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Decadal variability in seawater pH in the West Pacific: Evidence from coral δ^{11}B records

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Key Points:
- Coral δ^{11}B-based seawater pH record show large interannual to decadal variability
- Monsoon driven upwelling controls the decadal seawater pH variability
- PDO influences pH variability in the West Pacific with different effects

Supporting Information:
- Supporting Information S1
- Table S1
- Table S2

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Abstract Long-term seawater pH records are essential for evaluating the rates of ocean acidification (OA) driven by anthropogenic emissions. Widespread, natural decadal variability in seawater pH superimposes on the long-term anthropogenic variations, likely influencing the OA rates estimated from the pH records. Here, we report a record of annual seawater pH estimated using the δ^{11}B proxy over the past 159 years reconstructed from a *Porites* coral collected to the east of Hainan Island in the northern South China Sea (SCS). By coupling this time series with previously reported long-term seawater pH records in the West Pacific, the decadal variability in seawater pH records and its possible driving mechanisms were investigated. The results indicate that large decadal variability in seawater pH has occurred off eastern Hainan Island over the past 159 years, in agreement with previous records. The Qiongdong upwelling system, which controls nutrient supplies, regulates surface water productivity, and is driven by the East Asian summer monsoon, is the primary control of this decadal variability, while terrestrial inputs appear not influence significantly. Meanwhile the impacts of the Pacific Decadal Oscillation (PDO) and the El Nino and Southern Oscillation (ENSO) systems on seawater pH off eastern Hainan Island is likely limited. In contrast, the PDO is the main factor to influence the decadal seawater pH variability offshore the East Australia, while the mechanism controlling the decadal seawater pH variability in Guam is not clear yet. Meanwhile, The rate of decrease in seawater pH estimated from coral records are significantly different in different regions and over different time spans, which may reflect a combination of natural decadal variability in seawater pH and long-term variations. Therefore, understanding the mechanisms driving natural variability in seawater pH is important for improving estimates of ocean acidification rates driven by anthropogenic emissions.

1. Introduction

The rapid increase in atmospheric CO_2 concentrations as a result of post-Industrial era anthropogenic emissions has increased CO_2 dissolution in oceanic surface waters, resulting in a reduction in seawater pH [*Caldeira and Wickett*, 2003; *Intergovernmental Panel on Climate Changes*, 2007]. Ocean acidification is predicted to reduce the saturation state of carbonate minerals in seawater [*Feely et al*., 2004; *Orr et al*., 2005; *Scott et al*., 2009] and potentially threaten the existence and development of many marine calcareous organisms, such as calcareous microorganisms and corals [*Langdon and Atkinson*, 2005; *Hoegh-Guldberg et al*., 2007]. Model calculations have indicated an overall decrease in global seawater pH of 0.1 relative to the pre-Industrial era value, and a further pH reduction of 0.2–0.3 over the next century [*Haugan and Drange*, 1996; *Caldeira and Wickett*, 2003]. The currently available worldwide ocean CO_2-pH time series covering the past 20–30 years have shown a trend of acidification of the surface ocean, with OA rates varying from -0.0013 ± 0.0003 yr^{-1} to -0.0026 ± 0.0006 yr^{-1} [*Bates et al*., 2014, and references therein], which is in good agreement with the anticipated OA rates from model predictions [*Caldeira and Wickett*, 2003]. However, seawater pH has seldom been recorded owing to the nonroutine nature of its measurement, and thus continuous long-term seawater pH records are scarce. Therefore, very little is known about regional variability in ocean acidification on decadal to centennial time-scales, especially since the industrial era.

As boron isotopic compositions (δ^{11}B) of marine biogenic carbonates are a function of the ambient seawater pH during calcification, they provide a proxy for the reconstruction of seawater pH records [*Vengosh et al*., 1991; *Hemming and Hanson*, 1992; *Honisch et al*., 2004]. Several long-term seawater pH records

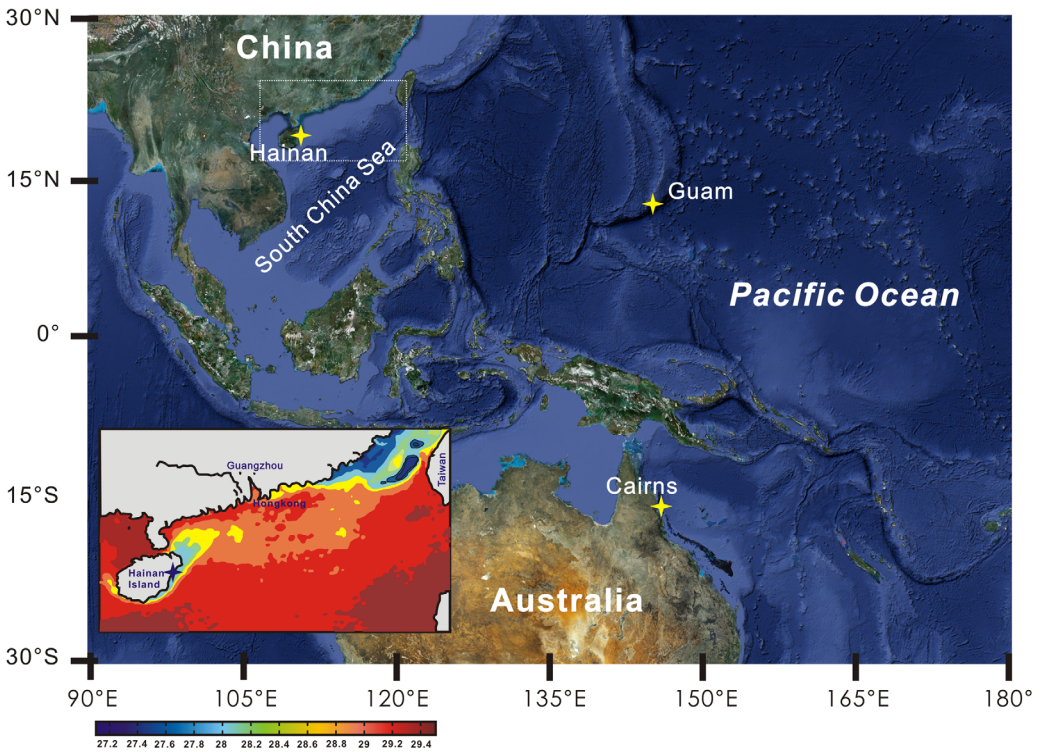

Figure 1. Map showing the location of the coral off eastern Hainan Island. Corals from the Great Barrier Reef (GBR) and Guam are also marked. The insert shows the climatological mean summer SST (°C) distributions in the northern SCS obtained from the Advanced Very High Resolution Radiometer from 1985 to 2006 (modified from *Jing et al.* [2009]).

covering the past 200–300 years have been reconstructed based on the δ^{11}B of several *Porites* corals from the West Pacific using 5 year or 1 year time resolutions [*Pelejero et al.*, 2005*; Wei et al.*, 2009*; Shinjo et al.*, 2013*; D'Olivo et al.*, 2014*; Liu et al.*, 2014]. These seawater pH records revealed different rates of ocean acidification, but most importantly, they all showed significant decadal variability. In particular, two long (>200 years) seawater pH records from the Great Barrier Reef (GBR) and the Coral Sea both exhibited robust decadal periodicities, which were likely influenced by the Pacific Decadal Oscillation (PDO) or Interdecadal Pacific Oscillation (IPO) of oceanic–atmospheric anomalies [*Pelejero et al.*, 2005*; Wei et al.*, 2009]. Seawater pH records from the past 40–60 years reconstructed from corals off Guam [*Shinjo et al.*, 2013] and the central GBR [*D'Olivo et al.*, 2014] also likely exhibited interannual to decadal periodicities, even though they spanned a relatively short time period. Therefore, interannual to decadal variability in seawater pH appears to be a general trend. However, the mechanisms driving such decadal variability are not well known because long-term seawater pH records are currently limited.

Herein, we report a new long-term seawater pH record from the past 159 years with a 1 year time resolution reconstructed from the δ^{11}B of a *Porites* coral from the northern South China Sea (SCS). We use comparisons between our records and the previous reported time series to investigate how the regional oscillations of oceanic–atmospheric anomalies influenced the variation in seawater pH. The results will provide a better understanding of the mechanisms driving long-term seawater pH variation, and hence reinforce our knowledge of ocean acidification.

