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Rising CO_2 and increased light exposure synergistically reduce marine primary productivity

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Carbon dioxide and light are two major prerequisites of photosynthesis. Rising CO_2 levels in oceanic surface waters in combination with ample light supply are therefore often considered stimulatory to marine primary production[1–3]. Here we show that the combination of an increase in both CO_2 and light exposure negatively impacts photosynthesis and growth of marine primary producers. When exposed to CO_2 concentrations projected for the end of this century[4], natural phytoplankton assemblages of the South China Sea responded with decreased primary production and increased light stress at light intensities representative of the upper surface layer. The phytoplankton community shifted away from diatoms, the dominant phytoplankton group during our field campaigns. To examine the underlying mechanisms of the observed responses, we grew diatoms at different CO_2 concentrations and under varying levels (5–100%) of solar radiation experienced by the phytoplankton at different depths of the euphotic zone. Above 22–36% of incident surface irradiance, growth rates in the high-CO_2-grown cells were inversely related to light levels and exhibited reduced thresholds at which light becomes inhibitory. Future shoaling of upper-mixed-layer depths will expose phytoplankton to increased mean light intensities[5]. In combination with rising CO_2 levels, this may cause a widespread decline in marine primary production and a community shift away from diatoms, the main algal group that supports higher trophic levels and carbon export in the ocean.

The oceans take up about one million tons of CO_2 per hour on average and remove a quarter of the CO_2 emitted to the atmosphere by anthropogenic activities[6], and therefore play a crucial role in modulating global warming. However, as more and more CO_2 dissolves in the oceans, seawater acidity is increasing, leading to ocean acidification. Under a fossil-fuel intensive emission scenario (A1F1)[4], the projected atmospheric CO_2 concentration of about 800–1,000 ppm by the end of this century will cause surface-ocean acidity to increase by 100–150% (pH reduced by 0.3–0.4; refs 7,8). Ocean acidification is known to affect the calcification of coccolithophores[2,9,10] and other marine photosynthetic[11] and animal calcifiers, such as corals[12]. Although some non-calcifying phytoplankton species or assemblages may benefit from the increasing CO_2 levels in sea water[1–3,13], growth rates of diatom-dominated phytoplankton assemblages were unaffected by CO_2-induced seawater acidification during shipboard studies[14], though the stoichiometry of carbon-to-nitrogen utilization was altered under high CO_2 partial pressure (pCO_2) in other studies[15,16]. Alternatively, phytoplankton biomass or net primary productivity in much of the surface ocean may decrease as shoaling of the upper mixed layer or enhanced stratification owing to global warming exposes phytoplankton cells to higher depth-integrated irradiance and reduced transport of nutrients from deeper layers[17,18]. Obviously, we still lack a comprehensive understanding of how ocean productivity will be affected by global change and, therefore, are unable to predict how important pelagic ecosystem services, such as food production and CO_2 sequestration, will evolve in the future. One reason for this is our lack of knowledge about synergistic effects of the main climate variables[5,19].

In an attempt to test for community-level responses to the projected ocean changes in future CO_2 and light conditions we conducted three cruises to the South China Sea (SCS). In a series of onboard microcosm experiments we observed primary productivity decrease when exposed to both high CO_2 levels and high light intensities (Fig. 1a,b). When grown at 91% incident surface solar radiation, the primary production of natural phytoplankton assemblages was significantly lower ($P < 0.05$) under increased pCO_2 (800 or 1,000 μatm) compared with ambient pCO_2 (385 μatm; seawater carbonate system parameters are given in Supplementary Table S1) at all stations except LE04 and C3 (Fig. 1a,b) when based on chlorophyll-*a* (chl.-*a*) concentration. Growth at the high-pCO_2 levels thus significantly (P values are given in Supplementary Table S3) reduced primary productivity by 12–81% per volume of sea water (Fig. 1a) and by 7–36% when normalized to chl.-*a* (Fig. 1b) based on the daytime 6 or 12 h ^{14}C-spiked incubations. At stations SEATS and C3, where also 24 h incubations were carried out (Fig. 1 inset), night-time respiration resulted in significant (Supplementary Table S3) loss of daytime photosynthetically fixed carbon, which was higher in the high- compared with the low-CO_2 microcosms, reflecting a high-CO_2 stimulation of respiration. At the same stations, where phytoplankton species composition was analysed, diatoms became less abundant in the high-CO_2 microcosms compared with the ambient CO_2 level, whereas haptophytes increased in relative abundance (Supplementary Fig. S1). In parallel, non-photochemical quenching (NPQ, an indicator of light stress) of the phytoplankton assemblages showed 54–196% higher values under high compared with ambient pCO_2 levels (Fig. 1c and Supplementary Fig. S2), reflecting a higher light stress in the high-CO_2 microcosms.

