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Responses of marine primary producers to interactions between ocean acidification, solar radiation, and warming

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ABSTRACT: Anthropogenic CO_2 is accumulating in the atmosphere and trapping reflected infrared radiation, resulting in warming of both terrestrial and ocean ecosystems. At the same time, the dissolution of CO_2 into seawater is increasing surface ocean acidity, a process known as ocean acidification. Effects of ocean acidification on marine primary producers have been documented to be stimulative, inhibitive, or neutral. Elevated CO_2 and reduced pH levels can interact with solar radiation, which fluctuates over different time scales from limiting to saturating or even stressful levels, to bring about synergistic, antagonistic, or balanced effects on marine primary producers at different depths or under changing weather conditions. However, shoaling of the upper mixed layer (enhanced stratification) due to ocean warming and freshening (rain, ice melting) can lead to additional photosynthetically active radiation (PAR) and ultraviolet (UV) exposure, which can have both benefits and costs to photosynthetic organisms. Elevated CO_2 concentrations under low or moderate levels of PAR have been shown to enhance photosynthesis or growth of both phytoplankton and macroalgae; excessive levels of PAR, however, can lead to additional inhibition of photosynthesis or growth under elevated CO_2, and addition of UV radiation (280 to 400 nm) can increase or down-regulate such inhibition, since solar UV-B (280 to 315 nm) radiation often harms algal cells, while UV-A (315 to 400 nm) at moderate levels stimulates photosynthetic carbon fixation in both phytoplankton and macroalgae. In view of warming effects, increased temperatures have been shown to enhance photorepair of UV-damaged molecules, though it simultaneously enhances respiratory carbon loss. The net effects of ocean acidification on marine primary producers are therefore largely dependent on the photobiological conditions (light limitation, light or UV stress), as well as interactions with rising temperature and other variables such as altered nutrient availability. Hence, feedbacks between changing carbonate chemistry and solar radiation across the entire spectrum present complications to interpret and understand ocean acidification effects based on single-factor experiments.

KEY WORDS: Algae · Carbon dioxide· Light · Phytoplankton · Photosynthesis · Ultraviolet radiation · Climate change

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OCEAN ACIDIFICATION AND GLOBAL CHANGE

The oceans are currently absorbing over one million tons of CO_2 from the atmosphere each hour, and play an important role in mitigating global warming (Sabine et al. 2004). At the same time, enhanced dissolution of CO_2 from the air is also acidifying the oceans, a process known as ocean acidification (Doney et al. 2009). While standing biomass in the oceans accounts for only about 1% of that in terres-

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trial habitats, marine primary producers contribute about half of the global primary productivity due to their faster growth and turnover rates (Falkowski & Raven 1997). The ocean's biological pump effectively removes CO_2 from near-surface waters through photosynthetic carbon fixation and sequesters it at depth (Falkowski et al. 2000), thus promoting the absorption of CO_2 from the atmosphere (Sabine et al. 2004, Behrenfeld et al. 2006). This mechanism can both affect and be affected by the process of ocean acidification (Hutchins et al. 2009).

When CO_2 dissolves in seawater, it combines with water to form carbonic acid, which dissociates to bicarbonate, releasing protons (H^+) and so ultimately reaching a new equilibrium state. However, as the H^+ concentration rises with CO_2 dissolution, 'excess' H^+ releases can partially reverse the secondary dissociation reaction, resulting in a decrease in carbonate ions:

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (1)$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \quad (2)$$

$$HCO_3^- \leftarrow H^+ + CO_3^{2-} \quad (3)$$

The carbonate chemistry of seawater is also strongly influenced by biological processes such as photosynthesis and respiration, which act to increase or decrease seawater pH, respectively. At the same time, assimilation of other nutrients such as nitrate or ammonia may also influence pH, as shown in the following assimilation equations (Stum & Morgan 1981):

$$106CO_2 + 16NO_3^- + HPO_3^- + 122H_2O + 18H^+ = [C_{106}H_{263}O_{110}N_{16}P_1] + 138O_2 \quad (4)$$

$$106CO_2 + 16NH_4^+ + HPO_3 + 108H_2O = [C_{106}H_{263}O_{110}N_{16}P_1] + 107O_2 + 14H^+ \quad (5)$$

However, considering the Redfield ratio (C:N:P stoichiometry), the hydrogen ion consumption or production due to nitrate or ammonia assimilation is small compared to changes in the seawater carbonate buffer system due to photosynthetic carbon removal.

Typical chemistry changes associated with ocean acidification are increased concentrations of CO_2, H^+, and HCO_3^- and decreased concentration of CO_3^{2-} and $CaCO_3$ saturation state (Gattuso et al. 2010). Since the beginning of the industrial revolution, the pH of oceanic surface seawater has been reduced by ~0.1 unit due to the increased atmospheric CO_2 concentration (Caldeira & Wickett 2003), corresponding to about a 30% increase in the H^+ concentration. With a further century-scale increase of CO_2 concentration in the atmosphere to 800–1000 ppmv (Intergovernmental Panel on Climate Change [IPCC] A1F1 scenario; Houghton et al. 2001), pH of the surface oceans will decrease by another 0.3 to 0.4 units (Feely et al. 2004, Sabine et al. 2004, Orr et al. 2005), thus increasing [H^+] by 100 to 150%. The exchange of CO_2 between the sea and atmosphere depends on diffusive fluxes, the dynamics of physical mixing, and the marine biological CO_2 pump. About 50% of the CO_2 taken up by the oceans since the industrial revolution is still present in the upper ocean down to 400 m (Sabine et al. 2004). Consequently, organisms in the euphotic zone are exposed to a high-CO_2 environment, and their physiologies may respond to the increased CO_2 as well as to chemical changes, such as ionic speciation (Millero et al. 2009), related to the altered carbonate system or reduced pH, which may also alter their thermal windows (temperature range for species survival; Pörtner & Farrell 2008).

Although the ecological consequences of ocean acidification are likely profound, they are largely uncertain (Turley et al. 2010), especially when other concomitant global change variables are taken into consideration (Wu et al. 2008, Boyd et al. 2010). For instance, at the same time as the ocean is acidifying, global warming associated with increasing atmospheric CO_2 accumulation is leading to a 'greenhouse ocean', with increased sea surface temperature (SST) and a shoaling of the upper mixed layer (UML) (Hays et al. 2005, Doney 2006, Capotondi et al. 2011). Freshwater inputs from increased precipitation in temperate areas and ice melting in the polar regions, increasing temperature, and decreasing or increasing wind speeds, are all important in determining the UML depth. Enhanced stratification would expose plankton to increasing levels of photosynthetically active radiation (PAR, 400 to 700 nm) and UV radiation (280 to 400 nm), as well as to reduced availability of nutrients from underlying deeper waters due to enhanced strength in the pycnocline at the base of the UML (Steinacher et al. 2010). However, the penetration of solar radiation in the water column largely depends on the amount of particles and dissolved organic matter (DOM), which may increase in various inland waters and coastal ecosystems due to an increase in rainfall. In addition, a feedback mechanism is the photo-degradation of DOM that would partially counteract the decrease in nutrients due to enhanced stratification (Hörtnagl et al. 2011, Vähätalo et al. 2011).

Multiple stressors or factors such as these will influence the effects of ocean acidification on primary producers and the food web in both direct and indirect ways (Boyd et al. 2010, Boyd 2011). In addition to direct effects of the chemical changes in seawater on

the physiology of marine primary producers (see reviews by Wu et al. 2008 and Beardall et al. 2009 and references therein), ocean acidification can also alter chemical speciation, thereby affecting the availability of iron (Shi et al. 2010) and ammonium (Hutchins et al. 2009, Beman et al. 2011) to plankton assemblages. Increased solar UV-B radiation (280 to 315 nm) along with depletion of stratospheric ozone and global warming can interact to influence planktonic primary producers (Häder et al. 2011). Consequently, other anthropogenic factors will synergistically or antagonistically act with ocean acidification to influence the oceanic biological uptake of CO_2, complicating the understanding of ecological impacts of ocean acidification.

Our present understanding of the sensitivity of photosynthetic organisms to ocean acidification is based primarily on short-term experiments under either saturating or sub-saturating constant light levels, in which organisms are exposed to increased concentrations of CO_2. In contrast, phytoplankton cells in natural environments experience diurnal fluctuations of solar radiation, from light-limiting to light-saturating and potentially to stressful light levels in the UML of the euphotic zone in the presence of UV radiation. Along with the diurnal variation of solar radiation, surface water temperature and pCO_2 also often follow a diel pattern, especially in coastal waters of high biological production. Obviously, phytoplankton cells are exposed to dynamic environments under the sun. In this review, we focus on the combined effects of ocean acidification and solar radiation, by summarizing our increasing understanding of the physiological responses of primary producers and addressing the potential ecological implications of their interactive effects in an acidified, warmer, and more stratified ocean.

RESPONSES TO INCREASING CO_2 AND DECREASING pH

As more CO_2 accumulates in the atmosphere, seawater pCO_2 increasingly affects marine photosynthetic processes and energetics in direct and/or indirect ways. Low pH and/or increased pCO_2 can alter periplasmic electro-potential (periplasm negative relative to the medium or the oxidation-reduction potential) and affect proton or ion channels by altering the structure of periplasmic proteins (Beardall et al. 2009, Lü et al. 2011) or the activity of periplasmic extracellular carbonic anhydrase (Aizawa & Miyachi 1986, Sültemeyer 1998, Bozzo & Colman 2000). Changes in energetics, associated with down-regulation of CO_2-concentrating mechanisms (CCMs) with increasing pCO_2 or with up-regulated cost to cope with increased H^+ concentration, are likely to be responsible for the major acclimation processes of oceanic phytoplankton to rising CO_2 (Hopkinson et al. 2011). Acclimation to a rapid change in CO_2 concentration has been shown by a lessening of maximum photosynthetic efficiency and increase in cell membrane permeability in a diatom (Sobrino et al. 2005). Nevertheless, most of the studies to date have been restricted to short-term periods of time and the responses might have been obscured by the lack of proper acclimation (Beardall et al. 2009).

The concentration of dissolved inorganic carbon (DIC) in surface seawater is approximately 100 to 200 times that of CO_2 in the atmosphere at the present; however, its predominant form is HCO_3^-, with CO_2 usually accounting for <1% in pelagic waters (Gattuso et al. 2010). In addition, since CO_2 in seawater diffuses about 10 000 times slower than in air, its supply rate can limit photosynthetic carbon fixation (Raven 1993, Riebesell et al. 1993, Morel et al. 1994). These facts led to early laboratory and shipboard studies to assess whether increasing atmospheric CO_2 concentrations would enhance the primary production or growth of marine photosynthetic organisms (Gao et al. 1991, Riebesell et al.1993, Hein & Sand-Jensen 1997, Schippers et al. 2004) or reduce algal calcification (Gao et al. 1993, Riebesell et al. 2000). At the same time, the extent of enhanced primary productivity at elevated atmospheric CO_2 levels has been questioned (Beardall & Raven 2004), since most of the species investigated so far possess CCMs (Giordano et al. 2005, Raven et al. 2011). Laboratory as well as mesocosm studies have suggested that increased atmospheric CO_2 can sometimes stimulate photosynthesis and/or growth in both micro- and macroalgae (Gao et al. 1991, 1999, Riebesell et al. 1993, 2007, Riebesell 2004, Hutchins et al. 2007, Fu et al. 2007, 2008a, 2010; see also reviews by Wu et al. 2008, Beardall et al. 2009, Riebesell & Tortell 2011). However, since different physiological processes are involved, whether or not phytoplankton or macroalgae will benefit from increased CO_2 remains controversial (Wu et al. 2008). Although photosynthetic carbon fixation rate was enhanced in a diatom, mitochondrial respiratory (Wu et al. 2010) or photorespiratory (Gao et al. 2012) carbon losses were also stimulated. Additionally, decadal-scale global decreases (Behrenfeld et al. 2006, Boyce et al. 2010) and increases (Chavez et al. 2011) of phytoplankton productivity have been reported.

The literature includes reports of effects of simulated future CO_2-induced seawater acidification that range from positive (Hein & Sand-Jensen 1997, Fu et al. 2007, 2010, Hutchins et al. 2007, Riebesell et al. 2007, Wu et al. 2010), to neutral (Tortell et al. 2000, Tortell & Morel 2002, Chen & Gao 2003, Fu et al. 2007), to negative (Wu et al. 2010, Gao et al. 2012) (our Table 1; also see review by Riebesell & Tortell 2011 and references therein). Elevated CO_2 concentrations up to 10 000–50 000 µatm are known to down-regulate CCMs (Kaplan et al. 1980, Tsuzuki & Miyachi 1989, Raven 1991, Matsuda et al. 2001), and induction of

Table 1. Representative effects of elevated CO_2 concentration reported on diatoms, coccolithophores, cyanobacteria, phytoplankton assemblages, and macroalgae grown under different levels or qualities of light or solar radiation. Groups of cyanobacteria or calcifying algae are indicated by genus or species names. L-PAR: photosynthetically active radiation (PAR) levels <300 µmol photons m^{-2} s^{-1}; M-PAR: PAR levels ≥300 µmol photons m^{-2} s^{-1}; SL: solar visible radiation; +UV: presence of UV radiation; POC: particulate organic carbon. Additional references on different phytoplankton groups' response to ocean acidification can be found in Riebesell & Tortell (2011)