2. Materials and Methods

A *Porites* coral marked as LW4 was collected in April 2011, in Longwan Bay, 2 km off the east coast of Hainan Island, located in the northern South China Sea (19°17′11.94″N, 110°39′21.06″E; Figure 1). This location is generally influenced by the Qiongdong upwelling system during summer, which is driven by variation in the alongshore wind stress associated with the East Asian summer monsoon [*Su and Pohlmann*, 2009]. The average summer sea surface temperature (SST) distribution in the northern SCS from 1985 to 2006

complied by *Jing et al*. [2009] (insert of Figure 1) showed that Longwan Bay is situated directly in the region influenced by the summer upwelling.

The coral cores were cut into 1 cm-thick, 5 cm-wide slabs along the major growth axis with a high-speed diamond saw. X-ray photographs were taken and used to reveal the annual density bands in the coral skeletons and to establish a continuous 159 year growth record from 1853 to 2011. Annual interval subsamples were collected between two adjacent high-density bands guided by the X-ray photographs continuously along the maximum growth axis using a digitally controlled milling machine. The milled coral subsamples generally consisted of fine particles. The samples were further ground into powder using an agate mortar and well mixed for geochemistry measurements. For further details of the sample collection and processing, see *Deng et al*. [2013].

The δ^{11}B values were measured from ~20 mg of each subsample, which contained $\sim 1 \times 10^{-6}$ g B. The preanalysis chemical treatments of these samples were conducted in the ultra-clean laboratory at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (SKLIG, GIG-CAS) following the procedure adopted by *Wei et al*. [2009] at the Australian National University. This procedure used a two-column separation and purification system, with the first column containing Bio-red AG50W-X8 cation resin to remove the Ca matrix and the second column containing Amberlite IRA 743 resin to concentrate and purify B. For details concerning the chemical treatments, refer to *Wei et al*. [2009]. In order to avoid the possible influence of Cs_2CNO^+ on $Cs_2BO_2^+$ during mass spectrometry analysis [*Wei et al*., 2009], caesium hydroxide (CsOH) was used in place of ammonium hydroxide (NH_4OH) to adjust the pH of the samples and to elute the column.

The δ^{11}B values were measured on a Finnigan TRITON thermal ionization mass spectrometer (TIMS) at SKLIG, GIG-CAS. The purified samples were loaded onto a single degassed Ta filament with 4 μL of 0.1 mol L^{-1} HCl and dried by passing a low current through the filament. Following *Xiao et al*. [1988], ~1 μL of a graphite suspension solution was added to the samples before they completely dried, and the samples were immediately loaded into the mass spectrometer for the δ^{11}B measurements. Positive ions with atomic masses of 309 and 308 amu ($Cs_2BO_2^+$) were measured, and the boron isotope ratios ($^{11}B/^{10}B$) were calculated from the $^{309}M/^{308}M$ ratio with a ^{17}O correction [*Spivack and Edmond*, 1986]: $^{11}B/^{10}B = {}^{309}M/{}^{308}M - 0.00078$. The δ^{11}B values are expressed relative to the NIST SRM 951 standard.

The TIMS was equipped with nine Faraday cups, H3 and H4, which were assigned to catch B isotope ions with mass-to-charge ratios (m/z) of 308 and 309, respectively. By adjusting the distance between H3 and H4 to the minimum and using the maximum zoom optics with a focus quad of 15.00 V and a dispersion quad of −100.00 V, the peaks of the m/e 308 and m/e 309 B isotope ions almost overlapped when scanning a mass of ~298.4 amu in the central cup. This enabled a static measuring mode and improved the internal precision of the 309/308 ratio significantly. The measurements for each sample consisted of 10 blocks, and each block contained 10 cycles. The 309/308 ratios measured in this manner generally had a $2\sigma_m$ (2 standard deviations of the mean) internal precision of <0.001%, corresponding to an error of better than $\pm$ 0.01‰ for δ^{11}B.

To evaluate the possible influence of Cs_2CNO^+ on $Cs_2BO_2^+$, after the first measurement on each filament was conducted the heating current was increased by 20 mA, the machine was tuned again, and another measurement was taken. This process was repeated three times for each filament. If the three measured $^{11}B/^{10}B$ ratios agreed well with each other (<0.01% of 1 standard deviation (SD)), the influence of Cs_2CNO^+ was considered negligible and the $^{11}B/^{10}B$ result reliable. Given that the internal precision of each measurement was too high (<0.001%), we used the average and the external precision (1 SD) of the three measurements to represent the results and precision of the sample, respectively (the supporting information Table S1).

The SRM 951 standard was measured repeatedly along with the samples, and had an average δ^{11}B value of 4.0529 $\pm$ 0.0004 (n = 30). Several other international B isotope standard materials (B1 seawater and JCp-1 coral) were chemically treated and measured repeatedly along with the samples. Their measured δ^{11}B values were identical to their certified values, within analytical errors ($\delta^{11}B = 39.50 \pm 0.22$‰ (1SD, n = 10) for B1 seawater and $\delta^{11}B = 24.61 \pm 0.14$‰ (1SD, n = 6) for JCp-1 coral.

Another set of annual resolution subsamples were milled next to the previous grooves for other geochemical measurements. δ^{11}B of the subsamples from 1982 to 2011 were measured to assess the reproducibility

of the coral boron isotope. Chemical treatments on these subsamples were the same as above, and their $\delta^{11}B$ were measured on a Neptune plus multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) in the same laboratory. Details of the instrumental measurement refer to *Wei et al*. [2013]. The internal precision for the $\delta^{11}B$ is very high too (0.02∼0.04 ‰ 2SE). We here used the maximum 0.05 ‰ to indicate the internal precision of a single measurement for $\delta^{11}B$. The results are presented in the supporting information Table S2. Again, B1 seawater and JCp-1 coral standards were repeatedly measured along with the samples, yielding 24.19 ± 0.23 ‰ (1SD, n = 7) and 39.32 ± 0.21 ‰ (1SD, n = 5), for JCp-1 and B1 respectively.

All the acids used in the analyses were prepared with distilled reagents; CsOH was purified by filling the B-specific column with Amberlite IRA 743 resin, and the mannitol used was of analytical grade. The blank values of all the reagents, including Milli-Q water, HCl, CsOH, and mannitol, as well as the blank value of the whole chemical procedure including loading the blank onto the Ta filament, have been tested using isotope dilution spiked with ^{10}B SRM 952. The blanks were measured using the negative ions $^{42}BO_2^-$ and $^{42}BO_2^-$ [*Pelejero et al*., 2005], which are extremely sensitive to small B signals. The amount of B in all of the blank samples was 10^{-9} g. The amount of B in each of the measured subsamples was $\sim 1 \times 10^{-6}$ g; Therefore, the influences of the reagents and procedural blanks were insignificant.

The paleo-pH was estimated from the measured $\delta^{11}B$ values of the samples using the following equation [*Zeebe*, 2005]:

$$pH = pK_b - log\left[\frac{\delta^{11}B_{SW} - \delta^{11}B_{carbonate}}{\alpha_{3-4}\delta^{11}B_{carbonate} - \delta^{11}B_{SW} + 1000(\alpha_{3-4}-1)}\right].$$

Given that the $\delta^{11}B$ values of the coral recorded the pH of the extracellular calcifying fluid (ECF) between the skeleton and the calicoblastic ectoderm rather than the ambient seawater, a further correction for the coral's physiological effects was needed to obtain the pH of the ambient seawater [*Krief et al*., 2010; *Trotter et al*., 2011; *McCulloch et al*., 2012]. We followed the procedure given by *McCulloch et al*. [2012] for correcting for the physiological effects of the *Porites* coral, with $\alpha_{3-4} = 1.0272$ [*Klochko et al*., 2006], $\delta^{11}B = 39.5‰$ (our unpublished data for the seawater in the same coral reef), and $pH_{SW} = (pH_{ECF} - 4.727)/0.466$ [*McCulloch et al*., 2012] to estimate the seawater pH. The calculated pH values of the samples are listed in the supporting information Table S1.

The Sr/Ca, $\delta^{18}O$ and $\delta^{13}C$ of this coral in annual resolution have previously reported by *Deng et al*. [2013], and these data enable us to discuss on the variations of related climatic and environmental factors. The sea surface temperature anomaly (SSTA) was adopted to estimate variability in the Qiongdong upwelling system [*Liu et al*., 2013]. The annual SSTs were calculated from the Sr/Ca ratios measured in this coral [*Deng et al*., 2013] using the equation of *Gagan et al*. [2012]: Sr/Ca (mmol/mol) = 0.084 × SST (°C) + 11.278. This equation has been corrected for the apparent attenuation effect from the skeletal mass accumulation of coral. It is identical to our calibration using the annually resolved Sr/Ca ratios and instrumental SST records from the GBR [*Deng et al*., 2014], thus it is suitable for calculating SST from annually resolved Sr/Ca ratios. The Sr/Ca ratios and the calculated SSTs of the samples are listed in Table 1. The SSTA was then calculated by subtracting the long-term mean annual temperature (T_{mean}) from the temperature in a definite year (T_i): $SSTA = T_i - T_{mean}$.

