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TECHNICAL ADVANCE

Dynamic energy budget modeling reveals the potential of future growth and calcification for the coccolithophore *Emiliania huxleyi* in an acidified ocean

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Abstract

Ocean acidification is likely to impact the calcification potential of marine organisms. In part due to the covarying nature of the ocean carbonate system components, including pH and CO_2 and CO_3^{2-} levels, it remains largely unclear how each of these components may affect calcification rates quantitatively. We develop a process-based bioenergetic model that explains how several components of the ocean carbonate system collectively affect growth and calcification rates in *Emiliania huxleyi*, which plays a major role in marine primary production and biogeochemical carbon cycling. The model predicts that under the IPCC A2 emission scenario, its growth and calcification potential will have decreased by the end of the century, although those reductions are relatively modest. We anticipate that our model will be relevant for many other marine calcifying organisms, and that it can be used to improve our understanding of the impact of climate change on marine systems.

Keywords: calcification, calcite saturation state, coccolithophores, Dynamic Energy Budget Theory, *Emiliania huxleyi*, ocean acidification

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Introduction

The increase in atmospheric pCO_2 since the onset of the industrial revolution has brought about a change in ocean surface carbonate chemistry, notably a decline in pH and carbonate concentration and an increase in dissolved CO_2 (IPCC, 2007). This change, commonly referred to as ocean acidification (OA), is expected to intensify during this century, resulting in an increasingly challenging environment for calcifying organisms to produce calcareous skeletons (Fabry *et al*., 2008; Rost *et al*., 2008). Indeed, numerous accounts, summarized in several recent reviews (Fabry *et al*., 2008; Rost *et al*., 2008; Doney *et al*., 2009), attest to declines in calcification rates with decreasing pH or ambient carbonate levels in marine calciferous organisms.

The impact of OA on coccolithophores is of special concern because of their large role in primary production and calcium carbonate precipitation in the ocean. Much about the impact of OA on their calcification potential and other physiological processes remains unclear. For instance, species and even strains differ considerably in their sensitivities to a changing ocean carbonate system (Langer *et al*., 2006, 2009). Furthermore, conflicting reports about the best studied coccolithophorid, *E. huxleyi*, have appeared. While most authors have found that per-cell calcification rates in *E. huxleyi* decrease with increasing pCO_2 beyond current atmospheric levels (Riebesell *et al*., 2000; Rost *et al*., 2008; Bach *et al*., 2011, 2013; Hoppe *et al*., 2011), others have observed the opposite trend (Feng *et al*., 2008; Iglesias-Rodriguez *et al*., 2008; Shi *et al*., 2009), possibly because of differences in experimental design or data normalization (Riebesell *et al*., 2008; Field *et al*., 2011). Finally, it remains unclear to what extent the different components in the carbonate system determine the rate of calcification. For example, it seems reasonable to expect photosynthesis to be a major driver of calcification, as the latter is an energy requiring process, and consequently to expect a positive relationship between pCO_2 levels and calcification rates. However, calcification rates in marine organisms generally depend, among all of the ocean carbonate system components, most clearly on the ocean CO_3^{2-} concentration (or, equivalently, the calcite or aragonite saturation state) (Fabry *et al*., 2008). A thorough quantification of the impact of OA on calcification requires an integrative framework with which the impact of the distinct components of the ocean carbonate system on relevant physiological processes can be evaluated.

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Our aim was to develop such an integrative framework, based on Dynamic Energy Budget (DEB) theory, to evaluate the impact of OA on the growth and calcification rate of calciferous organisms, such as coccolithophores. DEB theory describes the rates at which organisms acquire resources from the environment (here: CO_2, light energy, and nutrients) and use the energy and nutrients therein for maintenance, development, and production of biomass (Nisbet *et al*., 2000; Sousa *et al*., 2008; Kooijman, 2010). We develop process-based models that treat calcification as a secondary process whose dynamics are implied by DEB theory and describe the impact of ocean carbonate system components, such as H^+ and CO_3^{2-}, on production and calcification rates. We then evaluate the model with published data describing growth and calcification rates in three *E. huxleyi* strains at a wide range of combinations of environmental inorganic carbon chemistry parameters (Bach *et al*., 2011; Hoppe *et al*., 2011). With parameters estimated from those data, we investigate implications of a changing ocean carbonate system in the Pacific, north of 50°, on primary production and calcification in *E. huxleyi*.

Materials and methods

Data were downloaded from the EPOCA database (EPOCA, 2011) in August 2012 (NZEH 'open DIC' treatment data were omitted because of poor mixing leading to cell sedimentation and erratic growth behavior). Parameters not directly affecting the calcification rate were estimated from data on growth rates and cellular organic carbon content and held constant at their respective estimated values during the analysis of data on calcification rates. Because the data do not contain sufficient information for the estimation of all model parameters, some simplifications needed to be considered. The maximum photosynthetic carbon fixation and maintenance rates could not be estimated (as this would require additional data, such as gross CO_2 fixation and dark/light respiration rates), and were, therefore, fixed at values selected from a range that yielded satisfactory model fits; this element of subjectivity doesn't affect the main findings of this article, which depend relatively little on the exact value of parameters (see Results and discussion). Furthermore, it was impossible to delineate the individual contributions of assimilation, growth, and maintenance to the calcification rate (as this would require additional data, such as gross CO_2 fixation, dark/light respiration, and dark/light calcification rates). It was necessary to assume two of the three energy fluxes contributed negligibly to calcification. It seems reasonable to assume that photosynthesis is a major driver of calcification. Accordingly, the yield coefficient quantifying the contribution of assimilation to calcification was chosen as a free estimable parameter and those quantifying the contribution of maintenance and growth were set at zero. It should be noted that fitting results obtained while assuming a negligible contribution of assimilation rather than growth to calcification were nearly identical, because the rates of photosynthetic carbon fixation (as implied by parameter values and environmental conditions) and growth (as measured) covary to a great extent in the experiments analyzed here.

