



Letter

Ocean acidification trend in the tropical North Pacific since the mid-20th century reconstructed from a coral archive

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ABSTRACT

Ocean acidification caused by anthropogenically elevated CO₂ concentration in the atmosphere can pose a critical threat to calcifying marine organisms and coral reef ecosystems. However, because of temporally and spatially limited instrumental pH records, little is known about the actual long-term trend and natural variability of seawater pH during the past century. We present an annually resolved time series of a pH proxy record for 1940–1999 using boron-isotope composition ($\delta^{11}\text{B}$) in a modern massive *Porites* coral from Guam Island (NW Pacific). When superimposed onto interannual variability, the data show a slightly decreasing trend of $\sim 0.39\%$ (equivalent to $\sim 0.05\text{--}0.08$ pH units for surface water pH) in the northwestern tropical Pacific since the mid-20th century. This first reported, coral-based reconstruction of long-term open ocean pH is a unique archive for ocean acidification trend in the North Pacific Ocean for the past, which, along with $\delta^{11}\text{B}$ records from South Pacific corals, can be an important key to ascertaining the extent and rapidity of actual acidification in the Pacific Ocean in the future.

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1. Introduction

Ocean acidification has been accelerating as a result of absorption of increasing anthropogenic CO₂ in the atmosphere emitted by fossil-fuel combustion and land-use practices since the Industrial Revolution, which is probably resulting in decreased surface ocean pH and posing a critical threat to marine ecosystems in the future (e.g. Sabine et al., 2004; Orr et al., 2005; De'ath et al., 2009; Pelejero et al., 2010; Joos et al., 2011). By the end of the 21st century, predictions based on different scenarios indicate that ocean pH will decrease by 0.3–0.4 pH units (Orr et al., 2005; Steinacher et al., 2009). This declining pH trend is quite extreme relative to typical variations in surface water pH during glacial–interglacial cycles, which ranged from 8.3 to 8.1 pH units over the last 800,000 years (Hönisch et al., 2009). Since the 1990s, a significant decline has occurred in coral calcification in the Great Barrier Reef because of the influence of global factors such as acidification or

warming of the oceans (De'ath et al., 2009). Meanwhile, there is no widespread pattern of consistent decline in the calcification rates during the 20th century in the West Australian coast (Cooper et al., 2012).

Only a few long-term continuous observations of sea surface pH have been conducted at Station ALOHA off the Hawaiian Islands (Hawaii Ocean Time-series [HOT]) in the North Pacific Ocean, near the Bermuda Islands (Bermuda Atlantic Time-series Study), and near the Canary Islands in the North Atlantic Ocean. However, records for ocean pH, as estimated from direct measurements of carbonic acid parameters on collected water samples, cover a few decades. A decreasing pH trend in the western North Pacific surface waters for 1983–2007 was estimated from the observational data of oceanic CO₂ partial pressure and related properties in latitudinal zones from 3° to 33°N at 137°E (Midorikawa et al., 2010). To elucidate the natural variability of ocean pH and assess the actual trend in ocean acidification more accurately, we must go further back in time. For these reasons, we rely on paleo-pH archives or other related parameters.

Massive *Porites* sp. corals, an informative archive of past ocean environments, precipitate annually banded aragonite skeletons at a relatively rapid rate, allowing for accurate chronological control and high-resolution sampling. Many studies have documented the seasonal-to-centennial scale variability of sea surface temperature and salinity in the tropics and subtropics over the last several centuries using oxygen-isotope composition ($\delta^{18}\text{O}$) and Sr/Ca records of

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modern *Porites* corals (e.g. Charles et al., 2003; Linsley et al., 2004; Calvo et al., 2007; Felis et al., 2009). Because of pH-dependent isotopic fractionation between the two dominant boron species in seawater, boron-isotope systematics in marine carbonates provide a potential proxy for pH of ancient oceans. Calibrations of *Porites* corals showed good agreement with the theoretically inferred relation (e.g. Hemming and Hanson, 1992; Hönisch et al., 2004). A few attempts have been made to reconstruct seawater pH using boron-isotope composition ($\delta^{11}\text{B}$) of modern and fossil corals. Nevertheless, only two previous studies (Pelejero et al., 2005; Wei et al., 2009) generated $\delta^{11}\text{B}$ time series from long-lived *Porites* corals from the Great Barrier Reef (GBR) in the southwestern Pacific Ocean for the last 300 years. Unlike seawater temperature and salinity records (e.g., Urban et al., 2000; Asami et al., 2005; Felis et al., 2009), no coral-based reconstruction of long-term pH variation in the North Pacific Ocean has been reported.

