

The fate of fossil fuel CO₂ in geologic time

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Abstract

A model of the ocean and sea floor carbon cycle is subjected to injection of new CO₂ pulses of varying sizes to estimate the resident atmospheric fraction over the coming 100 kyr. The model is used to separate the processes of air-sea equilibrium, an ocean temperature feedback, CaCO₃ compensation, and silicate weathering on the residual anthropogenic pCO₂ in the atmosphere at 1, 10, and 100 kyr. The mean lifetime of anthropogenic CO₂ is dominated by the long tail, resulting in a range of 30-35 kyr. The long lifetime of fossil fuel carbon release implies that the anthropogenic climate perturbation may have time to interact with ice sheets, methane clathrate deposits, and glacial/interglacial climate dynamics.

Introduction

The idea that anthropogenic CO₂ release may affect the climate of the earth for hundreds of thousands of years has not reached general public awareness. The End of the Age of Oil, for example, published in 2004 by David Goodstein [2004], reports that fossil fuel CO₂ will disappear within a few centuries. This misconception is widespread in scientific and public discussion. It certainly makes sense to focus our attention on the century time scale within which we live out our lives, and within which most of the CO₂ will be absorbed by the natural carbon cycle. According to economic theory, application of a discount rate largely eliminates our concern about an effect that is projected tens of thousands of years in the future [*Grossman and Krueger, 1995*]. However, the long-term consequences of fossil fuel CO₂ release have never reached the same level of public awareness and concern as does the production of long-lived nuclear wastes, for example.

Potential sources of new CO₂ to the ocean / atmosphere carbon pools include fossil fuel carbon, changes in the size of the terrestrial biosphere including soil organic carbon, and changes in the amount of methane sequestered in frozen clathrate deposits in terrestrial permafrost and ocean margin sediments. The amount of fossil fuel carbon available for energy use is generally considered to total about 5000 Gton of carbon, dominated by coal . Ultimately extractable oil resources are thought to be about 250 Gton C, potentially expanding severalfold if unconventional oil sources such as oil sands are considered. Traditional natural gas reserves represent about 200 GtonC, again with the potential to expand severalfold with future exploration and technological advances[Rogner, 1997; Sundquist, 1985]. Humankind has already released about 300 Gton C from fossil fuels and deforestation, and the IPCC business-as-usual scenario (IS92a) projects about 1600 Gton of carbon released from a combination of fossil fuels and terrestrial fluxes, with emissions beyond 2100 unspecified. The maximum amount of fossil fuel carbon that could ultimately be released would seem to be about 5000 Gton C, on a time scale of several centuries.

At present, the terrestrial biosphere appears to be a net sink of carbon, in spite of anthropogenic deforestation, predominantly in the tropics [Keeling *et al.*, 1996]. Future carbon uptake or release from the terrestrial biosphere will be determined by land-use decisions, climate change, and CO₂ fertilization of land plants. The terrestrial biosphere is about 500 Gton in size, with an additional 1500 Gton of carbon stored in soils [Siegenthaler and Sarmiento, 1993]. Long-term modeling studies predict a reversal of present-day carbon uptake, resulting in net release of carbon by the end of the century

[Cox *et al.*, 2000]. The ultimate magnitude of the release is difficult to predict, but seems unlikely to exceed 1000 Gton C.

Hundreds of Gton C are frozen into methane hydrate deposits in permafrost [MacDonald, 1990], and approximately 5,000-10,000 Gton C exists as methane frozen into methane clathrate deposits under the floor of the deep sea [Buffett and Archer, 2004; Kvenvolden, 1995]. Carbon release from these deposits by the end of this century have been projected to be of order 100 Gton C [Harvey and Huang, 1995], but it has been projected that the ultimate methane carbon release could be comparable in size to the fossil fuel carbon release that initiates it [Archer and Buffett, in press].

The aim of this paper is to diagnose the atmospheric lifetime of a several-century timescale release of new carbon to the atmosphere. Methane clathrate decomposition would probably take longer than this; the effect of this process on the long-term pCO₂ trajectory is presented by [Archer and Buffett, in press] and neglected here. The remaining sources, fossil fuel and terrestrial biosphere, we group together under the designation "anthropogenic" carbon sources. Although any projection of carbon release beyond the usual window of the year 2100 is extremely speculative, the worst case we will consider is a net anthropogenic release of 5000 Gton C, which is dominated by the large size of the coal reserves. Anthropogenic carbon slugs of 300, 1000, 2000, and 5000 Gton C are released following a Gaussian trajectory of 150 years half-width centered on the year 2100.