Source	Group	Study type	Light	Variables
Positive				
Riebesell et al. (1993)	Diatom	Lab	L-PAR	Growth
Schippers et al. (2004)	Diatom	Lab	L-PAR	Growth & photosynthesis
Chen & Gao (2004a)	Diatom	Lab	L-PAR	Photosynthesis
Wu et al. (2010)	Diatom	Lab	L-PAR	Growth & photosynthesis
Tortell et al. (2008)	Diatom	Ship-board	30% SL	Growth
Kim et al. (2006)	Diatom assemblage	Mesocosm	SL	Growth
Riebesell et al. (2007)	Diatom assemblage	Mesocosm	SL	POC production
Egge et al. (2009)	Phytoplankton assemblage	Mesocosm	SL	Photosynthesis
Hein & Sand-Jensen (1997)	Phytoplankton assemblage	Ship-board	L&M-PAR	Photosynthesis
Iglesias-Rodriguez et al. (2008a,b)	*Emiliania huxleyi*	Lab	L-PAR	Calcification
Feng et al. (2009)	Coccolithophore assemblage	Ship-board	SL	Calcification
Fu et al. (2007)	Pico-cyanobacteria	Lab	L-PAR	Abundance
Hutchins et al. (2007)	*Trichodesmium*	Lab	L-PAR	Growth
Fu et al. (2008a)	*Crocosphaera*	Lab	L-PAR	Growth & N_2 and CO_2 fixation
Fu et al. (2008b)	Raphidophyte	Lab	L-PAR	Growth & N_2 and CO_2 fixation
Gao et al. (1991, 1993, 1999)	Macroalgae	Lab	L-PAR	Growth
Chen & Gao (2003)	Diatoms	Lab	L-PAR	Photosynthesis
Kim et al. (2006)	Diatoms	Mesocosm		Growth
Gao et al. (2012)	Diatoms	Lab	Low SL	Growth
Neutral				
Tortell et al. (2000)	Phytoplankton assemblage	Ship-board	M-PAR	Growth
Tortell & Morel (2002)	Phytoplankton assemblage	Ship-board	30% SL	Growth
Feng et al. (2010)	Phytoplankton assemblage	Ship-board	7 and 33% SL	Photosynthesis
Fu et al. (2007)	Pico-cyanobacteria	Lab	L-PAR	Growth
Zou et al. (2011)	Macroalgae	Lab	L-PAR	Photosynthesis
Israel & Hophy (2002)	Macroalgae	Lab	SL	Growth
Fu et al. (2008b)	Dinoflagellate	Lab	L-PAR	Growth
Feng et al. (2008)	*Emiliania huxleyi*	Lab	L-PAR	Growth and photosynthesis
Gao et al. (2012)	Diatoms	Lab	~30% SL	Growth
Negative				
Wu et al. (2010)	Diatom	Lab	L-PAR	Respiration & photoinhibition
Gao et al. (2012)	Diatoms	Lab	>40% SL	Growth
Rokitta & Rost (2012)	*Emiliania huxleyi*	Lab	M-PAR	Growth
Levitan et al. (2010)	*Trichodesmium* sp.	Lab	L-PAR	Electron transport rate
Riebesell et al. (2000)	*Emiliania huxleyi*	Lab	L-PAR	Calcification & morphology
Feng et al. (2008)	*Emiliania huxleyi*	Lab	M-PAR	Calcification
Gao et al. (2009)	*Emiliania huxleyi*	Lab	PAR+UV	Calcification & photosynthesis
Gao & Zheng (2010)	Coralline algae	Outdoor	SL+UV	Calcification & photosynthesis & growth
Zou et al. (2011)	Macroalgae	Lab	L-PAR	Respiration
Chen & Gao (2011)	*Phaeocystis globasa*	Outdoor	SL+UV	Growth & photochemical yield
Russell et al. (2009)	Coralline algae	Lab	L-PAR	Abundance

CCMs is suggested to be closely related to the intracellular inorganic carbon (C_i) pool and be dependent on oxygen availability (Woodger et al. 2005). CO_2 levels (up to 1000 µatm) relevant to future CO_2 levels projected for 2100 have also been confirmed to down-regulate CCMs in marine diatoms (Chen & Gao 2003, 2004a, Rost et al. 2003, Wu et al. 2010), though CO_2 concentrations at which CCMs become completely switched off have not confirmed for different taxa. Down-regulation of CCMs can include decreased CO_2 affinity or increased CO_2 requirements for photosynthesis, inhibited carbonic anhydrase activity, and depressed HCO_3^- transport. Such down-regulation was found to be synchronized with diurnal photosynthetic performance in the diatom *Skeletonema costatum* (Chen & Gao 2004a,b). In a freshwater cyanobacterium (*Synechocystis* PCC6803), CO_2 concentration *in vitro* acts as a signal to control the activity of the NDH-1 complex (involved in cyclic electron flow around Photosystem I [PSI]), which in turn functions in the regulation of CO_2 uptake (Deng et al. 2003). Notably, doubling of ambient [CO_2] was recently suggested to save about 20% of the CCM-related energy expenditure in some diatoms, decreasing the total energy expended on carbon fixation by between 3 and 6% (Hopkinson et al. 2011). This estimate of saved energy expenditure parallels the 5% increase in growth rate observed in *Phaeodactylum tricornutum* when grown under 1000 µatm CO_2 (Wu et al. 2010). However, in the same diatom, CO_2-induced seawater acidification was shown to increase mitochondrial respiration and inhibit photosynthetic electron transport (Wu et al. 2010; our Fig. 1), which indicates an additional energy demand to re-equilibrate the perturbed acid–base balance during the night period under ocean acidification conditions. Although this additional energy demand should also happen during the daytime, this may be offset by the saved energy from down-regulation of CCM activity. On the other hand, cAMP metabolism was shown to be involved in controlling CCM in a diatom under elevated CO_2 levels (Harada et al. 2006). Recently, across a CO_2–pH gradient off the volcanic island of Vulcano (NE Sicily), periphyton communities altered significantly as CO_2 concentrations increased, with significant increases in chlorophyll *a* concentrations and in diatom abundance (Johnson et al. in press). This implies a possibility that the 'winners' could have increased their photosynthetic antenna to capture additional light energy to cope with the extra energy demand (such as enhanced respiration) due to increased seawater acidity.

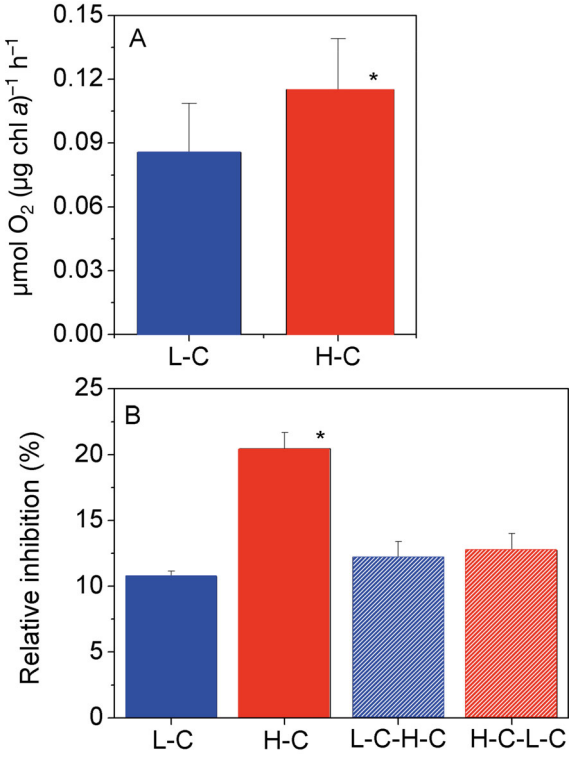

Fig. 1. *Phaeodactylum tricornutum*. (A) Dark respiration rate of low (L-C, 390 µatm) and high CO_2 (H-C, 1000 µatm) grown diatom cells, and (B) inhibition of electron transport measured under an actinic light level of 1200 µmol m^{-2} s^{-1} in L-C, H-C, or L-C grown cells measured under H-C condition (L-C-H-C) and vice versa (H-C-L-C); error bars represent SD (n = 3 to 12). *Significant ($p < 0.05$) differences. (Redrawn from Wu et al. 2010)

For calcifying coccolithophores, the efficiency of CCMs is still controversial. *Emiliania huxleyi* is able to concentrate inorganic carbon within its cells to a level about 10 times higher than the ambient (Sekino & Shiraiwa 1994); however, other studies show that the coccolithophorids *Pleurochrysis carterae* and *E. huxleyi* do not operate highly efficient CCMs (Nimer & Merrett 1992, Israel & Gonzalez 1996). On the other hand, it is still uncertain whether intracellular calcification in coccolithophores, which use bicarbonate and calcium ions to generate calcite and CO_2 ($2HCO_3^- + Ca^{2+} = CaCO_3 + CO_2 + H_2O$) (Hutchins 2011), provides a source of CO_2 for photosynthesis in these organisms (Zondervan 2007). A recent study demonstrated a photoprotective role of the calcification in *E. huxleyi* (Xu & Gao 2012). Calcification in some species of coccolithophores does not seem to be affected by elevated CO_2 and reduced pH (Langer et al. 2006). Calcification of one *E. huxleyi* strain was stimulated at low pH on a per-cell basis (Iglesias-Rodriguez et al. 2008a), a result that supported an earlier study on the same species (Fritz 1999). How-

ever, the Iglesias-Rodriguez et al. (2008a) results showed no increases in the cellular particulate inorganic carbon (PIC) to particulate organic carbon (POC) ratio (PIC:POC) at high pCO_2, and their methods and interpretations are still being debated (Riebesell et al. 2008, Iglesias-Rodriguez et al. 2008b). Notably, a recent global-scale water column and sediment core study found that coccolith mass declines nearly linearly with increasing pCO_2 or decreasing CO_3^{2-} ion levels (Beaufort et al. 2011). Other photosynthetic calcifiers may respond differently to ocean acidification; for instance, elevated DIC resulted in both enhanced photosynthesis and calcification in a coralline alga (Gao et al. 1993).

From a physiological point of view, increased CO_2 availability and the associated decline of pH should act differentially to affect primary producers, with the former saving energy required for active inorganic carbon acquisition and the latter potentially increasing energy demand to maintain cellular homeostasis relative to the increased acidity of seawater. Therefore, effects of ocean acidification on algal species or cyanobacteria would largely depend on their species-specific energetics and related physiological regulation, and subsequently their responses to ocean acidification would be altered by light as well as other environmental factors. Growth or photosynthetic responses to elevated pCO_2 are generally modulated by light energy availability, being typically most pronounced under low (Gao et al. 2012, Rokitta & Rost 2012) or stressful high (Gao et al. 2012) light levels. In a high-CO_2 ocean, increased pCO_2 and lowered pH cannot be considered separately as 2 independent factors, and double-edged effects of ocean acidification would be expected under different environmental conditions. Over long adaptation periods, ocean acidification may cause genetic alteration such as loss of CCM capabilities, and the evolved communities of the future are likely to be genetically different from contemporary communities (Collins et al. 2006). For instance, adaptation under ocean acidification condition for about 500 generations led to restored calcification in *Emiliania huxleyi* (Lohbeck et al. 2012).

PRIMARY PRODUCERS IN A WARMER AND ACIDIFIED OCEAN

The accumulation of CO_2 in the atmosphere traps heat reflected as infrared radiation (>700 nm), and both terrestrial and aquatic environments are thus being warmed. Although global mean SSTs are rising at only half the rate of those on land (0.13 vs. 0.27°C per decade since 1979), increasing temperature is one of the most pervasive of present-day influences on marine systems (Halpern et al. 2008). Warming trends are already believed to be changing the distributions and ecological niches of major phytoplankton groups like dinoflagellates (Peperzak 2003, Cloern et al. 2005, Hallegraeff 2010, Fu et al. 2012, this Theme Section), diatoms, and coccolithophores (Merico et al. 2004, Hare et al. 2007). A 50 yr (1960 to 2009) time series survey revealed a decline in dinoflagellate abundance in the northeast Atlantic and North Sea (Hinder et al. 2012) due to ocean warming and windy conditions. The combination of warming and higher light intensities during a mesocosm experiment resulted in significant acceleration of the spring phytoplankton bloom and changes in dominant species (Lewandowska & Sommer 2010).

Different habitats or latitudes have differences in annual and daily temperature means and ranges, and marine primary producers are subjected to substantial changes of temperature on various timescales. These include rapid shifts associated with tidal displacement of the thermocline or tidal immersion/emersion, diurnal fluctuations caused by clouds and changes in solar elevation, seasonal variations caused by changes in solar declination, and long-term inter-annual variability associated with natural climatic cycles and likely, human influence (Raven & Geider 1988, Davison 1991). These changes in temperature can influence the thermal windows of marine organisms by influencing their enzymatic efficiency and heat tolerance (Pörtner & Farrell 2008).

For primary producers, photosynthesis usually increases with increased temperature to reach an optimum and then declines with further warming, while respiration increases with increased temperatures, in a similar way to terrestrial plants (Zou et al. 2011). The respiration coefficient (Q_{10}, change in respiration rate over 10°C temperature change) increased with increased CO_2 concentrations in the brown macroalga *Hizikia fusiformis* (Zou et al. 2011). These authors documented a steeper slope of respiration versus temperature under increased levels of CO_2, reflecting a synergistic effect of elevated CO_2 and temperature on respiration. Respiration of phytoplankton may also increase under ocean acidification. In the diatom *Phaeodactylum tricornutum*, increase of pCO_2 from 390 to 1000 µatm (equivalent to 1000 ppmv in air) resulted in about a 30% increase in respiration (our Fig. 1; Wu et al. 2010), though combined effects of ocean acidification and warming on phytoplankton respiration, to the best of our know-

ledge, have not been documented. Since both photosynthesis and respiration will likely be influenced by ocean warming and ocean acidification, but probably to a different extent, the ratio of photosynthetic carbon fixation to respiratory carbon loss within the euphotic zone will vary in future warmer and acidified oceans.

Despite the obvious environmental relevance of these types of interactions between rising temperature and CO_2, there have been surprisingly few studies in which the effects of both factors have been considered together on marine primary producers. Recently, Connell & Russell (2010) found that simulated future CO_2 and temperature interacted synergistically to have a positive effect on the abundance of algal turfs. Species diversity and richness or ecological niche partitioning may be altered, since growth responses to the combined effects of ocean acidification and warming are likely to be species-specific. Two strains of the marine picocyanobacteria *Synechococcus* and *Prochlorococcus* responded differentially to warming as well as to elevated CO_2, with the growth rate of the former increasing and that of the latter not changing under the combined 'greenhouse' treatment (our Fig. 2) (Fu et al. 2007). Growth and nitrogen fixation rates of 2 isolates of the filamentous cyanobacterium *Trichodesmium* were strongly enhanced by either increasing CO_2 (750 µatm) or a 4°C temperature increase, but synergistic effects between the 2 variables were not observed (Hutchins et al. 2007). Levitan et al. (2010) reported similar findings for these 2 parameters in one of these same *Trichodesmium* isolates under the combination of warmer temperature (+6°C) and higher CO_2 (900 µatm).