Diatoms are responsible for about 40% of total primary production in the oceans[20] and they were the predominant phytoplankton group in our study areas (Supplementary Fig. S1). To explore the mechanisms responsible for the decrease in primary

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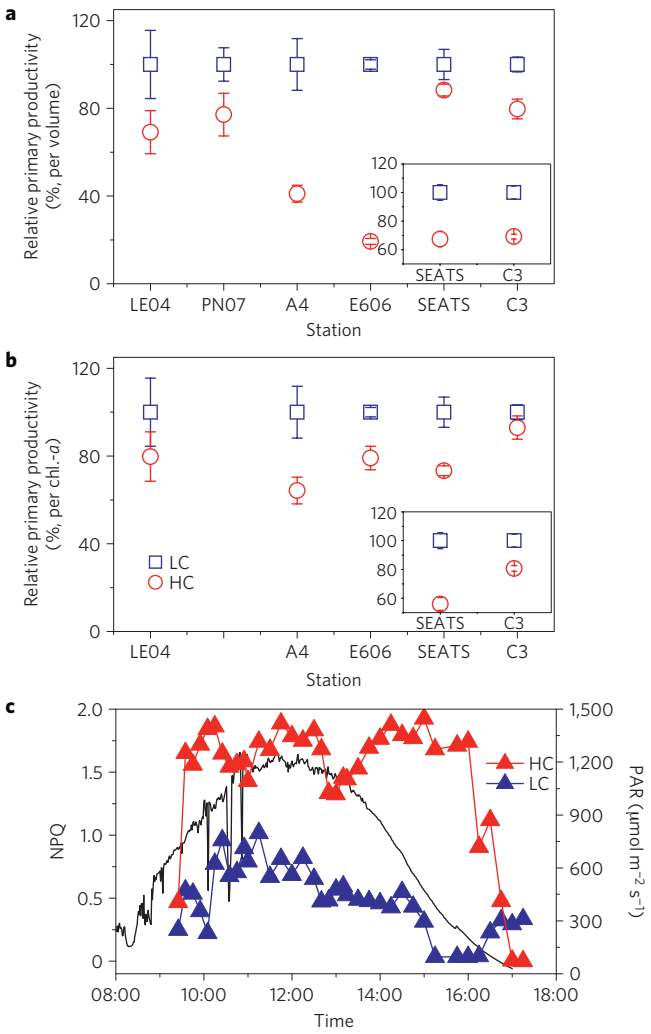

