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Journal of Marine Systems 59 (2006) 120-142

JOURNAL OF MARINE SYSTEMS

www.elsevier.com/locate/jmarsys

Is there any relationship between phytoplankton seasonal dynamics and the carbonate system?

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> Received 14 April 2005; received in revised form 9 September 2005; accepted 6 November 2005 Available online 27 December 2005

Abstract

Production of calcium carbonate by marine calcifying organisms has been shown to decrease under increasing CO_2 . This effect appears to be driven by a decrease in $[CO_3^{2-}]$. The modelling study here described aims at investigating whether the success of a marine calcifying phytoplankton species, the coccolithophore *Emiliania huxleyi*, may be tied to $[CO_3^{2-}]$. The work highlights the complex interactions between the carbonate system variables and spring blooms, and the possibility of a link to the competition between calcifying vs. non-calcifying species on the Bering Sea shelf. We find that the strong seasonal cycle in $[CO_3^{2-}]$ is driven primarily by carbon drawdown during spring blooms. The interesting outcome of this work is the fact that *E. huxleyi* bloom timings always coincide with periods of high $[CO_3^{2-}]$, which is consistent with studies showing coccoliths malformations and a slowdown in calcification at low $[CO_3^{2-}]$. Whether the condition of high $[CO_3^{2-}]$ can be considered a crucial ecological factor for the success of *E. huxleyi*, however, remains an open and important question needing further investigation.

Keywords: Modelling; Phytoplankton seasonal dynamics; Emiliania huxleyi; Bering Sea; Carbonate system

1. Introduction

Many recent laboratory experiments, but also mesocosms and natural field studies, show a reduction in the production of calcium carbonate by marine calcifying organisms under increasing CO₂ (Spero et al., 1997; Kleypas et al., 1999; Gattuso et al., 1999; Riebesell et al., 2000). According to the "business-as-usual" scenario (IPCC, 2001), atmospheric CO₂ will have doubled from the pre-Industrial Revolution concentration by the middle of this century. As the anthropogenic CO₂ diffuses across the sea surface, surface ocean pH will fall by as much as 0.4 units (Caldeira and Wickett, 2003) and $[CO_3^{2-}]$ will fall by as much as 50% (Zeebe and Wolf-Gladrow, 2001) by the end of the century. The consequences of such a change on calcifiers may be dramatic (Feely et al., 2004). The Bering Sea (Fig. 1) has recently shown drastic (but temporary) changes in its ecosystem with a shift in the dominant summer phytoplankton. Particularly since 1996 (Merico et al., 2003), but most noticeably in 1997 and following years (Vance et al., 1998; Sukhanova and Flint, 1998), the coccolithophore *Emiliania huxleyi* (*E. huxleyi*) appeared in the Eastern Bering Sea (EBS) in very high concentrations (as high as $2.1-2.8 \times 10^6$ cells L⁻¹).

Because of the concern over upcoming ocean acidification and the consequences for marine calci-

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Fig. 1. Map of the Bering Sea with bathymetric contour lines indicating the three hydrographic regions on the shelf: (1) the coastal region from the coast line to the 50 m isobath; (2) the middle region from the 50 m isobath to the 100 m isobath; and (3) the outer region approximately between the 100 m and 150 m isobaths. M2, at $56.8^{\circ}N,164^{\circ}W$, marks mooring station 2 around which the current model is applied.

fiers, in this paper we investigate whether the natural occurrence of *E. huxleyi* in the Bering Sea could in any way be linked with natural variations in $[CO_3^{2^-}]$.

It is important to note that an earlier work (Merico et al., 2004) addressed the question of which environmental factors (e.g. nutrients, grazing, light) could best explain the *E. huxleyi* blooms in the EBS between 1996/1997 and 2000. That topic is not revisited in this paper, except in as much as we look at the possible influence of $[CO_3^{2-}]$, which was not considered in the earlier study. Our focus in the present study is limited to the investigation of a possible link between *E. huxleyi* success in the natural environment and the ambient values of $[CO_3^{2-}]$. More specifically, the following questions are tackled:

- (1) Was the interannual variability in $[CO_3^{2-}]$ between 1995 and 2001 consistent with the interannual variability of *E. huxleyi* blooms, such that especially high $[CO_3^{2-}]$ in 1996/1997–2000 could have caused the blooms?
- (2) Was the seasonal pattern of [CO₃²⁻] from winterspring-summer-autumn consistent with the seasonal distribution of *E. huxleyi* blooms, such that

especially high $[CO_3^{2-}]$ in summer could have caused the blooms?

- (3) Is there any evidence from the natural ecology of *E. huxleyi* blooms in the EBS (or in other locations) that support a link between [CO₃²⁻] and *E. huxleyi* success?
- (4) Will acidification of the oceans in the future undermine coccolithophores such as *E. huxleyi* or leave them largely unaffected?

1.1. Calcifiers and the carbonate system

The development of a coccolithophore bloom is a major process for the export of calcite $(CaCO_3)$ to the deep ocean. Biogenic calcification, however, causes a shift in the equilibrium of the carbonate system toward higher concentrations of CO_2 and it can represent a small sink or a potential source of CO_2 to the environment (Holligan et al., 1993; Paasche, 2002), depending on the degree to which coccolith-weighted faecal pellets lead to enhanced co-transport of organic matter (Buitenhuis et al., 2001).

The processes of inorganic precipitation and dissolution of $CaCO_3$ in seawater are driven by the saturation state of (degree of supersaturation with respect to) calcite (Ω_{cal}):

$$\Omega_{\rm cal} = \frac{\left[{\rm Ca}^{2+}\right] \left[{\rm CO}_3^{2-}\right]}{k_{\rm sp}'} \tag{1}$$

where k'_{sp} is the stoichiometric solubility product for a particular mineral phase, which can be aragonite (ara), calcite (cal) or high-magnesian calcite (hmc). Values of $\Omega < 1$ indicate undersaturation and values of $\Omega > 1$ indicate supersaturation. Given that Ca²⁺ concentrations are more or less constant both horizontally, vertically and seasonally in the ocean, variations in Ω are largely determined by variations in $[CO_3^{2-}]$. Note that k'_{sp} depends on temperature, salinity and pressure (Zeebe and Wolf-Gladrow, 2001).

The saturation state value appears to have an important influence on calcifying organisms. For example, coral reefs are restricted to low latitudes, most probably because of a dependence of these organisms on the calcium carbonate saturation state, Ω_{ara} , (Kleypas et al., 1999), which attains highest values between about 0 and 30°N and becomes smaller towards the poles (see Fig. 6 in Opdyke and Wilkinson, 1990). Note, however, that also temperature may play an important role the biogeography of coral reefs. Laboratory experiments have shown that foraminifera shell weight is strongly dependent on carbonate ion concentration (Spero et al., 1997). Finally, coccolithophores showed a decline in calcification rate when cultured at low Ω_{cal} (Riebesell et al., 2000). Coccolith malformations were also apparent as a consequence of such growing conditions (Riebesell et al., 2000). More recently, Sciandra et al. (2003) showed that net cell calcification can be significantly and rapidly reduced in coccolithophores following an increase of pCO_2 of the medium. However, in contrast to Riebesell et al. (2000), they found that this effect was not accompanied by a significant decrease in the calcification to photosynthesis ratio, since organic carbon production decreased roughly in proportion to inorganic carbon production. The main difference between the two studies was that in the work of Sciandra et al. (2003) experimental growth was nitrogen-limited.

The sensitivity of coral reef calcification to Ω_{ara} translates into a restriction on where this species can live. Coccolithophores are also largely absent from polar (low $[CO_3^{2-}]$) waters (McIntyre and Bé, 1967). Foraminifera, on the other hand, occur in reasonable numbers even in the Arctic and Southern Oceans (Hemleben et al., 1989) where $[CO_3^{2-}]$ is rather low, although these high-latitude foraminifera are smaller than those closer to the equator (Schmidt et al., 2004).

1.2. A possible temperature effect on the carbonate system

If the biogeography of calcifiers is to some extent controlled by $[CO_3^{2-}]$, it may be expected that the changes in $[CO_3^{2-}]$ predicted for the future (IPCC, 2001) in the global ocean may force alterations in coccolithophore distribution. It is also worthwhile to remember here of the strong correlation between sea surface temperature and Ω_{ara} in today's ocean (see Figs. 1 and 2 in Opdyke and Wilkinson, 1993). In this context, it is interesting to investigate whether the temporary colonisation of the Bering Sea by E. huxlevi, which started in a year (1997) of unusually high sea surface temperature (SST), represented an example of such a migration. In this respect, a relevant question is: could higher SST in 1997 have caused a raise in $[CO_3^{2-}]$ (for instance through outgassing of CO_2 and/or through a redistribution of carbon species towards higher CO_3^{2-}) so as to promote E. huxleyi success by making it easier to synthesise more strongly calcified coccoliths?

