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Simple ocean carbon cycle models

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for submission to the proceedings of the
Snowmass Global Change Institute on the Global Carbon Cycle

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Abstract

Simple ocean carbon cycle models can be used to calculate the rate at which the oceans are likely to absorb CO₂ from the atmosphere. For problems involving steady-state ocean circulation, well calibrated ocean models produce results that are very similar to results obtained using general circulation models. Hence, simple ocean carbon cycle models may be appropriate for use in studies in which the time or expense of running large scale general circulation models would be prohibitive. Simple ocean models have the advantage of being based on a small number of explicit assumptions. The simplicity of these ocean models facilitates the understanding of model results.

Introduction

Homo sapiens has been significantly perturbing the global carbon cycle for the past several hundred years. We have been taking ancient organic carbon from subterranean environments and modern organic carbon from terrestrial ecosystems, oxidizing it, and injecting the resulting CO₂ into the atmosphere. Not all of this CO₂ remains in the atmosphere. Some of it is absorbed by the oceans, and some is probably absorbed by terrestrial ecosystems (Siegenthaler and Sarmiento, 1993). A major focus of ocean carbon cycle modelers has been to try to develop models that will lead to more accurate predictions of the rate at which anthropogenic carbon dioxide has been and will be absorbed by the oceans.

The residence time in the atmosphere/biosphere/ocean system of most chemical species of importance to the global carbon cycle gas is greater than 10³ years (Broecker and Peng, 1982). Hence, on the decadal to century time scale, natural changes in atmospheric CO₂ concentration generally reflect a redistribution of carbon among atmosphere, biosphere, and ocean reservoirs, and not a change in the total amount of carbon in those reservoirs taken as a whole. The anthropogenic perturbation to the global carbon cycle can be divided into two classes. The first, the burning of fossil fuels,

involves adding carbon to Earth's surficial reservoirs. The second, the reduction of biomass associated with land use changes, involves a redistribution of carbon among those reservoirs. With the anthropogenic addition and redistribution of carbon, the atmosphere, biosphere and oceans are perturbed away from their steady-state condition. Barring further perturbation, the atmosphere, ocean, and biosphere will probably tend towards some new steady-state.

Simple ocean carbon cycle models are constructed to reflect the interaction between the atmospheric and oceanic components of the global carbon cycle. These models have been used to predict possible new steady-states of the coupled atmosphere/ocean system, and the transient approach to that steady state. However, accurate prediction of past or future changes on the decadal to century time scale requires a coupled atmosphere/biosphere/ocean carbon cycle model. However, the biospheric component of the Earth's carbon cycle is discussed elsewhere in this volume (ref?), and is outside the scope of this paper.

Box models

The standard approach to modeling the global carbon cycle and its oceanic component has been the multi-box mass exchange method (Revelle and Suess, 1957; Bolin and Eriksson, 1959; Broecker et al., 1971; Machta, 1973; Hoffert, 1974; Keeling, 1973, 1977; Bacastow and Keeling, 1973, 1977). Transient multi-box formulations are intuitively appealing for finding the time-variation of the mass (N_i) of carbon, carbon isotopes, nutrients or other oceanic tracers in each of a number of well-mixed carbon cycle reservoirs in response to a specified source or sink term (S_i).

Box models normally assume first-order transport kinetics in which the outflux from box i to some adjacent box j is $k_{ij} N_i$ leading to reservoir differential equations of the form

$$\frac{d N_i}{dt} = \sum_{j=1}^n (\kappa_{ji} N_j - \kappa_{ij} N_i) + S_i \quad (1)$$

where n is the number of boxes. The exchange coefficients κ_{ij} have inverse time units and are normally calibrated to recover the observed distribution of carbon-isotopes and other tracers among the various ocean reservoirs in steady state ($d N_i/dt = 0$). (Before the availability of simulated three-dimensional internal ocean currents from numerical ocean circulation models, there were no data sets representing advective, diffusive, and convective fields in the global ocean.) In practice, it is often more convenient to work with concentrations rather than masses of tracers. These two forms are mathematically equivalent.

Any of the models presented here (see Table 1) can be used in at least two modes, depending on whether the atmospheric CO_2 concentration is considered part of the model, or whether that concentration is considered an upper boundary condition for the ocean model. In the forward calculations, when we are computing the effect of anthropogenic CO_2 releases, the change in atmospheric CO_2 mass is computed as the sum of fossil fuel and net biosphere CO_2 emissions, less the net CO_2 absorption from the oceans. In the inverse calculation, when we are determining what CO_2 emissions would be consistent with attaining specified atmospheric CO_2 concentration targets, the permissible fossil fuel emissions would be the change in atmospheric CO_2 mass plus the rate of net CO_2 absorption by the oceans less the net emission of CO_2 by the biosphere.

The simplicity of box-ocean carbon cycle models is deceptive. As we will discuss here, critical features of the ocean carbon cycle, including chemical buffering by the surface oceans, the subjective choice of how to disaggregate the ocean into subreservoirs (Table 1), the transition from continuous versus discrete formulations, and the calibration of empirical exchange coefficients, are fraught with pitfalls. Some of these are well-understood, other uncertainties remain.

A one-box ocean carbon cycle model

Before we look at how simple models calculate a response of the global carbon cycle to atmospheric CO₂ perturbations, we will look at what controlled the pre-industrial state of ocean chemistry.

In the long-term (>10⁵ yr) carbon cycle, the atmospheric CO₂ concentration is thought to be controlled by relations among geologic CO₂ degassing, silicate-rock weathering and atmospheric CO₂ concentration (Walker et al, 1981). The chemical weathering of silicate rocks supplies Ca²⁺ to the oceans. Most of that Ca²⁺ is eventually deposited as CaCO₃ (= CaO•CO₂) on the continental shelves or the ocean floor. In this way, each mole of Ca²⁺ weathered out of silicate rocks generally results in a mole of CO₂ sequestered in marine sediments. The silicate-rock weathering rate is thought to be positively correlated with atmospheric CO₂ content. This creates a negative feedback loop whereby atmospheric CO₂ adjusts such that the Ca²⁺ (and Mg²⁺) flux to the oceans derived from silicate-rock weathering balances the CO₂ degassing flux from the mantle and metamorphism. (A study of the long-term fate of anthropogenic CO₂ emissions involving these processes in a multi-box ocean model can be found in Walker and Kasting, 1992).

Perhaps the simplest model of the ocean carbon cycle is a one-box model, in which the entire ocean is considered to be a single well-mixed reservoir. Such an approach was taken by Berner et al. (1983) in their model of the long-term (>10⁵ yr) carbon cycle.

