6 Geological Carbon Sinks

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6.1 Introduction

The sequestering (locking up) of carbon in geological formations and removal of carbon dioxide (CO_2) from the atmosphere is not a unique, human-driven invention thought up for ameliorating (reducing) the degree of greenhouse gas–driven climate change in the future. CO_2 has been spewing from volcanoes on land and the spreading ridges of the ocean throughout geological time. Yet, CO_2 levels are not thought to have risen inexorably since the Earth was formed some 4.5 billion years ago. Quite the opposite – geological evidence suggests that we live in a period in which atmospheric CO_2 concentrations are probably amongst the lowest to have occurred on Earth, at least for the past 600 million years (Royer *et al.*, 2004) (Fig. 6.1a). Indeed, compared to the 'pre-Industrial' atmosphere (i.e. immediately prior to the Industrial Revolution *c.*1765 and the onset of industrialization and increasingly rapid fossil fuel consumption), which was characterized by a CO_2 concentration of 278 ppm (Enting *et al.*, 1994), geological periods such as the Jurassic (200–145 million years ago) and Devonian (416–359 million years ago) saw about ten times as much carbon residing in the atmosphere. The ocean carbon reservoir would also have been much larger at times in the past (Ridgwell, 2005) (Fig. 6.1b). But where has this carbon gone? There must exist greenhouse gas sinks that are able not only to sequester large amounts of carbon but also to keep a tight hold of it for extended periods of time. The amount of carbon stored in vegetation and soils has varied significantly through time, with as much as ~1000 Gt C less at the height of the last glacial period, and is associated with major shifts in vegetation type and coverage, compared to the ~2200 Gt C in the modern terrestrial biosphere (Fig. 6.2). However, the fall in atmospheric CO_2 between the Devonian and Carboniferous (369–299 million years ago) equates to ~5000 Gt C reduction in carbon stored in the atmosphere (and a considerably greater reduction in the ocean inventory) (Fig. 6.1a). It is not easy to envisage how the terrestrial biosphere could possibly have accommodated this increase in carbon storage. The terrestrial biosphere is also not a 'safe' long-term store for carbon. For instance, the devastation wrought by the Indonesian wildfires of 1997 has been estimated to have resulted in the release of 0.8–2.6 Gt C (Page *et al.*, 2002). This is equivalent to 13–40% of the annual emissions from anthropogenic fossil fuel combustion, and could help explain why the growth rate of CO_2 in the atmosphere approximately doubled during the 1997–1998 period (Schimel and Baker, 2002).

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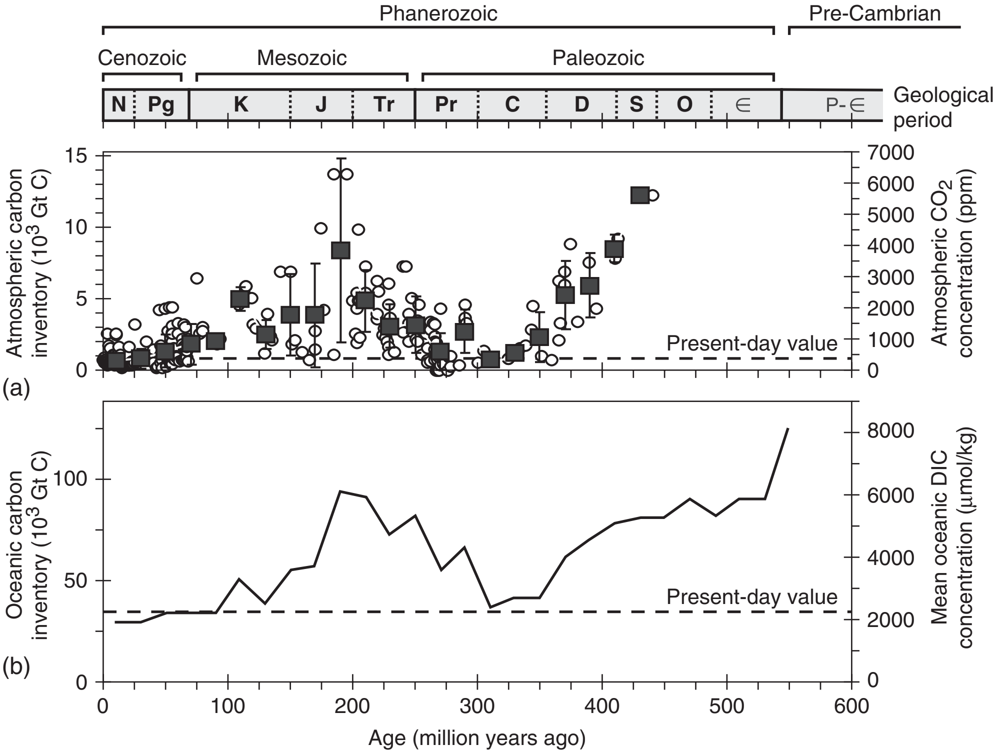
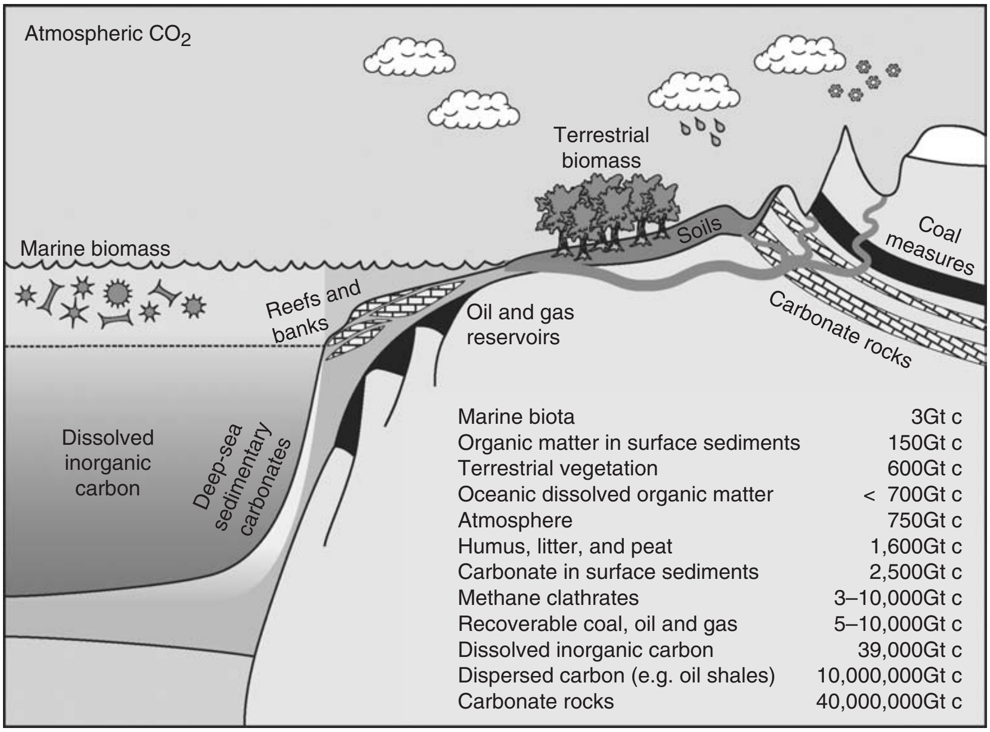


Fig. 6.1. Evolution of atmospheric and oceanic carbon reservoirs through time. (a) Phanerozoic evolution of atmospheric CO_2 reconstructed from proxy records (Royer *et al*., 2004). The filled squares show the data binned into intervals of 20 million years, with one standard deviation of the error shown as a vertical black line for each point. The raw proxy data is plotted as open circles. There are two vertical scales; atmospheric concentration (right) and the corresponding total carbon inventory (left). (b) Model-estimated evolution of the ocean carbon reservoir (Ridgwell, 2005). The vertical scales are mean dissolved inorganic carbon (DIC) concentration (right) and total ocean carbon inventory (left). The horizontal lines in both panels indicate the size of the present-day carbon inventories. The geological timescale abbreviations for the periods are: D, Devonian; C, Carboniferous; P, Permian; J, Jurassic. [AU1]

Clues as to the ultimate fate of CO_2 released to the atmosphere lie in the rocks around us. Fossil fuel deposits such as coal measures, oil and gas reservoirs, as well as oil shales and other organic matter rich sedimentary rocks, all hold substantial quantities of carbon (Fig. 6.2). The relationship of these reservoirs to atmospheric CO_2 is conceptually fairly straightforward – sequestration of organic matter in geological formations must result in less carbon in the atmosphere and ocean. Past increases in organic carbon burial driven by evolutionary and tectonic factors have been linked to decreases in atmospheric CO_2, particularly the CO_2 'trough' during the Carboniferous and Permian periods (Berner, 1990) (Fig. 6.1a). We are all too familiar with the converse link: the burning of deposits of ancient carbon and increasing CO_2 concentrations in the atmosphere. However, if the rate of burial of organic matter were to increase in the future, perhaps in response to climate change, there would presumably be an additional removal of fossil fuel CO_2 from the atmosphere. Is this likely to occur, and how important might this be? To answer this question we are going to have to look at how organic matter is deposited and preserved in accumulating sediments.

The formation of carbonate rocks such as limestones (the remains of ancient reefs) and



Marine biota	3Gt c
Organic matter in surface sediments	150Gt c
Terrestrial vegetation	600Gt c
Oceanic dissolved organic matter	< 700Gt c
Atmosphere	750Gt c
Humus, litter, and peat	1,600Gt c
Carbonate in surface sediments	2,500Gt c
Methane clathrates	3–10,000Gt c
Recoverable coal, oil and gas	5–10,000Gt c
Dissolved inorganic carbon	39,000Gt c
Dispersed carbon (e.g. oil shales)	10,000,000Gt c
Carbonate rocks	40,000,000Gt c

Fig. 6.2. Estimated inventories of the various carbon reservoirs on Earth. (Adapted from Kump *et al.*, 2004.) Units are in Gt C; 1 Gt C = 1 Pg (10^{15} g) of carbon or about 8.3°–10^{13} mol carbon. To put this into some perspective, the 750 Gt C in the atmosphere is equivalent to an average concentration of CO_2 of 351 ppm, and the average emission of anthropogenic CO_2 (from fossil fuels and cement production) during the 1990s was 6.3 Gt C/year. (From Houghton *et al.*, 2001.)

chalks (the microscopic shells of dead calcifying marine plankton) also represents a sink of carbon from the Earth's surface. This turns out to be an even more important reservoir of carbon than fossil fuels and other forms of ancient organic matter (Fig. 6.2). The relationship between carbonate deposition and atmospheric CO_2 is also less straightforward – when marine carbonates are precipitated from solution, the concentration of CO_2 in the atmosphere actually goes up. How the burial of carbonate can at the same time be a geologic sink for carbon needs some explanation. We also need to quantify how this sink might change in the future, and whether it will be important on the (century and shorter) timescales that matter to us most.

In this chapter we examine the role played by 'geologic' sinks for fossil fuel CO_2 emitted to the atmosphere. We tell the inorganic (carbonate) carbon and organic carbon sides of the story separately (in Sections 6.2 and 6.3, respectively), and look in detail at the underlying mechanisms involved. We also consider how human (anthropogenic) activities and climate change may perturb these processes in ways that will affect the rate at which fossil fuel CO_2 is removed from the atmosphere. Finally, we provide a summary and perspective in Section 6.4. Box 6.1 contains a basic '101' tutorial on carbonate chemistry and the key geochemical reactions involved in the geologic carbon sink (see Zeebe and Wolf-Gladrow, 2001 for a more detailed primer).

Box 6.1. Carbonate chemistry '101'.

The mineral calcium carbonate ($CaCO_3$) has a crystal lattice consisting of calcium ions (Ca^{2+}) ionically bound to carbonate ions (CO_3^{2-}). The lattice can take one of several different 'polymorphic' forms (i.e. the same chemical composition but different crystalline structure) such as *calcite*, or a higher symmetry *aragonite* phase. Calcite is the more abundant of the two polymorphs that are biologically precipitated in the open ocean. Because it is also more thermodynamically stable than aragonite it is the phase responsible for almost all carbonate burial in the deep sea. In contrast, aragonite is abundant amongst shallow water carbonates (e.g. corals). Biogenic carbonates are not always pure $CaCO_3$ and a range of substitutions of magnesium (Mg^{2+}) for Ca^{2+} are possible in the crystal structure to give natural carbonates a generic formula: $Mg_x \times Ca_{(1-x)} \times CO_3$. We will, however, focus on the more abundant $CaCO_3$ end member here.

