Multiple timescales for neutralization of fossil fuel CO_2

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Abstract. The long term abiological sinks for anthropogenic CO_2 will be dissolution in the oceans and chemical neutralization by reaction with carbonates and basic igneous rocks. We use a detailed ocean / sediment carbon cycle model to simulate the response of the carbonate cycle in the ocean to a range of anthropogenic CO_2 release scenarios. $CaCO_3$ will play only a secondary role in buffering the CO_2 concentration of the atmosphere because $CaCO_3$ reaction uptake capacity and kinetics are limited by the dynamics of the ocean carbon cycle. Dissolution into ocean water sequesters 70-80% of the CO_2 release on a time scale of several hundred years. Chemical neutralization of CO_2 by reaction with $CaCO_3$ on the sea floor accounts for another 9-15% decrease in the atmospheric concentration on a time scale of 5.5 - 6.8 kyr. Reaction with $CaCO_3$ on land accounts for another 3-8%, with a time scale of 8.2 kyr. The final equilibrium with $CaCO_3$ leaves 7.5-8% of the CO_2 release remaining in the atmosphere. The carbonate chemistry of the oceans in contact with $CaCO_3$ will act to buffer atmospheric CO_2 at this higher concentration until the entire fossil fuel CO_2 release is consumed by weathering of basic igneous rocks on a time scale of 200 kyr.

Introduction

The terrestrial biosphere appears to be taking up CO_2 today [*Keeling et al.*, 1996] but future biospheric uptake may be swamped by the magnitude of the fossil fuel CO_2 release, potentially several times larger than the biosphere plus soil carbon reservoirs. The oceans have the capacity to take up far more CO_2 than can the terrestrial biosphere [*Sarmiento and Sundquist*, 1992], and ocean chemistry is buffered by $CaCO_3$ on the sea floor and on land. Predicting the millenial scale fate of fossil fuel CO_2 is therefore largely an oceanographic problem.

Methods

We simulated the assimilation of fossil fuel CO_2 into the ocean carbon cycle using the HAMOCC global ocean carbon cycle model [*Maier-Reimer and Hasselmann*, 1987; *Maier-Reimer*, 1993] coupled with a model of carbonate sediment diagenesis [*Archer*, 1991; *Archer and Maier-Reimer*, 1994]. The HAMOCC circulation code has been shown to reproduce the observed distribution of ^{14}C in the ocean, a reflection of the rate of atmospheric ventilation of the deep sea [*Maier-*

Reimer, 1993]. The sediment model resolves the physics of $CaCO_3$ dissolution within the diffusive sediment pore water, and is consistent with in situ pore water chemistry [*Archer et al.*, 1989; *Hales et al.*, 1993] and sea floor $CaCO_3$ distribution data [*Emerson and Archer*, 1990; *Archer*, 1996]. Carbonate dissolution on land (weathering) adds a constant prescribed flux of carbonate ion ($CO_3^=$) to the surface ocean, with no attempt to predict anthropogenic changes in global chemical weathering rate. In the model as in nature, the burial rate of $CaCO_3$ in deep sea sediments is controlled by the deep sea concentration of $CO_3^=$, which ultimately adjusts to maintain steady state between weathering and burial; this process is called $CaCO_3$ compensation. Ocean circulation and biological production in the model are maintained at present-day values, unaffected by any changes in climate forcing.

The release of fossil fuel CO_2 was simulated by increasing the atmospheric CO_2 concentration following projections from IPCC 1990 [*Houghton et al.*, 1990] to the year 2100, and in some cases extrapolating the year 2100 emission for one or two centuries more, for net releases of 900, 1500, 3000, and 4500 Gton C as CO_2, approaching the estimated 5000 Gton C of potentially recoverable coal, oil and gas [*Sundquist*, 1985]. The IPCC scenarios incorporated projections of biospheric uptake, but for simplicity no further biospheric uptake was allowed following the end of the emission period, as the model was run to the year 40,000 for the 3000 Gton scenario and the year 10,000 for the others (Figure 1a). All scenarios were also run to the year 10,000 in the absence of weathering and burial of $CaCO_3$.