1.3. The Bering Sea case

A number of climatic anomalies took place in 1997 in the Bering Sea (Overland et al., 2001; Stabeno et al., 2001). Particularly calm and warm weather in 1997 increased sea surface temperatures to at least 4 °C above the seasonal average (Stabeno et al., 2001). In addition to climate, several biotic components of the ecosystem were also disrupted (Brodeur et al., 2002; Baduini et al., 2001). These anomalies resulted in a striking visual phenomenon: all the continental shelf was covered for the first time ever reported by discoloured bright waters caused by a massive bloom of the coccolithophore E. huxleyi. These blooms persisted for a few years after 1997 but have not been observed during 2001 or any subsequent years. The increased temperature represented probably the most remarkable observed anomaly of the whole physical system. In a recent modelling study, Merico et al. (2004) suggested that the blooms were stimulated in 1997 by increased solar irradiance through a particularly shallow upper mixed layer and proposed that E. huxleyi could outcompete other phytoplankton due to a lack of photoinhibition. Here our study is restricted solely to investigation of a possible relationship between *E. huxleyi* and Ω_{cal} .

2. Model description

The model used in the present study is a modified version of the existing two-layer, time-dependent eco-

Table 1

Parameters used in the model for calibration and main simulation runs

Parameter	Symbol	Unit	Value
Diatoms (P_d)			
Maximum growth rate at 0 °C	$\mu_{0,d}$	day^{-1}	1.2
Minimum sinking speed	$v_{\rm d}$	$m day^{-1}$	0.5
Mortality rate	m _d	day ⁻¹	0.08
Light saturation constant	I _{s.d}	Wm^{-2}	15
Nitrate half-saturation const.	N _{h.d}	mmol m ⁻³	1.5
Ammonium half-saturation const.	Ahd	mmol m ⁻³	0.05
Silicate half-saturation const.	Sh	$mmol m^{-3}$	3.5
Flagellates $(P_{\rm f})$			
Maximum growth rate at 0 C	$\mu_{0,\mathrm{f}}$	day^{-1}	0.65
Mortality rate	$m_{\rm f}$	day^{-1}	0.08
Light saturation const.	$I_{s,f}$	$W m^{-2}$	15
Nitrate half-saturation const.	$N_{\rm h,f}$	mmol m^{-3}	1.5
Ammonium half-saturation const.	$A_{\mathrm{h,f}}$	mmol m^{-3}	0.05
Dinoflagellates (P_{df})			
Maximum growth rate at 0 °C	$\mu_{0,\mathrm{df}}$	day^{-1}	0.6
Mortality rate	$m_{\rm df}$	day^{-1}	0.08
Light saturation const.	$I_{ m s,df}$	$W m^{-2}$	15
Nitrate half-saturation const.	$N_{ m h,df}$	mmol m^{-3}	1.5
Ammonium half-saturation const.	$A_{ m h,df}$	mmol m^{-3}	0.05
E. huxleyi (P _{eh})			
Maximum growth rate at 0 °C	$\mu_{0,\mathrm{eh}}$	day ⁻¹	1.15
Mortality rate	m _{eh}	day^{-1}	0.08
Light saturation const.	I _{s,eh}	$W m^{-2}$	45
Nitrate half-saturation const.	$N_{\rm h,eh}$	mmol m^{-3}	1.5
Ammonium half-saturation const.	$A_{\rm h,eh}$	mmol m^{-3}	0.05
Nitrate (N)			
Deep concentration	N_0	mmol m^{-3}	20
Nitrification rate	Ω	day^{-1}	0.05
Silicate (S)			
Deep concentration	S_0	mmol m^{-3}	35
Microzooplankton (Z _{mi})			
Assimilation efficiency ($S < 3 \mu M$)	$B_{\rm eh,mi}, B_{\rm f,mi}, B_{\rm d,mi}$	_	0.75, 0.75, 0.75
Assimilation efficiency ($S > 3 \mu M$)	$B_{\rm eh,mi}, B_{\rm f,mi}, B_{\rm d,mi}$	_	0.75, 0.75, 0.0
Grazing preferences ($S < 3 \mu M$)	$p_{\rm eh}, p_{\rm f}, p_{\rm d}$	_	0.33, 0.33, 0.33
Grazing preferences ($S > 3 \mu M$)	$p_{\rm eh,mi}, p_{\rm f,mi}, p_{\rm d,mi}$	_	0.5, 0.5, 0.0
Max. ingestion rates (S<3 μ M)	$g_{ m eh,mi}, g_{ m f,mi}, g_{ m d,mi}$	day ⁻¹	0.175, 0.7, 0.7
Max. ingestion rates ($S > 3 \mu M$)	$g_{ m eh,mi},g_{ m f,mi},g_{ m d,mi}$	day^{-1}	0.7, 0.7, 0.0
Grazing half-saturation const.	$Z_{ m h,mi}$	mmol m^{-3}	1.0
Mortality rate	$m_{ m mi}$	day^{-1} (mmol m ⁻³) ⁻¹	0.05
Excretion rate	e _{mi}	day^{-1}	0.025
Fract. of mort. going into amm.	$\delta_{ m mi}$	_	0.1
Mesozooplankton (Z_{me})			
Assimilation efficiency	$B_{d,me}, B_{mi,me}, B_{df,me}$	_	0.75, 0.75, 0.75
Grazing preferences	$p_{d,me}, p_{mi,me}, p_{df,me}$	-	0.33, 0.33, 0.33
Max. ingestion rates	gd,me, gmi,me, gdf,me	day ⁻¹	0.7, 0.7, 0.7
Grazing half-saturation const.	$Z_{\rm h,me}$	$mmol m^{-3}$	1.0
Mortality rate	m _{me}	day^{-1} (mmol m ⁻³) ⁻¹	0.2
Excretion rate	е	day ⁻¹	0.1
Fract. of mort. going into amm.	$\delta_{\rm me}$	_	0.1
Detritus (D)			
Sinking speed	ν _D	m day ⁻¹	0.4
Breakdown rate	m _D	day ⁻¹	0.05
Cross-thermocline mixing rate	k	m day ⁻ '	0.01

References for these values are given by Merico et al. (2004).

system model of the Bering Sea shelf, which was presented in detail by Merico et al. (2004) and used to investigate the biological and physical conditions behind the success of *E. huxleyi* in the area. The modifications adopted here comprise the inclusion of an extra layer representing the atmosphere (with constant pCO_2), the addition of two other state variables (dissolved inorganic carbon, DIC, and alkalinity, Alk) and the implementation of the carbon chemistry routines. The representations of *E. huxleyi* and other ecosystem processes and parameters are the same as in Merico et al. (2004).

All model variables and parameters are shown in Tables 1 and 2. The reader is referred to the previous work (Merico et al., 2004) for a justification of the values used. The model equations are given in Appendix A.

2.1. Physical aspects

The simple two-layer physical scheme adopted for the water column does not include lateral advection. Such an approximation is acceptable when considering that long-term average current speeds within the Bering Sea middle shelf domain are on the order of 1 cm s⁻¹ (Coachman, 1986). In the Bering Sea, the *E. huxleyi* blooms took place predominantly in the middle shelf domain (Merico et al., 2004), where the water column is typically stratified into two layers during the warm seasons and where tides have no direct effect on the upper mixed layer (Coachman, 1986). The model was intended to represent the southern part of the middle shelf region (Fig. 1). The biological activity was considered to take place only in the upper mixed layer. In the bottom layer, nutrient concentrations (A_0 , N_0 and S_0 for ammonium, nitrate and silicate, respectively) were kept constant throughout the year as also were the carbon state variables (DIC₀ and Alk₀). Nutrients were supplied to the upper mixed layer by entrainment or diffusive mixing across the interface using the method of Fasham (1993). Diffusive mixing was parameterised by means of a constant factor, *k*. On top of the water column, a box representing the atmosphere was added in order to allow exchanges of CO₂ at the air/sea interface. The $pCO_{2(air)}$ was assumed constant (Peng et al., 1987) and equal to 358 µatm (Murata and Takizawa, 2002). A scheme of the physical structure of the model is presented in Fig. 2 with a simplified diagram of the food web.