In the natural carbon cycle, unperturbed by human induced CO₂ emissions, the primary source of carbon to the oceans and atmosphere comes from volcanoes, mid-ocean-ridges, CO₂-rich hot springs, and the weathering of carbonate rocks and sedimentary organic carbon. Most of this carbon is subsequently sequestered in sediments as carbonate rock and organic carbon. In the model of Berner et al (1983), ocean calcium and carbon concentrations adjust to satisfy two conditions: (1) the partial pressure of CO₂ (*p*CO₂) in the surface ocean approaches the value determined by

considerations involving silicate-rock weathering and CO₂ degassing rates; and (2) calcite sedimentation balances sources of calcium and carbon to the ocean.

The ocean is approximately saturated with respect to calcite (CaCO₃). Berner et al (1983) reasoned that as the saturation state with respect to calcite increases, so would the rate of calcite sedimentation, and this would draw down the oceanic reservoir of calcium and dissolved CO₂. They schematically wrote this reaction as:

and parameterized the rate of calcite deposition as a function of the degree of disequilibrium of this reaction. This simple one-box ocean carbon-cycle model can give insight into factors controlling ocean chemistry on long time scales. It highlights that the long-term chemistry of the oceans, including factors such as ocean pH and the concentration of total dissolved carbon, is largely determined by the atmospheric CO₂ concentration, the rate at which rivers transport dissolved chemicals to the oceans, and the dissolution and/or precipitation of calcite.

A one-box model incorporates the assumption that the ocean can be treated as a well mixed reservoir. However, the ocean exhibits significant inhomogeneity with respect to dissolved concentrations of carbon, carbon isotopes, alkalinity, phosphate, nitrate, oxygen, cadmium, temperature, salinity, and many other tracer fields. A one-box model cannot reproduce the time-dependent structure of the response of the carbon cycle to the anthropogenic CO₂ perturbation, because the time scale of the perturbation is short relative to the ocean mixing time scale (~1000 yr).

After several centuries, interactions with ocean sediments become an important factor affecting atmospheric CO₂ content (Sundquist, 199x); hence, to obtain relatively precise results for predictions many centuries into the future, ocean and atmosphere models must consider interactions involving marine sediments. However, for most problems relating to the carbon cycle on the decadal to century time scale, the atmosphere, biosphere, and ocean may be considered jointly as a closed system.

A two-box ocean carbon cycle model

Ocean carbon pumps

The concentration of carbon is greater in the deep ocean than in the surface ocean. This is primarily due to two factors: the "biological pump" and the "solubility pump" (Volk and Hoffert, 1985).

The surface ocean provides the primary base of the marine food chain, because phytoplankton can grow only where there is sufficient light. Irradiance in seawater diminishes with depth on a length scale of some tens of meters (Parsons et al., 1984), so below the base of the ocean's surface mixed-layer, there is little photosynthesis. Some of the organic carbon generated in the mixed-layer falls through the base of the mixed-layer and is oxidized into CO_2 deeper in the ocean. Thus, biological production at the ocean's surface provides a CO_2 source to the deep ocean. This "biological pump" tends to make the deep ocean CO_2 rich relative to the surface ocean.

CO_2 is more soluble in cold water than in warm water. Cold water is also more dense than warm water of the same salinity. Hence, cold sinking water tends to have a higher total dissolved CO_2 concentration than warm buoyant water. This "solubility pump" tends to make the deep ocean CO_2 rich relative to the surface ocean.

The biological pump and the solubility pumps tend to produce a gradient in total dissolved CO_2 , with concentration increasing with depth. In steady-state, the upward and downward fluxes of carbon must balance; the balancing upward flux of carbon is provided by large-scale ocean mixing processes, which tend to return carbon to the surface ocean where the total dissolved carbon concentration is lower. In many simple models (e.g., Oeschger et al., 1975), this large-scale mixing is represented as a diffusive process. Hence, the ocean can be conceptualized as a system in which the biological and solubility pumps establish a surface-to-deep carbon gradient; this gradient is limited by the back diffusion of total dissolved CO_2 .

Fundamental two-box ocean model equations

The simplest model of the ocean that can represent the difference between surface and deep total dissolved inorganic carbon concentrations is a two-box ocean model (Fig. 1). In such a model, typically, the ocean is divided into two well mixed compartments, a surface ocean and a deep ocean, with some mixing flux specified between the two compartments. The equation for the time rate of change of total dissolved inorganic carbon in the surface-box, C_s , can be represented

$$M_s \frac{dC_s}{dt} = F_{\text{mix}} (C_d - C_s) - F_{\text{bio}}^C - F_{\text{sol}} + F_{\text{gasex}}, \quad (3)$$

where M_s is the mass of the surface ocean ($= \sim 3.6 \times 10^{19}$ kg for a 100 m layer), F_{mix} represents a mass mixing flux between the surface and deep boxes, C_d is the concentration of total dissolved inorganic carbon in the deep-ocean box, F_{bio}^C is the flux of carbon to the deep ocean produced by the biological pump, F_{sol} is the flux of carbon to the deep ocean produced by the solubility pump, and F_{gasex} represents the net flux of CO_2 into the oceans due to gas exchange with the atmosphere. A corresponding equation for the surface ocean can be written

$$M_d \frac{dC_d}{dt} = F_{\text{mix}} (C_s - C_d) + F_{\text{bio}}^C + F_{\text{sol}} \quad (3)$$

where M_d is the mass of the deep ocean ($= \sim 1.3 \times 10^{21}$ kg).

This simple model can yield some insight into the distribution of carbon in the ocean. For example, in steady-state we can set equation (2) equal to zero, and see that

$$C_d - C_s = \frac{F_{\text{bio}}^C + F_{\text{sol}}}{F_{\text{mix}}}, \quad (4)$$

i.e., the surface-to-deep carbon concentration difference is enhanced by more vigorous biological or solubility pumps, and is diminished by stronger ocean mixing.

A perturbation approach

If we make the assumptions that (1) the pre-industrial ocean was in steady-state, (2) ocean mixing, and the biological and solubility pumps, are unaffected by the change in atmospheric CO_2 in the industrial age, and (3) there was no net CO_2 flux into the oceans

(i.e., $F_{\text{gasex}} = 0$) in the pre-industrial state, we can develop a perturbation model corresponding to this two-box ocean model.

