The future of the carbon cycle: review, calcification response, ballast and feedback on atmospheric CO$_2$

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The operation of the carbon cycle forms an important part of the processes relevant to future changes in atmospheric carbon dioxide. The balance of carbon between terrestrial and oceanic reservoirs is an important factor and here we focus in particular on the oceans. Future changes in the carbon cycle that may affect air–sea partitioning of CO$_2$ are difficult to quantify but the palaeoceanographic record and modern observational studies provide important evidence of what variations might occur. These include changes in surface nutrient use, the oceanic inventory of nutrients, and the elemental composition and rain-rate ratio of marine particles. Recent work has identified two inter-linked processes of potential importance that we consider in some detail: the response of marine calcification to changes in surface water CO$_2$ and the association of particulate organic carbon with ballast minerals, in particular biogenic calcite. We review evidence from corals, coccolithophores and foraminifera, which suggests that the response of reduced calcification provides a negative feedback on rising atmospheric CO$_2$. We then use a box model to demonstrate how the calcification response may affect the organic carbon rain rate through the ballast effect. The ballast effect on export fluxes of organic and inorganic carbon acts to counteract the negative calcification response to increased CO$_2$. Thus, two oceanic buffers exert a significant control on ocean–atmosphere carbonate chemistry: the thermodynamic CO$_2$ buffer; and the ballast/calcification buffer. Just how tightly coupled the rain-rate ratio of CaCO$_3$/C$_{org}$ is to fluxes of ballast minerals is an important question for future research.

Keywords: climate change; carbon dioxide; oceans; calcification

1. Introduction

Evaluation of future changes in the carbon cycle forms a crucial part of the efforts to determine how climate will respond to changes in greenhouse gases. Within this work, assessing future changes in oceanic carbon uptake is of great importance. This is because of the quantitative importance of the oceanic carbon reservoir compared

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with the other reservoirs with which carbon exchange occurs on human time-scales (the oceanic reservoir of carbon is about 60 times larger than that of the atmosphere). There are two fundamental questions. How will increased atmospheric CO\textsubscript{2} alter the balance between terrestrial and oceanic carbon reservoirs? How well known are the factors affecting oceanic CO\textsubscript{2} uptake and their possible responses to future changes?

The most recent assessment of the Intergovernmental Panel on Climate Change (IPCC) (Houghton \textit{et al.} 2001) has provided estimates of the global climate of the twenty-first century. Using a variety of scenarios, estimated CO\textsubscript{2} levels in year 2100 are between ca. 500 and 1000 ppm compared with annual average levels which have recently reached 370 ppm (figure 1\textit{a}). The estimates of the associated temperature change are between 1.5 and 5.5 °C and those of sea-level change between 0.1 and 0.9 m. The uncertainties in the estimates reflect, in part, incomplete understanding of the carbon cycle.

Records of changes in atmospheric CO\textsubscript{2} over the last 420,000 years have been obtained from ice cores. Although some doubts exist as to the extent to which the past, or indeed the present, is a good analogue for future climate change (e.g. Mitchell 1990), there is no doubt that the mechanisms causing past changes in atmospheric CO\textsubscript{2} are extremely relevant. The message from the body of work on, for example, the causes of glacial–interglacial cycles in carbon dioxide is, according to the IPCC (Houghton \textit{et al.} 2001), that ‘given the complex timing of changes between climate changes and atmospheric CO\textsubscript{2}, it is plausible that more than one mechanism has been in operation; and indeed most or all of the hypotheses encounter difficulties if called upon individually to explain the full magnitude of the change’. In this paper, we shall comment on some ‘clues from the past’ as well as from the modern oceans, including laboratory and model simulations, to address some factors affecting the future of the carbon cycle.

2. The balance between terrestrial and oceanic carbon reservoirs

The pre-industrial oceanic carbon reservoir has been estimated at 38,240 Gt (1 Gt = 10^{15} g), as compared with 600 Gt in the atmosphere and 1,930 Gt in the terrestrial biosphere (850 Gt as biomass and 1,080 Gt as soil) (Brovkin et al. 2002). There appears to be a consensus that the availability of extra CO_2 and fixed nitrogen in the future will result in an increase in carbon storage but that soil warming will decrease carbon storage. However, the balance between these two factors is unknown. Here, we turn to the past and review the evidence as to what caused the atmosphere’s CO_2 to rise during the past 8,000 years (figure 1b).

Indermühle et al. (1999) proposed that the 20 ppm increase in CO_2 since the mid-Holocene (ca. 8,000 years ago) was caused by a ca. 200 Gt decrease in the terrestrial biomass over this period. This is very large and equivalent to ca. 30 years of fossil fuel CO_2 increase at the current rate. Broecker et al. (2001) have expressed surprise that such a large change in storage might reflect a small change in climate. It is therefore pertinent that the reasons for this rise in CO_2 are determined. In support of the interpretation for a massive biomass change is the observation that the increase in CO_2 is accompanied by a decrease in δ^{13}C of atmospheric CO_2 of ca. 0.3 ± 0.1‰ (Indermühle et al. 1999). Additionally, it is consistent with a decline in deep-ocean carbonate ion concentration over the same period (Broecker et al. 1999, 2001).