This model is a more quantitative accounting of the effect of ocean chemistry on atmospheric pCO_2, and of the reservoirs and fluxes of carbon in the deep sea, than has been applied previously to predicting the fate of anthropogenic CO_2. For example, we find that after an initial relaxation time, the dissolution flux from the sea floor is regulated in part by deep ocean flow , an effect best simulated using a three dimensional circulation model. Recent work [*Archer et al.*, 1989] shows that $CaCO_3$ dissolution kinetics are slower than had been used in previous models, and presumably therefore less responsive to CO_2 invasion. Also the inventory of $CaCO_3$ on the sea floor available for dissolution is a factor of three smaller than the value used in previous neutralization projections. Using these refinements, we hope to reduce the factor of four range in published estimates of the time scale for $CaCO_3$ compensation [*Broecker and Peng*, 1987; *Keir*, 1988; *Sundquist*, 1990].

Analysis

Ocean Invasion

Fossil fuel CO_2 is removed from the atmosphere by several geochemical pathways, each of which sequesters a distinct

fraction of the CO_2 release over a particular time scale. Uptake by dissolution in the ocean (invasion) can be seen most clearly in model runs which neglect the buffering effect of $CaCO_3$ weathering and burial (Figure 1a, dotted lines). The oceans ultimately absorbed between 70 and 80% of the CO_2 release, with lower uptake efficiency when the CO_2 release is larger (Figure 2). The e-folding time scale (τ) for the atmospheric decrease ranged from 200 to 450 years, slower for the larger release. An impulse CO_2 release to this model has been shown to invade the ocean on multiple time scales corresponding to different water masses in the ocean [*Maier-Reimer and Hasselmann*, 1987], but the faster time scales were here obscured by the 2-4 century time scale for CO_2 release.

Reaction with $CaCO_3$

CO_2 invasion into the ocean decreases deep ocean $[CO_3^=]$ (Figure 1b) by the reaction $CO_2 + CO_3^= + H_2O \leftrightarrow 2\ HCO_3^-$, which has two salient consequences. First, dissolution of previously deposited $CaCO_3$ on the sea floor (Figure 1c) reacts with CO_2 via the reaction $CaCO_3 + CO_2 + H_2O \leftrightarrow 2\ HCO_3^-$. This will be referred to as sea floor neutralization. Second, the decrease in the global burial rate of $CaCO_3$ in deep sea sediments creates an imbalance with terrestrial weathering,
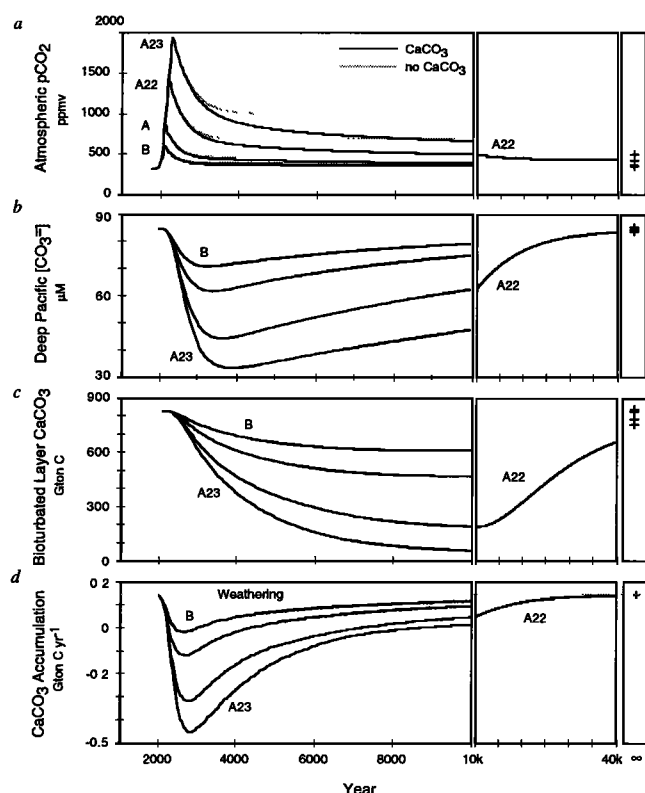
Figure 1. Model response to fossil fuel CO_2 invasion. Time series to the year 40,000, and the fully $CaCO_3$ neutralized state (t = ∞ excluding the igneous weathering effect). (a) Atmospheric pCO_2 was driven by atmospheric pCO_2 projections from extended IPCC [*Houghton et al.,* 1990] scenarios B, A (also referred to as BaU), and A extrapolated to the years 2200 and 2300 (A22 and A23). Dark lines include the effect of $CaCO_3$, light lines neglect $CaCO_3$. (b) Deep Pacific $[CO_3^=]$ (all results include $CaCO_3$). (c) Bioturbated layer deep sea $CaCO_3$. (d) Globally integrated accumulation rate of $CaCO_3$ in the deep sea; negative values indicate net dissolution.
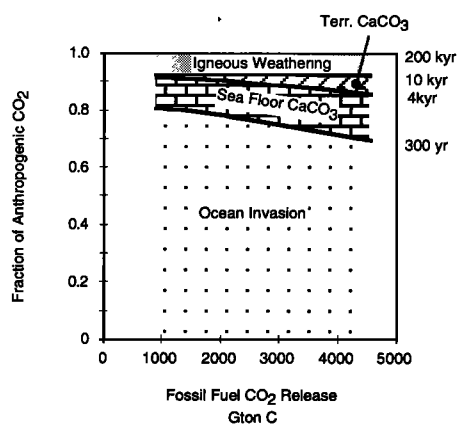
Figure 2. Fractions of anthropogenic CO_2 sequestered by various abiological processes plotted as a function of anthropogenic CO_2 release. The approximate e-folding time scales for each process are given at the right.