Precipitation of calcium carbonate may be described by the following reaction:

$$Ca^2 + 2HCO_3^- \rightarrow CaCo_3 + Co_{2(aq)} + H_2O$$

Because Ca^{2+} has a 'residence' time in the ocean counted in millions of years, we can assume that the concentration of Ca^{2+} does not change on the (100–100,000 year) timescales we are interested in, and that ocean mixing homogenizes its concentration throughout the ocean. The *bicarbonate ion* (HCO_3^-) required in the precipitation reaction is formed through the hydration and dissolution of CO_2 gas ($CO_{2(g)}$) to form a proton (H^+) and a bicarbonate ion (HCO_3^-):

$$H_2O + CO_{2(aq)} \rightarrow H^+ + HCO_3^-$$

(The first, hydration step is the formation of *carbonic acid* (H_2CO_3), but this is only present in very small concentrations and is commonly ignored.) A fraction of the HCO_3^- dissociates to form a *carbonate ion* (CO_3^{2-}) and another proton:

$$HCO_3^- \rightarrow H^+ + CO_3^{2-}$$

The sum total of carbon in all its dissolved (inorganic) forms (i.e. $CO_{2(aq)} + HCO_3^- + CO_3^{2-}$) is collectively termed *dissolved inorganic carbon* (DIC). The relationship between these different forms of DIC, and to hydrogen ion (H^+) concentrations and to pH is shown in Fig. 6.3 [AU2]

When $CaCO_3$ is precipitated from solution, although the total sum of DIC is reduced, the remaining carbon is re-partitioned in favour of the $CO_{2(aq)}$ species. One way of thinking about this is in terms of removing CO_3^{2-} and shifting the aqueous carbonate equilibrium reaction:

$$CO_{2(aq)} + CO_3^{2-} + H_2O \rightarrow 2HCO_3^-$$

to the left to compensate. The counterintuitive consequence of this is that the precipitation of carbonate drives an *increase* in the *partial pressure* of CO_2 (pCO_2) in the surface ocean, despite there being a reduction in total carbon (DIC). (pCO_2 is the variable that determines the exchange of CO_2 between ocean and atmosphere – if atmospheric pCO_2, which is equal to the CO_2 molar ratio at a surface pressure of 1 atmosphere is greater than the pCO_2 of the surface ocean, there will be a net transfer of CO_2 from the atmosphere to the ocean, and vice versa.)

Whether $CaCO_3$ precipitates or dissolves is dictated by the stability of its crystal structure relative to the ambient environmental conditions. This can be directly related to the concentrations of Ca^{2+} and CO_3^{2-} and written in terms of the 'saturation state' (also known as the solubility ratio) Ω of the solution, defined as

$$\Omega = (Ca^{2+}) \times (CO_3^{2-}) / K_{sp}$$

where K_{sp} is a solubility constant. The precipitation of calcium carbonate from sea water is thermodynamically favourable when Ω is greater than unity. Conversely, $CaCO_3$ will tend to dissolve at $\Omega < 1.0$. In addition to the concentrations of Ca^{2+} and CO_3^{2-}, depth is also important because K_{sp} scales with increasing pressure (as well as with decreasing temperature). Thus, the greater the depth in the ocean, the more the ambient environment will tend to be undersaturated (i.e. $\Omega < 1.0$) and the less likely that carbonate will be present in the sediments.

continued

Box 6.1 *continued*

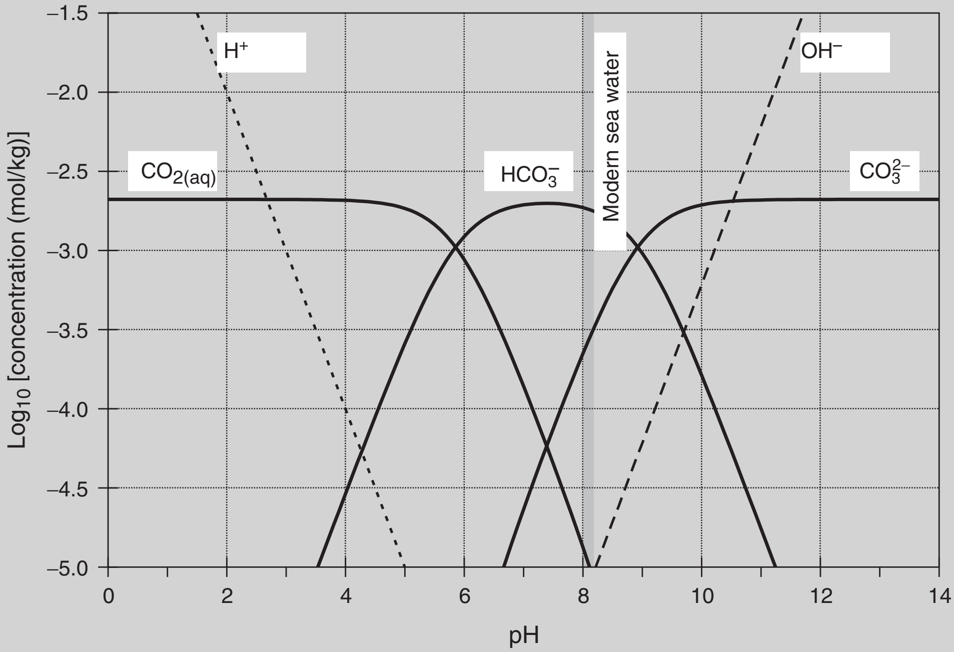
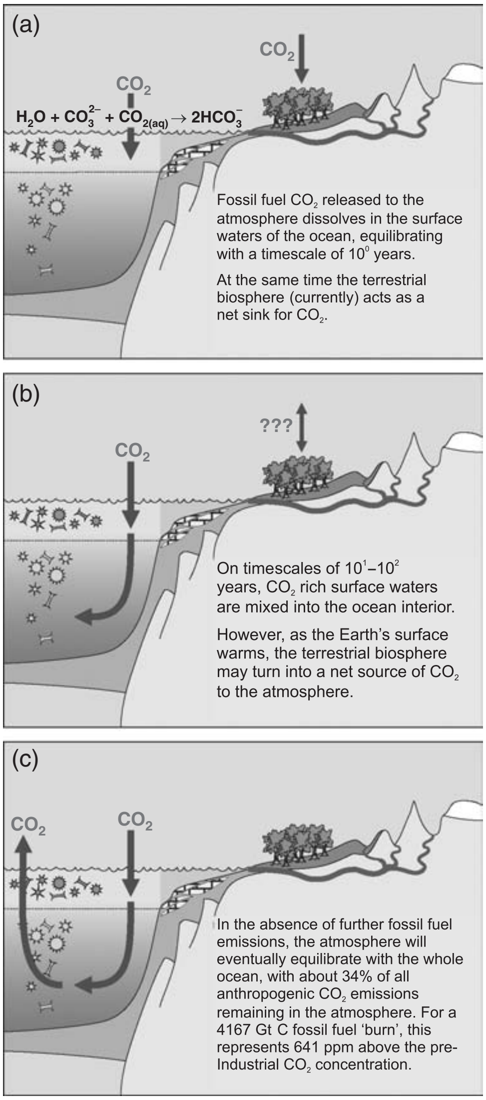


Fig. 6.3. The concentrations of the dissolved carbonate species as a function of pH (referred to as the Bjerrum plot; cf. Zeebe and Wolf-Gladrow, 1999): dissolved carbon dioxide ($CO_{2(aq)}$), bicarbonate (HCO_3^-), carbonate ion (CO_3^{2-}), hydrogen ion (H^+) and hydroxyl ion (OH^-). At modern sea water pH, most of the dissolved inorganic carbon is in the form of bicarbonate.

[AU3]

6.2 The Inorganic (Carbonate) Carbon Sedimentary Sink for Fossil Fuel CO_2

To see where carbonate rocks come into the greenhouse sink picture, we recap on the sequence of different fates that befall CO_2 released to the atmosphere through anthropogenic activities such as the burning of fossil fuels and cement production (Fig. 6.4). Some of the added CO_2 may be relatively quickly removed from the atmosphere and taken up by the terrestrial biosphere as a result of 'CO_2 fertilization' of plant productivity (although nutrient limitation may limit the importance of this effect; see Hymus and Valentini, Chapter 2, this volume) as well as forest regrowth and changes in land use practice. Current estimates suggest that 100–180 Gt C may already have been removed in this way, equivalent to 28–50% of total emissions from fossil fuels and cement production (Sabine *et al.*, 2004). The timescale for this CO_2 sink to operate is years to decades (for the aboveground vegetation response) to centuries (for the soil carbon inventory to adjust). At the same time, CO_2 dissolves in the surface ocean. If the ocean did not circulate or mix and if dissolved CO_2 remained as $CO_{2(aq)}$ (see Box 6.1), the ocean surface would quickly come into equilibrium with the atmosphere without having absorbed much anthropogenic CO_2. Fortunately, neither ocean dynamics nor CO_2 chemistry is simple, making the ocean a powerful carbon sink (Sabine and Feely, Chapter 3, this volume). However, once fossil fuel emissions to the atmosphere have ceased, sequestration by this means, termed 'ocean invasion', cannot continue indefinitely. Firstly, the ocean becomes less efficient at storing additional dissolved carbon at higher atmospheric CO_2 concentrations. Secondly, once CO_2-enriched surface waters have been mixed down to depth and throughout the ocean, outgassing of previously absorbed CO_2 will then tend to balance the rate of uptake from the atmosphere. Once this happens, the removal of anthropogenic CO_2 by the ocean will cease and the ocean and atmosphere can then be in 'equilibrium'.



Fossil fuel CO_2 released to the atmosphere dissolves in the surface waters of the ocean, equilibrating with a timescale of 10^0 years.

At the same time the terrestrial biosphere (currently) acts as a net sink for CO_2.

On timescales of 10^1–10^2 years, CO_2 rich surface waters are mixed into the ocean interior.

However, as the Earth's surface warms, the terrestrial biosphere may turn into a net source of CO_2 to the atmosphere.

In the absence of further fossil fuel emissions, the atmosphere will eventually equilibrate with the whole ocean, with about 34% of all anthropogenic CO_2 emissions remaining in the atmosphere. For a 4167 Gt C fossil fuel 'burn', this represents 641 ppm above the pre-Industrial CO_2 concentration.

Fig. 6.4. Mechanisms of carbon sequestration (I). Panels (a) through (c) illustrate the pathways of carbon uptake operating on timescales of years (10^1) to centuries (10^2) – ocean invasion and 'CO_2 fertilization' of the terrestrial biosphere.

We use a computer model of ocean–atmosphere carbon cycling (see Box 6.2 for details) to illustrate the importance of ocean invasion and the processes discussed in Chapter 3. This will give us something of a benchmark with which to compare the relative importance of the geologic sinks. The predicted evolution of atmospheric CO_2 in response to a future CO_2 emissions trajectory (Fig. 6.5a) and the operation of the ocean invasion sink is shown in Fig. 6.5b. For a total release (burn) of 4167 Gt C (Fig. 6.5a) and with global climate held in the modern state (i.e. global temperatures are not allowed to respond to rising CO_2), the final atmospheric CO_2 concentration reached is 919 ppm. This is equivalent to 2007 Gt C; ~1400 Gt C more than the amount prior to the Industrial Revolution (in *c*.1765). Thus, the ocean has taken up a little over 66% of the total release, storing it mainly in the form of bicarbonate ions (HCO_3^-) (the dotted line in Fig. 6.5c), with [AU4] the remainder in the atmosphere. We have not taken into account any net uptake (or release) by the terrestrial biosphere in this calculation.

One caveat to this assessment is that the fraction of fossil fuel CO_2 that is sequestered by ocean invasion actually declines with increasing total burn. In other words, if we had chosen a smaller quantity of carbon than 4167 Gt C, the proportion taken up by ocean invasion would be greater than 66%. Ocean invasion was found to account for 80.7% when the fossil fuel release was just 874 Gt C, but 69.7% when the fossil fuel release was 4550 Gt C in an ocean carbon cycle general circulation model (GCM) (Archer *et al.*, 1997, 1998). The results of the high-end CO_2 release of Archer *et al.* (1998) are thus comparable to what we obtain here, with the ~3% difference reflecting variations in the representation of ocean circulation and marine carbon cycling between the two models. A second caveat is that no change in ocean circulation, marine biological productivity or surface temperatures has yet been taken into account.