Given that the reef where the LW4 coral was collected extends to Hainan Island, terrestrial inputs may possibly influence the seawater chemistry on this reef. The influence of terrestrial inputs could be indicated by the oxygen isotope residual ($\Delta\delta^{18}O$) of this coral, which was calculated by subtracting the temperature contribution in the coral $\delta^{18}O$ values [*Gagan et al*., 1998]. Details of the $\Delta\delta^{18}O$ calculation of the LW4 coral were described in *Deng et al*. [2013], and the $\Delta\delta^{18}O$ values are also included in the supporting information Table S1 for comparison.

3. Results

The measured $\delta^{11}B$, Sr/Ca ratios and $\delta^{13}C$ of the samples, as well as the calculated pH_{SW}, temperature, and $\Delta\delta^{18}O$ are listed in the supporting information Table S1. The $\delta^{11}B$ varied from 20.82 to 26.00‰, corresponding to a seawater pH variation range of 7.66–8.40. The average calculated seawater pH over the past 159

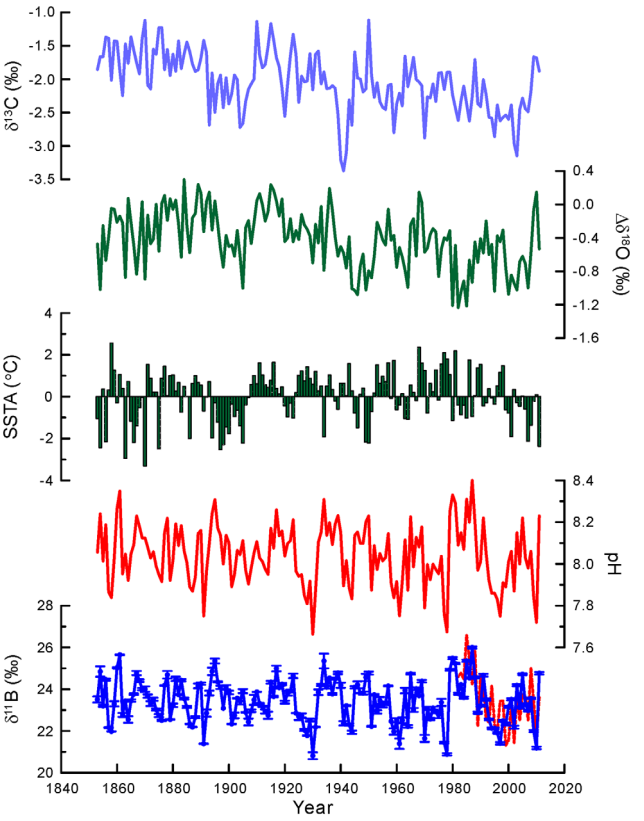

Figure 2. The δ^{11}B, pH, SSTA, $\Delta\delta^{18}$O and δ^{13}C time series from the LW4 coral off eastern Hainan Island. The red dashed line is the results of the duplicated δ^{11}B of the adjacent growth axis. The SSTA values were calculated from the Sr/Ca ratios previously reported by *Deng et al*. [2013], and the $\Delta\delta^{18}$O and δ^{13}C were from *Deng et al*. [2013].

years was 8.04, which is close to the annual mean value of the in-situ measured seawater pH in this region. The Sr/Ca ratios varied from 9.011×10^{-3} to 9.506×10^{-3}, corresponding to a calculated annual temperature range of 21.0–26.9°C. The δ^{13}C varied from -3.37 ‰ to -1.14 ‰ with an average of -2.04 ± 0.44 ‰ (1σ).

Figure 2 shows the temporal variations in δ^{11}B, seawater pH, SSTA, $\Delta\delta^{18}$O and δ^{13}C over the past 159 years. These time series show periodical variation patterns with apparent decadal periodicities. The duplicated δ^{11}B from 1982 to 2011 of the subsamples milled from the adjacent grooves are also shown in Figure 2. The two δ^{11}B data sets agree well with each other showing similar variation patterns, and the grand means of the original and duplicated δ^{11}B time series from 1982 and 2011 are 23.49 ‰ and 23.33 ‰, respectively. This suggests that these annual resolution coral δ^{11}B are reproducible, and they truthfully indicate changes in seawater pH over decadal time scales.

Figure 3 shows the power spectra of the pH, SSTA, $\Delta\delta^{18}$O and δ^{13}C time series. The pH time series exhibited robust ~18 year and ~5.6 year periodicities, the SSTA time series exhibited robust ~52 year and ~4.1 year periodicities, and the $\Delta\delta^{18}$O and δ^{13}C time series exhibited robust ~53 year and ~19 year, ~40 year and ~18 year periodicities, respectively.

4. Discussion

4.1. Mechanisms Driving Seawater pH Variability off Eastern Hainan Island

The large interannual to decadal variations in seawater pH off eastern Hainan Island reconstructed from the LW4 coral resembled those reconstructed from corals from the GBR [*Pelejero et al*., 2005*; Wei et al*., 2009*; D'Olivo et al*., 2014] and off Guam [*Shinjo et al*., 2013]. The rapid and large variations in seawater pH on coral reefs are generally believed to be the result of biological activities regulated by photosynthesis and respiration over short (i.e., diurnal) time scales [*Dai et al*., 2009; *Zhang et al*., 2013; *Chen et al*., 2015] and oceanic–atmospheric oscillations over interannual to decadal time scales [*Wei et al*., 2009]. Considering that nutrient supply is the key factor controlling biological activity on coral reefs, a recent study by *D'Olivo et al*. [2014] indicated that enhanced river runoff may transport more nutrients to coral reefs fringed to continents, significantly influenced the productivity and hence increased seawater pH. As the location of the LW4 coral is very close to Hainan Island, the runoff of the rivers, such as Wanquan River from the Island may have influenced the seawater chemistry. Meanwhile, regional atmospheric-ocean oscillations such as PDO, El Nino and Southern Oscillation (ENSO) and the East Asian monsoon significantly influence the climate in this region [*Deng et al*., 2013]. All these factors likely take effect on the decadal seawater pH variability recorded by the δ^{11}B time series of the LW4 coral.

4.1.1. Terrestrial Input

Whether or not river runoff influenced seawater pH in this region, similar to the situation described by *D'Olivo et al*. [2014] in the central GBR, could be evaluated by comparing the pH and $\Delta\delta^{18}$O and δ^{13}C

