

Decreasing marine biogenic calcification: A negative feedback on rising atmospheric $p\text{CO}_2$

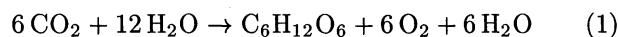
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Abstract. In laboratory experiments with the coccolithophore species *Emiliana huxleyi* and *Gephyrocapsa oceanica*, the ratio of particulate inorganic carbon (PIC) to particulate organic carbon (POC) production decreased with increasing CO_2 concentration ($[\text{CO}_2]$). This was due to both reduced PIC and enhanced POC production at elevated $[\text{CO}_2]$. Carbon dioxide concentrations covered a range from a preindustrial level to a value predicted for 2100 according to a “business as usual” anthropogenic CO_2 emission scenario. The laboratory results were used to employ a model in which the immediate effect of a decrease in global marine calcification relative to POC production on the potential capacity for oceanic CO_2 uptake was simulated. Assuming that overall marine biogenic calcification shows a similar response as obtained for *E. huxleyi* or *G. oceanica* in the present study, the model reveals a negative feedback on increasing atmospheric CO_2 concentrations owing to a decrease in the PIC/POC ratio.

1. Introduction

The ocean plays a major role in the global carbon cycle, representing the largest reservoir of carbon that is exchanged with the atmosphere in the form of CO_2 on timescales < 1000 years. The uptake of atmospheric CO_2 by the oceans is driven by physicochemical processes as well as biological fixation of inorganic carbon species. The biogenic production of organic material and carbonate minerals in the surface ocean and their subsequent transport to depth, termed the “biological carbon pumps” [Volk and Hoffert, 1985], generate a gradient of dissolved inorganic carbon (DIC), with relatively low values in the surface and higher values at depth. The biological carbon pumps are thought to be responsible for approximately three-quarters of the vertical DIC gradient [Volk and Hoffert, 1985]. Depending on their effect on ocean-atmosphere CO_2 exchange, two different biological pumps can be distinguished. The organic carbon pump is a sink for CO_2 , which is taken up during photosynthetic carbon fixation:

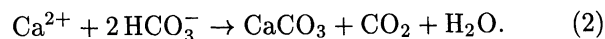


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and then transported as particulate organic carbon (POC) to deeper water layers. The carbonate pump transports particulate inorganic carbon (PIC) to the deep sea, which is formed in the surface ocean:



As the uptake of 2 moles of alkalinity in the form of HCO_3^- (or CO_3^{2-}) and 1 mole of DIC during calcification causes a shift in the equilibrium of the carbonate system toward higher $[\text{CO}_2]$ (see section 4), biogenic calcification represents a potential CO_2 source to the environment [Holligan *et al.*, 1993; Robertson *et al.*, 1994]. Since calcification often occurs in combination with production of organic matter, part of the CO_2 generated may be taken up by photosynthetic carbon fixation [Sikes *et al.*, 1980; Holligan and Robertson, 1996]. Thus compared to noncalcifying new production systems (for example diatom blooms), calcifying communities are a smaller sink or form a net potential source of CO_2 to the atmosphere [Ware *et al.*, 1991; Holligan *et al.*, 1993].

Although corals are the most conspicuous calcifying organisms in the ocean and are widely distributed in tropical shelf regions, they account for only 10% of the global CaCO_3 production [Ware *et al.*, 1991; Milliman and Drozler, 1996]. From a quantitative point of view, the most important groups of marine calcifying organisms are pelagic organisms like coccolithophores [Westbroek *et al.*, 1994; Winter *et al.*, 1994], planktonic foraminifera, and pteropods [Morse and Macken-

zie, 1990]. Among these groups, which contribute up to 70% to global CaCO_3 precipitation [Wollast, 1994; Milliman and Drozler, 1996], coccolithophores are thought to be the most productive calcifying group [Westbroek et al., 1993]. They form intensive blooms extending over large parts of the global ocean, mainly at subpolar latitudes [Brown and Yoder, 1994]. These blooms are mostly monospecific and formed by only a few coccolithophore species, of which the most prominent representatives are *Emiliania huxleyi* and *Gephyrocapsa oceanica* [Winter et al., 1994]. Mass development of coccolithophores is a main driving force for the export of calcium carbonate to the deep ocean. Although calcium carbonate cycling represents only a small fraction of the global carbon cycle, atmospheric CO_2 , which is largely a function of DIC and alkalinity in the surface ocean [Broecker and Peng, 1982], is intimately related to CaCO_3 production. *E. huxleyi* and *G. oceanica* are therefore of main importance in global carbon cycling.

Estimates of global calcium carbonate production ranges from 0.64 to 2 Gt C per year (1.03 Gt C [Morse and Mackenzie, 1990]); (0.64 Gt C [Milliman, 1993]); (1-2 Gt C [Shaffer, 1993]); (1.0-1.3 Gt C [Westbroek et al., 1993]); (1.13 Gt C [Wollast, 1994]); (1 Gt C [Milliman and Drozler, 1996]). Modern estimates of global annual marine primary production are ~ 45 Gt C [Antoine et al., 1996], of which ~ 10 Gt C are exported to the deep sea [Palmer and Totterdell, 2001]. The estimated export ratio of CaCO_3 to particulate organic carbon (rain ratio) is therefore relatively high, ranging from 0.17 to 0.4 (0.18 [Shaffer, 1993]); (0.17-0.33 [Westbroek et al., 1993]); (0.25 [Broecker and Peng, 1982]); (0.4 [Sigman et al., 1998]); (see Holligan and Robertson [1996] for review). Since the export of CaCO_3 and POC have opposite effects on the surface ocean CO_2 partial pressure, a change in the rain ratio affects the partitioning of CO_2 between ocean and atmosphere. It has been suggested that the rain ratio is not constant through time and is an important factor in the regulation of global climate [Archer and Maier-Reimer, 1994].

From the middle of the 18th century, the atmospheric partial pressure of CO_2 has increased steadily from 280 to 366 μatm in the year 1998 [Keeling and Whorf, 1999]. This rise in atmospheric CO_2 concentration has led to changes in the surface ocean chemistry [Brewer, 1978, 1997; Chen and Millero, 1979] and will continue to cause corresponding changes in the future. Following the International Panel on Climate Change (IPCC) "business as usual" scenario (IS92a, [Houghton et al., 1995]), it can be predicted that by the year 2100, when atmospheric $p\text{CO}_2$ is expected to have reached about 700 μatm , sea surface $[\text{CO}_2]$ will have tripled, and $[\text{CO}_3^{2-}]$ and pH will have dropped by 50% and 0.35 units, respectively, relative to preindustrial values [Wolf-Gladrow et al., 1999]. The present increase of

$[\text{CO}_2]$ in the ocean will decrease the CaCO_3 saturation state, which will make the conditions for calcification less favorable [Wollast, 1994]. The CaCO_3 saturation state Ω is defined as

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp}^*}, \quad (3)$$

where K_{sp}^* is the stoichiometric solubility product for the mineral phases of CaCO_3 (calcite or aragonite). Sensitivity to the CaCO_3 saturation state has been shown for corals [Gattuso et al., 1998; Kleypas et al., 1999, Langdon et al., 2000] and foraminifera [Bijma et al., 1999], where decreasing CaCO_3 saturation state caused a decrease in calcification rates.

