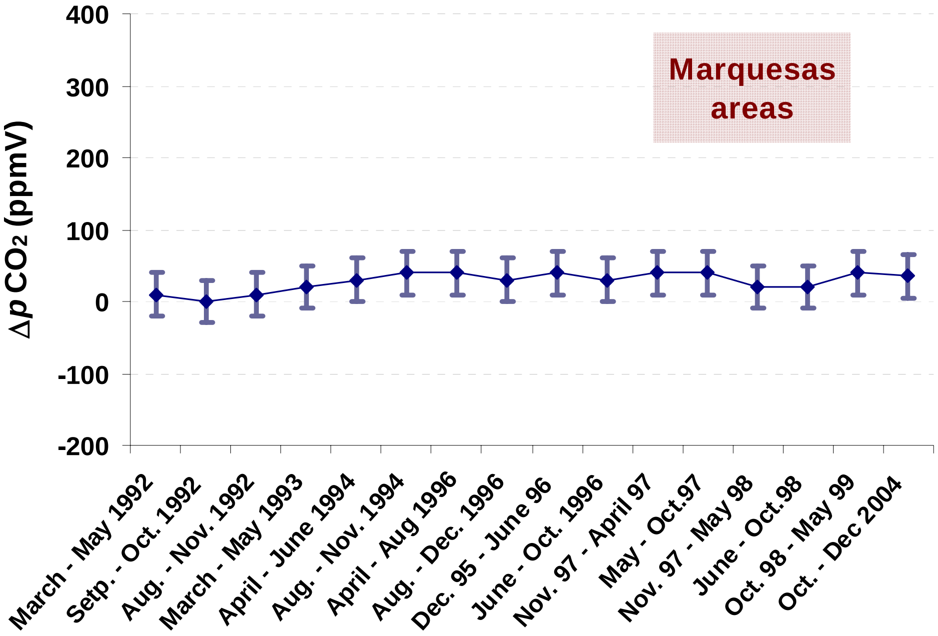


Figure 8 **- Douville et al. (2010 - submitted)**



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