The model was forced with variable photosynthetic active radiation (PAR) and wind speed by using 6hourly climatology data from the European Centre for Medium-Range Weather Forecasts (ECMWF). PAR attenuation through depth was then simulated using the attenuation model of Anderson (1993). Wind speed data were used in order to calculate the gas transfer velocity at the air-sea interface. A variable mixed layer depth (MLD) was also used to force the model. The MLD was reconstructed from mooring temperature (T) data as the depth at which T differs by 0.5 °C from its sea surface value (SST). SST was also used to control phytoplankton growth by using Eppley's formulation (Eppley, 1972). Seasonal variations of noon PAR, wind speed, MLD and SST from 1997 to 1999 are shown in Fig. 3.

2.2. The ecosystem

The food web (Fig. 2) comprised 3 common phytoplankton groups of the region (Sukhanova et al., 1999):

Table 2

Parameters used to model the calcification process (see Merico et al., 2004) and the carbonate variables (see text)

Parameter	Symbol	Unit	Value
Attached coccolith (L_a)			
Calcification rate	C_{\max}	mg cal C (mg org C) ^{-1} day ^{-1}	0.2
Light half-saturation constant	$I_{ m h}$	$W m^{-2}$	40
Max. number of coccoliths on a cell	$\Pi_{\rm max}$	coccolith $cell^{-1}$	30
Rate of detachment	γ	day ⁻¹	24.0
Calcite C content of a coccolith	$C_{\rm L}$	g cal C coccolith ^{-1}	0.25×10^{-12}
Organic C content of an E. huxleyi cell	$C_{\rm eh}$	g org C cell ^{-1}	10.0×10^{-12}
C/N ratio	$\rho_{\rm CN}$	_	6.625
Free coccolith $(L_{\rm f})$			
Dissolution rate	Θ	day ⁻¹	0.05
Fraction of grazed free coccoliths	$\delta_{ m f}$	_	0.5
Carbonate system (DIC, Alk)			
DIC deep concentration	DIC_0	μ mol kg ⁻¹	2100
Alkalinity deep concentration	Alk	$\mu Eq kg^{-1}$	2250
Atmospheric pCO_2	pCO _{2(air)}	μatm	358



Fig. 2. Physical structure of the model with main biological and chemical components. Arrows represent exchange of materials. Empty arrows indicate the material flowing between mixed layer depth and bottom layer. The arrow from *E. huxleyi* (P_{eh}) to attached coccoliths (L_a) is dashed indicating that attached coccoliths are produced proportionately to the *E. huxleyi* concentration rather than with a real flow of material between these two compartments. Note that mesozooplankton (Z_{me}) grazes also on microzooplankton (Z_{mi}). See text for more details.

diatoms (P_d), flagellates (P_f) and dinoflagellates (P_{df}), as well as the species *E. huxleyi* (P_{eh}). Three main nutrients were considered: silicate (*S*), nitrate (*N*) and ammonium (*A*), with silicate used only by diatoms. Two different classes of zooplankton were included: microzooplankton (Z_{mi}) and mesozooplankton (Z_{me}). Diatoms, dinoflagellates and microzooplankton were the food sources for mesozooplankton; flagellates and *E. huxleyi* were the food sources for microzooplankton. Microzooplankton were allowed to graze also on diatoms during summer when silicate concentration dropped below 3 μ M (further details on this aspect can be found in the earlier work (Merico et al., 2004). A single detrital compartment (*D*) was considered with a fixed sinking rate in order to simulate the remineralisation of zooplankton faecal pellets and dead plankton into ammonium. The breakdown of detritus (i.e. ammonification) to ammonium was also represented. Coccoliths were included in the model as attached (i.e. part of the coccosphere) and free coccoliths (i.e. those which have become detached from the coccosphere), L_a and L_b respectively.

2.3. The carbonate system

In the ocean, dissolved inorganic carbon (DIC) can be found in three different forms: as free carbon dioxide, $CO_{2(aq)}$, as bicarbonate, HCO_{3}^{-} , and as carbonate



Fig. 3. Forcing functions used in the ecosystem model. (a) Sea surface temperature, (b) mixed layer depth, and weekly running averages of (c) noon photosynthetically active radiation, and (d) wind speed.

ion, CO_3^{2-} . As suggested by Broecker (1974), to a first approximation, the carbonate ion concentration can be estimated as follows:

$$\left[\mathrm{CO}_{3}^{2-}\right] \approx \mathrm{Alk} - \mathrm{DIC} \tag{2}$$

with:

$$DIC = \left[CO_{2(aq)}\right] + \left[HCO_{3}^{-}\right] + \left[CO_{3}^{2-}\right]$$
(3)

$$Alk \approx [HCO_3^-] + 2[CO_3^{2-}]. \tag{4}$$

According to Eq. (2), as alkalinity decreases (for instance during calcification through HCO_3^- or CO_3^{2-} removal) or as DIC increases (for instance through respiration and/or input from the atmosphere), $[CO_3^{2-}]$ decreases.

The calculation of the carbon system variables was implemented in the model on the base of the carbon system equations of Millero (1995) and Peng et al. (1987). In the model, carbon was consumed by phytoplankton by assuming a C/N ratio equal to 6.625. The exchange of CO_2 across the air–sea interface was computed by using the formulation of Wanninkhof (1992). The effects of calcification and dissolution were taken into account as well. Deep DIC and alkalinity concentrations (DIC₀ and Alk₀) were set to 2100 µmol kg⁻¹ and 2250 µEq kg⁻¹, respectively (Walsh and Dieterle, 1994).

2.4. Method

The system of differential equations was solved numerically using the fourth-order Runge–Kutta method with a time step of 1 h. A linear interpolation of 6-hourly ECMWF data (i.e. PAR and wind speed) for the runs related to years from 1995 to 2001 was used to match the time step of the model. In order to minimise the dependency of the model results on the initial conditions of the state variables, the model was run repeatedly over a full seasonal cycle of the physical forcing prior to 1995. Only once it developed a repeatable annual cycle, was it then run with the forcing from 1995 to 2001.

3. Results

The model presented here was used in an earlier study (Merico et al., 2004) to investigate environmental factors other than the carbonate system that caused the blooms of *E. huxleyi* in the Bering Sea. The model was able to reproduce well the typical nutrient seasonal cycles and the magnitude of the chlorophyll seasonal concentration (Fig. 9 in Merico et al., 2004). *E. huxleyi* bloom timings were also studied in detail and the results compared favourably with SeaWiFS-derived bright waters and cell counts, (Figs. 9 and 11 in Merico et al., 2004). Pronounced spring diatom blooms, a typical feature of the Bering Sea shelf (Sukhanova et al., 1999), were correctly predicted for every year (Fig. 9 in Merico et al., 2004).

The model configuration that gave the best account of the recent succession patterns in the Bering Sea (1995–2001) including *E. huxleyi* (Merico et al., 2004) was used for all the runs presented in the following.

We stress the fact that we are not revisiting the topic of the causative factors for *E. huxleyi* blooms here. As explained in the Introduction, what we intend to investigate with the present study is whether there is any link between *E. huxleyi* success (as predicted by other environmental conditions discussed by Merico et al., 2004) and high $[CO_3^{2-}]$.

3.1. Bering Sea system prior to E. huxleyi arrival

A typical phytoplankton spring bloom in the Bering Sea (Fig. 4a) before the arrival of *E. huxleyi* (i.e. before 1997) caused a 10-fold depletion of surface nitrate to less than 1 μ M nitrate (Fig. 4b) and about 85 μ M (5%) drawdown of DIC (Fig. 4c). Such a change in DIC impacts on [CO₃²⁻] (the concentration of carbonate ion)



Fig. 4. Seasonal cycles of biological and carbonate variables in the Bering Sea before the arrival of *E. huxleyi*. (a) Modelled chlorophyll (solid line) as compared with a 20-year composite (1970–1990) of observations (dots), after Merico et al. (2004); (b) modelled nitrate (solid line) as compared with a 20-year composite (1970–1990) of observations (dots), after Merico et al. (2004); (c) modelled dissolved inorganic carbon (solid line) as compared with a 2-year composite (1980–1981) of observations (dots), after Codispoti et al. (1986); (d) modelled pCO_2 in seawater (solid line) and observed pCO_2 in air (dashed line) as compared with a 2-year composite (1980–1981) of observations (dots), after Codispoti et al. (1986); (e) modelled carbonate ion concentration and (d) modelled calcite saturation state.

by raising this variable by about 50% above its winter value (Fig. 4e). The degree of saturation state of the calcite form of calcium carbonate (Ω_{cal}) increases concomitantly, from about 2 (typical winter value) to about 3 (Fig. 4f).