which results in a net dissolution flux of terrestrial $CaCO_3$ to the sea, i.e. neutralization by terrestrial $CaCO_3$.

In the ocean, $CaCO_3$ is found in nearshore sediments such as coral reefs, and in sediments of the open ocean at depths shallower than the undersaturated abyssal waters. Respiration-driven dissolution in shallow water sediments could be enhanced by a decrease in overlying water supersaturation [*Walter and Burton,* 1990], but the greater area of $CaCO_3$ rich sediments in the deep sea, and the under-saturation of the deep ocean, argue that the shallow water contribution to fossil fuel neutralization will be smaller than that of the deep ocean. We make the simplifying assumption of neglecting it altogether.

The inventory of $CaCO_3$ on the deep sea floor which is available for dissolution is determined by the geometry of surface sediments. Bioturbation (sediment mixing by benthic macrofauna) exposes $CaCO_3$ from roughly 10 cm depth [*Berger and Killingley,* 1982] to the zone of dissolution at the sediment surface on time scales of hundreds of years. If the transient dissolution flux following CO_2 invasion exceeds the mass sedimentation rate to the sea floor, then old $CaCO_3$ can be exposed from below the bioturbated layer in a process called chemical erosion, which can potentially continue until the bioturbated layer becomes filled by non-$CaCO_3$ material, isolating $CaCO_3$ from the zone of dissolution. The inventory of erodable deep sea $CaCO_3$ in the model is approximately 1770 Gton C, comparable with a value of 1600 Gton C from a recent reassessment of sea floor data [*Archer,* 1996] (and a factor of three smaller than the *Broecker and Takahashi* [1978] estimate used in previous estimate fossil fuel uptake studies [*Broecker and Peng,* 1987; *Sundquist,* 1990; *Walker and Kasting,* 1992].

Chemical erosion is a transient condition which continues until the $CaCO_3$ supply to the bioturbated layer as sedimenting particles is balanced by losses due to dissolution and burial. This condition is hereafter referred to as local lysocline equilibrium. The global bioturbated layer $CaCO_3$ inventory in local lysocline equilibrium, determined from direct model experiments, is plotted as a function of the deep sea $CO_3^=$ concentration in Figure 3a. Superimposed upon this are model time trajectories from Figure 1. The model came close to local lysocline equilibrium by the year 10,000 in all cases. Most of the change in ocean chemistry during this time can be attributed to the decrease in sea floor $CaCO_3$ inventory, defining this time period as the sea floor neutralization stage.
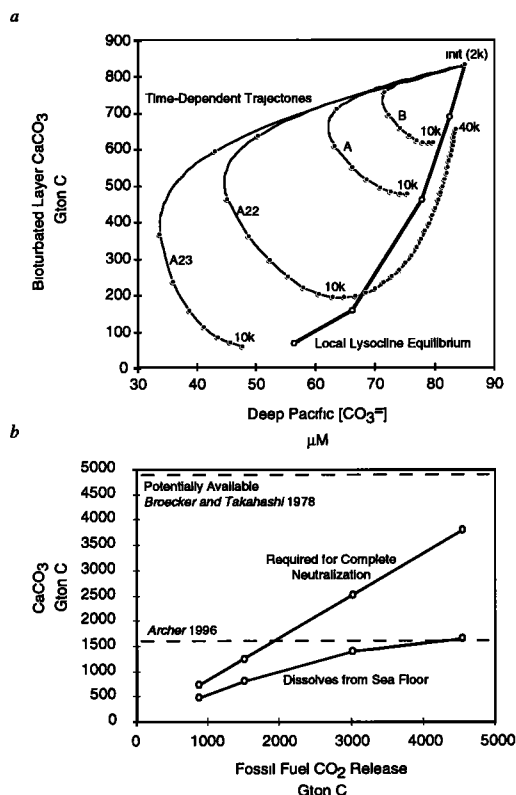
a