It has been calculated that marine calcification constitutes a larger source for CO_2 when the seawater buffer capacity decreases in the surface ocean as a consequence of increasing atmospheric CO_2 , a positive feedback on increasing CO_2 concentrations [Frankignoulle et al., 1994; Gattuso et al., 1996]. However, these calculations were done under the assumption that global calcification rates remain constant over time. If calcification by the dominant calcifying group, i.e., the coccolithophores, also shows to be sensitive to changing carbonate chemistry in the sea surface, potential CO_2 exchange between ocean and atmosphere could be affected over large areas of the world ocean. Riebesell et al. [2000] showed that the ratio of calcification to POC production in the coccolithophorid species *E. huxleyi* and *G. oceanica* is sensitive to the carbonate chemistry in the growth medium. In both laboratory experiments and natural phytoplankton assemblages this ratio decreased with increasing CO_2 concentration corresponding to surface ocean conditions ranging from preindustrial levels to values expected in the year 2100.

In this study we present results of laboratory experiments with *E. huxleyi*, where the effects of changing carbonate chemistry on calcification and particulate organic carbon production were tested. We compare the results with data obtained by Riebesell et al. [2000]. In addition, a model was employed to simulate short-term effects of increasing atmospheric CO_2 concentrations on the CO_2 release due to CaCO_3 precipitation in the surface ocean. As input to the model, we used the data from laboratory experiments with *E. huxleyi* and *G. oceanica* presented by Riebesell et al. [2000] and in the present study, to simulate different scenarios of changing calcification rates in the surface ocean.

2. Methods

Monospecific cultures of *E. huxleyi* (strain PML B92/11) and *G. oceanica* (strain PC 7/1) were grown in filtered (0.2 μm) seawater enriched with NO_3 and PO_4 to concentrations of 100 and 6.25 $\mu\text{mol L}^{-1}$, respec-

Table 1. Production of Particulate Organic Carbon (POC, pg C cell⁻¹ d⁻¹), Particulate Inorganic Carbon (PIC, pg C cell⁻¹ d⁻¹), and the PIC/POC Ratio in *G. oceanica* and *E. huxleyi* Under Two L/D Cycles and at Different CO₂ Concentrations (μmol L⁻¹) in the Growth Medium^a

<i>E. huxleyi</i> (16/8 L/D)				<i>E. huxleyi</i> (24/0 L/D)				<i>G. oceanica</i> (16/8 L/D)			
CO ₂	POC	PIC	PIC/POC	CO ₂	POC	PIC	PIC/POC	CO ₂	POC	PIC	PIC/POC
5.61	9.02 (0.26)	9.24 (0.27)	1.02	11.68	11.08 (0.51)	9.75 (0.83)	0.88	5.68	21.41 (0.87)	25.26 (1.06)	1.18
12.36	9.76 (0.19)	9.28 (0.35)	0.95	16.77	12.59 (0.84)	9.16 (0.73)	0.73	11.95	26.46 (1.36)	22.56 (0.07)	0.97
18.45	9.44 (0.12)	8.00 (0.25)	0.85	17.95	14.03 (0.21)	9.43 (0.39)	0.67	16.94	25.22 (1.18)	19.26 (2.27)	0.77
21.32	10.66 (0.24)	8.53 (0.54)	0.80	22.56	11.76 (0.52)	7.83 (0.30)	0.67	24.78	25.68 (1.29)	19.81 (2.97)	0.78
27.25	9.78 (0.15)	7.56 (0.23)	0.77	30.00	13.26 (1.10)	7.38 (0.38)	0.56	33.71	32.22 (1.51)	5.60 (1.61)	0.17

^aThe numbers in parentheses represent 1 s.d.

tively and with metals and vitamins according to *f/2* [Guillard and Ryther, 1962]. Cultures were preadapted to the experimental conditions for ~12 generations and maintained dilute by starting the experiment with low cell concentrations. The incident photon flux density was 150 μmol m⁻² s⁻¹ and the temperature 15°C. *E. huxleyi* was grown at a 16/8 and 24/0 hours L/D cycle, whereas *G. oceanica* was grown at a 16/8 hours L/D cycle only. Five different CO₂ levels (Table 1) were adjusted by adding 1 N HCl or 1 N NaOH to the medium. At the end of the experiment, after 8 generations, less than 7% of the DIC in the medium had been taken up by the cells. After inoculation in triplicate 2.4 L borosilicate bottles, the bottles were closed immediately with teflon lined screw caps without head space to avoid CO₂ exchange with the atmosphere.

Samples for DIC and alkalinity measurements were taken in 300 mL borosilicate bottles, fixed with 1 mL of a HgCl₂ solution (35 g L⁻¹) and stored, in case of DIC samples free of air bubbles at 4°C. DIC was measured coulometrically [Johnson *et al.*, 1985] in duplicate and alkalinity was calculated from linear Gran plots [Gran, 1952] after duplicate potentiometric titration [Bradshaw *et al.*, 1981; Brewer *et al.*, 1986]. The carbonate system of the medium was calculated from temperature, salinity, and the concentrations of DIC, alkalinity, and PO₄, using equilibrium constants of Goyet and Poisson [1989]. Subsamples for the determination of total particulate carbon (TPC) and particulate organic carbon (POC) were filtered on precombusted (12 hours, 500°C) QM-A filters (pore width ~0.6 μm) and stored at -20°C. Prior to analysis, the POC filters were fumed for 2 hours with a saturated HCl solution to remove all inorganic C. TPC and POC were subsequently measured on a mass spectrometer. Particulate inorganic carbon (PIC)

was calculated as the difference between TPC and POC. Samples for cell counts were fixed with 400 μL/20 mL sample of a 20% formaldehyde solution buffered with hexamethylenetetramine, and counted within one day by means of a Coulter "Multisizer II". The growth rate (μ) was calculated as

$$\mu = \frac{(\ln c_1 - \ln c_0)}{\Delta t}, \quad (4)$$

where c_0 and c_1 are the cell concentrations at the beginning and the end of the experiment, respectively, and Δt is the duration of the incubation in days. Inorganic and organic carbon production (P , pg C cell⁻¹ d⁻¹) was calculated according to