Simulations for predicting past and future productivity and calcification rates assumed the carbonate system of the Northern Pacific (Feely *et al*., 2009) as determined with CO2sys for Matlab (T = 10 °C; salinity = 3.5) and beta-distributed model parameter values (distribution parameter values = 2, which yields a symmetrical, hump-shaped distribution with upper and lower bounds), without affecting conclusions, $[H^+]_0^{env}$, was not randomized to avoid bimodal results due to the role of this parameter in a switch function. The lower and upper bounds for yield parameters differ 25% from their means (to constrain them within a biologically meaningful range); the bounds for other parameters differ 50% and 150%, respectively, from their means.

Models

This section briefly outlines the mathematical framework of DEB theory as needed for this article [assumptions, underpinnings, and further details can be found elsewhere (Kooijman, 2010; Muller, 2011; Sousa *et al*., 2008)], adds calcification to this theory, and describes the impact of OA on growth and calcification. A conceptual representation of the resulting modeling framework is depicted in Fig. 1.

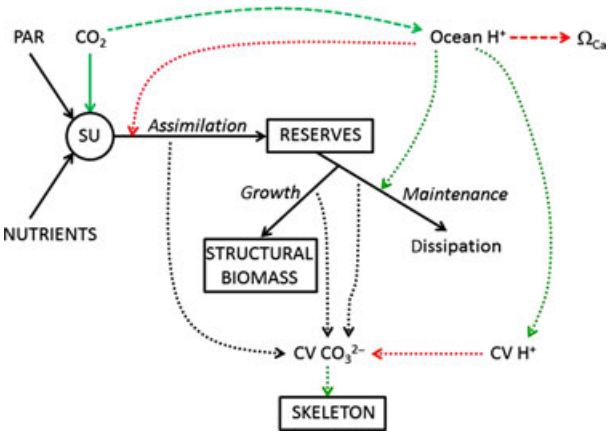

Fig. 1 Conceptual model representation of the impact of ocean acidification on calcification. Dynamic Energy Budget theory (sources and sinks connected by solid arrows) provides the energetic basis for the model and implicitly specifies energy allocation to calcification (broken black arrows). Additional modeling modules describe the impact of suboptimal pH on general physiological processes and the relationship between the pH of the coccolith vesicle (CV) and of the ocean (green and red arrows represent positive and negative relationships, respectively). See text for a full description and the Supplemental Equations for model derivation. 'PAR' is photosynthetically active radiation; 'SU' is synthesizing unit.

Dynamic energy budgets

The core DEB model for a population of dividing unicellular organisms has two state variables: the load of energy reserves in a cell, m_E, and the density of structural biomass, X_V. In this particular DEB model variant (for 'V1 morphs'; Hanegraaf & Muller, 2001), the mean structural biomass of a cell in an exponentially growing population is a constant, so the density of structural biomass is proportional to the density of cells, regardless of resource availability. Hence, we can normalize model quantities to cell numbers, i.e. *per capita*, rather than per mole of structural C as is customary in DEB theory. This is convenient as the data in our analysis are in expressed as *per capita*. The state equations are

$$\frac{dm_E}{dt} = j_{\mathrm{EA}} - k_E m_E \tag{1}$$

$$\frac{dX_V}{dt} = X_V \frac{K_E m_E - j_{\mathrm{ED}}}{m_E + 1/y_{\mathrm{VE}}} \tag{2}$$

in which j_{EA} is the specific assimilation rate (which in this article is the same as the *per capita* photosynthetic carbon fixation rate); k_E is the specific energy conductance; j_{ED} the specific maintenance rate and y_{VE} the growth efficiency. The specific assimilation rate is conveniently described with the concept of a synthesizing unit for two potentially limiting resources (Kooijman, 1998; Muller, 2011), i.e. here the environmental CO_2 concentration, $X_{\mathrm{CO_2}}$, and irradiance, $\{J_{L,F}\}$:

$$j_{\mathrm{EA}} = \frac{1}{\frac{1}{j_{\mathrm{EAm}}} + \frac{1}{p_1 X_{\mathrm{CO_2}}} + \frac{1}{p_2\{J_{L,F}\}} - \frac{1}{p_1 X_{\mathrm{CO_2}} + p_2\{J_{L,F}\}}} \tag{3}$$

in which j_{EAm} is the maximum specific assimilation rate and p_1 and p_2 are proportionality factors (HCO_3^- instead of CO_2 should be used with species with efficient carbon concentrating mechanisms). Equation (3) adequately describes published (Nimer & Merrett, 1993) photosynthetic carbon fixation rates in *E. huxleyi* (see Fig. S1). The specific growth rate, j_{VG}, is defined as $j_{\mathrm{VG}} = \frac{dX_V}{X_V dt}$, which equals the *per capita* growth rate in an exponentially growing population.

