

Multiple timescales for neutralization of fossil fuel CO₂

David Archer

Department of the Geophysical Sciences, University of Chicago, IL

Haroon Kheshgi

Exxon Research and Engineering Company, Annandale, NJ

Ernst Maier-Reimer

Max-Planck-Institut für Meteorologie, Hamburg, Germany

Abstract. The long term abiological sinks for anthropogenic CO₂ 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 CO₂ release scenarios. CaCO₃ will play only a secondary role in buffering the CO₂ concentration of the atmosphere because CaCO₃ reaction uptake capacity and kinetics are limited by the dynamics of the ocean carbon cycle. Dissolution into ocean water sequesters 70-80% of the CO₂ release on a time scale of several hundred years. Chemical neutralization of CO₂ by reaction with CaCO₃ 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 CaCO₃ on land accounts for another 3-8%, with a time scale of 8.2 kyr. The final equilibrium with CaCO₃ leaves 7.5-8% of the CO₂ release remaining in the atmosphere. The carbonate chemistry of the oceans in contact with CaCO₃ will act to buffer atmospheric CO₂ at this higher concentration until the entire fossil fuel CO₂ 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 CO₂ today [Keeling *et al.*, 1996] but future biospheric uptake may be swamped by the magnitude of the fossil fuel CO₂ release, potentially several times larger than the biosphere plus soil carbon reservoirs. The oceans have the capacity to take up far more CO₂ than can the terrestrial biosphere [Sarmiento and Sundquist, 1992], and ocean chemistry is buffered by CaCO₃ on the sea floor and on land. Predicting the millennial scale fate of fossil fuel CO₂ is therefore largely an oceanographic problem.

Methods

We simulated the assimilation of fossil fuel CO₂ 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 ¹⁴C 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 CaCO₃ 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 CaCO₃ distribution data [Emerson and Archer, 1990; Archer, 1996]. Carbonate dissolution on land (weathering) adds a constant prescribed flux of carbonate ion (CO₃⁼) 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 CaCO₃ in deep sea sediments is controlled by the deep sea concentration of CO₃⁼, which ultimately adjusts to maintain steady state between weathering and burial; this process is called CaCO₃ 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 CO₂ was simulated by increasing the atmospheric CO₂ 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 CO₂, 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 CaCO₃.

This model is a more quantitative accounting of the effect of ocean chemistry on atmospheric pCO₂, and of the reservoirs and fluxes of carbon in the deep sea, than has been applied previously to predicting the fate of anthropogenic CO₂. 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 CaCO₃ dissolution kinetics are slower than had been used in previous models, and presumably therefore less responsive to CO₂ invasion. Also the inventory of CaCO₃ 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 CaCO₃ compensation [Broecker and Peng, 1987; Keir, 1988; Sundquist, 1990].

Analysis

Ocean Invasion

Fossil fuel CO₂ is removed from the atmosphere by several geochemical pathways, each of which sequesters a distinct

Copyright 1997 by the American Geophysical Union.

Paper number 97GL00168.
0094-8534/97/97GL-00168\$05.00

fraction of the CO₂ 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 CaCO₃ weathering and burial (Figure 1a, dotted lines). The oceans ultimately absorbed between 70 and 80% of the CO₂ release, with lower uptake efficiency when the CO₂ 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 CO₂ 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 CO₂ release.

