



HAL
open science

Assessing the potential long-term increase of oceanic fossil fuel CO₂ uptake due to CO₂-calcification feedback

A. Ridgwell, I. Zondervan, J. C. Hargreaves, J. Bijma, T. M. Lenton

► To cite this version:

A. Ridgwell, I. Zondervan, J. C. Hargreaves, J. Bijma, T. M. Lenton. Assessing the potential long-term increase of oceanic fossil fuel CO₂ uptake due to CO₂-calcification feedback. *Biogeosciences*, 2007, 4 (4), pp.481-492. hal-00297628

HAL Id: hal-00297628

<https://hal.science/hal-00297628>

Submitted on 18 Jun 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Assessing the potential long-term increase of oceanic fossil fuel CO₂ uptake due to CO₂-calcification feedback

A. Ridgwell¹, I. Zondervan², J. C. Hargreaves³, J. Bijma², and T. M. Lenton⁴

¹School of Geographical Sciences, University of Bristol, Bristol, BS8 1SS UK

²Biogeosciences, Alfred Wegener Institute for Polar and Marine Research, Am Handelshafen 12, 27570 Bremerhaven, Germany

³Frontier Research Center for Global Change, 3173-25 Showa-machi, Kanazawa-ku, Yokohama, Kanagawa 236-0001, Japan

⁴School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK

Received: 27 September 2006 – Published in Biogeosciences Discuss.: 13 November 2006

Revised: 27 June 2007 – Accepted: 28 June 2007 – Published: 6 July 2007

Abstract. Plankton manipulation experiments exhibit a wide range of sensitivities of biogenic calcification to simulated anthropogenic acidification of the ocean, with the “lab rat” of planktic calcifiers, *Emiliania huxleyi* apparently not representative of calcification generally. We assess the implications of this observational uncertainty by creating an ensemble of realizations of an Earth system model that encapsulates a comparable range of uncertainty in calcification response to ocean acidification. We predict that a substantial reduction in marine carbonate production is possible in the future, with enhanced ocean CO₂ sequestration across the model ensemble driving a 4–13% reduction in the year 3000 atmospheric fossil fuel CO₂ burden. Concurrent changes in ocean circulation and surface temperatures in the model contribute about one third to the increase in CO₂ uptake. We find that uncertainty in the predicted strength of CO₂-calcification feedback seems to be dominated by the assumption as to which species of calcifier contribute most to carbonate production in the open ocean.

1 Introduction

Open ocean dwelling calcifying plankton, such as coccolithophorids and foraminifera produce shells by precipitating the mineral calcium carbonate (CaCO₃). The continued dissolution of fossil fuel CO₂ in the surface waters of the ocean and associated decrease in ambient carbonate ion (CO₃²⁻) concentration (Orr et al., 2005) and pH, termed ocean acidification (Caldeira and Wickett, 2003) could adversely affect the ability of these species of plankton to precipitate CaCO₃

Correspondence to: A. Ridgwell
(andy@seao2.org)

(e.g., Bijma et al., 1999; Riebesell et al., 2000; Zondervan et al., 2001). A reduction in marine carbonate production would, in turn, increase the capacity of the surface ocean to absorb CO₂ (Barker et al., 2003; Zondervan et al., 2001). Understanding the strength of this “CO₂-calcification” feedback, by which we mean: the acceleration of CO₂ uptake by the ocean due to lower calcification rates, is important to accurate prediction of the fate of CO₂ emitted to the atmosphere and the extent of future climate change.

The climatic importance of biogenic production of CaCO₃ in the surface ocean and its subsequent removal by gravitational settling arises because although the sum total of dissolved carbon species (DIC) is reduced upon CaCO₃ precipitation, the remaining carbon is re-partitioned in favor of CO_{2(aq)}. This results in a higher partial pressure of CO₂ (*p*CO₂) in the surface ocean by: Ca²⁺+2HCO₃⁻→CaCO₃+CO_{2(aq)}+H₂O. It has been found that biogenic carbonate production can be suppressed as CO₂ is added to the ocean (see Table 1) and the ambient concentration of carbonate ions (CO₃²⁻) is reduced (CO_{2(aq)}+CO₃²⁻+H₂O→2HCO₃⁻). This is not entirely unexpected because in the abiotic system, the precipitation rate of CaCO₃ can be related directly to concentration [CO₃²⁻] via:

$$R = k \times (\Omega - 1)^\eta \quad (1)$$

where Ω is the saturation state (or solubility ratio) of the aqueous environment, defined as $[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] / K_{sp}$ (with K_{sp} a solubility constant), and k is an overall scaling constant (Zhong and Mucci, 1993). The power parameter η controls how non-linear the response of calcification is to a change in saturation state (and $[\text{CO}_3^{2-}]$) – the higher the value of η , the more responsive calcification is to ambient saturation. Conversely, low values of η imply that calcification will be only

Table 1. Relative sensitivity to saturation changes (η) observed in different experimental calcification rate manipulations.

# ¹	Species	Experimental details	Ω (calcite)	Ω (aragonite)	Estimated η ²	Reference
–	<i>Calcidiscus leptoporus</i>	in vitro	~ 2 to ~10	–	n/a ³	Langer et al. (2006)
0	<i>Coccolithus pelagicus</i>	in vitro	~ 2 to ~10	–	0 ⁴	Langer et al. (2006)
1	<i>Emiliana huxleyi</i>	in vitro	2.0 to 4.8	–	0.20±0.09 ⁵	Zondervan et al. (2001)
2	<i>Emiliana huxleyi</i>	mesocosm bloom	2.0 to 5.3	–	0.32±0.20	Delille et al. (2005)
3	<i>Orbulina universa</i>	in vitro (high light)	1.0 to 4.1	–	0.32±0.08	Bijma et al. (1999)
3	<i>Orbulina universa</i>	in vitro (darkness)	1.7 to 4.1	–	0.49±0.23	Bijma et al. (1999)
4	<i>Gephyrocapsa oceanica</i>	in vitro	1.7 to 4.3	–	0.53±0.31	Zondervan et al. (2001)
5	Mixed assemblage	Ship-board incubation	1.7 to 4.4	–	0.75±0.10	Riebesell et al. (2000)
6	Corals ⁶	(various)	–	~ 1 to ~6	~ 1	Langdon and Atkinson (2005) ⁷
7	None (abiotic)	in vitro	–	–	1.9–2.8	Zhong and Mucci (1993)

¹ Sorted downwards by increasing apparent sensitivity of calcification to a change in saturation state. The ID number (#) corresponds to the number labeling in Fig. 4.

² Mean value and standard error.

³ For *C. leptoporus* the observed response of the inorganic carbon content per cell to saturation state was inconsistent with Eq. (1).

⁴ No significant carbonate production response was observed in *C. pelagicus*.

⁵ In an incubation experiment with *Emiliana huxleyi*, Sciandra et al. (2003) found a 25% decrease in net calcification rate in response to an increase in CO₂ from 400 to 700 ppm. This is a slightly larger calcification response than the 15% decrease observed by Zondervan et al. (2001) under a comparable increase in pCO₂, but still rather lower than the 43% decrease in mesocosm experiments with *E. huxleyi* (Delille et al., 2005).

⁶ Coral communities as well as individuals.

⁷ Also see: Yates and Halley (2006a, b) and Schneider and Erez (2006).

weakly affected by changes in saturation. A value of zero is the same as assuming that calcification is independent of saturation.

Marine carbonate production thus gives rise to a negative feedback on climate change, as by suppressing calcification, fossil fuel CO₂ emissions will cause a reduction in the rate of CO₂ release from CaCO₃ precipitation and accelerate the removal of CO₂ from the atmosphere (Zondervan et al., 2001). The net impact of fossil fuel CO₂ release on the climate system will therefore be reduced in the presence of this “CO₂-calcification feedback”.

