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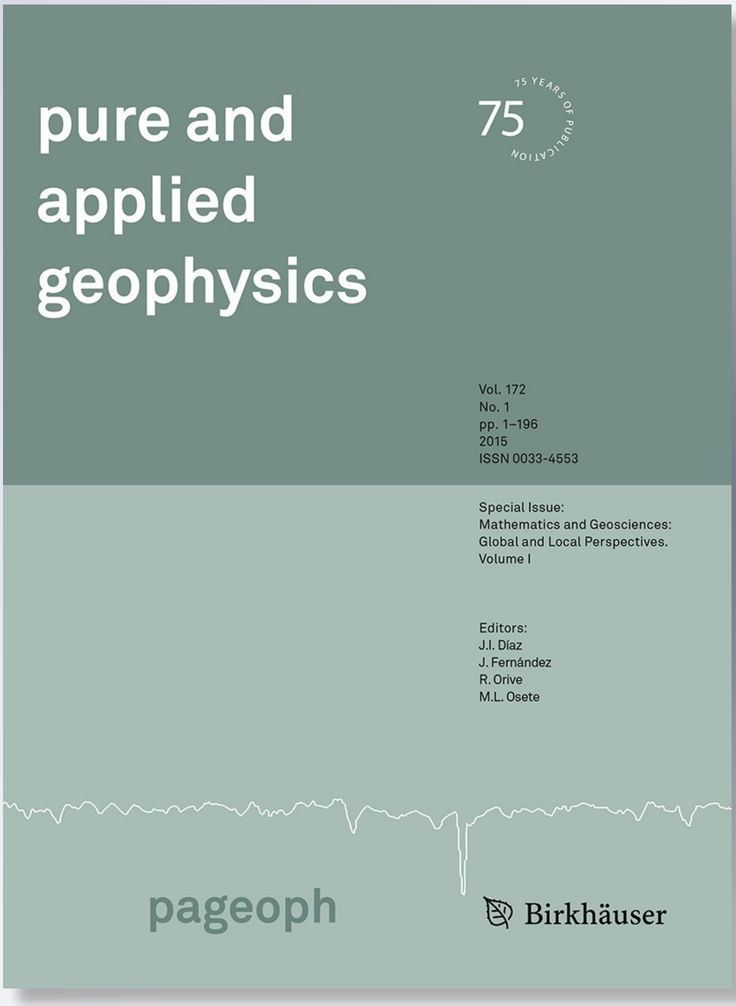

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A Simple Thousand-Year Prognosis for Oceanic and Atmospheric Carbon Change

A. C. Fowler[1,2]

Abstract—A simple carbon-cycle box model allows for very simple quantitative insight into the evolution of climate over the next millennium. While melting ice sheets, rising sea levels, and ocean acidification are well recognised, we show that a further consequence of the repartitioning of ocean carbon is a dramatic rise in atmospheric carbon dioxide on a millennial time scale.

Key words: Climate change, carbon cycle, ocean acidification.

1. Introduction

Climate change is prevalent in the news, and there is a growing consensus on some of the more pertinent facts and hypotheses. It is a simple consequence of radiative transfer theory that increasing CO_2 levels in the atmosphere cause atmospheric warming (Pierrehumbert 2010), with an approximate logarithmic dependence (Houghton 2009). It is well-known that CO_2 levels oscillated between 180 and 280 ppmv during the Pleistocene ice ages (Petit *et al.* 1999) but have risen since 1750 to a level near 400 ppmv. Here, we will preferentially use partial pressures for atmospheric CO_2 levels. Dalton's law of partial pressures states that, for a dilute perfect gas, the ratio of partial CO_2 pressure to air pressure is approximately the molar volume fraction. For an atmospheric pressure of 10^5 Pa and a partial CO_2 pressure of p_{CO_2}, we get a volume fraction $p_{CO_2}/10^5 = 10\,p_{CO_2}$ ppmv; thus, roughly, 400 ppmv = 40 Pa.