We can define, two new variables, ΔC_d and ΔC_s , representing the perturbation to their steady-state values, i.e.,

$$C_d = \Delta C_d + C_{d,0} \quad (5)$$

and

$$C_s = \Delta C_s + C_{s,0}, \quad (6)$$

where the subscript 0 indicates a steady-state value. Substituting equations (5) and (6) into equations (3) and (4) with the assumptions stated above, and subtracting the steady-state solution, yields the equations

$$M_d \frac{d \Delta C_d}{dt} = F_{\text{mix}} (\Delta C_s - \Delta C_d) \quad (7)$$

and

$$M_m \frac{d \Delta C_s}{dt} = F_{\text{mix}} (\Delta C_d - \Delta C_s) + F_{\text{gasex}}. \quad (8)$$

Note that, under these assumptions, the biological and solubility pumps "drop out" of the solution to the perturbation equations. This principal is utilized in many simple ocean models (e.g., Oeschger et al, 1975), as well as general circulation models (e.g., Sarmiento et al, 1992, Maier-Reimer and Hasselmann, 1987), to perform carbon cycle calculations without explicitly modeling ocean biology or the steady-state distribution of carbon in the oceans.

Because one of our primary interests is the absorption by the oceans of CO_2 injected into the atmosphere in the course of human activities, we need some way to estimate F_{gasex} , the net flux of CO_2 into the oceans due to gas exchange with the atmosphere. CO_2 fluxes into the ocean are typically modeled as some gas exchange coefficient (k_{gasex}) times the partial pressure of CO_2 in the atmosphere (P_{atm}) less the partial pressure of CO_2 in the ocean (P_{ocean}):

$$F_{\text{gasex}} = k_{\text{gasex}} (P_{\text{atm}} - P_{\text{ocean}}). \quad (9)$$

In steady-state, in this sort of two-box model, $P_{\text{atm}} = P_{\text{ocean}}$ and $F_{\text{gasex}} = 0$. In keeping with our perturbation approach, we can define variables ΔP_{atm} and ΔP_{ocean} , which correspond to the perturbation to the atmospheric and surface ocean partial pressures of CO_2 respectively. Furthermore, we can relate ΔP_{ocean} to ΔC_d , via a factor B:

$$\Delta P_{\text{ocean}} = B \Delta C_s, \quad (10)$$

i.e., in this simple model we will assume that a perturbation in the surface total dissolved CO_2 concentration is linearly related to a change in surface ocean $p\text{CO}_2$. Because the partial pressure of mixed-layer CO_2 is a non-linear function of total inorganic carbon concentration, this assumption is valid only for small changes in atmospheric CO_2 content (see Maier-Reimer and Hasselmann, 1987).

Many simple modes utilize a concept known as the buffer factor (ζ) to express the fractional change in the partial pressure of CO_2 in the mixed-layer ($p\text{CO}_2$) in relation to a fractional change in mixed-layer total dissolved inorganic carbon (ΣCO_2):

$$\zeta = \frac{\Delta p\text{CO}_2 / p\text{CO}_2}{\Delta [\Sigma\text{CO}_2] / [\Sigma\text{CO}_2]}. \quad (11)$$

The value B in equation (10) is equivalent to ζ times ΔC_s divided by P_{ocean} . From table (1), we can calculate that, in this case, the buffer factor ($\zeta = (75.1/279)/(48/1937)$) takes on a value of ~ 10.9 when calculated as a move from the pre-industrial steady-state to the present-day state. On the other hand, when calculated in the opposite direction, going from the present-day state to the pre-industrial state, the buffer factor ($\zeta = (75.1/354.1)/(48/1985)$) takes on a value of ~ 8.8 . This little example shows that even within the CO_2 changes experienced over the past several hundred years, the assumption of a constant buffer factor can introduce errors on the order of 10% or more. More advanced parameterizations (e.g., Sarmiento et al., 1992) make the buffer factor depend on the change in surface-ocean concentration of total dissolved inorganic carbon.

If we add an equation for the change of mass of CO_2 in the atmosphere, such as

$$M_{\text{atm}} \frac{d P_{\text{atm}}}{d t} = F_{\text{human}} - F_{\text{gasex}} \quad (12)$$

(where M_{atm} is the molar mass of the atmosphere, F_{human} is the flux of CO_2 into the atmosphere brought on by human activity, and net fluxes of CO_2 into the terrestrial biosphere are ignored!) this linear system is soluble analytically for the decay of a unit pulse of CO_2 into the atmosphere. Unfortunately, the result is an algebraically unwieldy.

From Table 2, we can see that a 2.47% change in total dissolved carbon concentration corresponds to a 26.9% change in atmospheric $p\text{CO}_2$. This corresponds to a value for B of 1.6 ppm/($\mu\text{mol kg}^{-1}$). Maier-Reimer and Hasselmann (1987) computed, using an ocean GCM, that the longest time scale for the absorption of CO_2 by the oceans was about 360 yr. If we take a 360 yr turnover time for the deep ocean as a representative number, then $F_{\text{mix}} = M_d/360 \text{ yr} = \sim 3.6 \times 10^{18} \text{ kg yr}^{-1}$. Net gas exchange between the surface and deep oceans is on the order of 0.06 mol C $\text{m}^{-2} \text{ yr}^{-1}$ per ppm difference in the partial pressure of CO_2 in the atmosphere and surface ocean (cf. Maier Reimer and Hasselmann, 1987). This corresponds to a value of $\sim 2.1 \times 10^{13} \text{ mol C yr}^{-1} \text{ ppm}^{-1}$ for k_{gasex} . Setting the molar volume of the atmosphere equal to $1.8 \times 10^{20} \text{ mol}$ permits the computation of the response of this two box model to a unit impulse of CO_2 (Fig. 2). The results of this calculation, compared with those of Maier-Reimer and Hasselmann (1987), are shown in Figure 1. The two box-model underestimates the uptake of CO_2 by the oceans in the first 100 years because the mixing time scales between the surface ocean and ocean thermocline waters is shorter than the mixing-time scale between the surface ocean and the deep ocean in its entirety. Nevertheless, this calculation demonstrates that even a model as simple as this two box perturbation model can capture some of the basic features of CO_2 absorption by the oceans. The ocean's initially absorb a pulse on a rapid time scale associated with the equilibration of the surface ocean waters with the atmosphere. Then the absorption process is dominated by slower process of transporting carbon from the surface ocean to the deep ocean.

The assumptions that ocean circulation, and the biological and solubility pumps, remain unchanged in a higher CO_2 world allowed these pumps to be ignored in this

perturbation calculation. However, if global warming were to significantly change ocean circulation, these assumption might no longer be valid.

A Simple Biological Carbon Flux Model

This two box model can be used to demonstrate how the biological pump may be explicitly modeled. The flux of biogenic matter from the surface-to-deep ocean alters the oceanic carbon, nutrient, oxygen and alkalinity fields. In such models, phosphate is typically taken to be the nutrient limiting biological productivity (e.g., Broecker and Peng, 1982), although nitrate (Fasham et al., 1993), iron (Martin, 1991), or zooplankton grazing (Fasham et al, 1993) may also limit productivity in the surface ocean.