We address the potential importance of CO₂-calcification feedback to the future sequestration of fossil fuel CO₂ by first collating the calcification responses of different marine organisms to changing CO₃²⁻ and then quantifying the implications of our findings using an Earth system model (Ridgwell et al., 2007; Ridgwell and Hargreaves, 2007). We consider changes in ocean carbon cycling occurring on up to a millennial timescale, when the most important control is the amount of fossil fuel emitted in conjunction with the impact of amplifying positive feedbacks between CO₂ and sea-surface temperature (due to reduced CO₂ solubility at higher temperatures) and ameliorating negative feedbacks such as between CO₂ and calcification. To simplify the analysis, we ignore the net loss or gain of carbon by the land surface (Lenton et al., 2006). Neither will we consider changes in: shallower water (coral reef) or benthic calcification or the

effect of temperature on calcification (e.g. coral bleaching), or potential changes in the efficiency of export of organic carbon to the deep sea, although we discuss their potential roles later. We also omit the impact of the dissolution of carbonates in deep-sea sediments as well as the enhancement of carbonate and silicate weathering on land under higher surface temperatures – such processes dominate ocean invasion only on time-scales rather longer than ca. 1000 years (Ridgwell and Hargreaves, 2007). Our focus in this paper is thus the direct modulating effect of changes in surface ocean calcification on atmospheric CO₂ through the remainder of the millennium.

2 Synthesis of experimental calcifier response

The response of a number of different calcifying marine organisms to changes in ambient carbonate chemistry have been investigated to date (summarized in Table 1). However, the experimental setups and chosen manipulations of the carbonate system differ, hindering simple comparison. We address this by calculating the relative change in calcium carbonate production (calcification rate) as a function of a common variable for which we utilize the widely-used description of the rate of precipitation of carbonate minerals as given in Eq. (1) (Zhong and Mucci, 1993).

For each set of experimental manipulations detailed in Table 1, Ω of calcite is calculated from mean dissolved

inorganic carbon and alkalinity concentrations, salinity, and temperature measured over the course of each experiment, and using the dissociation constants of Mehrbach et al. (1973), as refitted by Dickson and Millero (1987). For *Emiliania huxleyi* (in vitro) (Zondervan et al., 2001) (#1) we combine the two different light-dark cycle data-sets, whereas there is sufficient experimental data to separately fit the results of “high light” and “complete darkness” incubations of the foraminifera *Orbulina universa* (in vitro) (Bijma et al., 1999) (#3). For the *E. huxleyi* mesocosm experiments (Delille et al., 2005) (#2), we fit all the individual replicates across the three treatments. For the ship-board incubations of phytoplankton assemblages (Riebesell et al., 2000) (#5), we first normalize the calcification rate data to a value of 1.0 at the common CO_{2(aq)} concentration of 10 μmol l⁻¹, before fitting the results of all 5 experiments together.

In fitting the data, we assume that Eq. (1) holds true and seek the value of η that produces the best fit to the data. The value of the parameter η is crucial, since it represents the degree of non-linearity of response of calcification rate to a change in ambient carbonate ion (CO₃²⁻) concentration (and thus Ω). A high value of η implies that even a modest anthropogenically-driven reduction in ocean CO₃²⁻ (and pH) might drive a substantial decrease in CaCO₃ production, significantly enhancing fossil fuel CO₂ uptake by the ocean. We carry out 100 iterations using the Levenberg-Marquardt algorithm to minimize the least squares misfit between the theoretical curve and the experimental data. We report the standard error associated with the estimated fitted value of η in Table 1.

3 Model configuration and calibration

The range in sensitivities exhibited by calcifying plankton coupled with uncertainty in which plankton groups dominate past, present, and future marine carbonate production (e.g., Schiebel, 2002), means that a single estimate of the strength of CO₂-calcification feedback could be misleading. Instead, we have taken an ensemble approach to the problem and explored a wide range of possible responses, using an ensemble Kalman filter (EnKF) calibration (Annan et al., 2005) of ocean carbon cycling in the GENIE-1 Earth system model.

The GENIE-1 model comprises: 3-D ocean circulation model, 2-D energy-moisture balance model (EMBM) of the atmosphere, dynamic-thermodynamic sea-ice model, and representation of atmosphere-ocean-sediment carbon cycling (Ridgwell et al., 2007; Ridgwell and Hargreaves, 2007). We use the same relationship between calcification and saturation state (Ω) in the GENIE-1 model (Ridgwell et al., 2007) as we used to fit the calcification data (i.e., Eq. 1). In this, we apply a thermodynamically-based modifier of the rate of carbonate production, γ , as a function of the local surface ocean saturation state (Ω):

$$\gamma = (\Omega - 1)^\eta \quad \text{for } \Omega > 1.0 \quad (2a)$$

$$\gamma = 0.0 \quad \text{for } \Omega \leq 1.0 \quad (2b)$$

We link this to biological export production from the surface ocean by relating the export flux of CaCO₃ (F^{CaCO_3}) directly to the POC flux (F^{POC}) via a spatially-uniform scalar for the CaCO₃:POC rain ratio ($r_0^{\text{CaCO}_3:\text{POC}}$), but modified by γ :

$$F^{\text{CaCO}_3} = \gamma \times r_0^{\text{CaCO}_3:\text{POC}} \times F^{\text{POC}} \quad (3)$$

The biogenic export of CaCO₃ from the surface ocean in the model thus increases with a greater ambient environmental degree of super-saturation with respect to the solid carbonate phase ($\Omega > 1.0$). Carbonate production is zero at $\Omega \leq 1$ – i.e., we implicitly assume that super-saturation and thermodynamically favorable environmental conditions are required for pelagic carbonate production. However, while this assumption appears valid for corals, it may not hold for foraminifera. We discuss the implications of this later. In addition, although coccolithophorid and foraminiferal calcification rates have been observed to respond to changes in saturation (e.g., Bijma et al., 1999; Riebesell et al., 2000; Zondervan et al., 2001; Delille et al., 2005), we do not explicitly capture other important controls in our formulation of carbonate production. Instead, we have implicitly collapsed the (poorly understood) ecological and physical oceanographic controls on marine carbonate production onto a single, purely thermodynamic dependence on Ω . Furthermore, while POC production is affected by changes in climate (such as stratification) in the GENIE-1 model, for simplicity, we do not additionally modify POC production in response to changes in pH (Zondervan et al., 2001).

We utilized observed 3-D distributions of alkalinity (Key et al., 2004) and phosphate (Conkright et al., 2002) in the ocean, together with the 2-D distribution of CaCO₃ content in surface sediments (Archer, 1996) to constrain model parameters controlling the marine carbon cycle using an ensemble Kalman filter (EnKF) as described in Ridgwell et al. (2007) and Ridgwell et al. (2007). The EnKF solves the Kalman equation for optimal linear estimation by using the ensemble statistics to define the mean and covariance of the model’s probability distribution function. In other words, the resulting ensemble members are random samples from this probability distribution function. Although this method is only formally optimal in the case of a linear model and an infinite ensemble size, it has been shown to work well in cases similar to ours (Hargreaves et al., 2004; Annan et al., 2005). We employ Eqs. (2–3) in calculating CaCO₃ production, and calibrate both $r_0^{\text{CaCO}_3:\text{POC}}$ and η in the EnKF. Six additional parameters controlling the rate of organic carbon export as a function of available nutrients (PO₄) as well as the length scales of organic carbon and carbonate carbon remineralization in the ocean interior are also simultaneously calibrated, summarized in Table 2. The size of the ensemble is 54, which is chosen primarily for computational convenience and has no special significance.

Table 2. Summary of the mean EnKF calibrated biogeochemical parameters in the GENIE-1 model (Ridgwell and Hargreaves, 2007).

