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# Acceleration of modern acidification in the South China Sea driven by anthropogenic $CO_2$

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**Modern acidification by the uptake of anthropogenic $CO_2$ can profoundly affect the physiology of marine organisms and the structure of ocean ecosystems. Centennial-scale global and regional influences of anthropogenic $CO_2$ 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 $CO_2$. Moreover, pH value also varies in phase with inter-decadal changes in Asian Winter Monsoon intensity. As the level of atmospheric $CO_2$ 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 $CO_2$ is the highest known to occur for the past 2 million years[1]. One half of the total modern anthropogenic $CO_2$ emissions have been absorbed by the ocean with an estimated rate of up to 1 million metric tons per hour[2,3], resulting in a reduction of seawater pH ($pH_{sw}$) and so-called ocean acidification. Sea surface $pH_{sw}$ dropped by ~0.1 unit relative to preindustrial time, based on modeling estimates[4] and is projected to decrease by another 0.3–0.4 units by AD 2100 under the IS92a "business-as-usual" scenario[5]. 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 $CaCO_3$. This is a threat to marine organisms that rely on the process of calcification to construct their skeletons[6–8]. These studies are based on modern observations and model predictions[4] with a $pH_{sw}$ decrease rate of ~0.002 $year^{-1}$ (ref. 5). However, instrumental $pH_{sw}$ records are sparse and span no more than three decades[9,10]. Natural archives offer an alternative approach to reconstruct pre-instrumental $pH_{sw}$ records much further back in time.

Biogenic carbonate $\delta^{11}B$ data have been suggested as a promising proxy to reconstruct ambient $pH_{sw}$ since the 1990s (refs. 11,12). Recent studies[13–15] showed that coral $\delta^{11}B$ could faithfully record pH values of extracellular calcifying fluids ($pH_{cf}$) that depend directly on ambient (external) seawater $pH_{sw}$. Only two published $\delta^{11}B$-derived $pH_{sw}$ records provide decadal to centennial timescales records[16,17]. The two records from Flinders[16] and Arlington Reefs[17] of the Great Barrier Reef (GBR) (Fig. 1) express a signature of $pH_{sw}$ reduction over the last 50 years. However, the inconsistency of $pH_{sw}$ variations during AD 1800–2000 for the two records (Supplementary Fig. 4) cannot provide convincing evidence for a decrease in $pH_{sw}$ that can be unambiguously attributed to atmospheric $CO_2$ rising.

In this study, we present a new $pH_{sw}$ record inferred from skeletal $\delta^{11}B$ 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