The biomass of a cell, M, is the sum of its structural biomass, M_V, and its reserve biomass, M_E. In exponentially growing populations, the reserve load of a cell is constant, so from Eqn (1) and $M_E \equiv m_E M_V$

$$M = M_V + M_E = M_V\left(1 + \frac{j_{\mathrm{EA}}}{k_E}\right) \tag{4}$$

For populations that do not grow (approximately) exponentially, the (numerical) solutions of Eqns (1) and (2) should be used to calculate M_E.

To account for the impact of H^+ on physiological processes other than those directly involved in calcification, we use an effect model (Muller *et al.*, 2010) in which the specific assimilation rate and specific energy conductance are reduced and the specific maintenance rate is increased when the environmental H^+ concentration, $[H^+]^{\mathrm{env}}$, exceeds a threshold no-effect concentration, $[H^+]_0^{\mathrm{env}}$. These rates change according to

$$\begin{aligned} j_{\mathrm{EA}} &\to j_{\mathrm{EA}}\left(1 + \frac{\left([H^+]^{\mathrm{env}} - [H^+]_0^{\mathrm{env}}\right)_+}{K_{H^+}}\right)^{-1}, \\ k_E &\to k_E\left(1 + \frac{\left([H^+]^{\mathrm{env}} - [H^+]_0^{\mathrm{env}}\right)_+}{K_{H^+}}\right)^{-1} \\ \text{and } j_{\mathrm{ED}} &\to j_{\mathrm{ED}}\left(1 + \frac{\left([H^+]^{\mathrm{env}} - [H^+]_0^{\mathrm{env}}\right)_+}{K_{H^+}}\right) \end{aligned} \tag{5}$$

in which K_{H^+} is the effect scaling parameter.

Calcification

To describe the calcification rate, we need to specify how the internal carbonate system depends on metabolism and on the ocean carbonate system. Biological calcification generally requires at least four 'substrates': energy, biomolecules for skeletal structure, divalent cations, and inorganic carbon. Accordingly, the calcification rate depends on the rates at which these 'substrates' are supplied to the calcification process. Rather than following the dynamics of all 'substrates', we argue that for our purposes, it is reasonable to describe the dependency of the calcification rate on metabolism solely in terms of the rate at which energy is supplied to calcification. Energy is needed to build the biomolecules needed for skeletal structure, have all the compounds delivered in the coccolith vessicle (CV) and regulate the pH in the CV. If each of these compounds requires a fixed amount of energy to be built and supplied to the CV, their supply rate is proportional to the rate at which energy is allocated to calcification. Each of the DEB energy fluxes, i.e. assimilation, maintenance, and growth, potentially contributes to calcification. Because the core assumptions of DEB theory imply that the contribution of each of those fluxes is proportional to their respective magnitude (cf. product formation in Hanegraaf & Muller, 2001; Kooijman, 2010), the rate at which energy (and hence compounds) is allocated to calcification is, in principal, specified by the theory. Accordingly, we assume that the specific calcification rate, j_{Ca}, is proportional to the weighted sum of contributing energy fluxes, or

$$j_{\mathrm{Ca}} \propto w_1 j_{\mathrm{EA}} + w_2 j_{\mathrm{VG}} + w_3 j_{\mathrm{ED}}, \tag{6}$$

in which $w*$ are the weight coefficients specifying the contribution of each energy flux to calcification.

Equation (6) does not explicitly consider the role of the speciation and internal transport of inorganic carbon in determining the calcification rate. To retain simplicity, we assume that the time scale at which the slowest steps in inorganic carbon speciation operate, i.e. seconds to minutes (Ho & Sturtevant, 1963), is generally short relative to the time scale of environmentally induced changes in metabolism, such as those governed by diurnal cycles. With Bolton & Stoll (2013), we also assume that transport of inorganic carbon is sufficiently fast such that the CV carbonate system responds to changes in metabolic rates and in the ocean carbonate system without ecologically significant delay. The model acknowledges the role of carbon speciation and transport in determining the composition of the CV carbonate system through parameter values, but it ignores the dynamic aspects of these processes.

We model the dependency of the calcification rate on the ocean carbonate system with simple chemical equilibrium and thermodynamic considerations. The speciation of total dissolved inorganic carbon (DIC) is commonly summarized with two reaction equations:

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$ with equilibrium constant

$$K_{a1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \quad (7)$$

and

$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$ with equilibrium constant

$$K_{a2} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \quad (8)$$

Then, as in equilibrium in alkaline solutions $K_{a1} \gg [H^+]$,

$$[CO_3^{2-}] = \frac{K_{a1}K_{a2}[DIC]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \approx \frac{K_{a2}[DIC]}{[H^+] + K_{a2}} \quad (9)$$

or

$$[H^+] \approx \frac{K_{a2}([DIC] - [CO_3^{2-}])}{[CO_3^{2-}]} \quad (10)$$

Following Ries (2011), we assume that the energy that is required to maintain a proton gradient is proportional to the proton-motive force E_{H^+} given by the Nernst equation,

$$E_{H^+} = \frac{RT}{F} \ln \frac{[H^+]^{env}}{[H^+]^i} \quad (11)$$

in which the superscripts 'env' and '*i*' represent the environment and coccolith vesicle, respectively. This implies that for a given energy supply rate to maintain a proton gradient, $[H^+]^i = \psi\ [H^+]^{env}$, with ψ as a proportionality constant. For a given rate of energy invested in maintaining a proton gradient, this proportional relationship also links the internal carbonate concentration to the ocean carbonate system through substitution into Eqn (9) (applied to the environment) and Eqn (8) (applied to the coccolith vesicle). Cast in terms of the saturation state of calcite in the environment, $\Omega_{Ca} \equiv [Ca^{2+}]^{env}\ [CO_3{}^{2-}]^{env}/K_{sp}$ with K_{sp} as the calcite solubility constant, we get after some routine algebra

$$[CO_3^{2-}]^i = \frac{\frac{K^i_{a2}}{K^i_{a2} - \psi K^{env}_{a2}}[DIC]^i \Omega_{Ca}}{\frac{\psi K^{env}_{a2}[Ca^{2+}]^{env}}{K_{sp}\left(K^i_{a2} - \psi K^{env}_{a2}\right)}[DIC]^{env} + \Omega_{Ca}} \quad (12)$$