Broecker has proposed an alternative explanation for the increase in CO_2 since the mid-Holocene (Broecker et al. 1999, 2001): that of a long-term response of the oceanic carbonate system to a ca. 500 Gt increase in terrestrial biomass during the Early Holocene. This mechanism involves four stages:

(i) an ‘instantaneous’ increase in deep water [CO_3^{2-}] as a response to the biomass increase;

(ii) a deepening of the calcite lysocline resulting in an imbalance between carbonate input and output (see §5a);

(iii) calcite preservation to restore balance (a preservation spike is seen in North Atlantic sediments at ca. 9,000 14C yr BP (Broecker et al. 1993; Chapman et al. 1996));

(iv) leading to a decrease in [CO_3^{2-}] and long-term (of the order of 5 kyr) increase in atmospheric CO_2.

Brovkin et al. (2002) have recently used the CLIMBER-2 model in a transient Holocene simulation. Their simulation suggests that terrestrial carbon storage at 8 ka may have been ca. 90 GtC higher than the pre-industrial value (less than the 200 Gt estimated by Indermühle et al. (1999)) but an additional oceanic source is also required to explain the observed change of 20 ppm CO_2. Brovkin et al. (2002) also point out that the change in atmospheric CO_2 may be simulated solely by an increase in oceanic carbonate sedimentation, leading to lower deep-water carbonate ion concentrations and higher surface-ocean pCO_2. This finding is in line with the hypothesis posited by Broecker et al. (2001). As yet the available data are insufficient to discriminate between a terrestrial biosphere or deep oceanic source for the observed Holocene increase in atmospheric CO_2. Both higher precision δ^{13}CO_2 data and a better understanding of oceanic carbonate preservation are needed.
Table 1. Factors potentially important for the future oceanic uptake of CO₂ (after Houghton et al. 2001)

<table>
<thead>
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3. Factors affecting oceanic CO₂ uptake and their response to future changes

Maps of the distribution of $pCO_2$ in surface waters of the world’s oceans (e.g. Takahashi et al. 2002) demonstrate powerfully how complex the factors are that contribute to the exchange of CO₂ between atmosphere and oceans. According to the IPCC (Houghton et al. 2001), the estimated flux of CO₂ from the atmosphere to the oceans will be between ca. 4 and 6 Gt yr$^{-1}$ in the year 2100 compared with ca. 2 Gt yr$^{-1}$ today. A number of physical, chemical and biological factors (table 1) have the potential to affect future changes in the oceanic uptake of carbon dioxide (Houghton et al. 2001). Physical factors include changes in vertical mixing versus stratification of the oceans. Increasing vertical stratification (decreased mixing) would reduce CO₂ uptake by, in effect, reducing the oceanic volume available to CO₂ absorption from the atmosphere. Stratification may also affect the biological carbon cycle by reducing the available nutrients necessary for primary production in the euphotic zone. Chemical processes that may contribute to CO₂-uptake variability include the CO₂ buffer or Revelle factor (see §4b) and the effects of temperature on CO₂ solubility. Because CO₂ is less soluble in warm water than in cold water, $pCO_2$ in seawater increases by 10–20 ppm per degree increase in temperature, thereby increasing the sea-to-air flux and potentially increasing atmospheric CO₂. Biologically linked processes are perhaps the most difficult to evaluate, although evidence from palaeoclimate records suggests that changes are likely to have occurred over glacial–interglacial time-scales. Here, we focus on the relationships between several of these factors: changes in the effectiveness of the ocean CO₂ buffer, changes in marine ecosystems, specifically the potential fate of calcareous organisms and changes in the rain-rate ratio (the ratio of CaCO₃ flux to C$_{org}$ flux to the sea floor).

4. Response of marine calcification to changes in atmospheric CO₂

(a) Production of calcium carbonate as a source of CO₂

The major oceanic producers of calcium carbonate include coral reef communities and pelagic organisms such as foraminifera and coccolithophores (quantitatively the most important (Westbroek et al. 1993)). The production and burial of both organic carbon and biogenic carbonate within the marine system provide a potential sink for carbon and therefore play a role in the global carbon cycle. However, while the formation of organic matter provides a sink for atmospheric CO₂, the production
of carbonate causes an increase in $pCO_2$ of surface waters and therefore acts as a potential source of $CO_2$ to the atmosphere. The two processes may be represented by the following simplified equations.

Formation of organic matter:

$$CO_2 + H_2O = CH_2O + O_2.$$  

(4.1)

Formation of biogenic carbonate:

$$Ca^{2+} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O.$$  

(4.2)

Although the formation and burial of $CaCO_3$ provides a net sink for carbon, it is the production of $CO_2$ during calcification that is of interest here. The interplay between the formation of organic matter and calcium carbonate and their opposing effects on surface-ocean $pCO_2$ has led to considerable debate on the role of marine calcifying organisms in atmospheric $CO_2$ variability, i.e. do they act as sources or sinks of atmospheric $CO_2$? In particular, coral reefs have received much attention (e.g. Ware et al. 1992; Gattuso et al. 1995; Kawahata et al. 1997; Ohde & van Woesik 1999). The bloom episodes of coccolithophore production have also been investigated for their effects on the $CO_2$ system in surface waters (Holligan et al. 1993; Bates et al. 1996; Crawford & Purdie 1997; Murata & Takizawa 2002). Although the ‘source/sink’ debate is still active, it is the general consensus that coral communities, at least, provide a net source of $CO_2$ to the atmosphere. Ware et al. (1992) provide an estimate of the net global coral reef $CO_2$ source as 0.02–0.08 GtC each year. This may be compared with the estimated annual emission of 7 GtC from fossil fuel burning (Houghton et al. 1995).

