

**The Dynamics of Fossil Fuel CO₂ Neutralization
by Marine CaCO₃**

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Abstract

A detailed model of the ocean circulation and carbon cycle was coupled to a mechanistic model of CaCO_3 diagenesis in deep sea sediments to simulate the millennium-scale response of the oceans to future fossil fuel CO_2 emissions to the atmosphere and deep sea. Simulations of deep sea injection of CO_2 show that CaCO_3 dissolution is sensitive to passage of high- CO_2 waters through the Atlantic Ocean, but CaCO_3 dissolution has a negligible impact on atmospheric pCO_2 or the atmospheric stabilization CO_2 emission in the coming centuries. The ultimate fate of the fossil fuel CO_2 will be to react with CaCO_3 on the sea floor and on land. An initial CaCO_3 dissolution spike reverses the net sedimentation rate in the ocean until it is attenuated by an enhanced vertical gradient of alkalinity after about 1000 years. The magnitude of the initial spike is sensitive to assumptions about the kinetics for CaCO_3 dissolution, but subsequent behavior appears to be less model dependent. Neutralization by seafloor CaCO_3 occurs on a timescale of 5-6 kyr, and is limited to at most 60-70% of the fossil fuel release, even when the fossil fuel release is small. After sea floor neutralization is exhausted in the about the this time the CaCO_3 accumulation rate relaxes toward the weathering rate (the global steady state condition) on a time scale of 8.5 kyr, while the deficit of sea floor CaCO_3 (the lysocline) is replenished with an e-folding time scale of approximately 18 kyr. The final equilibrium with CaCO_3 leaves 7-8% of the fossil fuel CO_2 remaining in the atmosphere, to be neutralized by the silicate rock cycle on a time frame of hundreds of thousands of years.

Introduction

Mankind releases CO₂ to the atmosphere by combustion of fossil fuels and by deforestation, which converts relatively high biomass forests, mostly in the tropics, into lower biomass grasslands and farmlands, resulting in a net release of CO₂. Currently, the rate of atmospheric CO₂ increase corresponds to less than half of the anthropogenic release from fossil fuels and deforestation. The sink for the other half appears to be a combination of dissolution into the ocean and uptake by the terrestrial biosphere in regions other than regions of active deforestation [*Tans et al.*, 1990; *Schimel et al.*, 1994; *Ciais et al.*, 1995; *Jain et al.*, 1996; *Keeling et al.*, 1996; *Kheshgi et al.*, 1996]. Future uptake by the terrestrial biosphere is difficult to predict and is not the topic of this paper. In contrast, uptake by the oceans is describable by the physics of ocean circulation and the chemistry of CO₂ and CaCO₃, which we are beginning to be able to describe quantitatively. For our discussion of the oceanic CO₂ uptake, it will be convenient to combine anthropogenic emission and biospheric uptake into a quantity called the net terrestrial emission, such that future biosphere uptake acts to directly counteract fossil fuel and deforestation CO₂ emission.

The first and quantitatively most significant step in the processing of the terrestrial CO₂ release will be dissolution in the oceans, which we will call invasion. The time scale for invasion is determined by the circulation time scale of the ocean and by the buffer capacity of subducting surface sea water. Following the equilibration of the atmosphere with the water in the ocean, the CO₂ will react with solid CaCO₃ (a reaction called neutralization), decreasing the atmospheric component of the CO₂ release still further. Two processes contribute to neutralization: (1) the transfer of carbonate ion [CO₃⁼] from dissolving CaCO₃ on the sea floor to the ocean (sea floor neutralization), and (2) the imbalance between the rate of chemical weathering (dissolving) of CaCO₃ on land and accumulation of solid CaCO₃ on the sea floor, which results in a net dissolution flux of CaCO₃ on land to the ocean (terrestrial neutralization). Finally, on time frames of hundreds of thousands of years the pCO₂ of the atmosphere (and hence the ocean) is thought to be controlled by the balance between volcanic degassing of CO₂ and its consumption by reaction with basic components of silicate rocks [*Walker and Kasting*, 1992].

In this paper we subject a detailed model of ocean and sediment carbon chemistry to a range of fossil fuel release scenarios, to predict the impact of CaCO₃ dissolution on time frames of centuries to millennia. The first section describes the model in detail. The next sections analyze the effect of CaCO₃ on estimates of the net terrestrial emission which results in a specified time-evolution of atmospheric CO₂ concentration leading to a stable value, and results of deep sea CO₂ direct injection experiments. The next and longest section describes the sequence of invasion and sea floor and terrestrial neutralization to the year AD 10,000 and beyond in response to various CO₂ release scenarios. We explore the dynamics of fossil fuel neutralization to understand the details of the kinetics of neutralization in its various regimes, an understanding which may also guide future research into the transitions in global carbon cycle accompanying the transitions between glacial and interglacial states.

Model Description

We simulate the physics and chemistry of the ocean and sediment response to anthropogenic CO₂ release using a previously documented model of ocean circulation and water column chemistry [*Maier-Reimer*, 1993], coupled to a sedimentary diagenesis model for organic carbon and CaCO₃ in deep sea sediments [*Archer*, 1991; *Archer*, 1996b]. The

ocean carbon cycle model advects dissolved chemical tracers using the steady flow field from the Large Scale Geostrophic (LSG) circulation model, tuned to represent the present-day ocean [Maier-Reimer, 1993]. The model flow field was invariant during the model integration, neglecting climate feedbacks to ocean flow [Manabe and Stouffer, 1993]. A single nutrient, scaled to represent PO_4^{3-} , limits organic carbon export from the surface ocean according to the Michaelis-Menton rate expression

$$\text{Rate} = r_{lat} \frac{P^2}{P + P_{HS}}$$

where r_{lat} is a function of latitude (light) and temperature, P is the nutrient concentration, and P_{HS} is the half-saturation constant, set at a value of $0.01 \mu\text{mol l}^{-1}$. This production rate has been adjusted relative to the formulation of [Maier-Reimer, 1993] to slow the biological uptake of nutrients in the euphotic zone, decreasing the rate of biological productivity in high nutrient areas such as the equatorial Pacific, allowing transport of nutrients in surface currents to the oligotrophic subtropical gyres. This was necessary to attenuate the equator/oligotrophic contrast in the delivery rates of organic carbon and CaCO_3 to the sea floor. The resulting export productivity field of the ocean is shown in Figure 1a. The disadvantage of this adjustment was an increase in the nutrient concentration and pCO_2 of the sea surface, increasing the pCO_2 of the model atmosphere by approximately $20 \mu\text{atm}$. The mole production rate of CaCO_3 per unit area is taken to be 25% of that of organic carbon in low and mid latitudes, resulting in the CaCO_3 production rate field shown in Figure 1b. Global rates of organic carbon and CaCO_3 export production were 7.48 and $1.65 \text{ Gton C yr}^{-1}$, respectively.

Sediment rain rates to the sea floor in the real ocean estimated from sediment trap and benthic flux studies show values of roughly 12 and $18 \mu\text{mol cm}^{-2} \text{ yr}^{-1}$ for organic C and CaCO_3 , respectively [Tsunogai and Noriki, 1991; Dymond and Lyle, 1993; Archer, 1996b; Jahnke, 1996], and rates close to this are required by the sediment model to reproduce the observed calcite lysocline [Archer, 1996b]. Coupling the ocean and the sediment models constrains the extent of water column redissolution of sinking organic carbon and CaCO_3 , which for organic carbon was taken to be

$$\text{Flux}(z) = \text{Flux}(100\text{m}) \times \frac{z^{-0.7}}{100\text{m}}$$

following the form of Martin *et al.* [1987] but replacing the original coefficient 0.858 in the exponential to 0.7 to reproduce observed organic carbon fluxes to the sea floor. For water column redissolution of CaCO_3 ,

$$\text{Flux}(z) = \text{Flux}(100\text{m}) \times 0.3 + 0.7 \times e^{-\frac{z}{2000\text{m}}}$$

where 0.3 represents the contribution of large rapidly sinking shells to the CaCO_3 flux. At the finite average depth of the water column, this function results in approximately 50% water column redissolution for CaCO_3 . Particulate redissolution at depth is instantaneous,

and production and decay of dissolved and suspended biogenic matter is neglected. The sediment model requires also a finite rain rate of refractory non-CaCO₃ material; although in the real ocean this is a regionally and time varying quantity, we specify a uniform flux of 0.180 g cm⁻² kyr⁻¹ in pelagic sediments, and values of 10 and 1 g cm⁻² kyr⁻¹ in grid points adjacent and once-removed from land, respectively.