Because CO_2 solubility decreases at higher temperatures (Zeebe and Wolf-Gladrow, 2001), warming of the surface ocean due to a

Box 6.2. The ‘genie’ carbon cycle model.

The details of the computer model used to illustrate the different pathways and mechanisms for CO_2 sequestration are not central to the discussions in this chapter: ‘To retain respect for either models of sausages, one must not watch too carefully what goes into either of them’ (Ridgwell, 2001, adapted from a remark attributed to Otto Von Bismarck, 1st Chancellor of the German Empire, 1871–1890). However, we include a brief overview of the model for completeness.

To quantify the uptake of atmospheric CO_2 by the ocean we use the GENIE-1 (Ridgwell *et al*., submitted) coupled carbon-climate model, developed as part of the ‘genie’ Earth system modelling initiative (www.genie.ac.uk). The climate model component is fully described in Edwards and Marsh (2005, and references therein). In a nutshell, it is a coarse (i.e. low) resolution of a ‘frictional geostrophic’ general circulation model (Edwards and Shepherd, 2002) coupled to a 2D energy/moisture balance model atmospheric component (Weaver *et al*., 2001) including a simple thermodynamic and dynamic representation of sea ice. An ‘ensemble Kalman filter’ has been used to calibrate this model and thereby achieve a reasonable simulation of the modern climate (Hargreaves *et al*., 2004).

The (ocean) biogeochemical component of the GENIE-1 model calculates the (mainly vertical) redistribution of tracer concentrations occurring rapidly relative to transport by the large-scale circulation of the ocean. This happens through the removal from solution of nutrients (PO_4) together with dissolved inorganic carbon (DIC) and alkalinity (ALK) in the sunlit surface ocean layer (euphotic zone) by biological activity. The resulting export of particulate matter to the ocean interior is subject to remineralization processes, releasing dissolved constituent species back to the ocean (but at greater depth). Further redistribution of tracers occurs through gas exchange with the atmosphere as well as due to the creation and destruction of dissolved organic matter. An ensemble Kalman filter is also used to calibrate the biogeochemical model (and reproduce the observed 3D distributions of phosphate and alkalinity in the ocean) (Ridgwell *et al*., submitted).

To quantify the importance of carbonate burial and the role of the ‘geologic’ carbon sink, the GENIE-1 model is further extended by including a representation of the geochemical interaction between the ocean and deep-sea sediments (Ridgwell, 2001). This extension calculates the fraction (if any) of $CaCO_3$ reaching the ocean floor that is preserved and buried in the sediments, and described in full in Ridgwell and Hargreaves (in preparation). It also calculates the amount (and rate) of carbonate previously buried in the sediments that can be dissolved to neutralize fossil fuel CO_2.

The GENIE-1 model is uniquely suited for the analysis of the long-term fate of fossil fuel CO_2 because it can simulate over 1000 years in less than 1 h of CPU time, and achieves this speed on a ‘normal’ Linux-based PC. (Some much higher-resolution and more detailed climate models would literally take a year of supercomputer time to do this.) Another important feature is that climate can interact with the carbon cycle (i.e. climate is responsive to changes in atmospheric CO_2), allowing the importance of ‘feedbacks’ to be quantified (e.g. Ridgwell *et al*., in preparation). For instance, if the positive feedback between increasing atmospheric CO_2 and sea surface temperature warming is not taken into account, the amount of CO_2 taken up from the atmosphere by the ocean could be overpredicted by ~10% (see Fig. 6.5).

CO_2 is added to the atmosphere in the model to simulate anthropogenic CO_2 emissions. We chose a hypothetical time-history of fossil fuel consumption (and combustion) of 4167 Gt C (Fig. 6.5a), similar to the ‘4kfast’ scenario of Lenton (2000). This follows IS92a ‘business as usual’ to 2100, followed by a linear decline in emissions to use up all ‘conventional’ fossil fuel reserves (coal, oil, gas) of ~4000 Gt C. The total amount of carbon released to the atmosphere is 4167 Gt C, with 3784 Gt C released from year 2000 onwards. This scenario falls midway between the ‘A22’ (3028 Gt C) and ‘A23’ (4550 Gt C) scenarios analysed by Archer *et al*. (1998), and is slightly less than the 5270 Gt C scenario employed by Caldeira and Wickett (2003). If ‘exotic’ fossil fuels, including methane clathrates, are exploited, total fossil fuel release could be as much as 15,000 Gt C (Hasselmann *et al*., 2003). Fossil fuel CO_2 emissions to the atmosphere up to year 2000 are estimated from the increase in ocean + atmosphere carbon inventory in the experiment when atmospheric CO_2 was forced to conform to the observed CO_2 concentration trajectory – Enting *et al*. (1990) up until 1994, and Keeling and Whorf (2005) thereafter. [AU5]

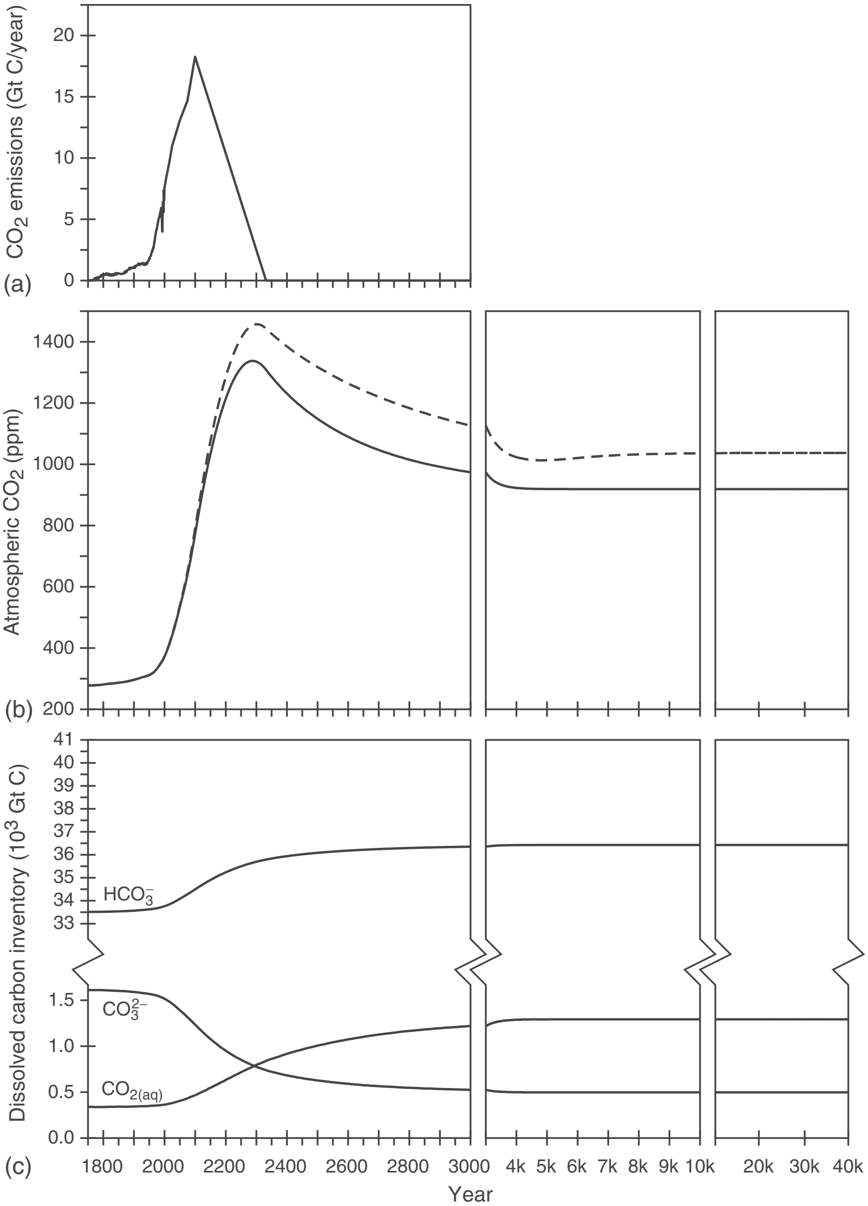


Fig. 6.5. Model analysis of the uptake of fossil fuel CO_2 by the ocean. (a) Time-history of the rate of CO_2 emissions to the atmosphere prescribed in the model (see Box 6.2). From 1765 to 2000, the emissions trajectory is deduced to be consistent with the observed trajectory of atmospheric CO_2 (Enting *et al.*, 1994; [AU5] Keeling and Whorf, 2005). Note that these calculated anthropogenic emissions are *net* of any uptake by the terrestrial biosphere (i.e. if the terrestrial 40 biosphere acts as a carbon sink over this interval, the CO_2 emissions will be underestimated). (b) Model-predicted trajectory of atmospheric CO_2 (assuming no change in the terrrestrial biosphere). The solid line shows predicted atmosphere CO_2 with climate (and ocean surface temperatures) held constant. The dotted line shows the impact of allowing the carbon cycle and climate to interact and produce 'feedback' between CO_2 and surface temperatures. (c) Predicted evolution of the different components of the ocean DIC reservoir: $CO_{2(aq)}$, HCO_3^- and CO_3^{2-}. Note the different *y*-axis scales used for $CO_{2(aq)}$ and CO_3^{2-} (bottom of panel c) and HCO_3^- (top of panel c).

stronger greenhouse effect will also render ocean invasion a less effective sink (Plattner *et al.*, 2001; see Chapter 3). This effect creates a 'feedback loop' (see Berner, 1999); Ridgwell, 2003); higher temperatures result in more CO_2 left in the atmosphere, which drives a stronger greenhouse effect causing yet higher temperatures, and so on. In this case the feedback has a 'positive' sign, and acts to amplify the impact of an initial perturbation (in our example, the release of fossil fuel CO_2). If we now take into account feedback between CO_2 and climate in the model, the final (steady-state) fraction of total emissions taken up by the ocean declines to 60%, with a residual 1037 ppm remaining in the atmosphere (Fig. 6.5b). The 2005 weakening of the ocean invasion sink due to feedback between CO_2 and climate in the GENIE-1 model used here (Box 6.2) is ~13%, compared with ~24% found by Plattner *et al.* (2001), most likely reflecting differences in the ocean circulation response to surface warming (and freshening).

With no other carbon sinks operating, our long-term future is thus looking decidedly on the warm side; the mean global ocean surface temperature is 23.1°C, ~4.5°C warmer than the pre-Industrial state of the model (18.6°C). To put this into some perspective, the 2005 value is 19.2°C in the model; just 0.6°C above the pre-Industrial estimate. This situation would persist indefinitely. There are important implications of the residual atmospheric fossil fuel fraction and degree of long-term greenhouse warming for stability of Greenland and Antarctic ice caps and of methane hydrates present in continental margin sediments (Archer and Buffett, 2004), as well as for the timing of the onset of the next ice age (Archer and Ganopolski, 2005).

6.2.1 Geologic carbon sinks: reaction with sedimentary carbonates

Where does the 'geologic' part come into the picture? In shallow water environments, carbonates are precipitated by corals and benthic shelly animals, with a smaller 'abiotic' contribution occurring as fill-in cements and coatings on mineral grains and biogenic matter. Approximately 0.3 Gt C equivalent of calcium carbonate ($CaCO_3$) is produced annually in these environments (Milliman and Droxler, 1996). Carbonate is also precipitated biologically in the open ocean (i.e. away from the continental shelf) by plankton such as coccolithophores and foraminifera, as well as by pteropods. Thus, ~0.8 Gt C/year of $CaCO_3$ is thought to be produced here (Milliman and Droxler, 1996; Feely *et al.*, 2004). What happens to this carbonate?

The shallow waters of the ocean margins are everywhere oversaturated with respect to the solid $CaCO_3$ phase (i.e. the saturation state, $\Omega > 1.0$; see Box 6.1). The dissolution loss of carbonate is therefore relatively small; of the ~0.3 Gt C/year produced, about 0.17 Gt C/year is thought to be buried virtually *in situ* while another 0.04 Gt C/year is exported to the adjoining continental slopes (Milliman, 1993; Milliman and Droxler, 1996). The total neritic accumulation of $CaCO_3$ today is therefore ~0.2 Gt C/year, and more than thousands of years of build-up of this material has given rise to large-scale topographical features such as barrier reefs and carbonate banks and platforms. The shallow-water accumulation rate encapsulated in these estimates is probably significantly higher than the long-term (glacial–interglacial, or >100,000 years) average because reef growth rates are still adjusting to the rise in sea level that accompanied the termination of the last glacial period (e.g. Ryan *et al.*, 2001; Vecsei and Berger, 2004).