In cultures of a Sargasso Sea isolate of the coccolithophore *Emiliania huxleyi*, growth and photosynthesis were stimulated by increases in both CO_2 and temperature, but no significant interactive effect was found between the 2 (Feng et al. 2008). That study found that although PIC production was affected by the combination of irradiance and acidification changes (see 'Light limitation and stress interactions with ocean acidification'), these calcification processes were independent of a 4°C temperature rise. In cultures of another *E. huxleyi* strain, De Bodt et al. (2010) found that elevated CO_2 stimulated photosynthetic carbon fixation, while both high CO_2 and temperature independently decreased calcification, but with no apparent interactions between the 2 factors. Another recent study found that temperature and CO_2 did have significant interactive effects on POC quotas and production rates in the coccolithophore

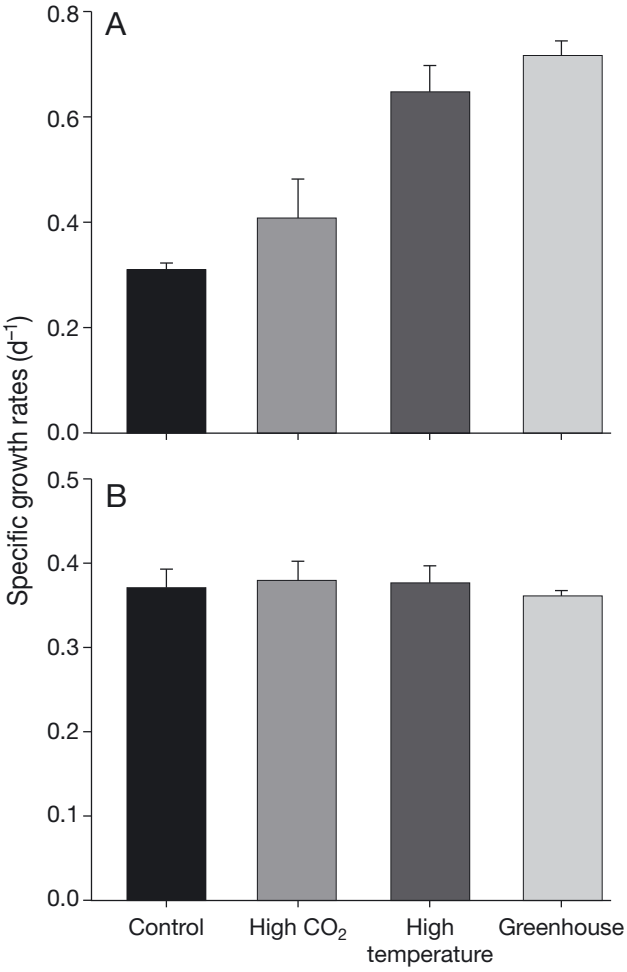

Fig. 2. Cell-specific growth rates of cultured (A) *Synechococcus* strain CCMP 1334 and (B) *Prochlorococcus* strain CCMP 1986 in a temperature and CO_2 matrix experiment. Treatments used were 20°C and 380 µatm CO_2 (control), 20°C and 750 µatm CO_2 (high CO_2), 24°C and 380 µatm CO_2 (high temperature), and 24°C and 750 µatm CO_2 (greenhouse). In (A), the right 2 bars are significantly different from the left 2, but no other differences; in (B), no significant differences. Error bars are SD of triplicate cultures for each treatment. (From Fu et al. 2007)

Syracosphaera pulchra, but these interactions were life-stage specific, with much greater impacts in haploid than in diploid cells (Fiorini et al. 2011). A 5°C temperature rise increased photosynthesis and calcification of *E. huxleyi* only at the ambient Ca^{2+} concentration (10 mM), whereas it decreased both processes in cells grown at 1% of ambient Ca^{2+} concentration (Xu et al. 2011). In contrast, in an experiment using a mixed natural North Atlantic bloom community, Feng et al. (2009) found that coccolithophore cell abundance was greatly increased under the 'greenhouse' combination of increased pCO_2 and temperature, but not when either one was increased

alone (our Fig. 3A). Paradoxically, they also found that calcite production was significantly lower in this greenhouse treatment (our Fig. 3B), even though it had by far the highest numbers of coccolithophores. They suggested that future trends in the North Atlantic bloom could include larger and denser blooms of coccolithophores, but that at the same time these cells might be much less calcified than under present-day conditions. Recent culture work, however, suggests large variability in the ability of different phytoplankton taxa to adapt to sequentially increasing temperatures, and 2 strains of *E. huxleyi* were among the species that were found to be unable to adapt to pronounced warming (e.g. a growth temperature increase from 22 to 30°C; Huertas et al. 2011). Further studies looking at the potential for long-term adaptation of algae to higher temperatures is needed, especially in combination with acidification and other global change variables.

While ocean acidification and warming lower coral-reef resilience (Anthony et al. 2011), algal reef builders also respond to these factors. Macroalgal calcifiers, which deposit $CaCO_3$ in their intercellular spaces or thallus surface, respond negatively to elevated pCO_2. Ocean acidification reduces the calcification of the red coralline algae (Gao et al. 1993, Gao & Zheng 2010), green algae *Halimeda* spp. (Sinutok et al. 2011), and brown algae *Padina* spp. (Johnson et al. 2012). The combination of ocean acidification and warming decreased photochemical yield, chlorophyll content, and calcification in *Halimeda* spp., indicating that 32°C and 1000 µatm CO_2 are the upper limits for survival of these organisms on the reef at Heron Island, Australia (Sinutok et al. 2011).

The combined effects of warming and acidification are likewise quite variable in other eukaryotic algae. In a comparative study of 2 co-occurring estuarine harmful bloom flagellate species, the maximum light-saturated carbon fixation rate (P^B_{max}) of the raphidophyte *Heterosigma akashiwo* was increased only with simultaneous increases in both CO_2 and temperature, whereas P^B_{max} of the dinoflagellate *Prorocentrum minimum* responded to CO_2 enrichment with or without increased temperature (Fu et al. 2008b). A shipboard incubation study that examined rising temperature and CO_2 in 2 natural Bering Sea assemblages found large community shifts away from diatoms and towards nanoflagellates in the 'greenhouse' treatment, although these appeared to be due more to changes in temperature than in CO_2 (Hare et al. 2007). Likewise, higher temperatures reduced the abundance of diatoms in the Feng et al. (2009) North Atlantic bloom incubation study, while

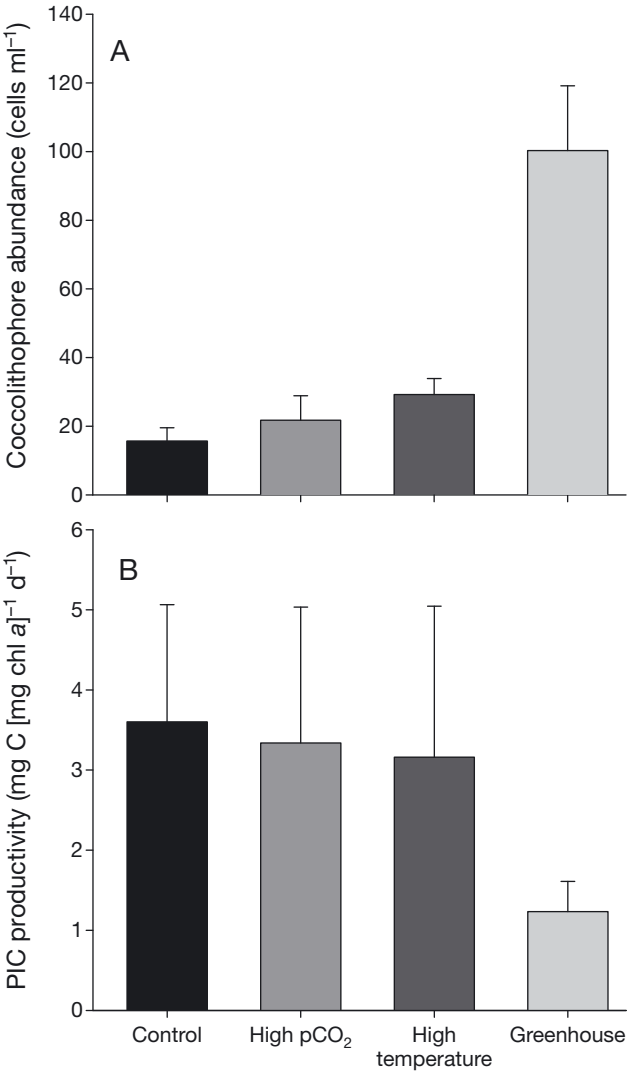

Fig. 3. (A) Final coccolithophore cell abundance and (B) particulate inorganic carbon (calcite or PIC) production rates in a temperature and CO_2 matrix experiment using a natural North Atlantic spring bloom phytoplankton community. Treatments used were 12°C and 390 µatm CO_2 (control), 12°C and 690 µatm CO_2 (high CO_2), 16°C and 390 µatm CO_2 (high temperature), and 16°C and 690 µatm CO_2 (greenhouse). In (A), right bar is different from the other 3 ($p < 0.05$), but none of the other 3 differ from each other ($p > 0.05$); in (B), same pattern as (A). Error bars are SD of triplicate treatments. (From Feng et al. 2009)

CO_2 changes had no apparent effect on diatom dominance. A similar finding was reported in a coastal regime, Daya Bay in China, where long-term inputs of thermal effluent from a power plant shifted the community from diatoms to dinoflagellates, although CO_2 was not considered in that study (T. Li et al. 2011). However, a 50 yr (1960 to 2009) survey in the northeast Atlantic and North Sea did not observe any decline in the abundance of diatoms (Hinder et al.

2012). On the other hand, there may be a strong shift in the biogeochemical cycling of organic matter in the upper ocean in response to increased temperature that will affect pelagic food web structure and the biological sequestration of organic matter (Wohlers-Zöllner et al. 2011), though interactive effects of ocean warming and acidification on important biogeochemical cycles are still uncertain.

LIGHT LIMITATION AND STRESS INTERACTIONS WITH OCEAN ACIDIFICATION

Visible light or PAR (400 to 700 nm) drives photosynthesis in the marine environment in a way that is more dynamic than in the terrestrial environment, since light quantity and quality changes rapidly with depth due to differential attenuation of different wavelengths. Light levels under which phytoplankton cells must photosynthesize can range from limiting to stressful depending on their mixing regime within the UML, as well as the season and time of day.

Under low light or reduced levels of solar PAR, growth or photosynthesis of many phytoplankton groups, including diatoms (Riebesell et al. 1993, Kim et al. 2006, Wu et al. 2010, Sun et al. 2011), coccolithophores (Riebesell et al. 2000, Leonardos & Geider 2005), dinoflagellates and raphidophytes (Fu et al. 2008b), and cyanobacteria (Hutchins et al. 2007, Fu et al. 2008a, Kranz et al. 2010, Levitan et al. 2010, Garcia et al. 2011), as well as some macroalgae (Gao et al. 1991, 1993, 1999, Zou et al. 2011), is often stimulated under elevated CO_2 conditions (our Table 1). For intertidal algae, increasing atmospheric CO_2 concentration enhances their photosynthetic CO_2 fixation rate during emersion at low tide (Gao et al. 1999, Zou & Gao 2002). However, non-responsiveness of photosynthetic carbon fixation to increased CO_2 or ocean acidification has also been shown in both phytoplankton (Tortell & Morel 2002) and macroalgae (Israel & Hophy 2002) (our Table 1).

Some of the best documented interactive effects between ocean acidification and PAR have been observed in *Trichodesmium*. Kranz et al. (2010), Levitan et al. (2010), and Garcia et al. (2011) all showed that CO_2-driven enhancement of N_2 fixation and growth rates is greatest at low, limiting light levels, while this effect is considerably muted at higher levels of PAR, possibly due to down-regulation of nitrogenase enzyme iron protein (NifH) synthesis (our Fig. 4). Under high light, elevated CO_2 concentration significantly depressed NifH levels compared to low light (our Fig. 4). Garcia et al. (2011) also found that gross:net N_2 fixation (gross being total N fixed, while net is N retained by the cell, as in gross or net photosynthetic carbon fixation) ratios were highest at low light and high pCO_2, and declined with successive increases in light or decreases in pCO_2. Trends in trichome (cell chain) length in the cultures were inversely related to those of the gross:net N_2 fixation ratios, although whether these 2 effects are connected, and why, is uncertain. These gross:net ratio effects imply that *Trichodesmium* cells exude or lose much more of their total fixed N at high CO_2. This effect is likely to be greatest deep in the euphotic zone, but may be reduced in future shallow mixed layers at high light intensities. In general, the overall

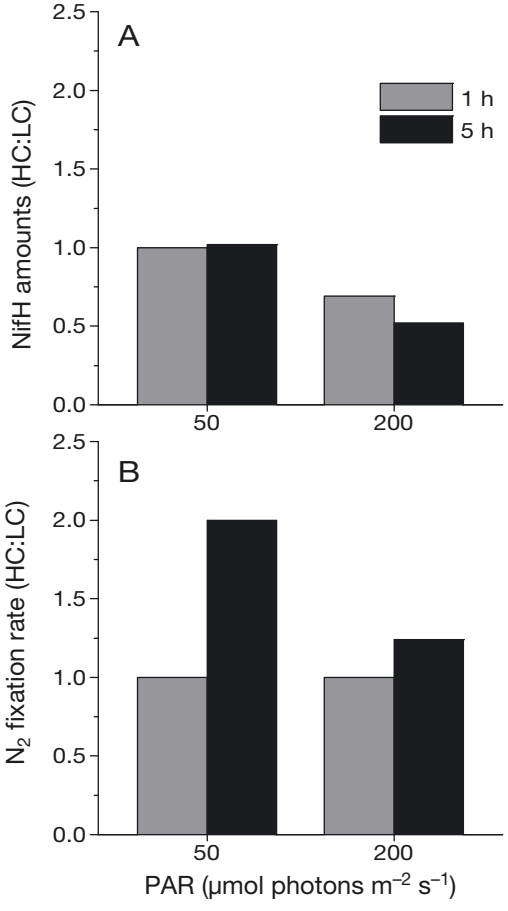

Fig. 4. *Trichodesmium* strain IMS101. (A) Changes in the amount of the nitrogenase iron protein, NifH (pmol mg protein^{-1}) and (B) nitrogen fixation rate in response to different light (50 and 200 µmol photons m^{-2} s^{-1}) and pCO_2 (150 and 900 µatm) levels. The values are indicated as the ratios of high (HC, 900 µatm) to low CO_2 (LC, 150 µatm), measured at 1 and 5 h after the onset of light. PAR: photosynthetically active radiation. (Data re-drawn from Kranz et al. 2010 and Levitan et al. 2010)

weakening of the well-documented positive effect of high pCO_2 on N_2 fixation in this biogeochemically critical cyanobacterium at higher irradiances also means that shoaled UML depth may need to be taken into account for accurate predictions of ocean acidification impacts on future N_2-supported new production. In addition, changes in PAR quality due to differential attenuation of different light wavelengths with changed UML depth might also interact with ocean acidification or warming to affect cyanobacterial physiology and N_2 fixation as well as that of other phytoplankton groups. Nevertheless, the high flexibility in resource and energy allocation by *Trichodesmium* should enable this important organism to flourish in future surface oceans characterized by elevated pCO_2, higher temperatures, and increased light exposures (Levitan et al. 2010), although little has been documented about its physiological performance under solar radiation.

Ocean acidification and PAR interactions can often be identified and quantified by examining photosynthesis versus light (*P–E*) relationships under varying pCO_2. For instance, in the toxic harmful bloom diatom *Pseudo-nitzschia multiseries*, Sun et al. (2011) found significant sequential increases in P^B_{max} (maximum biomass-normalized carbon fixation rates) across 3 pCO_2 levels. However, for this diatom, α values (the slope of the light-limited portion of the curve) and E_K (the light saturation point) did not change with acidification. Frequently, these types of experiments demonstrate non-linear effects on *P–E* parameters. For instance, Feng et al. (2008) found that in *Emiliania huxleyi* cultures grown under low light, P^B_{max} was much higher in combined high-pCO_2, high-temperature 'greenhouse' treatments than when either CO_2 or temperature were increased alone. Similar additive or non-linear 'greenhouse' enhancements of P^B_{max} have been seen in the raphidophyte *Heterosigma* sp. (Fu et al. 2008b), the cyanobacteria *Synechococcus* sp. and *Trichodesmium* sp. (Fu et al. 2007, Hutchins et al. 2007), and in a natural assemblage from the Bering Sea (Hare et al. 2007). In contrast, Feng et al. (2010) found no physiological interactive effects of light and CO_2 on community P^B_{max} in an experiment using a Ross Sea diatom–*Phaeocystis* assemblage. Instead, they observed a diatom community structure shift away from small pennate diatoms towards much larger centric diatoms when high CO_2 was combined with high light. This might be related to the difference in photo-physiological performance between large and small diatoms (Wu et al. 2011). Susceptibility to photo-inactivation under high light is less in larger than in smaller diatom species, and is higher under ocean acidification conditions compared to ambient CO_2 level (our Fig. 5; Key et al. 2010, McCarthy et al. 2012). Phytoplankton cell size controls the efficiency of elements or energy transfer, and thus the assembly of higher trophic levels in marine food chains (Raven 1998, Finkel et al. 2010). Light absorption (Fujiki & Taguchi 2002) and photosynthesis (Raven & Kübler 2002) are also known to differ among differently sized algal cells. The pigment-specific light absorption increases with decreasing cell size (Fujiki & Taguchi 2002), leading to higher light-use efficiency as well as solar radiation exposures per unit pigment or per cell volume (Jeffrey et al. 1996). On the other hand, even when experiencing the same pH reduction with the ongoing ocean acidification, smaller cells suffer differentially from the acidity increase due to differences in thickness of the diffusion layer surrounding cells (Flynn et al. 2012).