Parameter symbol	Calibrated mean ¹	Parameter description	Fig. 1 sub-plot
$u_0^{\text{PO}_4}$	$1.96 (\pm 0.34) \mu\text{mol kg}^{-1} \text{yr}^{-1}$	maximum PO ₄ uptake (removal) rate	(a)
K^{PO_4}	$0.22 (\pm 0.065) \mu\text{mol kg}^{-1}$	PO ₄ Michaelis-Menton half-saturation concentration	(b)
r^{POC}	$0.065 (\pm 0.011)$	initial proportion of POC export as recalcitrant fraction	(c)
l^{POC}	$550 (\pm 59) \text{m}$	e -folding remineralization depth of non-recalcitrant POC fraction	(d)
$r_0^{\text{CaCO}_3:\text{POC}}$	$0.044 (+0.038/-0.024)^{2,3}$	CaCO ₃ :POC: export rain ratio scalar (Eq. 3)	(e)
η	$0.81 (\pm 0.28)$	thermodynamic calcification rate power (Eq. 2)	(f)
r^{CaCO_3}	$0.468 (\pm 0.07)$	initial proportion of CaCO ₃ export as recalcitrant fraction	(g)
l^{CaCO_3}	$1083 (\pm 244) \text{m}$	e -folding remineralization depth of non-recalcitrant CaCO ₃ fraction	(h)

¹ Quoted as the mean of the entire EnKF ensemble plus 1 standard deviation of the calibrated parameter value.

² The rain ratio scalar parameter is not the same as the CaCO₃:POC export rain ratio as measured at the base of the euphotic zone because $r_0^{\text{CaCO}_3:\text{POC}}$ is further multiplied by $(\Omega - 1)^\eta$ to calculate the rain ratio, where Ω is the surface ocean saturation state with respect to calcite (see Sect. 3). Pre-industrial mean ocean surface Ω is ~ 5.2 in the GENIE-1 model, so that the global CaCO₃:POC export rain ratio can be estimated as being equal to $(5.2 - 1)^{0.81} \times 0.044 = 0.14$.

³ The \pm standard deviation values differ because EnKF calibration of this particular parameter was carried out in log space.

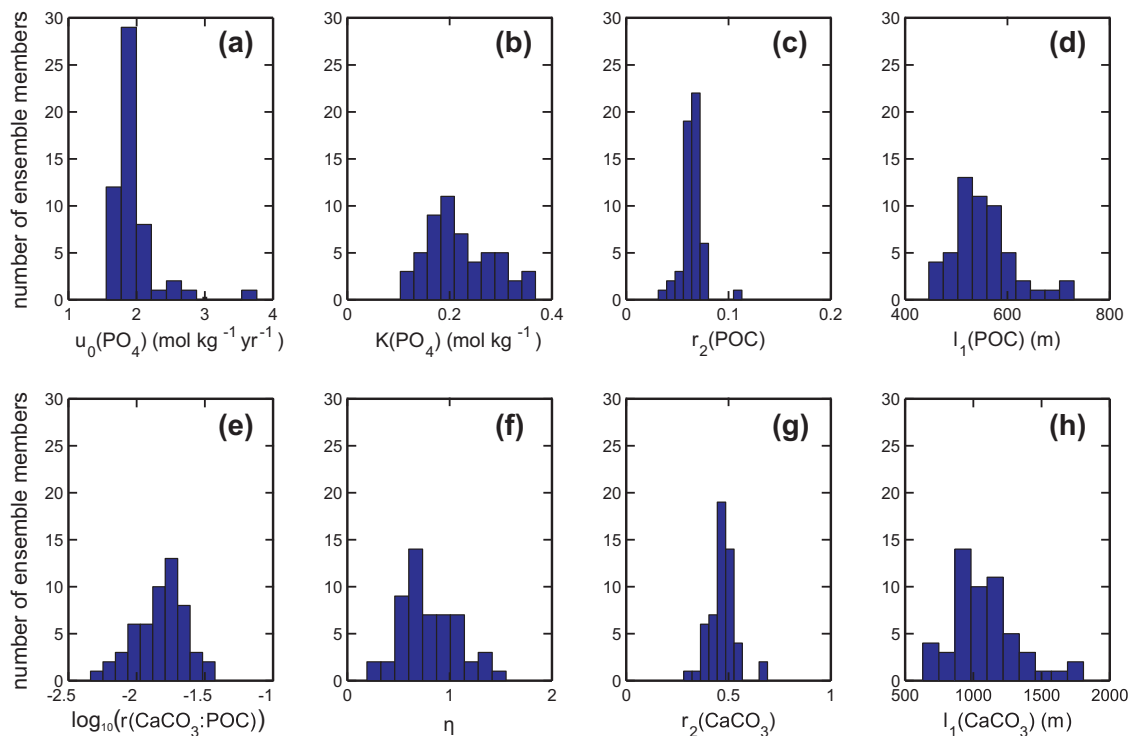


Fig. 1. Distributions of the eight parameters which were varied independently to produce a 54 member ensemble via calibration with the EnKF (<http://www.biogeosciences.net/4/481/2007/bg-4-481-2007-supplement.zip>). The parameters are described in Ridgwell et al. (2007) and summarized in Table 2.

The resulting frequency distribution of calibrated parameter values is shown in Fig. 1. Although all ensemble members are tuned to the observations, we obtain a large range of η across the ensemble members (0.19 to 1.55) because the scaling constant $r_0^{\text{CaCO}_3:\text{POC}}$ (Eq. 3) introduces a degree

of freedom in fitting modern ocean alkalinity and sedimentary CaCO₃ distributions (see Ridgwell et al., 2007). The values we obtain for η thus strongly reflect our prior assumption of a 1 standard deviation of η spanning the range 0–1.5, which is informed by the results of our analysis of

experimental manipulations (Table 1). The relationship between $r_0^{\text{CaCO}_3:\text{POC}}$ and η is determined by the EnKF itself, consistent with the ocean and sediment data. Thus, although this means that we cannot deduce the most probable value for η from marine geochemical observations using our model, we can address the sensitivity of the marine carbon cycle to the wide range of uncertainty in η by carrying out experiments using the full 54-member ensemble of model instances (rather than a just single model composed of the parameter value means).

We refer readers to Ridgwell and Hargreaves (2007) for critical assessment of the ensemble mean of this calibration and to Ridgwell et al. (2007) for a similar calibration but omitting sediment composition. For the analysis presented here, the most relevant model prediction is that of pelagic CaCO₃ production in the open ocean. In the calibrated model, mean CaCO₃ export is 1.2 PgC yr⁻¹, very close to other observational-based estimates (e.g., Feely et al., 2004; Jin et al., 2006). The GENIE-1 model also successfully captures the latitudinal trends in the zonal mean of ocean saturation (Ω) with respect to calcite, although it generally predicts Ω some ~ 0.5 units higher than observations and does not reproduce the distinct geochemistry characterizing continental margin upwelling zones, as shown in Fig. 2. The consequence of this model-data mismatch will be a slight under-estimate of the strength of CO₂-calcification feedback in the model because initial Ω is slightly further away from the threshold of zero calcification ($\Omega=1$, as defined by Eq. 2) than it should be.

4 Future impacts of reduced marine calcification on fossil fuel CO₂ uptake

We run the 54 member ensemble under a single illustrative CO₂ emissions scenario, based on the assumption of all conventional fossil fuel reserves (ca. 4000 PgC) being used up sometime early in the 24th century (Lenton et al., 2006) (Fig. 3a), an amount slightly less than that assumed by Caldeira and Wickett (2003). The ensemble members are run in each of four permutations of feedbacks operating: (i) no CO₂-calcification or CO₂-climate feedbacks, (ii) just the CO₂-climate feedback, (iii) just the CO₂-calcification feedback, and (iv) both CO₂-calcification and CO₂-climate feedbacks. The numerical efficiency of the GENIE-1 model is critical, as this combined sensitivity + feedback analysis represents a total of: $4 \times 54 \times 3000 = 648\,000$ years of coupled 3-D ocean carbon cycle/climate model simulation, which we achieve in just a few days on a small computing cluster.