Reaction with CaCO₃

CO₂ invasion into the ocean decreases deep ocean [CO₃⁼] (Figure 1b) by the reaction $\text{CO}_2 + \text{CO}_3^{=} + \text{H}_2\text{O} \leftrightarrow 2 \text{HCO}_3^-$, which has two salient consequences. First, dissolution of previously deposited CaCO₃ on the sea floor (Figure 1c) reacts with CO₂ via the reaction $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow 2 \text{HCO}_3^-$. This will be referred to as sea floor neutralization. Second, the decrease in the global burial rate of CaCO₃ in deep sea sediments creates an imbalance with terrestrial weathering,

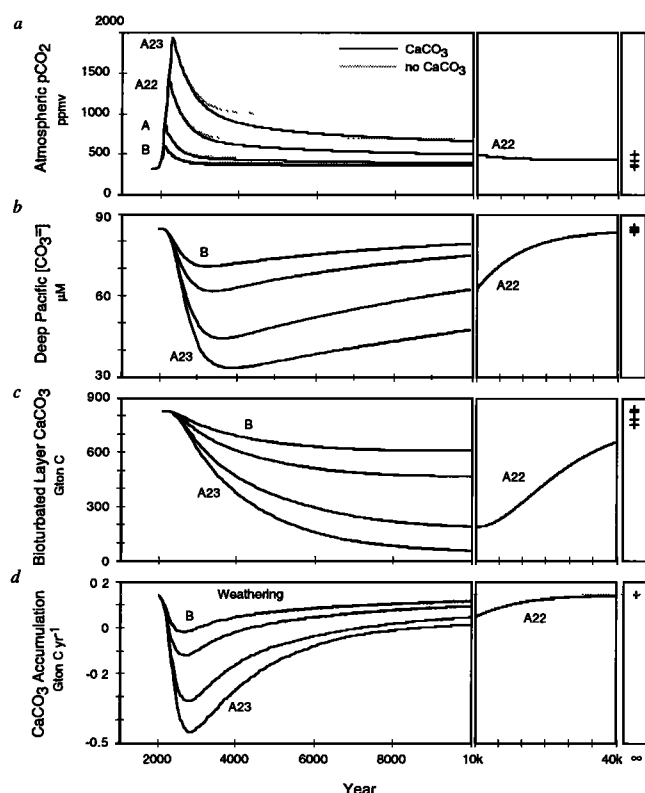


Figure 1. Model response to fossil fuel CO₂ invasion. Time series to the year 40,000, and the fully CaCO₃ neutralized state ($t = \infty$ excluding the igneous weathering effect). (a) Atmospheric pCO₂ was driven by atmospheric pCO₂ projections from extended IPCC [Houghton *et al.*, 1990] scenarios B, A (also referred to as BaU), and A extrapolated to the years 2200 and 2300 (A22 and A23). Dark lines include the effect of CaCO₃, light lines neglect CaCO₃. (b) Deep Pacific [CO₃⁼] (all results include CaCO₃). (c) Bioturbated layer deep sea CaCO₃. (d) Globally integrated accumulation rate of CaCO₃ in the deep sea; negative values indicate net dissolution.

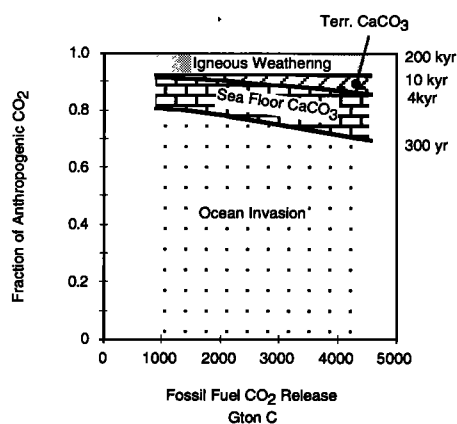


Figure 2. Fractions of anthropogenic CO₂ sequestered by various abiological processes plotted as a function of anthropogenic CO₂ release. The approximate e-folding time scales for each process are given at the right.

which results in a net dissolution flux of terrestrial CaCO₃ to the sea, i.e. neutralization by terrestrial CaCO₃.

In the ocean, CaCO₃ 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 CaCO₃ 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 CaCO₃ 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 CaCO₃ 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 CO₂ invasion exceeds the mass sedimentation rate to the sea floor, then old CaCO₃ 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-CaCO₃ material, isolating CaCO₃ from the zone of dissolution. The inventory of erodable deep sea CaCO₃ 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 CaCO₃ 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 CaCO₃ inventory in local lysocline equilibrium, determined from direct model experiments, is plotted as a function of the deep sea CO₃⁼ 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 CaCO₃ inventory, defining this time period as the sea floor neutralization stage.

