Larger CO₂ source at the equatorial Pacific during the last deglaciation

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While biogeochemical and physical processes in the Southern Ocean are thought to be central to atmospheric CO₂ rise during the last deglaciation, the role of the equatorial Pacific, where the largest CO₂ source exists at present, remains largely unconstrained. Here we present seawater pH and pCO₂ variations from fossil Porites corals in the mid equatorial Pacific offshore Tahiti based on a newly calibrated boron isotope paleo-pH proxy. Our new data, together with recalibrated existing data, indicate that a significant pCO₂ increase (pH decrease), accompanied by anomalously large marine ¹⁴C reservoir ages, occurred following not only the Younger Dryas, but also Heinrich Stadial 1. These findings indicate an expanded zone of equatorial upwelling and resultant CO₂ emission, which may be derived from higher subsurface dissolved inorganic carbon concentration.

Understanding the past condition of the surface ocean carbonate system and air-sea CO₂ exchange is crucial to projecting future changes in the carbon cycle under ongoing anthropogenic global warming and ocean acidification. Atmospheric CO₂ concentration increased by as much as 80 μatm during the last deglaciation, with ~50 μatm released during Heinrich Stadial 1 (HS1, from 17.5 to 14.6 kyr), followed by an additional ~30 μatm during the Younger Dryas (YD, from 12.9 to 11.7 kyr) (ref. 1). While the Southern Ocean is generally considered to be central to the deglacial CO₂ rise, the contribution from other oceanic regions remains relatively uninvestigated. Information on the partial pressure of CO₂ (pCO₂) is needed to directly constrain past air-sea CO₂ exchange, and this can be reconstructed from boron isotopes (δ¹¹B), a marine carbonate pH proxy. Regions where surface seawater CO₂ is out of equilibrium with the atmosphere are ideal for such studies, and the equatorial Pacific is particularly well suited because it represents the largest global CO₂ source at present (e.g. ref. 16). Corals broadly distributed in tropical to subtropical areas constitute excellent high-resolution geochemical archives for paleo-CO₂ studies because they may be precisely radiogenically dated (U-series), unlike foraminifers that are affected by uncertainty in radiocarbon reservoir age (R).

Two previous studies have attempted to constrain equatorial Pacific CO₂ changes. Palmer and Pearson showed increased CO₂ emission during the last deglaciation in the western equatorial Pacific (WEP) from δ¹⁵N measurements on the planktonic foraminifer (Globigerinoides sacculifer) in a sediment core recovered from offshore Papua New Guinea (ERDC-92, Fig. 1a). Further east, Douville et al. performed δ¹³C on fossil corals from the Marquesas (9.5°S 139.4°W, Fig. 1a) and also demonstrated increased CO₂ release at the end of the YD. However Douville et al. did not observe a significant CO₂ release during HS1, complicating interpretation of the equatorial contribution to deglacial atmospheric CO₂ rise. Integrated Ocean Drilling Program Expedition 310 (IODP Exp. 310) drilled the outer reef slope at Tahiti (17.6°S 149.5°W, Fig. 1a) recovering fossil corals from an open ocean environment spanning HS1, which enable us to assess the issue.

Results

δ¹³C-pH calibration. This study establishes a new empirical δ¹³C-pH calibration utilizing, for the first time, anthropogenic ocean acidification. Empirical calibration is needed to overcome the observed offsets from a theoretical δ¹³C-pH curve in culture experiments for zooxanthellate corals. (pH is reported using the total hydrogen scale, hereafter pH for simplicity). There are two primary approaches to overcoming the reported offsets. One is an empirical approach that assumes constant offsets in measured and theoretical δ¹³C (“offset a”; see Methods), while the other is an observational approach that considers potential pH modification by calcifiers.
The potential for pH-modification is of great concern for δ11B-based reconstruction of pH due to the implications for atmospheric pCO2 calculation. Such a phenomenon is consistent with indirect pH measurements of internal calcification fluid using pH sensitive dye that suggests a higher pH than ambient seawater, creating better conditions for calcification. The pH concept in the δ11B-pH calibration that reflects pH differences in seawater (pHsw) and internal calcification fluid has been proposed, however usage of this proposed relationship to calibrate δ11B of modern Porites spp. from Tahiti and Marquesas resulted in unrealistically high values (e.g., 8.34 in AD 1991), well above reported estimates (e.g., refs. 20, 21). Therefore the present study employs the empirical equation here (see Methods).