The sediment diagenesis model, described as the "Oxygen Only" model by Archer [1991], resolves the pore water profiles of oxygen and the carbonate buffer system to predict the dissolution of CaCO₃ using rain rates and overlying water chemistry as boundary conditions. The top 10 cm of the sediment are discretized into seven layers, with a minimum layer thickness near the top of 0.5 cm. The depth-integrated respiration rate within the sediment is assumed to be equal to the instantaneous sinking flux of organic carbon to the sea floor; this flux is instantly returned to the bottom ocean box. The sediment respiration rate is used to calculate the rate of CaCO₃ dissolution from the sediment. In the sediment, organic carbon degrades in the presence of O₂ with a rate constant of 2·10⁻⁹ sec⁻¹ and mixes into the bioturbated layer (10 cm deep) with a bulk mixing coefficient of 150 cm² kyr⁻¹. The solid organic carbon profile in the sediment is assumed to follow steady state balance between mixing and degradation (no time dependent mixing). CaCO₃ dissolution kinetics into undersaturated solution follow the rate law

$$J = k \frac{\text{g CaCO}_3}{\text{g solid}} \left(1 - \frac{[\text{CO}_3^{=}]}{[\text{CO}_3]_{\text{sat}}} \right)^n$$

where k , the dissolution rate constant, is taken to be 1 day⁻¹ using a rate order, n , of 4.5 [Archer, 1996b], except in a comparison case where $n=1.0$ and k ranges from 10⁻³ to 3·10⁻⁵ day⁻¹. The saturation state for CaCO₃ is based on the concentration of carbonate ion, [CO₃⁼], relative to the saturation condition [CO₃⁼]_{sat}. The heaviside function, H , is used to prevent crystallization of CaCO₃ from supersaturated conditions. CaCO₃ is considered well-mixed within the bioturbated layer. Accumulation of CaCO₃ is taken by difference between rain rate and dissolution. Maps of steady state CaCO₃ concentration and mass accumulation rate are given in Figure 1c and 1d.

The inventory of CaCO₃ on the sea floor which may become available for dissolution depends on the geometry of dissolution in surface sediments, as first described by [Broecker and Takahashi, 1978]. The zone of dissolution is isolated to the top few centimeters of the sediment surface, but bioturbation exposes sediment from below this depth, to a depth scale of order 10 centimeters, to the zone of dissolution. Thus at least the depth of the bioturbated layer is within reach of potential return to the ocean reservoir. If dissolution exceeds the total sedimentation rate, then the erosion of the sea floor can effectively mine old carbonates in a process called chemical erosion. Chemical erosion may continue until the entire bioturbated layer becomes filled with non-CaCO₃ refractory material. Thus, the potential reach of dissolution, which defines the lower boundary of the "erodable inventory" of CaCO₃ and will be referred to as the "erodable surface", is defined as the depth to the quantity of non-CaCO₃ material which would be required to fill the bioturbated layer.

The inventory of CaCO₃ above the erodable surface is very sensitive to the porosity [Archer, 1996a], defined as the ratio of pore volume to total volume. The porosity of surface sediments are found empirically to vary with sediment composition. In addition,

porosity is generally observed to increase in the top few centimeters of the sediment. In a fit to observations, we assume a porosity / depth relation of

$$\rho(z) = \rho_{max} + (1 - \rho_{max}) e^{-\frac{z}{L}}$$

where the depth scale, L , and the asymptotic porosity, ρ_{max} , are chosen to be functions of the CaCO_3 concentration as

$$L = 0.25\text{cm} \times \frac{\% \text{CaCO}_3}{100\%} + 3.0\text{cm} \times \left(1 - \frac{\% \text{CaCO}_3}{100\%}\right)$$

and

$$\rho_{max} = 1 - \frac{0.483 + 0.0045 \times \% \text{CaCO}_3}{2.5}$$

respectively. The average porosity of the bioturbated layer is then

$$\bar{\rho} = \rho_{max} - \frac{(1 - \rho_{max}) e^{-\frac{10\text{cm}}{L}} - 1}{10\text{cm}}$$

by integration. From the profiles of porosity with and without CaCO_3 , the depth to which chemical erosion can penetrate is

$$z_{erosion} = 10\text{cm} \times \frac{1 - \bar{\rho}_{no \text{CaCO}_3}}{1 - \bar{\rho}_{with \text{CaCO}_3}} \left(1 - \frac{\% \text{CaCO}_3}{100\%}\right)^{-1}$$

The global available inventory of CaCO_3 on the sea floor is 1770 Gton C, similar to the recent estimate of 1600 Gton C based on sea floor data [Archer, 1996a].

The model calculates the global rate of CaCO_3 dissolution and sedimentation in the ocean from the production of CaCO_3 in the surface ocean and from the chemistry of the bioturbated layer of the sea floor. In the model as in nature, the removal of CO_3^{2-} from the ocean by CaCO_3 burial is replenished by dissolution of carbonate and silicate rocks on land (terrestrial weathering). Weathering is simulated as a constant uniform input of CO_3^{2-} to surface waters at a rate of 0.145 Gton C as CO_3^{2-} per year, intended to balance the global deep sea burial rate of CaCO_3 . This is slightly lower than estimates of riverine dissolved CaCO_3 fluxes [Berner and Berner, 1987; Morse and MacKenzie, 1990] plus hydrothermal exchange of Mg for Ca [Wolery and Sleep, 1988], although the comparison should also include shallow water deposition of CaCO_3 , which is estimated to rival the rate of burial in

the deep sea [Milliman, 1993]. By neglecting shallow water deposition and its corresponding weathering flux, we are implicitly assuming that these fluxes will be constant throughout the simulations. The burial rate of CaCO_3 is ultimately driven to balance terrestrial weathering by the mechanism of CaCO_3 compensation, whereby ocean carbonate ion concentration ($[\text{CO}_3^{=}]$) increases or decreases until the fluxes balance.

The initial condition of the model is a steady state, with weathering balanced by deep sea burial, although there is some question about whether the present-day ocean has achieved this steady state following carbon cycle rearrangements accompanying the glacial termination [Milliman, 1993]. CO_2 additions from fossil fuel combustion were simulated as increases in the atmospheric concentration, or in some cases by direct injection to single grid cells in the ocean model. Except for these fluxes, the coupled ocean/sediment model conserved carbon to 10^{-5} Gton C over 10,000 years of model integration, the expected drift due to rounding errors at the 64-bit precision of the calculation.

In addition to time dependent runs, acceleration techniques were used to obtain various steady states of the model (which will be described more fully below). A balance between weathering and the global deep sea burial of CaCO_3 is referred to as "global steady state", and was approached by adding $\text{CO}_3^{=}$ to the water column homogeneously, ten times per century, for 800 years. The $\text{CO}_3^{=}$ concentration added was

$$\text{CO}_3^{=} \text{ added} = 50 \mu\text{mol l}^{-1} / \text{Gton C yr}^{-1} \cdot [\text{weathering} - \text{burial}]$$

The 800 year acceleration period was followed by 700 years of spin-up to allow the water column chemistry to relax toward a steady state.

A separate steady state condition can be called "local steady state", defined as a balance at each grid point between CaCO_3 rain, dissolution, and burial. In local steady state the CaCO_3 lysocline is stationary with respect to a snapshot of water column chemistry and sediment rain rates, but an ocean in local steady state can still bury less or more CaCO_3 than weathering, i.e. be out of global steady state. Thus the two steady state conditions are independent of each other. The local steady state condition was found by iterating sea floor CaCO_3 concentration at each grid point, to obtain the steady state lysocline corresponding to a snapshot of water column chemistry. This operation was also followed by 1000 years of model spin-up to relax the water column chemical distribution to a steady condition. The full steady state condition, which satisfied both of these constraints, was also obtained in some cases. Note that the model neglects CO_2 release from metamorphic decarbonation and uptake by silicate weathering, so that full steady state of this model does not imply this balance [Walker *et al.*, 1981].

Stabilization of Atmospheric CO_2 Concentration

The objective of the Framework Convention on Climate Change (FCCC) is, in part, to "achieve ... stabilization of greenhouse gas concentrations at a level that would prevent dangerous anthropogenic interference with the climate system". Implementing such a stabilization will require a means of translating atmospheric concentrations into corresponding emission rates by predicting uptake by the oceans and the biota. The IPCC [Schimel *et al.*, 1994] has tailored a series of illustrative CO_2 concentration time pathways in order to study the implications of the FCCC objective. The specified CO_2 concentration follows arbitrary time pathways to reach various constant atmospheric concentrations ranging from $350 \mu\text{atm}$ to $1000 \mu\text{atm}$ by AD 2400 [Houghton *et al.*, 1996]. Various

carbon cycle models have been used to estimate the rate of emissions that result in these CO₂ concentration time pathways [Enting *et al.*, 1994; Wigley *et al.*, 1996] by taking account of ocean and, in some cases, biospheric uptake of carbon. However, these studies have not included the effect of CaCO₃ dissolution. For the range of prescribed stabilization pathways, carbon emissions by AD 2300 have declined well below current emission rates. In this situation—low emission rates following a rise in atmospheric CO₂ spanning centuries—does the effect of CaCO₃ dissolution become apparent?

The time course of atmospheric pCO₂ specified by IPCC scenario s750 [Schimel *et al.*, 1994], offset by 33 μ atm (Figure 2a) because the initial steady state atmospheric pCO₂ of the model is higher than preanthropogenic by this amount (see Model Description). The allowed rate of terrestrial CO₂ release was determined by holding the atmospheric CO₂ at the specified value and tabulating the flux of CO₂ to the atmosphere/ocean system which was required to track this specified concentration. The results for the no-CaCO₃ model are given in Figure 2b; the results which included CaCO₃ are nearly indistinguishable on this scale. The difference between the two is plotted as absolute ocean uptake in Figure 2c and as a relative increase in Figure 2d; this is the extra CO₂ emission which is due to neutralization by sea floor CaCO₃. The extra CO₂ emission is at most a few percent, which is not significant relative to the uncertainty of uptake by the ocean or by the biosphere. We learn that the effect of deep sea CaCO₃ dissolution on the CO₂ concentration over the next several centuries is likely to be negligible, consistent with previous studies [Sundquist, 1986; Maier-Reimer, 1993; Archer *et al.*, 1997].