The atmospheric lifetime and uptake of anthropogenic CO₂ will involve a number of different mechanisms which operate on distinct timescales. (1) Anthropogenic CO₂ will equilibrate with seawater in the global ocean, on a timescale less than a millennium.

Although we assume atmospheric release of the anthropogenic carbon, the end result of atmosphere / ocean equilibration, and the subsequent trajectory of atmospheric $p\text{CO}_2$, will be very similar if the carbon is injected as unneutralized CO_2 into the ocean [Rau and Caldeira, 2002]. Ocean injection would simply eliminate the century-timescale transient peak in atmospheric $p\text{CO}_2$. A new component in the calculations presented here is the potential for a positive feedback between ocean temperature and atmospheric $p\text{CO}_2$, revising upward previous estimates of the atmospheric fraction of released CO_2 [Archer *et al.*, 1998; Archer *et al.*, 1997]. (2) Acidifying the ocean by adding CO_2 perturbs the CaCO_3 cycle by decreasing the global burial rate of CaCO_3 . This perturbation acts to restore the pH of the ocean back towards its initial pre-anthropogenic value, on a time scale of $\sim 10\text{kyr}$. As the pH of the ocean recovers, atmospheric $p\text{CO}_2$ decreases, in effect neutralized by CaCO_3 . (3) A silicate weathering feedback acts to restore $p\text{CO}_2$ to some equilibrium value on time scales of $\sim 100\text{ kyr}$, setting the ultimate maximum duration of an anthropogenic carbon cycle perturbation. This process is not resolved mechanistically in this paper, but rather imposed as an assumed 400 kyr timescale restoring of atmospheric $p\text{CO}_2$ toward 280 ppm, as a means of limiting our attention to processes that affect $p\text{CO}_2$ on timescales shorter than that.

The atmospheric $p\text{CO}_2$ trajectories presented in this paper do not account for the sorts of natural $p\text{CO}_2$ variability that drive the glacial / interglacial and shorter-term climate cycles. Our ignorance of the mechanisms behind these natural variations belies our ability to forecast precise future $p\text{CO}_2$, but past $p\text{CO}_2$ changes are not random, and the anthropogenic CO_2 perturbation cannot be simply wiped away by natural processes. The $p\text{CO}_2$ trajectories presented here are buffered by the large carbon reservoir of the ocean.

Adding carbon to the ocean/atmosphere system has the effect of moving the baseline about which natural variability might act. One might simply imagine natural variations of order 30% superimposed upon the projections here, by analogy to past perturbations about a steady baseline pCO₂ value. The drawdown of pCO₂ associated with a transition from interglacial to glacial climate states will not be an issue in the future if glaciation is forestalled by weak orbital forcing [Loutre and Berger, 2000] or by elevated pCO₂ [Archer and Ganapolski, submitted; Ruddiman, 2003]. We cannot rule out the possibility that the unknown mechanism [Archer et al., 2000] which amplifies the ocean temperature feedback upon glaciation [Martin, submitted] will act in reverse in the future to amplify future anthropogenic pCO₂ forcing. In conclusion we are unable to forecast precisely the pCO₂ of the atmosphere 10k or 100k years from now, but we can speak with more certainty about the anthropogenic perturbation to the pCO₂ at that time.

We evaluate the impact of these processes and effects by successively adding them to an ocean / sediment carbon cycle model. Some aspects of these calculations, such as the ocean temperature solubility feedback, are included here for the first time. These model results therefore supercede those presented by [Archer et al., 1998; Archer et al., 1997]. We need to know how long anthropogenic CO₂ will remain in the atmosphere if we are to predict its interaction with ocean methane clathrates [Archer and Buffett, 2005], for example, or the onset of the next glaciation [Archer and Ganapolski, submitted].