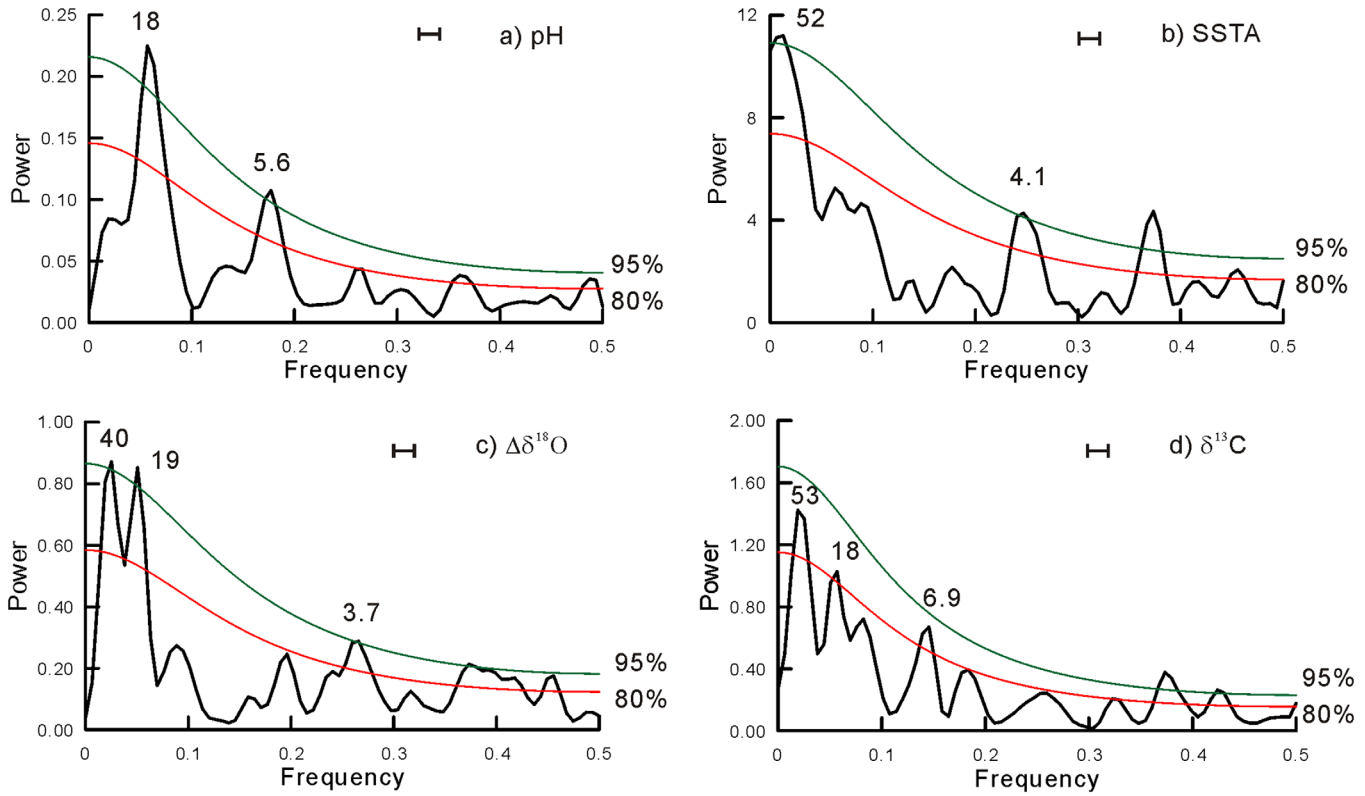

Figure 3. The power spectra of the LW4 coral time series calculated using REDFIT software [*Schulz and Mudelsee*, 2002]: (a) pH; (b) SSTA; (c) $\Delta\delta^{18}O$; and (d) $\delta^{13}C$. The horizontal bars indicate 6 dB bandwidths, and the thin lines indicate the 95% and 80% confidence intervals.

records of the LW4 coral.The $\Delta\delta^{18}O$ values of corals are good indicators of terrestrial input, as terrestrial water (river runoff and/or ground water) has lower $\delta^{18}O$ values than seawater; thus, the LW4 $\Delta\delta^{18}O$ record could adequately indicate changes in river runoff from Hainan Island over the past 159 years [*Deng et al*., 2013]. Additionally, the $\delta^{13}C$ values of corals from reefs fringed to continents are largely influenced by terrestrial input, in which $\delta^{13}C$ of dissolved inorganic carbon (DIC) is more negative than seawater, thus could also be good indicators of terrestrial input [*Deng et al*., 2013]. The $\Delta\delta^{18}O$ and $\delta^{13}C$ of the LW4 coral show a positive correlation with a coefficient of 0.38 ($N = 159$, $p < 0.000001$). This agrees with the fact that terrestrial input has more negative $\delta^{18}O$ and DIC $\delta^{13}C$, and enhanced terrestrial input can both decrease the $\Delta\delta^{18}O$ and $\delta^{13}C$ values of coral.

In order to compare the decadal to interdecadal variability among these time series, low-pass filtration with a 13 year cutoff was performed on the pH, $\Delta\delta^{18}O$ and $\delta^{13}C$ records using the software program PAST [*Hammer et al*., 2001] (Figure 4). The filtered time series all showed decadal variation patterns. However, the overall correlation between them was poor. The correlation coefficient between pH and $\Delta\delta^{18}O$ and between pH and $\delta^{13}C$ is -0.18 ($N = 159$, $p = 0.012$) and 0.04 ($N = 159$, $p = 0.31$), respectively (Figure 4). According to the scenario of *D'Olivo et al*. [2014] that increased terrestrial input may have transported more nutrients to the reef, increased productivity, and consequently increased seawater pH, if terrestrial input takes effect, there may be a negative correlation between pH and $\Delta\delta^{18}O$ (or $\delta^{13}C$). However, this has not been observed in Figure 4, thus terrestrial input may not have been the main factor controlling seawater pH variability around the LW4 coral over the past 159 years.

4.1.2. Monsoon Driven Upwelling

The Qiongdong upwelling system prevails off eastern Hainan Island during the summer [*Su and Pohlmann*, 2009], and Longwan Bay is situated within the low-temperature region influenced by this summer upwelling (Figure 1). Significant increasing in chlorophyll level in the coastal Hainan Island could generally be observed during summers when the Qiongdong upwelling system is activated [*Liu et al*., 2002]. Recent observations on the coral reefs off eastern Hainan Island by *Li et al*. [2015] again indicate that the seawater nutrients on the coral reefs in this region are significantly enriched when the Qiongdong upwelling is

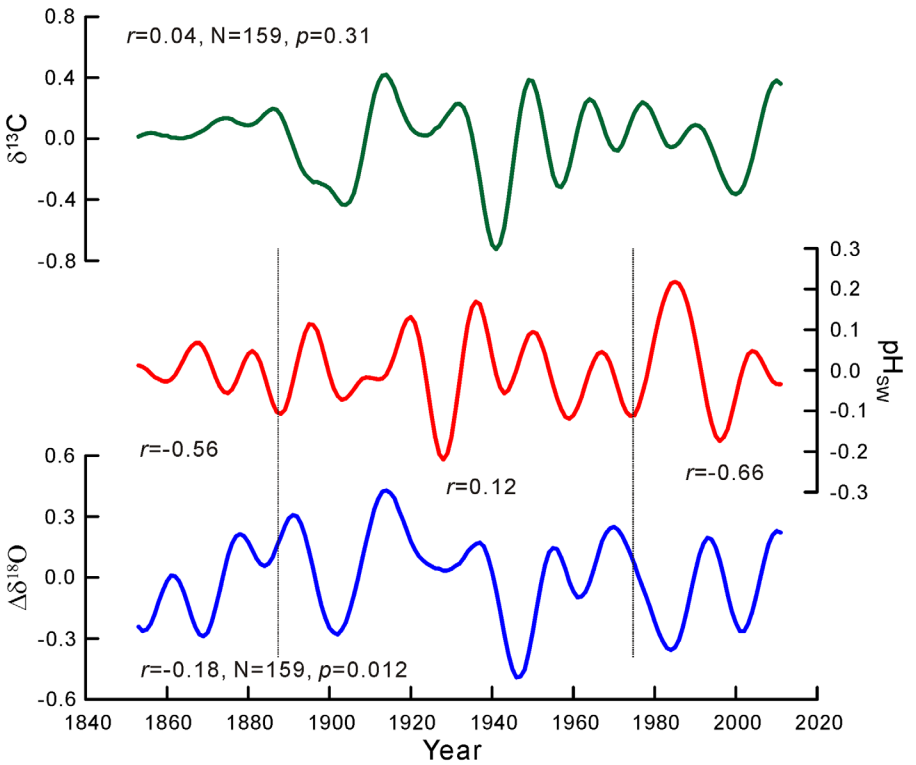

Figure 4. Temporal variations in pH, $\Delta\delta^{18}O$ and $\delta^{13}C$ from the LW4 coral after processing the data with a low-pass filter with a 13 year cutoff.

activated. Thus, the Qiongdong upwelling may be very important for supplying nutrients to this region [*Chen et al*., 2015a].

Variability in the Qiongdong upwelling could be indicated by the SSTA [*Liu et al*., 2013]. Figure 5 shows variations in the SSTA and pH time-series of the LW4 coral, both of which were low-pass filtered with a 13 year cutoff [*Hammer et al*., 2001] to highlight the decadal variability. As the summer monsoon is believed to be the main force driving the Qiongdong upwelling [*Su and Pohlmann*, 2009], the South China Sea summer monsoon index (SCSSMI), defined as a seasonal (June–July–August–September), area-averaged, dynamically normalized seasonality index at 925 hPa within the SCS monsoon domain (0°–25°N, 100°–125°E; data available from http://ljp.lasg.ac.cn/dct/page/65578) [*Li and Zeng*, 2002], was also included in Figure 5. The SCSSMI time series was filtered using the method described above. All three filtered time series showed similar variation patterns, with higher pH corresponding to more negative SSTA and higher SCSSMI values, and vice versa (Figure 5). Although the SCSSMI time series only covered 64 years, it was significantly negatively correlated with the SSTA ($r = -0.58$, $N = 64$, $p < 0.000001$). The negative correlation indicates that stronger summer monsoons increased the Qiongdong upwelling activity, bringing more cold deep water to the surface, which resulted in lower SSTs. This agrees with the previous result that the Qiongdong upwelling system is driven by variation in the alongshore wind stress associated with the East Asian summer monsoon [*Su and Pohlmann*, 2009]. Furthermore, a significant negative correlation was also observed between the pH and SSTA time series ($r = -0.37$, $N = 159$, $p < 0.000001$), indicating that the increased upwelling corresponds to a higher seawater pH. Deep water generally has a lower temperature and a lower pH (<7.5 in the northern SCS below 1000 m, according to our in-situ observations) than surface water, and lower temperatures favor the dissolution of CO_2, which leads to lower pH. Thus, the upwelled deep water likely decreased the pH of the surface water if physical mixing is considered only. This, however, is in contrast to the observed negative correlation between pH and SSTA, which indicated that the increased upwelling resulted in higher surface water pH. Thus, there was likely another process driving the change in seawater pH after the input of the cold and acid deep water from upwelling.