Figure 1 | Primary production in CO_2-perturbed microcosms by phytoplankton assemblages collected in the SCS and East China Sea (station PN07). a,**b**, Per volume of sea water (μg C l^{-1} h^{-1}) (**a**) and per chl.-*a* (μg C chl.-*a*$^{-1}$ h^{-1}) (**b**); chl.-*a* concentration at PN07 was not measured. For the high-pCO_2 (HC, 800 μatm, red circle) for all stations except SEATS and C3, where 1,000 μatm pCO_2 was applied and low-pCO_2 (LC, 385 μatm, blue square) experiments, triplicate microcosms (32 l) were used for each pCO_2 level (seawater carbonate system parameters are given in Supplementary Table S1). The phytoplankton assemblages in all microcosms were equally exposed to 91% incident solar visible radiation. Detailed information for the stations and related physicochemical and biological features are given in Supplementary Table S2. Insets: additional 24 h incubations carried out at the two stations. Error bars represent standard deviations of triplicate incubations of samples from triplicate microcosms. Details about the statistical comparisons among the treatments are given in Supplementary Table S3. Note, higher rates of photosynthetic carbon fixation were found in low-CO_2 microcosms. **c**, The NPQ of phytoplankton assemblages at station E606 grown under low pCO_2 (385 μatm, filled blue triangle) and high pCO_2 (800 μatm, filled red triangle) in the microcosms on day six. NPQ in other stations showed similar patterns (Supplementary Fig. S2). The black line represents the visible light intensity of that day. Note, higher NPQs were always found in the high-CO_2 microcosms.

production at increased CO_2 concentration observed in our shipboard experiments, we hypothesized that increased CO_2 concentration lowers the threshold for phytoplankton growth above which photosynthetic active radiation (PAR) becomes excessive or stressful, owing to reduced energy requirements for inorganic carbon acquisition at increased CO_2. We tested this hypothesis by investigating the growth rate and photosynthetic performance of three cosmopolitan diatom species (*Phaeodactylum tricornutum*, *Thalassiosira pseudonana* and *Skeletonema costatum*) grown over a range of PAR at both ambient and increased CO_2 concentrations as projected for the end of this century[4].

Unialgal cultures of the three diatoms were grown semicontinuously (dilution every 24 h) outdoors at 5%, 10%, 18%, 30%, 55% and 100% of incident solar radiation, mimicking deeper to shallower mixing depths, at ambient (390 μatm) and increased levels of pCO_2 (1,000 μatm) (related seawater chemical parameters are given in Supplementary Table S1). Although at low PAR levels specific growth rates (μ) of the high-CO_2-grown cells were higher than those kept under ambient CO_2, this trend reversed at higher PAR levels (Fig. 2), with the PAR thresholds (daytime mean PAR levels) at the reversion points being about 160, 125 and 178 μmol photons m^{-2} s^{-1} for *P. tricornutum*, *T. pseudonana* and *S. costatum*, respectively (corresponding daily PAR doses are given in Supplementary Table S4). These light levels correspond to 22–36% of incident surface solar PAR levels and are equivalent to PAR levels at 26–39 m depth in the SCS, based on the vertical profiles of PAR at the SEATS station. The mean PAR levels at which the growth rate of the low-CO_2-acclimated cells exceeded that of the high-CO_2 ones were 180, 163, and 201 μmol photons m^{-2} s^{-1} (corresponding daytime PAR doses are 1.59, 1.74 and 2.34 MJ m^{-2} d^{-1}) for *P. tricornutum*, *T. pseudonana* and *S. costatum*, respectively, corresponding to 25–42% of incident surface solar PAR levels (Fig. 2). These light levels also represent PAR levels at 22–36 m depth at the SEATS station. Under light-limiting levels of solar radiation, the high-CO_2-grown cells had higher light-use efficiencies (α) for growth, by 7–25% based on daytime mean PAR intensity or by 7–22% based on daily PAR dose ($P < 0.05$; Supplementary Table S4). The effective quantum yield (an indicator of the efficiency of photosynthetic energy use) decreased and NPQ increased more strongly ($P < 0.05$) in the high-CO_2-grown cells with increased PAR levels (Fig. 3), indicating an enhanced photosynthetic system II inactivation[21] and photoprotective strategy (as reflected in enhanced NPQ) under the high-CO_2 and acidified conditions. The increased NPQ in the high-CO_2-grown diatoms (Fig. 3) is comparable to that of the phytoplankton assemblages in the high-CO_2 microcosms (Fig. 1c and Supplementary Fig. S2), evidence that increasing seawater pCO_2 increased the light stress for the cells in both cases (Figs 1c and 3, and Supplementary Fig. S2). Furthermore, the increased CO_2 concentration stimulated photorespiration (Supplementary Table S5), a process by which oxygen is consumed and CO_2 released in the light. Mitochondrial respiration may have also increased in the high-CO_2 microcosm, as shown in the difference of 24 h over 12 h ^{14}C-traced incubations (Fig. 1 insets) and in the diatom *P. tricornutum*[22] grown under 1,000 μatm pCO_2, implying an additional carbon loss and O_2 consumption under low pH/high CO_2 stress.