Deep Ocean Disposal of CO₂

A number of geoengineering techniques have been proposed to control atmospheric greenhouse gas concentrations or to limit potential impacts [National Academy of Sciences *et al.*, 1992]. Marchetti [1977] proposed capturing CO₂ emissions from power plants, and disposing of it in the deep sea. Relative to human emissions, oceans have an immense capacity for CO₂, so that the added burden of CO₂ will be relatively small. Also, we will see below that the ultimate fate of most of the fossil fuel CO₂ will be to dissolve in the oceans eventually anyhow, so direct injection would only be catalyzing the transition to an already inevitable condition.

It appears that CO₂ retention times for the remaining atmosphere-bound fraction could exceed 500 years for marine disposal below a few km [Hoffert *et al.*, 1979]. Retention times can, however, be much shorter and have been found to be dependent on the location of injection [Haugan and Drange, 1995]. Furthermore, there has been speculation that sediment dissolution can effectively increase the CO₂ residence time by preferential dissolution of CaCO₃ in regions near or downstream of the injection site. To assess the effect of CaCO₃ dissolution on ocean disposal, we have run emissions scenario A with 25% of the CO₂ emissions injected equally into the deep Pacific (east of Japan at 152.5° E, 31.25° N, 3000 m depth) and the Atlantic (Mediterranean outflow water at 17.5° W, 36.25° N, 3000 m depth). Figure 3 shows that the effect of injecting 25% of the fossil fuel release directly into the oceans is much more significant than is the effect of CO₂ neutralization by CaCO₃.

In addition, we have run more mechanistically interpretable "impulse injection" experiments where 10 Gton C as CO₂ is impulse injected into the steady state ocean, comparing Atlantic (17.5° W, 36.25° N, 3000 m depth) vs. Pacific (152.5° E, 31.25° N, 3000 m depth), and CaCO₃ vs. no CaCO₃. Figure 4 shows the results of these experiments. Initially, the Atlantic injection models track each other, as do the Pacific,

regardless of the presence of CaCO_3 , as we would expect. The Pacific injection is somewhat "leakier" because the Pacific is closer to the end of the line of the deep sea circulation, which leads to a faster outgassing of the atmospheric fraction of the CO_2 impulse and also a slight overshoot on the approach toward atmosphere/ocean equilibrium. 1000 years after the injection, the model runs sort themselves according to the presence or absence of CaCO_3 . Dissolution fluxes (Figure 4b) are initially much higher in the Atlantic injection experiment than in the Pacific or atmospheric, and the accumulated dissolution anomaly due to the CO_2 injection is greatest for the Atlantic injection, presumably because of the abundance of CaCO_3 in Atlantic sediments. Interestingly, the atmospheric release results in greater accumulated dissolution anomaly after 1000 years than does the Pacific injection, because the pathway from the atmosphere to the ocean is through the Atlantic, which the Pacific injection skips. However, the benefits of lowering the atmospheric CO_2 transient by Pacific injection would appear to outweigh the drawbacks of leaking to the atmosphere and depressed CaCO_3 dissolution which Pacific injection appears to generate.

These results are consistent with earlier studies. *Bacastow and Dewey* [1996] speculated that CO_2 injection at sites near the east coast of the USA or in the North Atlantic would benefit more from calcite dissolution relative to injection in the Pacific. Using a 4-box model for atmosphere/ocean/sediment system, *Cole et al.* [1993; 1995] conclude that the extent of CaCO_3 dissolution will vary significantly with injection depth. *Nihous et al.* [1994] found extensive sediment dissolution when a model fast dissolution kinetics was used. However, we find that the effect of enhanced CaCO_3 dissolution in Atlantic CO_2 injection (relative to atmospheric release) will only have an effect on pCO_2 after roughly 500 years, and this effect will likely be compensated by the enhanced production of CO_2 [*Kheshgi et al.*, 1994] required to carry out the capture and deep-sea injection of CO_2 . For these reasons, we would not expect the extent of enhanced CaCO_3 dissolution to be an important factor in determining the effectiveness of deep sea disposal of CO_2 .

Long Term Fate of Fossil Fuel CO_2

We have done a series of time-dependent model integrations to characterize the millennial time scale fate of fossil fuel CO_2 . These results have been briefly described by *Archer et al.*, [1997]; here we present a more thorough and detailed analysis. IPCC [*Houghton et al.*, 1990; *Houghton et al.*, 1992] has put forth families of scenarios for future emissions of CO_2 which have been used as benchmarks for comparing carbon cycle models [*Enting et al.*, 1994] as well as making projections of global climate change and its impacts. Using simple ocean and biosphere carbon cycle models, IPCC projected the concentration of CO_2 in the atmosphere in response to these emissions scenarios. Because we have no land biota model, our strategy was to impose these projected CO_2 concentrations on the model atmosphere beginning at an initial steady state in the year AD 1750. For the period from 1750 to 1990 atmospheric CO_2 was imposed at historical values [*Marland et al.*, 1993]. From 1990 through to AD 2100 we specify atmospheric concentrations at projections based on the IPCC emissions scenarios labeled *Business-as-usual* and *B* [*Houghton et al.*, 1990]. These projections include the effect of a terrestrial biospheric sink for CO_2 . Following AD 2100 we chose several variants. The first two, which we label scenarios "A" and "B", follow the IPCC 1990 scenarios *Business-as-usual* and *B*, respectively, until AD 2100, and have zero emissions after AD 2100. Scenarios A22 and A23 follow *Business-as-usual* until AD 2100, then linearly extrapolate from the AD 2100 net terrestrial emission rate to AD 2200 or AD 2300, respectively, and thereafter the rate is set to zero. Following the emission period, no further biospheric uptake was allowed; the system was closed except for weathering and sedimentation. The rate of net terrestrial emission of CO_2 is shown in Figure 5, and the cumulative emissions of CO_2 are summarized in Table 1. Global reserves of fossil fuels have been estimated to be of order

5000 Gton C [Sundquist, 1985], which indicates that the eventual release (beyond AD 2100) could greatly exceed the cumulative release of the IPCC scenarios out to AD 2100. The models were run both with and without CaCO₃ compensation until AD 10,000, except for A22 which was extended to AD 40,000.

CO₂ Invasion Time Scale

Time series of atmospheric pCO₂ to AD 10,000 are shown in Figure 6. The initial increase in atmospheric CO₂ is determined by the emissions scenario, and the subsequent decline is caused by dissolution of CO₂ in the oceans (invasion) and reaction with CaCO₃ (neutralization). The characteristics of invasion alone can best be determined from the model results neglecting CaCO₃ dissolution (Figure 7a). Previous studies of the ocean uptake of a single impulse of CO₂ release ([Maier-Reimer and Hasselmann, 1987; Sarmiento *et al.*, 1992]) resolved CO₂ invasion into several distinct time scales corresponding to uptake into surface, thermocline, intermediate, and deep waters of the ocean. In our simulations, the hundred year time scale of the CO₂ release has obscured the shorter time scales for ocean invasion. However, we find that the overall CO₂ decline can be approximated with single e-folding time scales of 200 to 450 years, depending on the amount of CO₂ released (Table 2). When CaCO₃ dissolution is disallowed in the model, the final equilibrium between the ocean and the atmosphere finds 83-70% of the fossil fuel release sequestered in the oceans (Table 2). These results are consistent with Sundquist [1990].

Reaction with CaCO₃

The long-term effects of CaCO₃ weathering and sea floor dissolution on the pCO₂ of the atmosphere can be seen as the divergence between the solid lines (including CaCO₃) and the dashed lines (no CaCO₃) in Figure 6. In the initial millennium, there is little difference between the two model formulations, but beyond AD 3000, the reaction of CO₂ with CaCO₃ becomes significant. pH equilibrium chemistry of dissolved CO₂ leads to an inverse relationship between CO₂ and CO₃⁼, which can be seen as a decrease in deep Pacific [CO₃⁼] following the CO₂ invasion (Figure 8). This in turn provokes two distinct but complementary neutralization responses: dissolution of previously deposited CaCO₃ on the sea floor, and net dissolution of terrestrial CaCO₃ which is temporarily not balanced by sea floor deposition of CaCO₃. This distinction will be justified in the Analysis and Discussion section, below.

By the end of the simulations, significant fractions of the global inventories of CaCO₃ in the bioturbated layer and within reach of chemical erosion have been exhausted. The initial e-folding time for the removal of CO₂ by CaCO₃, relative to the case of no CaCO₃, is 5-6 kyr and relatively independent of the magnitude of CO₂ release (Figure 7b and Table 2), based on a plot of the log of the increase in the pCO₂ (CaCO₃ - no CaCO₃) toward the final steady state value given in Table 2. As we shall see, this can be taken to be the time scale of "sea floor" neutralization effect on the pCO₂ of the atmosphere.