To maintain a stable CV carbonate system, two protons need to be removed for each calcium carbonate deposited, i.e. the proton removal rate is proportional to the calcification rate (to avoid dilution effects due to growth, we assume that the total volume of the CVs in a cell is proportional to the amount of its structural biomass). A complicating factor is, however, that the marginal cost of proton removal increases as the proton gradient becomes steeper [cf. Eqn (11)]. To retain simplicity and tractability, we maintain our assumption that the calcification rate, and hence the proton removal rate, is directly proportional to energy allocated to proton removal.

We can now combine Eqns (6) and (12) to describe the impact of the ocean carbonate system and metabolism on calcification. To simplify the result, we assume constant calcium concentrations in the ocean and CV and ocean calcium concentrations and a constant DIC concentration in the CV (these assumptions can be relaxed when those concentrations are measured), and present aggregates of constants and proportionality factors as compound parameters. Then,

$$j_{Ca} = \left(y_{Ca,A} j_{EA} + y_{Ca,G} j_{VG} + y_{Ca,D} j_{ED}\right) \frac{\Omega_{Ca}}{K_{\Omega_{Ca}}[DIC]^{env} + \Omega_{Ca}} \quad (13)$$

in which the compound parameter $K_{\Omega_{Ca}}$ is the OA effect scaling parameter (when $[DIC]^{env}$ is constant, $K_{\Omega_{Ca}}\ [DIC]^{env}$ is a half-saturation constant) and y_{**} are yields of calcite from contributions of the respective energy fluxes that would be observed at very high calcite saturation states (e.g. $y_{Ca,A}$ is the number of calcite molecules that would be deposited for each CO_2 fixed during photosynthesis at very high calcite saturation states).

Results and discussion

The model developed in the previous section relates production and calcification rates to metabolic rates and ocean carbonate system parameters. To compare model predictions to data, those data need to meet three demanding criteria. First, to characterize the energy supplied to calcification, data should include measurements about some physiological processes, such as the rate of photosynthesis, dark respiration or growth or cellular composition. Second, the environmental inorganic carbon chemistry needs to be fully specified. Third, data need to be collected for a relatively large number and sufficiently wide range of combinations of environmental inorganic carbon chemistry parameters. To the best of our knowledge, only two publications reporting on three calcifying strains of *E. huxleyi* meet those criteria to an extent that permits a model evaluation. Bach *et al*. (2011) determined the organic carbon content of cells and the rates of growth and calcification in strain B92/11 for a wide range of environmental CO_2 concentrations at both constant and variable pH, whereas Hoppe *et al*. (2011) collected similar data for strains NZEH and RC1256 in experiments in which either the environmental total alkalinity or DIC varied.

The trends in the data from those studies are adequately described by the model (see Fig. 2 for model fits to data from strain B92/11 and Fig. S2 those to data from strains RC1256 and NZEH; see Table 1 for parameter estimates). A comparison of data and model fits across treatments is rather subtle, as the relationships among the components of the carbonate system vary greatly among treatments, while four components, namely CO_2, DIC, H^+, and Ω_{Ca}, are input variables in the model (see the legend to Fig. 2 for a model explanation of trends). This figure establishes two important