The Earth has been cooling since the Eocene, some 50 My (million years) ago (Bijl *et al.* 2013). This cooling is generally associated with declining levels of atmospheric carbon (Pearson and Palmer 2000) that are likely due to the increased weathering associated with Himalayan uplift following the collision of India with Asia, as well as the associated subduction of pelagic carbonates as the Tethys Ocean closed (Caldeira 1992).

The Antarctic continent was sub-tropical on its coasts (Pross *et al.* 2012), and the Antarctic Ice Sheet grew slowly thereafter, possibly originating as three separate ice caps (Pollard and DeConto 2005) before these coalesced at the Eocene–Oligocene transition at 34 My (Zachos *et al.* 1992). In model experiments, the hysteretic decay of the Antarctic Ice Sheet (Pollard and DeConto 2005) is associated with the increase of atmospheric CO_2 levels above about 900 ppmv (90 Pa), but one would expect melting to be initiated at levels well below that in conditions of rapid warming. And indeed, the great ice sheets do appear to be melting: outlet glaciers on Greenland and Antarctica have all shown dramatic signs of increased discharge and collapse in recent decades (Holland *et al.* 2008; Rott *et al.* 1996; Rignot *et al.* 2002).

Apart from the atmospheric warming caused by increased atmospheric CO_2 levels, a secondary effect is that of ocean acidification (Zeebe 2012a). The increased CO_2 in the atmosphere causes an increase in dissolved CO_2 in the ocean, and the effect of the bicarbonate buffering system is to cause a decrease in carbonate ion, and hence a decrease in pH (Archer *et al.* 1997; Archer 1999). Emphasis has been placed on the possible consequences for calcifiers in the ocean (Ridgewell and Zeebe 2005; Zeebe *et al.* 2008), with the suggestion that decreased calcium carbonate formation leads to lower oceanic burial rates, and thus, further enhancement of ocean carbon stocks. In addition, simulation models (Zeebe 2012b) indicate an associated increase in temperature of the

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order of ten degrees on a millennial time scale (Zeebe and Zachos 2013).

Much of the discussion concerning climate prediction focusses on details of recent warming over the last century, and restricts itself to a range of forecasts over the coming century based on ever more detailed numerical weather prediction models, as described in the 2007 Intergovernmental Panel on Climate Change (IPCC) report (Solomon *et al.* 2007), for example. Together with the increasing complexity of these models comes an inevitable uncertainty, due both to chaotic dynamics and model uncertainty (Palmer 2001), with much of the latter being attributable to uncertainty in cloud parameterisation (Tiedtke 1993).

Arguably, this ‘kitchen sink’ approach (include every process possible) misses the elephant in the room, which becomes visible when one adopts a ‘top-down’ approach (include only the essentials of the problem); indeed, this is partly the view of Archer, and of Zeebe and Zachos, who put an emphasis on ocean acidification beyond the century time scale.

There have been a number of recent studies which emphasise the long-term (millennial) evolution of atmospheric and oceanic carbon (Gillett *et al.* 2011; Solomon *et al.* 2009, 2010; Archer and Brovkin 2008; Eby *et al.* 2009). The studies use models of intermediate complexity, suitable for such longer time-scale studies, but still necessary to be solved numerically, so that the mechanisms of the processes are somewhat opaque.

The purpose of the present paper is to illustrate the way in which atmospheric carbon evolves over long time scales using the simplest model that still represents the essential exchange processes in the system, and particularly, to point out a third consequence of carbon injection (beyond warming and acidification). The criticism of over-simplicity must be balanced against the clarity of the insight that emerges.

2. *A Simple Model*

Our simplest model for climate prediction is based on a box model introduced by Fowler *et al.* (2013). Conceptually, the model is a generalised energy balance model of the type introduced by Budyko (1969) and Sellers (1969), and whose progeny are the models of intermediate complexity (Ganopolski *et al.* 2010), which are applied with some success to climate models, ocean models (Johnson *et al.* 2007; Toggweiler 2008), and biogeochemical models (Zeebe 2012b). Our approach here is to choose the very simplest such model that still encapsulates the essential physics of climate control. Because the energy balance part of the model simply reflects an essentially algebraic dependence of global average temperature on atmospheric CO_2, our focus is on the evolution of carbon within the ocean and atmosphere.