(b) Marine calcification as a positive feedback to rising atmospheric $CO_2$

The production of one mole of calcium carbonate does not result in the release of one mole of $CO_2$. This is due to the carbonate buffering capacity of seawater (figure 2). An increase in dissolved $CO_2$ will tend to lower the $pH$ of seawater but this will be partly compensated for by the reaction of $CO_2$ with $CO_3^{2-}$:

$$CO_2 + CO_3^{2-} + H_2O = 2HCO_3^-.$$  

(4.3)
In the modern ocean, the ratio of released CO$_2$ to precipitated carbonate, $\Psi$, is approximately 0.6 (Ware et al. 1992). Frankignoulle et al. (1994) proposed that $\Psi$ increases as a result of increasing atmospheric CO$_2$ concentration.† Specifically, a doubling of atmospheric CO$_2$ would cause $\Psi$ to increase to 0.76. This could provide a net CO$_2$ source of ca. 5 GtC between 1880 and 2050 (Frankignoulle et al. 1994). Therefore, if all else remained equal, marine calcification could be expected to provide a positive feedback to rising atmospheric CO$_2$. The CO$_2$ produced by formation of calcium carbonate does not necessarily evade into the atmosphere. It may be used during the formation of organic matter and therefore may not provide a direct source of CO$_2$ to the atmosphere. However, if the global production rate of organic matter and inorganic carbonate are considered to be constant, then an increase in $\Psi$ will provide a net source of CO$_2$ to the ocean atmosphere system.

(c) Correlation between calcification rate and pCO$_2$

The saturation state of seawater with respect to calcium carbonate may be defined as

$$\Omega = \frac{[Ca^{2+}] [CO_3^{2-}]}{K_{sp}},$$

(4.4)

where $K_{sp}$ is the stoichiometric solubility product for CaCO$_3$ (a function of temperature and pressure). When $\Omega = 1$, the solution is considered saturated with respect to carbonate; a value less than unity represents undersaturation and dissolution may occur, while a value greater than unity implies supersaturation. Since $[Ca^{2+}]$ is approximately conservative in seawater, $[CO_3^{2-}]$ may be considered as the dominant control over $\Omega$. On dissolution in seawater, CO$_2$ dissociates to form HCO$_3^-$ and CO$_3^{2-}$ ions. At average pH values, ca. 90% of the total dissolved inorganic carbon ($\sum$ CO$_2$) in seawater is in the form HCO$_3^-$, the remainder is mostly CO$_3^{2-}$ (figure 2). CO$_2$ represents less than 1% of dissolved inorganic carbon in average surface-ocean waters.‡ The partitioning between inorganic carbon species in seawater is such that, for a given temperature and salinity, pCO$_2$ is approximately inversely proportional to [CO$_3^{2-}$]. A similar relation exists between pCO$_2$ and $\Omega$.

† This decrease in the effective buffering capacity of seawater is analogous to the Revelle factor, which predicts that the capacity of ocean water to absorb atmospheric CO$_2$ by reaction with CO$_3^{2-}$ will decrease as atmospheric CO$_2$ rises and surface-ocean [CO$_3^{2-}$] decreases.

‡ The partitioning of marine inorganic carbon species between HCO$_3^-$, CO$_3^{2-}$ and CO$_2$ provides the explanation for the significantly larger capacity for carbon storage in the oceans than in the atmosphere and is the basis for assuming that the oceans ultimately control atmospheric CO$_2$ concentrations.

Figure 3. The effect of carbonate saturation on marine calcification. (a) Compilation of culture data from the BIOSPHERE-2 facility, showing the relation between saturation state and calcification rate for a coral reef mesocosm (Langdon et al. 2000; Langdon 2001). Although the data shown here represent several experiments involving a variety of chemical perturbations, there is a strong positive relation between calcification rate and saturation state. (b) Culturing experiments on two species of coccolithophore (Emiliania huxleyi, circles; Gephyrocapsa oceanica, squares) demonstrate a negative relation between calcification rate and pCO$_2$ (reproduced from Riebesell et al. (2000), with permission from the Nature Publishing Group). This is synonymous with a positive relation between calcification rate and [CO$_3^{2-}$]. Note also that organic matter production shows a slight positive response to increased pCO$_2$. (c) Data from Barker & Elderfield (2002) showing the relation between foraminiferal shell weight and [CO$_3^{2-}$] (the main controller of calcite saturation).