Despite having low pH and temperature, deep water generally contains nutrients that can increase surface productivity. Increased photosynthesis can rapidly consume dissolved inorganic carbon and significantly

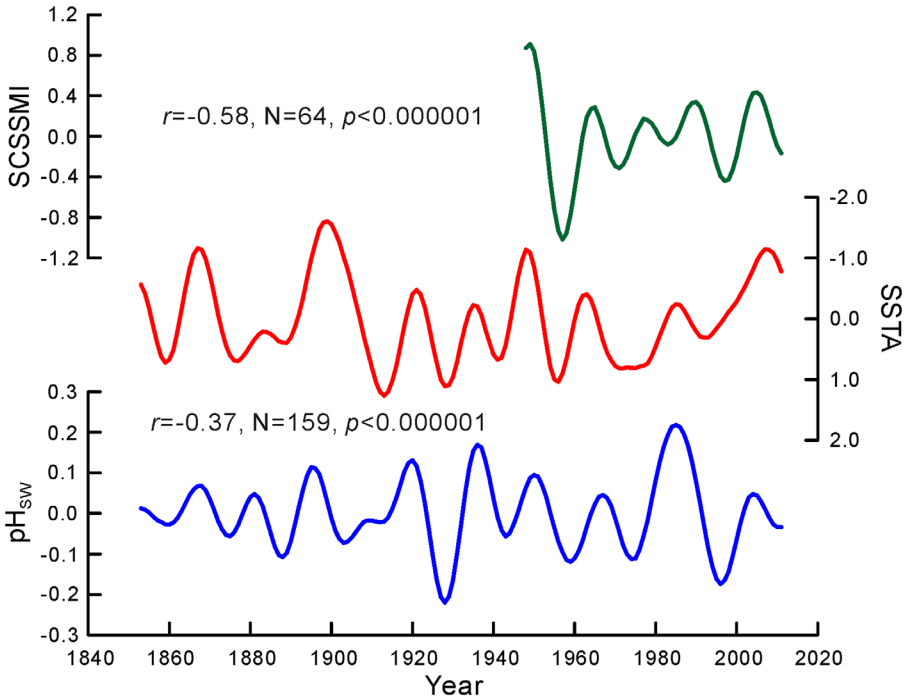

Figure 5. Temporal variations in pH and SSTA from the LW4 coral, as well as the SCS summer monsoon index time series, after processing the data with a low-pass filter with a 13 year cutoff. The SCSSIM is defined as a seasonal (June–July–August–September), area-averaged, dynamic normalized seasonality (DNS) index at 925 hPa in the SCS monsoon domain (0°–25°N, 100°–125°E) [*Li and Zeng*, 2002]. Data are available from http://ljp.lasg.ac.cn/dct/page/65578.

increase seawater pH on coral reefs over very short time scales (i.e., diurnally) [*Dai et al.*, 2009]. Such rapid pH increasing driven by enhanced photosynthesis has also been observed on the coral reefs in the coastal Hainan Island [*Zhang et al.*, 2013; *Chen et al.*, 2015b]. Diurnal variation of seawater pH on the coral reefs in this region is up to 0.6, and closely in pace with the variations of dissolved oxygen (DO), DIC content and its carbon isotope ($\delta^{13}C_{DIC}$), with high pH corresponding to high DO, $\delta^{13}C_{DIC}$ and low DIC content [*Chen et al.*, 2015b]. Thus, enhanced photosynthesis, a mean of increasing of productivity, can increase seawater pH on coral reefs. This may be the reason why increased upwelling resulted in increased surface water pH off eastern Hainan Island as shown in Figure 5. This situation also agrees with the scenario in which the input of low-pH but nutrient-rich river runoff increased productivity and seawater pH in the coastal region of the GBR [*D'Olivo et al.*, 2014]. It is therefore that the activity of the Qiongdong upwelling system, driven by the East Asian summer monsoon, largely controls the decadal variability in seawater pH off eastern Hainan Island.

4.1.3. PDO and ENSO

In addition to the above local forcing, regional oceanic–atmospheric oscillations such as PDO (or IPO) and ENSO, the most important climatic systems originating from the Pacific, influence climatic and environmental changes in the coastal Hainan Island significantly [*Deng et al.*, 2013]. Whether they take effect on the decadal variability of seawater pH could be assess by cross comparisons between these time-series. The PDO system, a pattern of interdecadal climate variability in the North Pacific Basin, and the closely related IPO system have widespread influences on the climate, such as temperature and precipitation anomalies in the Pan-Pacific Basin [*Mantua et al.*, 1997; *Power et al.*, 1999; *Folland et al.*, 2002; *Mantua and Hare*, 2002]. We used the averages of the leading principal component (PC) of the monthly (January–March) SST anomalies in the North Pacific Ocean poleward of 20°N as the PDO index after 1900 (data available from the University of Washington's Joint Institute for the Study of the Atmosphere and Oceans, http://jisao.washington.edu/pdo/PDO.latest [*Mantua et al.*, 1997]) for comparison with the coral-derived seawater pH. The ENSO system, originating in the tropical Pacific, is another important climate system that greatly influences interannual variability in the global climate [*Philander*, 1990]. Here we adopted the NINO3.4 index, which is represented by the yearly averages of monthly SST anomalies in the area bounded by 5°S–5°N and 120°–170°W from 1856 to the present, for comparison with seawater pH. The SST anomalies during the period from 1856 to 1949 were reconstructed using statistical methods (http://iridl.ldeo.columbia.edu/SOURCES/Indices/nino/KAPLAN/) [*Kaplan et al.*, 1998], and