Model Description

Atmosphere / Ocean Equilibrium

The ocean circulation field was derived from the annual mean of the Large Scale Geostrophic ocean model [Maier-Reimer, 1993]. The model is formulated on a 72×72 E-grid for an effective resolution of 3.5° . The offline tracer advection code HAMOCC2 [Maier-Reimer and Bacastow, 1990] carries concentrations of dissolved inorganic carbon (DIC), alkalinity, and nutrient PO_4^{3-} . An implicit scheme is used to compute CO_2 gas exchange over the annual timestep, as biological activity alters the carbon chemistry of surface waters. Plankton convert these dissolved tracers into particles which sink and redissolve as a function of depth. The model reproduces the distribution of nutrients, oxygen, and carbon chemistry of the real ocean. The air / water version of the model, which we explore first as the simplest case, does not allow any deposition of particles on the sea floor.

Temperature Feedback

Atmosphere / ocean partitioning of CO_2 may be affected by changes in the temperature of the deep ocean. One might have thought that deep ocean temperature ought to be insulated from climate change at the sea surface, since the surface ocean reaches the freezing point someplace in the world even under global-warming conditions. However, recent data from glacial time [Adkins *et al.*, 2002; Martin *et al.*, 2002], and coupled ocean / atmosphere climate models [Stouffer and Manabe, 1999; Stouffer and Manabe, 2003], predict significant changes in deep ocean temperature. Both paleoclimate and computational data are consistent with a deep-ocean temperature

sensitivity of about 3°C, which we will assume here. If the real temperature sensitivity is less, the feedback will be weaker than we present.

The ocean circulation model reads in a temperature and circulation field from a model of ocean physics, and then uses that “frozen” flow field to advect tracers, for the calculation of atmospheric invasion and ultimate equilibrium of CO₂. The advantage of the off-line tracer advection scheme is speed; we are able to present multiple runs each of which encompasses 10⁵ years of simulation. The downside of this strategy is that we are unable to simulate the effect of changing climate on the circulation and temperature fields of the ocean. We compromise by imposing a uniform temperature change on the waters of the ocean, whenever gas equilibrium and gas exchange kinetics calculations are done. The ocean temperature relaxes toward an equilibrium value

$$\Delta T_{\text{equil}} = 3^{\circ}\text{C}/\ln(2) \cdot \ln(p\text{CO}_2/278)$$

on a time scale of 1 kyr such that

$$\delta T/\delta t = (T_{\text{equil}} - T) / 1000 \text{ yr}$$

CaCO₃ Cycle Equilibrium

Acidifying the ocean by CO₂ addition perturbs the CaCO₃ weathering and burial cycle, and the eventual recovery of this cycle acts to further remove anthropogenic CO₂ from the atmosphere. We simulate these dynamics using an oxic-only model for the burial or redissolution of CaCO₃ as governed by the kinetics of diffusion and by pH equilibrium reactions in the pore water in the top 10 cm of deep sea sediment at each grid point of the Hamocc2 GCM. The coupled ocean sediment model is the same as was used by [Archer, 1991; Archer and Maier-Reimer, 1994]. The sediment model was ground-

truthed to pore-water microelectrode [Archer *et al.*, 1989] and sea floor CaCO₃ concentration [Archer, 1996] data.

Silicate Weathering Thermostat Equilibrium

Weathering of the CaO component of igneous rocks acts to drag carbon from the atmosphere/ocean and deposit it as CaCO₃ on the sea floor. The silicate-weathering thermostat hypothesis is that the rate of igneous rock weathering increases with increasing atmospheric CO₂, primarily by acceleration of the hydrologic cycle. However, the silicate-weathering thermostat is complicated by possible changes in carbon subduction and outgassing, and by continental crust uplift rates. It is also unclear how the silicate weathering thermostat interacts with the glacial / interglacial pCO₂ cycles in the Pleistocene. Forecasting the detailed dynamics of this mechanism in the future will be a big job and will not be attempted here. Instead I assumed a typical e-folding time for CO₂ relaxation of 400 kyr [Berner and Kothavala, 2001; Sundquist, 1991], toward a target value of preanthropogenic 278 ppm pCO₂. We parameterize the silicate-weathering thermostat as a Newtonian restoring of atmospheric CO₂ toward an assumed equilibrium value of preanthropogenic pCO₂, with a restoring time of 40 kyr. The ocean buffers atmospheric pCO₂ by a factor of close to 10:1, so that the effective time scale for pCO₂ approaching equilibrium is the desired 400 kyr. Rather than modeling the sensitivities of this silicate weathering mechanistically, we are parameterizing it in order to limit our attention to mechanisms that act more quickly than its assumed 400 kyr timescale.