Ocean acidification was estimated from a combination of in situ fCO2 values in the surface ocean, atmospheric CO2 concentration directly measured at the Mauna Loa observatory in Hawaii since AD 1960 (ref. 22), and CO2 concentrations within bubbles trapped in an Antarctic ice core (Figs. 2, S1–S4; Supplementary Methods). These data were then fit to the previously reported δ11B measurements of Porites spp. (refs. 11, 24), which are for the years AD 1991, 1950, and 1700 (Fig. 2, see Methods and Supplementary Methods for details of the δ11B-pH calibration and pH estimation since the Industrial Revolution).

**pH and pCO2 reconstruction.** Using our revised calibration, we reconstructed pH from our new δ11B measurements on Tahitian corals, as well as from previously reported data from both the Marquesas and Tahiti, and the overall result is consistent with the WEP foraminifer δ11B variations (Fig 3a and b). The oldest coral sample, dated to 20.7 ka BP during the last glacial maximum (LGM), exhibits a relatively high pH (8.26). From 15.5 to 9.0 ka BP, pH is generally constant within uncertainty (8.15–8.22) and consistent...
with the preindustrial value of 8.20. Four notable pH excursions are associated with HS1 and the YD. Two of our samples exhibit anomalously low pH at the end of HS1 (8.13 at 15.15 ka and 8.09 at 14.99 ka BP), in addition to those at end of the YD at the Marquesas11. The low pH following HS1 had been previously undetected at this location. Calculation of pCO₂ (see Methods) reveals deglacial values significantly above those of the atmosphere (Figs. 3c and 4a). Conversely, ΔpCO₂ during last glacial and the early Holocene was nearly zero, suggesting air-sea CO₂ equilibrium.

Results from a different portion of the same 14.99 ka BP coral sample deviate by as much as 1.4‰, which corresponds to 0.11 in pH and 100 μatm in pCO₂ (310-M0024A-11R-01W_77-90 and 310-M0024A-11R-1W_60-75, Table S1). Considering the average 4 year temporal resolution of each sample, these excursions occurred abruptly and persisted for several years, which differs from modern observations that show no clear interannual or decadal variability (Supplementary Methods, Fig. S1). This enhanced variability, which is also observed in Sr/Ca derived SST results from another Porites colony recovered from IODP Exp. 310 (ref. 25), may relate to Tahiti’s location at the rim of equatorial upwelling cell (Fig. 1a). Taken together, pCO₂ (pH) records indicate that the equatorial Pacific became a larger CO₂ source during the last deglaciation with excursions at the end of HS1 and the YD.

**Marine ¹⁴C reservoir age compilation.** Compiled marine ¹⁴C reservoir ages (R) throughout the equatorial Pacific resemble pCO₂ variability (see Methods; Figs. 4 and S5; Table S2). Larger and more variable values of R are evident in Tahiti during HS1 and the YD, and enhanced R variability is also seen in the Marquesas (Figs. 4 and S5). Paterne et al.26 sub-sampled different parts in the same fossil coral skeleton and analyzed both ¹⁴C and U/Th. They observed no difference in U/Th dates, but a much larger difference in ¹⁴C.
Possibilities of either a diagenetic alteration or a change in R were suggested. The latter is more probable because a large variation in R is also suggested from Vanuatu coral at 11.7–12.4 ka (~400 years; during the YD, ref. 27).

Though reported $R_{\text{a}}$ (difference between calculated R and modern R; see Methods) data around the upwelling zone during the LGM are sparse, calculations with the new Lake Suigetsu datasets suggests no substantial change in R (see Methods; Figs. 4 and S5). This implies that the CO$_2$ exchange rate in the surface equatorial Pacific during the last glacial was almost the same as present, which supports the above-mentioned observation that $\Delta$PCO$_2$ is essentially equivalent to zero and indicates that anomalous R values are limited to the last deglaciation.