$$P = \mu(\text{cellular carbon content}). \quad (5)$$

3. Experimental Results

Changes in the production of PIC and POC and the PIC/POC ratio are analyzed in relation to [CO₂]. Data of *E. huxleyi* grown at a 16/8 L/D and of *G. oceanica* are taken from Riebesell *et al.* [2000]. PIC and POC data for *G. oceanica* were incorrectly plotted by Riebesell *et al.* [2000] and have been corrected in the present study. However, note that trends remain exactly the same. With increasing [CO₂] in the growth medium and corresponding changes in *p*CO₂, pH, and [CO₃²⁻], POC production increases slightly in *E. huxleyi* at a 16/8 L/D. When grown at a 24/0 L/D cycle there was no significant change in the POC production in *E. huxleyi* (Figure 1a, Table 1). In contrast, there was a pronounced increase in the POC production in *G. oceanica* over the CO₂ range tested (Figure 1d, Table 1). The cellular organic carbon content of *G. ocean-*

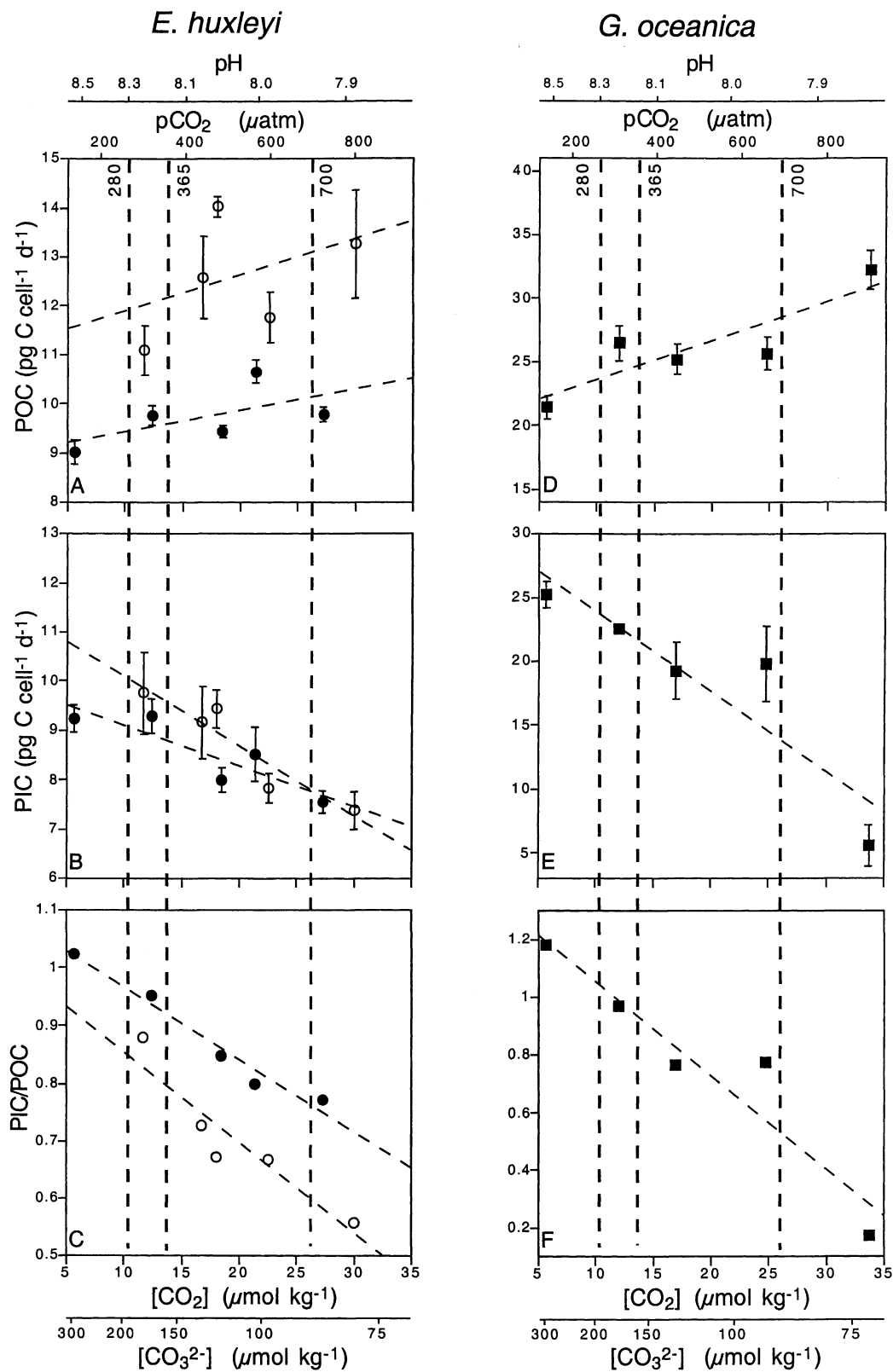


Figure 1. (a-c) Rates of production of particulate organic carbon (POC), particulate inorganic carbon (PIC), and the ratio of PIC/POC in *E. huxleyi* at L/D cycles of 16/8 hours (closed symbols) and 24/0 hours (open symbols) and (d-f) *G. oceanica* at 16/8 L/D. Error bars represent one standard deviation ($n=3$). The vertical dashed lines indicate atmospheric $p\text{CO}_2$ at pre-industrial times, at present, and as expected in 2100 according to a “business as usual scenario” [Houghton et al., 1995]. Note that the vertical axes have different scales and that DIC and total alkalinity differed slightly between the experiments, so that values for pH, $p\text{CO}_2$, and $[\text{CO}_3^{2-}]$ are approximations. Reprinted by permission from Nature (Riebesell et al. 2000) copyright (2000) Macmillan Magazines Ltd.

ica is 2 times higher than the organic carbon content of *E. huxleyi*. Moreover, *E. huxleyi* cells grown under continuous light have a higher organic carbon content than those grown at a 16/8 L/D cycle. In contrast to POC production, the production of PIC significantly decreases with increasing [CO₂] in *E. huxleyi* and even more pronounced in *G. oceanica* (Figures 1b and e, Table 1). There is no significant difference in PIC content between *E. huxleyi* cells grown at different L/D cycles. The decrease and increase in the production of PIC and POC, respectively, caused a decrease in the ratio of PIC to POC with increasing [CO₂] in both *E. huxleyi* ($r^2 = 0.98$ and 0.94 at 16/8 and 24/0 L/D, respectively) and *G. oceanica* ($r^2 = 0.95$) (Figures 1c and f).