Results

Atmosphere / Ocean Equilibrium

Results of all model runs are shown in Figures 1-3, and are summarized in Table 1. Atmospheric pCO₂ approaches equilibrium on a time scale of ~300 yr (Figure 1). The exact timing of this equilibration process in the real ocean will depend on interaction between climate and the circulation and biota of the ocean, which are better represented elsewhere [Sarmiento *et al.*, 2004]. After equilibration, the fraction of the carbon release that resides the ocean decreases as the anthropogenic CO₂ slug increases. At first glance, the high atmospheric fraction may seem puzzling. The ocean contains ~50 times more dissolved inorganic carbon than does the atmosphere, so it might seem as though pretty much all of the anthropogenic carbon should dissolve in the ocean. Roger Revelle [Revelle and Suess, 1957] realized, however, that the pH equilibrium chemistry of seawater will limit the uptake of CO₂, by a factor now known as the Revelle buffer factor. At the pre-anthropogenic pH of the ocean, the buffer factor ranged from ~9 in the tropics to 15 in high latitude surface waters. The effective "size" of the ocean CO₂ buffering capacity can be estimated as 40,000 Gtons of ocean DIC divided by the buffer factor from cold surface waters (~15) to yield about 2500 Gtons buffering capacity. We expect that added CO₂ will partition itself between the atmosphere and the ocean in proportion to the sizes of the reservoirs, and in the ocean we expect that size to be the buffering capacity. The relative sizes of the preanthropogenic atmosphere and the atmosphere plus ocean buffer are proportioned 560:(560+2500) equals ~18%. This crudely predicted atmospheric fraction is comparable to the model atmospheric fraction after 1000 years, which ranges from 14-30%, depending on the size of the fossil fuel release. As the

anthropogenic CO₂ acidifies the ocean, the Revelle buffer factor increases, decreasing the buffer capacity of the ocean. This effect can also be seen in the model results, which show a higher fraction of the anthropogenic carbon in the atmosphere after 1kyr when the release size is larger. Because atmospheric CO₂ never returns to its preanthropogenic level, the mean atmospheric lifetime of released CO₂ in this scenario is, strictly speaking, infinite.

Temperature Feedback

Resulting ocean temperature time-series are shown in Figure 2. The temperature feedback tends to drive CO₂ to remain in the atmosphere, because warming driven by higher CO₂ concentrations decreases the solubility of CO₂ in the ocean. We find that the temperature feedback increases the atmospheric fraction by about 11-15% relative to the constant temperature ocean case (Figure 1 and Table 1).

CaCO₃ Cycle Equilibrium

The effect of the CaCO₃ cycle is to decrease the atmospheric load of the anthropogenic carbon to ~8-13%, on a time scale of thousands of years (Figure 1, Table 1). The temperature feedback affects this 10kyr-timescale CaCO₃-equilibrium state similarly to how it affected the 1kyr-timescale atmosphere/seawater equilibrium state, by increasing the CO₂ load on the atmosphere. In this case, the amplification is a bit larger than in the last; an increase by ~20-25%, resulting in an atmospheric residual of 10-18% after 10kyr. For anthropogenic carbon releases of 2000 Gton C and less, the size of the anthropogenic slug has less impact on the CaCO₃-equilibrium partitioning of carbon between the atmosphere and ocean than it did on the atmosphere / seawater state. When

the anthropogenic release is 5000 Gton, CaCO_3 nears depletion in the deep ocean, and the atmospheric fraction rises. The CaCO_3 -equilibrium state does not restore atmospheric pCO_2 to its pre-anthropogenic value, so strictly speaking, if CaCO_3 equilibrium were where the process stopped, the mean lifetime of anthropogenic CO_2 would still be infinite.

Silicate Weathering Thermostat Equilibrium

The 400 kyr timescale of silicate weathering thermostat dominates the mean lifetime of a CO_2 perturbation. Without and with the T feedback, the values are about 30 and 34 kyr, respectively. These lifetimes are nearly independent of release magnitude, with a slight increase as the release approaches 5000 Gtons, exhausting the CaCO_3 dissolving capacity of the ocean.