None of the model results in Figure 6 have reestablished equilibrium by the end of their 10 kyr runs. This can be seen in Figure 8c as the imbalance between weathering and deep sea CaCO₃ accumulation and the depletion of the sea floor CaCO₃ inventory relative to the initial (steady state) condition. Figure 9 shows A22 to the year 40k, by which time the global ocean burial rate, and the sea floor CaCO₃ inventories, appear to have largely returned to their original values. The e-folding time scales for the approach to weathering / accumulation steady state ("terrestrial neutralization") can be estimated from semi-log plots in Figure 10. In the first 10 kyr, both the atmospheric CO₂ decline and the recovery of weathering / burial steady state relax to their final states with e-folding time scales of 5.5-

6.8 kyr (Figure 10a). After the year 10k, the slope shallows to an 8.3 kyr time scale. This is because the sea floor CaCO_3 inventory has reached a minimum value, and has been exhausted as a source of alkalinity to neutralize CO_2 (see Discussion). The remaining source, terrestrial CaCO_3 , is slower than sea floor neutralization. The replenishment of the sea floor CaCO_3 inventory after the year 20k appears to take place with an e-folding time scale of 18 kyr (Figure 10c).

The division of CaCO_3 compensation response of the ocean into several components has been a common finding of previous studies. *Sundquist* [1990] partitioned the alkalinity response of the ocean into primary and secondary responses based on the log slope of the model response; these ranged from 1500-2700 and 10,800-14,200 years, respectively. The former was identified as sea floor neutralization, because it was sensitive to sediment dissolution kinetics, while the latter corresponds to the CaCO_3 compensation (weathering / burial imbalance) timescales as estimated by *Broecker* [1987] and *Boyle* [1983]. *Walker and Kasting* [1992] assumed as an upper limit that sea floor dissolution occurs instantaneously, so that the several thousand year response time of their model to fossil fuel invasion represents only what we have called terrestrial neutralization.

CaCO₃ Steady State

The final state of the 40 kyr A22 integration has nearly restored the sea floor CaCO_3 inventory to original values, and the global burial rate balances weathering. This state has also been obtained directly by the acceleration technique described in the Methods section. The resulting alkalinity of the ocean and $p\text{CO}_2$ of the atmosphere are given in Table 2. We find that even after complete reaction with CaCO_3 , approximately 7-8% of the fossil fuel CO_2 remains in the atmosphere, consistent with *Sundquist* [1990] and *Walker and Kasting* [1992]. The equilibrium partitioning of fossil fuel CO_2 between the atmosphere and the CaCO_3 -buffered ocean can be understood from the aqueous CO_2 equilibrium reactions. Dissolved CO_2 equilibrium can be expressed as

$$\frac{p\text{CO}_2 [\text{CO}_3^{=}]}{[\text{HCO}_3^-]^2} = \frac{K_2' K_H}{K_1} = \text{constant}$$

which relates the partial pressure of CO_2 exerted by a sea water sample and the concentrations of carbonate and bicarbonate ions to the apparent dissociation constants for carbonic acid (K_1' and K_2') and the Henry's law solubility product for CO_2 (K_H). For the global ocean and atmosphere, the situation is complicated by heterogeneities in ocean chemistry and temperature, but we will retain the idea that the ratio on the left hand side will behave as a nearly constant value as the carbon inventories of the ocean and atmosphere change. Taking the ratio of initial and final states of the ocean/atmosphere and rearranging, we get the approximation

$$\frac{p\text{CO}_{2_{\text{final}}}}{p\text{CO}_{2_{\text{initial}}}} = \frac{\text{HCO}_{3_{\text{final}}}^-}{\text{HCO}_{3_{\text{initial}}}^-} \frac{\text{CO}_{3_{\text{initial}}}^=}{\text{CO}_{3_{\text{final}}}^=}$$

where the constants have canceled, and where we now replace concentrations of bicarbonate and carbonate with global inventories, which we denote by dropping the brackets. Equilibrium with CaCO_3 (the neutralization reaction) tends to restore $\text{CO}_3^=$ to

close to its initial (equilibrium) value, reducing the final factor on the right hand side to near 1. This leaves atmospheric $p\text{CO}_2$ to scale with the bicarbonate inventory of the ocean squared. We make a final approximation, that the relative increase in ocean bicarbonate should be about the same as the relative increase in total carbon in the ocean, since bicarbonate is the dominant form of carbon while the second most important form, carbonate ion, is held constant. This leaves us with the approximate relation

$$\frac{p\text{CO}_2_{\text{final}}}{p\text{CO}_2_{\text{initial}}} = \frac{\left(\text{CO}_{2\text{ocean}} + 2 \text{CO}_{2\text{ff}} \right)^2}{\text{CO}_{2\text{ocean}}^2}$$

where the final total CO_2 inventory of the ocean is approximated as the initial value plus twice the fossil fuel CO_2 release; the factor of two is due to the nearly 1:1 reaction of CO_2 with CaCO_3 , which releases additional carbon to the ocean. For the A22 scenario, the initial total CO_2 inventory is 38,400 Gton C, the fossil fuel release is 3,028, and the predicted equilibrium $p\text{CO}_2$ is 34% higher than the initial value (compared with 37% observed in the full model), accounting for 6.7% of the fossil fuel release (compared with 7.6% observed in the full model). We conclude that the residual CO_2 left in the atmosphere after complete reaction with CaCO_3 is a straightforward result of equilibrium chemistry of inorganic carbon. This result is therefore likely to be relatively robust and model independent.

The atmospheric residual will be buffered by the silicate rock cycle, which would tend toward equilibrium between CO_2 consumption associated with weathering of basic components of silicate rocks such as CaO , and the reverse of this reaction, metamorphic decarbonation and volcanic degassing of CO_2 [Walker *et al.*, 1981; Berner *et al.*, 1983]. This mechanism is thought to stabilize atmospheric CO_2 on a time frame of several hundred thousand years. The long time frame for this mechanism, relative to the glacial / interglacial cycles, raises the question of what value for atmospheric CO_2 is required to achieve balance between weathering and metamorphism. The question is complicated by fluctuations in both atmospheric CO_2 and presumably in silicate weathering associated with the climate cycles, but presumably the true equilibrium CO_2 value is somewhere between the glacial and interglacial values.

The 7-8% atmospheric residual of the fossil fuel CO_2 would, according to our current understanding, raise the baseline atmospheric CO_2 concentration, for a period of several hundred thousands years. This long tail on the fossil fuel CO_2 forcing of climate may well be more significant to the future glacial/interglacial time scale evolution of Earth's climate than will the brief period of greater intensity warming, since its duration is greater than a glacial cycle. The end result of a 3,000 Gton fossil fuel release (scenario A22) will be an atmospheric $p\text{CO}_2$ value of approximately 400 ppm. This represents an increase in the direct radiative forcing from CO_2 , relative to the preanthropogenic concentration of 280 ppm, that is as large as the CO_2 direct radiative forcing change on the glacial termination (from 200 ppm).

Sensitivity to CaCO_3 Dissolution Kinetics

Dissolution of CaCO_3 in the laboratory has been shown to exhibit a non-linear dependence on the undersaturation of the solution, attributed to dissolution as the sum of a range of elementary reactions (CaCO_3 reacting by itself to produce $\text{Ca}^{2+} + \text{CO}_3^-$, or reactions coupled with H^+ or H_2CO_3) and a range of types of crystal sites (corner and defect sites as opposed to flat surface sites) [Berner and Morse, 1974]. A dissolution

order, n , of 4.5 has been observed in the laboratory by Keir [1980], and has been assumed by *in situ* dissolution rate studies [Archer *et al.*, 1989; Berelson *et al.*, 1990; Cai, 1992], although the dissolution order is difficult to constrain using the range of saturation conditions found in the deep sea [Hales *et al.*, 1993]. Recently, Hales [1995] has argued that first-order rate kinetics ($n=1$) may be more appropriate for *in situ* conditions. Hales finds that the range of rate constant values, k , inferred from his *in situ* data spans nearly 3 orders of magnitude, while the same data can be fit using $n=1$ with only 1 order of magnitude variation, using k values between 0.1 and 0.01 % day⁻¹.

The effect of higher order dissolution kinetics is to increase the sensitivity of the dissolution rate to the degree of undersaturation as undersaturation becomes more extreme. Within the diffusive pore water medium, the effects of the dissolution rate constant are more difficult to predict, because the differences in the microscopic rate law may be compensated for by changes in the diffusion/reaction steady state pore water concentration profiles. In any case, we expect that the differences between the two formulations may become pronounced during the extreme acidification of the ocean after fossil fuel uptake. For the deep sea, undersaturation values (expressed as $\Delta\text{CO}_3 = [\text{CO}_3^{2-}] - [\text{CO}_3^{2-}]_{\text{saturation}}$) as low as -40 $\mu\text{mol kg}^{-1}$ are observed in the deep Pacific, but calcite is generally completely depleted from these sediments; the range of ΔCO_3 across the lysocline is of order 20-30 $\mu\text{mol kg}^{-1}$ in ΔCO_3 . Across this range in undersaturation, the difference between 1.0 and 4.5 order kinetic rate laws may be rather subtle. In contrast, the deep sea $[\text{CO}_3^{2-}]$ suddenly decreases 60 $\mu\text{mol kg}^{-1}$ following a large fossil fuel CO_2 release (Figure 8), in contact with sediments where CaCO_3 has not yet been depleted. Under these conditions, the two kinetic rate laws may make differ significantly in their neutralization and CaCO_3 compensation responses.