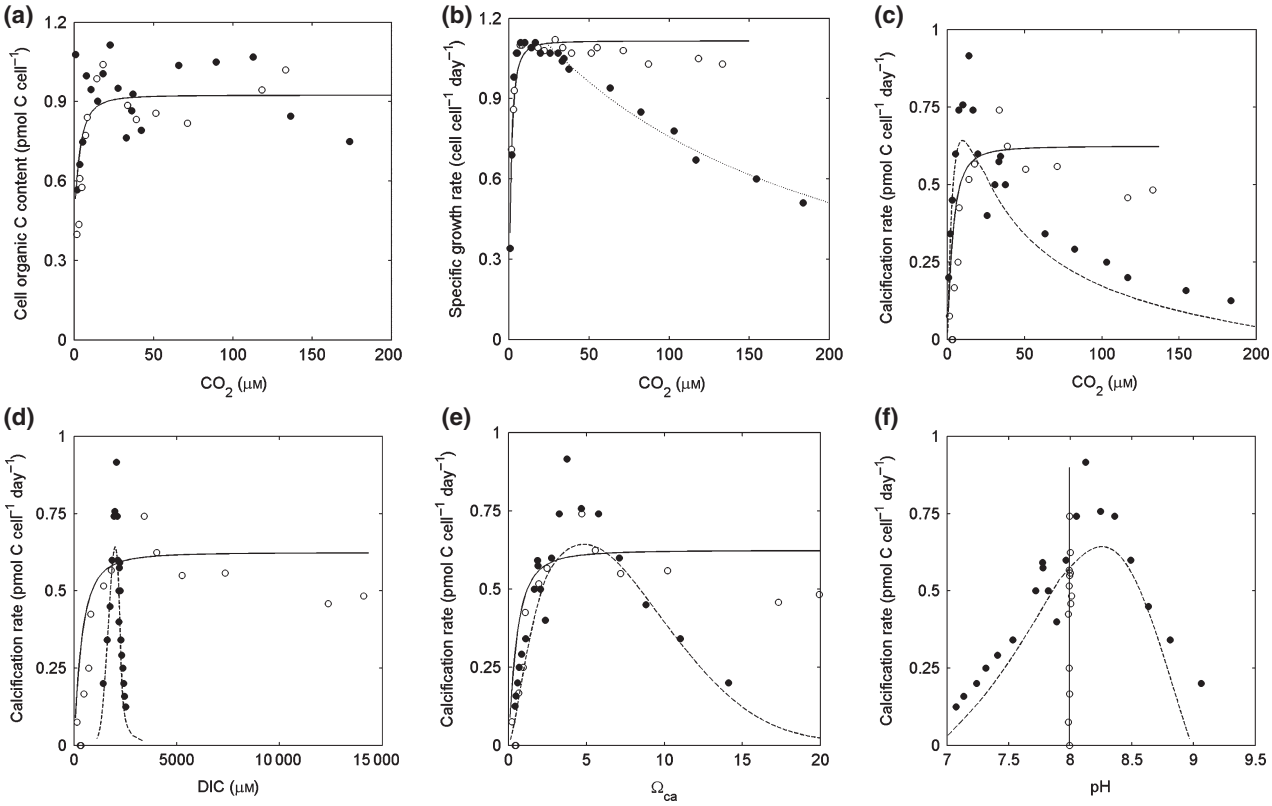

Fig. 2 Production and calcification in *Emiliania huxleyi* B92/11 as a function of carbonate system parameters with model fits to data from Bach *et al.* (2011). Two carbonate system manipulation techniques yielded different pH (free scale) vs. CO_2 patterns: one with a constant pH (open symbols and solid lines) and one in which the pH declines with increasing CO_2 concentrations (closed symbols and broken lines). Model fits to the mean cell organic carbon content (a) and specific growth rate (b) provide parameter estimates (see Table 1) used to fit the calcification rate as a function of CO_2 (c), DIC (d), Ω_{Ca} (e), and pH (f). With Ω_{Ca} as the reference independent variable (e), the model explains the trends as follows. The direct functional relationship between the calcification rate and Ω_{Ca} [see Eqn (13)] in part explains the initial increase and subsequent leveling-off of calcification rates with increasing Ω_{Ca}. At constant pH, an additional cause for depressed calcification rates at low Ω_{Ca} is the relatively low energy supply resulting from CO_2 limitation for photosynthesis. In contrast, at a variable pH, CO_2 limited photosynthesis occurs at high Ω_{Ca}; hence the declining calcification rates at values for Ω_{Ca} beyond 6. The low calcification rates observed at low Ω_{Ca} with this treatment are the result of pH conditions being suboptimal for metabolism. For parameter values, see Table 1. Mean relative error (Lika *et al.*, 2011) is 0.15 (data from constant and variable pH treatment combined; a), 0.04/0.05 (constant/variable pH; b), 0.39/0.21 Constant/variable pH excluding data for which calcification is nil; c–f).

points: (i) any search for a single component of the carbonate system that most prominently determines calcification potential of a particular strain is bound to be futile, as calcification depends on multiple, covarying factors whose relative impact on calcification depends on experimental protocol; but (ii) a process-based model such as ours can tease out the combined effect of these covarying factors.

Because *E. huxleyi* plays fundamental roles in the dynamics of marine food webs and CO_2 sequestration, it is informative to project the potential impact of changing ocean carbonate conditions on this species. We use simulations to illustrate this for a 'bad-case' scenario by assuming future CO_2 levels according to the relatively pessimistic IPCC A2 emission scenario (see Table 2), the projected ocean carbonate chemistry parameters for the Pacific, north of 50° (Feely *et al.*, 2009), and three irradiance levels, the lowest of which is likely the environmentally the most relevant (Zondervan *et al.*, 2002). Parameter values are drawn from wide-range beta distributions (see Methods) with the mean values for strain B92/11 (see Table 1) to account for the uncertainty about those values and/or for variability in parameter values among *E. huxleyi* strains.

Six major conclusions emerge from the simulations of primary production and calcification in *E. huxleyi* in the Pacific, north of 50° (see Table 1). First, up to the present, *E. huxleyi* has benefitted from CO_2 fertilization since the start of the Industrial Revolution as expected

Table 1 Parameter values with standard error (if estimated)

Symbol	Interpretation	*Emiliania huxleyi* strain			Units
		B92/11	RC1256	NZEH	
k_E	Specific energy conductance	1.45 (0.12)	2.38 (0.06)	2.74 (0.09)	day^{-1}
$[H^+]_0^{env}$	No-effect H^+ concentration	12.25 (4.5)	12.25	12.25	nM
K_{H^+}	H^+ effect scaling constant	83.4 (17.8)	83.4	83.4	nM
$K_{\Omega_{Ca}}$	OA effect scaling parameter	1.1187 (0.50)	0.55 (0.10)	0.16 (0.11)	mM^{-1}
j_{EAm}	Maximum specific assimilation rate	4	4	4	pmol C $cell^{-1}$ day^{-1}
j_{ED}	Specific maintenance rate	0.1	0.1	0.1	pmol C $cell^{-1}$ day^{-1}
M_V	Mean cellular structural biomass*	0.46 (0.04)	0.65	0.65	pmol C $cell^{-1}$
p_1	CO_2 assimilation constant	0.33 (0.04)	7.72 (14.52)	7.72	μmol C M CO_2^{-1} $cell^{-1}$ day^{-1}
p_2	Photon assimilation constant	15.36 (2.05)	11.80 (0.06)	11.40 (0.50)	fmol C m^2 mol $photons^{-1}$ $cell^{-1}$
$y_{Ca,A}$	Maximum calcite yield via assimilation	0.77 (0.15)	0.90 (0.04)	0.96 (0.08)	mol $CaCO_3$ mol C^{-1}
$y_{Ca,D}$	Maximum calcite yield via maintenance	0	0	0	mol $CaCO_3$ mol C^{-1}
$y_{Ca,G}$	Maximum calcite yield via growth	0	0	0	mol $CaCO_3$ mol C^{-1}
y_{VE}	Structural biomass yield	1.74	1.23	1.23	cell pmol C^{-1}

