

## Fate of fossil fuel CO<sub>2</sub> in geologic time

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[1] A model of the ocean and seafloor carbon cycle is subjected to injection of new CO<sub>2</sub> 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, CaCO<sub>3</sub> compensation, and silicate weathering on the residual anthropogenic pCO<sub>2</sub> in the atmosphere at 1, 10, and 100 kyr. The mean lifetime of anthropogenic CO<sub>2</sub> 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.

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### 1. Introduction

[2] The idea that anthropogenic CO<sub>2</sub> release may affect the climate of the earth for hundreds of thousands of years has not reached general public awareness. *Goodstein* [2004] reports that fossil fuel CO<sub>2</sub> will disappear after a millennium. This misconception is widespread in scientific and public discussion. It certainly makes sense to focus our attention on the century timescale within which we live out our lives, and within which most of the CO<sub>2</sub> 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 CO<sub>2</sub> release have never reached the same level of public awareness and concern as does the production of long-lived nuclear wastes, for example.

[3] Potential sources of new CO<sub>2</sub> 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 Gton C, 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 timescale of several centuries.

[4] 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 CO<sub>2</sub> 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.

[5] Hundreds of Gton C are frozen into methane hydrate deposits in permafrost [MacDonald, 1990], and approximately 5000–10,000 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, 2005].

[6] 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 pCO<sub>2</sub> trajectory is presented by [Archer and Buffett, 2005] 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.

[7] The atmospheric lifetime and uptake of anthropogenic CO<sub>2</sub> will involve a number of different mechanisms which operate on distinct timescales. (1) Anthropogenic CO<sub>2</sub> 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 pCO<sub>2</sub>, will be very similar if the carbon is injected as unneutralized CO<sub>2</sub> into the ocean [Rau and Caldeira, 2002]. Ocean injection would simply eliminate the century-timescale transient peak in atmospheric pCO<sub>2</sub>. A new component in the calculations presented here is the potential for a positive feedback between ocean temperature and atmospheric pCO<sub>2</sub>, revising upward previous estimates of the atmospheric fraction of released CO<sub>2</sub> [Archer et al., 1998, 1997]. (2) Acidifying the ocean by adding CO<sub>2</sub> perturbs the CaCO<sub>3</sub> cycle by decreasing the global burial rate of CaCO<sub>3</sub>. This perturbation acts to restore the pH of the ocean back toward its initial preanthropogenic value, on a timescale of ~10 kyr. As the pH of the ocean recovers, atmospheric pCO<sub>2</sub> decreases, in effect neutralized by CaCO<sub>3</sub>. (3) A silicate weathering feedback acts to restore pCO<sub>2</sub> to some equilibrium value on timescales of ~100 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 pCO<sub>2</sub> toward 280 ppm, as a means of limiting our attention to processes that affect pCO<sub>2</sub> on timescales shorter than that.

[8] The atmospheric pCO<sub>2</sub> trajectories presented in this paper do not account for the sorts of natural pCO<sub>2</sub> 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 pCO<sub>2</sub>, but past pCO<sub>2</sub> changes are not random, and the anthropogenic CO<sub>2</sub> perturbation cannot be simply wiped away by natural processes. The pCO<sub>2</sub> 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 pCO<sub>2</sub> value. The drawdown of pCO<sub>2</sub> 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 pCO<sub>2</sub> [Archer and Ganopolski, 2005; 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 et al., 2005] will act in reverse in the future to amplify future anthropogenic pCO<sub>2</sub> forcing. In conclusion we are unable to forecast precisely the pCO<sub>2</sub> of the atmosphere 10,000 or 100,000 years from now, but we can speak with more certainty about the anthropogenic perturbation to the pCO<sub>2</sub> at that time.

[9] 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, 1997]. We need to know how long anthropogenic CO<sub>2</sub> 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 Ganopolski, 2005].