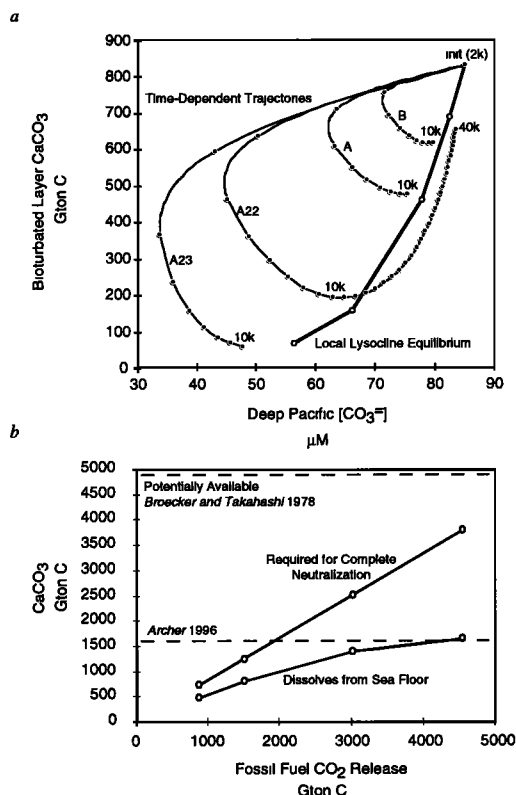


Figure 3. a) Deep ocean [CO₃⁼] plotted against bioturbated layer CaCO₃ inventory. Model time-trajectories are shown with solid circles every 1000 years of model time. Open circles are model-calculated state of local lysocline equilibrium, where CaCO₃ equals dissolution plus burial at every grid point, 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

$$\frac{p\text{CO}_2 [\text{CO}_3^{=}]}{[\text{HCO}_3^-]^2} = \frac{K_H K_2}{K_1} = \text{constant} \quad (1)$$

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

$$\frac{\text{atm CO}_{2f}}{\text{atm CO}_{2i}} = \left(\frac{[\text{HCO}_3^-]_f}{[\text{HCO}_3^-]_i} \right)^2 = \frac{(\Sigma\text{CO}_{2i} + 2 \cdot \text{CO}_{2ff})^2}{\Sigma\text{CO}_{2i}^2} \quad (2)$$

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 (ΣCO_2). 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 CO_{2i} as 625 Gton C, ΣCO_{2i} as 38,000 Gton C, and CO_{2ff} 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

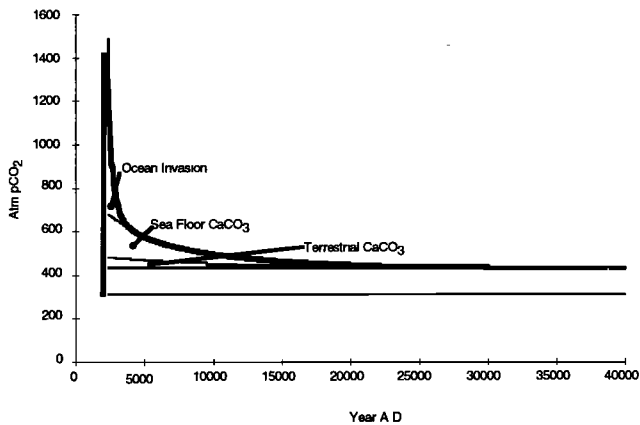


Figure 4. Atmospheric CO₂ concentration from the model, scenario A22, compared with uptake fractions and response times derived in the text.