Seasonal overturn of the water column in September evidently restocks both the pools of nitrate and DIC when the winter light limitation halts the autumn bloom of 3–4 mg Chl m⁻³ (Fig. 4a). In the absence of calcifying organisms, pCO_2 in seawater remains undersaturated throughout the year with respect to pCO_2 in air (Fig. 4d), as expected at these latitudes (Takahashi et al., 1993). Note, however, that Takahashi et al. (1993) have show that during the winter months the sub-arctic Pacific (up to 54 °N) may be a source for atmospheric CO_2 . Their data, unfortunately, do not cover our region of interest on the Bering Sea shelf (around 56.8°N– 164°W, see Fig. 1), and lower pCO_2 values are to be expected over the shelf, which experiences spring blooms, than in the open ocean subarctic Pacific, which does not. In addition, water conditions of 344 μ atm *p*CO₂ were observed in February 1970 within ice-covered waters of the middle shelf region (Kelly and Hood, 1971). Note also that a much greater undersaturation of the water column was observed, *p*CO₂~260 μ atm, in February 1983 (Chen, 1985, 1993).

The described DIC and pCO_2 dynamics predicted by the model and compared in Fig. 4c and d with observations reported by Codispoti et al. (1986) are consistent with the general understanding of carbon cycling at high latitudes (Takahashi et al., 1993) and agree well with the numerical analysis of carbon cycling in the southeastern Bering Sea done in the past by Walsh and Dieterle (1994). The seasonal variations of $[CO_3^{2-}]$ and Ω_{cal} in high latitude waters have not previously been calculated.



Fig. 5. Biological and carbonate system variables from 1995 to 2001. (a) Modelled DIC (black line) and modelled chlorophyll (red line) as compared with weekly averages of SeaWiFS-derived chlorophyll data (red dots); (b) modelled carbonate ion concentration; (c) modelled calcite saturation state (black line) and modelled *E. huxleyi* abundance (red line) as compared with observed concentrations (red dots), after Merico et al. (2004); (d) modelled CO_2 partial pressure in seawater (black line) and observed CO_2 partial pressure in atmosphere (dashed line), after Murata and Takizawa (2002), and modelled dissolved CO_2 (red line); (e) modelled alkalinity (black line) and modelled free coccolith concentration (red line).

3.2. Bering Sea system with E. huxleyi: standard run

The arrival of E. huxleyi in the Bering Sea caused a perturbation to the carbonate system with respect to non-E. huxlevi years. The model results suggest that the intensive E. huxleyi bloom of 1997 caused seawater pCO_2 to become supersaturated with respect to atmospheric pCO_2 (Fig. 5d). Changes of this order of magnitude in pCO_2 have been observed in connections with these blooms (taking place at similar latitudes but in different locations) in the past (Holligan et al., 1993; Robertson et al., 1994). The pCO_2 increases occur because calcification lowers alkalinity (in 1997 by approximately 70 μ Eq kg⁻¹, see Fig. 5e). Such a decrease is in agreement with observations carried out during a bloom of E. huxleyi in the north Atlantic (see Fig. 13 in Holligan et al., 1993), where a drawdown in alkalinity of about 65 μ Eq kg⁻¹ was reported.

The arrival of *E. huxleyi* produced noticeable changes also to DIC and other variables (compare Figs. 4 and 5). It appears, however, that the large change in SST (4 $^{\circ}$ C

above climatological mean) in summer of 1997 had no significant effect on the carbonate concentrations. Indeed, this can be seen with a simple experiment, consisting of a run which does not include *E. huxleyi* in the ecosystem during 1995–2001 (Fig. 6). The higher SST of 1997 (Fig. 3) does not produce a noticeably higher calcite saturation state in 1997 with respect to other years. This experiment allows decoupling of the effects that calcification and higher SST conditions have on the carbonate system and shows that yearly fluctuations in post-spring bloom carbonate ion concentrations appear more strongly connected to the intensity of the spring bloom rather than to interannual SST variations (Fig. 6).

Changes in alkalinity are mainly driven by the processes of calcification (i.e. the production of attached coccoliths), dissolution and upper to bottom water fluxes (see Eq. (4)). Therefore, a realistic simulation of the process of production of attached coccoliths will result in a realistic prediction of alkalinity drawdown, provided that dissolution is negligible at the surface. However,



Fig. 6. Modelled carbonate system variables from 1995 to 2001 with ecosystem including *E. huxleyi* (red line) and with ecosystem not including *E. huxleyi* (blue line). The dotted line in the pCO_2 plot represents the concentration of this variable in atmosphere.

since the details of how coccoliths are produced and afterward detached in nature are not fully understood, the modelling of these processes represents a challenge. The approach used here was to tune the amount of coccoliths produced in the model so that the concentrations of free coccoliths compared favourably with the observations available: the SeaWiFS-derived concentration of calcite. Daily SeaWiFS normalized water leaving radiance data were utilized in order to obtain estimates of calcite concentrations during E. huxlevi blooms in the Bering Sea (1997–1999). The radiance data were processed with the SeaWiFS Data Analysis System software (Baith et al., 2001) according to the coccolithophore detection algorithm proposed by Gordon et al. (2001). The essence of this algorithm is to minimize the influence from the absorption by chlorophyll and dissolved organic material in the visible channels in Case 1 waters and to empirically relate the backscatter coefficient at 550 nm to calcite concentration. The algorithm, however, does overestimate calcite concentrations in Case 2 waters (e.g. Cokacar et al., 2004), such as the Bering Sea shelf waters. Therefore, although these data represent the best information that can be obtained in order to constrain the carbon chemistry routines, their significance should not be overestimated. Selected calcite data (criteria for selection was best cloud-free scene) for the summer periods from 1997 to 2000 are presented in Fig. 7 (1 mol C m⁻³=12 g C m⁻³).

Coccolith concentrations were also measured in situ in the Bering Sea on one occasion (September 1997) and a value of 0.1 g C m^{-3} was reported by Napp and Hunt (2001).

The model results of free coccoliths for the year 1997 (shown in Fig. 5e) are consistent with the data just mentioned and also with observations carried out in the north Atlantic (see Fig. 6D in Holligan et al., 1993, where a value of 0.2 g C m⁻³ was reported) and in the western English Channel (see Fig. 11A in Garcia-Soto et al., 1995, where a value of about 0.3 g C m⁻³ was reported).

An interesting result of this investigation is that high concentrations of *E. huxleyi* are always coincidental in



Fig. 7. SeaWiFS-derived concentration of calcite (in mol m^{-3}) for (a) 16 September 1997, (b) 20 July 1998, (c) 11 September 1999 and (d) 15 September 2000.

the seasonal cycle with times of high calcite saturation state (see Fig. 5c).

It appears, however, that with today's typical $[CO_3^{2-}]$ values (ranging from about 100 to 160 μ mol kg⁻¹, Fig. 5b), interannual variations of the calcite saturation state (from about 2.3 to 4, Fig. 5c) are too small to favour or prevent an E. huxleyi bloom. However, this may well change in the future, given that $[CO_3^{2-}]$ will fall by as much as 50% by the end of the century (IPCC, 2001).

4. Sensitivity analyses

A series of sensitivity analyses have been carried out to examine the effects of changing the values of some crucial parameters or to test certain assumptions.

4.1. Parameters

0.6

0.5

Three parameters were investigated to assess the sensitivity of the carbonate variables to the calcification

1996

1997

1995

Free Coccoliths

process: the maximum calcification rate, C_{max} , the halfsaturation constant of the light-dependent calcification, $I_{\rm h}$ (see Table 2) and the total number of attached coccoliths that an *E. huxleyi* cell can hold, Π_{max} . All the parameters were changed independently by $\pm 50\%$ (it was decided to change the calcification parameters by $\pm 50\%$ because preliminary investigations showed that a $\pm 25\%$ change would produce only small effects) and the effects of these changes were investigated on free coccoliths $(L_{\rm f})$, attached coccoliths $(L_{\rm a})$, alkalinity (Alk), dissolved carbon dioxide (DIC) and carbonate ion concentration ($[CO_3^{2-}]$). Almost no effect was observed on these variables due to changes in the total number of attached coccoliths (results not shown). Conversely, the impact of C_{max} is more important, as shown in Fig. 8, but the effect of $I_{\rm h}$ (see Fig. 9) is less important.

Given the uncertainties related to these parameters and in general on the functioning of the calcification process (Paasche, 2002), the model results have to be

2000

2001



1998

1999

Fig. 8. Sensitivity of modelled free and attached coccoliths, alkalinity, DIC and carbonate ion concentrations to changes in maximum calcification rate (C_{max}). The black line represents the result obtained with C_{max} as in the standard run (SR), the red line shows the result with C_{max} increased by 50% from its SR value, and the blue line shows the result with $C_{\rm max}$ decreased by 50% from its SR value.