In order to calculate the effect of changes in biological export from the mixed-layer might have on the carbon cycle, this export must be linked to the carbon cycle. This is typically done through a concept known as "Redfield ratios" (Redfield et al., 1963; Broecker and Peng, 1982). The proportions of carbon, alkalinity, phosphate, and nitrate in the organic matter transported out of the base of the mixed-layer are approximately constant throughout the world ocean. The ratios of silica and carbonate minerals to the organic constituents are more highly variable, as upwelling zones tend to be dominated by siliceous diatoms, whereas carbonate secreting organisms tend to dominate in more oligotrophic regions. Redfield ratios express the proportions of elements in the biogenic flux of matter transported out of the base of the mixed-layer.

The ratios of carbon-to-phosphate ($R_{C:P}$) and alkalinity-to-phosphate ($R_{Alk:P}$) in the detrital "rain" out of the mixed-layer has classically been taken to be 132.5 and 38, respectively. (This assumes that 80% of the detrital rain is composed of organic matter and that 20% is composed of calcite and aragonite.) The phosphate and carbon cycles are then linked by assuming

$$F_{bio}^C = R_{C:P} F_{bio}^P \quad (13)$$

Changes in marine biological productivity would affect the surface alkalinity concentration. Since this will have an impact on the partial pressure of CO_2 in the

surface waters, and thereby affect the atmospheric CO₂ concentration, the alkalinity field must be calculated to properly estimate the distribution of carbon in the ocean and atmosphere. Equations for alkalinity parallel the equations for carbon, except that there is no exchange in the atmosphere, and alkalinity transport in the detrital rain is the product of R_{Alk:P} and F_{bio}^P.

The equations for the time rate of change of the surface phosphate concentration (P_s) may be written

$$M_s \frac{d P_s}{d t} = F_{mix} (P_d - P_s) - F_{bio}^P \quad (14)$$

and the deep-ocean phosphate concentration (P_d) may be calculated by assuming a constant total ocean phosphate reservoir (P_{tot}).

$$P_{tot} = M_s P_s + M_d P_d \quad (15)$$

In the simplest form of such models, surface phosphate concentrations are taken to be constant, and the F_{bio}^P is calculated to maintain a constant concentration (e.g., Toggweiler and Sarmiento, 1984). In the next level of complexity, F_{bio}^P may be taken to be an increasing function of phosphate concentration. The simplest such statement would be

$$F_{bio}^P = k_{bio} P_s, \quad (16)$$

where k_{bio} is a constant relating biological export from the mixed-layer to mixed-layer phosphate concentration. More complicated formulation may involve Michaelis-Menton kinetics (e.g., Maier Reimer, 1993) or represent ecosystem structure (Fasham et al, 1993).

With equations (14) to (16), it can be shown that in steady-state, the fraction of nutrients imported into the mixed-layer that gets exported as biological detritus (f = F_{bio}^P/(F_{mix} P_d)) is

$$f = \frac{k_{bio}}{F_{mix} + k_{bio}}, \quad (17)$$

In this model, as ocean mixing slows, the difference between surface and deep phosphate concentration gets larger. With slower ocean mixing rates, the residence time for water in the mixed-layer is greater, and, hence, nutrients might be expected to be stripped more

efficiently from the mixed-layer. Consequently, surface-ocean nutrient utilization may become more efficient at slower ocean mixing rates.

Carbonate Chemistry

Once we are concerning ourselves with changing biological productivity and alkalinity, a constant buffer factor is no longer an acceptable approximation. Typically, at this point, we would have to consider some carbonate chemistry.

The concentration of total dissolved inorganic carbon (ΣCO_2) is

$$[\Sigma\text{CO}_2] = [\text{CO}_2] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]. \quad (18)$$

The concentration of total alkalinity (ΣAlk) is the sum of the charge concentration of all of the negative ions in the ocean for compounds that can easily change their charge (i.e., the weakly dissociated acids):

$$[\Sigma\text{Alk}] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{H}^+] + \dots \quad (19)$$

Because the oceans are electrically neutral, this quantity is equivalent to the sum of the positive charge of all of the ions in the ocean that cannot easily change their charge:

$$[\Sigma\text{Alk}] = [\text{Na}^+] - [\text{Cl}^-] + 2 [\text{Ca}^{2+}] + 2 [\text{Mg}^{2+}] - 2 [\text{SO}_4^{2-}] + \dots \quad (20)$$

That part of total alkalinity (ΣAlk) that whose charge is balanced by inorganic carbon species is known as carbon alkalinity (Alk_C). The concentration of carbon alkalinity is equal to the sum of the concentration of negative charge associated with dissolved inorganic carbon species:

$$[\text{Alk}_\text{C}] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}]. \quad (21)$$

The speciation of all of the ions that can easily change charge adjusts such that they balance the charge required by the ions that cannot easily change their charge. This coupled with conservation of mass for each element, and the equilibrium constants for each reaction, determines the speciation of the various compounds in the ocean.

The basic reactions involving the dissolution and speciation of carbon in the oceans are (see Stumm and Morgan, 1981).

This simplest form of carbonate chemistry is to consider only dissociation reactions involving HCO_3^- and CO_3^{2-} , and ignores the relatively minor contribution from CO_2 and H_2CO_3 (Broecker and Peng, 1982). When dissolved CO_2 and H_2CO_3 are neglected, the partitioning of dissolved inorganic carbon into carbonate and bicarbonate ions can be solved as a simple linear function of dissolved carbon and carbon alkalinity concentrations. These relations, with the rate constants as specified in Broecker and Peng (1982) are useful for demonstrating the basic behavior of the response of CO_2 partial pressure to changes in temperature, alkalinity, and ΣCO_2 concentration.

Some basic behaviors common to the Broecker and Peng simplification and more elaborate carbonate chemistry models are:

1. Higher total dissolved inorganic carbon concentration $\rightarrow$
higher CO_2 partial pressure.
2. Lower alkalinity concentration $\rightarrow$ higher CO_2 partial pressure.
3. Warmer water $\rightarrow$ higher CO_2 partial pressure.

Marine biological productivity tends to diminish both the inorganic carbon and alkalinity concentrations of the surface ocean waters. However, the diminution of inorganic carbon concentration has a large effect on the $p\text{CO}_2$ in the surface ocean; hence, enhanced biological productivity would tend to diminish the partial pressure of CO_2 in the surface ocean.

Improved accuracy can be gained by considering the sum of the concentrations of CO_2 and H_2CO_3 , in addition to the concentrations of HCO_3^- , CO_3^{2-} . This turns the solution of the chemical speciation problem into a quadratic equation, and considerably improves accuracy of the calculation. However, this solution of the system is still

inaccurate for large CO₂ perturbations because it neglects the role of borate in the absorption of CO₂ by the oceans.

Boric acid dissociates according to the following schematic reaction.