Most of the surface ocean is supersaturated with respect to both the calcite and aragonite forms of calcium carbonate. Therefore, it may be assumed that small changes in surface-ocean carbonate chemistry will not have a perceptible effect on marine calcification. However, a range of studies has shown a strong dependence of carbonate production rates on the degree of supersaturation. Several studies on...
coralline calcification have concluded that rates of carbonate production are positively correlated with the carbonate saturation state of seawater (Gattuso et al. 1998; Langdon et al. 2000; Marubini et al. 2001; Leclercq et al. 2002) (figure 3a). Similar findings (figure 3b) have been reported for calcification rates in coccoliths (Riebesell et al. 2000). The shell weights of planktonic foraminifera have also been shown to vary in response to increasing saturation state (figure 3c) of seawater during growth (Spero et al. 1997; Bijma et al. 1999; Barker & Elderfield 2002). An increase in shell weight is thought to reflect higher rates of calcification. All of these studies are in line with inorganic precipitation experiments that demonstrate a positive relation between saturation state and precipitation or calcification rate (Zhong & Mucci 1989; Zuddas & Mucci 1998). Since the carbonate saturation state of the surface ocean is intimately linked to \( p\text{CO}_2 \), it follows that rates of marine calcification will be sensitive to changes in atmospheric \( \text{CO}_2 \).

(d) Past evidence of marine calcification response to changing atmospheric \( \text{CO}_2 \)

Evidence from ice cores suggests that atmospheric \( \text{CO}_2 \) during the last glacial maximum (LGM) was ca. 30% lower than pre-industrial values. From our knowledge of the marine carbonate system, we can predict that surface ocean \([\text{CO}_3^{2-}]\) would have been correspondingly higher during glacial times. This proposition is supported by isotopic evidence for a lower pH in the glacial oceans (Sanyal et al. 1995). A record of planktonic foraminiferal shell weights from the North Atlantic reveals that similarly sized shells of \( \text{Globigerina bulloides} \) were ca. 70% heavier (figure 4a) during the LGM than during the Holocene (Barker & Elderfield 2002). By using an empirical calibration of shell weight to \([\text{CO}_3^{2-}]\) and combining chemical proxies to attain estimates of temperature and salinity, Barker & Elderfield (2002) showed that
The continued increase in atmospheric CO$_2$ will cause a lowering of surface ocean [CO$_2^-$] and a lowering of the saturation state with respect to calcite and aragonite. Due to the observed sensitivity of calcification rates in corals, coccoliths and foraminifera to changes in carbonate saturation, it may be predicted that carbonate production by these groups will decrease into the future. This phenomenon is significant not only to the ecological stability of these types of organism but also to their role in the global carbon cycle. On the time-scales relevant to modern society, the immediate impact will be a decrease in evolved CO$_2$ due to reduced CaCO$_3$ formation.

Kleypas et al. (1999) presented future projections of surface-ocean \( \Omega_{\text{aragonite}} \) distributions based on thermodynamic constraints and results from the HAMOCC (Hamburg Ocean Carbon Cycle) global model (Maier-Reimer 1993) (figure 5a, b). They also predicted consequent global changes in reef calcification rates over the next 100 years, based on average calcification responses of tropical marine algae and corals (figure 5c). It is clear from their estimates that the possible impact of increasing atmospheric CO$_2$ on coral communities is significant. In a recent review of the experimental evidence for effects of CO$_2$ on calcification of reef-building organisms, the observed weight difference was appropriate for the observed decrease in glacial atmospheric CO$_2$ (figure 4b).

\( \text{(e) Marine calcification as a negative feedback to rising atmospheric CO}_2 \)
Langdon (2001) states that based on recent studies, calcification rates on coral reefs could decline by 11–44% by the middle of this century. Further, due to a long-term reduction in skeletal growth it is likely that corals will be more susceptible to bioerosion, storm damage and possibly disease (Langdon 2001). Other factors related to elevated atmospheric CO$_2$ may also influence coral reef ecology, notably the ‘bleaching’ effect of increased temperatures.

As discussed previously, increasing the atmospheric concentration of CO$_2$ will decrease the carbonate buffering capacity of the surface ocean. This means that more CO$_2$ will be produced per mole of calcium carbonate precipitated and therefore constitutes a positive feedback to rising CO$_2$. However, due to the observed negative impact of increased atmospheric CO$_2$ on marine calcifying organisms, it is probable that global marine biogenic carbonate production will decrease into the future. This will counter the positive feedback effect of a reduced buffering capacity and may provide a net negative feedback to rising CO$_2$. Zondervan et al. (2001) present a model for this scenario based on experimental evidence for coccolith-calcification-rate dependence on $p$CO$_2$. They predict that global production of CO$_2$ by precipitation of CaCO$_3$ may decrease by up to 0.4–0.5 GtC yr$^{-1}$ by the year 2150 (even accounting for the decreased buffering capacity), given a modern global carbonate production rate of ca. 1 GtC yr$^{-1}$ (figure 6).

5. The ballast hypothesis

(a) Rain-rate ratio

Considerable dissolution of marine carbonate occurs within the upper few centimetres of sediment at the sea floor. This dissolution is driven by a lowering of [CO$_3^{2-}$] within sediment pore waters as a result of increased CO$_2$ released during respiration of organic matter within the sediments (Emerson & Bender 1981).Obviously, the amount of organic matter entering the sediments and therefore available to respiration dictates the amount of dissolution that may occur in this way. A higher ratio
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of organic matter to inorganic carbonate will cause an increase in the proportion of carbonate that dissolves. The rain-rate ratio or rain ratio may be considered as the molar ratio of particulate organic carbon to particulate inorganic carbon (i.e. carbonate) arriving at the sea floor. Changes in the rain ratio may alter the extent of carbonate dissolution or preservation on a global scale due to its influence on sediment pore-water chemistry (Archer 1991).