b

Figure 3. *a)* Deep ocean [CO₃⁼] plotted against bioturbated layer CaCO₃ inventory. Model time-trajectories are shown with solid circles every 1000 years of model time. Open circles are model-calculated state of local lysocline equilibrium, where CaCO₃ equals dissolution plus burial at every grid point, for a range of deep ocean [CO₃⁼] values. The initial invasion of CO₂ depletes deep ocean [CO₃⁼], which is subsequently replenished as bioturbated layer CaCO₃ is depleted. Once the model trajectory reaches local lysocline equilibrium, neutralization of CO₂ by dissolution of seafloor CaCO₃ ceases.

b) The inventory of CaCO₃ on the sea floor available to neutralize fossil fuel CO₂. The reassessment of the maximum potential dissolvable CaCO₃ inventory by *Archer* [1996] is a factor of three lower than the estimate by *Broecker and Takahashi* [1978] used in previous fossil fuel modeling studies [*Broecker and Peng*, 1987; *Sundquist*, 1990; *Walker and Kasting*, 1992]. Solid lines show the actual model sea floor dissolution response as a function of the amount of CO₂ released, compared with the amount of CaCO₃ required for complete neutralization. Sea floor neutralization does not reach the maximum potential dissolvable CaCO₃ inventory except in the case of the highest fossil fuel CO₂ release, because of the limitation imposed by reestablishment of local lysocline equilibrium, at which time sea floor neutralization stops.

After the lysocline reaches local equilibrium with the water column, as marked by the intersection of the model trajectories with the local lysocline equilibrium line, there is no longer a thermodynamic driving force for further chemical erosion, and both the ocean CO₃⁼ and the sea floor CaCO₃ inventories await replenishment by the imbalance between weathering and accumulation (terrestrial neutralization), as can be seen by the change in the path of the model trajectories toward higher inventories in Figure 3.

If the fossil fuel CO₂ release is less than our maximum 4500 Gton C value, then only a fraction of the "potentially available" CaCO₃ can dissolve before the end of sea floor dissolution associated with reestablishment of local lysocline equilibrium (Figure 3b). Sea floor neutralization sequestered 10-15% of the atmospheric concentration of anthropogenic CO₂ (greater for larger CO₂ release: Figure 2). A log-linear plot of the approach of atmospheric CO₂ to final neutralized values (discussed below) reveals τ values in the sea floor neutralization stage (before A.D. 10k) of 5.5 - 6.8 kyr, and a value of 8.3 kyr for the A22 scenario for the terrestrial neutralization stage (after A.D. 10k). These time scales could be decreased by dissolution of shallow water carbonates or a climate-related increase in terrestrial weathering or perturbed, probably increased, by changes in deep sea circulation driven by anthropogenic climate change [*Manabe and Stouffer*, 1993]. The magnitude of the atmospheric decrease is most sensitive to the availability of CaCO₃ for dissolution, determined in the deep sea by the depth of bioturbation and the porosity of surface sediments.

Return to CaCO₃ Steady State

The state of complete CaCO₃ neutralization was calculated directly by accelerating the GCM approach to global (burial = weathering) and local lysocline equilibrium after fossil fuel release. The results of these direct endpoint calculations are plotted in the rightmost panels in Figure 1. Atmospheric pCO₂ from the A22 scenario calculated by acceleration was within 2 ppm of the end state of the 40,000 year integration. After complete CaCO₃ neutralization, 7.5 - 8% of the CO₂ release remained in the atmosphere for all scenarios. This result is consistent with carbonate equilibrium chemistry, which is described by the relation

$$\frac{pCO_2 \left[CO_3^=\right]}{\left[HCO_3^-\right]^2} = \frac{K_H \, K_2}{K_1} = \text{constant} \tag{1}$$

where K_H, K_1, and K_2 are the Henry's Law and first and second dissociation constants for CO₂ and carbonic acid. Based on this, the ratio of the final and initial atmospheric CO₂ inventories can be written