reactions such as CaO (silicate rock) + CO₂ → sedimentary CaCO₃. This mechanism is thought to stabilize atmospheric pCO₂ with $\tau = 200$ kyr. Approximating the silicate weathering mechanism as a simple 200 kyr exponential approach to an atmospheric pCO₂ of 280 ppm, the time dependent response of the atmospheric pCO₂ to a 3,000 Gton anthropogenic CO₂ IPCC injection scenario (scenario A22) can be written as

$$\text{atmCO}_{2,t} = \text{atmCO}_{2,\text{minal}} + 3000 \text{ GtC} \left[0.75 \cdot e^{-\frac{t}{365\text{yr}}} + 0.135 \cdot e^{-\frac{t}{5.5\text{kyr}}} + 0.035 \cdot e^{-\frac{t}{8.2\text{kyr}}} + 0.08 \cdot e^{-\frac{t}{200\text{kyr}}} \right] \quad (3)$$

(Figure 4) where the four terms in brackets represent the time dependent uptake by ocean invasion, sea floor and terrestrial CaCO₃ neutralization, and silicate weathering, respectively.

While this expression summarizes our best estimate of known long-term sinks of CO₂, it does not account for the observed modulation of atmospheric CO₂ concentration over the glacial cycles [Barnola *et al.*, 1987] which are poorly understood and which highlight our limited ability to predict long-term atmospheric CO₂. Nevertheless, we can predict that the carbonate chemistry of the oceans in contact with CaCO₃ will act to buffer atmospheric pCO₂ at these higher levels. In order for the terrestrial biosphere or silicate rock weathering, for example, to restore atmospheric CO₂ to its preanthropogenic value, we require uptake not only of the atmospheric CO₂ excess, but of the entire fossil fuel CO₂ load, including that which has reacted with CaCO₃, reducing the cumulative net atmospheric release to zero. If the atmospheric fraction of the fossil fuel CO₂ (*atmCO*_{2,t}) is removed from the atmosphere, degassing from the ocean and precipitation of CaCO₃ would replenish most of the drawdown of *atmCO*_{2,t}. Future variability in the global carbon cycle, such as accompanied the glacial cycles, would then drive atmospheric CO₂ perturbations starting from a new robust baseline value, *atmCO*_{2,t}.

Acknowledgements. This work was supported in part by the Petroleum Research Fund and the National Center for Atmospheric Research. We thank several anonymous reviewers for helpful criticism.

References

- Archer D., S. Emerson and C. Reimers, Dissolution of calcite in deep-sea sediments: pH and O₂ 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 Biogeochem. 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 CO₂ 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 CO₂, *Nature*, 329, 408-414, 1987.
- Berger W. H. and J. S. Killingley, Box cores from the equatorial Pacific: ¹⁴C 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 CaCO₃ compensation in the glacial to interglacial atmospheric CO₂ change, *Global Biogeochem. Cycles*, 1, 15-29, 1987.
- Broecker W. S. and T. Takahashi, Neutralization of fossil fuel CO₂ by marine calcium carbonate, in *The Fate of Fossil Fuel CO₂ 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 CO₂ sinks deduced from changes in atmospheric O₂ 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. Preindustrial tracer distributions, *Global Biogeochem. Cycles*, 7, 645-678, 1993.
- Maier-Reimer E. and K. Hasselmann, Transport and storage of CO₂ 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 CO₂ 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 CO₂: 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 CO₂, *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, *Palaeoecology, Palaeoecology, 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.
- D. Archer, Department of the Geophysical Sciences, University of Chicago, Illinois 60637 (email d-archer@uchicago.edu)
- H. Khesghi, Exxon Research and Engineering Company, Route 22E, Annandale, NJ 08801 (email hskhes@erenj.com)
- E. Maier-Reimer, Max-Planck-Institut fuer Meteorologie, Bundesstrasse 7, D-2000 Hamburg 54, Germany (email maier-reimer@dkrz.de)
- D. Archer,

(Received October 7, 1996; revised January 13, 1997; accepted January 16, 1997)