The evolution with time of the strength of the CO₂-calcification feedback is shown in Fig. 3 for the ensemble mean model, and for the individual members in Fig. 4. We find that historical fossil fuel CO₂ emissions drive an ensemble mean reduction in calcite saturation state (Ω) from 5.2 to 4.5 by the year 1994, leading to a 13% decrease in marine

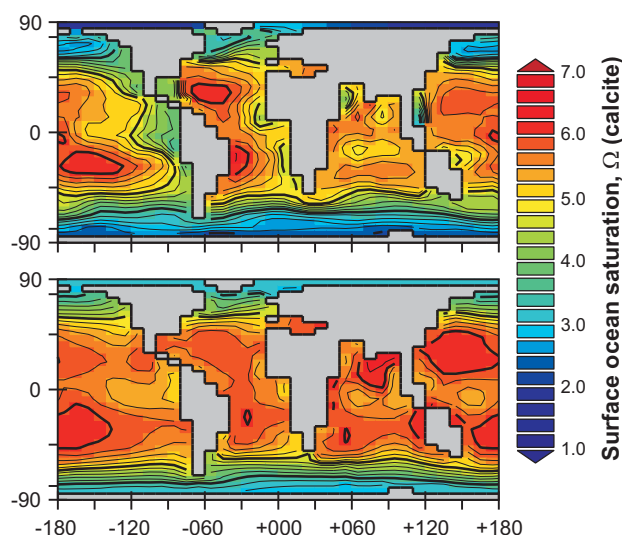


Fig. 2. Surface ocean saturation state. The top panel shows the observationally-derived annual average pre-Industrial saturation state (Ω) for calcite, which we calculate from 3-D data-sets of DIC and ALK (Key et al., 2004) together with temperature, salinity, PO₄, and H₄SiO₄ (Conkright et al., 2002), transformed onto the GENIE-1 model 36×36 equal area model grid and integrated over the uppermost 75 m. We use the same carbonate chemistry scheme as used in GENIE-1 (Ridgwell et al., 2007) in this calculation. The lower panel shows the model-predicted annual average Ω based on the calibrated parameter value means (Ridgwell and Hargreaves, 2007) (see Table 2).

carbonate production (Fig. 3d) as a consequence of Eq. (2). The contribution to the 1994 oceanic anthropogenic CO₂ inventory (estimated at 118 ± 19 PgC (Sabine et al., 2004)) due to CO₂-calcification feedback (ΔCO_2) and including climate feedbacks in the model is no more than 3.2 PgC at this time (Fig. 4), even under the ensemble end-member with the highest sensitivity to ocean acidification ($\eta=1.55$).

Deviations from the best fit line across the ensemble (Fig. 4) reflect the influence of factors that affect CO₂ sequestration, other than differences in the value of η . For instance, the ensemble exhibits initial (year 1765) global CaCO₃ export of between 1.05 and 1.59 PgC yr⁻¹, similar to recent data-based production estimates of 0.8–1.4 PgC yr⁻¹ (Feely et al., 2005; Jin et al., 2006). Because there is no significant correlation with the value of η across the ensemble ($R^2 \sim 0.03$), our model experiment encapsulates a sensitivity test of the strength of CO₂-calcification feedback to uncertainties in initial (pre-industrial) global carbonate production. The relatively muted scatter ($R^2 > 0.94$) of the ensemble members about the best fit line (Fig. 4) indicates that CO₂ sequestered due to ocean acidification is relatively insensitive to assumptions regarding initial carbonate production in the open ocean in the ensemble. Particulate organic carbon (POC) export varies from 7.9 to 12.0 PgC yr⁻¹

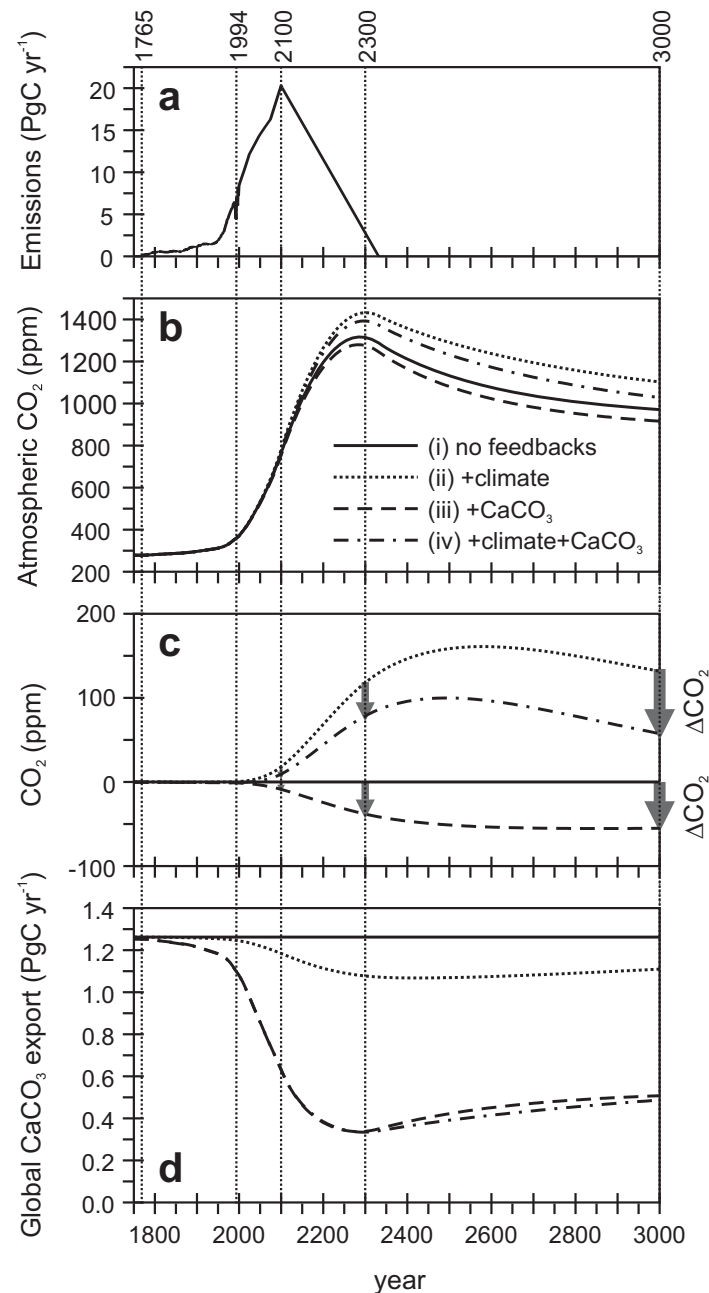


Fig. 3. Atmospheric CO₂ and marine carbonate production responses to fossil fuel CO₂ release. In this, a single model instance employing the ensemble mean parameter set (Table 2) rather than all individual members of the ensemble is used here to illustrate the impact of CO₂-calcification feedback. **(a)** Time-history of the rate of CO₂ emissions to the atmosphere prescribed in the model (see Lenton et al., 2006). **(b)** Evolution of atmospheric CO₂ in experiments with: (i) neither climate nor calcification changes (solid line), (ii) “CO₂-climate” feedbacks operate (dotted line), (iii) calcification responds to atmospheric CO₂ (i.e., “CO₂-calcification” feedback) (dashed line), and (iv) both CO₂-calcification and CO₂-climate feedbacks operate (dot-dash line). **(c)** The impact on the evolution of atmospheric CO₂ of the two feedbacks is shown, both individually, and combined (and compared to the baseline (i.e., no feedbacks) scenario). The grey arrows illustrate how the strength of CO₂-calcification feedback (ΔCO_2) is calculated – i.e., as the difference between the atmospheric CO₂ responses with and without calcification responding to acidification. The ΔCO_2 values themselves are plotted in Fig. 4 for all the ensemble members, while the time-slices at which CO₂ is calculated (years; 1994, 2100, 2300, 3000) are marked by vertical dotted lines. **(d)** The response of global carbonate export under the different permutations of feedback. In the absence of any response of calcification to changing carbonate saturation, CaCO₃ export declines in response to fossil fuel emissions as a result of changes in ocean circulation (stratification) when feedbacks between CO₂ and climate are allowed to operate. (Legend as per 1b.)