The comparison between linear and non-linear CaCO_3 dissolution kinetics required first spinning up the model to a steady state using linear dissolution kinetics in the sediments. We found that simply changing the dissolution order and rate constant to linear kinetics consistently underrepresented the inventory of CaCO_3 in surface sediments (Figure 11). This becomes significant as CaCO_3 is depleted from surface sediments; the lower inventory decreases the dissolution flux, obscuring the differences between the two kinetics formulations. Linear kinetics generate a lower CaCO_3 inventory when everything else is equal because the lysocline tends to be sharper using linear kinetics. For a given weathering rate (which determines the area of high- CaCO_3 sediments where most of the CaCO_3 burial occurs) there is a smaller area of moderate- CaCO_3 concentration sediments to contribute to the CaCO_3 inventory using linear kinetics; CaCO_3 concentration tends to be more focused into areas of high accumulation. Varying the dissolution rate constant, k , had the effect in the steady state of changing the saturation state of the whole ocean (represented in Figure 11 by the alkalinity inventory), without much of a change in the bioturbated layer CaCO_3 inventory, which is determined by the global burial rate. In other words, the rate constant affects the ΔCO_3 of the lysocline without changing the thickness of the transition zone very much. We found that to reproduce both the alkalinity and the CaCO_3 inventories of the non-linear model, we were forced to increase the weathering rate from 0.145 Gton C yr⁻¹ to 0.175 Gton C yr⁻¹, thus increasing the global burial rate of CaCO_3 . However, the global burial rate is not known to this precision, so that the contrast in burial rates cannot be construed as an argument either for or against linear kinetics.

A comparison of the global burial rate of CaCO_3 is presented as deviations from the initial steady state value in Figure 12. We see that for $n=1$ and $k=10^{-3}$ day⁻¹ (the fast linear

model), the results are indistinguishable from the results using $n=4.5$ and $k=1 \text{ day}^{-1}$ (the nonlinear model). This is also true for the slow nonlinear model ($n=4.5$ and $k=0.1 \text{ day}^{-1}$). However, when $n=1$ and $k=10^{-4} \text{ day}^{-1}$ (the slow linear model), the initial spike in dissolution intensity is attenuated, but the long-term trend in dissolution converges on the time trend of the other models. The CO_2 histories of the three models are shown in Figure 12b, and again we find relatively minor differences. The slow nonlinear model lags in the uptake of fossil fuel CO_2 by about 10 ppm throughout the simulation, which the pCO_2 of the fast linear model is consistently about 5 ppm lower than the nonlinear model (largely an offset due to the difference in steady state initial conditions). The formulation of the kinetic rate law has surprisingly little effect on the neutralization of fossil fuel CO_2 , except for the magnitude of the dissolution spike immediately following invasion for the slow linear model, and interestingly, only the linear model is sensitive even in this time period. The dynamics of the dissolution spike are explored below.

Analysis and Discussion

A Phase Diagram for CaCO_3 Compensation

Anthropogenic CO_2 can be viewed as a perturbation of two natural cycles of carbon on the surface of the earth: CaCO_3 compensation in the ocean and the silicate rock weathering / volcanic degassing balance [Walker *et al.*, 1981; Berner *et al.*, 1983]. The interaction of the CO_2 perturbation with these natural cycles is controlled by the dynamics of the system, which we undertake to analyze here. These dynamics will also eventually apply to our understanding of carbon cycle rearrangements corresponding to the glacial interglacial transitions.

The response of the model to fossil fuel invasion is a relaxation toward a new steady state condition. An analogy can be drawn to the dissolution of a solid material in a beaker in the lab. The kinetics of this system are described by rate equations, which will require at least two pieces of information, the extent of disequilibrium (in this case a property of the solution), and the quantity of the solid phase reactant (or more precisely the surface area). We will characterize the dynamics of the ocean/sediment model by ignoring spatial heterogeneity and reducing the complex three dimensional calcite saturation state (defined by the deviation of $\text{CO}_3^{=}$ from saturation, CO_3) and % CaCO_3 fields to single values. These values will be the concentration of $\text{CO}_3^{=}$ from a single arbitrary location in the western equatorial Pacific (170°W , 1.25°S , 2000 m) representing the saturation state, and the global inventory of CaCO_3 in the sediment bioturbated layer, representing the surface area of substrate. By reducing the state of the ocean to these two variables, we are assuming that the ocean state associated with a given value of one of these variables is single valued; i.e. that a single pair of numbers is all that is required to describe the carbon cycle in the ocean. Of course, the state of the ocean cannot be exactly represented by these two variables alone. But as we will show, this approximation simplifies our interpretation of the behavior of the model as a dynamical system. Also, we shall see that the limitations of this approach are themselves revealing of the dynamics of the model.

These two state variables for the ocean carbonate system correspond to reservoirs for carbonate with fluxes between them. The reservoirs are the $[\text{CO}_3^{=}]$ of the ocean, determined by the alkalinity and CO_2 , and the inventory of sea floor CaCO_3 available for dissolution (Figure 13). The input to the system is weathering, which transfers alkalinity to the ocean. Output consists of the imbalance between the rain rate of CaCO_3 to the sea floor and the sea floor dissolution flux, which we will call the "accumulation" rate of CaCO_3 (the middle arrow in Figure 13). Finally, CaCO_3 is effectively removed from the

system as it escapes the potential reach of sea floor dissolution. The final removal of sediment from the ocean system will be called "burial", the bottom arrow in Figure 13. Because the burial rate is defined relative to the deepest possible reach of chemical erosion, its value can never be negative, since by definition CaCO_3 below the erodable depth can never be redissolved. The rate of burial as defined here is determined by the accumulation rate of non- CaCO_3 material on the sea floor multiplied by the concentration of CaCO_3 at the erodable depth.

Stages of the Neutralization Process

The differential equation describing ocean $[\text{CO}_3^{=}]$ is

$$\frac{d[\text{CO}_3^{=}]}{dt} = \beta \times [\text{weathering} - \text{accumulation}] - \gamma \times \text{CO}_2 \text{ invasion} \quad (1)$$

where β and γ represent buffering of ocean $[\text{CO}_3^{=}]$ by the reaction with dissolved CO_2 . These coefficients are nonlinear functions of the concentrations of $\text{CO}_3^{=}$, HCO_3^- , and CO_2 , but are always positive; so that an excess of weathering over accumulation always drives an increase in ocean $[\text{CO}_3^{=}]$, CO_2 invasion always decreases ocean $[\text{CO}_3^{=}]$, and a balance between weathering and accumulation, in the absence of CO_2 invasion, is the steady state. Beyond this, the complexity intrinsic to β and γ need not concern us here.

The equation for the bioturbated layer CaCO_3 inventory is

$$\frac{d(\text{erodable } \text{CaCO}_3)}{dt} = \text{accumulation} - \text{burial} \quad (2)$$

where accumulation is defined as the net sedimentation rate, which can be negative indicating chemical erosion, and burial is the rate at which CaCO_3 crosses the erodable depth and becomes unavailable for chemical erosion, a flux which by definition can never be negative. We leave a detailed characterization of these fluxes, in particular the accumulation flux, to a next section, but for the time being it is instructive to derive numerically the steady state conditions for these two variables, where the input and output fluxes balance and the time derivatives equal zero.

The steady state condition for the erodable CaCO_3 inventory (equation 2) is the condition of local balance in the budget for CaCO_3 in the sediment mixed layer, where at each model grid point

$$\text{CaCO}_3 \text{ Rain} = \text{Dissolution} + \text{Burial}$$

For any distribution of $[\text{CO}_3^{=}]$, there is a concentration field of CaCO_3 on the sea floor which satisfies this condition. Because the equilibrium condition can be calculated locally, this steady state condition will hereafter be called local lysocline equilibrium. The set of local lysocline equilibrium states can be described by a line on a deep Pacific $[\text{CO}_3^{=}]$ / bioturbated layer CaCO_3 phase plot (Figure 14a). This line was calculated by (1) adjusting the $[\text{CO}_3^{=}]$ of the deep sea by imposing a homogeneous offset to the total CO_2 of the water

column, then (2) calculating the steady state concentration of CaCO_3 by iteration [Archer, 1990] as the model chemistry spun up over 1,000 years. The resulting inventory of CaCO_3 was tallied and plotted against the corresponding value of deep Pacific $[\text{CO}_3^{=}]$, to make up the steady lysocline line in Figure 14a. To the right of the steady lysocline line, the inventory of CaCO_3 is smaller than the steady state value, implying that *erodable* $\text{CaCO}_3 / t > 0$. To the left, the erodable CaCO_3 is declining.