On time-scales of thousands of years, the supply rate of calcium carbonate to the oceans by terrestrial weathering is balanced by deposition and burial of carbonate at the sea floor. If this steady-state situation is perturbed, for example by a decrease in carbonate burial rates, the system will tend to respond in such a way as to regain the balance (Broecker & Peng 1987). In this example, reduced burial of carbonate at the sea floor will cause an increase in deep-water \([\text{CO}_3^{2-}]\). This in turn will lead to an increase in the preservation potential of carbonate sediments and will result in an increase in carbonate output to match the original input. This process is known as carbonate compensation (Broecker & Peng 1987).

Archer & Maier-Reimer (1994) presented a model that combined changes in the rain ratio (and subsequent adjustment of pore-water calcite dissolution) with carbonate compensation to explain the observed decrease in atmospheric \(\text{CO}_2\) during glacial times. They suggested that a 40% decrease in carbonate production with respect to organic production in the surface ocean would cause a decrease in carbonate burial and an increase in deep ocean \([\text{CO}_3^{2-}]\). This in turn would cause a lowering of atmospheric \(\text{CO}_2\) to near glacial values due to the inverse relation between \([\text{CO}_3^{2-}]\) and \(p\text{CO}_2\).

As discussed earlier, the effect of continued atmospheric \(\text{CO}_2\) increase in the future will probably lead to reduced production of marine carbonate. It may seem likely that we should expect a corresponding decrease in the ratio of carbonate to organic matter falling to the deep sea. This would lead to changes in carbonate burial rates similar to those described by Archer & Maier-Reimer (1994) and possibly to long-term changes in deep-sea \([\text{CO}_3^{2-}]\) and atmospheric \(\text{CO}_2\).

(b) The ballast hypothesis

Quantifying the vertical flux of organic matter from the surface to the deep ocean is important for investigations into the role of the oceanic biological pump in the global carbon cycle. Models attempting to represent the cycling of organic matter and nutrients in the upper ocean (e.g. Sarmiento et al. 1993) have used power-law functions, based on empirical observations (e.g. Martin et al. 1987), to represent variations in the sinking flux of organic matter with depth. These models imply an independence between organic and inorganic material fluxes to the deep sea. However, recent work by Armstrong et al. (2002) and Klaas & Archer (2002) suggests that fluxes of organic and inorganic matter are in fact intimately related to one another. This interdependence implies that deep-sea rain ratios may ultimately be fixed at least on regional scales.

The dominant role of large particles and aggregates in the flux of material to the ocean floor is well documented (e.g. McCave 1975; Honjo 1980). Apart from an organic component, inorganic mineral phases such as opaline silica, calcium carbonate and lithogenic dust (collectively termed ‘ballast’ minerals) represent a major constituent of these particles (Honjo 1980) and presumably play an important role.
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Figure 7. Scatter plots showing the correlation between POC flux and ballast flux below 1000 m from a global coverage of sediment traps. CaCO₃ is thought to be the most important transporter of POC to the deep sea. (a) \( r = 0.829 \), (b) \( r = 0.595 \), (c) \( r = 0.536 \); \( P < 0.0001 \). (Reproduced by permission from Klaas & Archer (2002). Copyright 2002 American Geophysical Union.)

in the rate of sinking due to their relatively high densities (Smayda 1970; McCave 1975; Ittekkot & Haake 1990). Armstrong et al. (2002) present a new model for describing the flux of sinking particulate organic carbon (POC) through the water column. They suggest that below ca. 1800 m the flux of organic matter is in direct quantitative proportion to the fluxes of ballast minerals. This may be illustrated by the relative constancy of POC flux normalized to total mass flux (i.e. the mass proportion of organic matter to total material flux) as compared to the absolute flux of POC. Klaas & Archer (2002) present a compilation of sediment trap data from around the globe from which they conclude that most (80–83%) of the organic carbon rain to the deep sea is carried by calcium carbonate (figure 7). They argue that this is because carbonate is denser than opal (and therefore has a greater carrying coefficient) and more abundant than terrigenous material.

6. Modelling the effects of POC ballasting: a positive feedback to rising atmospheric CO₂

The intimate relation between deep vertical fluxes of carbonate and organic matter suggested by Armstrong et al. (2002) and Klaas & Archer (2002) has implications not only for theories involving past changes in the rain-rate ratio (e.g. Archer & Maier-Reimer 1994) but also for atmospheric CO₂ uptake related to the burial of organic matter. The formation of organic carbon in the surface ocean involves an uptake of CO₂ (equation (4.1)). As POC sinks through the water column, most is remineralized back to inorganic CO₂ in the upper 1–2 km (Armstrong et al. 2002). The rest is transported to the deep sea and sediments and provides a net sink for atmospheric CO₂ on centennial time-scales. A reduction in the proportion of POC sinking to deeper waters will reduce the effective capacity of organic matter formation as an atmospheric CO₂ sink. We propose that as a result of decreased carbonate production in response to rising atmospheric CO₂, the flux of POC to the deep ocean will also be reduced due to the ballast effect. The resulting redistribution of POC remineralization with depth will then provide a positive feedback for increasing atmospheric CO₂.

