Acceleration of modern acidification in the South China Sea driven by anthropogenic CO₂

Yi Liu1,2, Zicheng Peng1, Renjun Zhou1,3, Shaohua Song2, Weiguo Liu2, Chen-Feng You4, Yen-Po Lin4, Kefu Yu5, Chung-Che Wu6, Gangjian Wei7, Luhua Xie7, George S. Burr6 & Chuan-Chou Shen6

1CAS Key Laboratory of Crust-Mantle Material and Environment, School of Earth and Space Science, University of Science and Technology of China, Hefei 230026, China, 2State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi’an 710071, China, 3CAS Key Laboratory of Geospace Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China, 4Earth Dynamic System Research Center (EDSRC), National Cheng Kung University, Tainan 701, Taiwan, 5South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China, 6High-Precision Mass Spectrometry and Environment Change Laboratory (HISPEC), Department of Geosciences, National Taiwan University, Taipei 10617, Taiwan, 7State Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China.

Modern acidification by the uptake of anthropogenic CO₂ can profoundly affect the physiology of marine organisms and the structure of ocean ecosystems. Centennial-scale global and regional influences of anthropogenic CO₂ remain largely unknown due to limited instrumental pH records. Here we present coral boron isotope-inferred pH records for two periods from the South China Sea: AD 1048–1079 and AD 1838–2001. There are no significant pH differences between the first period at the Medieval Warm Period and AD 1830–1870. However, we find anomalous and unprecedented acidification during the 20th century, pacing the observed increase in atmospheric CO₂. Moreover, pH value also varies in phase with inter-decadal changes in Asian Winter Monsoon intensity. As the level of atmospheric CO₂ keeps rising, the coupling global warming via weakening the winter monsoon intensity could exacerbate acidification of the South China Sea and threaten this expansive shallow water marine ecosystem.

The present-day level of atmospheric CO₂ is the highest known to occur for the past 2 million years. One half of the total modern anthropogenic CO₂ emissions have been absorbed by the ocean with an estimated rate of up to 1 million metric tons per hour, resulting in a reduction of seawater pH (pHsw) and so-called ocean acidification. Sea surface pHsw dropped by ~0.1 unit relative to preindustrial time, based on modeling estimates and is projected to decrease by another 0.3–0.4 units by AD 2100 under the IS92a “business-as-usual” scenario. Ocean acidification could lead to significant shifts in the structure and dynamics of ocean ecosystems. One of the direct impacts of acidification is that it may lead to a decrease in the saturation state of surface ocean waters with respect to CaCO₃. This is a threat to marine organisms that rely on the process of calcification to construct their skeletons. These studies are based on modern observations and model predictions with a pHsw decrease rate of ~0.002 year⁻¹ (ref. 5). However, instrumental pHsw records are sparse and span no more than three decades. Natural archives offer an alternative approach to reconstruct pre-instrumental pHsw records much further back in time.

Biogenic carbonate δ¹¹B data have been suggested as a promising proxy to reconstruct ambient pHsw since the 1990s (refs. 11,12). Recent studies showed that coral δ¹¹B could faithfully record pH values of extracellular calcifying fluids (pHcf) that depend directly on ambient seawater pHsw. Only two published δ¹¹B-derived pHsw records provide decadal to centennial timescales records. The two records from Flinders and Arlington Reefs of the Great Barrier Reef (GBR) (Fig. 1) express a signature of pHsw reduction over the last 50 years. However, the inconsistency of pHsw variations during AD 1800–2000 for the two records (Supplementary Fig. 4) cannot provide convincing evidence for a decrease in pHsw that can be unambiguously attributed to atmospheric CO₂ rising.

In this study, we present a new pHsw record inferred from skeletal δ¹¹B data of modern and fossil corals from Xiaodonghai Reef (18°12.46’N, 109°29.93’E), located in the South China Sea (SCS) (Fig. 1). The modern coral record spans from AD 1838–2001, before the beginning of the Industrialization Period and covers the current
warm period (CWP, since 1950s). The δ11B-inferred record of a precisely 230Th-dated fossil coral records values from AD 1048–1079, within the Medieval Warm Period (MWP)\(^9\). Understanding pH\(_{sw}\) variations in the MWP of the last millennia without anthropogenic CO\(_2\) perturbation will be helpful in understanding modern acidification in the CWP.

**Results**

Measured δ11B values of modern and fossil corals are given in Supplementary Figure 3 and Supplementary Tables 2–4. The pH\(_{sw}\) values (total scale) were calculated from measured δ11B data (see Methods and ref. 15). The coral-reconstructed pH\(_{sw}\) record from AD 1838–2001 varies from 7.82 to 8.21 (Fig. 2b). There is a ~30-yr period with maximal pH\(_{sw}\) values of 8.20–8.21 during AD 1830–1870. A minimum pH\(_{sw}\) value of 7.82 occurred from AD 1990–1993. Striking features of this record includes a decreasing trend of −0.0015 ± 0.0002 pH year\(^{-1}\) from AD 1838–2001 (R\(^2\) = 0.63, p < 0.0001) and inter-decadal variations with amplitudes of 0.1–0.2 units (Fig. 2b). The reconstructed bi-weekly pH\(_{sw}\) data in AD 2000 displays strong seasonality, from high values of ~8.1 in winter to low values of ~7.6 in summer (Fig. 3b). This seasonal pH\(_{sw}\) change is consistent with local instrumental data (Supplementary Fig. 7), and follows intra-annual seawater pCO\(_2\) variations of SCS reef water, from a high value of ~500 μatm in summer to a low value of ~380 μatm in winter\(^{20,21}\). A 32-yr fossil coral-derived pH\(_{sw}\) record is characterized by a high average value of 8.17 ± 0.08 (2σ, n = 8) (Fig. 2c).