Summary

The carbon cycle of the biosphere will take a long time to completely neutralize and sequester anthropogenic CO_2 . We show a wide range of model forecasts of this effect. For the best-guess cases, which include air/seawater, CaCO_3 , and silicate weathering equilibria as affected by an ocean temperature feedback, we expect that 17-33% of the fossil fuel carbon will still reside in the atmosphere 1kyr from now, decreasing to 10-15% at 10kyr, and 7% at 100 kyr. The mean lifetime of fossil fuel CO_2 is about 30-35 kyr.

A mean atmospheric lifetime of order 10^4 years is in start contrast with the "popular" perception of several hundred year lifetime for atmospheric CO_2 . In fairness, if the fate of anthropogenic carbon must be boiled down into a single number for popular discussion, then 300 years is a sensible number to choose, because it captures the

behavior of the majority of the carbon. A single exponential decay of 300 years is arguably a better approximation than a single exponential decay of 30,000 years, if one is forced to choose. However, the 300-year simplification misses the immense longevity of the tail on the CO₂ lifetime, and hence its interaction with major ice sheets, ocean methane clathrate deposits, and future glacial/interglacial cycles. One could sensibly argue that public discussion should focus on a time frame within which we live our lives, rather than concern ourselves with climate impacts tens of thousands of years in the future. On the other hand, the 10-kyr lifetime of nuclear waste seems quite relevant to public perception of nuclear energy decisions today. A better approximation of the lifetime of fossil fuel CO₂ for public discussion might be "300 years, plus 25% that lasts forever".

Citations

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Tables

Table 1. Air/seawater, CaCO₃, and silicate weathering equilibrium runs, with and without ocean temperature feedback.

T feedback	CaCO ₃ Weat.	Silicate Weat.	Anthro. Release, Gton C	Atmospheric Fraction			Mean Lifetime, kyr	T Feedback Amp. Fac.
				1kyr	10kyr	100kyr		
no	no	no	300	13.9%	13.9%	13.9%		
			1000	15.9%	15.9%	15.9%		
			2000	19.7%	19.7%	19.7%		
			5000	30.4%	30.4%	30.4%		
yes	no	no	300	15.8%	15.8%	15.8%		13.6%
			1000	18.0%	18.0%	18.0%		13.5%
			2000	22.2%	22.2%	22.2%		12.7%
			5000	33.7%	33.7%	33.7%		10.7%
no	yes	no	300	15.0%	8.6%	8.6%		
			1000	17.1%	8.7%	8.7%		
			2000	21.5%	9.4%	9.4%		
			5000	30.3%	13.8%	13.8%		
yes	yes	no	300	17.0%	10.3%	10.3%		19.0%
			1000	19.8%	10.8%	10.8%		24.0%
			2000	24.1%	11.4%	11.4%		21.0%
			5000	33.9%	17.5%	17.5%		26.3%
no	yes	yes	300	14.8%	8.3%	5.8%	30.3	
			1000	16.9%	8.4%	5.6%	29.3	
			2000	21.2%	8.9%	5.7%	29.7	
			5000	29.8%	12.5%	5.8%	31.2	
yes	yes	yes	300	16.8%	9.8%	6.7%	34.7	14.2%
			1000	19.2%	9.9%	6.5%	33.7	14.4%
			2000	23.8%	10.7%	6.5%	34.1	14.7%
			5000	32.9%	15.1%	6.7%	36.1	15.2%

Figure Captions

Figure 1. Model $p\text{CO}_2$ results to the year 100k A.D. Results neglecting (left) and including (right) the ocean temperature feedback. The ocean-only case runs go to 9kyr only, CaCO_3 equilibrium runs to 35 kyr, and silicate weathering runs go all the way to 100 kyr. Top is for 300 Gton C anthropogenic emission, followed by 1000, 2000, and 5000 Gton.

Figure 2. Ocean temperature trajectories from the model runs. The ocean-only case runs go to 9kyr only, CaCO_3 equilibrium runs to 35 kyr, and silicate weathering runs go all the way to 100 kyr. Top is for 300 Gton C anthropogenic emission, followed by 1000, 2000, and 5000 Gton.