These findings support our hypothesis that rising pCO_2 and high light exposure can act synergistically to reduce marine primary productivity. Mechanistically, the increased pCO_2 and seawater acidity increased light stress, as indicated by higher NPQ (Fig. 1c and Supplementary Fig. S2), reduced PAR threshold (Fig. 2) and enhanced photorespiration (Supplementary Table S5). Furthermore, respiratory carbon loss in the phytoplankton assemblages (Fig. 1 inset) and as reported for a diatom species[22] could also be at least partially responsible for the decreased growth rates of the diatoms grown under moderate to high levels of solar radiation at the high CO_2 concentration. The fact that increased CO_2 stimulated growth rate (Figs 2, 3) and quantum yield (Fig. 3) under low levels (5–18%) of incident solar PAR is consistent with previous findings[1–3,13,22]. Notably, doubling of pCO_2 was recently

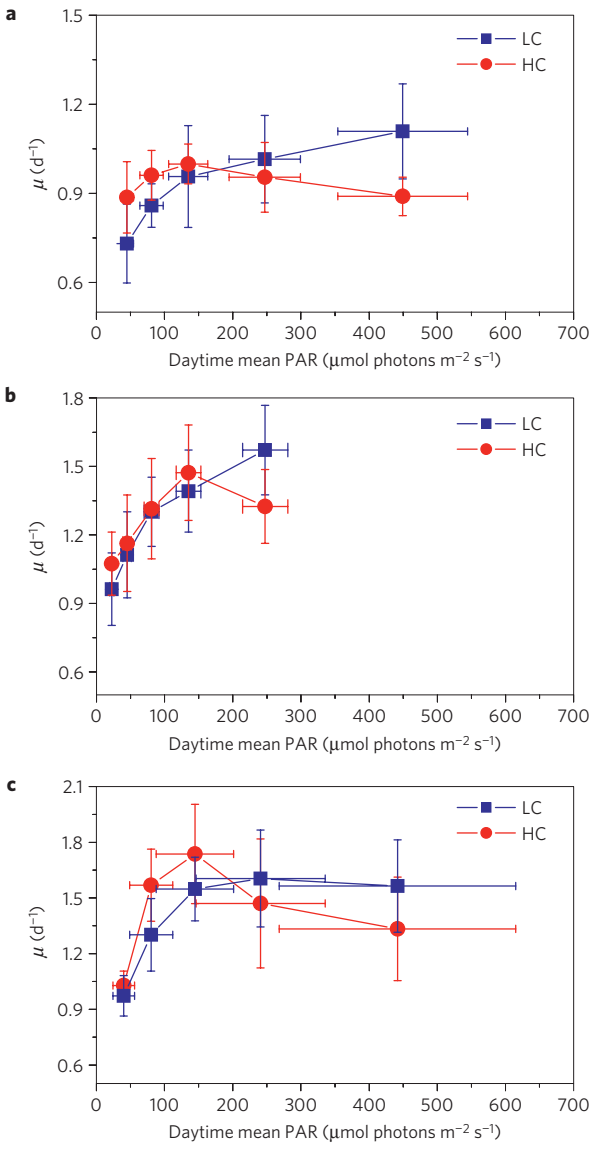

Figure 2 | Growth rates of cultured diatoms as a function of pCO_2 and light. a–c, μ of the diatoms *Phaeodactylum tricornutum* (**a**), *Thalassiosira pseudonana* (**b**) and *Skeletonema costatum* (**c**) grown under ambient (390 μatm, LC, blue square) and increased CO_2 (1,000 μatm, HC, red circle) conditions under 5%, 10%, 18%, 30%, 55% or 100% levels of incident sunlight for *P. tricornutum* (December 2010) and 5%, 10%, 18%, 30% and 55% for *T. pseudonana* (March 2011) and *S. costatum* (April 2011). Each symbol represents the average of six replicate cultures under each treatment. Seawater carbonate system parameters are given in Supplementary Table S1. Horizontal and vertical error bars denote standard deviations for variation of solar radiation and μ, respectively.