*Coccoliths are not part of structural biomass.

Table 2 Calculated changes in growth and calcification rates in *Emiliania huxleyi* B92/11 in the Pacific, north of 50°, relative to the present with IPCC A2 emission scenario*

Irradiance†	% change in growth rate (SD)			% change in calcification rate (SD)		
	Low	Medium	High	Low	Medium	High
Preindustrial	−0.8 (0.5)‡	−2.2 (1.0)	−3.8 (1.4)	−1.3 (0.7)	−5.1 (2.0)	−10.8 (2.5)
2050	−0.6 (0.4)	−0.5 (0.8)	2.0 (1.2)	−0.2 (0.5)	2.8 (1.8)	9.0 (3.1)
2100	−8.6 (2.3)	−6.3 (2.3)	−3.6 (2.8)	−6.9 (1.9)	−2.3 (3.4)	8.6 (6.4)

*Impact of change in CO_2 only; pCO_2 in preindustrial, present, 2050, and 2100 is 280, 387, 560, and 840 μatm, respectively.
†Low, medium, and high irradiance is 50 (natural conditions(Zondervan *et al*., 2002)), 150 (laboratory conditions(Bach *et al*., 2011; Hoppe *et al*., 2011)), and 500 (light saturated conditions) μmol m^{-2} s^{-1}, respectively.
‡Negative values in the preindustrial era mean that current rates are higher.

primary production and calcification rates have increased, although those increases are very modest at the lowest irradiance considered. Second, in agreement with observations (Rokitta & Rost, 2012), the negative impact of OA on primary production and calcification rates is most pronounced at low irradiance levels as CO_2 fertilization cannot enhance photosynthesis at light limited conditions. Third, at the lowest, environmentally most relevant irradiance, the gain in primary production and calcification rates since the preindustrial era will be reversed before midcentury. Fourth, OA has impacts on both primary production and calcification rates. There is a relatively minor difference in impact at environmentally relevant light levels, i.e. expected end of century declines relative to the present of 8.6% and 6.9% in the rates of primary production and calcification, respectively. Yet, this minor difference might have negative implications for atmospheric CO_2 sequestration in the ocean as the organic carbon pump, which draws CO_2 from the atmosphere through primary production, might be impacted more severely than the carbonate counter pump, which releases CO_2 into the atmosphere through the reduction in ocean water alkalinity due to calcification (Riebesell, 2004; Riebesell *et al*., 2007). Fifth, although parameter values are drawn from wide distributions, the distributions of expected changes in primary production and calcification rates are surprisingly narrow (see Fig. 3). In addition, simulation results with parameter values for strain RC1256 and NZEH deviate at most 2% from those obtained with strain B92/11 at the environmentally most relevant irradiance. This lends substantial credibility to the general conclusions of this paper and supports our expectation that the numerical results in Table 1 are indicative for the response of a wide range of *E. huxleyi* strains and potentially other coccolithophores. Sixth, our results are in line with those studies that report a negative impact of OA on calcification (Riebesell *et al*., 2000; Sciandra *et al*., 2003; Bach *et al*., 2011, 2013), but our estimate of the expected loss in calcification by the end of the century relative to today (6.9% under the low light scenario) is rather modest.

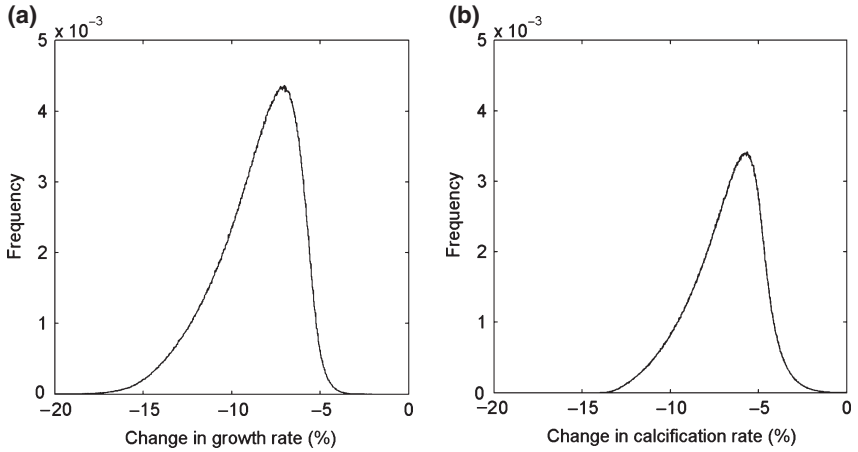

Fig. 3 Distribution of declines in per-cell growth (a) and calcification (b) rates in *Emiliania huxleyi* by the end of the century relative to present day as predicted by simulations with randomized parameter values. The simulations assume the IPCC A2 emission scenario, the expected ocean carbonate characteristics of the Pacific, north of 50°, and an irradiance of 50 μmol m^{-2} s^{-1}. Ocean acidification is expected to have a somewhat larger impact on growth than on calcification. Most parameter values are drawn from a beta distribution with shape parameters fixed at 2, with the parameter values of strain B92/11 (see Table 1) as means and with upper and lower boundaries differing 50% from the mean.