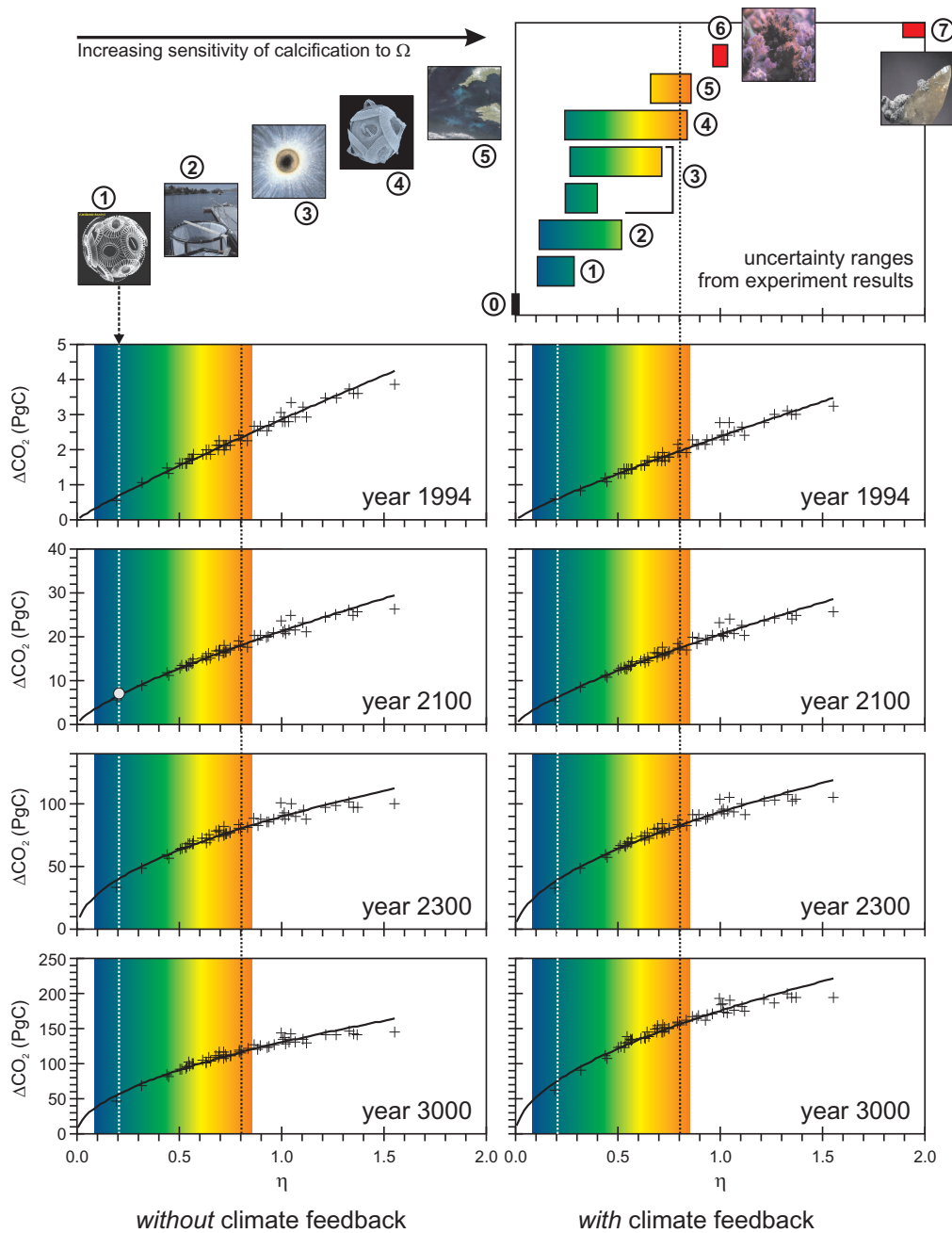


Fig. 4. Response of the 54-member ensemble of realizations of the GENIE-1 Earth system model to CO₂ emissions. The strength of the CO₂-calcification feedback (see Fig. 3) is plotted against the calcification rate sensitivity (η) (Eq. 2) for each of 4 time-slices. Crosses represent individual ensemble members with results shown for the strength of the CO₂-calcification feedback both with (RH side panels) and without (LH side) further feedbacks with climate. The filled grey circle represents the year 2100 prediction of the ocean GCM of Heinze (2004), which assumed the calcification sensitivity of *Emiliana huxleyi* (Zondervan et al., 2001) (indicated by the vertical dotted white line) and no feedbacks with climate (and calculated at a comparable atmospheric CO₂ concentration). The values of η corresponding to the characteristics of different calcifying systems are highlighted at the top, with mean η value and uncertainty limits as given in Table 1: #0 the coccolithophorid *Coccolithus pelagicus* (in vitro) (Langer et al., 2006), #1, the coccolithophorid *Emiliana huxleyi* (in vitro) (Zondervan et al., 2001), #2, *E. huxleyi* mesocosms (Delille et al., 2005), #3, the foraminifer *Orbulina universa* (in vitro) (Bijma et al., 1999), #4, the coccolithophorid *Gephyrocapsa oceanica* (in vitro) (Zondervan et al., 2001), and #5, ship-board incubations of phytoplankton assemblages (Riebesell et al., 2000). Shown for comparison only are: #6, corals (as summarized by Langdon and Atkinson (2005)), and #7, “abiotic” precipitation (i.e., occurring in the absence of any biological intervention) (Zhong and Mucci, 1993). The ensemble mean value ($\eta=0.81$) is indicated by a vertical dotted black line. We chose a simple power law fit to illustrate the trend across the ensemble (solid line). However, while this provides a close approximation with $R^2>0.94$ in each case, a rather more complex function might provide a better fit.