The dissolution of CO₂ in the oceans primarily occurs by two avenues. The first, which involves reactions (22) and (23) going to the right, with (24) going to the left, is equivalent to

This results in no change to carbon alkalinity, because now the negative charge on one CO₃²⁻ ion is distributed among two HCO₃⁻ ions. The second main avenue for the CO₂ to dissolve in the oceans involves reactions (22) and (23) going to the right, with (26) going to the left; this is equivalent to

This net reaction increases carbon alkalinity, at the expense of borate alkalinity, i.e., in this reaction negative charge is transferred from dissolved borate to dissolved carbon. Near present-day atmospheric CO₂ concentrations, approximately two-thirds of the dissolving CO₂ dissolves by equation (27) and one-third by reaction (28). If reaction (k+6) is not considered, calculated changes in CO₂ partial pressure may be off by 30%.

Many carbon cycle modelers use the calculation methods described in Peng et al. (1987). The algorithm presented in this paper includes the minor contributions from the dissociation of species containing Si and P, and considers changes in salinity, pressure, and temperature.

One consequence of carbonate buffering of the surface oceans is that it is difficult to measure the direct uptake of carbon by the oceans. The small percentage change in ocean total dissolved inorganic carbon concentration at any location is masked by natural variability. For this reason ocean carbon cycle models calibrated on other tracers have

been employed to estimate the historical and projected future stable carbon uptake rates by the oceans.

N-box ocean carbon cycle models

Three box models

Cold CO₂-rich water penetrates to the deep ocean, where as warm CO₂-depleted water tends to stay near the surface. This tends to diminish the ΣCO_2 concentration in the surface ocean. To represent this "solubility pump" (Volk and Hoffert, 1985), at least two surface boxes are necessary (Fig. 3). The solubility pump plays a role in the three-box models of Toggweiler and Sarmiento (1985), Knox and McElroy (1984), and Siegenthaler and Wenk (1984). In these models, there are warm and cold surface boxes, and a deep-water box. Instead of including a term explicitly specifying the strength of the solubility pump, as was done for the two-box model developed above, these models calculate the solubility of CO₂ in each of the surface boxes as a function of temperature. The solubility of CO₂ in the surface boxes affects the CO₂ fluxes between the atmosphere and surface ocean boxes, and, hence, the concentration of CO₂ in the surface boxes. In these models, the cold surface box tends to have a greater total dissolved CO₂ concentration than the warm surface box. Furthermore, in these models, the cold surface box is specified as being the primary locus of deep-water formation. Hence, the higher solubility of CO₂ in the cold surface box tends to increase the total dissolved CO₂ concentration in the deep ocean box.

Many-box models

Most organic carbon that falls out of the mixed-layer is oxidized in the upper km of the ocean, whereas most carbonate carbon dissolves in the bottom km of the ocean. This consideration suggests the possible division of subsurface waters into an intermediate-water box and a deep-water box (Volk and Liu, 1988; Caldeira and Rampino, 1993). The

inclusion of an intermediate water box permits four-box models to capture features such as the oxygen concentration minimum, a phosphate maximum, and so on.

The desire to represent individual ocean basins and or water masses has led researchers to add even more boxes into simple ocean models constructed along the lines outlined above. Notable efforts in this area have been made by Broecker and Peng (1987; Fig. 4) and Keir (1988, 1989).

The Box-Diffusion Model

On decadal to century timescales the infusion of anthropogenic CO₂ into the ocean may be primarily due to small scale vertical transport in eddies, and not the large scale ocean circulation. This suggests a pure diffusion approach to a perturbation model: Assume that the anthropogenic diffuses into the ocean

A notable perturbation ocean carbon cycle model is the box-diffusion model (Oeschger et al., 1975; Fig. 5). This model represents the ocean as a vertical column of boxes, with neighboring boxes exchanging water parcels at a specified rate. The governing equations for this model, with a finite number of vertical boxes, can be stated in the form of equation (1). However, in the limit of a large number of boxes, the governing equation for the box-diffusion model becomes

$$\frac{d \Delta C}{d t} = \frac{d}{d z} \left(k \frac{d \Delta C}{d z} \right), \quad (28)$$

where z is depth in meters and ΔC is generally the perturbation to the carbon concentration. At the bottom boundary there is a zero-flux boundary condition. At the surface boundary the flux of carbon into the ocean is specified much as the net gas flux into the ocean was specified in the one-box model.

The box-diffusion carbon cycle model of Oeschger et al. (1975) was a major step demonstrating this relationship between discrete multilayer ocean box models and continuous pure diffusion models. When the ocean is modeled by a vertical stack of boxes (or layers) of constant thickness Δz , the net mass exchange between interior layers

and their top and bottom neighbors is purely diffusive if the exchange coefficient between adjacent layers is a constant. In that case the effective eddy diffusivity is $k = \kappa \Delta z^2$, where $\kappa = \kappa_{i,i+1} = \kappa_{i,i-1}$ (see equation 1).

Maier-Reimer and Hasselmann (1987) produced impulse-response functions for the absorption of a CO_2 -pulses of various sizes injected into the atmosphere using a perturbation approach with an ocean general circulation model. They found that the model response was similar to that of the box-diffusion model of Siegenthaler and Oeschger (1978). That this simple model has been shown to absorb atmospheric CO_2 at rates comparable to a much more complicated three-dimensional ocean general circulation model, indicates that a properly calibrated box-diffusion model can be used in applications in it is important to retain moderate accuracy and use a model that is inexpensive to run. A well calibrated box-diffusion model can produce results that are within the uncertainties inherent in ocean general circulation modeling efforts.

Typically, box-diffusion models are calibrated using ^{14}C . There are two basic ways of doing this: one is to try to reproduce the steady-state distribution (or inventory) in the ocean of ^{14}C produced by natural processes in the atmosphere; the other is to try to reproduce, as a function of time, the distribution (or inventory) in the ocean of ^{14}C produced during atmospheric atomic bomb tests. Unfortunately, the diffusion coefficients are not the same for the two different calibration methods. Box-diffusion models calibrated using natural ^{14}C absorb CO_2 more slowly than box-diffusion models calibrated using bomb ^{14}C . Natural ^{14}C has been penetrating into the oceans for as long as there have been oceans, whereas bomb ^{14}C has been penetrating into the oceans only for several decades. Hence, it is thought that natural ^{14}C calibrations may represent a mean ocean-mixing rate on long time scales; whereas bomb ^{14}C calibrations may represent the mean ocean-mixing rate in the upper several hundred meters of the ocean, where most of the bomb ^{14}C resides.