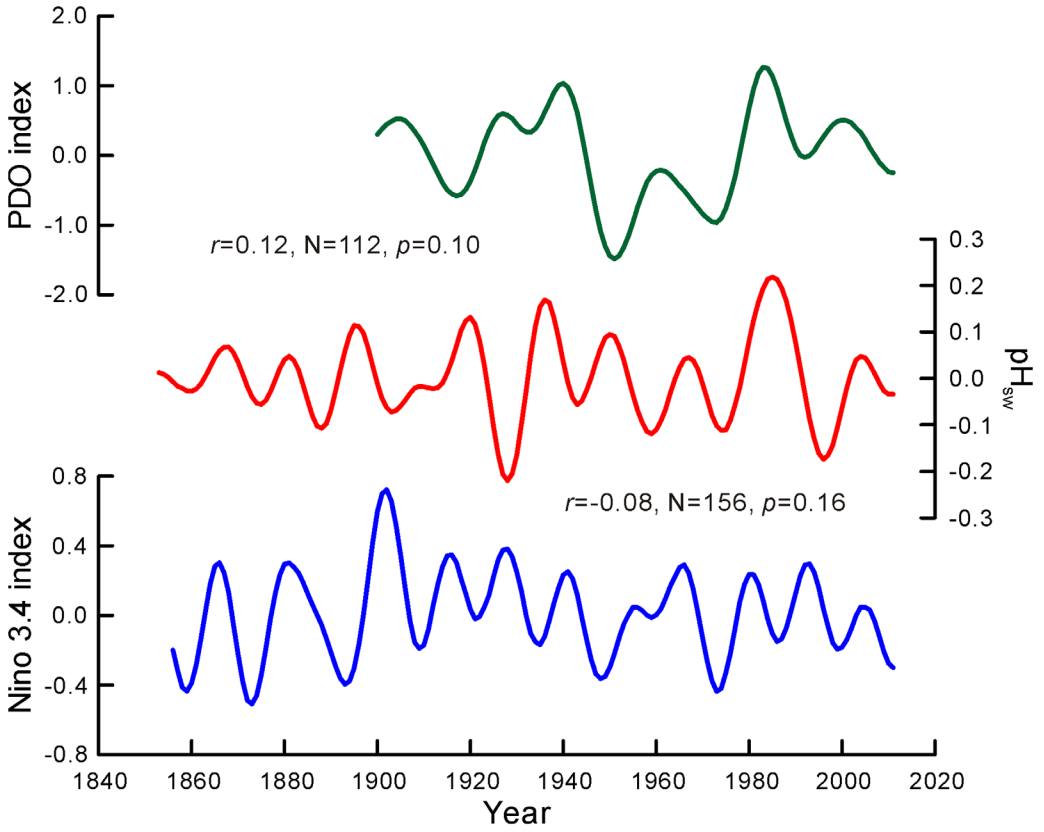

Figure 6. Temporal variations in the pH time series off eastern Hainan Island and the PDO index and the Nino 3.4 index after processing the data with a low-pass filter with a 13 year cutoff. The time series of the PDO index data are from *Mantua et al.* [1997] (http://jisao.washington.edu/pdo/PDO.latest). The Nino 3.4 index are from *Kaplan et al.* [1998] (http://iridl.ldeo.columbia.edu/SOURCES/Indices/nino/KAPLAN/), and *Reynolds et al.* [2002] (http://www.cpc.ncep.noaa.gov/data/indices/).

those from 1950 to the present were obtained from the Reynolds OI SST data set (http://www.cpc.ncep.noaa.gov/data/indices/) [*Reynolds et al.*, 2002].To highlight the decadal variability, all the time series were low-pass filtered with a 13 year cutoff [*Hammer et al.*, 2001], and the results are shown in Figure 6.

The correlation between variations in seawater pH off eastern Hainan Island and the PDO ($r = 0.12$, N = 112, $p = 0.10$) and the ENSO ($r = -0.08$, N = 156, $p = 0.16$) were poor over the entire time period (Figure 6). The influence of the PDO on the climatic and environmental changes in the northern SCS is largely conducted by regulating precipitation in this region [*Chan and Zhou*, 2005; *Mao et al.*, 2011]. As for the ENSO system, its impacts on climate of the East Asia is complicate, but precipitation change in South China may be influenced by the ENSO [*Wang et al.*, 2000]. Changes in precipitation can influence terrestrial inputs to the coral reefs off eastern Hainan Island. However, terrestrial input appears not the main factor influencing seawater pH variations in this region as mentioned above. Therefore, the PDO and ENSO were not the main factor controlling the decadal variability of seawater pH changes in this region over the past 159 years.

4.2. Decadal Variability of Seawater pH in the West Pacific

The currently available high-resolution seawater pH records reconstructed from coral B isotopes that are longer than 50 years are mostly from the West Pacific (including the SCS) [*Pelejero et al.*, 2005; *Wei et al.*, 2009; *Shinjo et al.*, 2013; *Liu et al.*, 2014; *D'Olivo et al.*, 2014]. Similar to the record off eastern Hainan Island, these seawater pH records all exhibit significant decadal variability. The mechanism for such decadal variability, however, is not well known yet. As mentioned above, variations of seawater pH off eastern Hainan Island in the northern SCS actively responded to changes in the East Asian summer monsoon. Terrestrial input likely influences seawater pH on the coral reefs at the inner shelf of the GBR [*D'Olivo et al.*, 2014], whereas changes in seawater pH in the middle shelf of the GBR [*Wei et al.*, 2009] and in the Coral Sea

[*Pelejero et al*., 2005] were closely related to changes in the PDO or IPO. Both local and regional factors apparently influence the decadal variability of seawater in the west Pacific. How changes in seawater pH in these regions respond to local or regional oceanic-atmospheric oscillations should be the key to understand the mechanism for such decadal variability. We here focus on the records with annual time resolutions from the northern GBR [*Wei et al*., 2009], and off Guam *[Shinjo et al*., 2013] to compare to our above results off eastern Hainan Island.

4.2.1. The Great Barrier Reefs

Previous studies have indicated that seawater pH in the GBR [*Wei et al*., 2009] and the Coral Sea [*Pelejero et al*., 2005] actively responds to the IPO. Recent studies by *D'Olivo et al*. [2014] indicate that nutrient rich river water carried to the reefs in the inner shelf of the GBR can increase phytoplankton productivity and hence increase seawater pH. In addition to terrestrial input, upwelling driven by the East Australian Current (EAC) could be another source for the seawater nutrients in the GBR [*Andrews and Gentien*, 1982]. However, time-series of the activity of this upwelling system that can be compared with the seawater pH records is not available currently. We here focus on terrestrial input (local factor) and PDO (regional factor) to seek for their possible influence on decadal seawater pH variability.

Considering that river water is mainly from precipitation in the arid subtropical Australia, we here used the precipitation time series in Cairns to indicate changes in terrestrial input to the region around Arlington Reef. Annual rainfall values for the period 1943–2009 were calculated from the monthly rainfall data recorded at the Cairns Aero Weather Station (16.87°S, 145.75°E; ~46 km from the sampling site at Arlington Reef, http://www.bom.gov.au/climate/data/?ref=ftr). Given that the PDO and IPO time series are similar [*Folland et al*., 2002], we here adopt the PDO index of *Mantua et al*. [1997] in the discussions. Figure 7 shows the time series filtered with a 13 year cutoff of the seawater pH from Arlington Reef, the PDO index and the precipitation in Cairns. A significant negative correlation is observed between seawater pH and the PDO time series ($r = -0.48$, N = 105, $p < 0.0000001$). This agrees with the previous studies [*Pelejero et al*., 2005*; Wei et al*., 2009], and again indicates that pH variation in the seawater off eastern Australia is largely associated with the PDO or IPO.

A similar negative correlation ($r = -0.42$, N = 62, $p < 0.0003$) can also be observed between the PDO index and the precipitation in Cairns (Figure 7), suggesting that important linkage may occur between changes in precipitation in this region and the PDO or IPO. According to *Folland et al*. [2002], the South Pacific Convergence Zone (SPCZ) tends to move further southwest during negative IPO (or PDO) phases. Therefore, during negative PDO phases, the precipitation in northern Australia may increase. This may be the reason for the negative correlation between precipitation in Cairns and the PDO.

However, the correlation between precipitation and seawater pH is very poor, with coefficient of 0.07 (N=62, p=0.29) even though their variation patterns are similar (Figure 7). This suggests that terrestrial input likely not influence the variations of seawater pH around Arlington Reef directly. According to *D'Olivo et al*. [2014], the nutrients supplied from river runoff can raise seawater pH in the inner shelf of the GBR, and such influence is very small in the middle shelf. Given that Arlington Reef is located at the middle shelf, the influence of terrestrial input on seawater pH should be negligible. Therefore, the close association between seawater pH and the PDO indicated by the significant negative correlation between them (Figure 7) may be linked by local factors other than terrestrial input driven by precipitation.

The upwelling system that supplies nutrients to the GBR [*Andrews and Gentien*, 1982] could be another local factor that drives the decadal variability of the seawater pH. As the upwelling system is largely activated by the East Australia Current (EAC), and the EAC is the pole-ward flowing branch of the South Equatorial Current (SEC) which is generally driven by winds [*Church*, 1987*; Kessler and Cravatte*, 2013]. The activity of the SEC is closely associated with the PDO [*Pelejero et al*., 2005]. However, direct evidences linking changes in seawater pH, the activity of the EAC and the PDO are not available currently. This could be an open question for further studies.