We simulate the effect of increased atmospheric CO$_2$ on calcification and mineral ballasting of POC using a modified version of the eight-box ocean–atmosphere model of Toggweiler (1999). The ocean is represented as an eight-box reservoir consisting of four surface boxes, three intermediate boxes, and a deep box (table 2, figure 8). The four surface-ocean boxes represent the sinking region of the North Atlantic (n), the low-latitude surface-ocean (l), the Subantarctic (s), and the upwelling region of the polar ocean (p). The intermediate ocean is divided into a polar-intermediate region (pi), a region corresponding to the thermocline (m), and the rest of the intermediate depth water (a). Oceanic conveyor circulation (denoted T), originates with deep water formation in the North Atlantic, which upwells to the surface in the Southern Ocean. Exchange terms (fppi, fpid, flm and fpia) simulate bi-directional exchange between boxes, fppi and fpid representing specifically the formation of Antarctic bottom water. Values for exchange and circulation fluxes were set so as to reproduce
the observed distribution of phosphorus in the surface, intermediate, and deep ocean. The magnitudes of the fluxes are significantly larger than similar box-model studies, owing to the high surface-ocean production values (14 GtC yr\(^{-1}\) and 3.5 GtC yr\(^{-1}\) for POC and CaCO\(_3\), respectively). We attribute this apparent inconsistency within our model as a result of the equations of Armstrong et al. (2002), which may underestimate dissolution and remineralization of CaCO\(_3\) and POC in the upper water column.

A full set of input parameters for the model are given in table 2. Carbon speciation in all the oceanic boxes and the surface-ocean partial pressure of CO\(_2\) are calculated after Zeebe & Wolf-Gladrow (2001). The Redfield ratio C\(_{\text{org}}\):N:P, linking the production and remineralization of POC to changes in phosphorus and alkalinity is set to 106:16:1 (Redfield et al. 1963). Production rates of POC and CaCO\(_3\) were set at 14 GtC yr\(^{-1}\) and 3.5 GtC yr\(^{-1}\), respectively, using the equations of Armstrong et al. (2002), the ballast parametrizations listed in table 1, and the estimates for benthic CaCO\(_3\) and associated POC fluxes (0.9 GtC yr\(^{-1}\), 0.6 GtC yr\(^{-1}\)) of Archer et al. (2000). Sediment burial is not simulated in the model and all of the sinking POC and CaCO\(_3\) is remineralized within the water column.

Primary productivity and the rain of both organic and inorganic carbon out of the surface ocean are defined by the numerical model of Armstrong et al. (2002), which accounts for the observed close correlation between POC fluxes and ballast mineral fluxes (calcium carbonate, opal and lithogenic material). For simplicity, we consider only calcium carbonate (CaCO\(_3\)) in our calculations of POC fluxes: a reasonable assumption given the results presented by Klaas & Archer (2002), which suggest that the majority of the benthic flux of organic carbon (80–83%) is associated with CaCO\(_3\). According to Armstrong et al. (2002), the total flux of POC at depth is partitioned between quantitatively associated POC and the remaining or excess POC.
The inverse relationship between calcification and atmospheric CO$_2$ should not be neglected when evaluating the role of the ocean in mitigating changes in atmospheric CO$_2$. Where $\delta_B$ and $\delta_E$ are the remineralization length-scales for ballast (CaCO$_3$) and excess POC. In this preliminary study, we used the additional simplification of Armstrong et al. (2002) that $\delta_B = \delta_E$, reducing equation (6.1) to

$$F_{OC}(z) = F_{OC}(\infty) + [F_{OC}(z_0) - F_{OC}(\infty)] \exp\{-(z-z_0)/\delta_F\},$$

where $F_{OC}(\infty)$ is evaluated from a prediction of $F_B(z_0)$ by

$$F_{OC}(\infty) = \rho F_B(\infty) = \rho F_B(z_0) / F_B(z_0),$$

and $\rho$ is the asymptotic POC-to-ballast ratio (the rain ratio), i.e. $F_{OC}(\infty)/F_B(\infty)$. Similarly, the dissolution of CaCO$_3$ is described as an exponential decay to the burial flux of CaCO$_3$:

$$F_B(z)/F_B(z_0) = F_B(\infty)/F_B(z_0) + [1 - F_B(\infty)/F_B(z_0)] \exp\{-(z-z_0)/\delta_B\}.$$  

The inverse relationship between calcification and $p$CO$_2$ is modelled using an exponential equation of Barker (2002),

$$F_B(z_0, t) = F_{B0}(z_0, t_0) \exp\{0.0083([\text{CO}_3^{2-}]_t - [\text{CO}_3^{2-}]_{t_0})\},$$

where $[\text{CO}_3^{2-}]_{t_0}$ is the initial steady-state carbonate ion concentration. Over a range of concentrations of atmospheric CO$_2$ (300–700 ppm), equation (6.5) gives a decrease in marine calcification of 40%, consistent with a predicted decrease in calcification over a comparable range of CO$_2$ in coccoliths (16–45%) (Zondervan et al. 2001), corals (40%) (Langdon et al. 2000) and natural planktonic assemblages (36–83%) (Riebesell et al. 2000).