In this study, we derived a 60-year-long record of seawater pH from $\delta^{11}\text{B}$ data for a *Porites* coral collected in Guam Island and found an ocean-acidification trend in the northwestern tropical Pacific Ocean extending from the mid-20th century. Guam Island is located in the Western Pacific Warm Pool (WPWP), which contains the highest annual sea surface waters $> 28^\circ\text{C}$, which serves as a heat engine for the earth's climate and provides an optimal environment for the greatest diversity of corals (e.g., Veron, 2000; Veron et al., 2009). From this perspective, the results of this study will provide improved constraints on global atmosphere–ocean interaction models and understanding of the future coral reef ecosystems.

2. Materials and methods

2.1. Coral sample

A long core of a massive *Porites* coral, with clear high/low-density skeletal banding (Supplementary Fig. S1), was collected on April, 2000 in Guam (13.6°N, 144.8°E), an island in the Mariana Islands group located in the tropical Northwest Pacific (Fig. 1A). The study site, characterized by a narrow fringing reef, is in the path of the North Equatorial Current (NEC) and exposed directly to open ocean conditions (Asami et al., 2004; Lindahl et al., 2011) (Fig. 1B). The NEC splits into two branches around the Philippines; one branch turns to the south and feeds the Equatorial Counter Current, and the northern extension of the northward-turning NEC forms the Kuroshio Current (Fig. 1A). The coral chronology was established in previous studies (Asami et al., 2004, 2005), in which X-radiographic and coral $\delta^{18}\text{O}$ analyses were determined with high-temporal resolution. The rigorous tests for diagenetic alteration showed evidence of well-preserved aragonite skeleton. We used annual skeletal growth increments (approximately from January to December) for $\delta^{11}\text{B}$ analysis for 1940–1999. The samples were cleaned ultrasonically in ultrapure water (18.2 M Ω), air dried, and were then ground into a homogeneous powder using a pre-cleaned agate mortar.

2.2. Boron-isotope measurements

We used a micro-sublimation technique for boron purification (Wang et al., 2010). $\delta^{11}\text{B}$ measurement was performed using a Neptune multi-collector ICP-MS (ThermoFisher Scientific) at the National Cheng Kung University, Taiwan, following an analytical protocol modified from a previous method (Foster, 2008). Boron-isotope ratios are expressed in the conventional delta (δ) notation relative to the NBS-951 boric acid international standard. The reported $\delta^{11}\text{B}$ value of a coral sample was determined as the average of 1–3 measurements. The external reproducibility throughout a long-term measurement of a 20-ppb NBS-951 was 0.24‰ (2SD, $n = 125$). The JCP-1 (*Porites* sp.; Geological Survey of Japan) standard was measured to evaluate the analysis of natural coral samples, yielding a mean value of $24.41 \pm 0.25\%$ (2SD, $n = 25$), which shows excellent

agreement with previously reported values (Douville et al., 2010; Wang et al., 2010; Ishikawa and Nagaishi, 2011). This translates into an error of ~ 0.03 pH units (2SD) in reconstructed pH. Further details can be found in the Supplementary materials.

2.3. Estimation of past seawater pH

Using the following equation (e.g. Zeebe et al., 2001), pH values for the past were estimated from coral $\delta^{11}\text{B}$ records.

$$\text{pH}_{\text{sw}} = \text{p}K_{\text{B}} - \log \left[\left(\delta^{11}\text{B}_{\text{sw}} - \delta^{11}\text{B}_{\text{carbonate}} \right) / \left\{ \alpha_{(\text{B3-B4})} \delta^{11}\text{B}_{\text{carbonate}} - \delta^{11}\text{B}_{\text{sw}} + 10^3 \left(\alpha_{(\text{B3-B4})} - 1 \right) \right\} \right]$$