General circulation models transport carbon vertically in three (and sometimes four) different ways (Fig. 6). The first way is by advective transport of water masses computed using some form of the Navier-Stokes equations. The second way is by a parameterization of convective overturning. Typically, in ocean general models, if a more dense water mass were to sit in a grid cell above a less dense water mass in the grid cell below, the water in the two grid cells is mixed. This tends to transport the anthropogenic carbon perturbation deeper into the ocean. The third way ocean GCMs transport carbon to the deep ocean is by parameterized sub-grid-scale diffusion between neighboring grid cells. This is modeled as some transfer coefficient times the difference in concentration between the neighboring cells, much as the transfer in neighboring layers is modeled in a box-diffusion model. (The fourth method of carbon transport, included in some ocean GCMs, is the biological transport of carbon. See Maier-Reimer, 1993, and Sarmiento et al, 1993.)

Of these methods of carbon transport, only one (advective transport) is calculated from first principals. All of the other methods of carbon transport are computed using quasi-empirical parameterizations. Hence, it is not terribly surprising that a highly parameterized model such as the box-diffusion model can so closely mimic the CO₂-uptake behavior of oceanic general circulation models.

The Outcrop Diffusion Model

There is considerable vertical density stratification in the ocean. In the ocean, warm water tends to sit above denser, cooler, water. Similarly, less saline water tends to sit above denser, more saline, water. But, largely because of the equator-to-pole surface temperature gradient, there is a surface ocean density gradient. Surface waters are less dense in equatorial regions and more dense near the poles. The ocean's dense deep and bottom waters tend to form in the densest polar regions.

Vertical eddies are damped by vertical density stratification, because buoyancy forces tend to counteract the movement a parcel of water into waters of a different density. In contrast, these forces do little to damp eddies that evolve along surfaces of constant density. Because mixing across surfaces of constant density (diapycnal mixing) is damped, mixing along surfaces of constant density (isopycnal mixing) tends to be much greater. Eddy transport processes in the ocean can be modeled simply as a macroscopic diffusion process, with an effective diffusion coefficient orders of magnitude greater than the value for pure molecular diffusion. Typical isopycnal eddy-diffusion coefficients may be 10^6 times larger than diapycnal eddy-diffusion coefficients. This suggests that it is about as easy for a tracer to diffuse 1000 km along a nearly horizontal isopycnal surface as it would for the tracer to diffuse 1 m in the nearly vertical diapycnal direction.

Because the surface ocean is more dense at the poles than in tropical regions, isopycnal surfaces at depth in the tropics tend to outcrop at the poles. Hence, CO_2 absorbed by the surface ocean in polar regions may be efficiently transported to deeper, more equatorial waters, along surfaces of constant density.

The box-diffusion model effectively has an isopycnal eddy-diffusion coefficient equal to zero, as water at depth is never exposed to the surface. Siegenthaler (1983) bounded the isopycnal mixing problem by studying what would happen in the limiting case with infinitely rapid isopycnal mixing (and a finite diapycnal eddy-diffusion coefficient). (A one-box model calculates the limiting case with infinite isopycnal and diapycnal eddy-diffusion coefficients. Hence, a one-box model, with properly calibrated gas exchange coefficients, calculates the maximum, gas-exchange limited, rate of CO_2 absorption by the oceans.)

Siegenthaler (1983) constructed the "outcrop-diffusion" model in which all deeper layers of the ocean were taken to be in direct contact with the atmosphere (Fig. 7). Transport to these deeper layers through the outcrop regions was limited by gas-exchange; additional carbon was transported to these deeper layers via diffusion

processes as in the box-diffusion model. Even when the vertical exchange coefficients in these two models were tuned to produce the steady-state natural ^{14}C profile, it was found that the two models produce significantly different results when calculating the rate of absorption of anthropogenic CO_2 by the oceans (Fig. 8). As might be expected, the outcrop-diffusion model absorbs CO_2 more readily than the box-diffusion model; and probably absorbs CO_2 faster than the real ocean.

The Upwelling-Diffusion model

Vertical globally averaged concentration profiles for ocean tracers such as carbon, nitrate, phosphate and oxygen show extrema in the first kilometer or so of the deep ocean. Such extrema at intermediate depths cannot be calculated in a one-dimensional pure diffusion model, as pure-diffusion models tend towards constant or linear profiles. This is because the real ocean not only diffuses, but on the mean there is a large scale overturning of the oceans.

Deep-water forms in relatively limited areas in the polar regions, and, in the mean, water tends to upwell outside of the polar regions. (In fact, much of this upwelling is localized in certain coastal and equatorial regions, but this geographic variability cannot be captured in a one-dimensional ocean carbon cycle model.) This fact suggests the construction of a model in which polar water is injected in the base of a one-dimensional column representing the non-polar regions of the global ocean (Fig. 9). This model is very similar to the box-diffusion model, except that, in addition to diffusing, tracers are advected towards the ocean surface. The governing equation for distribution of tracers in this model can be represented (Munk, 1966)

$$\frac{dc}{dt} = \frac{d}{dz} \left(k \frac{dc}{dz} \right) + w \frac{dc}{dz} \quad (29)$$

Calibration of this model using nutrient and other tracer fields suggests an upwelling velocity (w) of 4 m yr^{-1} and a diffusion coefficient (k) on the order of $2000 \text{ m}^2 \text{ yr}^{-1}$ (Hoffert et al., 1981). Other symbols are as in the box-diffusion model. The bottom

boundary condition of this model reflects the composition of newly formed deep water. With the appropriate choice of the composition of newly formed deep water, this model reproduces observed tracer fields reasonably well (e.g., Volk, 1984; Khesghi et al., 1991). This type of model can be calibrated with a constant value for the eddy-diffusion coefficient (k) to do a reasonably good job reproducing both the bomb and natural ^{14}C profiles (Jain et al., 1993), and was used to compute the thermal inertia of the oceans for the 1990 IPCC report. Perhaps, the two greatest objections that can be made to this model are: (1) there is no unique and obvious way to determine the composition of newly formed deep water, and (2) not all newly formed deep water is bottom water; some newly formed deep water leaves the deep-water forming regions at intermediate depth.

A form of upwelling-diffusion model, known as the HILDA model, has been developed by Shaffer (1989) and Siegenthaler and Joos (1992). This model appends two polar water boxes to the classical upwelling diffusion model. In this model, the deep-layers exchange water with the polar deep-water box, so that polar-water effectively enters the ocean at all depths. Furthermore, this feature also mimics some of the properties of isopycnal mixing. When calibrated using a diffusion coefficient that decreases with depth, this model is able to reproduce the vertical profiles of both bomb and natural ^{14}C (Siegenthaler and Joos, 1992).

Convolution models

The ocean models discussed above all explicitly consider some kind of ocean buffer factor and explicitly calculate the change in concentrations of various chemical species. However, there is another type of model that is based on parameterized results of general circulation models (Maier-Reimer, 1987; Harvey, 1989; Wigley, 1991). Maier-Reimer (1987) produced exponential curve fits to the change in atmospheric CO_2 concentration as a function of time for a variety of CO_2 -emission pulse sizes using a perturbation approach with an ocean general circulation model. In the appendix to this paper, for a

variety of emission scenarios, Maier-Reimer compared the full model results with results of a convolution integral calculation.