**Discussion**

The longest in-situ pH\(_{sw}\) record at Station ALOHA in Hawaii shows a significant decreasing trend of −0.018 pH year\(^{-1}\) in surface water of the central North Pacific Ocean over the past two decades (AD 1988–2011) (Supplementary Fig. 4)\(^9\). Our coral-inferred pH\(_{sw}\) reconstruction from the SCS provides the first evidence of a decreasing trend, traced back to the Industrialization Period (Fig. 2b). Atmospheric CO\(_2\) increased slightly between AD 1840 and 1950 at a rate of 0.270 ± 0.010 ppm year\(^{-1}\) (R\(^2\) = 0.97, p < 0.0001), after which the rate increases dramatically to 1.135 ± 0.062 ppm year\(^{-1}\) (R\(^2\) = 0.97, p < 0.0001) (Fig. 2). Our pH\(_{sw}\) sequence follows the temporal pattern of CO\(_2\). The coral-inferred pH\(_{sw}\) values of 8.1–8.2 in AD 1830–1870 are not significantly different from those in the MWP (Fig. 2). The values decreased at a rate of −0.0011 ± 0.0003 pH year\(^{-1}\) (R\(^2\) = 0.35, p = 0.0009) in a 110-yr interval after AD 1840. This rate of decline almost tripled to −0.0029 ± 0.0013 pH year\(^{-1}\) (R\(^2\) = 0.33, p = 0.04) after AD 1950. This pH\(_{sw}\) follows changes observed in the CO\(_2\) time series (Pearson correlation coefficient: R\(^2\) = 0.63, n = 41, p < 0.0001). The long-term decreasing trend of pH\(_{sw}\) also corresponds to a shift to more negative δ13C values (~−0.0037 ± 0.00100 ppm year\(^{-1}\), R\(^2\) = 0.26, p = 0.0007, AD 1838–2001) (Supplementary Fig. 5b), where a significant positive correlation (R\(^2\) = 0.21, n = 41, p = 0.003) exists between pH\(_{sw}\) and δ13C. This suggests synchronous changes between seawater acidification and decreasing dissolved inorganic carbon (DIC) in this region. The δ13C change could be attributed to the “Suess effect”, which is due to uptake of atmospheric CO\(_2\) by the oceans that has been progressively depleted in 13C by combustion of fossil fuels, as supported by previous studies\(^{22–23}\). These signatures all reflect the remarkable absorption of anthropogenic CO\(_2\) by the ocean, and induced acidification in response to the rapid rise in atmospheric CO\(_2\) since the Industrialization Period.

While atmospheric CO\(_2\) governs the long-term SCS pH\(_{sw}\) trend, the inter-decadal cycles of 0.1–0.2 pH must be linked to other mechanism, in the absence of significant inter-decadal variability in atmospheric CO\(_2\). The physical-biogeochemical conditions of the SCS are strongly influenced by the Asian monsoon\(^{23,24}\). During summer, this region is affected by the southwest Asian summer monsoon (ASM), which brings warm and wet tropical air masses to the study area, resulting in increased precipitation (Supplementary Fig. 1b). However there is no correlation between the coral-inferred pH\(_{sw}\)
and the precipitation record (Supplementary Fig. 6). The Asian winter monsoon (AWM) prevails during November to March, bringing cold and dry continental air associated with the Siberian High. From AD 1994 to 2011, the monthly mean wind speed varied from 0.4 to 11 m s\(^{-1}\), with prominent peaks occurring during the winter monsoon season (Supplementary Fig. 1c). We found a significant correlation (\(R^2 = 0.20\), \(n = 41\), \(p = 0.003\)) between the pH\(_{sw}\) and Siberian High pressure, an index of AWM intensity\(^{24}\). Low and high pH\(_{sw}\) values respectively co-vary with weak and strong Siberian High phases on an inter-decadal timescale (Fig. 3c). It is a robust feature that the significant correlation (\(R^2 = 0.18\), \(n = 41\), \(p = 0.006\)) still exists for the two detrended sequences (Fig. 3d). This concurrence suggests that the AWM may contribute to changes in regional pH\(_{sw}\) in the SCS.