## 2. Model Description

### 2.1. Atmosphere/Ocean Equilibrium

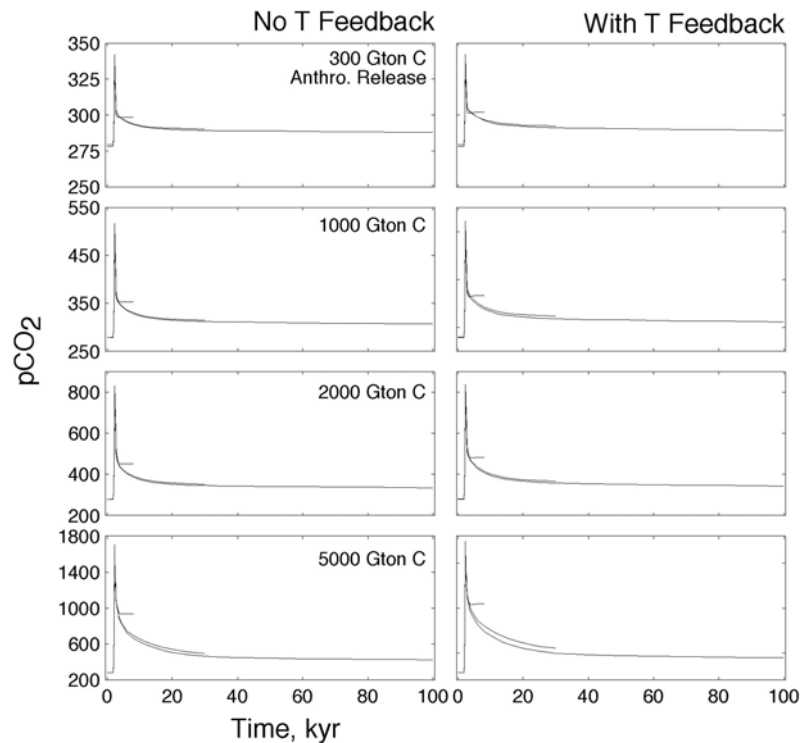
[10] The ocean circulation field was derived from the annual mean of the Large-Scale Geostrophic Ocean Model [Maier-Reimer, 1993]. The model is formulated on a 72 × 72 E-grid for an effective resolution of 3.5°. The offline tracer advection code HAMOCC2 [Maier-Reimer and Bacastow, 1990] carries concentrations of dissolved inorganic carbon (DIC), alkalinity, and nutrient PO<sub>4</sub><sup>3-</sup>. An implicit scheme is used to compute CO<sub>2</sub> gas exchange over the annual time step, 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 seafloor.

### 2.2. Temperature Feedback

[11] Atmosphere/ocean partitioning of CO<sub>2</sub> 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, 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.

[12] 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 CO<sub>2</sub>. The advantage of the off-line tracer advection scheme is speed; we are able to present multiple runs each of which encompasses 10<sup>5</sup> 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

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



**Figure 1.** Model pCO<sub>2</sub> results to the year 100,000 A.D. Results (left) neglecting and (right) including the ocean temperature feedback. The ocean-only case runs go to 9 kyr only, CaCO<sub>3</sub> equilibrium runs go 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.

on a timescale of 1 kyr such that

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

### 2.3. CaCO<sub>3</sub> Cycle Equilibrium

[13] Acidifying the ocean by CO<sub>2</sub> addition perturbs the CaCO<sub>3</sub> weathering and burial cycle, and the eventual recovery of this cycle acts to further remove anthropogenic CO<sub>2</sub> from the atmosphere. We simulate these dynamics using an oxic-only model for the burial or redissolution of CaCO<sub>3</sub> 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] and Archer and Maier-Reimer [1994]. The sediment model was ground truthed to pore water microelectrode [Archer *et al.*, 1989] and seafloor CaCO<sub>3</sub> concentration [Archer, 1996] data.