In a convolution-integral calculation of the ocean carbon cycle, the CO₂ concentration in the atmosphere above the pre-industrial concentration (ΔC), given some CO₂ source flux ($E(t)$), is calculated by computing the integral:

$$\Delta M(t) = \int_0^t E(u) G(t-u) du = \int_0^t E(t-u) G(u) du, \quad (30)$$

where 0 represents the time at some initial condition when $\Delta M = 0$, and $G(t)$ represents the response of the system to a unit impulse of CO₂. The impulse-response function, $G(t)$, is "defined as the CO₂ signal observed in the atmosphere for a δ -function atmospheric input at time $t = 0$ (or equivalently a unit step-function change in the initial atmospheric CO₂ concentration)" (Maier-Reimer and Hasselmann, 1987).

In general, convolution integrals produce accurate results only for nearly linear systems. This modeling approach may be useful for small perturbations in which the linearizing assumption of a constant buffer factor. All of the impulse-response functions calculated by Maier-Reimer and Hasselmann represent injections of CO₂ into a 265 ppm CO₂ atmosphere. Because the response to a CO₂ impulse is a function of the initial condition, no convolution of impulses into a 265 ppm atmosphere will appropriately reflect the behavior of pulse injected into an atmospheric CO₂ content that differs significantly from that value. However, Harvey (1989) and Wigley (1991) have modified the pure impulse-response function calculation to mimic the effects of a changing buffer factor in a way that produces reasonable results for some common CO₂ scenarios.

Offline Ocean General Circulation Tracer Models

One type of model that begins to stretch the notion of a simple ocean carbon cycle model is the offline ocean GCM tracer model (e.g., Maier-Reimer, 1993; Eliason, pers. comm.). First, an ocean GCM is run to a quasi-steady state, and then and the advective,

diffusive and convective fields (and sea-ice and any other fields that may affect gas exchange or tracer transport) computed by the ocean GCM are stored in a data base. Then a model is run that computes gas exchange fluxes, and moves tracers around in the ocean, using the transport fields from the ocean GCM. In this way ocean GCM tracer results are obtained at a fraction of the expense needed to run the full ocean GCM in a dynamic mode. The primary limitation of this approach is that it cannot be used in scenarios in which changes in atmospheric CO₂ affect climate, which in turn affects ocean circulation and, hence, the rate at which the ocean absorbs CO₂ from the atmosphere.

Conclusions and discussions

Why would someone want to use a simple ocean carbon cycle model when complex three-dimensional ocean carbon cycle models such as that of Maier-Reimer (1993) or Sarmiento et al (1992) are available? Simple ocean carbon cycle models, relative to ocean GCMs, are easy to develop, constrain, and test, execute rapidly, and produce understandable output. It is not clear that the added complexity of an ocean GCM produces a better estimate of the rate of CO₂-absorption by the oceans than a well-calibrated simple ocean carbon cycle model. Complex scenarios involving the dynamic coupling of the atmosphere and ocean may need to be simulated using ocean GCMs.

It would be more satisfying if the parameterization in simple ocean models were based on physical principals, instead of calibration to tracer fields. One of the reasons we have some faith in simple ocean carbon cycle models is that their results are generally consistent with ocean GCM results. Ocean GCMs have the satisfying property of being based, in part, on the fundamental physics of fluid motion, but these models too contain quasi-empirical parameterizations of convection and sub-grid-scale eddy-diffusive processes (Schlesinger and Jiang, 1990). Simple ocean carbon cycle models can be constructed to closely mimic the CO₂ uptake behavior of general circulation models (e.g.,

Caldeira and Kasting, 1993), and these models can be used in contexts in which the time and expense associated with general circulation models would be prohibitive.

In a model comparison study, Siegenthaler and Sarmiento (1993) showed that schematic ocean models of the type discussed here predict similar present-day carbon uptake rates to models using the current distributions of three-dimensional ocean circulation models when calibrated to recover the global mean penetration depth of bomb radiocarbon measured by the Geochemical Ocean Sections (GEOSECS) Program. Both simple and more complicated ocean carbon cycle models alike predict recent (1980-1989) oceanic carbon uptake rates in the range 2.0 ± 0.6 Gt C yr⁻¹, when calibrated to the (roughly 1974) global mean bomb-¹⁴C penetration depth measured by GEOSECS (Geochemical Ocean Sections Program) of ~354 m.

Interestingly, balances of the global carbon cycle budget based on ocean model estimated uptake rates have led to increased emphasis on the terrestrial carbon cycle. Current ocean models suggest the oceans absorbed ~140 Gt C since pre-industrial times in addition to the ~160 GtC that has remained in the atmosphere (Sundquist, 1993). The sum of atmospheric and oceanic "sinks" from 1750 to 1990 (~300 Gt C) is less than estimates of carbon "sources" during this time frame. Sundquist's (1993) mean estimates are ~220 Gt C from fossil fuel burning and ~160 Gt C from changes in land use giving a total integrated carbon source of ~380 Gt C. The imbalance, ~80 Gt C, is believed to be larger than the uncertainties, and implies an additional sink in the terrestrial biosphere from increased plant fertilization by higher atmospheric CO₂ and nitrate in the environment. Of course, this conclusion depends on how realistic the oceanic uptake estimates are.

Acknowledgement

This work was performed under the auspices of the U.S. Department of Energy Environmental Sciences Division by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

Table 1. Taxonomy of Ocean Carbon Cycle Models

<p>1. Classical multibox Minimum number of boxes is atmosphere, surface mixed layer deep sea). Single-box ocean fails because downward mixing is limited by thermocline diffusion bottleneck, not gas exchange at the surface.</p>	<p>Revelle and Suess, 1957; Bolin and Eriksson, 1959; Broecker et al., 1971; Machta, 1973; Hoffert, 1974; Keeling, and 1973, 1977; Bacastow and Keeling, 1973 Bjorkstrom, 1979; 1986; Broecker and Peng, 1982</p>
<p>2. High-latitude surface box Attempts to explain $p\text{CO}_2$ variations in icecores though changes in circulation, solubility or biological carbon pumps leveraged by high-latitude gas exchange.</p>	<p>Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984; Knox, F., and M. McElroy, 1984; Volk and Hoffert, 1985; Toggweiler and Sarmiento, 1985; Volk and Liu, 1988.</p>
<p>3. Multiocean multibox Pandora and related models calibrated on tracers to include many physically distinct water mass regimes and process</p>	<p>Broecker and Peng, 1986, 1987; Bjorkstrom, 1986; Kier, 1988, 1989; Walker, 1991; Walker and Kasting, 1992</p>
<p>4. Box-diffusion Vertically-stacked boxes equivalent to pure diffusion finite-difference formulation beneath a well-mixed layer; steady state calibrated on pre-bomb radiocarbon.</p>	<p>Oeschger et al., 1975; Siegenthaler and Oeschger, 1978; Hoffert et al. , 1979; Keeling et al., 1989a,b; Caldeira and Kasting, 1993</p>
<p>5. Outcrop-diffusion Combines diffusion with high-latitude connection to deep sea to simulate isopycnal mixing outcrop.</p>	<p>Siegenthaler, 1983</p>