$$\frac{\text{atm CO}_{2_f}}{\text{atm CO}_{2_i}} = \left(\frac{HCO_{3_f}^-}{HCO_{3_i}^-}\right)^2 \approx \frac{\left(\Sigma CO_{2_i} + 2 \cdot CO_{2_{ff}}\right)^2}{\Sigma CO_{2_i}^2} \tag{2}$$

where ocean [CO₃⁼] is held constant by equilibrium with CaCO₃, and the relative increase in HCO₃⁻ is approximated by the increase in the ocean CO₂ inventory (ΣCO₂). C_{ff} is the magnitude of the anthropogenic CO₂ release, and the factor of 2 is derived from the nearly 1:1 stoichiometry of CO₂ reaction with CaCO₃, eventually releasing two carbons to the ocean per carbon of fossil fuel. Taking atm CO₂ᵢ as 625 Gton C, ΣCO₂ᵢ as 38,000 Gton C, and CO₂ff as ranging from 800-4,500 Gton C, we estimate that the atmospheric partition of fossil fuel carbon should be between 6.7-7.3% after complete neutralization, consistent with the model result.

In nature, the residual atmospheric CO₂ will ultimately be consumed by the silicate rock cycle, which maintains a long-term balance between CO₂ degassing from the mantle and CO₂ uptake by weathering of calcium and magnesium silicates by
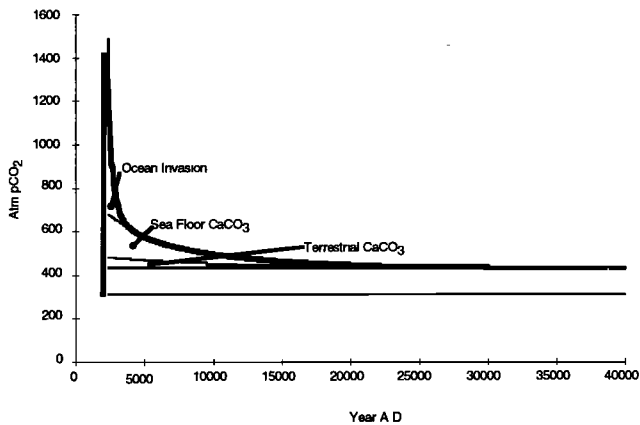
Figure 4. Atmospheric CO_2 concentration from the model, scenario A22, compared with uptake fractions and response times derived in the text.

reactions such as CaO (silicate rock) + $CO_2 \rightarrow$ sedimentary $CaCO_3$. This mechanism is thought to stabilize atmospheric pCO_2 with τ = 200 kyr. Approximating the silicate weathering mechanism as a simple 200 kyr exponential approach to an atmospheric pCO_2 of 280 ppm, the time dependent response of the atmospheric pCO_2 to a 3,000 Gton anthropogenic CO_2 IPCC injection scenario (scenario A22) can be written as

$$atmCO_{2_t} = atmCO_{2_{innal}} + 3000 \ GtC \left[0.75 \cdot e^{\frac{-t}{365\,yr}} \right.$$

$$\left. + 0.135 \cdot e^{\frac{-t}{5.5\,kyr}} + 0.035 \cdot e^{\frac{-t}{8.2\,kyr}} + 0.08 \cdot e^{\frac{-t}{200\,kyr}} \right] \qquad (3)$$

(Figure 4) where the four terms in brackets represent the time dependent uptake by ocean invasion, sea floor and terrestrial $CaCO_3$ neutralization, and silicate weathering, respectively.

While this expression summarizes our best estimate of known long-term sinks of CO_2, it does not account for the observed modulation of atmospheric CO_2 concentration over the glacial cycles [*Barnola et al.*, 1987] which are poorly understood and which highlight our limited ability to predict long-term atmospheric CO_2. Nevertheless, we can predict that the carbonate chemistry of the oceans in contact with $CaCO_3$ will act to buffer atmospheric pCO_2 at these higher levels. In order for the terrestrial biosphere or silicate rock weathering, for example, to restore atmospheric CO_2 to its preanthropogenic value, we require uptake not only of the atmospheric CO_2 excess, but of the entire fossil fuel CO_2 load, including that which has reacted with $CaCO_3$, reducing the cumulative net atmospheric release to zero. If the atmospheric fraction of the fossil fuel CO_2 ($atmCO_{2_f}$) is removed from the atmosphere, degassing from the ocean and precipitation of $CaCO_3$ would replenish most of the drawdown of $atmCO_{2_f}$. Future variability in the global carbon cycle, such as accompanied the glacial cycles, would then drive atmospheric CO_2 perturbations starting from a new robust baseline value, $atmCO_{2_f}$.