### 2.4. Silicate Weathering Thermostat Equilibrium

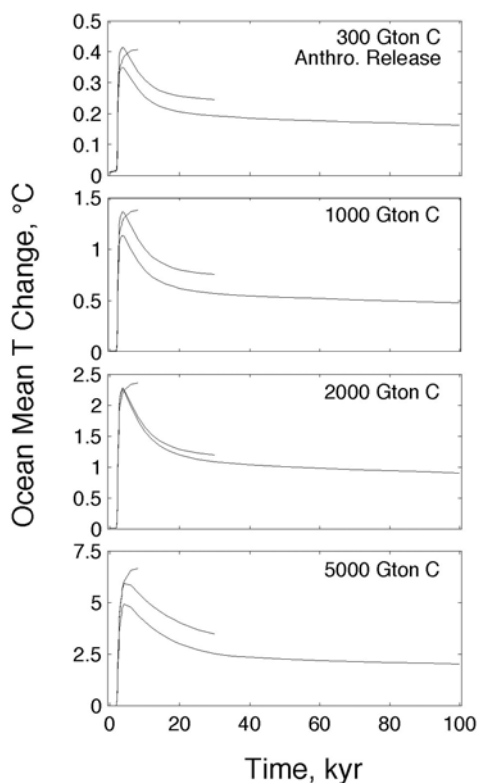
[14] Weathering of the CaO component of igneous rocks acts to drag carbon from the atmosphere/ocean and deposit it as CaCO<sub>3</sub> on the seafloor. The silicate weathering thermostat hypothesis is that the rate of igneous rock weathering increases with increasing atmospheric CO<sub>2</sub>, primarily 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 pCO<sub>2</sub> 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 CO<sub>2</sub> relaxation of 400 kyr [Bernier and Kothavala, 2001; Sundquist, 1991], toward a target value of preanthropogenic 278 ppm pCO<sub>2</sub>. We parameterize the silicate weathering thermostat as a Newtonian restoring of atmospheric CO<sub>2</sub> toward an assumed equilibrium value of preanthropogenic pCO<sub>2</sub>, with a restoring time of 40 kyr. The ocean buffers atmospheric pCO<sub>2</sub> by a factor of close to 10:1, so that the effective timescale for pCO<sub>2</sub> 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.

## 3. Results

### 3.1. Atmosphere/Ocean Equilibrium

[15] Results of all model runs are shown in Figures 1–3, and are summarized in Table 1. Atmospheric pCO<sub>2</sub> approaches equilibrium on a timescale of ~300 years (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 CO<sub>2</sub> slug increases.



**Figure 2.** Ocean temperature trajectories from the model runs. The ocean-only case runs go to 9 kyr only, CaCO<sub>3</sub> equilibrium runs go 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.

At first glance, the high atmospheric fraction may seem puzzling. The ocean contains  $\sim 50$  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 CO<sub>2</sub>, by a factor now known as the Revelle buffer factor. At the preanthropogenic pH of the ocean, the buffer factor ranged from  $\sim 9$  in the tropics to 15 in high-latitude surface waters. The effective “size” of the ocean CO<sub>2</sub> buffering capacity can be estimated as 40,000 Gtons of ocean DIC divided by the buffer factor from cold surface waters ( $\sim 15$ ) to yield about 2500 Gtons buffering capacity. We expect that added CO<sub>2</sub> 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  $\sim 18\%$ . This crudely predicted atmospheric fraction is comparable to the model atmospheric fraction after 1000 years, which ranges from 14 to 30%, depending on the size of the fossil fuel release. As the anthropogenic CO<sub>2</sub> 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

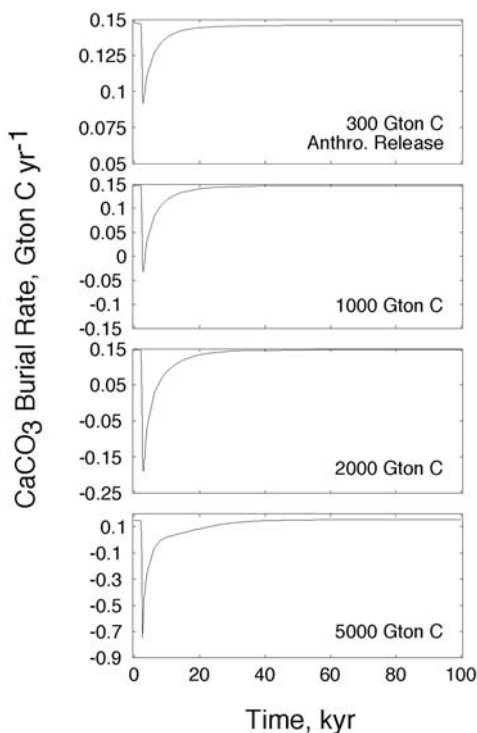
fraction of the anthropogenic carbon in the atmosphere after 1 kyr when the release size is larger. Because atmospheric CO<sub>2</sub> never returns to its preanthropogenic level, the mean atmospheric lifetime of released CO<sub>2</sub> in this scenario is, strictly speaking, infinite.