The parameters $\text{p}K_{\text{B}}$ and $\alpha_{(\text{B3-B4})}$ are the equilibrium constant and the fractionation factor for isotope exchange, respectively, between boric acid $\text{B}(\text{OH})_3$ and borate ions $\text{B}(\text{OH})_4^-$ in seawater. $\delta^{11}\text{B}_{\text{sw}}$ and $\delta^{11}\text{B}_{\text{carbonate}}$ represent the $\delta^{11}\text{B}$ in seawater and in carbonate, respectively. We used $\text{p}K_{\text{B}} = 8.60$ (DOE, 1994; Hönisch et al., 2004), $\delta^{11}\text{B}_{\text{sw}} = 39.5\%$ (Foster, 2008), and $\alpha_{(\text{B3-B4})} = 1.0204$ at 25°C (Xiao et al., 2006) to compare with results from GBR corals (Pelejero et al., 2005; Wei et al., 2009). These values were widely used for *Porites* coral-based pH reconstructions in previous studies (Pelejero et al., 2005; Liu et al., 2009; Wei et al., 2009; Douville et al., 2010). Although selection of the $\alpha_{(\text{B3-B4})}$ value is critical in the use of the $\delta^{11}\text{B}$ -pH proxy, the value of 1.0204 suggested for massive *Porites* corals is close to the theoretically estimated value of 1.0194 (Kakihana et al., 1977). Whereas, a couple of complexities such as $\alpha_{(\text{B3-B4})}$, reef environment, and biological processes possibly influence estimation of past seawater pH values. Recent studies suggest that a higher $\alpha_{(\text{B3-B4})}$ value of 1.026–1.028 than previously used values can be recommended and that there exists a variable offset of 0.5–1.1 between ambient seawater pH and internal pH at calcification sites of *Porites* corals (Klochko et al., 2006; Krief et al., 2010; Trotter et al., 2011; McCulloch et al., 2012). In this study, we also estimated seawater pH based on the approach shown in recent articles (Krief et al., 2010; Trotter et al., 2011) using the $\alpha_{(\text{B3-B4})}$ value of 1.0272 (Klochko et al., 2006) with a correction for relationship between ambient seawater pH and internal calcifying fluid pH for *Porites* sp. (McCulloch et al., 2012: $\text{Calcifying fluid pH} = 5.95 + 0.32 \times \text{Seawater pH}$). It should be noted that absolute seawater pH values will be acquired once the robust quantification of internal-external pH offsets caused by physiological process (vital effects) and the validated $\alpha_{(\text{B3-B4})}$ value for *Porites* sp. corals are established (Trotter et al., 2011). Therefore, we believe that reconstruction of relative change in pH values is more important than the absolute values in this study.

Although the $\text{p}K_{\text{B}}$ value depends on seawater temperature and salinity, variations in these parameters would only change the reconstructed pH values by ~ 0.03 and ~ 0.01 pH units, when temperature and salinity change by $\sim 3^\circ\text{C}$ and ~ 2 , respectively (Liu et al., 2009). Around Guam, annual instrumental data derived from Met Office Hadley Centre's sea surface temperature (Hadl 1.1 SST) and Etudes Climatiques de l'Océan Pacifique tropical sea surface salinity (ECOP SSS) show slight variations, with a standard deviation (1σ) of $\pm 0.25^\circ\text{C}$ for 1940–1999 and ± 0.16 for 1970–1995, respectively, and potential long-term trends of $\sim 0.30^\circ\text{C}$ and ~ 0.14 since 1940, suggesting that the effects of these variations in $\text{p}K_{\text{B}}$ and thus on the reconstructed pH are negligible. Using CO_2 system calculations (Lewis and Wallace, 1998), the deviations and long-term trends of seawater temperature and salinity correspond to minor errors of less than 0.003 in estimated pH values.

3. Results and discussion

A 60-year-long annual time series of $\delta^{11}\text{B}$ values ranging from 22.1 to 23.9‰ was generated from the Guam coral sample (Fig. 2 and Supplementary Table S1). Using the $\alpha_{(\text{B3-B4})}$ value of 1.0204 (Xiao et

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