The global steady state of the model balances input of $[\text{CO}_3^{=}]$ to the ocean from continental weathering against removal by CaCO_3 accumulation on the sea floor (equation 1). This condition was also found by acceleration. For each of the steady lysocline experiments described above, after the distribution of CaCO_3 was calculated at some value of deep Pacific $[\text{CO}_3^{=}]$, the concentration of $[\text{CO}_3^{=}]$ was increased iteratively over a relaxation time of 1,000 years, until the global accumulation rate balanced the weathering rate. In contrast to local lysocline equilibrium, the weathering = accumulation steady state is a global condition, and for this reason this state will be referred to as global throughput steady state. For any value of the CaCO_3 inventory there is a corresponding value of ocean $[\text{CO}_3^{=}]$ at which global throughput steady state will obtain, so that global throughput steady state also describes a line on the deep Pacific $[\text{CO}_3^{=}] / \text{bioturbated layer } \text{CaCO}_3$ phase plot (Figure 14b). The trend of this line is toward increasing deep Pacific $[\text{CO}_3^{=}]$ with increasing bioturbated CaCO_3 inventory (a positive slope). This is a somewhat counterintuitive result; one might have expected that more CaCO_3 on the sea floor would tend to increase CaCO_3 accumulation, requiring a lower $[\text{CO}_3^{=}]$ to compensate. The observed behavior of the model can be understood as follows. The steady state requires that input from weathering, which is held constant in the model, balance the rain of CaCO_3 to the sea floor, which is also held constant, minus sea floor CaCO_3 dissolution, which is predicted by the model. Throughput balance is therefore determined entirely by the dissolution flux, which increases with increasing CaCO_3 inventory on the sea floor. As the CaCO_3 inventory increases, a higher value of $[\text{CO}_3^{=}]$ (lesser undersaturation) is required to maintain the requisite dissolution flux. The steady throughput line exhibits positive slope as does the steady lysocline line, but a much steeper slope. The steady throughput line describes the state $[\text{CO}_3^{=}] / t = 0$; area to the left of the line has a positive growth, and area to the right negative.

The division of the phase plane (Figure 14c) into four quadrants determines the behavior of the dynamical system shown in Figure 13. The signs of d/dt for both state variables of the system are indicated in Figure 14. In region "A", the sediment inventory tends to decrease while the ocean $[\text{CO}_3^{=}]$ tends to increase. The opposite situation is found in region "C". In this region, a transfer of carbon between the sediment and the ocean will act to satisfy the requirements of both reservoirs; the evolution of both reservoirs are "complementary" with each other. In the case of excess dissolution (region A), we have already named this response sea floor neutralization. The response time of sea floor neutralization is relatively fast because the accumulation rate, the middle arrow in Figure 13, is limited only by the kinetics of CaCO_3 diagenesis. The weathering rate is held fixed and constant, and burial, the flux of CaCO_3 across the erodable line, is by definition non-negative. In contrast, the accumulation rate flux is free to exceed weathering or to reach negative values. Sea floor neutralization can be envisioned as an internal transfer of $\text{CO}_3^{=}$ within the ocean / sediment system, unbounded by the weathering and burial fluxes.

In the "incomplementary" regions of the phase space, regions "B" and "D", both the ocean and the sediment evolve in the same direction; in the case of fossil fuel neutralization, both await replenishment by the excess of weathering over burial (terrestrial neutralization). In this regime, the steady accumulation flux can be no greater than the weathering influx,

nor smaller than the burial flux (which is limited to non-negative values). The accumulation flux is therefore less dynamic in this case than it was when the model was in one of the complementary regions of the phase plot (A and C). Sea floor CaCO_3 no longer contributes to the neutralization of fossil fuel CO_2 . For this reason, model evolution in this regime is slower than in the complementary regimes. The transition of the model into the incomplementary regime at around the year 10k is the reason for the increase in e-folding time scale for CaCO_3 burial after this time in Figure 10b. By 10k, the alkalinity of the ocean has increased to 60-75% of its final (fully neutralized) value (Figure 15). Most of this increase corresponds to the decrease in erodable CaCO_3 inventory on the sea floor, leaving only a small role for terrestrial CaCO_3 through this time.

The directions of model evolution in the complementary quadrants in phase space tends to drive the model toward the incomplementary regions, which serve as dynamical attractors for the model state (Figure 14c). This is demonstrated by the model trajectories in Figure 14d. Once the model reaches one of the incomplementary regions, it slowly evolves back to the model starting point (the full steady state condition). As it does so, it veers to the left, toward the steady throughput line, indicating that the model achieves steady throughput (nearly steady ocean $[\text{CO}_3^-]$) while the lysocline lags behind.

The relationship of model behavior with the two equilibrium conditions is summarized in Figure 16, which relates the global accumulation rate of CaCO_3 to deep ocean $[\text{CO}_3^-]$ and bioturbated layer CaCO_3 inventory in three dimensional space and in three two dimensional projections. The global throughput equilibrium condition (green cubes) can be seen to satisfy the constraint that accumulation = weathering, while the local lysocline equilibrium (red spheres) does not satisfy this condition except where it intersects the global throughput equilibrium line. The model trajectories intersect the equilibrium conditions in three-space, supporting our contention that the equilibrium conditions (which were determined independently of the model trajectories) are relevant to the evolution of the model state. And finally, symmetry of the model evolution is demonstrated by a mirror image B scenario which removed CO_2 rather than releasing it, which traces a complementary path to B.

Control of the CaCO_3 Accumulation Rate

We have seen that the behavior of the model is determined by the rates of addition and removal of CO_3 from the ocean and surface sedimentary reservoirs, and the response of those rates to the fossil fuel perturbation. In particular, the accumulation flux of CaCO_3 on the sea floor dominates the fast sea floor neutralization response in the 5 kyr or so of the model runs. Previous estimates of the CaCO_3 compensation time scale [Boyle, 1983; Broecker and Peng, 1987; Sundquist, 1990; Walker and Kasting, 1992] differed in part because of differences in the presumed sensitivity of the global CaCO_3 accumulation rate to ocean acidification. In this section we characterize the global CaCO_3^- accumulation rate of the model as a function of CO_3 and the bioturbated CaCO_3 inventory, for use in (1) understanding the model results and (2) for use in simpler parameterized models of CaCO_3 compensation. Because we are parameterizing the dissolution flux as a function of deep Pacific $[\text{CO}_3^-]$ and bioturbated layer CaCO_3 , we refer to these as the parametric model experiments.

The CaCO_3 distribution on the sea floor ought to resemble a natural model state, so we adjusted the bioturbated CaCO_3 inventory of the model by adjusting the water column $[\text{CO}_3^-]$ (a homogeneous perturbation of water column total CO_2), spinning up, and then calculating the steady state CaCO_3 distribution. Following this, we again perturbed the

water column $[\text{CO}_3^{=}]$. A sample result from one of these model experiments (the standard distribution of CaCO_3 and a homogeneous addition of $100 \mu\text{M CO}_2$) is shown in Figure 17. During spin-up, $[\text{CO}_3^{=}]$ increases somewhat and the bioturbated layer CaCO_3 inventory decreases, as the model begins to neutralize the added CO_2 . Dissolution intensity reaches an intense maximum (a minimum in CaCO_3 burial) directly after the CO_2 addition and stabilizes at lower values after 1,000 years. At this time the model is out of steady state (by design), but the accumulation rate is relatively stable with respect to the current values of $\text{CO}_3^{=}$ and CaCO_3 .

Summarizing results of many such model runs, the steady (1000 yr) CaCO_3 accumulation rates in Table 3 were empirically fit to yield the equation

$$\begin{aligned} \text{Accumulation} = & 3.12542 \cdot 10^{-3} \text{ Gton C yr}^{-1} (\mu\text{mol kg}^{-1})^{-1} \cdot [\text{CO}_3^{=}] \\ & - 8.25096 \cdot 10^{-4} \text{ Gton C yr}^{-1} (\text{Gton C})^{-1} \cdot \text{CaCO}_3 \\ & + 9.06625 \cdot 10^{-6} \text{ Gton C yr}^{-1} (\text{Gton C } \mu\text{mol kg}^{-1})^{-1} \cdot [\text{CO}_3^{=}] \cdot \text{CaCO}_3 \\ & - 8.626211 \cdot 10^{-2} \text{ Gton C yr}^{-1} \end{aligned}$$

with a fit to the individual model results shown in Figure 18.

The accumulation fluxes expected from the model evolution of $\text{CO}_3^{=}$ and bioturbated CaCO_3 inventory are compared with the actual model values in Figure 19. It can be seen that the empirically predicted accumulation rate corresponds well except for a significant spike in dissolution immediately following the fossil fuel invasion. Similar behavior was observed in the parametric model runs, a simple example of which was shown in Figure 17. The magnitude of the transitional dissolution spike was calculated by subtracting the model accumulation rate from the empirical prediction, in Figure 19(b). Both the magnitude and the decay time of the transient dissolution spike correspond well to the initial spike of dissolution from the model run in Figure 17.