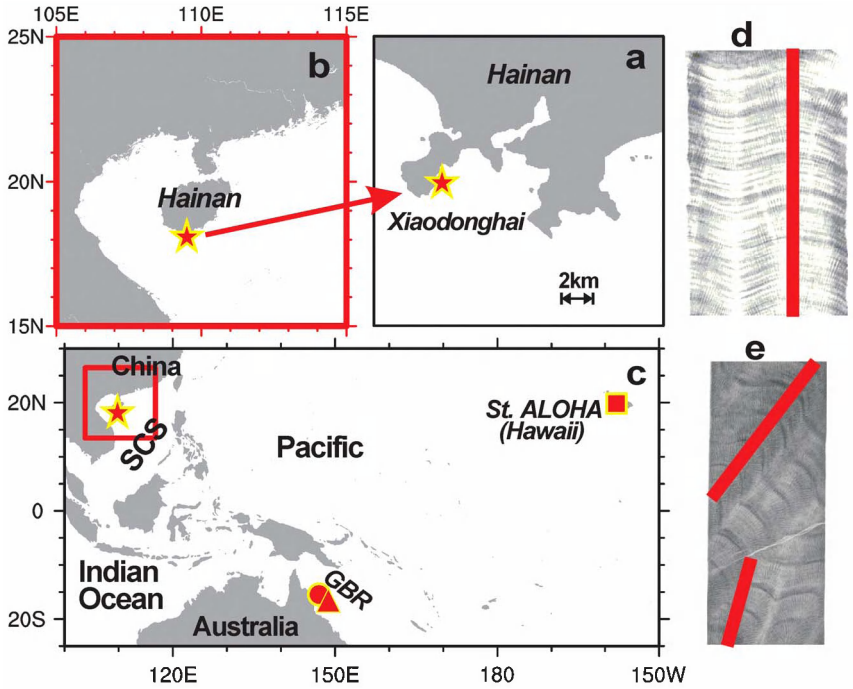


**Figure 1 | Maps with study sites.** Modern and fossil *Porites* cores were drilled from (a) Xiaodonghai Reef (star), located off (b) southern Hainan in (c) the northern South China Sea (SCS). Circle, triangle and square symbols denote the locations of Arlington Reef[17] and Flinders Reef[16] in the Great Barrier Reef (GBR) and Station of ALOHA[9] in Hawaii, respectively. The maps created using NCAR Command Language (http://www.ncl.ucar.edu/) and MapPlot the Earth.4 dataset (http://www.ncl.ucar.edu/Document/HLUs/Classes/MapPlotData4_1_earth_4.shtml). Representative X-radiographs of slices of (d) modern coral sample Song-5 and (e) fossil coral sample Dong-5 are also shown. Red lines denote the subsampling transect along the maximum growth axis.

warm period (CWP, since 1950s). The $\delta^{11}B$–inferred record of a precisely $^{230}Th$-dated[18] fossil coral records values from AD 1048–1079, within the Medieval Warm Period (MWP)[19]. Understanding $pH_{sw}$ variations in the MWP of the last millennium without anthropogenic $CO_2$ perturbation will be helpful in understanding modern acidification in the CWP.

## Results

Measured $\delta^{11}B$ 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 $\delta^{11}B$ 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 $-0.0015 \pm 0.0002$ 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 $\mu$atm in summer to a low value of ~380 $\mu$atm in winter[20,21]. A 32-yr fossil coral-derived $pH_{sw}$ record is characterized by a high average value of $8.17 \pm 0.08$ ($2\sigma$, $n = 8$) (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 $0.270 \pm 0.010$ ppm year$^{-1}$ ($R^2 = 0.97$, $p < 0.0001$), after which the rate increases dramatically to $1.135 \pm 0.062$ 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 $-0.0011 \pm 0.0003$ 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 $-0.0029 \pm 0.0013$ 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 $\delta^{13}C$ values ($-0.0037 \pm 0.0010$ 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 $\delta^{13}C$. This suggests synchronous changes between seawater acidification and decreasing dissolved inorganic carbon (DIC) in this region. The $\delta^{13}C$ 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 $^{13}C$ by combustion of fossil fuels, as supported by previous studies[16,17]. 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[22,23]. 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 $pH_{sw}$