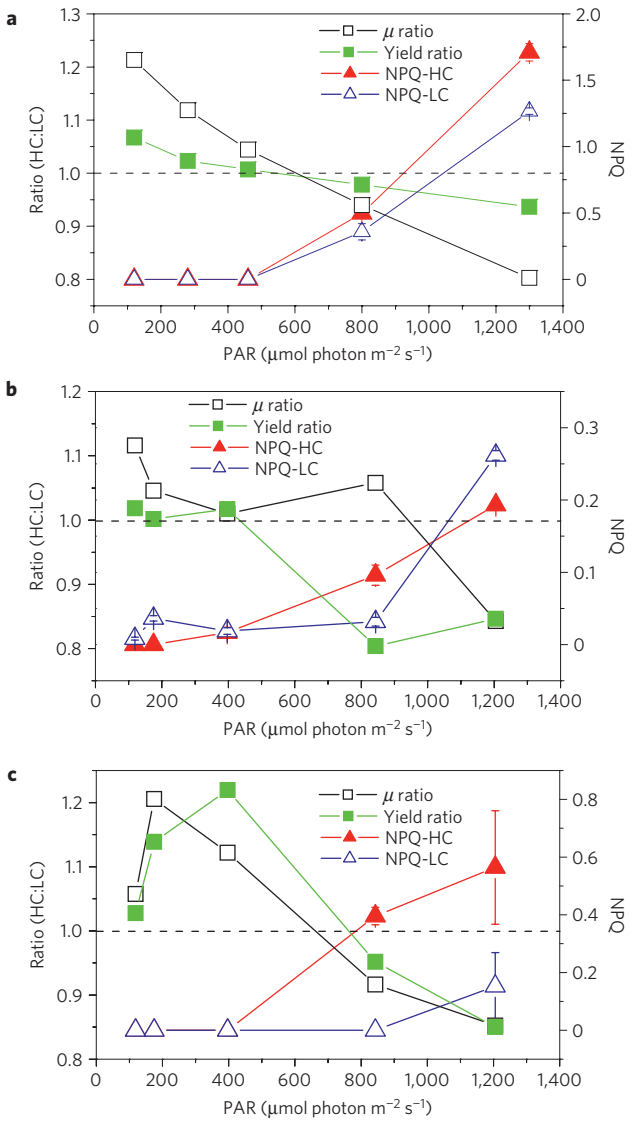

Figure 3 | High- to low-pCO_2 ratios for growth rates and photosynthetic parameters in cultured diatoms. a–c, The ratios of μ (open square) and effective yields (green filled square) in high-CO_2-grown cells (HC, 1,000 μatm) to those in low-CO_2-grown cells (LC, 390 μatm), and their NPQ (red filled triangle for HC and blue open triangle for LC) in the diatoms, *Phaeodactylum tricornutum* (**a**), *Thalassiosira pseudonana* (**b**) and *Skeletonema costatum* (**c**), as a function of PAR levels, equivalent to solar PAR levels during noon period for the same cultures grown outdoors (Fig. 2). Note, both growth rate and yield reversed with increased PAR levels and NPQ increased faster with increased PAR levels in the high-CO_2-grown cells.

found to decrease the energy expended on carbon fixation by up to 6% in the diatom *P. tricornutum*[23], which agrees well with the increased growth rate of 5% in the same species grown under a pCO_2 of 1,000 μatm (ref. 22). However, such stimulation is probably owing to reduced energetic costs rather than increased intracellular CO_2 availability, as most photosynthetic organisms down-regulate their CO_2-concentrating mechanisms (CCMs) under increased CO_2 levels[24]. Previously, both *P. tricornutum*[22] and *S. costatum*[25,26] were found to down-regulate their CCMs when grown under increased CO_2 concentrations. Enrichment of CO_2 and increased acidity were also found to increase photoinhibition of electron transport in *P. tricornutum*[22].