The linkage between pH\(_{sw}\) and AWM is attributable to the flushing efficiency of waters over the reefs as observed in the GBR\(^{16}\) and monsoon-driven productivity. During weak AWM periods with reduced wind forcing\(^{25}\) in the SCS, the build-up of CO\(_2\) due to calcification and respiration could lower pH\(_{sw}\) due to poor flushing of reef waters by open seawater. In contrast, periods of relatively strong AWM with strengthened surface currents\(^{22}\) could result in higher pH\(_{sw}\) values. At the same time, surface primary productivity of the SCS is also controlled by AWM intensity\(^{23}\). A weak (strong) AWM would cause the nutricline to deepen (shallow) and result in lower (higher) surface productivity\(^{23}\) and decreased (increased) pH\(_{sw}\). This mechanism is strongly supported by the co-variation of biweekly-resolved coral-inferred pH\(_{sw}\) and AWM wind speed data from AD 2000 (Fig. 3b).

The most acidic condition in AD 1990 is coincident with a sharp drop in the Siberian High index (Fig. 3c), an unprecedented weak event during the past four centuries\(^{21}\). Global warming preferentially warms the high latitudes of Eurasia and this decreases the land-sea pressure gradient and weakens the AWM\(^{27}\). The expected rise in atmospheric CO\(_2\) will likely reduce the AWM intensity in the coming decades\(^{23}\) and exacerbate the impact of acidification on the SCS, and threaten the most diverse collection of shallow water marine organisms on Earth\(^{26}\). Under the stress of current accelerated ocean acidification, an in-depth understanding of the ecological and socioeconomic repercussions in the SCS and other monsoon regions is imperative.

**Methods**

**Coral cores.** A 3-m long core of Porites sp. coral, Song-5, was drilled from Xiaodonghai Reef (18°12.46′N, 109°29.93′E), at a water depth of 8.5 m offshore south Hainan in April 2002 (Fig. 1). Slabs, 7 mm in thickness, were sectioned, washed with ultrapure water, and then dried for X-ray images. Annual banding counts were used to establish the chronology. Subsamples were milled from the AD 2000 segment. One more 1-m long core fossil Porites sp. coral, Dong-5, was also drilled. Subsamples were milled at 4-year intervals along the maximum growth axis on a 32-yr section. X-ray diffraction analysis shows coral samples are 100% aragonite and scanning electron microscopy image indicates an absence of secondary aragonite. After ground into a homogeneous powder using a pre-cleaned agate, all the subsamples (1–3 mg) were treated with 10% NaOCl and ultrapure water (18.2 MO) in an ultrasonic bath.

**Isotopic analysis and dating.** Micro-sublimation techniques were used for boron purification\(^{27}\). Aliquots (~50 μL) containing 50–100 ng of boron were then diluted to 20 ppb boron for the isotopic measurements. \(^{6}B/\(^{10}B\) compositions were determined by a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), Thermo Neptune, at the Earth Dynamic System Research Center, National Cheng Kung University. Instrumental mass bias was calibrated using standard-sample bracketing techniques\(^{28 - 29}\) with NIST SRM 951 boric acid. At each analytical sequence, two JCP-1 and JCt-1 carbonate standards (Porites sp. and giant clam Geological Survey of Japan) and one in-house standard Alfa-B (B ICP-MS solution, Alfa Aesar) were used to monitor the micro-sublimation procedure and plasma condition in...
order to maintain analytical accuracy. The ICP-1 and ICl-1 standard yielded a mean value of 24.20 ± 0.24% (2σ, n = 9) and 16.21 ± 0.05% (2σ, n = 3) respectively. The external precision of δ18O measurements are better than ±0.28% (2σ)5. The precision blank is <5 pg of boron. Instrument sensitivity for 20 ppb B was 0.4–0.5 V for 11B signal intensity, and the effect of total blanks (<0.01 V, including procedure blank and instrument background) can be negligible. Boron isotopic ratios are expressed are expressed using delta (δ) notation relative to the NIST SRM 951. The δ13C and δ18O measurements are carried out using an isotope ratio mass spectrometer MAT-252 equipped with a micro carbonate automatic sample input Kiel II device in the Institute of Earth Environment, Chinese Academy of Sciences. Results are expressed using delta (δ) notation relative to the Vienna Pee-Dee Belemnite (V-PDB) standard. The external error of the laboratory standard is ±0.1% and ±0.2% (1σ) for δ13C and δ18O, respectively.

The fossil coral 5 Dong was dated by 230Th techniques5 (Supplementary Table 1) by a MC-ICP-MS, Thermo Neptune, at the High-Precision Mass Spectrometry and Geochemistry Laboratory (HISPEC), National Taiwan University. The first order of better than 2. Sabine, C. L. et al. The oceanic sink for anthropogenic CO2. Science 305, 367–371 (2004).

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Author contributions

Y.L., Z.P. and C.-F.Y. designed and initiated the research. Y.L., Y.-B.L. and C.-F.Y. analyzed B isotope. S.S. and L.X. drilled the cores. C.-C.W. and C.-C.S. conducted $^{230}$Th dating. W.L. analyzed O and C isotopes. R.Z., C.-F.Y., K.Y., G.W. and G.B. contributed significantly to the discussion of results and manuscript. Y.L. and C.-C.S. wrote the paper.

Additional information

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