(b) Results

The model is initialized with steady-state partitioning of total CO$_2$, alkalinity and phosphorus. At each model time-step, CO$_2$ is added to the atmosphere at a constant rate. This increase in atmospheric CO$_2$ lowers the concentration of CO$_3^{2-}$ in the surface ocean in accordance with the inverse relationship between CO$_2$ and CO$_3^{2-}$. The decrease in CO$_3^{2-}$ results in a reduction in marine planktonic calcification, in accordance with equation (6.5), from an initial production rate of 3 GtC yr$^{-1}$ to a value of 1.8 GtC yr$^{-1}$. This decrease in CaCO$_3$ production lowers the amount of CO$_2$ produced via calcification. Alternatively, the decrease in CaCO$_3$ production can be interpreted as a relative increase in surface-ocean alkalinity which is equivalent to an increase in the capacity of the surface ocean for CO$_2$ uptake. As a result, the calcification response acts as a negative feedback on increasing atmospheric CO$_2$ (figure 9a). The net draw-down of atmospheric CO$_2$ resulting from the calcification response is small (17.4 ppm or ca. 5% of the total atmospheric CO$_2$ increase), but should not be neglected when evaluating the role of the ocean in mitigating changes in atmospheric CO$_2$. 

Figure 9. (a) Negative feedback of calcification response to increasing atmospheric CO$_2$. The dashed line is the control run with no calcification effect. The decrease in effective CO$_2$ uptake with increasing pCO$_2$ in the control run is due to the positive-feedback effect of lowering the carbonate-buffering capacity (Frankignoulle et al. 1994). CO$_2$ fluxes were calculated using only CaCO$_3$ production; the effect of CaCO$_3$ dissolution on subsequent CO$_2$ uptake was neglected. (b) Positive feedback of mineral ballasting of POC as a consequence of the calcification response. CO$_2$ fluxes were calculated using POC export to the deep sea. The dashed line represents CO$_2$ uptake by POC export with no ballast effect.

Mineral ballasting of POC adds a further complication to the response of calcification to changes in atmospheric CO$_2$ as changes in ballast production drive simultaneous changes in the POC flux (equation (6.3)). A decrease in CaCO$_3$ production results in an upward shift in the locus of POC remineralization, thereby lowering the flux of POC to the deep sea (figure 10). As illustrated in figure 10b, this decrease in calcification in response to increasing atmospheric CO$_2$ results in a significant reduction in the POC flux (10–50%) below ca. 1500 m. Reducing the deep-sea POC flux effectively increases the reservoir of CO$_2$ in the surface and intermediate ocean. This increase in CO$_2$ in the surface ocean acts as a positive feedback on increasing atmospheric CO$_2$ (figure 9b). Adding the effect of mineral ballasting to the model causes the amount of surface ocean CO$_2$ and atmospheric CO$_2$ to increase by 3 µmol kg$^{-1}$ and 3 ppm, respectively.

The combined model results of calcification response and ballast effect on atmospheric CO$_2$ are shown in figure 11a. The negative feedback effect of reduced calcification acts to lower predicted atmospheric CO$_2$ values by ca. 2.5% (by 2250) below a control scenario with neither calcification nor ballast effects included. Adding in the ballast effect goes some way to counteracting the calcification effect, but is insufficient to completely reverse it. In response to this, we considered the effect of changing the rates of dissolution and remineralization of CaCO$_3$ and POC. When the dissolution and remineralization rates are increased (by using a shorter length-scale of dissolution/remineralization), less CO$_2$ is exported to the deep ocean, resulting in higher concentrations of CO$_2$ in the surface and intermediate ocean. Lowering the length-scale of dissolution by 20% increases surface-ocean CO$_2$, alkalinity and atmospheric CO$_2$ by 21 µmol kg$^{-1}$, 13 µmol kg$^{-1}$ and 20 ppm, respectively. This enables the ballast effect to completely counter the negative feedback of reduced calcifica-
Figure 10. (a) The effect of the calcification response on mineral ballasting of POC to the deep sea. Including the effect causes an increase in the amount of POC remineralized before sinking to the deep sea. (b) Modelled future POC fluxes based on IPCC estimates of $pCO_2$ increase and the response of marine calcification.

In addition to $CaCO_3$ and POC dissolution and remineralization rates, we investigated the sensitivity of the model to changes in the burial flux of $CaCO_3$ ($F_B(z_0)/F_B(\infty)$) and the asymptotic transport ratio, $\rho$, equivalent to the rain-rate ratio ($F_{OC}(\infty)/F_B(\infty)$). The asymptotic transport ratio is a measure of the POC carrying capacity of $CaCO_3$. As a result, changes in $\rho$ are important with respect to the flux of POC at depth. A change in the rain-rate ratio from 0.6 to 0.7 (mol POC/mol $CaCO_3$) yields a 16% increase in the POC flux at 3000 m. How-
Figure 11. (a) $\Delta p\text{CO}_2$ curves for calcification response and mineral ballasting of POC. (b) $\Delta p\text{CO}_2$ curves for calcification response and mineral ballasting with increased dissolution/remineralization rates of CaCO$_3$ and POC. Remineralization length-scales are shortened by 20% as a consequence of a reduction in the saturation state of the ocean with increasing atmospheric CO$_2$.