The situation is quite different in the open ocean because oceanic waters become increasingly less saturated at greater depth (and more pressure). When the ambient environment becomes undersaturated ($\Omega < 1.0$) carbonates will start to dissolve. This occurs at ~4500 m in the Atlantic Ocean and ~3000 m in the Pacific Ocean. At more than 1000 m deeper than this, sediments are typically completely devoid of any carbonate particles. Topographic 'highs' on the ocean floor such as the mid-Atlantic ridge (where the ocean floor is 'only' ~3000 m deep and $\Omega > 1.0$) can thus be picked out by sediments rich in $CaCO_3$ while the adjacent deep basins ($\Omega < 1.0$) are low in $CaCO_3$ content (Fig. 6.6); an effect likened to 'snow-capped mountains'. The situation is actually much

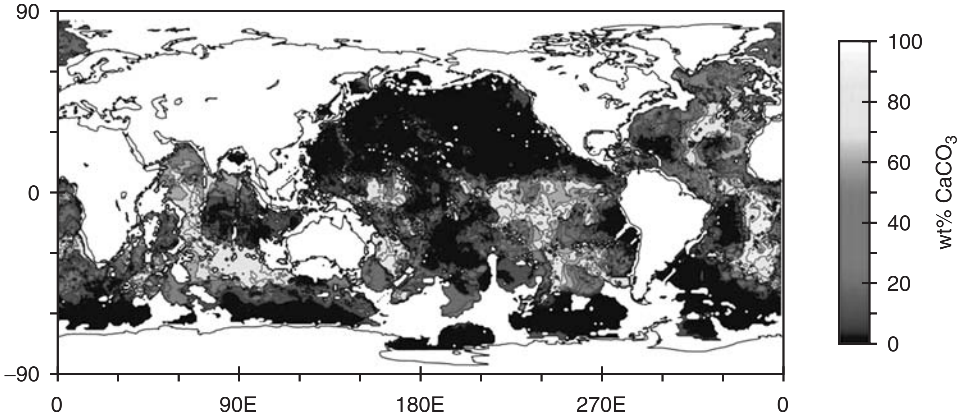


Fig. 6.6. Observed distribution of the calcium carbonate content (as percentage dry weight (wt%) in each sample) of the surface sediments of the deep sea. (From Archer, 1996a.) Areas with no data coverage (parts of the Southern Ocean, and many of the continental margins) are left blank.

more complicated than this and other factors are required to completely explain the whole observed pattern of sediment composition, such as the breakdown of organic matter in surface sediments and the release of metabolic CO_2 into the sediment pore - waters (see Archer, 1996b; and Ridgwell and Zeebe, 2005). At a global scale, only ~10–15% (equal to 0.1 Gt C/year) of carbonate produced at the surface ever escapes dissolution to be buried in accumulating deep-sea sediments (Milliman and Droxler, 1996; Archer, 1996b; Feely *et al.*, 2004).

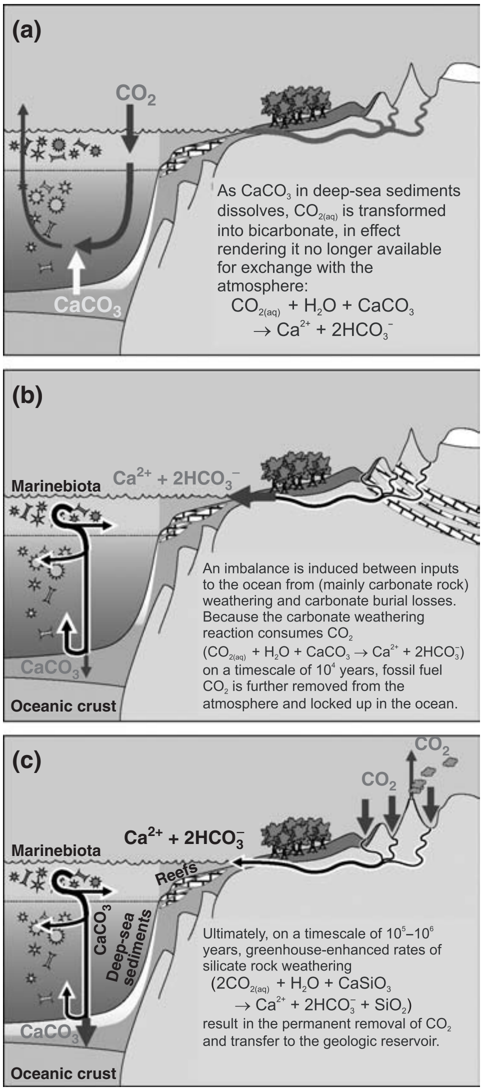
Although $CaCO_3$ burial in shallow waters currently appears to be greater than in deep-water sediments, we will focus on the latter carbon sink. We justify this simplification because carbonate preservation and burial in the deep sea is much more important in regulating atmospheric CO_2 (Archer, 2003). Although it is beyond the scope of this chapter, note that sea-level and evolutionary changes occurring during the Phanerozoic period have altered the balance between shallow- and deep-water $CaCO_3$ burial. This must have had a profound impact on the regulation of ocean chemistry and climate (Ridgwell *et al.*, 2003; Ridgwell, 2005).

Carbonate burial (in the deep ocean) represents a 'geologic' sink of carbon. How does this relate to the long-term fate of fossil fuel CO_2? The first mechanism we will discuss is illustrated in Fig. 6.7a. Dissolution of CO_2 in surface waters results in a decrease in ambient carbonate ion (CO_3^{2-}) concentration (see Figs 6.4c, 6.7c). Think about shifting the aqueous carbonate equilibrium reaction $CO_{2(aq)} + CO_3^{2-} + H_2O \leftrightarrow 2HCO_3^-$ to the right to (partly) compensate for the addition of CO_2. Because a reduction in CO_3^{2-} reduces the stability of carbonates (see Box 6.1), the invasion of fossil fuel CO_2-enriched waters into the deep ocean will drive an increase in the rate of dissolution of $CaCO_3$ in the sediments (Sundquist, 1990; Archer *et al.*, 1997, 1998). If this rate of dissolution overtakes the rate of supply of new biogenic carbonate from above, previously deposited carbonate will start to dissolve (erode) (Fig. 6.8a).

Each mole of $CaCO_3$ that dissolves removes one mole of $CO_{2(aq)}$ to form two moles of bicarbonate:

$$CaCO_3 + CO_{2(aq)} + \mathrm{H2O} \rightarrow Ca^{2+} + 2HCO_3^-$$

(the difference between dotted and dashed HCO_3^- inventory trajectories in Fig. 6.8c). Thus, water masses that have passed over carbonate-rich sediments become, in a sense, 'recharged', and are able to absorb more CO_2 from the atmosphere (Fig. 6.7a). One can think of this as anthropogenic CO_2 being 'neutralized' by the reaction with sedimentary $CaCO_3$. We will refer to this carbon



As $CaCO_3$ in deep-sea sediments dissolves, $CO_{2(aq)}$ is transformed into bicarbonate, in effect rendering it no longer available for exchange with the atmosphere:

$$CO_{2(aq)} + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$

An imbalance is induced between inputs to the ocean from (mainly carbonate rock) weathering and carbonate burial losses. Because the carbonate weathering reaction consumes CO_2 ($CO_{2(aq)} + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$) on a timescale of 10^4 years, fossil fuel CO_2 is further removed from the atmosphere and locked up in the ocean.

Ultimately, on a timescale of 10^5–10^6 years, greenhouse-enhanced rates of silicate rock weathering ($2CO_{2(aq)} + H_2O + CaSiO_3 \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$) result in the permanent removal of CO_2 and transfer to the geologic reservoir.

Fig. 6.7. Mechanisms of carbon sequestration (II). Panels (a) through (c) illustrate the pathways of carbon uptake occurring on timescales of millennia (103 years) and beyond – the 'geologic' carbon sinks. (a) Operation of the sea-floor $CaCO_3$ neutralization; (b) operation of terrestrial $CaCO_3$ neutralization; and (c) operation of the silicate weathering carbon sink.

sequestration process as the 'sea-floor $CaCO_3$ neutralization' sink. It should be carefully considered that although the dissolution of sedimentary $CaCO_3$ results in an *increase* in the *total* amount of carbon dissolved in the ocean, the proportion of dissolved inorganic carbon (DIC) that is in the form of $CO_{2(aq)}$ actually decreases (compare dotted and dashed lines in Fig. 6.8c) as a result of reaction with $CaCO_3$. It is the associated reduction in ambient pCO_2 that allows further transfer of CO_2 from the atmosphere to the ocean.

Clearly we need to quantify how much $CaCO_3$ will dissolve from the sediments and what effect it will have on the removal of CO_2 from the atmosphere. We therefore use an extended carbon cycle model that includes the relevant interaction with carbonates in deep-sea sediments (Box 6.2). The evolution of atmospheric CO_2 is shown in Fig. 6.8b. Now, CO_2 is declining slightly faster at year 3000 compared with when the ocean invasion sink is operating alone. It is important to recognize, however, that the peak atmospheric CO_2 value reached (and thus the maximum extent of 'global warming') is virtually unaffected by the inclusion of the buffering of ocean chemistry by carbonate-rich sediments. The effect of sediment dissolution is rather more pronounced over the following few thousand years, and atmospheric CO_2 reaches a new, lower steady state of 715 ppm not long after year 10,000. Thus, neutralization with sea-floor carbonates eventually results in the additional removal of 444 Gt C from the atmosphere, or about 11% of the initial fossil fuel burn that we assumed. Again, the relative importance and fraction of CO_2 sequestered by this mechanism depends on the magnitude of the fossil fuel burn – sea-floor carbonate neutralization has been estimated to account for 9.0% of an 874 Gt C fossil fuel release, rising to 14.8% for a 4550 Gt C release (Archer *et al.*, 1998). Thus, the buffering response in the GENIE-1 model is slightly less than in a previous model study.

6.2.2 Geologic carbon sinks: the weathering of carbonate rocks on land

CO_2 in the atmosphere dissolves in rainwater to form a weak carbonic acid solution, which dissolves carbonate minerals in rocks exposed at the land surface and mineral grains in soils:

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$

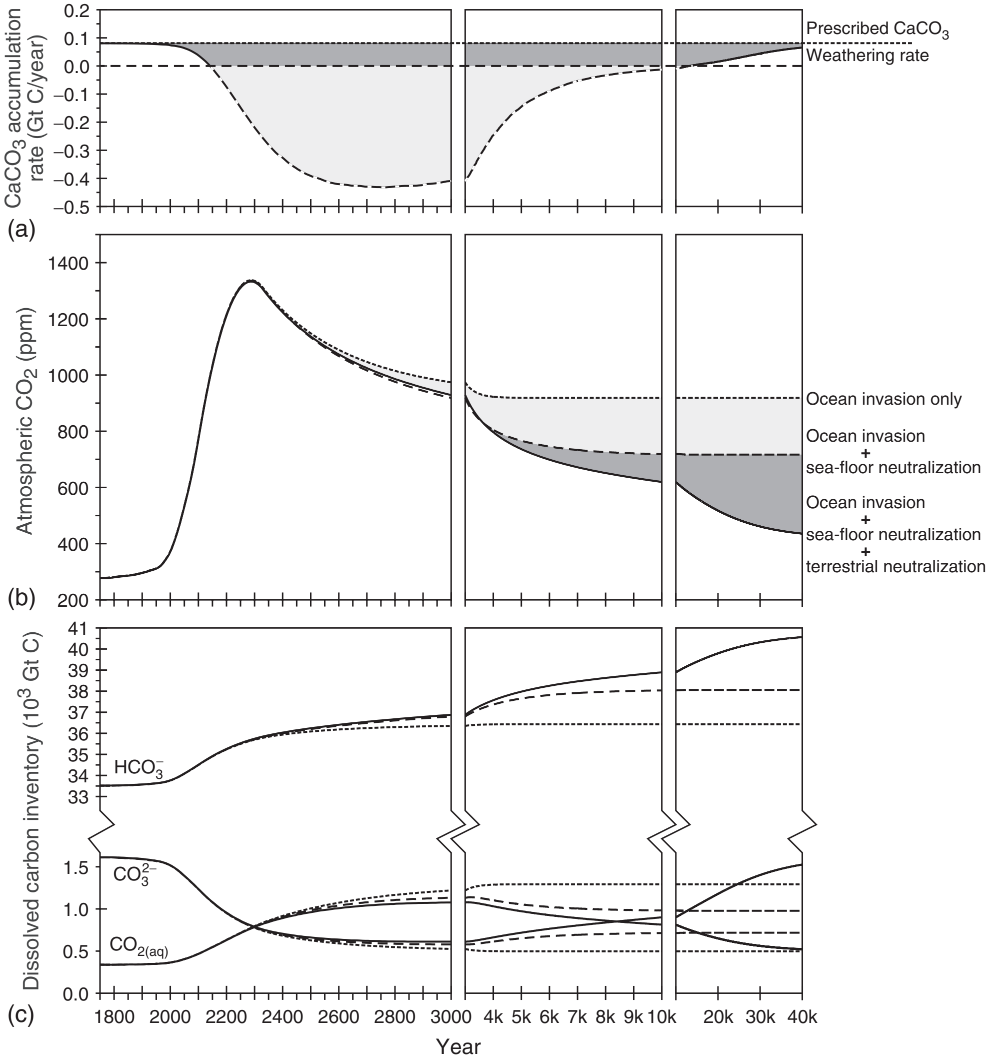


Fig. 6.8. Model analysis of the role of 'geologic' carbon sinks in the sequestration of fossil fuel CO_2. (a) Model-predicted global accumulation rate of $CaCO_3$ in deep-sea sediments. The lighter shaded area under the curve (negative $CaCO_3$ accumulation rate) represents the net erosion of carbonates previously deposited in deep-sea sediments – sea-floor $CaCO_3$ neutralization. The darker shaded region represents periods characterized by a positive accumulation rate of $CaCO_3$, but at a rate lower than the supply by carbonate weathering on land – terrestrial neutralization. (b) Trajectory of atmospheric CO_2. The dotted line represents anthropogenic uptake by the ocean only (same as the curve shown in Fig. 6.5 solid line). The dashed line shows the effect of seafloor neutralization (Fig. 6.7a) in addition to the ocean invasion carbon sink. The lighter shaded region thus indicates the reduction of atmospheric CO_2 due to sea-floor neutralization alone. The solid line shows the effect of terrestrial neutralization (Fig. 6.7b) in addition to ocean invasion and sea-floor neutralization. The darker shaded region thus indicates the reduction of atmospheric CO_2 due to terrestrial neutralization alone. Note that weathering rates are held constant for this experiment, meaning that the ultimate CO_2 sequestration mechanism of silicate weathering (Fig. 6.7c) is not 'switched on'. (c) Evolution of the different components of the ocean dissolved inorganic component (DIC) reservoir: $CO_{2(aq)}$, HCO_3^- and CO_3^{2-}.

[AU6]

The solutes that result from this reaction are carried by rivers to the ocean. All the while that anthropogenic acidification of the ocean is causing carbonate accumulation in the deep ocean to be reduced and then reversed (Fig. 6.8a), the input of solutes derived from carbonate weathering on land continues. The accumulation rate of new marine carbonates is thus slower than the terrestrial weathering rate. The consequence of this is a net removal of CO_2 from the atmosphere and transformation into HCO_3^- (Fig. 6.8b). At the same time, the carbonate ion concentration in the ocean increases (the solid $CO_3{}^-$ inventory line in Fig. 6.8c), raising the saturation state of the ocean (higher Ω) and increasing carbonate preservation in deep-sea sediments. Eventually, the preservation and burial of $CaCO_3$ in deep-sea sediments will once again balance the weathering input (Fig. 6.8a) and this second 'geologic' sequestration process comes to an end. We will refer to this process as the 'terrestrial $CaCO_3$ neutralization' sink.

How much CO_2 can be sequestered by reaction with terrestrial carbonates? The evolution of atmospheric CO_2 with this additional process enabled is shown in Fig. 6.8b. Now, even at year 40,000, steady state has not quite been attained and CO_2 is still continuing to fall slightly. (A model run of 120,000 years' duration (not shown) reveals that atmospheric CO_2 would fall by only another 18 ppm.) At year 40,000, the concentration of CO_2 in the atmosphere is 435 ppm, which equates to an atmospheric inventory of 951 Gt C. Thus, terrestrial $CaCO_3$ neutralization has removed 15% of the original 4167 Gt C burn (in addition to the initial ocean invasion and erosion of $CaCO_3$ in deep-sea sediments). Just 344 Gt C (8%) of anthropogenic CO_2 is then left in the atmosphere – a finding that is consistent with previous estimates (with a range of 7.4–7.9%, depending on the magnitude of the assumed fossil fuel burn (Archer *et al.*, 1998)).

6.2.3 Geologic carbon sinks: the weathering of silicate rocks on land

Some tens of thousands of years after the burning of fossil fuels has ceased, ~8% of fossil fuel CO_2 emissions (assumed to be 4167 Gt C here) will remain in the atmosphere. The atmospheric CO_2 concentration is 435 ppm, compared with 376 ppm in 2003 (Keeling and Whorf, 2005) and a pre-Industrial value of 278 ppm (Enting *et al.*, 1994). This would probably give half as much climate change as has already occurred till date. Is this the 'end of the road', or does the geologic carbon sink have any further cards to play?

Estimates of the evolution of the amount of carbon in the ocean and atmosphere through Earth history have both reservoirs generally paralleling each other over very long periods of time (>1 million years); i.e. CO_2 and DIC tend to increase and decrease together (Fig. 6.1). In contrast, our model has so far predicted that when atmospheric CO_2 declines, the ocean inventory increases (Fig. 6.8b and c); an antiphased relationship. It would not be unreasonable to conclude from this that we are missing (at least) one important mechanism. We now come to the final geologic (carbonate) carbon sink and one of the most fundamental regulatory mechanisms of the Earth system – the weathering of silicate rocks.

The reaction involved in the weathering of calcium silicate minerals (particularly the feldspar family, which are the most abundant group of minerals in continental rocks) can be written as:

$$2CO_2 + 3H_2O + CaAl_2Si_2O8 \rightarrow Ca^{2+} + 2HCO^-{}_3 + A1_2Si_2O_5(OH)_4$$

This differs from the weathering of carbonate rocks (in contrast to the weathering reaction listed in Section 6.2.2) in one fundamental regard; it takes two moles of CO_2 to weather each mole of $CaAl_2Si_2O_8$ and release a single mole of calcium ions (plus 2 of bicarbonate ions). The calcium ion is subsequently removed from solution in the same precipitation reaction as before, meaning that only one mole of CO_2 is released back to the ocean (and atmosphere). The weathering of silicate rocks is thus a net sink for atmospheric CO_2 (Berner, 1992) (Fig. 6.7c) – i.e. one mole of CO_2 is being sequestered for each mole of calcium silicate mineral weathered. In the long term, the rate of silicate weathering should balance the rate of volcanic release of CO_2 to the atmosphere (Berner and Caldeira, 1997). If this mechanism is then already busy removing volcanic CO_2 emissions, how can it help in removing the final fraction of anthropogenic CO_2 from the atmosphere?

The rate at which the weathering reaction proceeds depends on a variety of variables. The ones that interest us here are ambient temperature and CO_2 concentration (which is enhanced in soils through the metabolic activity of plants, animals and microbes) (Berner, 1990, 1992). Now we can see how the ultimate fate of fossil fuel CO_2 and the final 'geologic' (carbonate) carbon sink arises – a faster rate of weathering of silicate rocks under a fossil fuel–elevated CO_2 atmosphere (and a warmer, wetter climate), which acts to remove the excess carbon from the atmosphere and sequesters it in marine carbonates. In fact, silicate weathering could remove not only the remaining ~8% fraction of fossil fuel CO_2 left in the atmosphere, but also the fossil fuel CO_2 stored (as bicarbonate ions – see Fig. 6.8c). No trace of our meddling with the environment would remain, except for a slightly more weathered continental surface than before and a fresh thick layer of carbonates covering the ocean floor. Unfortunately, the planetary cleaners will not finish their work any time soon – the timescale for this process is counted in hundreds of thousands of years (Berner and Caldeira, 1997).

6.2.4 Other considerations in the geologic (carbonate) carbon sink

The reduction in pH and carbonate ion (CO_3^{2-}) concentration in the ocean caused by anthropogenic CO_2 emissions has another important consequence, in addition to the dissolution of carbonates deposited on the sea floor (Section 6.2.2). This arises because even if surface waters do not quite become undersaturated ($\Omega < 1.0$), the marine organisms that produce carbonate shells and skeletons will be affected (Royal Society, 2005). If $CaCO_3$ precipitation becomes less thermodynamically favourable, the metabolic (energy) cost of making shells and skeletons will rise. The result is that organisms will precipitate less carbonate and/or will be disadvantaged in the ecosystem. The implications of this for coral reef ecosystems and associated biodiversity and economic impacts are already being widely recognized (Kleypas *et al.*, 2001; Hughes *et al.*, 2003). There is also increasing evidence that calcifying plankton could also be affected by higher atmospheric CO_2 (Bijma *et al.*, 1999; Riebesell *et al.*, 2000; Zondervan *et al.*, 2001; Delille *et al.*, 2005) as well as by pteropods, which make aragonite shells (Orr *et al.*, 2005). To understand the implications of this effect for geologic carbon sequestration one must first recognize that the precipitation of $CaCO_3$ by calcifying plankton in the surface ocean and its subsequent removal through gravitational settling raises the partial pressure of CO_2 (pCO_2) at the surface (see Box 6.1). This acts to reduce the rate of fossil fuel CO_2 uptake from the atmosphere. Thus, if carbonate production were to decrease, surface ocean pCO_2 would fall and the rate of CO_2 invasion into the ocean would increase (Zondervan *et al.*, 2001; Barker *et al.*, 2003; Zeebe and Westbroek, 2003). Secondly, a reduction in the flux of $CaCO_3$ to deep-sea sediments brings forward the year in which the net accumulation of carbonate first becomes negative and 'erosion' starts to occur. This means that neutralization by sea-floor carbonates would have an earlier and potentially more extensive impact compared to the case where $CaCO_3$ production does not change.

These effects are illustrated with the help of the model. Carbonate production in the open ocean is now allowed to decrease in response to anthropogenic acidification and reduced surface carbonate ion concentrations. The result is that atmospheric CO_2 is 82 ppm lower in year 3000 compared to the control run (solid line = no calcification change in Fig. 6.9), and 36 ppm lower in year 10,000. Interestingly, the final (steady-state) CO_2 concentration is virtually identical (Ridgwell and Hargreaves, in preparation). The important point is that the maximum CO_2 value attained, and thus the maximum

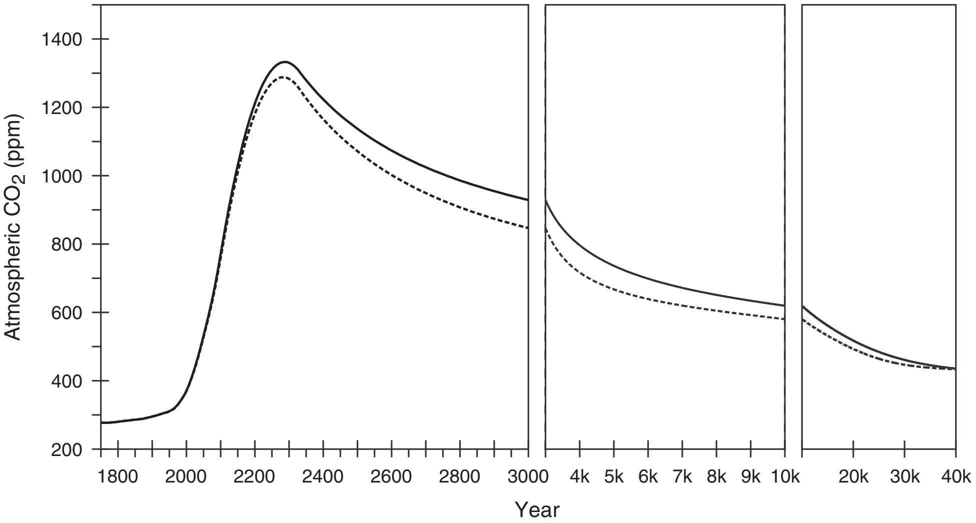


Fig. 6.9. Model analysis of the impact of a reduction in marine calcification (Ridgwell and Hargreaves, in preparation) on the 'geologic' carbon sink and sequestration of fossil fuel CO_2. The CO_2 trajectory resulting from a combination of ocean invasion, sea-floor neutralization and terrestrial neutralization is shown as a solid line (i.e. the same as the solid line in Fig. 6.8b). The dashed line shows the impact of a reduction in calcification rates in the open ocean.

degree of greenhouse warming, is lower in the presence of CO_2-calcification feedback (Ridgwell *et al.*, in preparation). Changes in the production and burial of carbonates in shallow waters (not represented in the model) are likely to drive an additional reduction in the CO_2 maximum. However, we have not taken into account in this analysis any impact of reduced carbonate production on the transport of organic matter into the deep ocean – the 'ballast hypothesis' (Armstrong *et al.*, 2002; Klaas and Archer, 2002). If this hypothesis is correct, the amount of CO_2 sequestered due to the CO_2-calcification feedback will be less than we have predicted (Barker *et al.*, 2003; Ridgwell, 2003; Heinze, 2004). There are also significant uncertainties as to just how sensitive biogenic calcification is to a reduction in CO_3^{2-} (and saturation state), particularly at the ecosystem (and global) level (Ridgwell *et al.*, in preparation).