Fig. 9. Sensitivity of modelled free and attached coccoliths, alkalinity, DIC and carbonate ion concentrations to changes in the half-saturation constant of the light-dependent calcification (I_h) . The black line represents the result obtained with I_h as in the standard run (SR), the red line shows the results with I_h increased by 50% from its SR value, and the blue line shows the result with I_h decreased by 50% from its SR value.

interpreted with caution. However, despite these weaknesses in the quantitative predictions of the carbonate variables in the presence of biocalcification and dissolution processes, the general patterns are consistent with previous studies, as explained in the previous section. Moreover, note that the calcification process has a firstorder impact on alkalinity but only a second-order impact on DIC (as also shown by Figs. 8 and 9).

4.2. Tests

4.2.1. Gas transfer velocity (v_{α})

We tested the sensitivity of our model results with respect to two different parameterisation of the gas transfer velocity (see Eq. (A.21)). In the first case (the standard run), a quadratic function of the wind speed is used (as from Wanninkhof, 1992) and in the second case a cubic function of the wind speed is used (as from Wanninkhof and McGillis, 1999). The model results are very similar in both cases (see Fig. 10) indicating that either parameterisation could be used in our study.

4.2.2. Thermocline mixing rate (k)

A model sensitivity analysis to vertical mixing (results not shown) revealed that when the ecosystem experiences low vertical diffusion (k set to 0.01 m day⁻¹, see Eq. (A.1)), any exchange of material between the two boxes is primarily driven by the dynamics of the upper mixed layer depth itself, via entrainment or detrainment. By increasing k, diffusive mixing becomes more and more important up to the limit of when (with k=6 m day⁻¹) the concentrations of nutrients in the upper box are forced to the same values as in the deep box and with no more biological activity due to a complete loss of phytoplankton cells. A turbulent environment tends to favour diatoms and *E. huxleyi* in our model due to their high maximum growth rates. Note that runs in conditions of reduced diffusive mixing



Fig. 10. Modelled carbonate system variables from 1995 to 2001 obtained by using: (1) the gas transfer velocity as a quadratic function of the wind speed (red line), and (2) the gas transfer velocity as a cubic function of the wind speed (blue line). The dotted line in the pCO_2 plot represents the concentration of this variable in atmosphere.

during 1997 with respect to other years have not produced appreciable interannual differences (also in terms of carbonate ion concentration and saturation state) probably due to the complex dual effect of k in supplying nutrients but also in removing plant cells (Evans, 1988).

4.2.3. Choice of deep DIC (DIC₀) and deep alkalinity (Alk_0)

During the years 1980–1981, Codispoti et al. (1986) measured the following values (we use here the notation of our model): $DIC_0 \sim 2000 \ \mu\text{mol kg}^{-1}$, $Alk_0 \sim 2100 \ \mu\text{Eq} \ \text{kg}^{-1}$, and $pCO_2 \sim 350 \ \mu\text{atm}$. However, for their modelling study, Walsh and Dieterle (1994) used $DIC_0 \sim 2120 \ \mu\text{mol kg}^{-1}$, $Alk_0 \sim 2250 \ \mu\text{Eq} \ \text{kg}^{-1}$, and $pCO_2 \sim 345 \ \mu\text{atm}$. Note also that in February 1983 within ice-covered waters, Chen (1993) measured: $DIC_0 \sim 2053 \ \mu\text{mol kg}^{-1}$, $Alk_0 \sim 2200 \ \mu\text{Eq} \ \text{kg}^{-1}$, which lead to a much greater undersaturation of the water column of $\sim 260 \ \mu\text{atm}$. In February 1970, water conditions of 344

 μ atm pCO₂ were observed under pack ice at the same temperature, salinity and isobath (Kelly and Hood, 1971).

Walsh and Dieterle (1994) suggested that there might have been a decadal change towards increasing DIC over the shelf probably resulting from DIC on-welling of deep-sea stocks (i.e. from the deep-basin). They then simulated the possible variations in the onshore upwelling of DIC and found steady-state values of 15.5 mmol m^{-3} for nitrate and of 2128 µmol kg⁻¹ for DIC.

For the run investigating the Bering Sea prior to the *E. huxleyi* arrival, we used Codispoti's data because we compared the model results directly to these data (see Fig. 4). But we used the parameterisation of Walsh and Dieterle for the 1995–2001 run because in this way we could compare our model results with those of Walsh and Dieterle.

We have investigated the sensitivity of our model results with respect to the choice of these two different conditions (see Fig. 11). It appears that the carbonate ion



Fig. 11. Modelled carbonate system variables from 1995 to 2001 obtained by forcing the model with: (1) $DIC_0 \sim 2000 \ \mu mol \ kg^{-1}$, $Alk_0 \sim 2100 \ \mu Eq \ kg^{-1}$ (data by Codispoti et al., 1986), and (2) $DIC_0 \sim 2120 \ \mu mol \ kg^{-1}$, $Alk_0 \sim 2250 \ \mu Eq \ kg^{-1}$ (data by Walsh and Dieterle, 1994). The dotted line in the *p*CO₂ plot represents the concentration of this variable in atmosphere.

concentration can differ by $20-30 \ \mu\text{mol kg}^{-1}$ depending on whether using Walsh and Dieterle's or Codispoti's data but the seasonal patterns of $[\text{CO}_3^{2-}]$ and Ω_{cal} are otherwise identical: (1) low winter time values, (2) large increase at time of spring blooms, and (3) high summer values (until upper mixed layer deepens again in autumn). This sensitivity analysis highlights that the paucity of data, particularly the lack of data from winter of each year, compromises our ability to say whether 1997 was a special year in terms of saturation state.

4.2.4. Effect of temperature on $[CO_3^{2-}]$

We have argued in Section 3.2 that year-to-year variations in SST did not produce appreciable changes in the carbonate chemistry. Here we present a test in which the biology is completely switched off in order to better discern the magnitude of the impact that temperature has on $[CO_3^{2-}]$ and compare the results with the standard run. As it is obvious, the temperature effect becomes dominant (through CO₂ de-gassing) when the

biology is switched off (see Fig. 12). Interestingly, there is an increase in carbonate ion concentration during 1997 due to the higher SST relatively to the other years. However, the effect of the spring bloom is distinctly more important. This test suggests that temperature has a large effect on pCO_2 (via Henry's law) but a small effect on the dissolution constants and therefore on $[CO_3^{2-}]$ and saturation state.

5. Discussion

5.1. Phytoplankton succession and the calcite saturation state

Motivated by recent evidence that increasing sea water acidification (Caldeira and Wickett, 2003), due to increasing CO_2 concentrations in the atmosphere, may cause a calcification slowdown of the most important calcifying organisms (Gattuso et al., 1999; Kleypas et al., 1999; Riebesell et al., 2000; Spero et al., 1997), it



Fig. 12. Modelled carbonate system variables from 1995 to 2001 obtained with: (1) the standard run (solid line), and (2) the biological activities switched off (dashed line). The dotted line in the pCO_2 plot represents the concentration of this variable in atmosphere.

has become important to understand how these changes will affect the competitive success of calcifiers. Will lower pH, lower $[CO_3^{2-}]$, and lower saturation state over the next few centuries lead to fewer coccolithophores in the ocean? More fragile coccoliths, with malformations, could make coccolithophores more susceptible to grazers and viruses, for instance.¹

Given the strong latitudinal correlation between temperature and calcite saturation state (Opdyke and Wilkinson, 1990, 1993), we had hypothesized that the anomalously high SST in the Bering Sea in the summer of 1997 had raised calcite saturation state so as to make it easier for *E. huxleyi* to synthesise more strongly calcified coccoliths (see Section 1.2). However, this hypothetical effect (i.e. higher temperature \Rightarrow higher calcite saturation state) was not confirmed by the model results for 1997 (Fig. 5). This finding suggests that interannual variations in spring-summer SST do not have an appreciable impact on interannual variations of $[CO_3^{2-}]$ and of calcite saturation state.

It was shown that the period of seasonally high *E. huxleyi* abundance always coincides with high calcite saturation state, typically after the spring diatom bloom (due to the drawdown of DIC), and that the magnitude of the seasonal peak of Ω_{cal} depends on the intensity of spring blooms (Fig. 6). The periods of *E. huxleyi* blooms correspond to values of calcite saturation state ranging from 3 to 4 (Fig. 5c). Correlation does not prove causation, and the temporal association could equally be due to coincidence. The temporal association is in agreement with, but does not prove, an importance of high Ω_{cal} for *E. huxleyi* blooms.