Table 1 (continued). Taxonomy of Ocean Carbon Cycle Models

6. Upwelling-diffusion and HILDA

Classical deep sea recipes
for temperature and tracers up-
dated by circulation and mixing
connections to polar sea surface
plus surface and high-latitude
mixed layer

Wyrski, 1962; Munk, 1966; Hoffert
et al., 1981; Volk, 1984; Shaffer, 1989;
Khesghi et al., 1991; Siegenthaler
and Joos, 1992; Jain et al., 1993;
Shaffer and Sarmiento, 1994

7. GCM

Transport by three-dimensional
internal current fields, but vertical
mixing input either as subgrid
diffusivity or numerical diffusion;
solutions depend on mixing
assumptions

Sarmiento, 1986;
Maier-Reimer and Hasselmann, 1987;
Toggweiler et al., 1989a,b;
Maier-Reimer and Bacastow, 1990;
Bacastow and Maier-Reimer, 1990;
1992; Sarmiento et al., 1993

8. Convolution integral

A calculational method to estimate
ocean carbon cycle model results
without performing full model
calculation.

Maier-Reimer and Hasselmann, 1987;
Harvey, 1989; Wigley, 1991

TABLE 2. Pre-industrial to present variation in the surface ocean of dissolved inorganic carbon $[\Sigma\text{CO}_2] = [\text{CO}_2] + [\text{CO}_3^{2-}] + [\text{HCO}_3^-]$ computed for constant total alkalinity $[\Sigma\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{H}_2\text{BO}_3^-] + \dots + [\text{OH}^-] - [\text{H}^+] = 2252 \mu\text{eq kg}^{-1}$, $[\Sigma\text{B(OH)}_3] = [\text{B(OH)}_3] + [\text{B(OH)}_4^-]$, water temperature $T_m = 19.2^\circ\text{C}$ and salinity $S = 34.262 \text{‰}$ using the carbonate chemistry equilibrium constants in Peng et al. (1987).

		<u>pre-industrial</u>	<u>present</u>	<u>change</u>	<u>% change</u>
$p\text{CO}_2$	[ppm]	279.0	354.1	75.1	26.9
$[\text{CO}_2]$	$[\mu\text{mol kg}^{-1}]$	9.3	11.8	2.5	26.9
$[\text{CO}_3^{2-}]$	$[\mu\text{mol kg}^{-1}]$	215.8	185.5	- 30.3	- 14.0
$[\text{HCO}_3^-]$	$[\mu\text{mol kg}^{-1}]$	1711.9	1787.7	75.8	4.4
$[\Sigma\text{CO}_2]$	$[\mu\text{mol kg}^{-1}]$	1937.0	1985.0	48.0	2.4
$[\text{B(OH)}_3]$	$[\mu\text{mol kg}^{-1}]$	299.2	313.4	14.2	4.7
$[\text{B(OH)}_4^-]$	$[\mu\text{mol kg}^{-1}]$	102.8	88.6	- 14.2	- 13.8
$[\Sigma\text{B(OH)}_3]$	$[\mu\text{mol kg}^{-1}]$	402.0	402.0	0.0	0.0

Figure Captions.

Fig. 1. Schematic diagram of the two-box ocean carbon cycle model described in the text.

Fig. 2. Comparison of the response of the two-box model described in the text with the results of Maier-Reimer and Hasselmann (1987) for a CO₂ pulse equal to 25% of the pre-industrial atmospheric CO₂ content.

Fig. 3. Schematic diagram of the three-box ocean carbon cycle model developed by Toggwiler and Sarmiento (1984).

Fig. 4. Schematic diagram of the PANDORA model developed by Broecker and Peng (1987). Shown are the names of the ten reservoirs, their fractional volumes and fractional outcrop areas, their temperatures, the fluxes of water between them, the rules governing the particulate cycles for organic matter, silica and silica, and the fluxes of organic carbon for the standard case.

Fig. 5. Schematic diagram of a box-diffusion model similar to that developed by Oeschger et al. (1975).

Fig. 6. From Schlesinger and Jiang (1990).

Fig. 7. Schematic diagram of an outcrop-diffusion model (Siegenthaler, 1983).

Fig. 8. Comparison of the box-diffusion (Siegenthaler and Oeschger, 1978) and outcrop-diffusion model (Siegenthaler, 1983) results for an anthropogenic CO₂ emission scenario. Even though both models were calibrated using the same ¹⁴C data, the model structure has a large effect on model results. It is thought that the box-diffusion model gives more accurate predictions than the outcrop-diffusion model. Curve 1 and 3, box-

diffusion model; curves 2 and 4, outcrop-diffusion model. Solid curves, calibrated to natural ^{14}C ; dashed curves, calibrated to bomb ^{14}C . (From Siegenthaler, 1983)

Fig. 9. A schematic representation of an upwelling-diffusion model. The Hoffert et al. (1981) version considers a cold water box, but does not explicitly resolve it as a separate reservoir. The HILDA model (Shaffer, 1989;; Siegenthaler and Joos, 1992) divides the polar water box into two explicit reservoirs and considers mixing transport between the deep polar water box and all levels in the one-dimensional deep ocean compartment.

Fig 1.

Fig 2

Fig 3.

Fig 4

Fig 5

OSU

GFDL

— diffusion
— convection

Fig. 6a and b. Annual global-mean heat flux by advection ($\overline{FADVV}^G$), diffusion ($\overline{FDIFV}^G$) and convection ($\overline{FCONV}^G$) for a year 12 of the OSU 2 x CO₂ - 1 x CO₂ difference (upper panel), 2 x CO₂ (middle panel) and 1 x CO₂ (lower panel) simulations and b years 20-30 of the GFDL 4 x CO₂ - 1 x CO₂ difference (upper panel), 4 x CO₂ (middle panel) and 1 x CO₂ (lower panel) simulations from Bryan and Spelman (1985)

Fig 6

Figure 7 illustrates the mathematical model of the atmospheric-oceanic system.

Fig 7

... is ... pulse
 ... for ...
 ... by comb-

Fig 8.

Fig 9.

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