4.2.2. Guam

The annual resolution seawater pH time series reconstructed from a coral off Guam [*Shinjo et al*., 2013] provides good archives for investigating decadal variability of pH in this region. Located in the ENSO core region [*Burdick et al*., 2008], the variation in climate and environment (e.g., SST and salinity) off Guam is largely controlled by the ENSO system [*Asami et al*., 2004, 2005]. In contrast to the coastal environments where the corals from Hainan Island and the northern GBR were located, the coral from off Guam was

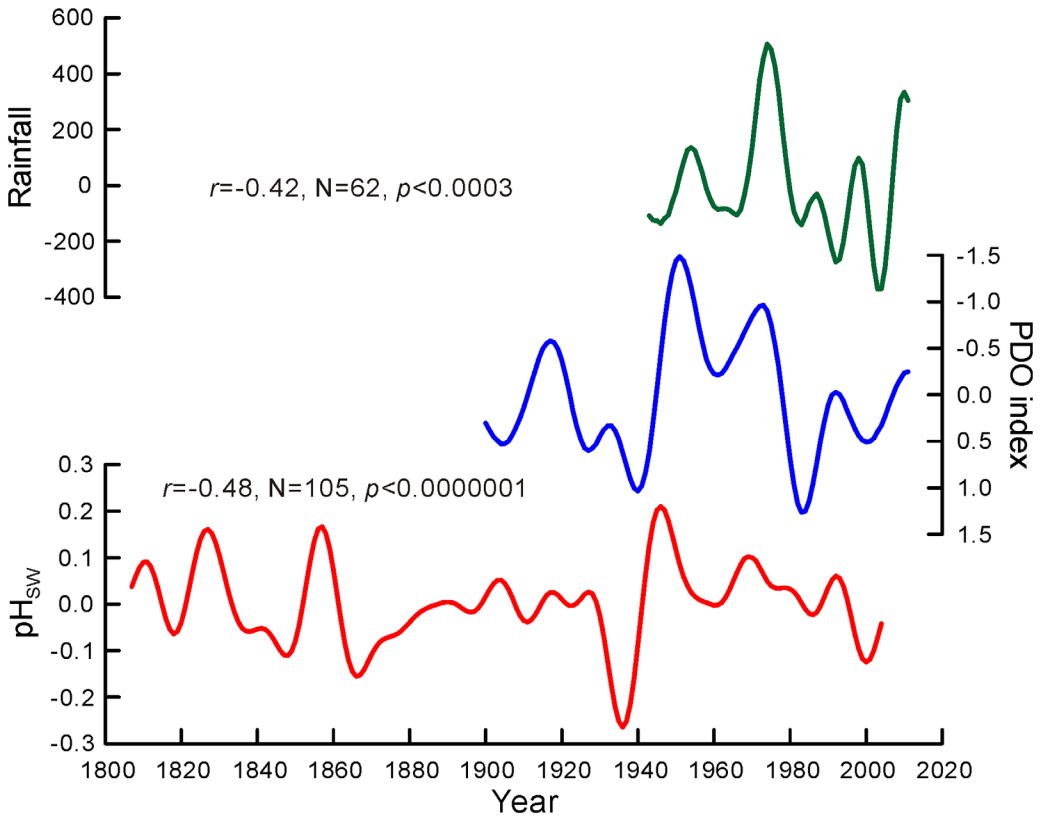

Figure 7. Temporal variations in the time series of pH of the Arlington Reef in the GBR, rainfall in Cairns and the PDO index after processing the data with a low-pass filter with a 13 year cutoff. The pH time series is from *Wei et al*. [2009]. The rainfall records are from the Cairns Aero Weather Station (http://www.bom.gov.au/climate/data/?ref=ftr).

located in a typical open ocean environment far away from continents [*Asami et al*., 2004*; Shinjo et al*., 2013]. However, because Guam is a large volcanic island with heavy rainfall, runoff from the island can significantly influence the seawater in coastal region [*Burdick et al*., 2008]. Thus, precipitation driven runoff may possibly influence seawater pH off Guam like that in the inner shelf of the GBR [*D'Olivo et al*., 2014]. We here compare the seawater pH record of *Shinjo et al*. [2013] with the precipitation time series of the past 50 years in Guam [*Lander and Guard*, 2003], the PDO [*Mantua et al*., 1997] and the NINO3.4 index time series [*Kaplan et al*. 1998; *Reynolds et al*. 2002] to show their relationships.

The filtered time series of these records are shown in Figure 8. A moderate positive correlation ($r = 0.39$, $N = 42$, $p < 0.006$) occurs between the Nino 3.4 index and rainfall time series. This agrees with the primary controls of the ENSO system on climatic and environmental changes in Guam [*Asami et al*., 2004, 2005; *Burdick et al*., 2008]. However, the correlations between the seawater pH and all the other time series are poor of the overall data from 1940 to 2000, with correlation coefficients of -0.04 ($N = 60$, $p = 0.38$), 0.05 ($N = 60$, $p = 0.36$) and -0.10 ($N = 42$, $p = 0.26$) for the PDO, Nino 3.4 and rainfall time series, respectively. This likely indicates that the decadal variability of seawater pH off Guam is neither driven by local runoff nor the PDO and ENSO system directly.

However, when the pH time series was separated into two sections, a significant correlation with the PDO was measured. A robust positive correlation was observed for the records before 1968 ($r = 0.92$, $N = 29$, $p < 0.0000001$), whereas a significant negative correlation was seen for the records after 1968 ($r = -0.91$, $N = 31$, $p < 0.0000001$; Figure 8). The positive correlation likely occurred during the period when the PDO switched from a positive to a negative phase, whereas the negative correlation occurred during the period when the PDO switched from a negative to a positive phase. Very little is known about how the PDO regulates seawater changes off Guam. Terrestrial input is not likely a significant factor as mentioned above and upwelling was not identified in nearby regions. Thus, the mechanisms explaining the variation in seawater pH off Hainan Island

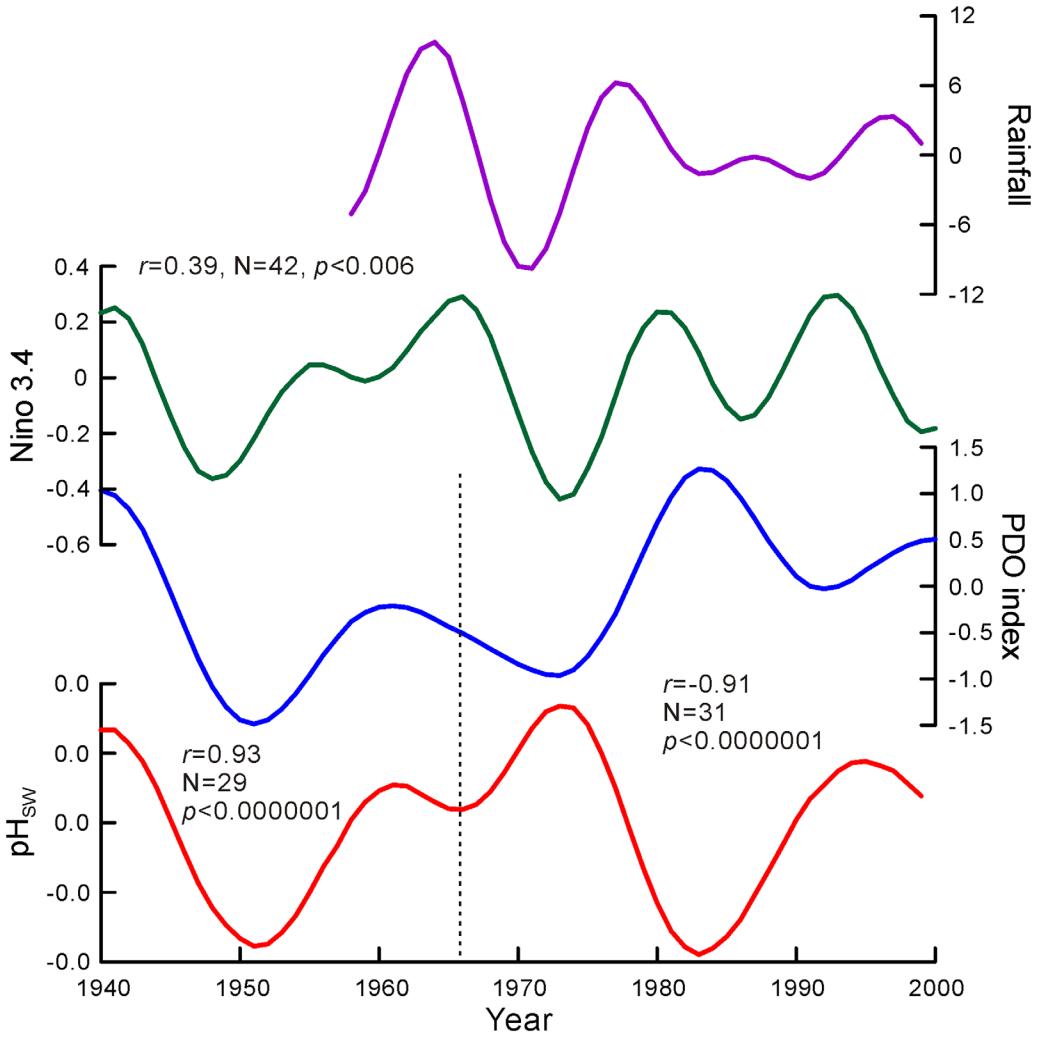

Figure 8. Temporal variations in the time series of pH off Guam, rainfall in Guam, the PDO index and the Nino 3.4 index after processing the data with a low-pass filter with a 13 year cutoff. The pH time series is from *Shinjo et al*. [2013]. The rainfall records are from *Lander and Guard* [2003]. The Nino 3.4 index is from *Kaplan et al*. [1998] (http://iridl.ldeo.columbia.edu/SOURCES/Indices/nino/KAPLAN/), and *Reynolds et al*. [2002] (http://www.cpc.ncep.noaa.gov/data/indices/).

and in the northern GBR could apparently not explain the observations off Guam. Moreover, the SST changes in this region were very small over decadal time scales, and the influence of the PDO on SST changes off Guam was unclear [*Asami et al*., 2005]. Despite the lack of a driving mechanism, the correlation shown in Figure 8 was evident. The robust correlation between seawater pH off Guam and the PDO time series over different time periods suggests that the PDO may take effect on seawater pH variation off Guam over decadal time scales.