The calcite saturation hypothesis cannot be considered as a "sufficient" condition for *E. huxleyi* success otherwise this species would also have been present in

¹ It is presumed here that the possession of coccoliths is beneficial to *E. huxleyi* in competition with other phytoplankton, and that thicker coccoliths are more beneficial than thinner ones. If not so, natural selection would be expected to favour the "cheap" option of building a less heavily reinforced covering. Note however that the true purpose of coccoliths is not well understood (Young, 1994).

the Bering Sea and in all temperate regions with a strong seasonal cycle, which is evidently not the case.² But this does not exclude the high calcite saturation state from being a "necessary" condition, i.e. one out of several factors that must be met before E. huxlevi bloom can occur. In other words, if there had been no spring blooms of diatoms in the Bering Sea (so that $[CO_3^{2-}]$ had remained at its typical winter values, around 100 μ M kg⁻¹, see Fig. 5b), would we still have observed E. huxleyi blooms in the period 1996/ 1997-2000? The work by Riebesell et al. (2000), showing slowing-down of calcification and coccolith malformations at $[CO_3^{2-}]$ values of about 85 μ M kg⁻¹ suggests "no" as the most likely answer. Our study therefore is particularly important in the context of the future increase in atmospheric CO₂, which will cause $[CO_3^{2-}]$ to drop by about 50% (thus, for example, bringing the Bering Sea [CO₃²⁻] typical summer values down to about 80 μ M kg⁻¹.

Notwithstanding the importance of other environmental parameters, such as silicate concentration or light intensities (Tyrrell and Merico, 2004; Merico et al., 2004), we suggest that high $[CO_3^{2-}]$ may also play a role in providing *E. huxleyi* with a favourable niche during summer. Whether the calcification control mechanism will prevail against other mechanisms will only depend on how severe will be the drawdown of $[CO_3^{2-}]$ in the future.

5.2. A potential mechanism that may link high $[CO_3^{2-}]$ to E. huxleyi success

The importance of the calcite saturation state may be related to the ability of *E. huxleyi* to synthesise more heavily calcified coccospheres in more highly supersaturated summer waters as compared to in less saturated winter waters. Indeed, Beaufort and Heussner (2001), studying the seasonal variation between lightly and heavily calcified morphotypes of *E. huxleyi* in a temperate location (i.e. with strong seasonal cycles), the Bay of Biscay, found a clear succession between morphotypes, with higher percentages of the heavily calcified morphotype in summer and of the lightly calcified morphotype in winter (see Beaufort and Heussner, 2001, Fig. 3 and Plate I).

A mechanism, although speculative, that can potentially explain the typical diatom–coccolithophore succession sequence in regions with strong seasonal cycles may therefore be that microzooplankton grazing responds to frustule silicification and coccosphere calcification (see also Merico et al., 2004, in relation to grazing during *E. huxleyi* years in the Bering Sea). Lightly (or heavily) silicified frustules may make diatoms more (or less) susceptible to microzooplankton grazing and lightly (or heavily) calcified coccospheres may make coccolithophore more (or less) susceptible to microzooplankton grazing. Rousseau et al. (2002), for example, observed in the Belgian coastal waters a dominance of heavily silicified diatom species in early spring as opposed to a dominance of lightly silicified diatom species in summer.

We propose therefore a combined role of microzooplankton grazing and silicate and carbonate concentrations in controlling phytoplankton seasonal dynamics. The CO_2 levels that may occur in the oceans by the end of the century could reduce the amount of calcium carbonate in shells by 25% to 45%, which might well cause major changes in the structure of phytoplankton assemblages (Feely et al., 2004).

5.3. Analogies with the past

The importance of calcite saturation state to biogenic calcification may be also inferred from the geological past. Most similar to the situation unfolding today (i.e. the increasing of atmospheric CO₂ concentrations) is probably the Palaeocene-Eocene Thermal Maximum (PETM) event, a period of intense greenhouse warming characterised by a sudden change (for geological timescales) in atmospheric pCO_2 (a rise of probably 80 ppm within 10,000 years (Dickens et al., 1997)) with Ca^{2+} and Mg²⁺ ion concentrations remaining constant, due to their much longer residence times of millions of years (Berner and Berner, 1996). One of the key effects of the atmospheric carbon increase during the PETM on marine sediments is the decrease in CaCO₃ concentration. Elevated concentrations of pCO_2 in the atmosphere likely caused a rise of the Calcite Compensation Depth (CCD), the depth at which $\Omega_{cal} < 1$ and the accumulation rate of calcite is lower than the rate of dissolution. Relevant to the present study is the fact that the PETM event coincided with a massive extinction of benthic foraminifera (Kaiho et al., 1996; Thomas, 1998). Steineck and Thomas (1996) reported also of a dramatic faunal change in deep-water faunas during this event. In their own words: ostracodes at the ODP site 689 "underwent a sudden, dramatic turnover synchronous with a global extinction in deep-sea benthic foraminifers and with large-scale, short- lived negative excursions in the stable isotope record of foraminiferal

² Note, however, that *E. huxleyi* is the most abundant and ubiquitous coccolithophore living in today's oceans and is the only species found in nearly every sample of ocean water (Winter et al., 1994).

calcite. A previously stable and long-lived ostracode assemblage, dominated by heavily calcified, chiefly epifaunal taxa, was replaced ... by a taxonomically novel association of small, thin-walled opportunistic and generalist forms".

The expected decrease of biogenic calcification (and therefore coccolithophore competitiveness) with increasing pCO_2 seems at odds with the massive accumulations of sedimentary calcium carbonate during the Cretaceous. During this period, atmospheric CO_2 levels were 2 to 6 times higher than at present (Berner, 1990). However, recent evidence from fluid inclusions suggest that calcium concentrations in the Cretaceous were 2 or 3 times higher than in the modern ocean (Horita et al., 2002; Lowenstein et al., 2001). Note also that a high saturation state at low $[Ca^{2+}]$ can easily be maintained by the lysocline dynamics itself (Zeebe and Westbroek, 2003). These possibilities imply that despite high atmospheric CO_2 levels, the calcite saturation state in this period need not necessarily have been much different from today.

6. Conclusions

A three-layer model (a two-layer ocean with an atmosphere on top) was used here to investigate the relationship between the seasonal diatoms-coccolithophores succession and the carbonate system on the Bering Sea shelf. In the years 1997–2000, intensive blooms (concentrations as high as $2.1-2.8 \times 10^6$ cells L⁻¹) of the coccolithophore *E. huxleyi* took place in this region. Such blooms were never documented before on the Bering Sea shelf except for a small bloom in 1996 (Merico et al., 2003).

This work contains the first calculation of the seasonal cycles of carbonate ion concentration and calcite saturation state in temperate waters in relation to phytoplankton dynamics.

With regards to the four questions that were put forward in the Introduction, we found the following:

- (1) Our model produced only minor interannual variations in calcite saturation state, that we suggest were not responsible for interannual patterns of *E. huxleyi* blooms in the Bering Sea from 1995 to 2001. This study also showed that the effect of increasing temperature on saturation state does not play a crucial role. Interannual variations of 4–5 °C do not appreciably alter carbonate ion concentration or calcite saturation state in our model.
- (2) We have shown that both $[CO_3^{2-}]$ and Ω_{cal} are typically low during winter and early spring,

rising to higher values immediately after the spring blooms, due to biological drawdown of DIC. These results point to the potential importance of carbonate ion concentration for the success of *E. huxleyi*, because the blooms of this species are seen to post-date the late spring shift to high $[CO_3^{2^-}]$. This is compatible with the hypothesis of a negative effect of more fragile coccoliths on coccolithophore competitiveness, for instance because of increasing the susceptibility to grazing (Merico et al., 2004).

- (3) Our findings suggest that the natural ecology of *E. huxleyi* blooms in the EBS (but also in other locations like, for example, the Bay of Biscay, see Beaufort and Heussner, 2001) may support a link between the calcite saturation state and *E. huxleyi* success.
- (4) If high [CO₃²⁻] effectively provides an ecological advantage to this species, increasing CO₂ could potentially decrease the competitiveness of *E. huxleyi*. The present study points towards this direction by offering complementary evidence consistent with the works of Riebesell et al. (2000) and Feely et al. (2004).

This work sheds some lights on how *E. huxleyi* success may be related to $[CO_3^{2-}]$, but its validity remains to be proved by field observations.

Acknowledgements

We are very grateful to Andrew Yool for his kind cooperation at an early stage of this work. Important discussions pertaining this work were also had with Joanie Kleypas, Patrick Holligan, John Shepherd and Rachel Mills. We especially thank Richard Zeebe for helpful comments which greatly improved the manuscript.