**Discussion**

PCO$_2$ variability in subtropical oligotrophic water can be explained by mixing of water masses that exhibit distinctly different dissolved inorganic carbon (DIC) concentrations. A southward migration of the intertropical convergence zone (ITCZ) that partly controls thermocline depth is hypothesized during Heinrich Events including HS1 and the YD (e.g. ref. 29). At present, the ITCZ does not seem to affect surface PCO$_2$ variability (Fig. 1a), and if it is displaced southward, the locus of equatorial upwelling remains at the equator due to the influence of inter-hemispheric asymmetry of Coriolis force (e.g. refs. 30, 31). Enhanced upwelling (shallower thermocline, La Niña–like conditions) or increased subsurface DIC concentration are more likely to drive PCO$_2$ variability based on sedimentary evidence from the equatorial Pacific for higher nutrient content, e.g., enhanced biogenic opal export production and lower stable carbon isotopes ($\delta^{13}$C) (TT013-PC72, ODP Site 1240 and TR163-19)32–35 (Fig. 1a). Semi-conservative radiogenic neodymium isotopes (147Nd) from sediment cores at the eastern equatorial Pacific (EEP) (ODP Site 1240) and off Baja California (MV99-MC99-GC31/PC08) indicates stronger subsurface water transport from the south33,36 (Fig. 1). Covariation of geochemical properties between the Southern Ocean and the equatorial Pacific suggest a subsurface connection during the last deglaciation (e.g. refs. 32–38). Thus, PCO$_2$ variability may be explained by an increase in DIC in the upwelled, subsurface water masses as opposed to physical processes alone.

Water mass subduction along the subtropical front, mainly off Chile39, forms Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) that upwells at the equatorial Pacific via the Equatorial Undercurrent (EUC) (Fig. 1). SAMW and AAIW are characterized by higher/lower concentrations of oxygen/silicic acid (Fig. 1b,c). It is suggested that the abyssal DIC reservoir around the Southern Ocean increased during the last glacial period39–41,45, which would have contributed to lower atmospheric PCO$_2$. Carbon dioxide was released to the surface through deep ocean ventilation during HS1 and the YD ( refs. 2–9), however export production was insufficient to fully compensate the increased carbon flux. This is consistent with residual radiocarbon content ($\Delta^{14}$C) of intermediate water at the EEP (V21–30)42 and off Baja California (MV99-MC99-GC31/PC08)43 that indicates anomalously older water was incorporated into SAMW/AAIW (Fig. 1), as well as with depleted $\delta^{13}$C of surface and lower thermocline dwelling foraminifers from sediment cores at both equatorial (TT013-PC72, ODP Site 1240 and TR163-19) and South Pacific sites32,33,37,38. Moreover, enhanced export production of biogenic opal suggest more silicic acid was transported via the EUC to thermocline water at the equatorial Pacific (V19-30 and TT013-PC72) without being consumed completely within the Southern Ocean33,34,44. Stronger Ekman transport in association with sea ice retreat and a poleward shift of southern westerlies is suggested to be a driver.43

A similarity between R and PCO$_2$ variability during the last deglaciation supports an interpretation that older DIC was incorporated to subtropical surface water through mixing with SAMW/AAIW, though, contrary evidence comes from the current formation sites off Chile44 and New Zealand45. However, a key sediment record off Chile was recently reevaluated, and the new interpretations indicate stronger upwelling and subsequent larger R in surface water in the Southern Ocean46, which agrees well with our interpretation. Yet, further work is still needed to fully understand both the physical and biogeochemical dynamics in the Southern Ocean and the equatorial Pacific4.