As global warming will cause surface stratification to increase and upper-mixed-layer depths to decrease in the future ocean, phytoplankton will be exposed to higher mean light intensities[5]. This in combination with increased CO_2 levels, which down-regulate CCMs and reduce energy spending on carbon acquisition, may act synergistically to trigger additional light stress and photodamages, thus stimulating cellular defenses as shown in increased NPQ (Figs 1c and 3, and Supplementary Fig. S2), enhancing mitochondrial respiration (Fig. 1 insets) and photorespiration (Supplementary Table S5), which is known to play crucial protective roles against photodamage caused by reactive oxygen species[27]. However, at or close to the reversion point where the growth of high-CO_2-grown cells declined (Fig. 2), neutral effects of ocean acidification

can be observed, such as those reported from shipboard CO_2 perturbation studies under 30% solar radiation[14].

Ocean acidification is not proceeding in isolation. Both synergistic and antagonistic effects of increased CO_2/decreased pH with other changes in environmental conditions may occur, thus complicating the overall ecosystem response. For instance, increasing surface ocean temperatures of 2–3 °C by the end of this century can affect the growth of phytoplankton, as well as the distributions of species at different trophic levels[28]. Moreover, ultraviolet-B irradiances can harm primary producers to a greater extent with progressing ocean acidification[29,30].

Whether the observed synergistic effects of high levels of CO_2 and light are unique for diatoms or are widespread among phytoplankton taxa remains to be seen. Considering the key role of diatoms in the ocean, both as the predominant source of food for higher trophic levels and as the main driver of export production[2], the impacts this effect may have on ocean productivity would be severe and independent of whether it is restricted to diatoms or common also to other key groups of phytoplankton. As the sign and strength of the CO_2 effect depend on the level of solar radiation, the impact it will have on ocean productivity is going to vary with season, latitude, cloud cover and mixed-layer depth. However, with much of the surface ocean experiencing light intensities above the crossover point, where a stimulating CO_2 effect shifts to an adverse one, the observed response could become widespread from the tropical to the temperate ocean as CO_2 concentrations continue to rise.

Methods

Field-assemblage studies. The effects of increased pCO_2 levels at 800 or 1,000 µatm on photosynthetic rate were investigated at six different stations in different seasons during three consecutive cruises in the SCS (five stations) and East China Sea (one station, PN07; detailed station information is given in Supplementary Table S2). Surface sea water (0–2 m) was collected before sunrise with a 10 l acid-cleaned plastic bucket, filtered (180 µm) to remove large grazers and dispensed into six microcosms (cylindrical polymethyl methacrylate tanks with water jacket, 32 l, 0.34 m water depth), which allowed 91% PAR, 63% ultraviolet-A (315–400 nm) and 6% ultraviolet-B (280–315 nm) transmissions under incident solar radiation. Microcosm temperature was controlled using a circulating cooler at levels similar to the sea surface temperature of the sampling stations (Supplementary Table S2).

The seawater carbonate system in the microcosms was maintained stable (Supplementary Table S1) by aerating with ambient air (385 µatm CO_2) and CO_2-enriched air (800 or 1,000 µatm CO_2) at a flow rate of 0.5 l min^{-1}. Stable CO_2 equilibrium with the sea water (variation <5%) was achieved within 25 h using a CO_2 enricher (CE-100, Wuhan Ruihua Instrument & Equipment Ltd, China). CO_2 preconditioning at each station lasted for seven days (except station E606, six days).

Photosynthetic carbon fixation was determined by inoculating 5 µCi (0.185 MBq) $NaH^{14}CO_3$ (ICN Radiochemicals, USA) in 50 ml samples, incubating for 6 h, 12 h or 24 h (details in Supplementary Table S2) and measuring the incorporated radioactivity by liquid scintillation counting (LS 6500, Beckman Coulter, USA; ref. 31).