When these data are interpolated between preindustrial $p\text{CO}_2$ values and values expected in 2100 (280 and 700 ppm, respectively, indicated in Figure 1), an 8.5 and 10% increase in POC production and a 15.7 and 25.7% decrease in PIC production is observed in *E. huxleyi* under a L/D cycle and continuous light, respectively. This causes the PIC/POC ratio to decrease by 21 and 31.5%, respectively. In *G. oceanica* the POC production increases by 18.6% over this range, whereas the PIC production and PIC/POC ratio decreases by 44.7 and 52.5%, respectively.

4. Effects of Calcification on the Surface Ocean Carbonate Chemistry

From (2) it can be seen that dissolved inorganic carbon (DIC) and total alkalinity (TA) drop by one and two units, respectively, for each unit of CaCO₃ precipitated. The new equilibrium concentrations of the carbonate species in solution after calcification can therefore be calculated from the change in DIC and TA. DIC and TA are defined as

$$\text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}], \quad (6)$$

where $[\text{CO}_2] = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3]$ and

$$\text{TA} = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+], \quad (7)$$

where minor contributions to the TA from seawater constituents such as phosphate and silicate have been neglected. Figure 2 shows an example typical for surface ocean conditions ($T = 15^\circ\text{C}$, $S = 35$), with initial values of $\text{DIC} = 2.0 \text{ mmol kg}^{-1}$, $\text{TA} = 2.3 \text{ mmol kg}^{-1}$, and $[\text{CO}_2] = 10.5 \mu\text{mol kg}^{-1}$. The surface ocean is assumed to be in equilibrium with the atmosphere with respect to CO₂. The effect of calcification on the carbonate system is illustrated by the light-shaded vector. The origin of the vector is located at initial conditions, whereas the final point corresponds to conditions after

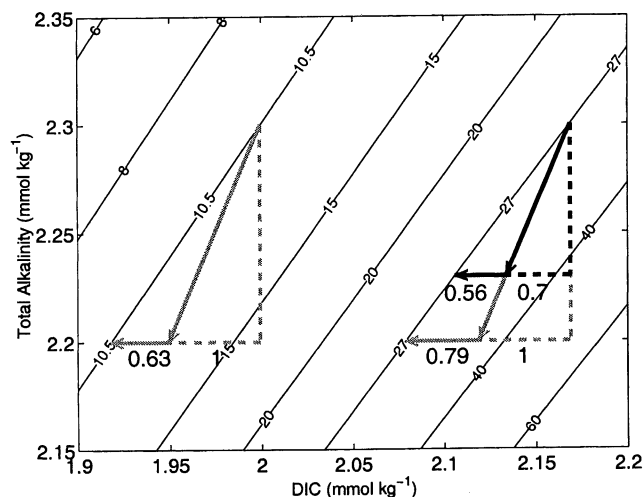


Figure 2. Changes in the concentrations of DIC, total alkalinity, and CO₂ owing to calcification (light-shaded vectors) at (left) preindustrial times and in (right) 2100. Numbers at the vectors are relative numbers. Thus when 1 mole C as DIC is taken up during calcification, 0.63 mole C as CO₂ is released to the environment during preindustrial times, and 0.79 C in 2100, owing to a decreasing buffer capacity (light-shaded vectors, see text). Assuming calcification is only 70% of the preindustrial value in 2100, CO₂ release due to calcification would then be 0.56 C (solid black vectors, see text).

removal of 50 μmol calcium carbonate per kg seawater. Since DIC and TA decrease in a ratio of 1:2, the slope of a line through the vector in this representation is 2. The concentration of dissolved CO₂ increases from 10.5 to 12.4 $\mu\text{mol kg}^{-1}$ during this process. Thus, for values of DIC, TA, T , and S given above, the production of 50 μmol calcium carbonate results in an increase of [CO₂] of 1.9 $\mu\text{mol kg}^{-1}$.

After the formation of calcium carbonate the water is left oversaturated in CO₂ with respect to the atmosphere, so that CO₂ is subsequently released in order to reestablish equilibrium. This effect is indicated by the horizontal solid light-shaded vector in Figure 2. Starting at conditions after calcification at [CO₂] = 12.4 $\mu\text{mol kg}^{-1}$, carbon dioxide is released until aqueous CO₂ (and the corresponding $p\text{CO}_2$) is restored to the value of the atmosphere. Concomitantly, the DIC concentration decreases, while the TA remains constant. The precipitation of 50 $\mu\text{mol kg}^{-1}$ CaCO₃ and the subsequent equilibration with the atmosphere then finally leads to degassing of $\sim 32 \mu\text{mol CO}_2 \text{ kg}^{-1}$ in this example.

With rising atmospheric CO₂ and the resulting decrease in pH of the surface seawater, the buffer capacity of the ocean for CO₂ decreases. The ratio of CO₂-released:carbonate-precipitated (Ψ) during CaCO₃ precipitation depends on the physicochemical properties of the seawater and will increase with decreasing buffer ca-

capacity [Frankignoulle et al., 1994; Gattuso et al., 1996]:

$$\Psi = -\frac{\delta(\text{CO}_2)}{\delta(\text{CO}_3^{2-})} = -\frac{\left[\frac{\delta p\text{CO}_2}{\delta(\text{CO}_3^{2-})}\right]}{\left[\frac{\delta p\text{CO}_2}{\delta(\text{CO}_2)}\right]}, \quad (8)$$

where $\delta(\text{CO}_2)$ and $\delta(\text{CO}_3^{2-})$ refer to variation of dissolved CO_2 and CO_3^{2-} , respectively. The buffer factors $\delta p\text{CO}_2/\delta(\text{CO}_2)$ and $\delta p\text{CO}_2/\delta(\text{CO}_3^{2-})$ can be used to describe the dynamics of the seawater carbonate system during calcification and to estimate the resulting release of CO_2 . Here Ψ is expected to increase from the calculated preindustrial value of 0.63 [Frankignoulle et al., 1994; Gattuso et al., 1996] to ~ 0.79 in the year 2100 and to ~ 0.84 in 2150, following an IPCC “business as usual scenario” (IS92a, [Houghton et al., 1995]). Thus, assuming that calcium carbonate production in the oceans stays constant this represents an additional source of CO_2 .

A decrease in the production of CaCO_3 with increasing atmospheric CO_2 concentrations, as found in corals [Gattuso et al., 1998], foraminifera [Bijma et al., 1999], and coccolithophores [Riebesell et al., 2000; this study], will immediately influence the surface ocean carbonate chemistry. In order to quantify this effect we employed a model where we used the laboratory results of the present study and those obtained by Riebesell et al. [2000] to simulate the possible impact of decreasing marine calcification on the CaCO_3 -related CO_2 release in the surface ocean.