Positive $\Delta$PCO$_2$ indicates CO$_2$ flux from the ocean to the atmosphere. Previous studies4,47 indicated that the equatorial Pacific contributed to deglacial CO$_2$ rise, however the timing of anomalously higher pCO$_2$ events recorded in radioactively dated fossil corals do not systematically correspond to those of atmospheric CO$_2$ rise recovered from Antarctic ice core on the GICC05 timescale4 (Figs. 3 and 4). Moreover our new calibration reveals a modest CO$_2$ emission continued through the Bolling/Allerød/Antarctic Cold Reversal when no atmospheric CO$_2$ increase is observed (Figs. 3 and 4). Though we demonstrate that the equatorial Pacific became a larger CO$_2$ source during the last deglaciation, it is too early to conclude its exact contribution to atmospheric CO$_2$ rise. The Southern Ocean is suggested to be central in CO$_2$ degassing48 and the contribution of the terrestrial biosphere should be further evaluated49. More evidence spanning the YD and the early part of HS1, in particular the sharp rise in atmospheric CO$_2$ and the sudden drop of $\delta^{13}$C of CO$_2$ (refs. 1,46), as well as more spatial coverage is needed.

**Methods**

$\delta^{13}$B analyses. The $\delta^{11}$B values of fossil Porites spp. were measured following the protocol of Ishikawa and Nagashii. Fossil corals were screened for diagenetic alteration with X-ray diffraction and geochemical analyses, as well as visual using a Scanning Electron Microscope48. Bulk sampling was conducted along the growth axis, and time resolution of each sample is several years (1–8 years) depending on growth rate of each coral. Typically 6 mg of carbonate was used for $\delta^{11}$B measurement. After removals of organic matter using 30% H$_2$O$_2$, for ~12 hours, boron was purified by cation and anion exchange using AG 50W X12 and 1X4 resin (Bio-Rad, USA) and then $\delta^{11}$B were measured using the positive polarity thermal ionization mass spectrometer (P-TIMS; Thermo Finnigan TRITON) installed at Kochi Core Center, Japan Agency for Marine-Earth Science and Technology. All reported $\delta^{11}$B values are the mean of duplicate analyses (Table S1). Repeated analysis of the 1C1–carbonate standard provided by Geological Survey of Japan yielded 24.21 ± 0.18‰ (2σ; n = 18), which is the finest precision to date50. Differences between the duplicates are 0.08‰ on average with the largest one of 0.28‰ (Table S1), which is within the measurement uncertainty of 1C1–. We conservatively report ±0.18‰ as the analytical uncertainty of our $\delta^{11}$B measurements.

$\delta^{11}$B-pH calculation and PCO$_2$ calculation. First, the analytical procedure-specific isotopic offset was corrected using the equation below (modified after Zeebe & Wolf-Gladrow51) in order to reduce inter-laboratory offsets in reported $\delta^{11}$B values, $

\delta^{11}$B$_{\text{Carbonate-corrected}} = \delta^{11}$B$_{\text{BSW-stacked + measured}} + 10^{\delta^{11}$B$_{\text{Carbonate-measured}} - \delta^{11}$B$_{\text{BSW-stacked}}}$ \tag{1}

where $\delta^{11}$B$_{\text{Carbonate-corrected}}$ is the boron isotopic value of carbonate after correction and $\delta^{11}$B$_{\text{BSW-stacked}}$ is the global average $\delta^{11}$B of seawater. We used the recommended value of 39.61‰ for $\delta^{11}$B$_{\text{BSW-stacked}}$ (ref. 49). $\delta^{11}$B$_{\text{Carbonate-measured}}$ and $\delta^{11}$B$_{\text{BSW-stacked}}$ are $\delta^{11}$B of carbonate samples and of seawater measured in different laboratories. Without performing inter-laboratory correction of 1C1–results of Douville et al.11 and this study differ by 0.25‰, equivalent to ~0.03 pH units. After the correction using the reported value of $\delta^{11}$B$_{\text{BSW-stacked}}$ (refs. 11,47), the difference improved to be 0.07‰, indicating that correction should be performed. After the correction, the empirical calibration equation reported by Hönisch et al.12 was utilized. In this equation, the model offset ‘a’ and fractionation factor ‘$\alpha$’ that yield the lowest $\text{rms}_{\text{root}}$ (root–mean–square error) is determined.