6.2.5 Even the geologic sink is not 'for ever'

On the longest timescales we actually come full circle – carbonates deposited in marine settings are destined to be weathered (i.e. dissolved) or undergo 'decarbonation', a reaction that proceeds at high temperatures (and pressures) according to:

$$CaCO_3 + SiO_2 \rightarrow CO_{2(g)} + CaSiO_3$$

The carbon that was formally locked up in the form of $CaCO_3$ is thus released back to the atmosphere and ocean. In the case of carbonates laid down in shallow seas such as limestones or chalks, these can be exposed to weathering during mountain-building episodes and as a result of sea-level fall. In contrast, carbonates deposited in deep-sea sediments are only infrequently exposed at the Earth's surface. Instead, the primary recycling of deep-sea $CaCO_3$ occurs through the decarbonation reaction when sea-floor sediments are subducted under (i.e. dragged beneath) continental margins (Caldeira, 1991; Berner, 1999; Edmond and Huh, 2003).

While virtually all fossil fuel CO_2 will be sequestered in ocean floor carbonates over the next million years or so, the ultimate fate of this material is subduction followed by decarbonation and the release of stored carbon back to the atmosphere. Fortunately, the sequestered CO_2 will not be released all at once, or anytime soon, because the opening and closing of ocean basins and recycling of oceanic crust takes place on 100 million year timescales.

Interestingly, we are currently short-circuiting the 'natural' geologic process of decarbonation through cement manufacture, although limestones are quarried as the reactant rather than deep-sea carbonate oozes. This process is something of a 'double whammy' (two problems at the same time) to the environment because fossil fuels are used to create the high temperatures needed for the CO_2-releasing decarbonation reaction to proceed. Annually, ~0.2 Pg C is released as a result of this activity (Houghton *et al.*, 2001), which is about twice the rate of burial of carbonates in the entire deep ocean (~0.1 Pg C/year).

6.3 The Geologic Organic Carbon Sink

The burial of organic carbon produced as a result of biological photosynthetic activity represents a net sink for CO_2, and can be encapsulated in the reaction $CO_2 + H_2O$ (+ sunlight) $\rightarrow CH_2O + O_2$. This reaction explains how burial of organic matter could have driven the changes in atmospheric oxygen concentrations during the Phanerozoic period (see Berner *et al.*, 2000, 2003 and references therein). Considerably more organic carbon is 'fixed' from CO_2 by photosynthesis than is ever eventually buried. For instance, global primary productivity by phytoplankton in the ocean is estimated to be ~45 Gt C/year (Houghton *et al.*, 2001). Of this, 11 Gt C/year escapes consumption and respiration (called 'remineralization') by zooplankton grazers and bacteria at the surface, and sinks in particulate form to the ocean interior. In turn, only a tiny fraction of this flux –0.05 Gt C/year is ever buried in marine sediments. The remainder (>99%) is remineralized either in the water column or in the surface sediments. This gives us some clues as to ways in which the strength of the geologic organic carbon sink could be enhanced and thus help sequester fossil fuel CO_2 from the atmosphere. We will outline the individual mechanisms that could give rise to a higher burial flux in the following sections, and discuss their possible response (if any) to future global change. The terrestrial geologic organic carbon sink (coal) is discussed separately at the end of the chapter.

6.3.1 Mechanisms of organic carbon burial: marine productivity and sedimentation

We can expect that the sedimentary burial flux of carbon will scale in some way with the strength of productivity in the overlying ocean. All we have to do in order to obtain a stronger geologic sink is to increase primary productivity. One way would be to increase the rate of upwelling of deep waters, thus supplying more nutrients such as phosphate (PO_4) to the ocean surface where photosynthesis takes place. However, most ocean circulation models predict that the ocean is likely to become more stratified in the future as the surface warms, reducing rather than enhancing ocean productivity (Sarmiento *et al.*, 1998; Plattner *et al.*, 2001; Schmittner, 2005).

As an alternative to increasing the rate of upwelling, we could increase the total amount of PO_4 dissolved in the ocean (i.e. raising the concentration everywhere). Phosphate is supplied to the ocean by the dissolution of phosphate-bearing minerals (e.g. apatites) in exposed rocks and soils on land. An increase in weathering rate, which we already expect might occur as a result of higher CO_2 and surface temperatures (Section 6.2.3), will thus act in the 'right' direction. However, PO_4 has a relatively long residence time in the ocean – estimated to be 10,000–80,000 years (Benitez-Nelson, 2000). Thus, even if the global weathering rate were to be instantaneously doubled, we would have to wait at least until the year 10,000 for PO_4 concentrations (and productivity) to have increased by 1055% (depending on the residence time chosen). Assuming that burial scaled linearly with productivity, this equates to an increase in the strength of the geologic carbon sink of 0.005–0.027 Gt C/year, which is insignificant compared to a total fossil fuel CO_2 release of 4176 Gt C. An increase in weathering rate would also increase the rate of erosion and oxidation of ancient organic matter (kerogens) sequestered in sedimentary rocks and, rather unhelpfully, release additional CO_2 to the atmosphere.

Finally, not everywhere in the ocean is all the PO_4 that is supplied to the ocean surface fully utilized by the phytoplankton. In places such as the Southern Ocean, and Eastern Equatorial and North Pacific, insufficient iron availability (a micronutrient essential for parts of the photosynthetic machinery of cells) limits productivity (Jickells *et al.*, 2005). Supply of this iron ultimately comes from dust deposited to the ocean surface. Thus, if dust supply were to increase, presumably so would productivity (e.g. Watson *et al.*, 2000), and with it, an increase in the rate of burial of organic carbon in sediments and sequestration of CO_2. Although the factors affecting dust production, transport and deposition are complex (Jickells *et al.*, 2005; Ridgwell and Kohfeld, in press), it seems that on balance, dust supply is likely to decrease rather than increase in response to future climate change, further restricting biological productivity. Overall, therefore, future productivity changes in the open ocean would seem to be of little help in the sequestering of fossil fuel CO_2.

Bulk sedimentation rate also appears to be an important control on carbon burial (see Arthur and Sageman, 1994; Hedges and Keil, 1995). This is because a faster accumulation rate reduces the residence time of organic matter in the surface sediments, giving bacteria and benthic animals less chance to consume and metabolize it. However, if productivity were to decline in the future, there is little a priori reason to expect an increase in bulk sedimentation rate, particularly if carbonate production were also to be suppressed (which could give rise to a decrease in the efficiency of transport of organic matter to the sediments if the 'ballast hypothesis' is correct – see Section 6.2.4). In contrast, soil erosion and poor land use management might be expected to contribute to increased sedimentation rates on the continental margins, which could result in increased rates of organic matter burial. For instance, increased Himalayan erosion during the Neogene has been hypothesized to have driven lower atmospheric CO_2 by just such a mechanism (France-Lanord and Derry, 1997). However, the damming of rivers for irrigation and power generation could prevent much of the clay mineral supply from reaching the continental margins, thus reducing the potential importance of this effect.

6.3.2 Mechanisms of organic carbon burial: marine anoxia

Most of the organic carbon that is consumed in the water column and surface sediments is preferentially utilized by bacteria and small animals that metabolize aerobically. Oxygen is used by these organisms because it allows the maximum energy to be extracted out of each molecule of organic matter (represented by 'CH_2O'): $CH_2O + O_2 \rightarrow CO_2 + H_2O$ (+ metabolic energy). If oxygen runs out and conditions become 'anoxic', other bacteria that can utilize nitrate (NO_3^-) or even sulphate (SO_4^{2-}) as the electron receptor for the reaction take over. It is less efficient doing it this way and toxic by-products such as H2S can build up. The result is that the fraction of organic matter that escapes degradation should be greater under anoxic conditions (Hedges and Keil, 1995). Another effect of anoxia is that burrowing animals, efficient scavengers and consumers of particulate organic matter from the surface sediments are excluded. This will also tend to increase the preservation and burial of organic carbon. In the geological record, the occurrence of 'organic-rich' (defined as sediments containing >1% carbon by dry weight) sedimentary formations called 'black shales' (of which 'sapropels' are a specific case) have often been interpreted as being caused by local anoxia (Arthur and Sageman, 1994). A contemporary example is the Black Sea, where anoxic conditions prevail deeper than about 150 m in the water column and the organic carbon content of the underlying sediments is typically 1–3% (Arthur and Dean, 1998).

Any increase in the occurrence of anoxia in the ocean should therefore enhance the geologic organic carbon sink. The solubility of oxygen decreases with increasing water temperatures, so a warmer Earth should have a less oxygenated ocean (all other things being equal). Increased stratification will also reduce the downward transport of oxygenated surface waters to depth. An increase in carbon preservation and burial in marine sediments in response to global warming is therefore starting to look like a distinct possibility.

The story gets more complicated because NO_3^- is consumed in anoxic regions, and lower ocean oxygen concentrations means less NO_3^-. Because nitrate, like PO_4 and Fe, is an essential nutrient for plant growth, lower NO_3^- concentrations will restrict productivity, and thus carbon burial. Decreased productivity will result in less oxygen consumed during remineralization, and ocean waters will be driven back away from anoxia. This is a 'negative' feedback loop, helping to stabilize oceanic oxygen concentrations. The net outcome of all these competing processes is not obvious, and this is still not including all the relevant factors (see Berner, 1999). This is where the importance of computer models is felt that can calculate the net impact on oceanic oxygen concentrations due to the interacting effects of surface warming, circulation changes and reduced productivity. The results of long-term climate experiments with such models suggest that no deep anoxia is likely to develop in the future, although in regions such as the eastern equatorial Pacific Ocean, an increase in the volume of hypoxic (i.e. not completely anoxic, but with <10 μmol/kg oxygen) thermocline waters is possible (Matear and Hirst, 2003). The oceanic distributions of dissolved oxygen predicted in the GENIE-1 model under our fossil fuel oxygen release experiment also remained oxygenated, although hypoxia became more extensive within the thermocline of the northern Indian Ocean in this particular model (not shown).

To put the potential importance of this mechanism into some sort of perspective, even if ocean anoxia doubled the global rate of carbon sequestration (adding another 0.05 Gt C/year) in the future, it would still take almost 84,000 years for all of the 4176 Gt C of emitted fossil fuel CO_2 to be removed by this mechanism operating alone.