The basic ingredient of the model of Fowler *et al.* (2013) is the dependence of mean atmospheric temperature on CO_2 content. To describe the atmospheric CO_2, we must balance anthropogenic or volcanic sources with fluxes to the ocean via dissolution or indirectly through weathering of silicate and carbonate rocks. At the ocean surface, the CO_2 concentration is related to the dissolved CO_2 in the water by Henry’s law:

$$p^s_{\mathrm{CO}_2} = \frac{[\mathrm{CO}_2]}{K_\mathrm{H}}; \tag{2.1}$$

K_H is Henry’s constant, and has units M Pa^{-1}, where 1 M = 1 mol kg^{-1}. Similarly, we may take the dissolved CO_2 in raindrops to be $K_\mathrm{H} p_{\mathrm{CO}_2}$, where p_{CO_2} is atmospheric CO_2 partial pressure. If P is the global rate of precipitation, then this leads to a net CO_2 precipitation of $K_\mathrm{H}\rho_{\mathrm{H_2O}} P p_{\mathrm{CO}_2}$, with units of mol y^{-1}. This leads us to a form of Fowler *et al.*’s (2013) equation (3.21):

$$\frac{A_\mathrm{E}}{M_a g}\dot{p}_{\mathrm{CO}_2} = I - K_\mathrm{H}\rho_{\mathrm{H_2O}} P p_{\mathrm{CO}_2} - h_{oc}(p_{\mathrm{CO}_2} - p^s_{\mathrm{CO}_2}), \tag{2.2}$$

which describes conservation of CO_2 in the atmosphere; the units are mol y^{-1}. The constants are as described in Table 1.

In order to determine p_{CO_2}, we need to know the dissolved CO_2 concentration in the ocean, which itself depends on the carbon balance. Particularly, carbon is buffered in the ocean by means of the following reactions:

Table 1

*Values and description of the constants in the model. The pre-industrial CO_2 production rate is based on an estimated volcanic production rate of 3×10^{11} kgCO_2 y^{-1} (*Walker et al. *1981), while the anthropogenic value corresponds to a fossil fuel and cement emissions rate of 6 GtC y^{-1}, a value typical of the 1990s (*Denman et al. *2007; indicating production rates of 5.4, 6.4 and 7.2 GtC y^{-1} in the 1980s, 1990s, and early 2000s, respectively)*

Symbol	Meaning	Typical value	Comment
A_E	Earth surface area	5.1×10^{14} m^2	
A_L	Land surface area	1.5×10^{14} m^2	
g	Acceleration due to gravity	9.81 m s^{-2}	
h_{oc}	Interfacial transport coefficient	1.8×10^{13} mol Pa^{-1} y^{-1}	
I	CO_2 production rate	0.7×10^{13} mol y^{-1}	Pre-industrial
		5×10^{14} mol y^{-1}	Anthropogenic
K_H	Henry's law coefficient	4.5×10^{-7} M Pa^{-1}	
M_a	Molecular weight of air	2.88×10^{-2} kg mol^{-1}	
m_{oc}	Ocean mass	1.38×10^{21} kg	
P	Global precipitation	5×10^{14} m^3 y^{-1}	
w	Net carbonate loss	0.5×10^{13} mol y^{-1}	
ρH_2O	Density of sea water	1.025×10^3 kg m^{-3}	

$$\begin{aligned}(H_2O) + CO_2 &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCO_3^- + H^+,\\ HCO_3^- &\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CO_3^{2-} + H^+.\end{aligned} \tag{2.3}$$