\[
\text{pH} = \text{pK}_a - \log \left( \frac{(\delta^{11}$B$_{\text{BSW-stacked}} - \delta^{11}$B$_{\text{Carbonate-measured}} + a)}{(\delta^{11}$B$_{\text{Carbonate-corrected}} - a) \times 10^ {\delta^{11}$B$_{\text{Carbonate-measured}} - \delta^{11}$B$_{\text{BSW-stacked}}}} \right) \tag{2}
\]

Three previously reported $\delta^{11}$B values for modern Porites spp. from Tahiti and Marquesas were fit to estimated pH at AD 1991, 1950 and 1700 (refs. 11,24) (Fig. 2, Table S1). In the calibration ‘a’ was determined as ~6.0 when we chose recently reevaluated 1C1– of 1.0273 (ref. 21). When this calibration was conducted, both ‘a’ and ‘$\alpha$’ were allowed to vary freely, and the resultant ‘$\alpha$’ with the lowest $\text{rms}_{\text{root}}$ was very close to that of Klochko et al.14 rather than the previously accepted value of Kakihana et al.52. Thus we used Klochko’s fractionation factor. pH was calculated from

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both previously reported and newly obtained δ¹⁸O values considering a local difference of seawater pH between Tahiti and Marquesas (see Supplementary Methods for details).

$\Delta ^{14}C_{marine}$ was further calculated from obtained pH values from δ¹³C corrected using CO2SYS program under assumptions of constant temperature, salinity and total alkalinity (see also Supplementary Methods for details). The δ¹³C values of $\text{G. saccifer}$ are not included here due to large uncertainties in the δ¹³C-pH calibration (e.g. refs. 12,15).

R compilation. Published $\Delta ^{14}C$ (radiocarbon years) and U/Th ages of fossil coral samples obtained during IODP Exp. 310 were compiled in order to calculate residual radiocarbon activities (ΔC and R). We verified via IODP sample ID and core photographs that the exact same samples were selected (Table S2). In some cases different portion of the skeleton of the same coral was dated. Given that lifetimes of coral are generally less than several decades, temporal gaps derived from sub-sampling are negligible in calculations of ΔC and R. We did not use 14C ages from either microbialite (carbonate created by bacteria) or encrusting coralline algae from equivalent down-core depths due to a possibility of post-depositional growth (for details, see ref. 53). Calculation was done according to equations (3) and (4) where 14C-age is an original radiocarbon data before a local R correction;ΔC:

$$\Delta ^{14}C_{marine} = \left( C_{Ca}^{e} - C_{Ca}^{atm} \right) / C_{Ca}^{atm}$$

$\text{R} = \frac{10^{4} \Delta ^{14}C_{marine}}{\Delta ^{14}C_{atm} + 1} \times 10^{3}$

Atmospheric ΔC (ΔCair) from INTCAL09 (ref. 56). We used R calculated of 14C samples that span 29–30 ka BP were calculated using the recently published Lake Suigetsu ΔCair dataset, since as much as $\sim 100\%$ offsets are observed between INTCAL09 in this interval (Fig. S5a). Southon et al. points out that the INTCAL09 curve heavily relies on Cariaco Basin varve sediment data beyond the dendrochronological limit (12,15). During the Last Deglaciation, and modern R (Fig. S5b; Table S2). Other 14C and U/Th datasets for fossil corals from the equatorial Pacific islands were also used to calculate R including Tahiti 58, 664, 303, Marquesas 352, 410, 353, Kiritimati 56, 300, 2445–2459 (2010). Calculation was done according to equations (3) and (4) where 14C-age is an original radiocarbon data before a local R correction;ΔC:

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56. Takahashi, T. et al. Climatological mean and decadal change in surface ocean pCO$_2$ and net sea–air CO$_2$ flux over the global oceans. Deep-Sea Res. II 56, 554–577 (2009).
62. Deschamps, P. et al. Ice-sheet collapse and sea-level rise at the Belling warming 14,600 years ago. Nature 483, 559–564 (2012).