This observation motivates a closer inspection of the transient behavior of the parametric model run in Figure 17. Over 1000 years following the homogeneous addition of CO_2 , the dissolution flux decreased more than can be explained by the changing values of $\text{CO}_3^{=}$ or bioturbated CaCO_3 inventory. This behavior was caused by a rearrangement of the distribution of $\text{CO}_3^{=}$ in the water column, by a process analogous to the formation of a whole-ocean boundary layer, caused by surface / deep fractionation of alkalinity in the ocean analogous to the biological pump. The global production rate of CaCO_3 in the model is approximately $1.6 \text{ Gton C yr}^{-1}$. Most of this CaCO_3 redissolves in the water column or at the sea floor, concentrating alkalinity in the deep waters. The dissolution flux from the sediments reached $0.5 \text{ Gton C yr}^{-1}$, which acts as an added source of alkalinity to the deep waters comparable to the flux attributable to the biological pump. Over the course of the 1,000 year circulation time of the ocean, the alkalinity of deep waters increased until a balance between dissolution and deep ocean circulation was reached. This relaxation is analogous to the formation of a whole ocean boundary layer. Profiles of ocean alkalinity during the dissolution spike and 500 years later are shown in Figure 20. The highest $[\text{CO}_3^{=}]$ blanket regions of high % CaCO_3 on the sea floor. In the IPCC model runs, the transient dissolution spike is responsible for 50% of the dissolution flux to year 3000, and roughly 10% of the flux to the year 40k. This transient dissolution spike is the only case

where the approximation of the ocean carbonate system as representable by two simple variables, deep Pacific $[\text{CO}_3^-]$ and bioturbated layer CaCO_3 inventory, breaks down.

Summary

According to our current understanding, CO_2 uptake by rock cycles of the earth will be slow, with no significant impact on the pCO_2 of the atmosphere for the next thousand years. The net terrestrial emission calculated to meet an IPCC atmospheric stabilization scenario (s750) is only a few percent higher when CaCO_3 is included in the model simulation, which is negligible compared with uncertainties in biospheric uptake or other aspects of the ocean carbon cycle. Direct ocean injection experiments demonstrate a coupling between dissolution and ocean circulation, as CaCO_3 dissolution proceeds somewhat more rapidly for atmospheric and Atlantic injection cases than for Pacific injection. However, CaCO_3 dissolution will play only a minor role in determining the fate of fossil fuel CO_2 in the coming millennium.

On longer time scales, neutralization of fossil fuel CO_2 by the oceans and by CaCO_3 takes five stages. (1) Invasion of fossil fuel into the oceans will sequester 70-80% of the net terrestrial CO_2 release on an e-folding time scale of 200-450 years depending on the magnitude of the fossil fuel release. (2) A fast sea floor dissolution spike after CO_2 dissolves in the oceans but before alkalinity has a chance to reorganize accounts for half of the neutralization in the coming millennium, and 10% of the total CaCO_3 dissolution in response to fossil fuel CO_2 . Beginning in this stage, mankind will have reversed the sedimentation rate of the ocean, by dissolving CaCO_3 faster than it is deposited on the sea floor; this is projected to peak by the year AD 3000 and last up to 5000 years. (3) Steady sea floor dissolution continues until the lysocline reaches local equilibrium with the water column saturation state, by about the year AD 10,000. Sea floor neutralization overall accounts for 60-70% of the fossil fuel CO_2 , and has an e-folding time scale of 5-6 kyr. (4) Terrestrial weathering replenishes ocean $[\text{CO}_3^-]$ on a time scale of 8 kyr after AD 10,000, and restores the lysocline to its original depth on a time scale of 18 kyr. Completion of this stage leaves 7-8% of the fossil fuel CO_2 remaining in the atmosphere in a new local and global CaCO_3 steady state. (5) Neutralization by the silicate rock cycle (not included in the model) restores atmospheric CO_2 to some unknown "set point", at which metamorphic decarbonation balances silicate weathering, with a time constant of several hundred thousand years.

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Tables

Table 1. Cumulative CO₂ emissions for model runs driven by extended-IPCC emission scenerios.

Scenario	CO ₂ Release, Gton C
B	874
A	1506
A22	3028
A23	4550
B Mirror	-878

Table 2. Summary of ocean effects in the model analyses of the extended-IPCC emission scenarios.

	B	A	A22	A23
Initial alkalinity Gton C equivalents ¹	40510	40510	40510	40510
Initial CO ₂ inventory Gton C	38400	38400	38400	38400
Initial erodable CaCO ₃ Gton C ²	1570	1570	1570	1570
Initial pCO ₂	310	310	310	310
Invasion , yr ³	212	255	365	453
Invasion final pCO ₂ ⁴	394	463	685	995
Invasion CO ₂ uptake ⁵	80.7%	79.6%	75.1%	69.7%
Sea floor neut. , yr (<AD 10,000) ⁶	5480	5490	5870	6810
Sea floor neut. pCO ₂	355	390	497	661
Sea floor neut. CO ₂ uptake ⁵	9.0%	9.8%	12.5%	14.8%
Sea floor neut. final alkalinity ¹	41611	42337	43831	44761
Sea floor neut. erodable CaCO ₃ ²	1230	975	424	129
Terr. weat. ⁷			8260	
Equilibrium ⁸ pCO ₂	343	366	425	489
Equil. ⁸ CO ₂ uptake	2.9%	3.2%	4.8%	7.6%
Equil. ⁸ alkalinity ¹	42015	43060	45588	48104
Equil. ⁸ CO ₂ atm. residual ⁵	7.5%	7.4%	7.6%	7.9%

¹The ocean inventory of alkalinity, scaled to be directly comparable to carbon inventories. The scaling factor is 12 g eq.⁻¹.

²Expressed in mass of C, not CaCO₃, for direct comparison with other carbon inventories.

³Determined by linear regression of ln[pCO₂(t) - pCO₂(final)] vs. time, for a time interval 2250 < t < 3000 A.D.

⁴Final pCO₂ of the model neglecting CaCO₃.

⁵Expressed as percentage of the released CO₂

⁶Determined by linear regression of the log of approach to the full effect of CaCO₃ on pCO₂, vs. time as defined in the caption to Figure 7b. Regression was performed on model results from 2000 < t < 10000. Final pCO₂ values for the CaCO₃ experiments are taken from the equilibrium results (8).

⁷Same as (6) but over time interval from 10,000 < t < 40,000. Model results for the A22 scenario only.

⁸Determined by acceleration of the model to steady state where weathering is balanced by burial and the lysocline is in local equilibrium with the water column saturation horizon.

Table 3. Results of the dissolution flux parameterization experiments. Ocean $[\text{CO}_3^{2-}]$ and sea floor CaCO_3 inventories were perturbed independently of each other. The steady model CaCO_3 accumulation rate is taken to be the flux 1100 years after the perturbation, as a function of the $[\text{CO}_3^{2-}]$ and CaCO_3 values at that time.

Deep Pacific $[\text{CO}_3^{2-}]$ μM	Bioturbated Layer CaCO_3 Inventory, Gton C	Global CaCO_3 Burial Rate, Gton C yr^{-1}
86.4	1298	0.113
79.1	1244	0.031
72.0	1187	-0.053
65.2	1130	-0.135
58.8	1072	-0.215
52.6	1015	-0.289
47.0	958	-0.359
87.0	834	0.144
78.4	763	0.073
70.2	699	0.000
60.3	662	-0.053
52.7	613	-0.109
45.8	565	-0.161
39.5	522	-0.205
85.3	440	0.170
76.5	382	0.099
67.1	330	0.049
58.5	318	0.011
50.2	284	-0.028
42.9	252	-0.061
36.3	225	-0.087
85.0	245	0.178
75.7	185	0.117
66.1	135	0.068
58.8	139	0.043
50.1	117	0.017
42.3	102	0.000
35.6	90	-0.015

Figure Captions

1. Model steady state. (a) Organic Carbon export production, mol m⁻² yr⁻¹. (b) CaCO₃ export production, mol m⁻² yr⁻¹. (c) Sediment %CaCO₃, g / g dry solid. (d) Sediment CaCO₃ mass accumulation rate, g cm⁻² kyr⁻¹.
2. (a) Atmospheric pCO₂ specified by IPCC for a case (s750) where atmospheric CO₂ approaches a stable concentration of 750 ppm, offset by 33 μatm because of the higher than observed model preanthropogenic pCO₂. (b) Calculated net terrestrial emission of CO₂ to match the s750 atmospheric concentration, for both the CaCO₃ and the no-CaCO₃ models (which are indistinguishable from each other in the graph). (c) and (d) The difference between the calculated emissions using the CaCO₃ and no-CaCO₃ models, in Gton C (c) and as a percent of net terrestrial emission (d). The kink at AD. 2250 is the transition to a constant atmospheric CO₂ specified by the s750 scenario.
3. The calculated atmospheric response to a direct ocean disposal of 25% of the net terrestrial emission derived from IPCC scenario A to the year 2100, both with and without CaCO₃. CO₂ is injected directly to two grid points, located at 3000 meters depth, in the Atlantic (17.5° W, 36.25° N, 3000 m depth) and Pacific (152.5° E, 31.25° N, 3000 m depth) oceans.
4. Impulse injection experiment results, comparing the effects of the location of the injection and the presence or absence of CaCO₃ in the model. Ten gigatons of CO₂ is injected into a steady state ocean (no rising atmospheric value) in the Atlantic or the Pacific oceans, both with and without CaCO₃, and into the atmosphere (which is equivalent to a 4.96 μatm step-increase in atmospheric CO₂ concentration) with CaCO₃ dissolution.
5. (a) Time series of atmospheric CO₂ concentration imposed on the model. Scenarios A, A22, and A23 stop their CO₂ release at the year 2100, 2200, and 2300 respectively. (b) Cumulative net terrestrial CO₂ release for the four scenarios.
6. Model response to anthropogenic CO₂ release to the year AD 10,000, including the effect of CaCO₃ (solid line), and neglecting CaCO₃ (dashed line). pCO₂ is held to IPCC projections for scenarios A and B to the year 2100, and extrapolated to the years 2200 and 2300 at the scenario A year 2100 emission rate, for runs B, A, A22, and A23, respectively. After those times, a zero net terrestrial release of CO₂ is specified.
7. (a) The e-folding time for invasion of CO₂ into the oceans can be estimated from the slope of the log of the model pCO₂ (in μatm) for the case of no CaCO₃ dissolution (model - initial) vs. time. The time scale is indicated to be order 250-400 years, longer for higher CO₂ release scenarios. (b) The time scale for the effect of CaCO₃ on the pCO₂ of the atmosphere can be estimated from the slope of the log of the difference between the model runs with and without CaCO₃ vs. time, pCO₂, defined as