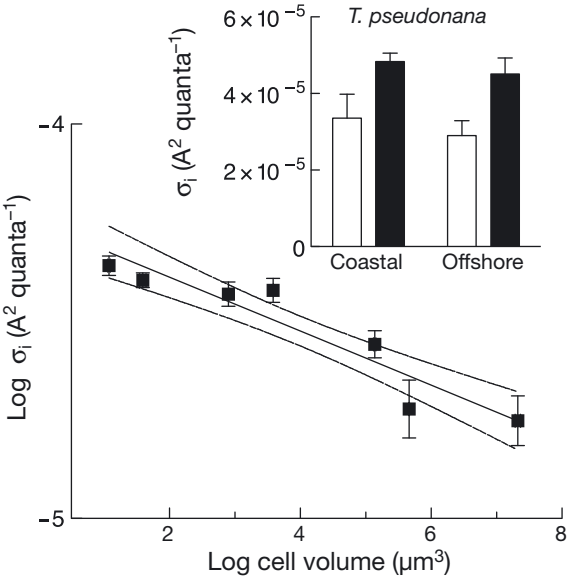

Fig. 5. *Thalassiosira* and *Coscinodiscus* spp. Smaller diatoms show higher susceptibility to photo-inactivation than large diatoms. Susceptibility to photo-inactivation of Photosystem II (PSII) (log σ_i) estimated under moderately high light for a size range of marine centric diatoms from the genera *Thalassiosira* and *Coscinodiscus*, plotted versus log cell volume (μm^3). Error bars are SD (n = 4 to 6 independent culture replicates for each strain), and dotted lines plot the 95% confidence interval for the regression. (Data re-drawn from Key et al. 2010 and Wu et al. 2011.) Inset: Susceptibility to photo-inactivation of PSII (σ_i) under moderately high light increases under increased pCO_2 for small diatoms from coastal and offshore habitats. Open bars: cells grown under 390 µatm CO_2; closed bars: cells grown under 750 µatm CO_2. Error bars are SD (n = 3 to 4). (Data re-drawn from McCarthy et al. 2012)

This implies that the combination of light and ocean acidification influences competition among species or differently sized groups, and is likely to change phytoplankton community structure in the future shoaled UML. Under laboratory constant-light levels, growth of larger diatoms is stimulated to higher extents than smaller ones, with differentially affected elemental stoichiometry (C:N:Si ratios) (Y. Wu, Z. Finkel, D. Campbell unpubl. data). Hoogstraten et al. (2012) found that growth rates of the colonial prymnesiophyte *Phaeocystis globosa* decreased with increasing pCO_2 in saturating light treatments, and suggested that this harmful bloom species could be less competitive in the future ocean as a consequence. Chen & Gao (2011) also showed depressed quantum yield and growth rate under high levels of sunlight, but they also found stimulated rates under heavy cloud cover when this species was grown under ocean acidification conditions under solar radiation.

While many laboratory or indoor studies under constant low or high PAR levels have demonstrated differential responses of different taxa to ocean acidification, few experiments have been performed under natural sunlight with changing light levels (Chen & Gao 2011). Notably, phytoplankton assemblages or diatoms showed different responses when grown under different levels of solar radiation and elevated pCO_2 (Gao et al. 2012). When exposed to CO_2 concentrations projected for the end of this century in combination with high light intensities representative of the UML, natural phytoplankton assemblages from the oligotrophic South China Sea responded with decreased primary production and increases in photo-physiological indicators of light stress (non-photochemical quenching, NPQ). At the same time, community dominance shifted away from diatoms and towards prymnesiophytes. However, under reduced sunlight intensities representing a deeper mixed layer, simulated ocean acidification did not cause such reduction in primary production (K. Gao et al. unpubl. data). To model this interactive acidification and light effect in the laboratory, Gao et al. (2012) grew representative diatoms at CO_2 concentrations of 390 and 1000 µatm across a range of solar radiation typically experienced by phytoplankton at different depths of the euphotic zone (5 to 100% of incident surface irradiance). Growth and photochemical quantum yield of the high-pCO_2 cultures were positively related to light intensity at lower light levels (5 to 36% of incident surface irradiance), but at higher light levels these parameters were negatively related to an increase in light intensity and significantly decreased compared to the cells grown at ambient CO_2 levels. This reversal of the effects of ocean acidification with increasing light levels suggests that under low levels of sunlight or at deeper depths, ocean acidification could stimulate diatom growth, but would be inhibitory under high solar exposures at shallower depths or at midday. Down-regulated CCMs due to increased availability of CO_2 and up-regulated energy demands due to acid–base perturbation appear to act synergistically to induce additional light stress to the cells, as evidenced by the increased NPQ in both the diatom cultures and the natural phytoplankton assemblages from the South China Sea and decreased PAR threshold in the diatoms grown at the elevated pCO_2 (Gao et al. 2012). Such enhanced light stress under ocean acidification and stimulated mitochondrial and photo-respiration could be mechanistically responsible for the decline of primary production or growth rate (our Fig. 6, based on the results presented in Gao et al. 2012). Hypothetically, with increasing availability of CO_2 and progressive acidification of seawater, phytoplankton cells at deeper depths receiving low light levels would increase their growth, while those near the surface receiving higher levels of sunlight would decrease their growth, with the PAR threshold at which growth becomes saturated declining (Fig. 7). Whether such a synergistic effect of high levels of CO_2 and light are unique for diatoms or are widespread among phytoplankton taxa remains to be investigated. However, 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, the impacts this effect may have on ocean productivity would be severe. Since future shoaling of UML depths is expected to expose phytoplankton to increased mean light intensities, reduced marine primary production along with community structure changes seem likely in future high-CO_2 oceans.

Photoautotrophs experience subsaturating, saturating, and stressful light levels even during a single daily solar movement. Under supra-optimal light-saturated conditions, algal cells need to dissipate additional energy they receive, and any other environmental stresses could affect the threshold at which PAR becomes excessive (Fig. 7). Therefore, increased acidity or a disturbed acid–base balance could affect light use efficiency or lower the PAR levels above which light becomes excessive (Gao et al. 2012). Photoinhibition of electron transport was exacerbated under ocean acidification when the diatom *Phaeodactylum triconutum* was exposed to high light levels

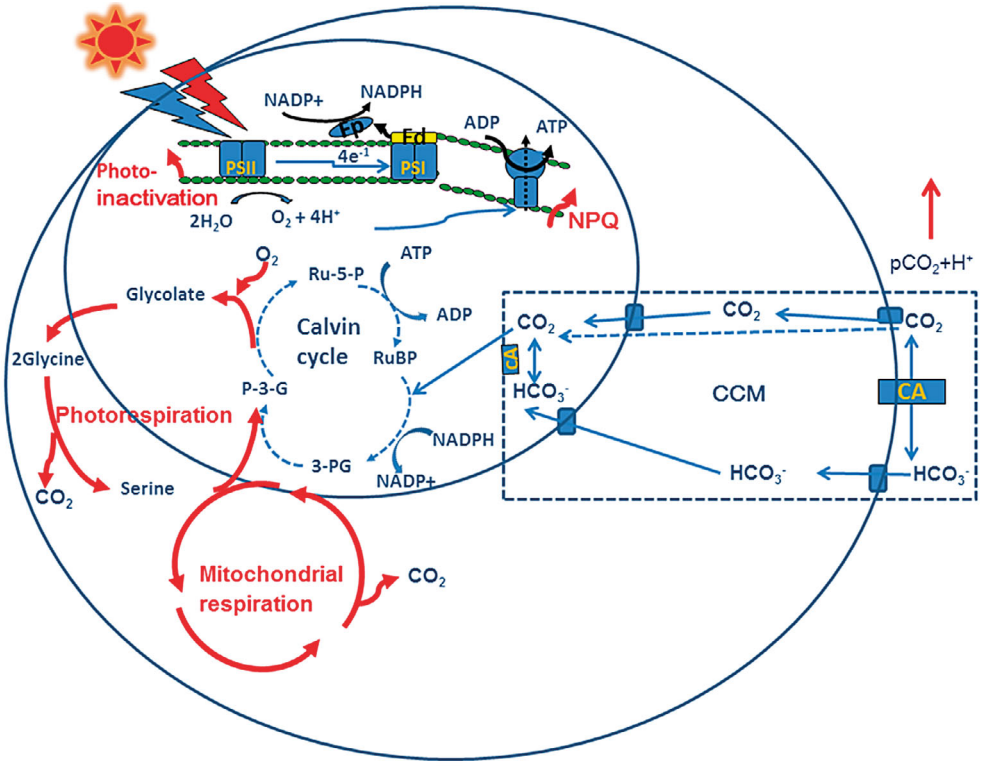

Fig. 6. Metabolic pathways up-regulated (red and solid) and down-regulated (blue and dotted) under ocean acidification. Phytoplankton down-regulate their CO_2-concentrating mechanisms (CCMs) under increased CO_2 levels and save energy expenditure on carbon acquisition, but this may trigger additional light stress when cells are exposed to high light intensity at the same time. Meanwhile, cellular defenses are enhanced, including increased non-photochemical quenching (NPQ), enhanced mitochondrial respiration, and photorespiration. However, these protective activities are not enough to fully compensate for photodamage, thus carbon fixation (the Calvin cycle) and growth rate are ultimately reduced under sunlight. PSI: Photosystem I; PSII: Photosystem II; CA: carbonic anhydrase; Fd: ferredoxin (Generated from the concepts in Gao et al. 2012)

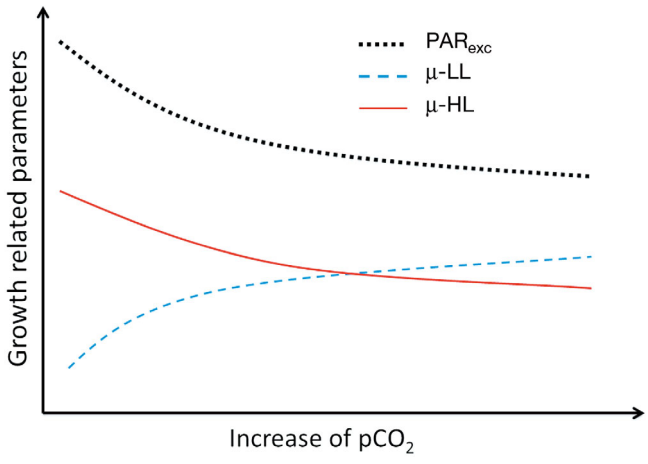

Fig. 7. Hypothetical relationship between growth-related parameters and increasing pCO_2, based on recent findings in some diatoms (Gao et al. 2012). PAR_{exc}: photosynthetically active radiation (PAR) threshold beyond which growth rate of a phytoplankton species declines with increasing light levels; μ-LL: specific growth rate under sub-saturating light levels; μ-HL: specific growth rate under super-saturating light levels

(our Fig. 1; Wu et al. 2010). In another diatom, *Thalassiosira pseudonana*, however, such an inhibition was not observed under the same CO_2 level (Yang & Gao 2012). In *Skeletonema costatum*, growth was not affected by elevation of CO_2 concentration (up to 1000 μatm) under either 30 or 210 μmol photons m^{-2} s^{-1} of PAR; however, at 30 μmol photons m^{-2} s^{-1} PAR and reduced CO_2 levels of 100 μatm, the growth of this diatom was significantly decreased (Chen & Gao 2003), likely reflecting that light energy availability affects the operation of CCMs that provide the carbon source for carboxylation. In contrast, in a mesocosm study under reduced levels of natural solar radiation, only the diatom *S. costatum* showed an increased growth rate with increased pCO_2 (Kim et al. 2006). In cultures of the diatom *Chaetoceros muelleri*, low-light treatments showed lower growth rates in elevated CO_2 or reduced pH conditions, but no CO_2 or pH effect was recorded under high light exposure, reflecting that light supply does alter the cell's response to ocean acidification (Ihnken et al. 2011). In *T. pseudonana*, since photosynthetic carbon fixation and respiratory

carbon loss were equally stimulated under the ocean acidification, growth rate was not affected (Yang & Gao 2012). Although indoor laboratory studies have provided useful information about the relationship of ocean acidification and light levels, it should be noted that fluctuating light levels in the mixed layer might modulate C_i acquisition efficiencies in different ways compared to the constant light levels under which cultures are usually maintained in the laboratory. Further interactive ocean acidification–light experiments are needed that use more realistic variable-irradiance regimes.

Coccolithophores, as key photosynthetic $CaCO_3$ producers, form extensive blooms in many regimes, and are sensitive to both acidification and PAR (Boyd et al. 2010). A recent field survey in the North Sea–Arctic Ocean identified pH and light as the 2 key environmental controls on coccolithophore community composition throughout this region (Charalampopoulou et al. 2011). When grown under indoor conditions (either light-limiting or -saturating), they usually demonstrate a decline of calcification rates under high pCO_2 and low pH conditions (Riebesell et al. 2000, Sciandra et al. 2003, Delille et al. 2005, Gao et al. 2009). In *Emiliania huxleyi,* different light:dark cycles (16:8 or 24:0 h) did not result in significant growth rate differences, and both PIC and POC production per cell increased with increased PAR within a range of 20 to 150 µmol photons m^{-2} s^{-1}, leading to insignificant changes in the PIC:POC ratio at the lowest irradiance, at which it was much lower. Increased CO_2 up to about 1050 µatm did not affect the specific growth rate as much as increased light levels, which increased POC content per cell (Zondervan et al. 2001). In the same species, the PIC:POC ratio was decreased when the cells were grown at 400 µmol photons m^{-2} s^{-1} compared to those at 50 µmol photons m^{-2} s^{-1}, and were further decreased by increased CO_2 and lowered pH, but only at the elevated PAR intensity (Feng et al. 2008). On the other hand, seawater acidification associated with elevated pCO_2 enhanced photosynthesis in coralline algae under indoor low PAR (Gao et al. 1993), but reduced it under incident high solar PAR (Gao & Zheng 2010). Photosynthetic carbon fixation or POC production often shows a positive relationship with calcification or PIC generation in coccolithophores (Paasche 2001, Zondervan et al. 2001, Feng et al. 2009, Xu & Gao 2012) and coralline algae (Borowitzka 1981, Gao et al. 1993) with increased light. Light limitation would result in less availability of ATP to drive algal calcification. However, under ocean acidification conditions, even photosynthesis-saturating levels led to decreased calcification in *E. huxleyi* (Feng et al. 2008, Gao et al. 2009). When grown at a PAR level of 300 µmol photons m^{-2} s^{-1}, the growth rate of both diploid and haploid *E. huxleyi* decreased at the elevated pCO_2 compared to those grown at the ambient level (Rokitta & Rost 2012). These findings indicate that, even when there is sufficient light energy, calcification is still suppressed by altered seawater chemistry under ocean acidification, which contrasts to the finding that calcification in some bivalves (Melzner et al. 2011) or corals (Holcomb et al. 2010) is not affected by ocean acidification when sufficient energy (food) is available.