5. Model Simulation

Changes in the surface ocean carbonate chemistry from conditions prevailing in preindustrial times to those expected for the years 2100 and 2150 were simulated according to the “business as usual” anthropogenic CO_2 emission scenario (IS92a) of the IPCC report 1995 [Houghton et al., 1995; see also Wolf-Gladrow et al., 1999]. The atmospheric CO_2 concentrations for the period from 2100 to 2150 were obtained from a projection of the IS92a scenario by fitting an exponential function to the atmospheric CO_2 concentrations given by Houghton et al. [1995]. Simulation of the temporal change of global calcification rates are based on the laboratory results described in this study. We assume that CO_2 -related responses of the coccolithophores *E. huxleyi* or *G. oceanica* as described in this study are representative for overall marine biogenic calcification.

The potential impact of decreasing calcification on the CO_2 release to the environment is investigated using the following scenarios (see Figure 3): (1) calcification stays at a constant rate of 1 Gt C per year (similar to present-ocean values [Milliman and Drozler, 1996]), (2) calcification decreases as in *E. huxleyi* grown at a 16/8 L/D cycle, (3) calcification decreases as in *E. hux-*

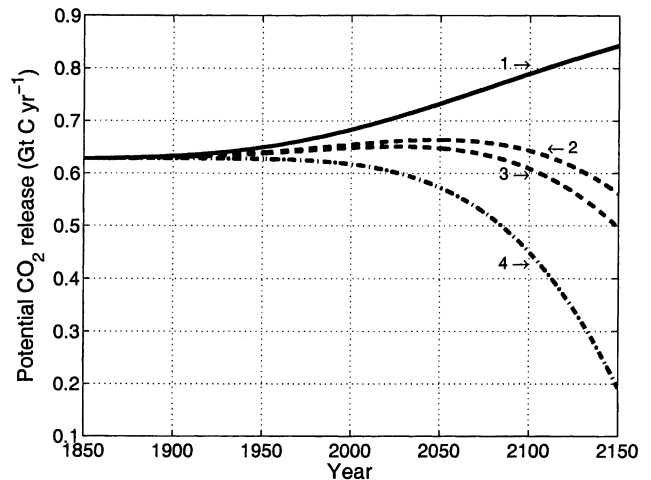


Figure 3. Potential CO_2 release in Gt C yr^{-1} from 1850 to 2150 when annual CaCO_3 production remains constant at 1 Gt C yr^{-1} (scenario 1, solid line), CaCO_3 production decreases as in *E. huxleyi* at a 16/8 L/D cycle (scenario 2, dashed line), or at a 24/0 L/D cycle (scenario 3, dashed line), and CaCO_3 production decreases as in *G. oceanica* (scenario 4, dashed-dotted line).

leyi grown at a 24/0 L/D cycle, (4) calcification decreases as in *G. oceanica* grown at a 16/8 L/D cycle, (5) PIC/POC ratio decreases as in *E. huxleyi* grown at a 16/8 L/D cycle, (6) PIC/POC ratio decreases as in *E. huxleyi* grown at a 16/8 L/D cycle and (7) PIC/POC ratio decreases as in *G. oceanica*. Since the POC production in *E. huxleyi* grown at a 16/8 L/D cycle shows no significant trend, a decrease in the PIC/POC ratio is only due to decreasing calcification rates. The model results for this scenario (5) are thus very similar to the results for scenario 2.

When global CaCO_3 production is kept at a preindustrial level of 1 Gt C per year, the annual CO_2 release to the environment increases with time due to increasing atmospheric CO_2 and the subsequent decreasing buffer capacity of the surface ocean (a positive feedback, see section 4; scenario 1, Figures 3 and 4). When global CaCO_3 production decreases as in scenario 2 and 3, the decrease in CO_2 release integrated between 1850 and 2100 (2150) is 8.7 (19.1) or 10.7 (23.5) Gt C , respectively (Figure 3, see also Figure 2). When global CaCO_3 precipitation decreases as in scenario 4, the integrated decrease in CO_2 release would be 20.1 (44.2) Gt C .

In our laboratory experiments *E. huxleyi* grown at a 24/0 L/D cycle and *G. oceanica* increased their cellular POC production with increasing CO_2 concentrations (Figure 1). When an increase in the POC production by marine calcifying organisms is accounted for in our model, the integrated difference in CO_2 released to the environment between 1850 and 2100 (2150) is 8.7 (19.1)

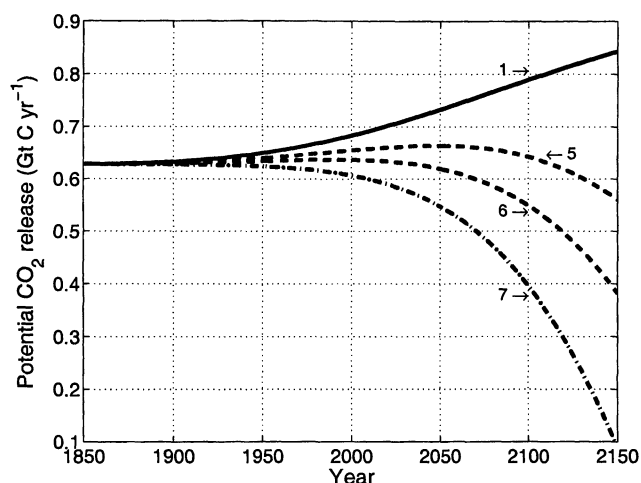


Figure 4. Potential CO₂ release in Gt C yr⁻¹ from 1850 to 2150 when annual CaCO₃ production remains constant at 1 Gt C yr⁻¹ (scenario 1, solid line), PIC/POC ratio decreases as in *E. huxleyi* at a 16/8 L/D cycle (scenario 5, dashed line), or at a 24/0 L/D cycle (scenario 6, dashed line), and PIC/POC ratio decreases as in *G. oceanica* (scenario 7, dashed-dotted line).

and 14.2 (31.3) Gt C for scenario 5 and 6, respectively, and 23.3 (51.2) for scenario 7 (Figure 4). This larger difference in CO₂ release is due to a further reduction in the PIC/POC ratio when cellular POC production increases. The relatively strong decrease in CO₂ release in the different scenarios after 2100 (Figures 3 and 4) is due to the exponential increase in atmospheric CO₂ concentrations with time and the decreasing calcification correlating linearly to the CO₂ concentration.