Our model enables us to evaluate the net impact of a complex set of interdependent carbonate system components on the production and calcification potential of marine calcifiers. This alone represents major progress. Further progress could be achieved by adding formalism describing the role of nutrient limitation and by estimating model parameters for a more diverse group of marine calcifiers. Modeling nutrient limitation is important, because, unlike the cultures analyzed here, natural populations of *E. huxleyi* are commonly faced with oligotrophic environments, with major impacts on growth and calcification. Although it would be straightforward, in principle, to extend our representation of assimilation to include an arbitrary number of additional potentially limiting factors (Kooijman, 2010), there are currently insufficient data to validate such an extension in the context of OA. Such an extended model would predict that nutrient limitation has a qualitatively similar impact on growth and calcification as light limitation.

The value of the model would greatly increase if it could be shown that it successfully describes the impact of OA on the vital rates and calcification rates of marine calcifiers other than coccolithophores. To the best of our knowledge, sufficient relevant data have not yet been published; what would be needed are data on multiple physiological processes, such as photosynthesis, feeding, respiration, calcification, growth, and cell composition, for a sufficiently wide range of combinations of carbonate system components. However, with the recent explosive growth of interest in the consequences of OA, this situation is likely to improve rapidly. We are optimistic that our model will be relevant to other taxa, as its assumptions are generic. In particular, the fundamental assumptions describing the direct impact of ocean pH on calcification only require that a calcifying organism must have a space with a carbonate system composition that may differ from that of the environment and the rest of the organism. The model thus opens the way to synthesis of data from many taxa and environments. With that prospect, the model has a potential use in large-scale models in need of more biological realism.

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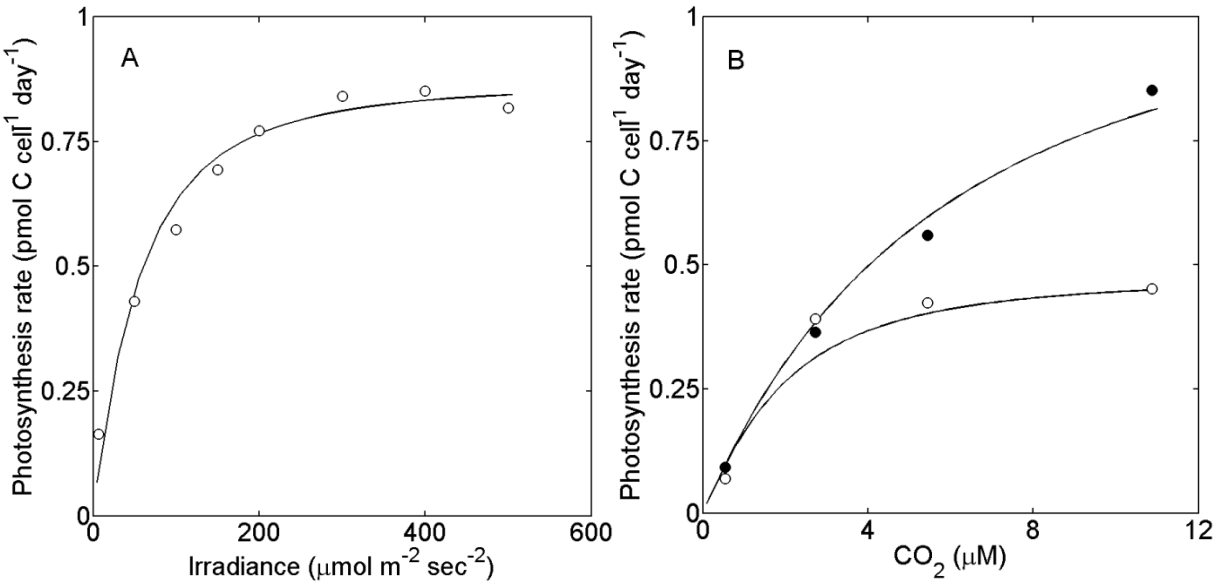
Supporting Information

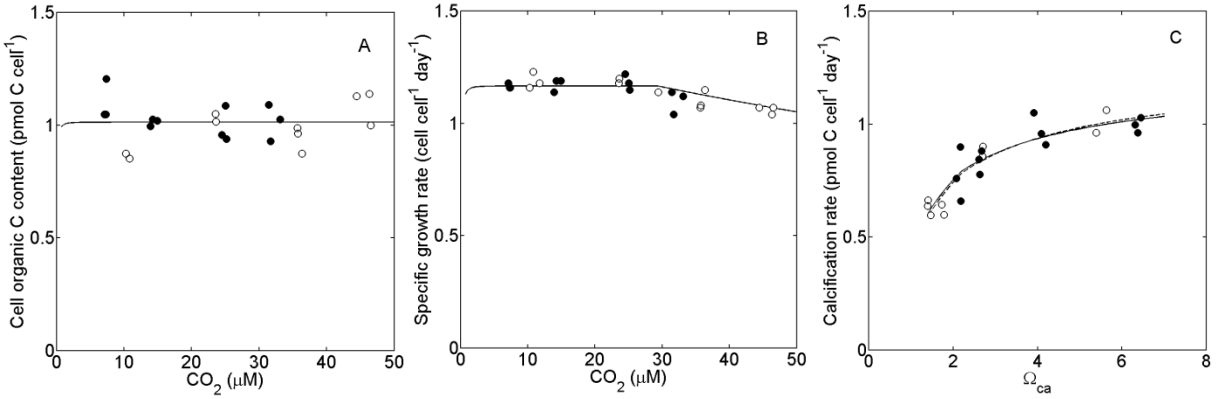
Additional Supporting Information may be found in the online version of this article:

Figure S1. The rate of photosynthesis in *E. huxleyi* as a function of irradiance (A; CO_2 concentration is 10.9 μM) and CO2 (B; irradiance is 50 and 300 μmol m^{-2} s^{-1} for open and closed symbols, respectively).
Figure S2. Production and calcification in *E. huxleyi* RC1256 as a function of carbonate system parameters with model fits to data from Hoppe *et al*., 2011.
Figure S3. Production and calcification in *E. huxleyi* NZEH as a function of carbonate system parameters with model fits to data from Hoppe *et al*., 2011.

Supplementary Figures

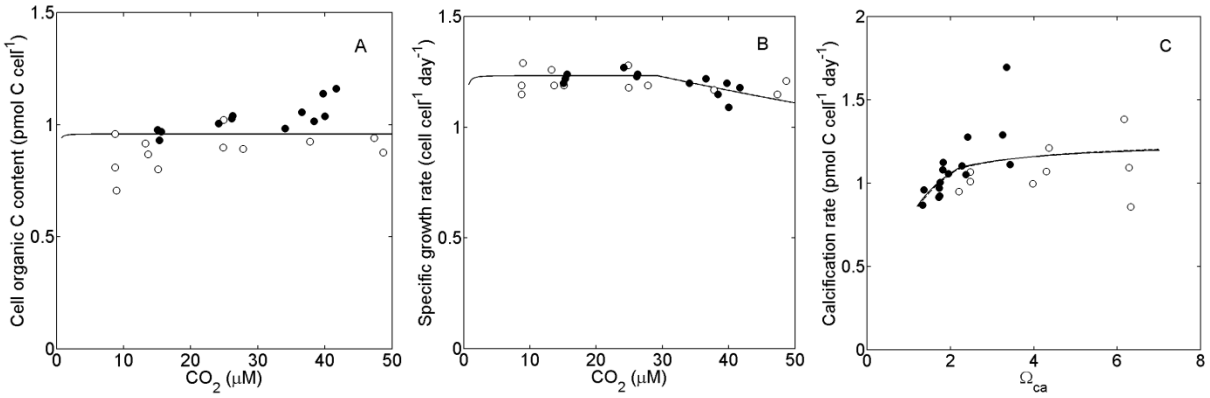


Supplementary Figure 1. The rate of photosynthesis in *E. huxleyi* as a function of irradiance (A; CO_2 concentration is 10.9 μM) and CO2 (B; irradiance is 50 and 300 μmol m^{-2} sec^{-1} for open and closed symbols, respectively). The curves represent fits of Equation 3 in the paper to all data simultaneously, with $j_{EAm} = 1.48$ pmolC cell^{-1} day^{-1}, $p_1 = 0.193\ (\pm\ 0.025)$ pmolC μmol CO_2^{-1} cell^{-1} day^{-1} and $p_2 = 0.014\ (\pm\ 0.001)$ pmolC m^2 sec μmol quanta^{-1} cell^{-1} day^{-1}; error measures are standard errors and the mean relative error is 0.099. pH=8.3 in all treatments; data from Nimer and Merrett (Nimer & Merrett, 1993).



Supplementary Figure 2.

Production and calcification in *E. huxleyi* RC1256 as a function of carbonate system parameters with model fits to data from Hoppe *et al.* (Hoppe *et al.*, 2011). Data were obtained with two carbonate system manipulation methods: total alkalinity manipulation (open symbols and solid curves) and DIC manipulation (closed symbols and broken curves). Model fits to the mean cell organic carbon content (A) and specific growth rate (B) provide parameter estimates used to fit the calcification rate as a function of Ω_{Ca} (C). The small differences in fits between manipulation methods are the result of minor differences between DIC levels at corresponding Ω_{Ca}. According to the model, calcification rates at low Ω_{Ca} are relatively low because of the impact of a suboptimal pH on general metabolism. The calcification rates at Ω_{Ca} above approximately 4 tend to decline because of a diminished energy supply to calcification due to CO_2 limitation of photosynthesis; the relatively narrow range of Ω_{Ca} in this data set precluded a clearly noticeable impact of CO_2 limitation at high Ω_{Ca}. For parameter values, see Table 1. Mean relative error is 0.07 (data both treatments combined; A), 0.02 (data both treatments combined; B), 0.07 and 0.06 (TA and DIC treatment, respectively, C).



Supplementary Figure 3.

Production and calcification in *E. huxleyi* NZEH as a function of carbonate system parameters with model fits to data from Hoppe *et al.* (Hoppe *et al.*, 2011). For explanation of data and model fits see legend to Supplementary Figure 2. Mean relative error is 0.09 (data both treatments combined; A), 0.03 (data both treatments combined; B), 0.13 and 0.07 (TA and DIC treatment, respectively, C).

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