COMBINED EFFECTS OF OCEAN ACIDIFICATION AND UV RADIATION

Solar UV radiation (280 to 400 nm) harms both primary producers and their consumers in aquatic ecosystems, decreasing productivity and disturbing reproduction and development (Häder et al. 2011). Although enforcement of the Montreal Protocol has slowed down ozone depletion, recent studies indicate a 10% increase in UV-B irradiance (280 to 315 nm) reaching northern temperate regions between 1983 and 2003 (Josefsson 2006). Most recently, a massive ozone hole was discovered in the Arctic, reflecting an interactive impact of climate change on ozone depletion (Manney et al. 2011). Global warming leads to less heat release to the stratosphere, and thereby enhances ozone depletion reactions, which occur faster when the stratosphere becomes further cooled. UV irradiances can penetrate as deep as 80 m in pelagic oceans (Tedetti et al. 2007), depending on the transparency of seawater. Open-ocean phytoplankton cells are generally more sensitive to UV inhibition than coastal assemblages (Fritz et al. 2008, G. Li et al. 2011). This may be because positive UV-A effects on photosynthetic carbon fixation were only found in coastal water phytoplankton assemblages, and because pelagic phytoplankton species are often smaller and more light-acclimated due to less mixing, and must deal with less availability of nutrients compared to those in coastal waters (G. Li et al. 2011).

Solar UV-B irradiance is known to decrease photosynthetic carbon fixation (Helbling et al. 2003, Gao et al. 2007, Häder et al. 2011), damage DNA (Buma et al. 2001, 2006, Gao et al. 2008) and proteins (Bouchard et al. 2005, Wu & Gao 2009), and even alter morphology (Wu et al. 2005) of photosynthetic organisms. It is also suggested to reduce genome stability in terrestrial plants (Ries et al. 2000). On the other hand, mod-

erate levels of UV-A (315 to 400 nm) are recognized to stimulate photosynthetic carbon fixation of phytoplankton assemblages (Barbieri et al. 2002, Helbling et al. 2003, Gao et al. 2007) and macroalgae (Gao & Xu 2008, Xu & Gao 2010), and enhance the activity of carbonic anhydrase, which facilitates bicarbonate utilization in a diatom (Wu & Gao 2009). Low levels of UV-A irradiances are known to stimulate repair of UV-B-induced DNA damage (Buma et al. 2001). DNA repair is also enhanced at higher temperatures (Gao et al. 2008). Therefore, contrasting effects of UV radiation (280 to 400 nm) on photosynthetic organisms can be observed between cloudy periods, when light is limiting and UV-A stimulative, and sunny days, when PAR becomes excessive and UV radiation more harmful (Gao et al. 2007). When the negative and positive effects are in balance, UV impacts can be neutral and disappear entirely (Wahl et al. 2004, Molis & Wahl 2009). Since UV-A and UV-B can affect photosynthetic CO_2 fixation in various and even opposing ways, it may interact with ocean acidification to affect marine primary producers differently under varying climate conditions (Chen & Gao 2011).

For the coccolithophore *Emiliania huxleyi* (Gao et al. 2009) and a coralline alga *Corallina sessilis* (Gao & Zheng 2010), reduced levels of calcification due to ocean acidification are further decreased by the addition of UV radiation. This reflects that the calcified layer for both the micro- and macro-algal calcifiers plays a protective role against UV. The coccoliths of *E. huxleyi* reduce the transmission of harmful UV radiation by about 26% (Gao et al. 2009), and reduced coccolith thickness leads to decreased electron transport rate as well as a lower PIC:POC ratio (our Fig. 8).

While ocean acidification increases the sensitivity of photosynthesis and calcification of some algal calcifiers to UV radiation (Gao et al. 2009, Gao & Zheng 2010), the presence of UV stimulates the calcification of *Emiliania huxleyi* when grown at ambient CO_2 levels under natural solar radiation, but at the cost of reduced growth rates (Guan & Gao 2010). Although increased accumulation of UV-screening compounds, such as mycosporine-like amino acids (MAAs), is a defensive strategy employed under ocean acidification conditions by coralline algae (Gao & Zheng 2010), it is usually not sufficient for the plant to cope with the combined impacts of both stressors at once, reflecting a likely future decrease of vegetation cover by these reef-building organisms.

Elevated CO_2 levels have been shown to increase the sensitivity of some marine and freshwater phytoplankton to UV-B (Sobrino et al. 2008). In contrast, ocean acidification and moderate levels of UV-A stimulated photochemical yield and specific growth rate of the harmful bloom prymnesiophyte *Phaeocystis globosa* (Chen & Gao 2011). Intense UV-B exposure on sunny days, however, caused significant reductions of the photochemical yield and growth of this alga, and these were further decreased under ocean acidification conditions in acclimated cultures of *P. globosa* grown under natural solar radiation (Chen & Gao 2011).

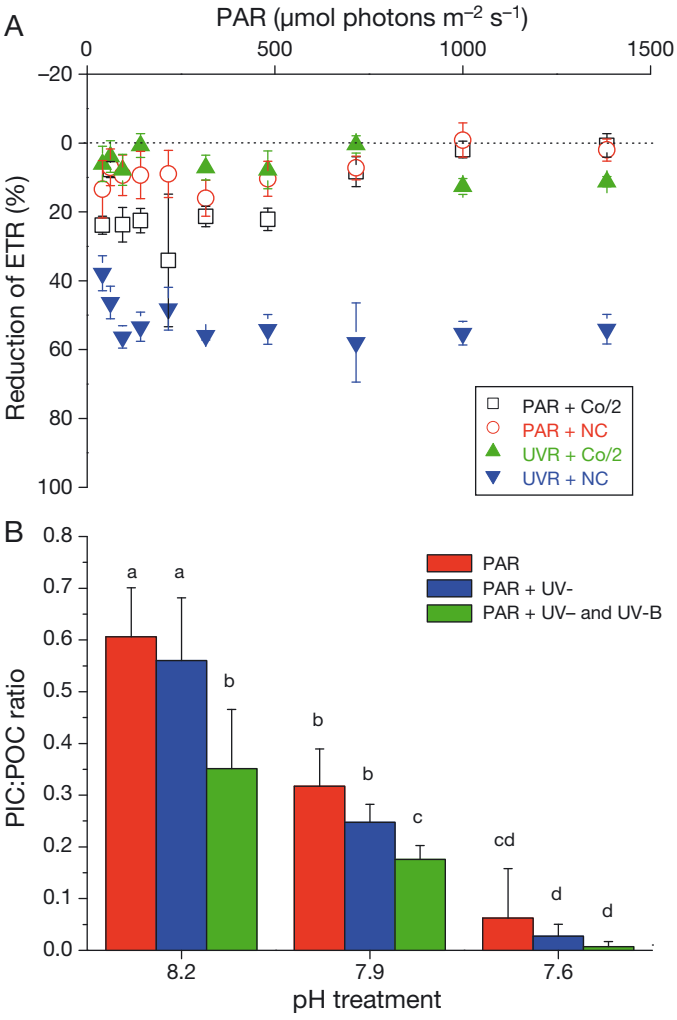

Fig. 8. *Emiliania huxleyi*. (A) Coccoliths play an important role in shielding cells from UV radiation (UVR). Removal of the coccoliths barely affects the electron transport rate (ETR) in the absence of UV (red, NC), but leads to about a 60% reduction in the presence of UV (blue, NC). PAR: photosynthetically active radiation. (Z. X. Ruan & K. Gao unpubl. data.) (B) UV-A and UV-B act synergistically with CO_2-induced seawater acidification to reduce the production ratio of particulate inorganic to organic carbon (PIC:POC ratio). Different letters indicate significant differences among the treatments. (Gao et al. 2009, with copyright permission from the Association for the Sciences of Limnology and Oceanography)

Interactive effects of UV radiation and CO_2-induced seawater acidification on phytoplankton are likely to differ between algal taxa due to species-specific differences in tolerance of UV radiation or UV-defensive strategies. For instance, coastal and pelagic phytoplankton species and assemblages can exhibit different responses to the effects of UV-A and UV-B (G. Li et al. 2011), and the extent of diel variations in seawater carbonate chemistry also differs between these 2 ecosystems. For many major functional groups of primary producers, like harmful algal species, N_2-fixing cyanobacteria, and picocyanobacteria, however, virtually nothing is presently known about their responses to combined ocean acidification and UV exposure. It is clear though that the net or balanced effects of ocean acidification on primary producers in general will depend on mixing depths, mixing rates, and fluctuations of solar radiation, which together mediate the balance between UV-induced damage and repair. Photosynthetic performance in phytoplankton assemblages (Helbling et al. 2003) or in diatoms (Guan & Gao 2008) is inhibited by UV to a lesser extent under fluctuating solar radiation or during the mixing path as compared to static (non-mixed) conditions. Therefore, it is likely that effects of ocean acidification on phytoplankton would differ when they are exposed to fluctuating light or solar radiation, as when they receive changing levels of solar radiation during vertical mixing. In general, how an organism responds to UV radiation under ocean acidification conditions may give insight as to which organisms may operate with better physiological performance in future lower-pH oceans. Li et al. (2012) showed that ocean acidification appears to counteract UV-B-induced harm to the diatom *Phaeodactylum tricornutum*. In addition, beneficial effects of increased temperature on photosynthesis under UV radiation stress have been previously documented (Sobrino & Neale 2007, Gao et al. 2008, Halac et al. 2010, Helbling et al. 2011), showing lower UV-induced inhibition or damages at higher temperatures. Differential sensitivities to UV radiation have been reported in marine picoplankters when grown under elevated CO_2 concentrations, with *Nannochloropsis gaditana* having lower sensitivity and *Nannochloris atomus* showing a neutral response (Sobrino et al. 2005). The diatom *Thalassiosira pseudonana*, when grown at elevated CO_2 concentration, became more sensitive to UV radiation (Sobrino et al. 2008). These issues require further studies to look into the physiological energetic costs and benefits in changing oceans.

CONCLUSIONS AND FUTURE WORK

Heat from solar radiation trapped in oceanic surface waters together with global warming is responsible for ocean warming. Surface ocean warming enhances stratification and reduces nutrient availability due to lower diapycnal transport of nutrients from deeper layers, as well as increases in UV exposure to phytoplankton cells circulating in a shallower mixed layer (our Fig. 9; Steinacher et al. 2010). In the tropics and at mid-latitudes, phytoplankton are typically nutrient-limited, and stratification with upper-ocean warming could lead to reduced nutrient supply and decreased growth (Fig. 9); at higher latitudes, phytoplankton cells are often light-limited, so stratification would keep them close to the surface where light levels are higher and may stimulate growth (Doney 2006). Nitrogen, phosphorus, and iron are key elements that limit marine primary production. The concentrations of these elements vary in different oceanic waters, and therefore may affect the physiological responses of phytoplankton to ocean acidification, probably differentially under different quality or intensity of solar radiation. However, only a few studies have addressed ocean acidification and nutrient interactions (Lefebvre et al. 2012), although like CO_2 and solar radiation, changes in nutrient supply rate and ratios could have large implications for biogeochemical cycles and food web interactions (e.g. the food quality of phytoplankton). Iron-limited phytoplankton in the Gulf of Alaska increase their growth rates and biomass when incubated at high CO_2 levels, probably due to increases in photosynthetic efficiency through reduced energetic demands for CCMs (Hopkinson et al. 2010). Irradiance and temperature both have documented interactions with phytoplankton iron requirements (Rose et al. 2009, Sunda & Huntsman 2011), but how these multi-variate feedbacks may change in a high-CO_2 ocean remains speculative. Even phytoplankton vitamin B_{12} requirements can be affected by acidification, and B_{12} and CO_2 levels together can help determine cellular quotas of iron and other trace metals (King et al. 2011).

Reduced thickness of surface mixed layer or UML with stratification can increase UV exposure to phytoplankton cells (Fig. 9). Increased PAR or UV dose exposure can decrease the ratio of chlorophyll to organic carbon in phytoplankton, and reduced availability of nutrients and iron can further alter this ratio, since both nutrient limitation and light stress decrease the pigmentation of photosynthetic organisms. Ocean acidification can lead to increased C:N

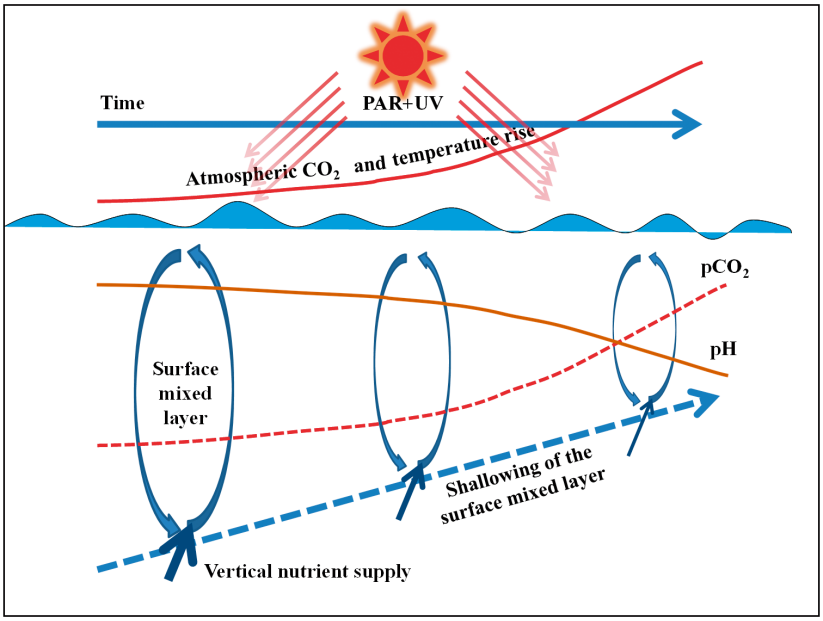

Fig. 9. Conceptual illustration of ocean changes associated with climate change. Atmospheric CO_2 and global temperature increases (red lines) lead to more CO_2 (dashed red line) dissolving in surface oceans, decreased pH (solid yellow line), and ocean warming. Increases in stratification and decreases in the thickness of the surface mixed layer due to ocean warming and freshening lead to less vertical transport of nutrients (decreasing size of upward arrows) and increasing exposure of cells to solar photosynthetically active radiation (PAR) and UV radiation. These multiple driving factors may synergistically or antagonistically interact to influence the physiology of marine plankton

and/or C:P ratios (Riebesell et al. 2007, Hutchins et al. 2009), consistent with trends in many terrestrial plants, whose food value can consequently decrease under elevated CO_2 (Ziska & Bunce 2006). P:N:C ratios changed from 1:6.3:121 to 1:7.1:144 to 1:8.25:168 in a pelagic phytoplankton assemblage when pCO_2 was raised from 350 to 700 to 1050 µatm (Bellerby et al. 2008), with enhanced organic carbon transport to the deeper layer (Schulz et al. 2008). Ocean acidification effects on the elemental stoichiometry of phytoplankton can also alter the ocean's large-scale biogeochemical cycles (Hutchins et al. 2009, Finkel et al. 2010, Tagliabue et al. 2011). Since reduced mineralization of algal mineralizers may affect their UV sensitivity (Gao et al. 2009; our Fig. 8), ocean acidification and UV may act synergistically to alter the PIC:POC rain ratio (Hutchins 2011).