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42. Stott, L., Southon, J., Timmermann, A. & Koutavas, A. Radiocarbon age anomaly at intermediate water depth in the Pacific Ocean during the last deglaciation. *Paleoceanography* **24**, PA001690 (2009).
43. Marchitto, T. M., Lehman, S. J., Ortiz, J. D., Flückiger, J. & van Green, A. Marine Radiocarbon Evidence for the Mechanism of Deglacial Atmospheric CO₂ Rise. *Science* **316**, 1456–1459 (2007).
44. De Pol-Holz, R., Keigwin, L., Southon, J., Hebbelin, D. & Mohtadi, M. No signature of abyssal carbon in intermediate waters off Chile during deglaciation. *Nature Geosci.* **3**, 192–195 (2010).
45. Ciais, P. et al. (2012) Large inert carbon pool in the terrestrial biosphere during the Last Glacial Maximum. *Nature Geosci* 5, 74–79.
46. Schmitt, J. et al. Carbon Isotope Constraints on the Deglacial CO₂ Rise from Ice Cores. *Science* **336**, 711–714 (2012).
47. Ishikawa, T. & Nagaishi, K. High-precision isotopic analysis of boron by positive thermal ionization mass spectrometry with sample preheating. *J. Anal. At. Spectrom.* **26**, 359–365 (2011).
48. Inoue, M. et al. Trace element variations in fossil corals from Tahiti collected by IODP Expedition 310: Reconstruction of marine environments during the last deglaciation (15 to 9 ka). *Mar. Geol.* **271**, 303–306 (2010).
49. Foster, G. L., Pogge von Strandmann, P. A. E. & Rae, J. W. B. Boron and magnesium isotopic composition of seawater. *Geochim. Geophys. Geosyst.* **11**, GC003201 (2010).
50. Zeebe, R. E. & Wolf-Gladrow, D. in *CO₂ in Seawater: Equilibrium, kinetics, isotopes.* (Elsevier Oceanography Series, 2001).
51. Klochko, K. et al. Experimental measurement of boron isotope fractionation in seawater. *Earth Planet. Sci. Lett.* **248**, 276–285 (2006).
52. Kakihana, H., Kotaka, M., Satoh, S., Nomura, M. & Okamoto, M. Fundamental Studies on the Ion-Exchange Separation of Boron Isotopes. *Bull. Chem. Soc. Japan* **50**, 158–163 (1977).
53. Seard, C. et al. Microbialite development patterns in the last deglacial reefs from Tahiti (French Polynesia; IODP Expedition #310): Implications on reef framework architecture. *Mar. Geol.* **279**, 63–86 (2011).
54. Adkins, J. F. & Boyle, E. A. Changing atmospheric Δ13C and the record of deepwater paleoventilation ages. *Paleoceanography* **12**, 337–344 (1997).
55. Burr, G. S. et al. Modern and Pleistocene reservoir ages inferred from South Pacific Corals. *Radiocarbon* **51**, 319–335 (2009).
56. Reimer, P. J. et al. IntCal09 and Marine09 radiocarbon age calibration curves, 0–50,000 years cal BP. *Radiocarbon* **51**, 1111–1150 (2009).
57. Southon, J., Noronha, A. L., Cheng, H., Edwards, R. L. & Wang, Y. A high-resolution record of atmospheric 14C based on Hula Cave speleothem H82. *Quat. Sci. Rev.* **33**, 32–41 (2012).
58. Bard, E., Arnold, M., Hamelin, B., Tisnerat, L. N. & Cabioch, G. Radiocarbon calibration by means of mass spectrometric 230Th/234U and 14C ages of corals: an updated database including samples from Barbados, Mururoa and Tahiti. *Radiocarbon* **40**, 1085–1092 (1998).
59. Fairbanks, R. G. et al. Radiocarbon calibration curve spanning 0 to 50,000 years BP based on paired 230Th/234U/238U and 14C dates on pristine corals. *Quat. Sci. Rev.* **24**, 1781–1796 (2005).
60. Schlitzer, R. Ocean Data View. <http://odv.awi.de>, (2014) Date of access:29/01/2014.

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**Author contributions**
Y.Y. designed the study and obtained samples. K.K. and T.I. measured coral boron isotope ratios. A.S. prepared samples. S.O. performed the statistical analysis of the data. K.K., Y.Y., T.I., S.O. and A.S. contributed to the interpretation and the preparation of the final manuscript.

**Additional information**
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