4.3. Implications for the Ocean Acidification Rate

The gradual increase in atmospheric CO_2 since the industrial era has caused a definitive decrease in global ocean surface water pH and a trend toward ocean acidification [*Caldeira and Wickett*, 2003*; Intergovernmental Panel on Climate Changes*, 2007]. The current estimate of the global ocean acidification rate is based on model calculations and suggests that the mean pH has decreased by ~0.1 over the past 200 years [*Haugan and Drange*, 1996*; Caldeira and Wickett*, 2003]. The long-term seawater pH records reconstructed from coral B isotopes may provide another way to estimate the rate of decrease in seawater pH or the rate of ocean acidification (OA).

A simple way to estimate the rate of ocean acidification is to linearly regress the pH values against time [*Shinjo et al*., 2013*; D'Olivo et al*., 2014*; Liu et al*., 2014]. The estimated OA rates by this method may be

Table 1. The Ocean Acidification Rates Estimated From Coral δ^{11}B pH Records

Location	Year	Rate (U/yr)	Resolution (year)	Source
East Hainan Is. (northern SCS)	1853–2011	-0.00039 ± 0.00025	1	This study
South Hainan Is. (northern SCS)[a)]	1840–2000	-0.0011 ± 0.0003	5	*Liu et al.* [2014]
	1950–2000	-0.0029 ± 0.0013	5	
Coral Sea[a]	1781–1990	-0.0000 ± 0.0015	5	*Pelejero et al.* [2005]
	1938–1990	-0.0008 ± 0.0015	5	
Arlington Reef, Northern GBR[a]	1807–2004	-0.00034 ± 0.00022	1, 5	*Wei et al.* [2009]
	1941–2004	-0.0033 ± 0.0006	1	
Havannah Is., Central GBR[b]	1966–2005	-0.0020 ± 0.0030	1	*D'Olivo et al.* [2014]
Havannah Is., Central GBR	1940–2009	-0.0023 ± 0.0011	1	
Pandora Reef, Central GBR	1963–2002	-0.0008 ± 0.0038	1	
Rib Reef, Central GBR	1964–2009	-0.0023 ± 0.0020	1	
Rib Reef, Central GBR	1973–2009	-0.0013 ± 0.0021	1	
Guam	1940–1999	-0.00094 ± 0.00036	1	*Shinjo et al.* [2013]
In field observation: Bermuda	1983–2005	-0.0017 ± 0.0003	monthly	*Bates* [2007]
In field observation: Hawaii	1988–2007	-0.0019 ± 0.0002	monthly	*Dore et al.* [2009]

[a]The different rates are calculated from different sections of the same record, respectively.
[b]The different rates from the Havannah Island and Rib Reef are calculated from different coral records.

influenced by the large decadal variations of seawater pH for that all the δ^{11}B-based pH time series are not linearly response to increasing of atmospheric CO_2, and the errors for the estimated OA rates might be large. This, however, is still one of the best ways currently available to estimate OA rate after the Industrial Era from continuous pH time series. We here estimate the OA rates from the two long (>150 years) annually resolved pH records from the northern SCS (this study) and the northern GBR [*Wei et al.*, 2009], and the results indicate annual rates of -0.00039 ± 0.00025 yr^{-1} and -0.00034 ± 0.00022 yr^{-1} for the northern SCS and the northern GBR, respectively. It is worth noting that the errors of these estimates are fairly large with RSD of ~65% for that these two time-series do not show significant decreasing trend for pH. Despite of such large errors, estimated from these rates, the seawater pH has decreased by about 0.07–0.08 U over the past 200 years in these regions. These results are similar to those from previous model calculations [*Haugan and Drange*, 1996; *Caldeira and Wickett*, 2003], and they may represent the long-term effect of ocean acidification driven by the increase in atmospheric CO_2 over the past 200 years in these regions.

Table 1 compiles all the available estimates of OA rates generated from coral δ^{11}B pH records, as well as two long-term, in-situ observational time series from Bermuda in the North Atlantic [*Bates*, 2007] and Hawaii in the North Pacific [*Dore et al.*, 2009]. The rates of decrease in pH showed large variation among different locations and during different time spans. The rates based on in-situ observations conducted in the open ocean were similar (about -0.0018 yr^{-1} over the past two decades). However, the estimated decrease rates in pH from the two coral-reconstructed pH records from the open ocean near Guam and in the Coral Sea were much smaller (about -0.0008 to -0.0009 yr^{-1}). As for the seawater pH records from coastal regions such as off Hainan Island and in the GBR, the variation in range of the rates was much larger than that in the open ocean. The records from the central GBR from the 1960s to the 2000s showed decrease rates in pH ranging from -0.0008 to -0.0023 yr^{-1}, with an average of -0.0017 ± 0.0007 yr^{-1} [*D'Olivo et al.*, 2014], which were similar to the rates based on in-situ observations in the open ocean. However, records from the northern GBR and south of Hainan Island showed very large decrease rates in pH, about -0.003 yr^{-1} after the 1940s, whereas those records covering more than 150 years from off eastern Hainan Island and the northern GBR showed very small rates (<0.0005 yr^{-1} as the absolute value). Therefore, the seawater pH variation in coastal regions appears to be more complicated than that in the open ocean, and the influence of local/regional oceanic–atmospheric oscillations on seawater pH variation may be an important factor.

The different OA rates in Table 1 also suggest that the estimates of OA rate may be influenced by the time span and resolution of the reconstructed pH time-series. Thus, a more reasonable estimation on OA rate should be conducted based on seawater pH records covering similar same time intervals and in the similar resolution. However, the currently available records are not numerous enough to do this. More long-term records (>100 years) from different climate regions (particularly those from the open ocean, which are essential for determining natural seawater pH variability) are needed to separate the natural seawater pH variations driven by oceanic–atmospheric oscillations from the long-term decreases in pH driven by anthropogenic emissions, for more accurate estimates of OA rates.

5. Summary

We reported an annually resolved seawater pH record from the past 159 years reconstructed from a *Porites* coral off eastern Hainan Island, in the northern SCS. The decadal variability in seawater pH was investigated based on this record coupled with previously reported long-term seawater pH records from the West Pacific. The results describe the long-term variation in seawater pH and provide hints for identifying the mechanisms driving the decadal variability in seawater pH in the West Pacific. The main findings of this study are as follows:

1. Similar to previous seawater pH records, seawater pH off eastern Hainan Island in the northern SCS showed large decadal variability over the past 159 years. The activity of the Qiongdong upwelling system, driven by the summer monsoon, primarily controlled the decadal variability by regulating nutrient supplies and surface water productivity. Terrestrial inputs likely did not affect the decadal pH variability significantly, and the influence of the PDO and ENSO system was apparently not significant either.
2. The influence of the PDO on the decadal pH variability in the northern GBR was significant over most of the past 200 years. However, precipitation driven terrestrial runoff appeared not the intermediate process linking the PDO and seawater pH variations in the middle shelf of the GBR. The variations of seawater pH off Guam did not response to the PDO and the ENSO directly, but the response to the PDO likely existed and exhibited decadal variations. However, the mechanisms are still not known.
3. The rates of decrease in pH estimated from seawater pH records reconstructed from coral $\delta^{11}B$ were significantly different among different regions and during different time spans or in different resolution. The combination of the natural interannual to decadal variability in seawater pH and the long-term variations may have contributed to the uncertainty of these estimates. Therefore, understanding the mechanisms causing the interannual to decadal variability in seawater pH is essential for better estimates of ocean acidification rates driven by anthropogenic emissions.

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