Despite an apparent need to consider all of these many environmental changes in a holistic context, most of the ocean acidification studies so far have been conducted under laboratory conditions without considering multiple factors (Boyd 2011). This is one of the main limitations on our knowledge about the ecosystem-level impacts of ocean acidification and other global change factors in the real ocean. The relevance of changes in PAR and temperature to photoautotrophic organisms in the ocean is obvious, but surprisingly few phytoplankton studies have addressed their physiological and ecological interactions with high CO_2 and lower pH. Future studies may also need to focus on the impacts of elevated CO_2 levels under different concentrations or ratios of nutrients, such as N, P, and Fe. Additionally, effects of solar UV radiation have not been considered in indoor laboratory experiments due to the common use of UV-free light sources or UV-opaque vessels. Solar UV radiation can be either harmful or beneficial for photosynthetic carbon fixation by phytoplankton assemblages, depending on the incident levels of solar radiation, and its presence definitely raises daily production in coastal water columns (Gao et al. 2007). Experimental tests of the ecological effects of ocean acidification under real sunlight would allow more realistic predictions of future biological processes in a high-CO_2 ocean.

Equally important is the need to assess the potential for algae to adapt in response to selection by the combination of changing pCO_2 and solar radiation exposure. Micro-evolutionary processes have the potential to result in responses to global change factors that differ considerably from those observed in short-term (typically weeks) experiments using phytoplankton that are physiologically acclimated, but not genetically adapted through extended natural selection. Pioneering studies on evolutionary responses of the freshwater green alga *Chlamydomonas* to long-term growth at high CO_2 demonstrated that some adapted cell lines lost CCM capabilities, although evolution of novel traits was not observed (Collins & Bell 2004, Collins et al. 2006). Beaufort et al. (2011) discovered a very heavily calcified coccolithophore morphotype growing in high-CO_2 coastal upwelling waters, suggesting the possibility of local adaptation to low pH. This field study was supported by experimental evolutionary culture studies by Lohbeck et al. (2012), who found that 500 generations of selection at high CO_2 resulted in recovery of coccolithophore growth rates and calcification. However, 100 generations of selection by high CO_2 resulted in no apparent

adaptation or clade selection in the diatom *Thalassiosira pseudonana* (Crawfurd et al. 2011). Obviously, more studies on genetic change in response to ocean acidification are needed, and flexible and reversible epigenetic changes beyond the DNA sequence have not been evaluated at all.

The evolutionary experimental studies cited in the previous paragraph have all addressed the adaptive responses of phytoplankton to increased pCO_2, and at least one study has taken a similar approach to understanding evolution driven by warming (Huertas et al. 2011). It seems reasonable to suppose that larger cell types might be favored if ocean acidification helps relieve diffusion limitation by CO_2, while at the same time warmer temperatures and lower nutrient supplies might exert selection for smaller cell sizes. To date though, no published data exist on evolutionary responses of phytoplankton to multiple simultaneous selection factors, such as elevated CO_2, light, and warming together, and complex adaptive responses to multiple variables are likely to be extremely difficult to rigorously attribute and interpret. Nevertheless, phytoplankton communities of the future will clearly be forced to adapt to many concurrent environmental changes, and so more realistic multi-variate experimental evolution studies are necessary if marine scientists are to accurately predict the trajectory of potential adaptive changes in the ocean biota.

In light of the studies summarized here, we suggest that priorities for future research in this field should include:

(1) Comparative studies of coastal water with open-ocean species or phytoplankton assemblages. Coastal water species might respond to ocean acidification differently from open-ocean species due to their acclimation to fluctuating and diel pH regimes, respectively. In coastal waters, high primary productivity results in day–night reversals of pH changes, that is, pH increases with increasing solar radiation due to photosynthetic CO_2 fixation and decreases with time after sunset due to respiration. Typically, light exposures of coastal phytoplankton are often lower due to near-shore turbidity, while incident visible and UV light penetrate much deeper in clearer offshore waters. Thus, these 2 types of communities may offer valuable lessons about the net effects of changes in both pCO_2 and solar radiation together.

(2) Community-level studies. Community structure changes or dominant species may differ under future lower pH, warmer, and higher light conditions. It is important to explore the involved mechanisms that are responsible for the establishment of 'winners', the species that are superior competitors under future ocean conditions. Studies on the responses of different taxa or different life stages to ocean acidification and altered light and temperature levels are needed that specifically assess their relative competitive abilities under global change scenarios.

(3) Combined effects of multiple stressors or factors, including light, UV, temperature, hypoxia, and eutrophication or nutrient limitation. While more interactive studies of this nature are appearing in the literature, capturing the net responses of marine algae and cyanobacteria to the full spectrum of expected environmental changes remains a daunting logistical challenge for experimentalists and modelers.

(4) Species living at different layers within the euphotic zone experience different light qualities and quantities, and therefore, their physiological responses to ocean acidification should be distinguished. As an example, work comparing the effects of elevated pCO_2 on high-light- and low-light-adapted ecotypes of the cyanobacterium *Prochlorococcus* (Moore et al. 1998) may yield insights into the physiological mechanisms governing interactions between light and ocean acidification. Notably, recent work looking into the effects of elevated pCO_2 under different levels of sunlight on diatoms revealed that different metabolic pathways are involved for the algae to adapt to ocean acidification and increased light exposures (Gao et al. 2012).

(5) For field studies, phytoplankton physiological responses to pH changes in upwelling areas or low pH waters should be studied as a natural analog to ocean acidification. However, upwelling waters are usually also colder and nutrient-rich, whereas much of the future ocean is expected to be warmer and more oligotrophic. Consequently, it is important to keep in mind when interpreting such studies that present-day upwelling regions are not perfect analogs for the future greenhouse ocean. Nevertheless, pH, temperature, and nutrient gradients and mixing depths in upwelling areas are the driving forces for abundance or primary production of phytoplankton, and the interaction of these variables have been little explored.

(6) Long-term adaptation studies. Key phytoplankton species should be grown for thousands of generations, under solar radiation and pCO_2 levels projected in their future natural environments, and their physiological, genetic, and epigenetic responses should be followed. Comparison of adaptation in cells grown under sunlight and constant indoor light would be of interest to evaluate the tremendous number of studies based on indoor experiments.

(7) Molecular methods should be used to examine gene regulation in model organisms and natural phytoplankton communities during acclimation or adaptation to altered pCO_2 and solar radiation, and these transcriptomic studies should be linked to simultaneous studies of adaptive genetic changes and physiological performance.

(8) For macroalgae, effects of fluctuating pH during the diel cycle on their physiological behavior should be investigated, which would enhance understanding of their mechanistic strategies to cope with coastal ocean acidification. At the same time, different life stages of a macroalga's life cycle may respond differently to ocean acidification, so long-term experiments either indoor or in the field should be launched. Some species may experience difficulties in completing their life cycles due to the impact of ocean acidification, such as the red algal genus *Porphyra*, which depends on calcified shells for the conchocelis stage.

(9) Growth as a function of different levels of CO_2 should be examined for different taxa acclimated or adapted to the CO_2 levels. Such a relationship should be examined under sub-, optimal, and supra-saturating light conditions as well as different levels of temperature and/or nutrients.

In conclusion, it is clear that combinations of ocean warming, PAR, UV radiation, and ocean acidification are all likely to interact to influence species competition, community structure, and biogeochemical cycles in the oceans. Biogeography and ecological niches of marine phytoplankton will also shift due to the combined effects of these factors. A full understanding of the ecological and physiological impacts of global change on marine ecosystems will require that future studies do a much better job of addressing the challenge of understanding the individual and combined effects of ocean acidification and solar irradiance across the entire electromagnetic spectrum.

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LITERATURE CITED

Aizawa K, Miyachi S (1986) Carbonic anhydrase and CO_2 concentrating mechanisms in microalgae and cyanobacteria. FEMS Microbiol Lett 39:215–233

Anthony KRN, Maynard JA, Diaz-Pulido G, Mumby PJ and others (2011) Ocean acidification and warming will lower coral reef resilience. Global Change Biol 17:1798–1808

Barbieri ES, Villafane VE, Helbling EW (2002) Experimental assessment of UV effects on temperate marine phytoplankton when exposed to variable radiation regimes. Limnol Oceanogr 47:1648–1655

Beardall J, Raven JA (2004) The potential effects of global climate change on microalgal photosynthesis, growth and ecology. Phycologia 43:26–40

Beardall J, Sobrino C, Stojkovic S (2009) Interactions between the impacts of ultraviolet radiation, elevated CO_2, and nutrient limitation on marine primary producers. Photochem Photobiol Sci 8:1257–1265

Beaufort L, Probert I, De Garidel-Thoron T, Bendif EM and others (2011) Sensitivity of coccolithophores to carbonate chemistry and ocean acidification. Nature 476:80–83

Behrenfeld MJ, O'Malley RT, Siegel DA, McClain CR and others (2006) Climate-driven trends in contemporary ocean productivity. Nature 444:752–755

Bellerby RGJ, Schulz KG, Riebesell U, Neil C and others (2008) Marine ecosystem community carbon and nutrient uptake stoichiometry under varying ocean acidification during the PeECE III experiment. Biogeosciences 5: 1517–1527

Beman JM, Chow CE, King AL, Feng Y and others (2011) Global declines in oceanic nitrification rates as a consequence of ocean acidification. Proc Natl Acad Sci USA 108:208–213

Borowitzka LJ (1981) Photosynthesis and calcification in the articulated coralline algae *Amphiroa anceps* and *A. foliacea*. Mar Biol 62:17–23

Bouchard JN, Campbell DA, Roy S (2005) Effects of UV-B radiation on the D1 protein repair cycle of natural phytoplankton communities from three latitudes (Canada, Brazil, and Argentina). J Phycol 41:273–286

Boyce DG, Lewis MR, Worm B (2010) Global phytoplankton decline over the past century. Nature 466:591–596

Boyd PW (2011) Beyond ocean acidification. Nat Geosci 4:273–274

Boyd PW, Strzepek R, Fu F, Hutchins DA (2010) Environmental control of open-ocean phytoplankton groups: now and in the future. Limnol Oceanogr 55:1353–1376

Bozzo GG, Colman B (2000) The induction of inorganic carbon transport and external carbonic anhydrase in *Chlamydomonas reinhardtii* is regulated by external CO_2 concentration. Plant Cell Environ 23:1137–1144

Buma AGJ, De Boer MK, Boelen P (2001) Depth distributions of DNA damage in Antarctic marine phyto-and bacterioplankton exposed to summertime UV radiation. J Phycol 37:200–208

Buma AGJ, Wright SW, van den Enden R, van de Poll WH, Davidson AT (2006) PAR acclimation and UVBR-induced DNA damage in Antarctic marine microalgae. Mar Ecol Prog Ser 315:33–42

Caldeira K, Wickett ME (2003) Oceanography: anthropogenic carbon and ocean pH. Nature 425:365

Capotondi A, Alexander MA, Bond NA, Curchitser EN, Scott J (2011) Enhanced upper-ocean stratification with climate change in the CMIP3 models. J Geophys Res