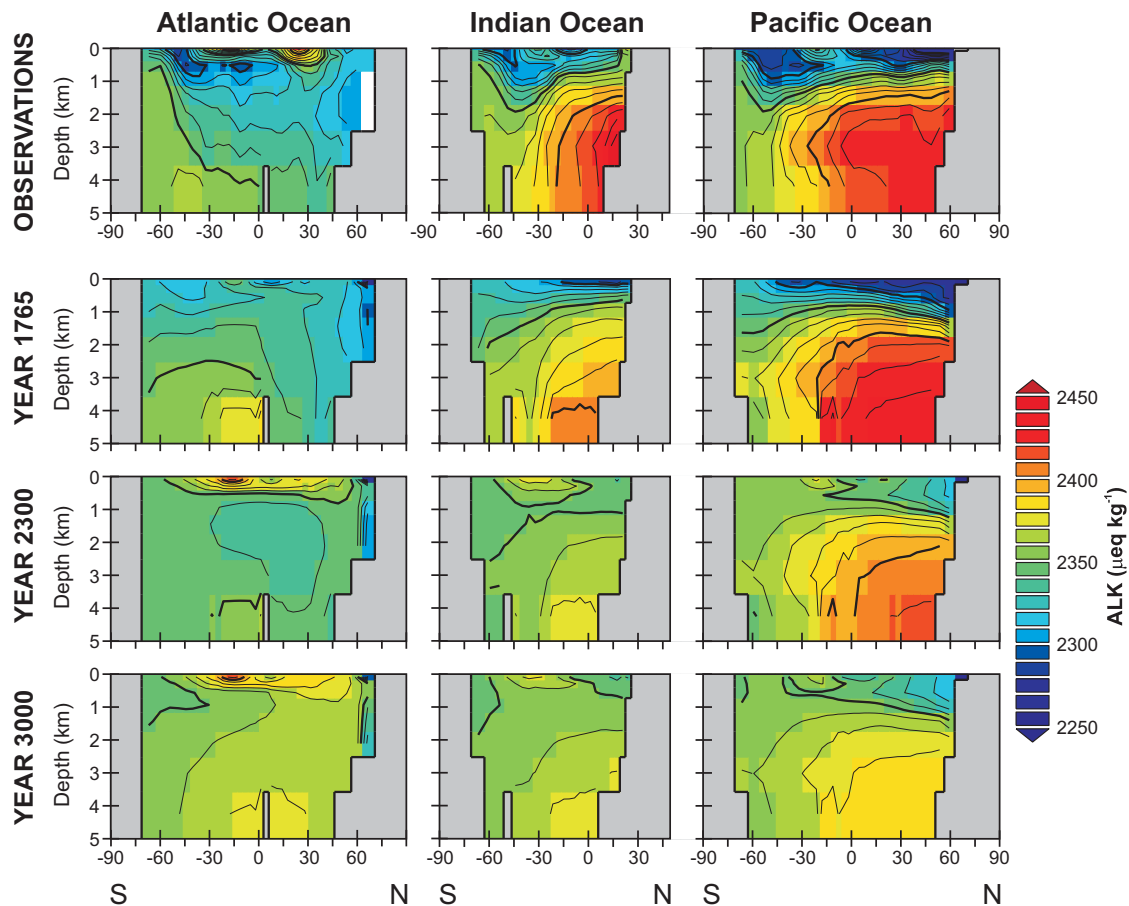


Fig. 5. Reorganization of the ocean alkalinity structure. The zonal mean distribution of alkalinity (ALK) undergoes a large-scale reorganization in response to the reduction in marine carbonate production. Shown compared to observations (Key et al., 2004) (top panel) are the predictions of the ensemble mean model ($\eta=0.81$) for the years: 1765, 2300, and 3000.

across the ensemble, but with only 2 members exhibiting POC export greater than 9.9 PgC yr^{-1} . The clustering in the range $\sim 8\text{--}10 \text{ PgC yr}^{-1}$ is consistent with published inter-model variability (e.g., Aumont et al., 2003; Heinze et al., 1999; Schmittner et al., 2005).

Ocean saturation and marine carbonate production decline (Fig. 3d) until around the year 2300 when a peak atmospheric CO₂ concentration of ~ 1400 ppm is reached in response to emissions. Our model ensemble predicts the additional sequestration of 33–107 PgC due to CO₂-calcification feedback at this time (Fig. 4). Although marine carbonate production starts to recover thereafter, the effect of CO₂-calcification feedback (ΔCO_2) continues to increase, reaching 62–199 PgC by the next Millennium.

The persistence of the impact of reduced calcification reflects the time needed to establish a new alkalinity (ALK) structure in the ocean (Fig. 5). By the year 3000 a profound reorganization has occurred, in which the ALK gradients induced by nitrate uptake and remineralization start to dominate over the initially much stronger opposite effect

due to the precipitation and dissolution of CaCO₃. For instance, ALK becomes almost as high in the deep North Atlantic compared to the North Pacific by year 3000, whereas in the modern ocean there is a very pronounced Atlantic \rightarrow Pacific gradient.

5 Discussion

Calcifying organisms studied in vitro exhibit a wide range of sensitivities of calcification to saturation state (e.g., Table 1). In contrast, marine ecosystem models have generally assumed a single species (*Emiliania huxleyi*) is representative of carbonate production in the open ocean (e.g., Moore et al., 2002; Le Quéré et al., 2005). This is problematic, because while *E. huxleyi* forms large blooms over wide areas of the ocean is not thought to be a particularly important calcifying coccolithophorid (Broerse et al., 2000; Ziveri and Thunell, 2000). We find that this species also exhibits one of the lowest observed calcification sensitivities to a change in CO₂ in vitro (although it is somewhat higher in mesocosms

– see below). Furthermore, foraminifera such as *Orbulina universa* which appear to be rather more sensitive than *E. huxleyi*, may dominate carbonate export globally (Schiebel, 2002).

There are also substantial differences between the results of different experimental methodologies with the same species – for instance, an approximate tripling of atmospheric CO₂ concentration drove a 10–19% reduction in carbonate production by *Emiliania huxleyi* when studied in vitro (Riebesell et al., 2000; Zondervan et al., 2001) but 42% under a similar CO₂ change in a mesocosm bloom experiment (Delille et al., 2005). Furthermore, incubated natural phytoplankton assemblages from the North Pacific have shown decreases in the rate of calcification of up to 83% over this same atmospheric CO₂ range (Riebesell et al., 2000).

The assemblage incubation results may reflect a delay in coccolith production (Delille et al., 2005). Differences in methodologies also exist between the perturbation studies in how CO₂ is controlled and which could affect the deduced sensitivity of calcification: for instance Delille et al. (2005) bubbled CO₂ to achieve required CO₂ values whereas Riebesell et al. (2000) and Zondervan et al. (2001) added acid and base in some experiments. However, we think that the apparent progression observed in carbonate production sensitivity: in vitro → mesocosms → natural assemblages might be important. It could reflect either a higher calcification susceptibility of un-characterized calcifying plankton species or an amplification of acidification impacts on carbonate production by ecosystem dynamics, perhaps reflecting a lower fitness of calcifying plankton, which would result in fewer individuals in addition to less CaCO₃ production per individual. If so, in making species response inter-comparison, use of a standard experimental protocol would be advantageous.

The enhancement of marine sequestration of fossil fuel CO₂ by the next Millennium (Fig. 4) as a result of reduced surface ocean calcification represents 4–13% of the atmospheric fossil fuel CO₂ burden at this time (the anthropogenic excess over the pre-industrial inventory). Thus, while CO₂-calcification feedback reduces the peak atmospheric CO₂ concentration by ~15–49 ppm in our experiment, its importance relative to atmospheric CO₂ is rather greater on the millennial-scale (~29–93 ppm). The inclusion of a climate component (Edwards and Marsh, 2005) in the GENIE-1 Earth system model allows us to assess the importance of changes in climate on the CO₂-calcification feedback. Changes in ocean surface temperatures affect CO₂ solubility and ocean stratification, which in turn affects the rate of CO₂ invasion into the ocean and nutrient supply up to the surface. This amplifies by up to one third the change in CO₂ sequestration that is directly driven by reduced calcification (contrast the L.H. and R.H. panels in Fig. 4).

A number of mechanisms have not been taken into account in this Earth system model analysis, which could affect estimates of the overall importance of CO₂-calcification feedback. For instance, the effect of ecosystem changes on

the average sinking rate and penetration depth of POC may act in either direction depending on the species that become more abundant (e.g., Bopp et al., 2003), amplifying or diminishing the net response of the marine carbon cycle to ocean acidification. However, we do not distinguish the contribution of different phytoplankton “functional types” to total export production in the current model (Ridgwell et al., 2007). There are also physiological effects of higher ambient concentrations of dissolved CO₂ (and lower pH) in driving more POC production per cell, an effect that has been observed to be substantial in *E. huxleyi* and *G. oceanica* (Zondervan et al., 2001). The consequential increase in the efficiency of the biological pump would act as a negative feedback on rising atmospheric CO₂. Similarly, any future decline in coral calcification (Kleypas et al., 1999) or increase in the dissolution of aragonite and/or high magnesium calcite, none of which we consider here, would act to increase the sequestration of fossil fuel CO₂. Finally, a reduction in carbonate production could also affect the transport of organic matter into the deep ocean (Ridgwell, 2003) – the ballast hypothesis (Armstrong et al., 2002). The consequence of a mechanistic dependence of organic carbon transport on the carbonate flux would be a reduction in the strength of CO₂-calcification feedback (Barker et al., 2003; Heinze, 2004). However, alternative interpretations of sediment trap correlations do not require the efficiency of the organic carbon pump to be dependent on the CaCO₃ flux (Francois et al., 2002; Passow and De La Rocha, 2006).