6. Discussion

In previous studies, CO₂-related effects on calcification have been demonstrated in corals [Gattuso *et al.*, 1998; Kleypas *et al.*, 1999, Marubini and Atkinson, 1999], in a coralline algae [Gao *et al.*, 1993], and in a foraminiferal species [Bijma *et al.*, 1999]. The response of the two coccolithophore species to CO₂-related changes in carbonate chemistry shown by Riebesell *et al.* [2000] and in the present investigation, agrees with previous studies on other marine calcifying organisms. Compared to preindustrial times, the PIC-production in *E. huxleyi* may decrease by 16-26% and in *G. oceanica* by 45% when surface ocean chemistry changes to conditions expected in 2100. This is consistent with a predicted decrease in calcification over a similar range of CO₂ in corals [Langdon *et al.*, 2000 (40%); Kleypas *et al.*, 1999 (17-35%)] and in the foraminifera *Orbulina universa* [Bijma *et al.*, 1999 (18-21%)], although decreases are lower than the maximal reduction of 83% in calcification shown in natural plankton assemblages [Riebesell *et al.*, 2000].

Why *G. oceanica* shows higher sensitivity to changing carbonate chemistry than *E. huxleyi* remains unclear. Furthermore, the reason why *E. huxleyi* cells grown under continuous light show higher POC production compared to cells grown at a 16/8 L/D cycle (Figure 1a), whereas there is no difference in the PIC decrease between both conditions (Figure 1b), is also not clear. One explanation might be the time of sampling in the L/D experiment, which was at the end of the dark phase. At this point in the L/D cycle the cells have the lowest carbon content due to cell division during the dark period [Van Bleijswijk *et al.*, 1994]. If calcification continued in the dark, as was shown in some studies [e.g., Balch *et al.*, 1992], this could explain the decoupling of POC and PIC production, yielding a similar PIC production under a 16/8 L/D cycle as under continuous light. This raises the question whether the quantitative nature of the CO₂ effects on the PIC/POC ratio may be due to the time of sampling and whether results may be different when the PIC/POC ratio is averaged over a L/D cycle. We tested this by monitoring diurnal variation in cellular carbon content over a 38-hour period at a 16/8 L/D cycle. A consistent significant offset in cellular PIC and POC content and the PIC/POC ratio was observed between high and low CO₂ treatments throughout the diurnal cycle (I. Zonder van *et al.*, Effect of increasing CO₂ concentration on the PIC/POC ratio in the coccolithophore *Emiliania huxleyi* grown under light-limiting conditions and different daylengths, submitted to *Marine Ecology Progress Series*, 2000), showing that the CO₂ effect reported here is not an artifact due to the time of sampling.

In our model we assume that CO₂-related responses of the coccolithophores *E. huxleyi* or *G. oceanica* as described in the present study are representative for overall marine biogenic calcification. We used two coccolithophore species, one of them at two different daylengths, obtaining different scenarios for the model simulation. Assuming a constant annual global carbonate production of 1 Gt C through time, it can be calculated that as a result of increasing anthropogenic CO₂ and the subsequent decrease in the seawater buffer capacity, biogenic calcification would act as an additional source for CO₂. Frankignoulle *et al.* [1994] calculated an additional input of 5 Gt C to the atmosphere from 1880 to 2030-2050 as a result of the change of the carbonate buffer in the surface ocean. When CO₂-related effects on biogenic calcification are accounted for, our model predicts a significant decrease in potential CO₂ release to the atmosphere when PIC/POC ratios decrease. Thus the expected positive feedback on increasing CO₂ concentrations is completely reversed by the effect of decreasing global calcification and becomes a negative feedback. This effect is rather small compared to the current anthropogenic CO₂ emission (~7

Gt C annually [Houghton et al., 1995]). Riebesell et al. [2000] showed a reduction in calcification rates by 36–83% in high relative to low CO₂ treatments in natural plankton assemblages, which were dominated by coccolithophores. *E. huxleyi* is the most abundant coccolithophore and possibly the most productive calcifying organism on Earth today [Holligan, 1992; Westbroek et al., 1994]. If the observed response to increasing CO₂ concentrations of the two coccolithophore species in this study and in the study by Riebesell et al. [2000] is a general phenomenon in the world's oceans, a decrease in the PIC/POC ratio could affect different processes in areas where coccolithophores play a dominant role.

First, as mentioned above, it directly affects the carbonate system. When coccolithophore carbonate production in the surface ocean slows down, the potential release of CO₂ to the atmosphere, as a consequence of calcification, is reduced [Holligan and Robertson, 1996] (see section 4 and Figure 2b). In addition to a decrease in PIC content, we found higher cellular POC production with increasing CO₂ concentration in both *E. huxleyi* and *G. oceanica* (the cells become larger). In a natural field situation, growth is ultimately limited by nutrient availability. Total production of POC will therefore not change if nutrient concentration remains constant. However, when the cellular POC content increases relative to the PIC content, this decreases the PIC/POC ratio. Experiments in the present study were done under nutrient replete conditions, which poorly mimics the natural situation. Therefore we also tested CO₂-related effects on the PIC/POC ratio under nutrient limitation. Preliminary results show a similar effect as described in the present study, i.e., a decrease in the PIC/POC ratio at elevated [CO₂] (I. Zondervan and U. Riebesell, unpublished data, 2000).

Second, trophic interactions may be influenced if feeding on coccolithophores by microzooplankton and copepods is dependent on cell size or the PIC/POC ratio. A decrease in the calcification rate could also decrease the competitiveness of coccolithophores with other phytoplankton functional groups. The malformation of the coccospheres under high CO₂ concentrations as shown by Riebesell et al. [2000] may be an indication for this. However, since the function and regulation of calcification by coccolithophores is not known [Young, 1994], it remains highly speculative what the role of calcification for coccolithophore physiology and ecology is. Nejstgaard et al. [1997] demonstrated in a mesocosm experiment that *E. huxleyi* dominated blooms provided a superior food source for reproduction of the copepod *Calanus finmarchicus* compared to diatom-dominated blooms. Holligan et al. [1993] found selective grazing on *E. huxleyi* cells by microzooplankton in the North Atlantic. Thus a shift in the dominance of phytoplankton species may affect regulation at higher trophic levels.

Third, sinking of coccolithophore-derived particulate material may become reduced when coccolithophore cells are less calcified [Fritz and Balch, 1996; Lecourt et al., 1996] or when the composition of faecal pellets changes owing to changes in the phytoplankton species composition or abundance [Harris, 1994; Holligan et al., 1993]. A decrease in calcification could actually reduce sinking rate of *E. huxleyi* cells [Fritz and Balch, 1996; Lecourt et al., 1996], and thus CO₂ uptake in the surface water, due to a decrease of organic carbon export to depth. However, we find an increase in POC production at elevated [CO₂], which could also affect particle sinking rate. Thus it remains speculative what the ultimate effect of a decrease in the PIC/POC ratio on particle sinking rate will be. Since this topic is beyond the scope of the present study we will not discuss this in further detail here.