References

Archer D., S. Emerson and C. Reimers, Dissolution of calcite in deep-sea sediments: pH and O_2 microelectrode results, *Geochim. Cosmochim. Acta, 53,* 2831-2846, 1989.

Archer D. E., Modeling the calcite lysocline, *J. Geophys. Res., 96,* 17,037-17,050, 1991.

Archer D. E., An atlas of the distribution of calcium carbonate in sediments of the deep sea, *Global Biogeoche. Cycles, 10,* 159-174, 1996.

Archer D. E., A data-driven model of the global calcite lysocline, *Global Biogeochem. Cycles,* 1996.

Archer D. E. and E. Maier-Reimer, Effect of deep-sea sedimentary calcite preservation on atmospheric CO_2 concentration, *Nature, 367,* 260-264, 1994.

Barnola J. M., D. Raynaud, Y. S. Korotkevich and C. Lorius, Vostok ice core provides 160,000 year record of atmospheric CO_2, *Nature, 329,* 408-414, 1987

Berger W. H. and J. S. Killingley, Box cores from the equatorial Pacific: ^{14}C sedimentation rates and benthic mixing, *Mar. Geol., 45,* 93-125, 1982.

Berner R. A., A. C. Lasaga and R. M. Garrels, The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years, *Am. J. Sci., 283,* 641-683, 1983.

Broecker W. S. and T. H. Peng, The role of $CaCO_3$ compensation in the glacial to interglacial atmospheric CO_2 change, *Global Biogeochem. Cycles, 1,* 15-29, 1987.

Broecker W. S. and T. Takahashi, Neutralization of fossil fuel CO_2 by marine calcium carbonate, in *The Fate of Fossil Fuel CO_2 in the Oceans,* edited by N. R. Andersen and A. Malahoff, 213, Plenum Press, New York, 1978.

Emerson S. and D. Archer, Calcium carbonate preservation in the ocean, *Phil. Trans. R. Soc. Lond, A331,* 29-41, 1990.

Hales B., S. Emerson and D. Archer, Respiration and dissolution in the sediments of the western North Atlantic: estimates from models of in situ microelectrode measurements of porewater oxygen and pH, *Deep-Sea Res., 41,* 695-719, 1993.

Houghton J. T., G. J. Jenkins and J. J. Ephraums (Ed.), *Intergovernmental Panel on Climate Change The IPCC Scientific Assessment,* pp., Cambridge University Press, Cambridge, U.K., 1990.

Keeling R. F., S. C. Piper and M. Heimann, Global and hemispheric CO_2 sinks deduced from changes in atmospheric O_2 concentration, *Nature, 381,* 218-221, 1996.

Keir R. S., On the late Pleistocene ocean geochemistry and circulation, *Paleoceanography, 3,* 413-445, 1988.

Maier-Reimer E., Geochemical cycles in an ocean general circulation model. Preindusrial tracer distributions, *Global Biogeochem. Cycles, 7,* 645-678, 1993.

Maier-Reimer E. and K. Hasselmann, Transport and storage of CO_2 in the ocean -- an inorganic ocean-circulation carbon cycle model, *Climate Dynamics, 2,* 63-90, 1987.

Manabe S. and R. J. Stouffer, Century-scale effects of increased atmospheric CO_2 on the ocean-atmosphere system, *Nature, 364,* 215-218, 1993.

Sarmiento J. L. and E. T. Sundquist, Revised budget for the oceanic uptake of anthropogenic carbon dioxide, *Nature, 356,* 589-593, 1992.

Sundquist E. T., Geological perspectives on carbon dioxide and the carbon cycle, in *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present,* edited by S. E.T. and B. W.S., 5, American Geophysical Union, Washington D.C., 1985.

Sundquist E. T., Influence of deep-sea benthic processes on atmospheric CO_2, *Phil. Trans. R. Soc. Lond. A, 331,* 155-165, 1990.

Walker J. C. G. and J. F. Kasting, Effects of fuel and forest conservation on future levels of atmospheric carbon dioxide, *Palaeogeography, Palaeoclimatology, Palaeoecology (Global and Planetary Change Section), 97,* 151-189, 1992.

Walter L. M. and E. A. Burton, Dissolution of recent platform carbonate sediments in marine pore fluids, *Am. J. Sci., 290,* 601-643, 1990.

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