The model calculations suggest that mineral ballasting of POC acts as a positive feedback on increasing atmospheric CO$_2$. The magnitude of this positive feedback is sensitive to the dissolution/remineralization rates of CaCO$_3$ and POC. Assuming a 20% increase in the dissolution/remineralization rates of CaCO$_3$ and POC, we calculate a small net increase in atmospheric CO$_2$ (positive feedback on increasing atmospheric CO$_2$) related to the combined effects of mineral ballasting and reduced calcification (figure 11b). While these results depend critically on an increase in dissolution/remineralization rates, we suggest that such a response is plausible given the relationship between increasing atmospheric CO$_2$ and the saturation state of the surface ocean with respect to CaCO$_3$.

While our model does reproduce the expected changes in oceanic CO$_2$ partitioning, there are a number of further experiments which will contribute to the future analysis of the ballast hypothesis on the global carbon cycle. Of particular interest is the effect of mineral ballasting on the regulation of atmospheric CO$_2$ on glacial–interglacial time-scales. Simulating the effect of mineral ballasting of POC on glacial–interglacial time-scales will require a model that includes all three types of ballast minerals (opal, calcium carbonate and lithogenic material), weathering/sediment burial and carbonate compensation. Additionally, a more mechanistic understanding of mineral ballasting is required. Given the apparent importance of biologically mediated dissolution of CaCO$_3$ (e.g. Milliman et al. 1999), it is clear that ballast mineral fluxes...
are not independent variables, but themselves depend on the flux of POC. From the perspective of changes in the global carbon cycle, oceanic productivity, and on longer time-scales POC and CaCO$_3$, burial fluxes are considered important regulators of atmospheric CO$_2$. However, scant attention has been given to the underlying mechanisms governing POC and CaCO$_3$ remineralization/dissolution. As these mechanisms ultimately determine the sediment fluxes of both organic carbon and calcium carbonate, a more quantitative treatment may shed light on additional important feedbacks within the global carbon cycle.

### 7. Conclusions

Understanding the role of the ocean in the global carbon cycle is critical to our ability to predict the Earth’s response to the current anthropogenic rise in atmospheric CO$_2$. Much of the uncertainty surrounding the role of the ocean in the global carbon cycle can be attributed to a dearth of knowledge concerning the mechanisms involved in the ocean’s biological carbon pump and how these might respond to changes in atmospheric CO$_2$. Frankignoulle et al. (1994) first calculated that marine calcification acts as a positive feedback on increasing atmospheric CO$_2$, resulting from the decreased buffer capacity of the surface ocean. However, Frankignoulle et al. (1994) assumed that calcification rates remained constant over time. Subsequent studies on coccoliths (e.g. Zondervan et al. 2001), corals (Langdon et al. 2000) and foraminifera (Barker 2002) have established an inverse relationship between calcification and atmospheric CO$_2$. From simple calculations of projected marine calcification rates, Zondervan et al. (2001) and Barker (2002) demonstrated that the inverse relationship between calcification and atmospheric CO$_2$ resulted in a net negative feedback on increasing atmospheric CO$_2$. The appearance of the ballast hypothesis has provided additional complication to the question of marine calcification as a feedback on changes in atmospheric CO$_2$ because it explicitly relates POC export fluxes to CaCO$_3$ export fluxes. We have shown that the ballast effect may act to counter the negative feedback effect of reduced calcification and may constitute a net positive feedback depending on the choice of the dissolution/remineralization rates of CaCO$_3$ and POC.

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### References


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1998

S. Barker, J. A. Higgins and H. Elderfield


Toggweiler, J. R. 1999 Variation of atmospheric CO$_2$ by ventilation of the ocean’s deepest water. Paleoceanography 14, 571–588.


Discussion

I. N. McCave (Department of Earth Sciences, University of Cambridge, UK). Have you included, or can you include, in your box model the consequences of glacial–interglacial and stadial–interstadial carbon-system variations for δ$^{13}$C in bottom sea water (and benthic foraminifera)?

H. Elderfield. The consequences have not been included as we were concerned with the response only to future CO$_2$ change. This is straightforward to do, although in the context of the approach taken we would have to decide whether the ocean configuration in the model is appropriate, for example, the depth and vigour of NADW production, for past times.

J. G. Shepherd (School of Ocean & Earth Science, University of Southampton, UK). How constant do you think the rain ratio may be?

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H. Elderfield. The implication of the ballast model is that the rain ratio may be more constant than has been surmised. It is important, though, to make it perfectly clear what is meant by this term. It was used by Archer & Maier-Reimer explicitly to refer to the ratio of inorganic to organic carbon at the sea bed (disregarding nepheloid layer resuspension), because this ratio affects sediment respiration and has the potential to separate the depths of the lysocline and saturation horizon. However, it has also been used to refer to the ratio of the export flux and the ratio of the production flux, and it is perhaps here that misunderstanding occurs. Clearly, there are large regional (and probably temporal) differences in production and export ratios (the diatom/phaeocystis ratio in the Southern Ocean, for example) and these will affect atmospheric CO$_2$ on 102-year time-scales. Interaction with sediments leads to carbonate compensation, which also changes CO$_2$ but on 103-year time-scales.