Finally, the optical properties in the surface ocean may be altered due to decreasing calcification or coccolithophore abundance in regions where coccolithophore blooms occur [Balch et al., 1991]. Tyrrell et al. [1999] modeled the optical impacts of coccolithophore blooms and demonstrated an increase in the reflectance of light due to the abundance of coccoliths, a stronger stratification and a decrease in total water column productivity due to intense shading and stratification in these areas. All potential changes mentioned above could alter ecosystem structure and regulation over large areas of the ocean, although the response of a complex, multiple species ecosystem, where each species reacts in its own particular way remains extremely difficult to predict [Ksheshgi et al., 1991; Westbroek et al., 1994].

In summary, what the response of marine biogeochemistry on increasing atmospheric CO₂ concentrations will be with respect to CO₂ partitioning between ocean and atmosphere remains speculative. Our model shows a complete reversal of the expected positive feedback on atmospheric CO₂ increase when CaCO₃ production remains constant, turning into a negative feedback when calcification rates decrease with increasing CO₂. The effect is small compared to the annual anthropogenic CO₂ emissions. However, further investigation is needed on potential secondary effects on the ocean-atmosphere CO₂ exchange. If the observed CO₂-related responses in calcification and POC production of coccolithophores are a general phenomenon, changes in ecosystem structure and functioning can be expected with increasing atmospheric CO₂ concentration.

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References

- Antoine, D., J.-M. André, and A. Morel, Oceanic primary production, 2, Estimation at global scale from satellite (coastal zone color scanner) chlorophyll, *Global Biogeochem. Cycles*, 10, 57-69, 1996.
- Archer, D., and E. Maier-Reimer, Effect of deep-sea sedimentary calcite preservation on atmospheric CO₂ concentration, *Nature*, 367, 260-263, 1994.
- Balch, W.M., P.M. Holligan, S.G. Ackleson, and K.J. Voss, Biological and optical properties of mesoscale coccolithophore blooms in the Gulf of Maine, *Limnol. Oceanogr.*, 36(4), 629-643, 1991.
- Balch, W.M., P.M. Holligan, and K.A. Kilpatrick, Calcification, photosynthesis and growth of the bloom-forming coccolithophore, *Emiliana huxleyi*, *Cont. Shelf Res.*, 12(12), 1353-1374, 1992.
- Bijma, J., H.J. Spero, and D.W. Lea, 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 G. Fischer and G. Wefer, pp. 489-512, Springer-Verlag, New York, 1999.
- Bradshaw, A.L., P.G. Brewer, D.K. Shaffer, and R.T. Williams, Measurements of total carbon dioxide and alkalinity by potentiometric titration in the GEOSECS program, *Earth Planet. Sci. Lett.*, 55, 99-115, 1981.
- Brewer, P.G., Direct observation of the oceanic CO₂ increase, *Geophys. Res. Lett.*, 5(12), 997-1000, 1978.
- Brewer, P.G., Ocean chemistry of the fossil fuel CO₂ signal: The haline signal of "business as usual", *Geophys. Res. Lett.*, 24(11), 1367-1369, 1997.
- Brewer, P.G., A.L. Bradshaw, and R.T. Williams, Measurement of total carbon dioxide and alkalinity in the North Atlantic ocean in 1981, in *The Changing Carbon Cycle - A Global Analysis*, edited by J.R. Trabalka and D.E. Reichle, pp. 358-381, Springer-Verlag, New York, 1986.
- Broecker, W.S., and T.-H. Peng, *Tracers in the Sea*, Lamont-Doherty Earth Observatory, Palisades, New York, 1982.
- Brown, C.W., and J.A. Yoder, Coccolithophorid blooms in the global ocean, *J. Geophys. Res.*, 99(C4), 7467-7482, 1994.
- Chen, G.-T., and F.J. Millero, Gradual increase of oceanic CO₂, *Nature*, 277, 205-206, 1979.
- Frankignoulle, M., C. Canon, and J.-P. Gattuso, Marine calcification as a source of carbon dioxide: Positive feedback of increasing atmospheric CO₂, *Limnol. Oceanogr.*, 39(2), 458-462, 1994.
- Fritz, J.J., and W.M. Balch, A light-limited continuous culture study of *Emiliana huxleyi*: determination of coccolith detachment and its relevance to cell sinking, *J. Exp. Mar. Biol. Ecol.*, 207, 127-147, 1996.
- Gao, K., Y. Aruga, K. Asada, T. Ishihara, T. Akano, and M. Kiyohara, Calcification in the articulated coralline alga *Corallina pilulifera*, with special reference to the effect of elevated CO₂ concentration, *Mar. Biol.*, 117, 129-132, 1993.
- Gattuso, J.-P., M. Pichon, J. Jaubert, M. Marchioretti, and M. Frankignoulle, Primary production, calcification and air-sea CO₂ fluxes in coral reefs: Organism, ecosystem and global scales, *Bull. Inst. Oceanogr., Monaco spécial*, 14, 39-46, 1996.
- Gattuso, J.-P., M. Frankignoulle, I. Bourge, S. Romaine, and R.W. Buddemeier, Effect of calcium carbonate saturation of seawater on coral calcification, *Glob. Planet. Change*, 18, 37-46, 1998.
- Goyet, C., and A. Poisson, New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity, *Deep Sea Res.*, 36(11), 1635-1654, 1989.
- Gran, G., Determination of the equivalence point in potentiometric titrations of seawater with hydrochloric acid, *Oceanol. Acta*, 5, 209-218, 1952.
- Guillard, R.R.L., and J.H. Ryther, Studies of marine planktonic diatoms, I, *Cyclotella nanna* (Hustedt) and *Detonula convervacea* (Cleve), *Can. J. Microbiol.*, 8, 229-239, 1962.
- Harris, R.P., Zooplankton grazing on the coccolithophore *Emiliana huxleyi* and its role in inorganic carbon flux, *Mar. Biol.*, 119, 431-439, 1994.
- Holligan, P.M., Do marine phytoplankton influence global climate?, in *Primary Productivity and Biogeochemical Cycles in the Sea*, edited by P.G. Falkowski and A.D. Woodhead, pp. 487-501, Plenum, New York, 1992.
- Holligan, P.M., and J.E. Robertson, Significance of ocean carbonate budgets for the global carbon cycle, *Glob. Change Biol.*, 2, 85-95, 1996.
- Holligan, P.M., et al., A biogeochemical study of the coccolithophore, *Emiliana huxleyi*, in the North Atlantic, *Global Biogeochem. Cycles*, 7, 879-900, 1993.
- Houghton, J.T., et al., (Eds.) in *Climate Change 1994: Radiative Forcing of Climate Change and An Evaluation of the IPCC IS92 Emission Scenarios*, Cambridge Univ. Press, New York, 1995.
- Johnson, K.M., A.E. King, and J.M. Sieburth, Coulometric TCO₂ analyses for marine studies; an introduction, *Mar. Chem.*, 16, 61-82, 1985.
- Keeling, C.D., and T.P. Whorf, Atmospheric CO₂ records from sites in the SIO air sampling network, in *Trends: A Compendium of Data on Global Change*, Carbon Dioxide Info. Analysis Cent., Oak Ridge, Tenn., 1999.
- Kheshgi, H.S., B.P. Flannery, and M.I. Hoffert, Marine biota effects on the compositional structure of the world oceans, *J. Geophys. Res.*, 96(C3), 4957-4969, 1991.
- Kleypas, J.A., R.W. Buddemeier, D. Archer, J.-P. Gattuso, C. Langdon, and B.N. Opdyke, Geochemical consequences of increased atmospheric CO₂ on coral reefs, *Science*, 284, 118-120, 1999.
- Langdon, C., T. Takahashi, C. Sweeney, D. Chipman, J. Goddard, F. Marubini, H. Aceves, H. Barnett, and M.J. Atkinson, Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef, *Global Biogeochem. Cycles*, 14, 639-654, 2000.
- Lecourt, M., D.L. Muggli, and P. Harrison, Comparison of growth and sinking rates of non-coccolith and coccolith-forming strains of *Emiliana huxleyi* (Prymnesiophyceae) grown under different irradiances and nitrogen sources, *J. Phycol.*, 32, 17-21, 1996.
- Marubini, F., and M.J. Atkinson, Effects of lowered pH and elevated nitrate on coral calcification, *Mar. Ecol. Prog. Ser.*, 188, 117-121, 1999.
- Milliman, J.D., Production and accumulation of calcium carbonate in the ocean: Budget of a nonsteady state, *Global Biogeochem. Cycles*, 7, 927-957, 1993.
- Milliman, J.D., and A.W. Droxler, Neritic and pelagic carbonate sedimentation in the marine environment: ignorance is not bliss, *Geol. Rundsch.*, 85, 496-504, 1996.
- Morse, J.W., and F.T. Mackenzie, *Geochemistry of Sedimentary Carbonates*, Dev. Sedimentol. Ser., Vol. 48, Elsevier Sci., New York, 1990.
- Nejstgaard, J.C., I. Gismervik, and P.T. Solberg, Feeding and reproduction by *Calanus finmarchicus*, and microzooplankton grazing during mesocosm blooms of