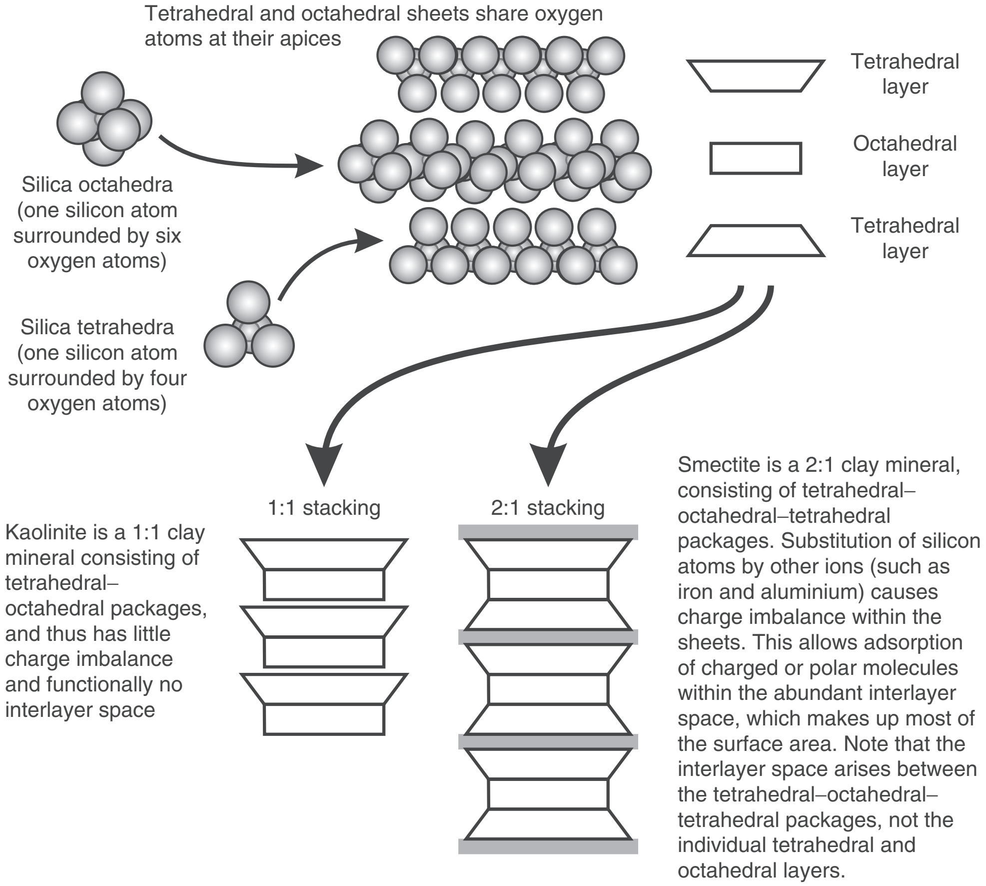
6.3.3 Mechanisms of organic carbon burial: trapping in clay mineral interlayers

There is a third proposed controlling mechanism for the preservation and burial of organic matter in sedimentary rocks – one involving a certain type of clay mineral. Dissolved organic molecules are ubiquitous in the ocean and in the pore spaces of accumulating sediments, and are attracted to the charged surfaces of clay minerals. Therefore, by burying clay minerals in sedimentary formations one would a priori expect a sink of carbon (Hedges and Keil, 1995). Not all clay minerals are created equally, and a mineral called smectite turns out to be 1–2 orders of magnitude more effective than other mineral grains. This is because unlike other clay minerals such as illite, kaolinite or chlorite, which have external surface areas of approximately 20–30 m^2/g, smectite also has an 'internal' (interlayer) surface, giving it a combined surface area of ~800 m^2/g (Kennedy *et al.*, 2002). These internal surfaces arise because of the particular way in which the individual crystalline sheets of smectite are stacked with 'large' interlayer gaps (Fig. 6.10). Polar (and even non-polar) organic molecules such as humic acids and proteins become sorbed into the interlayer sites from the surrounding pore water environment, thereby effectively protecting them from degradation by bacteria (Keil *et al.*, 1994).

Clay mineral formation is the result of the weathering of (mainly feldspar) minerals, such as the hydrolysis of orthoclase feldspar to form kaolinite:

$$4K\ AlSi_3O_8 + 4H^+ + 2H_2O \rightarrow 4K + Al_4Si_4O_{10}(OH)_8 + 8SiO_2$$

Chemical weathering of feldspars to form clays is complex, and is dependent on weathering intensity, rate and starting composition



Kaolinite is a 1:1 clay mineral consisting of tetrahedral–octahedral packages, and thus has little charge imbalance and functionally no interlayer space

Smectite is a 2:1 clay mineral, consisting of tetrahedral–octahedral–tetrahedral packages. Substitution of silicon atoms by other ions (such as iron and aluminium) causes charge imbalance within the sheets. This allows adsorption of charged or polar molecules within the abundant interlayer space, which makes up most of the surface area. Note that the interlayer space arises between the tetrahedral–octahedral–tetrahedral packages, not the individual tetrahedral and octahedral layers.

Fig. 6.10. Illustration of the structural units and stacking of two different common clay minerals – kaolinite and smectite. (Unlike the schema, real clays have vastly greater lateral dimension than shown: typically 3–8 layers thick (3–8 nm) and 1 μm in lateral extent. Therefore, for smectite, most surface is internal). Because clays are formed at surface temperatures and pressures, there is abundant substitution of ions such as aluminium and iron for silica. This results in a net charge imbalance, which is why clay minerals adsorb charged and polar molecules (organic molecules and water most commonly), and exchangeable cations such as calcium and potassium. However, simple substitution is not the only control on the degree to which exchangeable cations and polar molecules are attracted to, and sorbed onto, interlayer surfaces: the location of the substitution (tetrahedral vs. octahedral sheet) also has a large influence on the effectiveness of interlayer adsorption. Thus, 2:1 clays such as smectite have more substitution than 1:1 clays such as kaolinite, in addition to having greater interlayer space.

of the silicate minerals undergoing reaction. However, it is interesting to note that if the feldspar in question is calcium-rich plagioclase ($CaAl_2Si_2O_8$), the weathering reaction produces calcium ions in solution, which could then react with bicarbonate ions, forming inorganic carbonate.

An increase in the rate of formation and supply of smectite clays would strengthen the geologic organic carbon sink and help sequester fossil fuel CO_2. However, smectites are preferentially formed at high weathering *intensity*, which does not necessarily mean a high overall weathering *rate*. For instance, while a change in weathering regime in the Himalayas during the late Miocene resulted in significantly more smectite deposition, it is thought to have resulted in reduced physical erosion at the same time (Derry and France-Lanord, 1996). Thus, decreased

CO_2 consumption because of reduced silicate weathering might offset some (or all) of the 'gains' made by greater carbon burial associated with smectites.

6.3.4 Mechanisms of organic carbon burial: peatlands and coal formation

It is briefly worth mentioning one more geologic carbon sink. Carbon is buried on land in peatlands and swamps, eventually to form coal measures. Peat accumulation depends sensitively on seasonal temperatures and the height of the water table, as well as on biological productivity. With a warmer, wetter future climate we might therefore expect increased rates of peat accumulation. This effect would be enhanced by higher plant productivity induced (fertilized) by rising CO_2 concentrations in the atmosphere. How important this mechanism might be is difficult to quantify, and to date there has not been a systematic attempt to estimate the large-scale future peatland response. However, we can attempt to place it into context by considering past changes.

During the late Holocene (the past few thousand years) there appears to have been a significant increase in carbon storage in peatlands, particularly in the boreal latitudes of the northern hemisphere (Gorham, 1991; Laine *et al.*, 1996; Gajewski *et al.*, 2001). The estimates that have been made suggest an average accumulation rate over the late Holocene of 0.096 Gt C/year (Gorham, 1991). If true, this would make peatlands a potentially important additional long-term carbon sink. However, it is far from clear how much of this expansion of peatlands is in response to the retreat of the northern hemisphere ice sheets following the end of the last glacial period and the creation of new areas suitable for wetlands to develop, and what might have been a response to Holocene warming (and an increase in CO_2). Although 'mining' and drainage in the recent past have probably reversed the global rate of peatland and carbon accumulation, an important contribution from this mechanism to fossil fuel CO_2 sequestration cannot be ruled out, particularly since peatlands are increasingly coming under protection, and in some cases formerly drained peatland forests are being reflooded to promote long-term carbon sequestration and other beneficial reasons.

6.4 Summary and Perspectives

We have looked at the long-term fate of CO_2 released to the atmosphere and used an Earth system model to illustrate (and quantify) the role of some of the major geological carbon sinks. After the ocean has absorbed ~66% of the total release, reaction with sea-floor carbonates results in the sequestration of another 11% on a timescale of a few thousand years. Then, reaction with $CaCO_3$ on land consumes a further 15%, but at a slightly slower pace (tens of thousands of years). Finally, the fate of the remaining 8% in the atmosphere (as well as the 92% now in the ocean as bicarbonate) is removal through silicate rock weathering and burial as marine carbonates.

The situation is not quite this straightforward. Rising surface temperatures and changes in ocean circulation could reduce the effectiveness of the initial ocean invasion sink by 10–20%. Additional and as yet poorly quantified complications arise due to a probable reduction in biogenic calcification in the surface ocean that could lead to an acceleration of ocean invasion and the sea-floor $CaCO_3$ neutralization of CO_2.

We have also considered different mechanisms of organic carbon deposition and burial in accumulating sediments. There is much greater uncertainty here in what the response will be to future global change. A greater rate of clay deposition and of continental margin sedimentary burial seems possible, and would favour a stronger carbon sink. Acting against this will be a reduction in open-ocean productivity caused by increased ocean stratification. However, regardless of the net impact of these factors, it seems unlikely that the organic carbon sink will be as important in the removal of fossil fuel CO_2 from the atmosphere and ocean as changes in carbonate deposition. In contrast, the potential role for peatlands (and incipient coal formation) in the future may be greater.

A clue as to how the geologic carbon sinks might react in the future can be found in the distant past – there is good evidence for a 'catastrophic' release of carbon associated with an event called the 'Paleocene/Eocene thermal maximum' (PETM), some 55.5 million years ago (Dickens *et al.*, 1995). Associated with this was a CO_2 (and maybe CH4)-driven greenhouse warming of the Earth's surface (Bains *et al.*, 1999; Tripati and Elderfield, 2005). Of particular interest to us is that sediment cores document how carbonate accumulation in the deep sea at first declined, and then later recovered in response to this event (Zachos *et al.*, 2005). It has also been suggested that the observed timescale for this recovery (~60,000 years) was accelerated by increased productivity in the ocean (Bains *et al.*, 2000). This would imply that the action of organic carbon sinks in the marine environment might be more important in the future than we speculated earlier (Section 6.3). Paleo-analogues for future global change such as the PETM have a critical role in helping to elucidate the role that the geologic carbon sinks might play in the future.

In its geological carbon sinks, particularly involving silicate rock weathering, the Earth possesses powerful feedback mechanisms that are able to regulate the surface environmental conditions of the planet. There is therefore no doubt about the long-term survival of the biosphere, despite the currently accelerating rate of greenhouse gas emissions. Indeed, by transforming fossil fuel CO_2 into carbonates that are buried on the ocean floor, the geological carbon sink will eventually clean up our mess and return atmospheric composition to the pre-Industrial state. Can we rely on these 'geologic' sinks to stabilize atmospheric CO_2 and climate without any societal intervention, leaving us free to continue to burn fossil fuels in a 'business as usual' fashion? Unfortunately, 'Mother Earth' is not a quick healer and the geologic carbon sinks will be of little help in damping the maximum future 'greenhouse' warming of the planet. This warming, along with other global environmental impacts will occur much quicker than the geological sinks can cope with.

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References

Archer, D. (1996a) An atlas of the distribution of calcium carbonate in sediments of the deep sea. *Global Biogeochemical Cycles* 10, 159–174.

Archer, D. (1996b) A data-driven model of the global calcite lysocline. *Global Biogeochemical Cycles* 10, 511–526.

Archer, D. (2003) Who threw that snowball? *Science* 302, 791–780.

Archer, D. and Buffett, B. (2004) Time-dependent response of the global ocean clathrate reservoir to climatic and anthropogenic forcing. *Geochemical, Geophysics, Geosystems* 6; doi:10.1029/2004GC000854.

Archer, D. and Ganopolski, A. (2005) A movable trigger: fossil fuel CO_2 and the onset of the next glaciation. *Geochemical, Geophysics, Geosystems* 6; doi:10.1029/2005GL022449.

Archer, D., Kheshgi, H. and Maier-Reimer, E. (1998) Dynamics of fossil fuel CO_2 neutralization by marine $CaCO_3$. *Global Biogeochemical Cycles* 12, 259.

[AU7] Archer, D., Morford, J.L. and Emerson, S.R. (2002) A model of suboxic sedimentary diagenesis suitable for automatic tuning and gridded global domains. *Global Biogeochemical Cycles* 16; doi: 10.1029/2000GB001288.

Armstrong, R.A., Lee, C., Hedges, J.I., Honjo, S. and Wakeham, S.G. (2002) A new, mechanistic model for organic carbon fluxes in the ocean: based on the quantitative association of POC with ballast minerals. *Deep-Sea Research II* 49, 219–236.

Arthur, M.A. and Dean, W.E. (1998) Organic-matter production and preservation and evolution of anoxia in the Holocene Black Sea. *Paleoceanography* 13, 395–411.

Arthur, M.A. and Sageman, B.B. (1994) Marine black shales: depositional mechanisms and environments of ancient-deposits. *Annual Review of Earth and Planetary Sciences* 22, 499–551.