Appendix A. Model equations

Temperature mooring data (as detailed functions of time and depth) were used to reconstruct the mixed layer depth, M(t). h(t)=dM(t)/dt was used to calculate the time rate of change of the mixed layer depth. Exchange between the two layers was modelled as two processes, vertical diffusion and entrainment or detrainment caused by deepening or shallowing of the mixed layer depth. According to Fasham (1993), the variable $h^+(t)=\max[h(t),0]$ was used in order to take into account the effects of entrainment and detrain-

ment. The two zooplankton variables were considered capable of maintaining themselves within the mixed layer and thus the function h(t) was used in that case. Diffusive mixing across the thermocline, k, was parameterised by means of a constant factor. The whole diffusion term can be written as:

$$K = \frac{k + h^+(t)}{M(t)}.$$
 (A.1)

A.1. Phytoplankton

The phytoplankton growth rate, μ_d (for example in the case of diatoms), is a function of light, nutrients and temperature. These terms are assumed to limit growth independently so that:

$$\mu_{\rm d} = \mu_{0,\rm d} f(T) \Psi_{\rm d}(I) \Phi_{\rm d}(N, A, S) \tag{A.2}$$

where $\mu_{0,d}$ is the maximum intrinsic growth rate at temperature $T=0^{\circ}$ C, $f(T)=e^{0.063T}$, and the term $\mu_{0,d}f(T)$ represents the Eppley's formulation of temperature-dependent growth (Eppley, 1972). The light limitation term, is calculated by integrating PAR over the depth *z* by using the Steele's formulation:

$$\Psi_{\rm d}(I) = \frac{1}{M} \int_0^M \frac{I(z)}{I_{\rm s,d}} {\rm e}^{1 - \frac{I(z)}{I_{\rm s,d}}} {\rm d}z \tag{A.3}$$

where $I_{s,d}$ is the light level at which photosynthesis saturates in the case of diatoms, I(z) is calculated with Anderson's model (Anderson, 1993).

Following Fasham (1995), the nutrient limitation term $\Phi_d(N,A,S)$ is given by:

$$\Phi_{\rm d}(N,A,S) = \min\left(n_{\rm d} + a_{\rm d}, \frac{S}{S_{\rm h} + S}\right) \tag{A.4}$$

with:

$$n_{\rm d} = \frac{N/N_{\rm h,d}}{1 + N/N_{\rm h,d} + A/A_{\rm h,d}}$$
(A.5)

for nitrate limitation and

$$a_{\rm d} = \frac{A/A_{\rm h,d}}{1 + N/N_{\rm h,d} + A/A_{\rm h,d}}$$
(A.6)

for ammonium limitation. S_h , $N_{h,d}$ and $A_{h,d}$ are the half-saturation constants for diatom uptake of silicate, nitrate and ammonium, respectively. For phytoplankton other than diatoms, the limitation due to nutrient is simply given by the sum of Eqs. (A.5) and (A.6).

The equations for phytoplankton can now be written as:

$$\frac{\mathrm{d}P_{\mathrm{d}}}{\mathrm{d}t} = \mu_{\mathrm{d}}P_{\mathrm{d}} - m_{\mathrm{d}}P_{\mathrm{d}} - G_{\mathrm{d,me}}P_{\mathrm{d}} - G_{\mathrm{d,mi}}P_{\mathrm{d}} - \left(\frac{v_{\mathrm{d}}}{M} + K\right)P_{\mathrm{d}}$$
(A.7)

$$\frac{\mathrm{d}P_{\mathrm{f}}}{\mathrm{d}t} = \mu_{\mathrm{f}}P_{\mathrm{f}} - m_{\mathrm{f}}P_{\mathrm{f}} - G_{\mathrm{f},\mathrm{mi}}P_{\mathrm{f}} - KP_{\mathrm{f}} \tag{A.8}$$

$$\frac{\mathrm{d}P_{\mathrm{df}}}{\mathrm{d}t} = \mu_{\mathrm{df}}P_{\mathrm{df}} - m_{\mathrm{df}}P_{\mathrm{df}} - G_{\mathrm{df,me}}P_{\mathrm{df}} - KP_{\mathrm{df}} \qquad (A.9)$$

$$\frac{\mathrm{d}P_{\mathrm{eh}}}{\mathrm{d}t} = \mu_{\mathrm{eh}}P_{\mathrm{eh}} - m_{\mathrm{eh}}P_{\mathrm{eh}} - G_{\mathrm{eh},\mathrm{mi}}P_{\mathrm{eh}} - KP_{\mathrm{eh}} \qquad (A.10)$$

where (for example in the case of diatoms, Eq. (A.7)) m_d is the constant mortality rate, $G_{d,me}$ the grazing rate by mesozooplankton and $G_{d,mi}$ the grazing rate by microzooplankton, which is different from zero when silicate becomes less than 3 μ M (see Merico et al., 2004).

A.2. Zooplankton

Following Fasham (1993), the grazing rate of, for example, mesozooplankton on diatoms is assumed to take the following form:

$$G_{d,me} = \frac{g_{d,me} p_{d,me} Z_{me} P_d}{Z_{h,me} (p_{d,me} P_d + p_{df,me} P_{df} + p_{mi,me} Z_{mi}) + p_{d,me} P_d^2 + p_{df,me} P_{df}^2 + p_{mi,me} Z_{mi}^2}$$
(A.11)

where $g_{d,me}$ is the maximum ingestion rate, $Z_{h,me}$ is the half-saturation constant for ingestion and $p_{d,me}$ is the mesozooplankton preference for diatoms.

The grazing rates on other food sources are analogous. The equations for zooplankton are therefore:

$$\frac{\mathrm{d}Z_{\mathrm{mi}}}{\mathrm{d}t} = \left(B_{\mathrm{f,mi}}G_{\mathrm{f,mi}} + B_{\mathrm{eh,mi}}G_{\mathrm{eh,mi}} + B_{\mathrm{d,mi}}G_{\mathrm{d,mi}}\right)Z_{\mathrm{mi}}$$
$$- e_{\mathrm{mi}}Z_{\mathrm{mi}} - m_{\mathrm{mi}}Z_{\mathrm{mi}}^2 - G_{\mathrm{mi,me}}Z_{\mathrm{mi}} - \frac{h(t)}{M}Z_{\mathrm{mi}}$$
$$(A.12)$$
$$\frac{\mathrm{d}Z_{\mathrm{me}}}{\mathrm{d}t} = \left(B_{\mathrm{d,me}}G_{\mathrm{d,me}} + B_{\mathrm{df,me}}G_{\mathrm{df}} + B_{\mathrm{mi,me}}G_{\mathrm{mi}}\right)Z_{\mathrm{me}}$$

$$-e_{\rm me}Z_{\rm me} - m_{\rm me}Z_{\rm me}^2 - \frac{\langle \cdot \rangle}{M}Z_{\rm me}$$
(A.13)

 $B_{f,mi}$ is, for example, the assimilation efficiency of flagellates by microzooplankton, and e_{mi} and m_{mi} are the microzooplankton excretion and mortality rates, respectively. Note that zooplankton mortality is represented by a quadratic function of zooplankton biomass, which constitutes the so-called closure term (Steele and

Henderson, 1992). This formulation may be interpreted as representing either cannibalism within the same group, or an unmodelled higher predator whose bio-

mass is assumed to be proportional to that of the zooplankton. Such formulation reduces the likelihood of obtaining solutions with short-term oscillations or multi-year cycles (Edwards and Yool, 2000).