- diatoms and the coccolithophore *Emiliana huxleyi*, *Mar. Ecol. Prog. Ser.*, 147, 197-217, 1997.
- Palmer, J.R., and I. Totterdell, Production and export in a global ocean ecosystem model, *Deep Sea Res.*, in press, 2001.
- Riebesell, U., I. Zondervan, B. Rost, P.D. Tortell, R.E. Zeebe, and F.M.M. Morel, Reduced calcification of marine plankton in response to increased atmospheric CO₂, *Nature*, 407, 364-367, 2000.
- Robertson, J.E., C. Robinson, D.R. Turner, P. Holligan, A.J. Watson, P. Boyd, E. Fernández, and M. Finch, The impact of a coccolithophore bloom on oceanic carbon uptake in the northeast Atlantic during summer 1991, *Deep Sea Res.*, 41(2), 297-314, 1994.
- Shaffer, G., Effects of the marine biota on global carbon cycling, in *The Global Carbon Cycle*, edited by M. Heimann, *NATO ASI Ser., Ser. I*, 15, 431-455, 1993.
- Sigman, D.M., D.C. McCorkle, and W.R. Martin, The calcite lysocline as a constraint on glacial/interglacial low-latitude production changes, *Global Biogeochem. Cycles*, 12, 409-427, 1998.
- Sikes, C.S., R.D. Roer, and K.M. Wilbur, Photosynthesis and coccolith formation: Inorganic carbon sources and net inorganic reaction of deposition, *Limnol. Oceanogr.*, 25(2), 248-261, 1980.
- Tyrrrell, T., P.M. Holligan, and C.D. Mobley, Optical impacts of oceanic coccolithophore blooms, *J. Geophys. Res.*, 104(C2), 3223-3241, 1999.
- Van Bleijswijk, J.D.L., R.S. Kempers, and M.J. Veldhuis, Cell and growth characteristics of types A and B of *Emiliana huxleyi* (Prymnesiophyceae) as determined by flow cytometry and chemical analyses, *J. Phycol.*, 30, 230-241, 1994.
- Volk, T., and M.I. Hoffert, Ocean carbon pumps: analysis of relative strengths and efficiencies in ocean-driven atmospheric CO₂ changes, in *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present*, *Geophys. Monogr. Ser.*, Vol. 32 edited by E.T. Sundquist and W.S. Broecker, pp. 99-111, AGU, Washington, D. C., 1985.
- Ware, J.R., S.V. Smith, and M.L. Reaka-Kudla, Coral reefs: sources or sinks of atmospheric CO₂?, *Coral Reefs*, 11, 127-130, 1991.
- Westbroek, P., et al., A model system approach to biological climate forcing: The example of *Emiliana huxleyi*, *Glob. Planet. Change*, 8, 27-46, 1993.
- Westbroek, P., B. Buddemeier, M. Coleman, D.J. Kok, D. Fautin, and L. Stal, Strategies for the study of climate forcing by calcification, *Bull. Inst. Oceanogr., Monaco spécial*, 13, 37-60, 1994.
- Winter, A., R.W. Jordan, and P.H. Roth, Biogeography of living coccolithophores in ocean waters, in *Coccolithophores*, edited by A. Winter and W.G. Siesser, pp. 161-179, Cambridge Univ. Press, New York, 1994.
- Wolf-Gladrow, D.A., U. Riebesell, S. Burkhardt, and J. Bijma, Direct effects of CO₂ concentration on growth and isotopic composition of marine plankton, *Tellus, Ser. B*, 51(2), 461-476, 1999.
- Wollast, R., The relative importance of biomineralization and dissolution of CaCO₃ in the global carbon cycle, *Bull. Inst. Oceanogr., Monaco spécial*, 13, 13-34, 1994.
- Young, J.R., Functions of coccoliths, in *Coccolithophores*, edited by A. Winter and W.G. Siesser, pp. 63-83, Cambridge Univ. Press, New York, 1994.

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