### 3.2. Temperature Feedback

[16] Resulting ocean temperature time series are shown in Figure 2. The temperature feedback tends to drive CO<sub>2</sub> to remain in the atmosphere, because warming driven by higher CO<sub>2</sub> concentrations decreases the solubility of CO<sub>2</sub> 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).

### 3.3. CaCO<sub>3</sub> Cycle Equilibrium

[17] The effect of the CaCO<sub>3</sub> cycle is to decrease the atmospheric load of the anthropogenic carbon to  $\sim 8$ –13%, on a timescale of thousands of years (Figure 1, Table 1). The temperature feedback affects this 10 kyr–timescale CaCO<sub>3</sub> equilibrium state similarly to how it affected the 1 kyr–timescale atmosphere/seawater equilibrium state, by increasing the CO<sub>2</sub> load on the atmosphere. In this case, the amplification is a bit larger than in the last; an increase by  $\sim 20$ –25%, resulting in an atmospheric residual of 10–18% after 10 kyr. For anthropogenic carbon releases of 2000 Gton C and less, the size of the anthropogenic slug has less impact on the CaCO<sub>3</sub> equilibrium partitioning of carbon between the atmosphere and ocean than it did on the



**Figure 3.** CaCO<sub>3</sub> burial rates in model runs. Anthropogenic perturbation decreases CaCO<sub>3</sub> burial, often to negative values (net dissolution), which recover on timescales of 10–20 kyr. Plotted are the silicate weathering runs (CaCO<sub>3</sub>-only runs are indistinguishable).

**Table 1.** Air/Seawater, CaCO<sub>3</sub>, and Silicate Weathering Equilibrium Runs, With and Without Ocean Temperature Feedback

<i>T</i> Feedback	CaCO <sub>3</sub> Weathering	Silicate Weathering	Anthropogenic Release, Gton C	Atmospheric Fraction, %			Mean Lifetime, kyr	<i>T</i> Feedback Amp. Fac., %
				1 kyr	10 kyr	100 kyr		
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		
			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
			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		
			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
			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	
			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
			5000	32.9	15.1	6.7	36.1	15.2

atmosphere/seawater state. When the anthropogenic release is 5000 Gton, CaCO<sub>3</sub> nears depletion in the deep ocean, and the atmospheric fraction rises. The CaCO<sub>3</sub> equilibrium state does not restore atmospheric pCO<sub>2</sub> to its preanthropogenic value, so strictly speaking, if CaCO<sub>3</sub> equilibrium were where the process stopped, the mean lifetime of anthropogenic CO<sub>2</sub> would still be infinite.

### 3.4. Silicate Weathering Thermostat Equilibrium

[18] The 400 kyr timescale of silicate weathering thermostat dominates the mean lifetime of a CO<sub>2</sub> 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<sub>3</sub> dissolving capacity of the ocean.

## 4. Summary

[19] The carbon cycle of the biosphere will take a long time to completely neutralize and sequester anthropogenic CO<sub>2</sub>. We show a wide range of model forecasts of this effect. For the best guess cases, which include air/seawater, CaCO<sub>3</sub>, 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 1 kyr from now, decreasing to 10–15% at 10 kyr, and 7% at 100 kyr. The mean lifetime of fossil fuel CO<sub>2</sub> is about 30–35 kyr.

[20] A mean atmospheric lifetime of order 10<sup>4</sup> years is in start contrast with the “popular” perception of several hundred year lifetime for atmospheric CO<sub>2</sub>. 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 CO<sub>2</sub> 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 CO<sub>2</sub> for public discussion might be “300 years, plus 25% that lasts forever.”

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