The caveats discussed above are all, in principal at least, accessible to model analysis. The primary source of uncertainty in quantifying the impact of ocean acidification on future ocean CO₂ uptake lies in the model representation of the calcification response to ocean acidification. Estimates can be made of likely parameter values, as we have demonstrated in this paper in the context of the power η (Table 1, Fig. 1) but the form of the most appropriate parameterization to describe the calcification response is not known a priori. Here we have assumed that calcification ceases at $\Omega=1.0$ (Eq. 2), analogous to the abiotic precipitation response (Eq. 1). For corals, the general trend across a range studies appears consistent with our assumption (Langdon and Atkinson, 2005). However, organisms exerting a much stronger degree of control over the calcification process, particularly foraminifera, need not be so constrained.

It is outside the scope of this paper to address formally the importance of model structural uncertainty in quantifying the strength of the CO₂-calcification feedback. (By “model structural uncertainty”, we mean the uncertainty in the model representation of the mechanisms involved rather than due to uncertainties in observational data-sets, including those used for constraining parameter values.) Instead, we have evaluated the results of different GCM-based analyses of the CO₂-calcification feedback. For instance, Heinze (2004) parameterized a response of the CaCO₃:POC rain ratio to changes in surface ocean carbonate chemistry in the

HAMOCC ocean carbon cycle model by modifying carbonate production in proportion to the deviation from modern surface ocean conditions of CO₂ partial pressure. The parameter values in the relationship were informed by the laboratory experiments on *Emiliana huxleyi* (Zondervan et al., 2001). We find a very comparable response when we take our value of η from the same calcification manipulation experiments ($\eta=0.2$ for *Emiliana huxleyi* in vitro – see Table 1) and set climate invariant. Our predicted year 2100 (with 774 ppm CO₂ in the atmosphere) enhancement of marine CO₂ sequestration due to CO₂-calcification feedback is 6.5 PgC (Fig. 4), almost identical to the 3.5 ppm (~7 PgC) calculated by Heinze (2004) at year 2100 (~800 ppm CO₂ in the atmosphere).

In a more recent model analysis, Gehlen et al. (2007) predicted a 29% smaller calcification response at 4× CO₂ (1112 ppm) as compared to Heinze (2004) under a similar atmospheric CO₂ forcing. Gehlen et al. (2007) assumed a rather different, Michaelis-Menten type formulation, but like Heinze (2004) calibrated their calcification parameterization mainly against the in vitro experimental response of *Emiliana huxleyi* (Zondervan et al., 2002), although mesocosm data (Delille et al., 2003) was also included. Their curve fit can be approximated (over a range in Ω of 2–6) by a value of η of around 0.2–0.25 using our Eq. (2), from which we predict the additional CO₂ sequestration due to CO₂-calcification feedback of 6.5–7.7 PgC (Fig. 4) at ~3×CO₂, compared to 5.9 PgC in Gehlen et al. (2007) at 4×CO₂.

Although other model differences such as saturation-dependent water column dissolution of carbonates (Gehlen et al., 2007) prevent straight-forward inter-comparison, the spread across the 3 different models and associated parameterizations is no more than a factor of 2 in estimating the potential enhancement of CO₂ uptake. The greater uncertainty in predicting future rates of fossil fuel CO₂ uptake by the ocean is thus the species calcification response in conjunction with which species dominate pelagic carbonate production. Indeed, recent research reveals some species of coccolithophorid exhibit rather unexpected responses to simulated changes in ocean acidification in vitro, with *Calcidiscus leptoporus* actually increasing CaCO₃ production per cell at elevated CO₂ partial pressures (Langer et al., 2006).

6 Conclusions

Our analysis highlights the importance of the prevailing uncertainties regarding the controls on marine carbonate production and calcifier response to anthropogenic ocean acidification. We conclude from the experimental data currently available that the response of carbonate production to a change in environmental chemistry as measured in vitro is not a good indication of the ecosystem (or global) level response. We also find that the behavior of the coccolithophorid *Emiliana huxleyi* to increasing CO₂ is rather

small compared to coccolithophores species such as *Gephyrocapsa oceanica*, foraminifera, and corals. Ecosystem models that adopt this species as their “functional type” for carbonate production may underestimate the importance of CO₂-calcification feedback on future climate change. The importance of the differences in species response is underlined by our model inter-comparison, which suggests that uncertainty in the model predictions is dominated by assumptions regarding the representative carbonate-producing species rather than the form of the relationship linking calcification to ocean acidification per se. Further mesocosm experiments and higher level manipulations of more complete ecosystems, together with a better quantification of which calcifying species control CaCO₃ production globally and the spatial distribution and (environmental and ecological) controls on this production, will be critical in making more reliable assessments of the future impact of ocean acidification and feedback with atmospheric CO₂.

Acknowledgements. AR acknowledges support from Canada Research Chairs, the Canadian Foundation for Climate and Atmospheric Sciences, and the Trusthouse Charitable Foundation. IZ’s contribution was supported by Netherlands-Bremen Cooperation in Oceanography (NEBROC II). TML’s contribution is part of the NERC e-Science GENIEfy project (NE/C515904). Computer facilities for the EnKF calculations were provided by JAMSTEC.

Edited by: C. Heinze

References

- Annan, J. D., Hargreaves, J. C., Edwards, N. R., and Marsh, R.: Parameter estimation in an intermediate complexity earth system model using an ensemble Kalman filter, *Ocean Model.*, 8, 135–154, 2005.
- Archer, D.: An atlas of the distribution of calcium carbonate in sediments of the deep sea, *Global Biogeochem. Cy.*, 10, 159–174, 1996.
- Armstrong, R. A., Lee, C., Hedges, J. I., Honjo, S., and Wakeham, S. G.: A new, mechanistic model for organic carbon fluxes in the ocean: based on the quantitative association of POC with ballast minerals, *Deep-Sea Res. II*, 49, 219–236, 2002.
- Aumont, O., Maier-Reimer, E., Blain, S., and Monfray, P.: An ecosystem model of the global ocean including Fe, Si, P colimitations, *Global Biogeochem. Cy.*, 17, 1060, doi:10.1029/2001GB001745, 2003.
- Barker, S., Higgins, J. A., and Elderfield, H.: The future of the carbon cycle: review, calcification response, ballast and feedback on atmospheric CO₂, *Philos. T. Roy. Soc. A*, 361, 1977–1999, 2003.
- Bijma, J., Spero, H. J., and Lea, D.W.: Reassessing foraminiferal stable isotope geochemistry: Impact of the oceanic carbonate system (Experimental Results), in: *Use of proxies in paleoceanography: Examples from the South Atlantic*, edited by: Fischer, G. and Wefer, G., Springer-Verlag Berlin Heidelberg, 489–512, 1999.
- Bopp, L., Kohfeld, K. E., Le Quere, C., and Aumont, O.: Dust impact on marine biota and atmospheric CO₂ during glacial pe-