Figure 3. CaCO_3 burial rates in model runs. Anthropogenic perturbation decreases CaCO_3 burial, often to negative values (net dissolution) which recover on time scales of 10-20 kyr. Plotted are the silicate-weathering runs (CaCO_3 -only runs are indistinguishable).

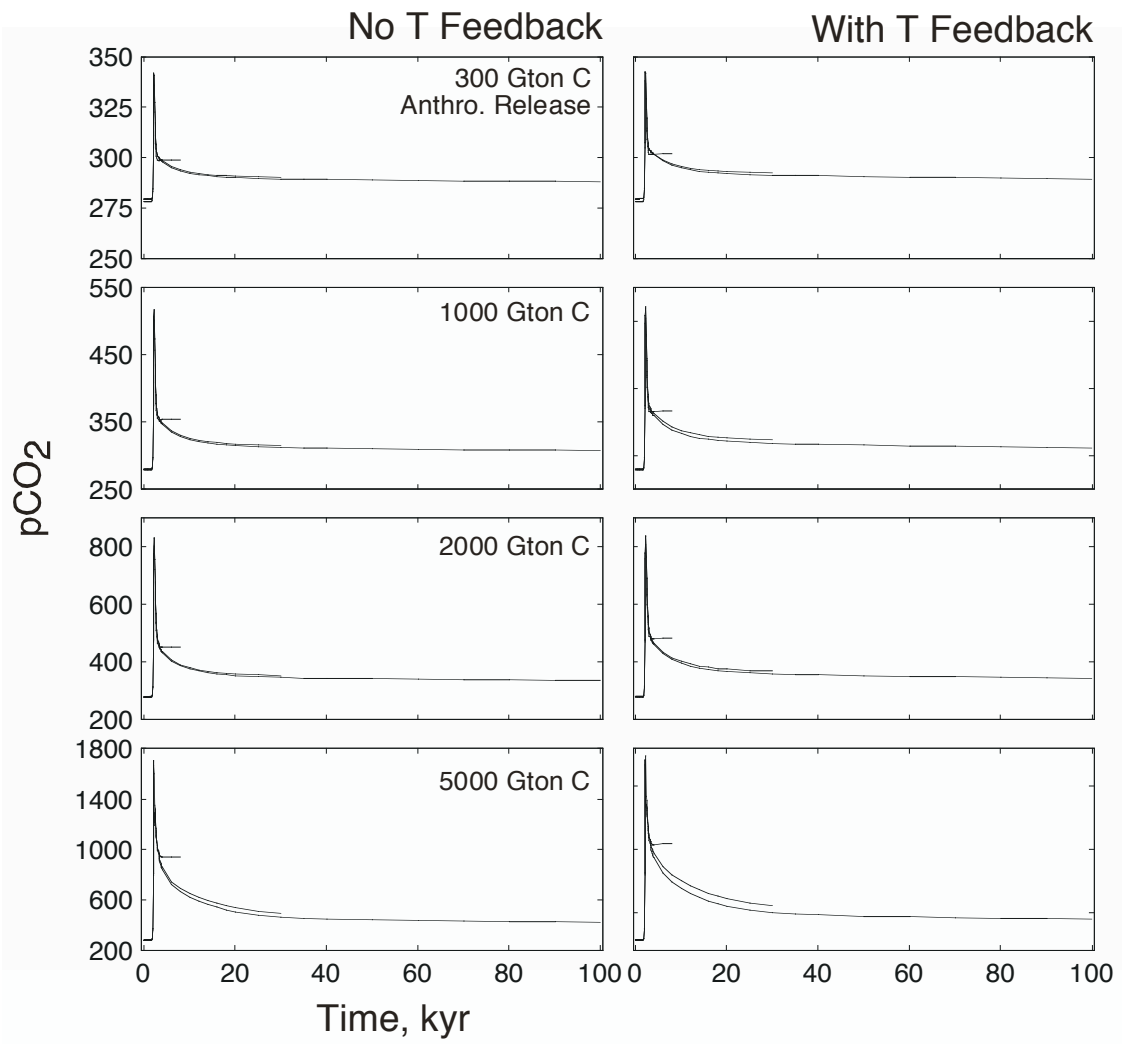


Figure 1

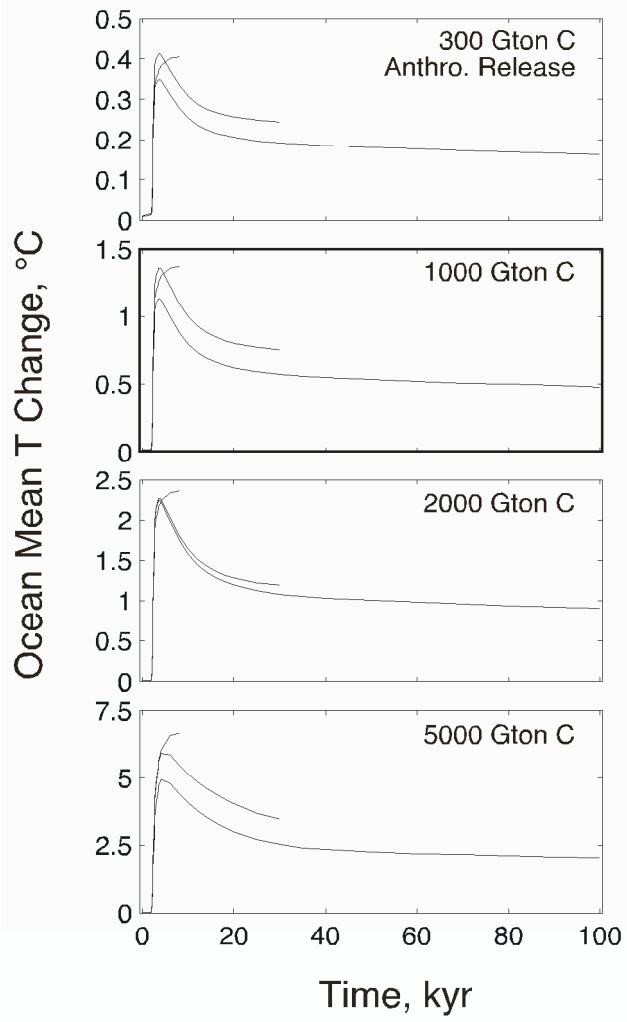


Figure 2

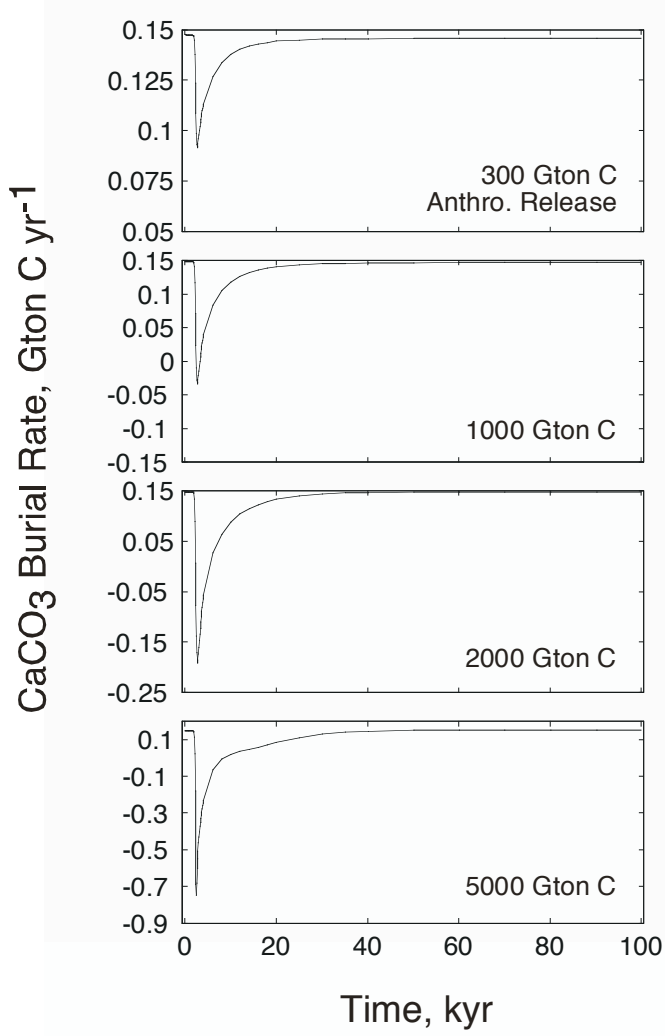


Figure 3