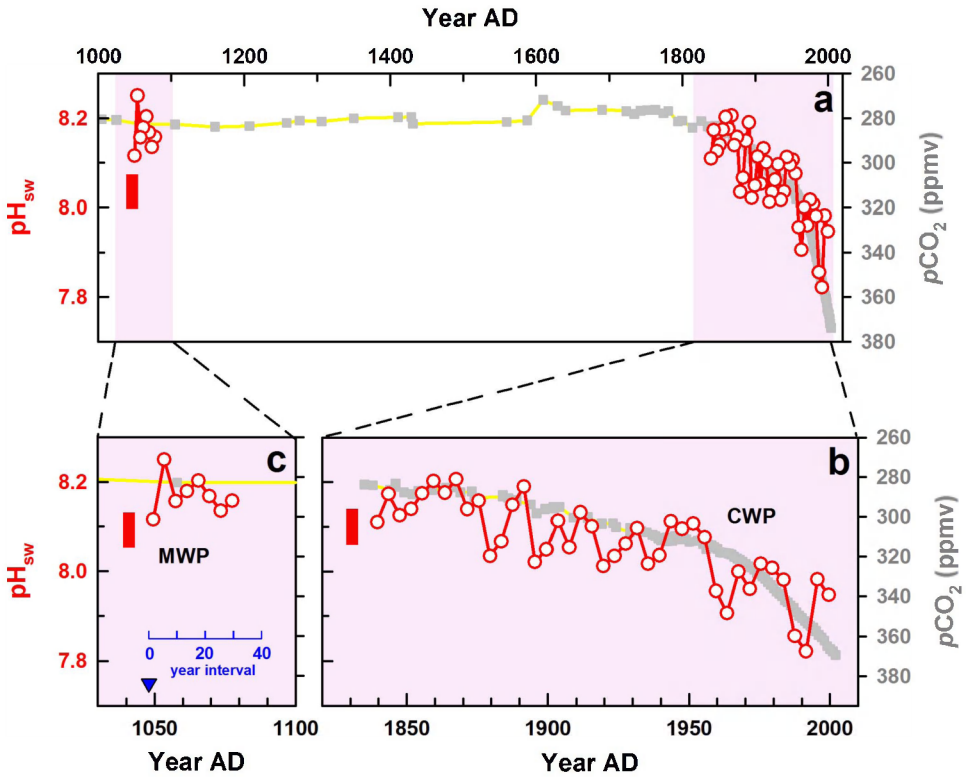


**Figure 2 | Coral-inferred $pH_{sw}$ in the SCS and atmospheric $CO_2$ (ref. 32).** Comparison of the $pH_{sw}$ (red circles and lines) based on boron isotope and atmospheric $CO_2$ (gray dots and yellow line) from (a) AD 1000–2000 and two enlarged sections during (b) AD 1030–1100 and (c) AD 1830–2000. $CO_2$ data after 1958 (included) are annual averages of direct observations from Mauna Loa and the South Pole[32]. $CO_2$ data before 1958 are from ice cores[33]. Vertical red bars denote the 2σ uncertainty of $pH_{sw}$. Dark blue triangle in (c) indicates position of $^{230}$Th-dated layer. The chronology of fossil sample was set by year intervals relative to the dating layer.

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[22] 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[24]. Global warming preferentially warms the high latitudes of Eurasia and this decreases the land-sea pressure gradient and weakens the AWM[25]. The expected rise in atmospheric $CO_2$ will likely reduce the AWM intensity in the coming decades[25] 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 in continuous 4-yr intervals down the full length of the core along the maximum growth axis for the period AD 1838 to 2001. A set of biweekly resolution subsamples was 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 MΩ) 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. $\delta^{11}B$ 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[27,28] 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