117:C04031, doi:10.1029/2011JC007409
Charalampopoulou A, Poulton AJ, Tyrrell T, Lucas MI (2011) Irradiance and pH affect coccolithophore community composition on a transect between the North Sea and the Arctic Ocean. Mar Ecol Prog Ser 431:25–43
Chavez FP, Messié M, Pennington JT (2011) Marine primary production in relation to climate variability and change. Annu Rev Mar Sci 3:227–260
Chen S, Gao K (2011) Solar ultraviolet radiation and CO_2-induced ocean acidification interacts to influence the photosynthetic performance of the red tide alga *Phaeocystis globosa* (Prymnesiophyceae). Hydrobiologia 675: 105–117
Chen X, Gao K (2003) Effect of CO_2 concentrations on the activity of photosynthetic CO_2 fixation and extracellular carbonic anhydrase in the marine diatom *Skeletonema costatum.* Chin Sci Bull 48:2616–2620
Chen X, Gao K (2004a) Characterization of diurnal photosynthetic rhythms in the marine diatom *Skeletonema costatum* grown in synchronous culture under ambient and elevated CO_2. Funct Plant Biol 31:399–404
Chen X, Gao K (2004b) Photosynthetic utilisation of inorganic carbon and its regulation in the marine diatom *Skeletonema costatum.* Funct Plant Biol 31:1027–1033
Cloern JE, Schraga TS, Lopez CB, Knowles N, Labiosa RG, Dugdale R (2005) Climate anomalies generate an exceptional dinoflagellate bloom in San Francisco Bay. Geophys Res Lett 32:L14608, doi:10.1029/2005GL023321
Collins S, Bell B (2004) Phenotypic consequences of 1,000 generations of selection at elevated CO_2 in a green alga. Nature 431:566–569
Collins S, Sultemeyer D, Bell G (2006) Changes in C uptake in populations of *Chlamydomonas reinhardtii* selected at high CO_2. Plant Cell Environ 29:1812–1819
Connell SD, Russell BD (2010) The direct effects of increasing CO_2 and temperature on non-calcifying organisms: increasing the potential for phase shifts in kelp forests. Proc R Soc Lond B Biol Sci 277:1409–1415
Crawfurd KJ, Raven JA, Wheeler GL, Baxter EJ, Joint I (2011) The response of *Thalassiosira pseudonana* to long-term exposure to increased CO_2 and decreased pH. PLoS ONE 6:e26695
Davison IR (1991) Environmental effects on algal photosynthesis: temperature. J Phycol 27:2–8
De Bodt C, Van Oostende N, Harlay J, Sabbe K, Chou L (2010) Individual and interacting effects of pCO_2 and temperature on *Emiliania huxleyi* calcification: study of the calcite production, the coccolith morphology and the coccosphere size. Biogeosciences 7:1401–1412
Delille B, Harlay J, Zondervan I, Jacquet S and others (2005) Response of primary production and calcification to changes of pCO_2 during experimental blooms of the coccolithophorid *Emiliania huxleyi.* Global Biogeochem Cycles 19:GB2023, doi:10.1029/2004GB002318
Deng Y, Ye J, Mi H, Shen Y (2003) Response of NAD(P)H dehydrogenase complex to the alteration of CO_2 concentration in the cyanobacterium *Synechocystis* PCC6803. J Plant Physiol 160:967–970
Doney SC (2006) Plankton in a warmer world. Nature 444:695–696
Doney SC, Fabry VJ, Feely RA, Kleypas JA (2009) Ocean acidification: the other CO_2 problem. Annu Rev Mar Sci 1:169–192
Egge JK, Thingstad TF, Larsen A, Engel A and others (2009) Primary production during nutrient-induced blooms at elevated CO_2 concentrations. Biogeosciences 6:877–885
Falkowski PG, Raven JA (1997) Aquatic photosynthesis. Blackwell Science, Malden, MA
Falkowski P, Scholes R, Boyle E, Canadell J and others (2000) The global carbon cycle: a test of our knowledge of earth as a system. Science 290:291–296
Feely RA, Sabine CL, Lee K, Berelson W and others (2004) Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. Science 305:362–366
Feng Y, Warner ME, Zhang Y, Sun J and others (2008) Interactive effects of increased pCO_2, temperature and irradiance on the marine coccolithophore *Emiliania huxleyi* (Prymnesiophyceae). Eur J Phycol 43:87–98
Feng Y, Hare CE, Leblanc K, Rose JM and others (2009) Effects of increased pCO_2 and temperature on the North Atlantic spring bloom. I. The phytoplankton community and biogeochemical response. Mar Ecol Prog Ser 388: 13–25
Feng Y, Hare C, Rose J, Handy S and others (2010) Interactive effects of iron, irradiance and CO_2 on Ross Sea phytoplankton. Deep-Sea Res I 57:368–383
Finkel ZV, Beardall J, Flynn KJ, Quigg A, Rees Ta V, Raven JA (2010) Phytoplankton in a changing world: cell size and elemental stoichiometry. J Plankton Res 32:119–137
Fiorini S, Middelburg JJ, Gattuso JP (2011) Effects of elevated CO_2 partial pressure and temperature on the coccolithophore *Syracosphaera pulchra.* Aquat Microb Ecol 64:221–232
Flynn KJ, Blackford JC, Baird ME, Raven JA and others (2012) Changes in pH at the exterior surface of plankton with ocean acidification. Nat Clim Change 2:510–513
Fritz JJ (1999) Carbon fixation and coccolith detachment in the coccolithophore *Emiliania huxleyi* in nitrate-limited cyclostats. Mar Biol 133:509–518
Fritz JJ, Neale PJ, Davis RF, Peloquin JA (2008) Response of Antarctic phytoplankton to solar UVR exposure: inhibition and recovery of photosynthesis in coastal and pelagic assemblages. Mar Ecol Prog Ser 365:1–16
Fu FX, Warner ME, Zhang Y, Feng Y, Hutchins DA (2007) Effects of increased temperature and CO_2 on photosynthesis, growth, and elemental ratios in marine *Synechococcus* and *Prochlorococcus* (Cyanobacteria). J Phycol 43:485–496
Fu FX, Mulholland MR, Garcia N, Beck A and others (2008a) Interactions between changing pCO_2, N_2 fixation, and Fe limitation in the marine unicellular cyanobacterium *Crocosphaera.* Limnol Oceanogr 53:2472–2484
Fu FX, Zhang Y, Warner ME, Feng Y, Hutchins DA (2008b) A comparison of future increased CO_2 and temperature effects on sympatric *Heterosigma akashiwo* and *Prorocentrum minimum.* Harmful Algae 7:76–90
Fu FX, Place AR, Garcia NS, Hutchins DA (2010) CO_2 and phosphate availability control the toxicity of the harmful bloom dinoflagellate *Karlodinium veneficum.* Aquat Microb Ecol 59:55–65
Fu FX, Tatters AO, Hutchins DA (2012) Global change and the future of harmful algal blooms in the ocean. Mar Ecol Prog Ser 470:207–233
Fujiki T, Taguchi S (2002) Variability in chlorophyll *a* specific absorption coefficient in marine phytoplankton as a function of cell size and irradiance. J Plankton Res 24: 859–874
Gao K, Xu J (2008) Effects of solar UV radiation on diurnal photosynthetic performance and growth of *Gracilaria lemaneiformis* (Rhodophyta). Eur J Phycol 43:297–307

Gao K, Zheng Y (2010) Combined effects of ocean acidification and solar UV radiation on photosynthesis, growth, pigmentation and calcification of the coralline alga *Corallina sessilis* (Rhodophyta). Global Change Biol 16:2388–2398

Gao K, Aruga Y, Asada K, Ishihara T, Akano T, Kiyohara M (1991) Enhanced growth of the red alga *Porphyra yezoensis* Ueda in high CO_2 concentrations. J Appl Phycol 3:355–362

Gao K, Aruga Y, Asada K, Ishihara T, Akano T, Kiyohara M (1993) Calcification in the articulated coralline alga *Corallina pilulifera*, with special reference to the effect of elevated CO_2 concentration. Mar Biol 117:129–132

Gao K, Ji Y, Aruga Y (1999) Relationship of CO_2 concentrations to photosynthesis of intertidal macroalgae during emersion. Hydrobiologia 398–399:355–359

Gao K, Wu Y, Li G, Wu H, Villafañe VE, Helbling EW (2007) Solar UV radiation drives CO_2 fixation in marine phytoplankton: a double-edged sword. Plant Physiol 144: 54–59

Gao K, Li P, Watanabe T, Helbling EW (2008) Combined effects of ultraviolet radiation and temperature on morphology, photosynthesis, and DNA of *Arthrospira* (*Spirulina*) *platesis* (Cyanophyta). J Phycol 44:777–786

Gao K, Ruan ZX, Villafañe VE, Gattuso JP, Helbling EW (2009) Ocean acidification exacerbates the effect of UV radiation on the calcifying phytoplankter *Emiliania huxleyi.* Limnol Oceanogr 54:1855–1862

Gao K, Xu J, Gao G, Li Y and others (2012) Rising CO_2 and increased light exposure synergistically reduce marine primary productivity. Nat Clim Change 2:519–523

Garcia NS, Fu FX, Breene CL, Bernhardt PW and others (2011) Interactive effects of irradiance and CO_2 on CO_2 fixation and N_2 fixation in the diazotroph *Trichodesmium erythraeum* (Cyanobacteria). J Phycol 47:1292–1303

Gattuso JP, Gao K, Lee K, Rost B, Schulz KG (2010) Approaches and tools to manipulate the carbonate chemistry. In: Riebesell U, Fabry VJ, Hansson L, Gattuso JP (eds) Guide to best practices for ocean acidification research and data reporting. European Commission, Luxembourg, p 41–51

Giordano M, Beardall J, Raven JA (2005) CO_2 concentrating mechanisms in algae: mechanisms, environmental modulation, and evolution. Annu Rev Plant Biol 56:99–131

Guan W, Gao K (2008) Light histories influence the impacts of solar ultraviolet radiation on photosynthesis and growth in a marine diatom *Skeletonema costatum.* J Photochem Photobiol B 91:151–156

Guan W, Gao K (2010) Impacts of UV radiation on photosynthesis and growth of the coccolithophore *Emiliania huxleyi* (Haptophyceae). Environ Exp Bot 67:502–508

Häder DP, Helbling EW, Williamson CE, Worrest RC (2011) Effects of UV radiation on aquatic ecosystems and interactions with climate change. Photochem Photobiol Sci 10:242–260

Halac SR, Villafañe VE, Helbling EW (2010) Temperature benefits the photosynthetic performance of the diatoms *Chaetoceros gracilis* and *Thalassiosira weissflogii* when exposed to UVR. J Photochem Photobiol B 101:196–205

Hallegraeff GM (2010) Ocean climate change, phytoplankton community responses, and harmful algal blooms: a formidable predictive challenge. J Phycol 46:220–235

Halpern BS, Walbridge S, Selkoe KA, Kappel CV and others (2008) A global map of human impact on marine ecosystems. Science 319:948–952

Harada H, Nakajima K, Sakaue K, Matsuda Y (2006) CO_2 sensing at ocean surface mediated by cAMP in a marine diatom. Plant Physiol 142:1318–1328

Hare CE, Leblanc K, DiTullio GR, Kudela RM and others (2007) Consequences of increased temperature and CO_2 for phytoplankton community structure in the Bering Sea. Mar Ecol Prog Ser 352:9–16

Hays GC, Richardson AJ, Robinson C (2005) Climate change and marine plankton. Trends Ecol Evol 20: 337–344

Hein M, Sand-Jensen K (1997) CO_2 increases oceanic primary production. Nature 388:526–527

Helbling EW, Gao K, Gonçalves RJ, Wu H, Villafañe VE (2003) Utilization of solar UV radiation by coastal phytoplankton assemblages off SE China when exposed to fast mixing. Mar Ecol Prog Ser 259:59–66

Helbling EW, Buma AGJ, Boelen P, van der Strate HJ, Fiorda Giordanino MV, Villaffñe VE (2011) Increase in Rubisco activity and gene expression due to elevated temperature partially counteracts ultraviolet radiation-induced photoinhibition in the marine diatom *Thalassiosira weissflogii*. Limnol Oceangr 56:1330–1342

Hinder SL, Hays GC, Edwards M, Roberts EC, Walne AW, Gravenor MB (2012) Changes in marine dinoflagellate and diatom abundance under climate change. Nat Clim Change 2:271–275

Holcomb M, McCorkle DC, Cohen AL (2010) Long-term effects of nutrient and CO_2 enrichment on the temperate coral *Astrangia poculata* (Ellis and Solander, 1786). J Exp Mar Biol Ecol 386:27–33

Hoogstraten A, Peters M, Timmermans KR, de Baar HJW (2012) Combined effects of inorganic carbon and light on *Phaeocystis globosa* Scherffel (Prymnesiophyceae). Biogeosciences 9:1885–1896

Hopkinson BM, Yan X, Dalin S, Mcginn PJ, Morel FMM (2010) The effect of CO_2 on the photosynthetic physiology of phytoplankton in the Gulf of Alaska. Limnol Oceanogr 55:2011–2024

Hopkinson BM, Dupont CL, Allen AE, Morel FMM (2011) Efficiency of the CO_2-concentrating mechanism of diatoms. Proc Natl Acad Sci USA 108:3830–3837

Hörtnagl P, Pérez MT, Sommaruga R (2011) Contrasting effects of ultraviolet radiation on the growth efficiency of freshwater bacteria. Aquat Ecol 45:125–136

Houghton JT, Ding Y, Griggs DJ, Noguer M and others (eds) (2001) Climate change 2001: the scientific basis. Cambridge University Press, Cambridge

Huertas IE, Rouco M, López-Rodas V, Costas E (2011) Warming will affect phytoplankton differently: evidence through a mechanistic approach. Proc R Soc Lond B Biol Sci 278:3534–3543

Hutchins DA (2011) Oceanography: forecasting the rain ratio. Nature 476:41–42

Hutchins DA, Fu FX, Zhang Y, Warner ME and others (2007) CO_2 control of *Trichodesmium* N_2 fixation, photosynthesis, growth rates, and elemental ratios: implications for past, present, and future ocean biogeochemistry. Limnol Oceanogr 52:1293–1304

Hutchins DA, Mulholland MR, Fu F (2009) Nutrient cycles and marine microbes in a CO_2-enriched ocean. Oceanography 22:128–145

Iglesias-Rodriguez MD, Halloran PR, Rickaby RE, Hall IR and others (2008a) Phytoplankton calcification in a high-CO_2 world. Science 320:336–340

Iglesias-Rodriguez MD, Buitenhuis ET, Raven JA, Schofield

O and others (2008a) Response to comment on 'Phytoplankton calcification in a high-CO_2 world.' Science 322: 1466

Ihnken S, Roberts S, Beardall J (2011) Differential responses of growth and photosynthesis in the marine diatom *Chaetoceros muelleri* to CO_2 and light availability. Phycologia 50:182–193

Israel AA, González EL (1996) Photosynthesis and inorganic carbon utilization in *Pleurochrysis* sp. (Haptophyta), a coccolithophorid alga. Mar Ecol Prog Ser 137:243–250

Israel A, Hophy M (2002) Growth, photosynthetic properties and Rubisco activities and amounts of marine macroalgae grown under current and elevated seawater CO_2 concentrations. Global Change Biol 8:831–840

Jeffrey WH, Aas P, Lyons M, Coffin RB and others (1996) Ambient solar radiation-induced photodamage in marine bacterioplankton. Photochem Photobiol 64:419–427

Johnson VR, Russell BD, Fabricius KE, Brownlee C and others (2012) Temperate and tropical brown macroalgae thrive, despite decalcification, along natural CO_2 gradients. Global Change Biol 18:2792–2803

Johnson VR, Brownlee C, Rickaby REM, Graziano M and others (in press) Responses of marine benthic microalgae to elevated CO_2. Mar Biol doi:10.1007/s00227-011-1840-2

Josefsson W (2006) UV-radiation 1983–2003 measured at Norrköping, Sweden. Theor Appl Climatol 83:59–76

Kaplan A, Badger MR, Berry JA (1980) Photosynthesis and the intracellular inorganic carbon pool in the bluegreen alga *Anabaena variabilis*: response to external CO_2 concentration. Planta 149:219–226

Key T, McCarthy A, Campbell DA, Six C, Roy S, Finkel ZV (2010) Cell size tradeoffs govern light exploitation strategies in marine phytoplankton. Environ Microbiol 12: 95–104

Kim JM, Lee K, Shin K, Kang JH and others (2006) The effect of seawater CO_2 concentration on growth of a natural phytoplankton assemblage in a controlled mesocosm experiment. Limnol Oceanogr 51:1629–1636

King AL, Sanudo-Wilhelmy SA, Leblanc K, Hutchins DA, Fu F (2011) CO_2 and vitamin B_{12} interactions determine bioactive trace metal requirements of a subarctic Pacific diatom. ISME J 5:1388–1396

Kranz SA, Levitan O, Richter KU, Prasil O, Berman-Frank I, Rost B (2010) Combined effects of CO_2 and light on the N_2-fixing cyanobacterium *Trichodesmium* IMS101: physiological responses. Plant Physiol 154:334–345

Langer G, Geisen M, Baumann KH, Kläs J and others (2006) Species-specific responses of calcifying algae to changing seawater carbonate chemistry. Geochem Geophys Geosyst 7:Q09006, doi:10.1029/2005GC001227

Lefebvre SC, Benner I, Stillman JH, Parker AE and others (2012) Nitrogen source and pCO_2 synergistically affect carbon allocation, growth and morphology of the coccolithophore *Emiliania huxleyi*: potential implications of ocean acidification for the carbon cycle. Global Change Biol 18:493–503