Bains, S. *et al*. (1999) Mechanisms of climate warming at the end of the Paleocene. *Science* 285, 724–727.

Bains, S., Norris, R.D., Corfield, R.M. and Faul, K.L. (2000) Termination of global warmth at the Palaeocene/Eocene boundary through productivity feedback. *Nature* 407, 171–174.

[AU8] Barker, S. and Elderfield, H. (2002) Foraminiferal calcification response to glacial-interglacial changes in atmospheric CO_2. *Science* 297, 833.

Benitez-Nelson, C.R. (2000) The biogeochemical cycling of phosphorus in marine systems. *Earth-Science Reviews* 51, 109–135.

Berner, R.A. (1990) Atmospheric carbon dioxide levels over Phanerozoic time. *Science* 249, 1382–1386.

Berner, R.A. (1992) Weathering, plants, and the long-term carbon cycle. *Geochimica et Cosmochimica Acta* 56, 3225–3231.

Berner, R.A. (1999) A new look at the long-term carbon cycle. *GSA Today* 9, 1–6.

Berner, R.A. and Caldeira, K. (1997) The need for mass balance and feedback in the geochemical carbon cycle. *Geology* 25, 955–956.

Berner, R.A. *et al*. (2000) Isotope fractionation and atmospheric oxygen: implications for Phanerozoic O_2 evolution. *Science* 287, 1630–1633.

Berner, R.A. *et al*. (2003) Phanerozoic atmospheric oxygen. *Annual Review of Earth and Planetary Sciences* 31, 105–134.

Caldeira, K. (1991) Continental-pelagic carbonate partitioning and the global carbonate-silicate cycle. *Geology* 19, 204–206.

Caldeira, K. and Wickett, M.E. (2003) Anthropogenic carbon and ocean pH. *Nature* 425, 365.

[AU9] Cameron, D.R., Lenton, T.M., Ridgwell, A.J., Shepherd, J.G., Marsh, R.J. and the GENIE team (submitted) A factorial analysis of the marine carbon cycle controls on atmospheric CO_2. *Global Biogeochemical Cycles*.

Derry, L.A. and France-Lanord, C. (1996) Neogene Himalayan weathering history and river 87Sr/86Sr: impact on the marine Sr record. *Earth and Planetary Science Letters* 142, 59–74.

Dickens, G.R. *et al*. (1995) Dissociation of oceanic methane hydrate as a cause of the carbon-isotope excursion at the end of the Paleocene. *Paleoceanography* 10, 965–971.

Edmond, J.M. and Huh, Y. (2003) Non-steady state carbonate recycling and implications for the evolution of atmospheric pCO_2. *Earth and Planetary Science Letters* 216, 125–139.

Edwards, N.R. and Marsh, R. (2005) Uncertainties due to transport-parameter sensitivity in an efficient 3-D ocean-climate model. *Climate Dynamics* 24, 415–433.

Edwards, N.R. and Shepherd, J.G. (2002) Bifurcations of the thermohaline circulation in a simplified three-dimensional model of the world ocean and the effects of interbasin connectivity. *Climate Dynamics* 19, 31–42.

Enting, I.G., Wigley, T.M.L. and Heimann, M. (1994) Future Emissions and Concentrations of Carbon Dioxide: Key Ocean/Atmosphere/Land Analyses. CSIRO Division of Atmospheric Research Technical Paper No. 31, Commonwealth Scientific and Industrial Research Organisation, Aspendale, Australia.

Feely, R.A. *et al*. (2004) Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. *Science* 305, 362–366.

France-Lanord, C. and Derry, L.A. (1997) Organic carbon burial forcing of the carbon cycle from Himalayan erosion. *Nature* 390, 65–67.

Gajewski, K., Viau, A., Sawada, M., Atkinson, D. and Wilson, S. (2001) Sphagnum peatland distribution in North America and Eurasia during the past 21,000 years. *Global Biogeochemical Cycles* 15, 297–310.

Gorham, E. (1991) Northern peatlands: role in the carbon cycle and probable responses to climatic warming. *Ecological Applications* 1, 182–195.

Hargreaves, J.C., Annan, J.D., Edwards, N.R. and Marsh, R. (2004) An efficient climate forecasting method using an intermediate complexity Earth system model and the ensemble Kalman filter. *Climate Dynamics* 23, 745–760.

Hasselmann, K. *et al*. (2003) The challenge of long-term climate change. *Science* 302, 1923–1925.

Hedges, J.I. and Keil, R.G. (1995) Sedimentary organic-matter preservation: an assessment and speculative. *Marine Chemistry* 49, 81–115.

Houghton, J.T. *et al*. (eds) (2001) *Climate Change 2001: The Scientific Basis*. Contribution of Working Group I. Third Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge.

Hughes, T.P. *et al*. (2003) Climate change, human impacts, and the resilience of coral reefs. *Science* 301, 929–933.

[AU10] IndermŸhle, A. *et al*. (1999) Holocene carbon-cycle dynamics based on CO_2 trapped in ice at Taylor Dome, Antarctica. *Nature* 398, 121–126.

Jickells, T.D. *et al*. (2005) Global iron connections between desert dust, ocean biogeochemistry and climate. *Science* 308, 67.

Keeling, C.D. and Whorf, T.P. (2004) Atmospheric CO_2 records from sites in the SIO air sampling network. In *Trends: A Compendium of Data on Global Change*. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee. Available at: http://cdiac.esd.ornl.gov/trends/co2/sio-mlo.htm

Keil, R.G., Montlucon, D.B., Prahl, F.G. and Hedges, J.I. (1994) Sorptive preservation of labile organic-matter in marine-sediments. *Nature* 370, 549–552.

Kennedy, M.J., Peaver, D.R. and Hill, R.J. (2002) Mineral surface control of organic carbon in black shale. *Science* 295, 657–660.

Klaas, C. and Archer, D.E. (2002) Association of sinking organic matter with various types of mineral ballast in the deep sea: implications for the rain ratio. *Global Biogeochemical Cycles* 16; doi: 10.1029/2001GB001765.

Kleypas, J.A., Buddemeier, R.W. and Gattuso, J.-P. (2001) The future of coral reefs in an age of global change. *International Journal of Earth Sciences* 90, 426–437.

[AU11] Klinger, L.F., Taylor, J.A. and Franzen, L.G. (1996) The potential role of peatland dynamics in ice-age initiation. *Quaternary Research* 45, 89–92.

Kump, L.R., Kasting, J.F. and Crane, R.G. (2004) *The Earth System*. Prentice-Hall, New Jersey.

Laine, J. *et al*. (1996) Effect of water-level drawdown on global climatic warming: northern peatlands. *Ambio* 25, 179–184.

Lenton, T.M. (2000) Land and ocean carbon cycle feedback effects on global warming in a simple Earth system model. *Tellus* B 52, 1159–1188.

Matear, R. J. and Hirst, A.C. (2003) Long-term changes in dissolved oxygen concentrations in the ocean caused by protracted global warming. *Global Biogeochemical Cycles* 17; doi:10.1029/2002GB001997.

Milliman, J.D. (1993) Production and accumulation of calcium carbonate in the ocean: budget of a nonsteady state. *Global Biogeochemical Cycles* 7, 927–957.

Milliman, J.D. and Droxler, A.W. (1996) Neritic and pelagic carbonate sedimentation in the marine environment: ignorance is not bliss. *Geologische Rundschau* 85, 496–504.

Orr, J.C. *et al*. (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* 437, 681–686.

Page, S.E. *et al*. (2002) The amount of carbon released from peat and forest fires in Indonesia during 1997. *Nature* 420, 61–65.

Plattner, G.K., Joos, F., Stocker, T.F. and Marchal, O. (2001) Feedback mechanisms and sensitivities of ocean carbon uptake under global warming. *Tellus B* 53, 564–592.

Ridgwell, A. (2005) Changes in the mode of carbonate deposition: implications for Phanerozoic ocean chemistry. *Marine Geology* 217, 193.

[AU12] Ridgwell, A. and Hargreaves, J. (in prep) Ocean sediment data assimilation within an Earth system model: the importance of deep-sea carbonates in the long-term sequestration of fossil fuel CO_2.

[AU13] Ridgwell, A. and Kohfeld, K.E. (in press) Dust in the Earth system: the biogeochemical linking of land, air, and sea. *Advances in Science*.

Ridgwell, A. and Zeebe, R.E. (2005) The role of the global carbonate cycle in the regulation and evolution of the Earth system. *EPSL* 234, 299.

Ridgwell, A. *et al*. (submitted) Ocean geochemical data assimilation within an Earth system model. *Global Biogeochemical Cycles*.

Ridgwell, A. *et al*. (in prep) Ensemble analysis of marine 'CO_2-calcification' feedback and fossil fuel CO_2 uptake.

Ridgwell, A. J. (2001) Glacial–interglacial perturbations in the global carbon cycle. PhD thesis, University of East Anglia at Norwich, UK. Available at: http://andy.seao2.org/publications/ridgwell_2001.pdf

Ridgwell, A. J. (2003) Implications of the glacial CO_2 'iron hypothesis' for quaternary climate change. *Geochemical, Geophysics, Geosystems* 4, 1076; doi:10.1029/2003GC000563.

Ridgwell, A. J., Kennedy, M. J. and Caldeira, K. (2003) Carbonate deposition, climate stability, and Neoproterozoic ice ages. *Science* 302, 859–862.

Riebesell, U., Zondervan, I., Rost, B., Tortell, P.D., Zeebe, R.E. and Morel, F.M.M. (2000) Reduced calcification of marine plankton in response to increased atmospheric CO_2. *Nature* 407, 364–367.

Royal Society (2005) *Ocean acidification due to increasing atmospheric carbon dioxide*. Royal Society Document 12/05, Royal Siociety, London.

Royer, D.L. *et al*. (2004) CO_2 as a primary driver of Phanerozoic climate. *GSA Today* 14, 4–10.

Ryan, D.A., Opdyke, B.N. and Jell, J.S. (2001) Holocene sediments of Wistari Reef: towards a global quantification of coral reef related neritic sedimentation in the Holocene. *Palaeogeography, Palaeoclimatology, Palaeoecology* 175, 173–184.

Sabine, C.L. *et al*. (2004) The oceanic sink for anthropogenic CO_2. *Science* 305, 367–371.

Sarmiento, J.L., Hughes, T.M.C, Stouffer, R. J. and Manabe, S. (1998) Simulated response of the ocean carbon cycle to anthropogenic climate warming. *Nature* 393, 245–249.

Schimel, D. and Baker, D. (2002) Carbon cycle: the wildfire factor. *Nature* 420, 29–30, 2002.

Schmittner, A. (2005) Decline of the marine ecosystem caused by a reduction in the Atlantic overturning circulation. *Nature* 434, 628–633.

Tripati, A. and Elderfield, H. (2005) Deep-sea temperature and circulation changes at the Paleocene-Eocene thermal maximum. *Science* 308, 1894–1898.

Vecsei, A. and Berger, W.H. (2004) Increase of atmospheric CO_2 during deglaciation: constraints on the coral reef hypothesis from patterns of deposition. *Global Biogeochemical Cycles* 18; doi:10.1029/2003GB002147.

[AU14]

Watson, A. J., Bakker, D.C.E., Ridgwell, A. J., Boyd, P.W. and Law, C.S. (2000) Effect of iron supply on Southern Ocean CO_2 uptake and implications for glacial atmospheric CO_2. *Nature* 407, 730–733.

Weaver, A. J. *et al*. (2001) The UVic Earth system climate model: model description, climatology and application to past, present and future climates. *Atmosphere-Ocean* 39, 361–428.

Zachos, J.C. *et al*. (2005) Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum. *Science* 308, 1611–1615.

Zeebe, R.E. and Westbroek, P. (2003) A simple model for the $CaCO_3$ saturation state of the ocean: the 'Strangelove,' the 'Neritan,' and the 'Cretan' ocean. *Geochemical, Geophysics, Geosystems* 4; doi:10.1029/2003GC000538.

Zeebe, R.E. and Wolf-Gladrow, D. (2001) *CO_2 in Seawater: Equilibrium, Kinetics, Isotopes*. Elsevier Oceanographic Series 65, Elsevier, New York.

Zondervan, I., Zeebe, R.E., Rost, B. and Riebesell, U. (2001) Decreasing marine biogenic calcification: a negative feedback on rising atmospheric pCO_2. *Global Biogeochemical Cycles* 15, 507–516.

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[Au8] Barker and Elderfield 2002 not cited. Text gives Barker et al. 2003, which is missing in References.
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