A.3. Nutrients

The nutrient equations are as follow:

$$\frac{dN}{dt} = -\mu_{0,d} f(T) \Psi_{d}(I) \Phi_{d}(N, A, S) \frac{n_{d}}{n_{d} + a_{d}} P_{d}
-\mu_{0,f} f(T) \Psi_{f}(I) n_{f} P_{f} - \mu_{0,df} f(T) \Psi_{df}(I) n_{df} P_{df}
-\mu_{0,eh} f(T) \Psi_{eh}(I) n_{eh} P_{eh} + \Omega A + K(N_{0} - N)$$
(A.14)

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -\mu_{0,\mathrm{d}}f(T)\Psi_{\mathrm{d}}(I)\Phi_{\mathrm{d}}(N,A,S)\frac{a_{\mathrm{d}}}{n_{\mathrm{d}}+a_{\mathrm{d}}}P_{\mathrm{d}}$$
$$-\mu_{0,\mathrm{f}}f(T)\Psi_{\mathrm{f}}(I)a_{\mathrm{f}}P_{\mathrm{f}}-\mu_{0,\mathrm{df}}f(T)\Psi_{\mathrm{df}}(I)a_{\mathrm{df}}P_{\mathrm{df}}$$
$$-\mu_{0,\mathrm{eh}}f(T)\Psi_{\mathrm{eh}}(I)a_{\mathrm{eh}}P_{\mathrm{eh}}+m_{\mathrm{D}}D$$
$$+(e_{\mathrm{mi}}+\delta_{\mathrm{mi}}m_{\mathrm{mi}}Z_{\mathrm{mi}})Z_{\mathrm{mi}}+(e_{\mathrm{me}}+\delta_{\mathrm{me}}m_{\mathrm{me}}Z_{\mathrm{me}})Z_{\mathrm{me}}$$
$$-\Omega A - KA \qquad (A.15)$$

$$\frac{dS}{dt} = -\mu_{\rm d} P_{\rm d} + K(S_0 - S).$$
(A.16)

The constant terms N_0 and S_0 represent the concentrations below the mixed layer depth for nitrate and silicate, respectively. Note that ammonium concentration below the MLD is assumed to be zero (Fasham, 1993). The equation for ammonium (A.15) shows the balance between the loss due to ammonium uptake by phytoplankton and due to nitrification (ΩA) and gains from zooplankton excretion and detrital remineralisation (see below). A Si/N ratio of 1:1 is assumed in Eq. (A.16) (Brzezinski, 1985; Dugdale et al., 1995).

A.4. Detritus

The equation for detritus is:

$$\frac{dD}{dt} = (1 - B_{d,me})G_{d,me} + (1 - B_{df,me})G_{df,me}
+ (1 - B_{mi,me})G_{mi,me} + (1 - B_{eh,mi})G_{eh,mi}
+ (1 - B_{f,mi})G_{f,mi} + (1 - B_{d,mi})G_{d,mi} + m_dP_d
+ m_fP_f + m_{df}P_{df} + m_{eh}P_{eh} - m_DD
- (\frac{v_D}{M} + K)D$$
(A.17)

where m_D is the breakdown rate of detritus to ammonium. The source of detritus in the mixed layer are assumed to be dead phytoplankton and zooplankton faecal pellets.

A.5. Coccoliths

Coccoliths are represented in the model as attached (i.e. part of the coccosphere) and free coccoliths (i.e. which have become detached from the coccosphere), L_a and L_f , respectively. The synthesis of new coccoliths is made proportional to the number of *E. huxleyi* cells and the changes in the two state variables are represented by:

$$\frac{\mathrm{d}L_{\mathrm{a}}}{\mathrm{d}t} = \rho_{\mathrm{CN}} C P_{\mathrm{eh}} - G_{\mathrm{eh,mi}} L_{\mathrm{a}} - m_{\mathrm{eh}} L_{\mathrm{a}} - \Gamma - K L_{\mathrm{a}} \tag{A.18}$$

$$\frac{\mathrm{d}L_{\mathrm{f}}}{\mathrm{d}t} = \Gamma + m_{\mathrm{eh}}L_{\mathrm{a}} - \delta_{\mathrm{f}}G_{\mathrm{eh,mi}}L_{\mathrm{f}} - \Theta L_{\mathrm{f}} - KL_{\mathrm{f}} \quad (\mathrm{A.19})$$

where $\rho_{\rm CN}$ is the C/N Redfield ratio. $C = C_{\rm max} f(T) \Psi(I)$, with C_{max} the constant rate of calcification (i.e. coccolith production) under optimal conditions, f(T) and $\Psi(I)$ representing temperature and light dependence of calcification, respectively. Note that $\Psi(I)$ in the case of coccoliths is calculated using the Michaelis-Menten formulation (rather than the Steel's one) since there are no evidence of photoinhibition of the calcification process. δ_{f} is the fraction of free coccoliths lost during microzooplankton grazing. Θ represents the constant dissolution rate. The transfer from attached to free coccoliths, Γ , is calculated by comparing the concentration of attached coccoliths with the concentration of E. huxleyi cells. When the ratio of these two variables is greater than the maximum number of coccoliths allowed per cell (Π_{max}), then all the excess coccoliths are transferred to the pool of free coccoliths. The number of coccoliths in excess is calculated with:

$$\Gamma = \gamma \left(L_{\rm a} - \Pi_{\rm max} C_{\rm L} \frac{\rho_{\rm CN} P_{\rm eh}}{C_{\rm eh}} \right) \tag{A.20}$$

where γ is the rate of detachment (which is equal to 100% of coccoliths in excess per time step).

A.6. Dissolved inorganic carbon

The change in total inorganic carbon in the upper box of the water column is affected by the utilisation of inorganic carbon by phytoplankton, breakdown of detritus, zooplankton excretion, the fraction of zooplankton mortality that rapidly decomposes into ammonium, and diffusive fluxes. The DIC cycle is affected also by CaCO₃ formation and dissolution. In the model, these processes are described by:

$$\begin{split} \frac{\mathrm{dDIC}}{\mathrm{d}t} &= -\rho_{\mathrm{CN}}(\mu_{\mathrm{d}}P_{\mathrm{d}} + \mu_{\mathrm{f}}P_{\mathrm{f}} + \mu_{\mathrm{df}}P_{\mathrm{df}} + \mu_{\mathrm{eh}}P_{\mathrm{eh}} + CP_{\mathrm{eh}}) \\ &+ \rho_{\mathrm{CN}}[m_{\mathrm{D}}D + (e_{\mathrm{mi}} + \delta_{\mathrm{mi}}m_{\mathrm{mi}}Z_{\mathrm{mi}})Z_{\mathrm{mi}} \\ &+ (e_{\mathrm{me}} + \delta_{\mathrm{me}}m_{\mathrm{me}}Z_{\mathrm{me}})Z_{\mathrm{me}}] + \Theta L_{\mathrm{f}} \\ &+ \nu_{\mathrm{g}}S_{\mathrm{CO}_{2}} \left[\frac{p\mathrm{CO}_{2(\mathrm{air})} - p\mathrm{CO}_{2(\mathrm{sea})}}{M(t)} \right] \\ &+ K(\mathrm{DIC}_{0} - \mathrm{DIC}) \end{split}$$
(A.21)

where the term $v_g S_{CO_2} [(pCO_{2(air)} - pCO_{2(sea)})/M(t)]$ describes the CO₂ fluxes at the air–sea interface, with v_g gas transfer velocity, S_{CO_2} solubility of CO₂ (expressed in units of concentration per pressure), and pCO_2 (partial pressure of CO₂ in air and seawater). A more correct form of this equation is written in terms of fugacity (fCO₂), which incorporates the changes of chemical potential as a function of pressure and temperature, rather than partial pressure. However, fugacity is approximately equal to partial pressure at sea level, and pCO_2 is more commonly used in the literature (Weiss, 1974).

The gas transfer velocity is given by Wanninkhof (1992, Eq. (8)). The solubility of CO₂ is obtained with a least squares polynomial fit vs. temperature and salinity with a method described first by Weiss (1974). As mentioned above, $pCO_{2(air)}$ is assumed to be constant at 358 µatm (measured in 2000 in the Bering Sea by Murata and Takizawa, 2002). The partial pressure of CO₂ in seawater was calculated from model variables of total alkalinity, temperature and DIC along with apparent dissociation constants of carbon acid, boric acid, the solubility of CO₂ and the hydrogen ion activity by using the iterative method presented by Peng et al. (1987).

Note that Alkalinity and DIC are independent of temperature and pressure; pCO_2 , and pH are not. The knowledge of any two of these parameters, along with the temperature, salinity, pressure, abundances of other constituents of seawater, and the relevant equilibrium constants, allow the determination of the other two.

A.7. Alkalinity

Alkalinity is formally defined as the amount of hydrogen ions (H^+) needed to convert all the weak acid anions back to their non-ionised acids. Another

definition is the equivalent sum of all the bases that can accept a proton to the carbonic acid endpoint. It can be seen from Eq. (4) that the precipitation of one unit of calcium carbonate lowers alkalinity by two units, due to the double negative charge of the carbonate ions. Therefore, in the model, changes of alkalinity are simply given by the balances between calcification, dissolution and diffusive fluxes:

$$\frac{\mathrm{dAlk}}{\mathrm{d}t} = -2_{\rho\mathrm{CN}}CP_{\mathrm{eh}} + 2\Theta L_{\mathrm{f}} + K(\mathrm{Alk}_0 - \mathrm{Alk}).$$
(A.22)

It is assumed that the effects of nitrate and ammonium ions are negligible (Peng et al., 1987).

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