Photosynthetic fluorescence parameters were measured with a fluorescence induction and relaxation system (FIRe, Satlantic, Canada) every 10–15 min (station E606) or every minute (stations SEATS and C3) in microcosm samples maintained under the ambient and increased CO_2 concentrations. NPQ was estimated by the equation[32]: $NPQ = (F_{md} - F'_m)/F'_m$, where F_{md} is the maximal fluorescence measured during night-time (station E606) or after 30 min early morning dark adaptation (SEATS, C3 stations) and F'_m is the effective yield during daytime measured at actinic light levels set to similar levels as the incident solar PAR levels at the time of each yield measurement. Both blue and green light sources were turned on and each saturating flash lasted for 80 µs.

Diatom-culture studies. *Phaeodactylum tricornutum* (CCMA 106) and *Skeletonema costatum* (CCMA110) were isolated from the SCS in 2004 and obtained from the Center for Collections of Marine Bacteria and Phytoplankton of the State Key Laboratory of Marine Environmental Science (Xiamen University), whereas *Thalassiosira pseudonana* (CCMP 1335, isolated off Long Island, New York, USA) was obtained from the Provasoli-Guillard National Center for Culture of Marine Phytoplankton. Monospecific cultures of all three species were grown semicontinuously by partially renewing the medium every 24 h with fresh medium equilibrated at ambient (390 µatm) or increased (1,000 µatm) pCO_2 levels. Culture medium was prepared with sterilized natural sea water collected from the SCS (18° N, 116° E) and enriched with Aquil nutrients[33] for *P. tricornutum* and f/2 medium[34] for *S. costatum* and *T. pseudonana*. Indoor *P. tricornutum*, *T. pseudonana* and *S. costatum* cultures were maintained for ~75, 220 and 20 generations, respectively, at 70 µmol photons m^{-2} s^{-1}, 20 °C, 14:10 light:dark under the two CO_2 levels before being transferred to outdoor growth experiments for solar exposures. Outdoor growth periods were 10–24 December 2010, 26 February–24 March 2011 and 10–24 April 2011, with mean daily surface incident PAR doses of 3.4, 4.3 and 7.1 MJ m^{-2} d^{-1}, respectively.

Target pH (pCO_2) was achieved by aerating (0.3 l min^{-1}) ambient air (outside, rooftop) or air with increased (1,000 µatm) CO_2 from a plant CO_2 incubator (HP1,000G-D, Ruihua, China) for indoor growth and with the portable CO_2 enricher (see above) for outdoor (sunlight) growth. Cell densities in the semicontinuous cultures were maintained between 5×10^4 ml^{-1} and 30×10^4 ml^{-1}, so that the pH of the culture medium varied <0.05 (Supplementary Table S1). Levels of 5%, 10%, 18%, 30%, 55% or 100% of incident solar PAR were achieved with neutral density screens. The temperature was controlled at 20 °C using the cooling unit (see above). Solar PAR and ultraviolet radiation for both the shipboard and outdoor experiments were measured every second with a broadband solar radiometer (ELDONET, Real Time Computer, Germany) and averaged over one-minute intervals. Chlorophyll fluorescence measurements of the three diatoms were carried out with a modulated fluorometer (XE-PAM, Walz, Effelrich, Germany)[26].

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Author contributions

On the basis of an original idea from K.G., the concept of this paper was developed in discussion between all authors. J.X. and G.G. contributed as equally as K.G. for their leading roles in laboratory and field experiments, respectively. U.R. and D.A.H. contributed to experimental designs, data analysis and the writing of the paper. D-P.H. contributed to the analysis of the data and writing of the paper. G.G., Y.Z., P.J., K.X., B.H., L.W. and N.L. carried out shipboard experiments; J.X., Y.L., X.C. and W.L. carried out laboratory experiments.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/natureclimatechange. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to K.G.