$$pCO_2 = \left(pCO_{2_{withCaCO_3}} - pCO_{2_{CaCO_3,final}} \right) - \left(pCO_{2_{noCaCO_3}} - pCO_{2_{noCaCO_3,final}} \right)$$

This time scale appears to be about 5000 years, and relatively independent of the CO₂ release magnitude.

8. Model response to the year AD 10,000 of (a) deep Pacific $[\text{CO}_3^{=}]$. (b) Alkalinity of the deep Pacific ocean. (c) Global accumulation rate of CaCO_3 ; negative values denote net erosion. (d) Inventory of CaCO_3 within the bioturbated layer on the sea floor. (e) Inventory of CaCO_3 within the potential reach of chemical erosion on the sea floor.

9. Model results of (a) atmospheric pCO_2 , (b) CaCO_3 accumulation rates, and (c) CaCO_3 inventories for the A22 emission scenario integrated to the year AD 40000. .

10. (a) E-folding time scales of the return to a balance between weathering and burial of CaCO_3 , for the A22 scenario. Slope of curves from AD 2000 to AD 10000 indicates time scales of 5480-6810 yr (see Table 2). (b) Return to weathering / burial steady state over 40 kyr of model time, A22 scenario. The relaxation time scale slows to 8260 yr after the year AD 10,000. (c) The time scale for restoration of the equilibrium depth of the lysocline is 18.1 kyr, from the 40 kyr A22 model results, based on the log of the bioturbated layer CaCO_3 inventory relative to the initial value.

11. Steady model states generated in an effort to tune the model for linear dissolution kinetics. Equilibrium model dependence of alkalinity and CaCO_3 inventories on weathering rate ($= 0.145 \text{ Gton C yr}^{-1}$ for open symbols and $= 0.175 \text{ Gton C yr}^{-1}$ for filled symbols). Circles are the linear rate law model with rate coefficients ranging from $3 \cdot 10^{-5}$ to $1 \cdot 10^{-3} \text{ d}^{-1}$ as indicated. Diamonds are 4.5 order rate law (Nonlinear) model with rate coefficients of 1 and 0.1 d^{-1} as indicated. Square is a data-based estimate from the real ocean.

12. (a) CaCO_3 burial anomaly (deviation from steady state value) and (b) atmospheric pCO_2 , a comparison between linear (first order) vs. nonlinear (4.5 order), and fast vs. slow dissolution kinetics. Rate constants are: Nonlin, 1.0 d^{-1} ; Nonlin Slow, 0.1 d^{-1} ; Linear, $1 \cdot 10^{-3} \text{ d}^{-1}$; Linear Slow, $1 \cdot 10^{-4} \text{ d}^{-1}$. Weathering rates are $0.145 \text{ Gton C yr}^{-1}$ for Nonlin models and $0.175 \text{ Gton C yr}^{-1}$ for Linear models.

13. Fossil fuel neutralization can be conceptualized as a perturbation to the system of weathering, CaCO_3 accumulation (defined as the instantaneous difference between CaCO_3 deposition and dissolution) and burial (defined as the permanent removal of CaCO_3 from the potential reach of chemical erosion; i.e. the flux of CaCO_3 past the erodable line in the sediments, defined in text).

14. (a) Steady state concentration of CaCO_3 at each grid point on the sea floor as a function of $[\text{CO}_3^{=}]$ at an arbitrary location in the Pacific Ocean (170°W , 1.25°S , 2000 m). Above this "steady lysocline" line, the CaCO_3 decreases with time, and below it increases. Vertical axis is the global inventory of CaCO_3 in the bioturbated layer. (b) Deep Pacific $[\text{CO}_3^{=}]$ at which the ocean CaCO_3 accumulation rate balances the terrestrial weathering rate, as a function of the CaCO_3 inventory results of part (a). To the left of this "steady throughput" line ocean $[\text{CO}_3^{=}]$ increases, to the right it decreases. (c) Time dependent behavior of both variables, $[\text{CO}_3^{=}]$ and CaCO_3 , from (a) and (b) tends to drive the model state toward one of the regions B and D. The full model steady state is given by the intersection of the steady lysocline and the steady throughput lines. (d) Model behavior for the IPCC B, A, A22, and A23 scenarios (see Table 1). Circles mark millennia. Simulations started in steady state, and all went to 10 kyr except for the A22 scenario, which went to 40 kyr, long enough to return to show the behavior of the return toward steady state. The "B Mirror" scenario is merely the opposite of the "B" scenario, with a CO_2 draw down flux that mirrors the CO_2 release flux of the B scenario.

15. (a) Inventory of dissolvable CaCO_3 on the sea floor. Dashed lines represent estimates of the total available inventories of CaCO_3 . Circles are amounts of sea floor CaCO_3 dissolved as a function of fossil fuel CO_2 release.

(b) (Circles) The fraction of neutralization of the model by the year 10,000, determined as the increase in model alkalinity relative to the difference between the initial and the fully neutralized state (calculated as explained in text; results in Table 2). (Squares) The increase in ocean alkalinity in the year 10,000 which corresponds to the decrease in erodable layer CaCO_3 inventory relative to the initial condition. The heavy line would be the result dissolving the entire 1800 Gton C erodable inventory of CaCO_3 on the sea floor (maximum neutralization). The figure shows that (1) sea floor neutralization accounts for most of the ocean alkalinity increase before year 10,000, but (2) sea floor CaCO_3 is unable to neutralize the entire net terrestrial CO_2 release, even when the CO_2 release is smaller than the "potentially erodable" CaCO_3 inventory. The reason for this limitation is explained in the text and in Figure 14.

16. The two variables which largely determine the global accumulation rate of CaCO_3 , deep ocean $[\text{CO}_3^-]$ and the bioturbated layer CaCO_3 inventory, are plotted against the model CaCO_3 burial rate response. Spheres and the red line represent synchrony between the calcite lysocline and the water column saturation state (the steady lysocline regime). Cubes and the green line represent the state of weathering / burial steady state for CaCO_3 (the steady throughput regime). Time dependent response to CO_2 invasion is shown as multicolored lines, with model time indicated by the color scale, which resets to zero every 10kyr for the 40 kyr A22 scenario run. Initial invasion of CO_2 depletes deep ocean $[\text{CO}_3^-]$, which is subsequently replenished as mixed layer CaCO_3 is depleted. Once the model trajectory intersects the steady lysocline line, neutralization of CO_2 by chemical erosion ceases. Symmetry of the model response is shown by removing CO_2 from the atmosphere in a mirror image to scenario B, which traces a complementary path to B.

17. The results of adding 100 μM CO_2 , homogeneously, to the water column of the model, in year 100 of the simulation. (a) Time trace of deep Pacific $[\text{CO}_3^-]$, (b) bioturbated CaCO_3 inventory, and (c) model CaCO_3 accumulation rate. The accumulation rate "spikes" immediately following the acidification, and decreases thereafter to a steady value. It appears that the decreasing dissolution flux over the next 1000 years is not simply a product of changes in deep Pacific $[\text{CO}_3^-]$ (a) or bioturbated layer CaCO_3 (b).

18. Comparison of the steady dissolution flux results from experiments such as shown in Figure 11, with a parameterized empirical function for dissolution as a function of deep Pacific $[\text{CO}_3^-]$ and bioturbated layer CaCO_3 inventory.

19. A comparison of the full time-dependent model results (A22) against predictions of the dissolution flux as a function of the time evolving values of deep Pacific $[\text{CO}_3^-]$ and bioturbated layer CaCO_3 inventory. The parameterized function describes the time evolution of the model well, except that it underestimates the magnitude of the time dependent model dissolution flux in the millennium following CO_2 release. (b) Detail of the first 5000 years of the experiment; same comparison as (a) but also showing the dissolution spike, defined as the difference between the time dependent model results and the parameterized function values. The time scale for decay of the dissolution spike resembles the behavior of the model to a homogeneous perturbation (Figure 11).

20. A comparison of profiles of CO_3^- immediately following and 500 years after a homogeneous addition of CO_2 to the water column. From 120°E, 0°N.