Leonardos N, Geider RJ (2005) Elevated atmospheric carbon dioxide increases organic carbon fixation by *Emiliania huxleyi* (Haptophyta), under nutrient-limited high-light conditions. J Phycol 41:1196–1203

Levitan O, Kranz SA, Spungin D, Prasil O, Rost B, Berman-Frank I (2010) Combined effects of CO_2 and light on the N_2-fixing cyanobacterium *Trichodesmium* IMS101: a mechanistic view. Plant Physiol 154:346–356

Lewandowska A, Sommer U (2010) Climate change and the spring bloom: a mesocosm study on the influence of light and temperature on phytoplankton and mesozooplankton. Mar Ecol Prog Ser 405:101–111

Li G, Gao K, Gao G (2011) Differential impacts of solar UV radiation on photosynthetic carbon fixation from the coastal to offshore surface waters in the South China Sea. Photochem Photobiol 87:329–334

Li T, Liu S, Huang L, Huang H and others (2011) Diatom to dinoflagellate shift in the summer phytoplankton community in a bay impacted by nuclear power plant thermal effluent. Mar Ecol Prog Ser 424:75–85

Li Y, Gao K, Villafañe V, Helbling EW (2012) Ocean acidification mediates photosynthetic response to UV radiation and temperature increase in the diatom *Phaeodactylum tricornutum.* Biogeosciences 9:3931–3942

Lohbeck KT, Riebesell U, Reusch TBH (2012) Adaptive evolution of a key phytoplankton species to ocean acidification. Nat Geosci 5:346–351

Lü W, Du J, Wacker T, Gerbig-Smentek E, Andrade SLA, Einsle O (2011) pH-dependent gating in a FocA formate channel. Science 332:352–354

Manney GL, Santee ML, Rex M, Livesey NJ and others (2011) Unprecedented Arctic ozone loss in 2011. Nature 478:469–475

Matsuda Y, Hara T, Colman B (2001) Regulation of the induction of bicarbonate uptake by dissolved CO_2 in the marine diatom, *Phaeodactylum tricornutum.* Plant Cell Environ 24:611–620

McCarthy A, Rogers SP, Duffy SJ, Campbell DA (2012) Elevated carbon dioxide differentially alters the photophysiology of *Thalassiosira pseudonana* (Bacillariophyceae) and *Emiliania huxleyi* (Haptophyta). J Phycol 48:635–646

Melzner F, Stange P, Trübenbach K, Thomsen J and others (2011) Food supply and seawater pCO_2 impact calcification and internal shell dissolution in the blue mussel *Mytilus edulis.* PLoS ONE 6:e24223

Merico A, Tyrrell T, Lessard EJ, Oguz T and others (2004) Modelling phytoplankton succession on the Bering Sea shelf: role of climate influences and trophic interactions in generating *Emiliania huxleyi* blooms 1997–2000. Deep-Sea Res I 51:1803–1826

Millero FJ, Woosley R, Ditrolio B, Waters J (2009) Effect of ocean acidification on the speciation of metals in seawater. Oceanography 22:72–85

Molis M, Wahl M (2009) Comparison of the impacts of consumers, ambient UV, and future UVB irradiance on mid-latitudinal macroepibenthic assemblages. Global Change Biol 15:1833–1845

Moore LR, Rocap G, Chisholm SW (1998) Physiology and molecular phylogeny of coexisting *Prochlorococcus* ecotypes. Nature 393:464–467

Morel FMM, Reinfelder JR, Roberts SB, Chamberlain CP, Lee JG, Yee D (1994) Zinc and carbon co-limitation of marine phytoplankton. Nature 369:740–742

Nimer N, Merrett M (1992) Calcification and utilization of inorganic carbon by the coccolithophorid *Emiliania huxleyi* Lohmann. New Phytol 121:173–177

Orr JC, Fabry VJ, Aumont O, Bopp L and others (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature 437:681–686

Paasche E (2001) A review of the coccolithophorid *Emiliania huxleyi* (Prymnesiophyceae), with particular reference to growth, coccolith formation, and calcification-photosyn-

thesis interactions. Phycologia 40:503–529
Peperzak L (2003) Climate change and harmful algal blooms in the North Sea. Acta Oecol 24:S139–S144
Pörtner HO, Farrell AP (2008) Physiology and climate change. Science 322:690–692
Raven J (1991) Physiology of inorganic C acquisition and implications for resource use efficiency by marine phytoplankton: relation to increased CO_2 and temperature. Plant Cell Environ 14:779–794
Raven JA (1993) Limits on growth rates. Nature 361:209–210
Raven JA (1998) Small is beautiful: the picophytoplankton. Funct Ecol 12:503–513
Raven JA, Geider RJ (1988) Temperature and algal growth. New Phytol 110:441–461
Raven JA, Kübler JE (2002) New light on the scaling of metabolic rate with the size of algae. J Phycol 38:11–16
Raven JA, Giordano M, Beardall J, Maberly SC (2011) Algal and aquatic plant carbon concentrating mechanisms in relation to environmental change. Photosynth Res 109: 281–296
Riebesell U (2004) Effects of CO_2 enrichment on marine phytoplankton. J Oceanogr 60:719–729
Riebesell U, Tortell PD (2011) Ocean acidification. In: Gattuso JP, Hansson L (eds) Effects of ocean acidification on pelagic organisms and ecosystems. Oxford University Press, Oxford, p 99–116
Riebesell U, Wolf-Gladrow DA, Smetacek V (1993) Carbon dioxide limitation of marine phytoplankton growth rates. Nature 361:249–251
Riebesell U, Zondervan I, Rost B, Tortell PD, Zeebe RE, Morel FMM (2000) Reduced calcification of marine plankton in response to increased atmospheric CO_2. Nature 407:364–367
Riebesell U, Schulz KG, Bellerby RG, Botros M and others (2007) Enhanced biological carbon consumption in a high CO_2 ocean. Nature 450:545–548
Riebesell U, Bellerby RG, Engel A, Fabry VJ and others (2008) Comment on 'Phytoplankton calcification in a high-CO_2 world'. Science 322:1466
Ries G, Heller W, Puchta H, Sandermann H, Seidlitz HK, Hohn B (2000) Elevated UV-B radiation reduces genome stability in plants. Nature 406:98–101
Rokitta SD, Rost B (2012) Effects of CO_2 and their modulation by light in the life-cycle stages of the coccolithophore *Emiliania huxleyi.* Limnol Oceanogr 57:607–618
Rose J, Feng Y, Ditullio GR, Dunbar RB and others (2009) Synergistic effects of iron and temperature on Antarctic phytoplankton and microzooplankton assemblages. Biogeosciences 6:3131–3147
Rost B, Riebesell U, Burkhardt S, Sültemeyer D (2003) Carbon acquisition of bloom-forming marine phytoplankton. Limnol Oceanogr 48:55–67
Russell BD, Thompson JI, Falkenberg LJ, Connell SD (2009) Synergistic effects of climate change and local stressors: CO_2 and nutrient-driven change in subtidal rocky habitats. Global Change Biol 15:2153–2162
Sabine CL, Feely RA, Gruber N, Key RM and others (2004) The oceanic sink for anthropogenic CO_2. Science 305: 367–371
Schippers P, Lürling M, Scheffer M (2004) Increase of atmospheric CO_2 promotes phytoplankton productivity. Ecol Lett 7:446–451
Schulz KG, Riebesell U, Bellerby RGJ, Biswas H and others (2008) Build-up and decline of organic matter during PeECEIII. Biogeosciences 5:707–718
Sciandra A, Harlay J, Lefèvre D, Lemée R, Rimmelin P, Denis M, Gattuso JP (2003) Response of coccolithophorid *Emiliania huxleyi* to elevated partial pressure of CO_2 under nitrogen limitation. Mar Ecol Prog Ser 261: 111–122
Sekino K, Shiraiwa Y (1994) Accumulation and utilization of dissolved inorganic carbon by a marine unicellular coccolithophorid, *Emiliania huxleyi.* Plant Cell Physiol 35: 353–361
Shi D, Xu Y, Hopkinson BM, Morel FMM (2010) Effect of ocean acidification on iron availability to marine phytoplankton. Science 327:676–679
Sinutok S, Hill R, Doblin MA, Wuhrer R, Ralph PJ (2011) Warmer more acidic conditions cause decreased productivity and calcification in subtropical coral reef sediment-dwelling calcifiers. Limnol Oceanogr 56:1200–1212
Sobrino C, Neale PJ (2007) Short-term and long-term effects of temperature on photosynthesis in the diatom *Thalassiosira pseudonana* under UVR exposures. J Phycol 43: 426–436
Sobrino C, Neale PJ, Lubian LM (2005) Interaction of UV radiation and inorganic carbon supply in the inhibition of photosynthesis: spectral and temporal responses of two marine picoplankters. Photochem Photobiol 81:384–393
Sobrino C, Ward ML, Neale PJ (2008) Acclimation to elevated carbon dioxide and ultraviolet radiation in the diatom *Thalassiosira pseudanana*: effects on growth, photosynthesis, and spectral sensitivity of photoinhibition. Limnol Oceanogr 53:494–505
Steinacher M, Joos F, Froelicher TL, Bopp L and others (2010) Projected 21st century decrease in marine productivity: a multi-model analysis. Biogeosciences 7:979–1005
Stum W, Morgan JJ (1981) Aquatic chemistry. Wiley, New York, NY
Sültemeyer D (1998) Carbonic anhydrase in eukaryotic algae: characterization, regulation, and possible function during photosynthesis. Can J Bot 76:962–972
Sun J, Hutchins DA, Feng Y, Seubert EL, Caron DA, Fu FX (2011) Effects of changing pCO_2 and phosphate availability on domoic acid production and physiology of the marine harmful bloom diatom *Pseudo-nitzschia multiseries.* Limnol Oceanogr 56:829–840
Sunda WG, Huntsman SA (2011) Interactive effects of light and temperature on iron limitation in a marine diatom: implications for marine productivity and carbon cycling. Limnol Oceanogr 56:1475–1488
Tagliabue A, Bopp L, Gehlen M (2011) The response of marine carbon and nutrient cycles to ocean acidification: large uncertainties related to phytoplankton physiological assumptions. Global Biogeochem Cycles 25:GB3017, doi:10.1029/2010GB003929
Tedetti M, Sempéré R, Vasilkov A, Charriere B and others (2007) High penetration of ultraviolet radiation in the south east Pacific waters. Geophys Res Lett 34:L12610, doi:10.1029/2007GL029823
Tortell PD, Morel FMM (2002) Sources of inorganic carbon for phytoplankton in the eastern Subtropical and Equatorial Pacific Ocean. Limnol Oceanogr 47:1012–1022
Tortell PD, Rau GH, Morel FMM (2000) Inorganic carbon acquisition in coastal Pacific phytoplankton communities. Limnol Oceanogr 45:1485–1500
Tortell PD, Payne CD, Li YY, Trimborn Sand others (2008) CO_2 sensitivity of Southern Ocean phytoplankton. Geophys Res Lett 35:L04605, doi:10.1029/2007GL032583
Tsuzuki M, Miyachi S (1989) The function of carbonic anhy-

drase in aquatic photosynthesis. Aquat Bot 34:85–104
Turley C, Eby M, Ridgwell AJ, Schmidt DN and others (2010) The societal challenge of ocean acidification. Mar Pollut Bull 60:787–792
Vähätalo AV, Aarnos H, Hoikkala L, Lignell R (2011) Photochemical transformation of terrestrial dissolved organic matter supports hetero- and autotrophic production in coastal waters. Mar Ecol Prog Ser 423:1–14
Wahl M, Molis M, Davis A, Dobretsov S and others (2004) UV effects that come and go: a global comparison of marine benthic community level impacts. Global Change Biol 10:1962–1972
Wohlers-Zöllner J, Breithaupt P, Walther K, Jürgens K, Riebesell U (2011) Temperature and nutrient stoichiometry interactively modulate organic matter cycling in a pelagic algal–bacterial community. Limnol Oceanogr 56: 599–610
Woodger FJ, Badger MR, Price GD (2005) Sensing of inorganic carbon limitation in *Synechococcus* PCC7942 is correlated with the size of the internal inorganic carbon pool and involves oxygen. Plant Physiol 139:1959–1969
Wu H, Gao K (2009) Responses of a marine red tide alga *Skeletonema costatum* (Bacillariophyceae) to long-term UV radiation exposures. J Photochem Photobiol B 94: 82–86
Wu H, Gao K, Villafane VE, Watanabe T, Helbling EW (2005) Effects of solar UV radiation on morphology and photosynthesis of filamentous cyanobacterium *Arthrospira platensis.* Appl Environ Microbiol 71:5004–5013
Wu H, Zou D, Gao K (2008) Impacts of increased atmospheric CO_2 concentration on photosynthesis and growth of micro- and macro-algae. Sci China C Life Sci 51: 1144–1150
Wu Y, Gao K, Riebesell U (2010) CO_2-induced seawater acidification affects physiological performance of the marine diatom *Phaeodactylum tricornutum.* Biogeosciences 7:2915–2923
Wu H, Cockshutt AM, Mccarthy A, Campbell DA (2011) Distinctive photosystem II photoinactivation and protein dynamics in marine diatoms. Plant Physiol 156: 2184–2195
Xu J, Gao K (2010) UV-A enhanced growth and UV-B induced positive effects in the recovery of photochemical yield in *Gracilaria lemaneiformis* (Rhodophyta). J Photochem Photobiol B 100:117–122
Xu K, Gao K (2012) Reduced calcification decreases photoprotective capability in the coccolithophorid *Emiliania huxleyi.* Plant Cell Physiol 53:1267–1274
Xu K, Gao K, Villafañe VE, Helbling EW (2011) Photosynthetic responses of *Emiliania huxleyi* to UV radiation and elevated temperature: roles of calcified coccoliths. Biogeosciences 8:1441–1452
Yang G, Gao K (2012) Physiological responses of the marine diatom *Thalassiosira pseudonana* to increased pCO_2 and seawater acidity. Mar Environ Res 79:142–151
Ziska LH, Bunce JA (2006) Plant responses to rising atmospheric carbon dioxide. In: Morison JIL, Morecroft MD (eds) Plant growth and climate change. Blackwell Publishing, Oxford, p 17–47
Zondervan I (2007) The effects of light, macronutrients, trace metals and CO_2 on the production of calcium carbonate and organic carbon in coccolithophores — a review. Deep-Sea Res II 54:521–537
Zondervan I, Zeebe RE, Rost B, Riebesell U (2001) Decreasing marine biogenic calcification: a negative feedback on rising atmospheric pCO_2. Global Biogeochem Cycles 15:507–516
Zou D, Gao K (2002) Effects of desiccation and CO_2 concentrations on emersed photosynthesis in *Porphyra haitanensis* (Bangiales, Rhodophyta), a species farmed in China. Eur J Phycol 37:587–592
Zou D, Gao K, Luo H (2011) Short- and long-term effects of elevated CO_2 on photosynthesis and respiration in the marine macroalga *Hizikia fusiformis* (Sargassaceae, Phaeophyta) grown at low and high N supplies. J Phycol 47:87–97

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