- riods, *Paleoceanography*, 18, 1046, doi:10.1029/2002PA000810, 2003.
- Broerse, A. T. C., Ziveri, P., Hinte, J. E. v., and Honjo, S.: Coccolithophore export production, seasonal species composition and coccolith CaCO₃ fluxes in the NE Atlantic (34° N, 21° W and 48° N, 21° W), *Deep-Sea Res. II*, 47, 1877–1905, 2000.
- Caldeira, K. and Wickett, M. E.: Anthropogenic carbon and ocean pH, *Nature*, 425, p. 365, 2003.
- Conkright, M. E., Antonov, J. I., Baranov, O. K., et al.: *World Ocean Database 2001, Volume 1, Introduction*, edited by: Levitus, S., NOAA Atlas, NESDIS 42, U.S. Government Printing Office, Washington, D.C., 167 pp., 2002.
- Delille, B., Harlay, J., Zondervan, I., et al.: Response of primary production and calcification to changes of pCO₂ during experimental blooms of the coccolithophorid *Emiliania huxleyi*, *Global Biogeochem. Cy.*, 19, GB2023, doi:10.1029/2004GB002318, 2005.
- Dickson, A. G. and Millero, F. J.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, *Deep-Sea Res.*, 34, 1733–1743, 1987.
- Edwards, N. R. and Marsh, R.: Uncertainties due to transport-parameter sensitivity in an efficient 3-D ocean-climate model, *Clim. Dynam.*, 2, 415–433, 2005.
- Feely, R. A., Sabine, C. L., Lee, K., et al.: Impact of anthropogenic CO₂ on the CaCO₃ system in the oceans, *Science*, 305, 362–366, 2004.
- Francois, R., Honjo, S., Krishfield, R., and Manganini, S.: Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean, *Global Biogeochem. Cy.*, 16, 1087, doi:10.1029/2001GB001722, 2002.
- Gehlen, M., Gangstø, R., Schneider, B., Bopp, L., Aumont, O., and Ethe, C.: The fate of pelagic CaCO₃ production in a high CO₂ ocean: A model study, *Biogeosciences Discuss.*, 4, 533–560, 2007, <http://www.biogeosciences-discuss.net/4/533/2007/>.
- Hargreaves, J. C., Annan, J. D., Edwards, N. R., and Marsh, R.: Climate forecasting using an intermediate complexity Earth System Model and the Ensemble Kalman Filter, *Clim. Dynam.*, 23, 745–760, 2004.
- Heinze, C., Maier-Reimer, E., Winguth, A. M. E., and Archer, D.: A global oceanic sediment model for long-term climate studies, *Global Biogeochem. Cy.*, 13, 221–250, 1999.
- Heinze, C.: Simulating oceanic CaCO₃ export production in the greenhouse, *Geophys. Res. Lett.*, 13, L16308, doi:10.1029/2004GL020613, 2004.
- Jin, X., Gruber, N., Dunne, J., Sarmiento, J. L., and Armstrong, R. A.: Diagnosing the contribution of phytoplankton functional groups to the production and export of POC, CaCO₃ and opal from global nutrient and alkalinity distributions, *Global Biogeochem. Cy.*, 20, GB2015, doi:10.1029/2005GB002532, 2006.
- Key, R. M., Kozyr, A., Sabine, C. L., et al.: A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), *Global Biogeochem. Cy.*, GB4031, 18, doi:10.1029/2004GB002247, 2004.
- Kleypas, J. A., Buddemeier, R. W., Archer, D., et al.: Geochemical consequences of increased atmospheric carbon dioxide on coral reefs, *Science*, 284, p. 118, 1999.
- Langdon, C. and Atkinson, M. J.: Effect of elevated pCO₂ on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment, *J. Geophys. Res.*, 110, C09S07, doi:10.1029/2004JC002576, 2005.
- Langer G., Geisen, M., Baumann, K.-H., Kläs, J., Riebesell, U., Thoms, S., and Young, J. R.: Species-specific responses of calcifying algae to changing seawater carbonate chemistry, *Geochem. Geophys. Geosyst.*, 7, Q09006, doi:10.1029/2005GC001227, 2006.
- Lenton, T. M., Williamson, M. S., Edwards, N. R., Marsh, R. J., Price, A. R., Ridgwell, A. J., Shepherd, J. G., Cox, S. J., and the GENIE team: Millennial timescale carbon cycle and climate change in an efficient Earth system model, *Clim. Dynam.*, 26, 687–711, doi:10.1007/s00382-006-0109-9, 2006.
- Le Quééré, C., Harrison, S. P., Prentice, I. C., et al.: Ecosystem dynamics based on plankton functional types for global ocean biogeochemistry models, *Glob. Change Biol.*, 11, 2016–2040, 2005.
- Mehrbach, C., Culbertson, C. H., Hawley, J. E., and Pytkowicz, R. M.: Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr.*, 18, 897–907, 1973.
- Moore, J. K., Doney, S. C., Kleypas, J. A., et al.: An intermediate complexity marine ecosystem model for the global domain, *Deep-Sea Res. II*, 49, 403–462, 2002.
- Orr, J. C., Fabry, V. J., Aumont, O., et al.: Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, *Nature*, 437, 681–686, 2005.
- Passow, U. and De La Rocha, C. L.: Accumulation of mineral ballast on organic aggregates, *Global Biogeochem. Cy.*, 20, GB1013, doi:10.1029/2005GB002579, 2006.
- Ridgwell, A. J.: An end to the ‘rain ratio’ reign?, *Geochem. Geophys. Geosys.*, 4, 1051, doi:10.1029/2003GC000512, 2003.
- Ridgwell, A., Hargreaves, J., Edwards, N., Annan, J., Lenton, T., Marsh, R., Yool, A., and Watson, A.: Marine geochemical data assimilation in an efficient Earth System Model of global biogeochemical cycling, *Biogeosciences*, 4, 87–104, 2007, <http://www.biogeosciences.net/4/87/2007/>.
- Ridgwell, A. and Hargreaves, J. C.: An efficient Earth System Model of Global biogeochemical cycling: Regulation of atmospheric CO₂ by deep-sea sediments, *Global Biogeochem. Cy.*, 21, GB2008, doi:10.1029/2006GB002764, 2007.
- Riebesell, U., Zondervan, I., Rost, B., Tortell, P. D., Zeebe, R. E., Morel, F. M. M.: Reduced calcification of marine plankton in response to increased atmospheric CO₂, *Nature*, 407, 364–367, 2000.
- Sabine, C. L., Feely, R. A., Gruber, N., et al.: The Oceanic Sink for Anthropogenic CO₂, *Science*, 305, 367–371, 2004.
- Schiebel, R.: Planktic foraminiferal sedimentation and the marine calcite budget, *Global Biogeochem. Cy.*, 16, 1065, doi:10.1029/2001GB001459, 2002.
- Schneider, K. and Erez, J.: The effect of carbonate chemistry on calcification and photosynthesis in the hermatypic coral *Acropora eurystoma*, *Limnol. Oceanogr.*, 51, 1284–1293, 2006.
- Schmittner, A., Oschlies, A., Giraud, X., Eby, M., and Simmons, H. L.: A global model of the marine ecosystem for long-term simulations: Sensitivity to ocean mixing, buoyancy forcing, particle sinking, and dissolved organic matter cycling, *Global Biogeochem. Cy.*, 19, GB3004, doi:10.1029/2004GB002283, 2005.
- Sciandra, A., Harlay, J., Lefèvre, D., Lemée, R., Rimmelin, P., Denis, M. and Gattuso, J.-P.: Response of the coccolithophorid

- Emiliana huxleyi* to elevated partial pressure of CO₂ under nitrate limitation, *Mar. Ecol.-Prog. Ser.*, 261, 111–122, 2003.
- Yates, K. K. and Halley, R. B.: CO₃²⁻ concentration and *p*CO₂ thresholds for calcification and dissolution on the Molokai reef flat, Hawaii, *Biogeosciences*, 3, 357–369, 2006a.
- Yates, K. K. and Halley, R. B.: Diurnal variation in rates of calcification and carbonate sediment dissolution in Florida Bay, *Estuaries Coasts*, 29, 24–39, 2006b.
- Ziveri, P. and Thunell, R. C.: Coccolithophore export production in Guaymas Basin, Gulf of California: Response to climate forcing, *Deep-Sea Res. II*, 47, 2073–2100, 2000.
- Zhong, S. J., Mucci, A.: Calcite precipitation in seawater using a constant addition technique – a new overall reaction kinetic expression, *Geochim. Cosmochim. Ac.*, 57, 1409–1417, 1993.
- Zondervan, I., Zeebe, R. E., Rost, B., and Riebesell, U.: Decreasing marine biogenic calcification: A negative feedback on rising atmospheric *p*CO₂, *Global Biogeochem. Cy.*, 15, 507–516, 2001.
- Zondervan, I., Rost, B., and Riebesell, U.: Effect of CO₂ concentration on the PIC/POC ratio in the coccolithophore *Emiliana huxleyi* grown under light-limiting conditions and different daylengths, *J. Exp. Mar. Biol. Ecol.*, 272, 55–70, 2002.