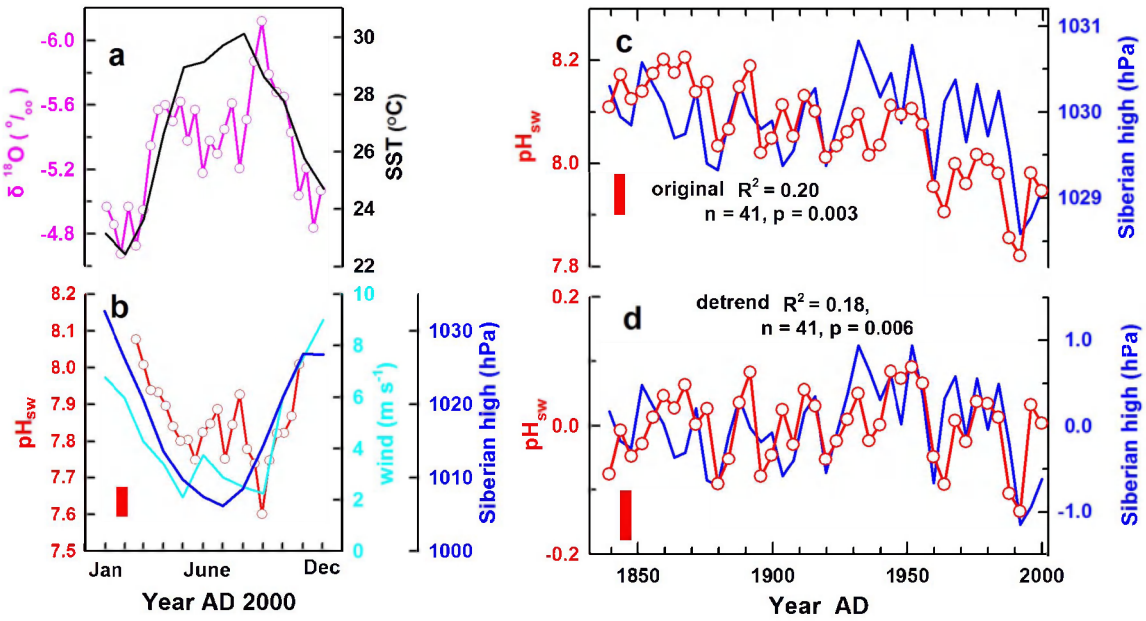


**Figure 3 | Biweekly-resolution coral data and environmental parameters in AD 2000 and time series of the reconstructed $pH_{sw}$ based on boron isotope and Siberian High index[24] from AD 1838–2001.** (a) Coral $\delta^{18}O$ (pink) and sea surface temperature (SST) (black line), and (b) coral-inferred $pH_{sw}$ (red), wind speed (cyan line) and Siberian High index[24] (blue line) in AD 2000. Monthly SST data (17–19°N, 115–117°E) with a 1° resolution were from the Optimum Interpolation Sea Surface Temperature, Version 2, National Oceanic and Atmospheric Administration (NOAA): (http://www.esrl.noaa.gov/psd/data/gridded/data.noaa.oisst.v2.html). Wind data (17–19°N, 115–117°E) with a 0.25° resolution were from the Blended Sea Winds provided by the NOAA National Climate Data Center: (http://www.ncdc.noaa.gov/oa/rsad/air-sea/seawinds.html). Intra-annual data were calendared by aligning coral $\delta^{18}O$ maxima with SST minima and applying a linear interpolation between anchor points. (c) Comparison of coral-inferred $pH_{sw}$ data and 4-yr averaged Siberian High index[24] (blue line), and (d) detrended $pH_{sw}$ data and Siberian High index. Vertical red bars denote the 2σ uncertainty of $pH_{sw}$.

order to maintain analytical accuracy. The JCp-1 and JCt-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 $\delta^{11}B$ measurements are better than ±0.28‰ (2σ)[27]. The procedure blank is <5 pg of boron. Instrument sensitivity for 20 ppb B was 0.4–0.5 V for $^{11}B$ 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 $\delta^{13}C$ and $\delta^{18}O$ measurements were 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 $\delta^{13}C$ and $\delta^{18}O$, respectively.

The fossil coral 5 Dong-was dated by $^{230}Th$ techniques[18] (Supplementary Table 1) by a MC-ICP-MS, Thermo Neptune, at the High-Precision Mass Spectrometry and Environment Change Laboratory (HISPEC), National Taiwan University. The first annual banding of the 32-yr section was sampled for dating.

**pH calculation**. The $pH_{cf}$ was converted by boron isotope systematics based on a following equation[29]:

$$pH_{cf} = pK_B - \log\left\{\left[\delta^{11}B_{SW} - \delta^{11}B_{coral}\right] / \left[\alpha_{(B3-B4)}\delta^{11}B_{coral} - \delta^{11}B_{SW} - 1000\left(\alpha_{(B3-B4)} - 1\right)\right]\right\},$$

where $\delta^{11}B_{sw}$ and $\delta^{11}B_{coral}$ represents $\delta^{11}B$ in seawater ($\delta^{11}B_{sw}$ = 39.5‰)[28] and in coral, respectively, and $\alpha_{(B3-B4)}$ = 1.0272 (ref. 30). The dissociation constant of boric acid $pK_B$ is 8.597 at 25°C and a salinity of 35 (ref. 31). The $pH_{sw}$ value was calculated using the empirical equation: $[pH_{sw} = (pH_{cf} - 4.72)/0.466)$, $R^2 = 0.99]$ (refs. 14,15). The external uncertainty of ±0.28‰ (2σ) (ref. 27) for $\delta^{11}B$ data corresponds to a precision of better than ±0.02 units for $pH_{cf}$ and ±0.04 for $pH_{sw}$. The biweekly $pH_{sw}$ was corrected by temperature effect[31] on $pK_B$.


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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

**Supplementary information** accompanies this paper at http://www.nature.com/scientificreports

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