These reactions are very fast (Zeebe and Wolf-Gladrow 2001), and thus can be taken to be in equilibrium, whence we have

$$X = \frac{K_2 Q}{S}, \quad Y = \frac{K_2 Q^2}{K_1 S}, \tag{2.4}$$

where we write

$$X = [H^+], \quad Y = [CO_2], \quad Q = [HCO_3^-], \quad S = [CO_3^{2-}], \tag{2.5}$$

and the equilibrium constants K_i are defined by

$$K_1 = \frac{k_1}{k_{-1}}, \quad K_2 = \frac{k_2}{k_{-2}}. \tag{2.6}$$

The total dissolved inorganic carbon concentration in the ocean is

$$C = Q + S + Y, \tag{2.7}$$

and a conservation law for total carbon is

$$\begin{aligned} m_{oc}\dot{C} = {} & h_{oc}(p_{CO_2} - p^s_{CO_2}) + \left(\frac{A_E - A_L}{A_E}\right) K_H \rho_{H_2O} P p_{CO_2} \\ & - r_c - r_p + W, \end{aligned} \tag{2.8}$$

in which m_{oc} is ocean mass, A_L is land surface area, r_c is the removal rate of bicarbonate by calcifiers, r_p is the removal rate of carbonate by calcium carbonate precipitation, and W represents the supply of bicarbonate to the ocean through weathering and riverine discharge. Fowler *et al.* (2013) provide further individual equations for the separate components, but in the present situation a more succinct discussion is appropriate.

The source and sink terms in (2.8) are relatively small; they cause adjustments to oceanic concentrations on time scales upwards of forty thousand years, which represents the normal adjustment time for carbonate. Because these time scales are much longer than the ocean mixing time, the box model makes sense on such long time scales. On the much shorter time scale associated with anthropogenic input to the atmosphere and thence, the ocean, the dissolved CO_2 adds no charge to the charge-neutral ocean. The concentration of the conservative ions chloride, sodium, etc., do not change at all, and the calcium also will not change, since its time scale for adjustment is so long, even if the calcifier populations were wiped out. Therefore, the net-negative charge $Q + 2S - X$ of the active ions H^+, HCO_3^-, and CO_3^{2-} must remain constant under conditions of rapid change. Since from Table 2 we see that $X \ll Q, S$, this implies

$$Q + 2S \approx \text{constant} \tag{2.9}$$

over relatively short (millennial) time scales. Since also $Y \ll S$, we see that (2.8) takes the form

$$\begin{aligned} -m_{oc}\dot{S} = {} & h_{oc}(p_{CO_2} - p^s_{CO_2}) + \left(\frac{A_E - A_L}{A_E}\right) K_H \rho_{H_2O} P p_{CO_2} \\ & - r_c - r_p + W. \end{aligned} \tag{2.10}$$

This completes our millennial-scale model. For such short time scales, we will eventually ignore the small

Table 2

Present estimates of the equilibrium constants K_i and the ionic species concentrations in units of M (1 M = 1 mol kg^{-1}) (Emerson and Hedges 2008). C is dissolved inorganic carbon

Species/constant	Typical value (M)
$[Ca^{2+}]$	1.03×10^{-2}
$[CO_2] = Y$	0.8×10^{-5}
$[CO_3^{2-}] = S$	0.24×10^{-3}
$[H^+] = X$	0.63×10^{-8}
$[HCO_3^-] = Q$	1.7×10^{-3}
K_1	1.4×10^{-6}
K_2	1.1×10^{-9}
C	2.0×10^{-3}

source and sink terms, but we retain them initially so that we can sensibly discuss the pre-industrial situation.

3. *The Past and the Future*

We take our model in the form (2.2) and (2.10), as follows:

$$\frac{A_{\mathrm{E}}}{M_a g}\dot{p}_{\mathrm{CO_2}} = I - K_{\mathrm{H}}\rho_{\mathrm{H_2O}}Pp_{\mathrm{CO_2}} - h_{oc}(p_{\mathrm{CO_2}} - p^s_{\mathrm{CO_2}}),$$
$$m_{oc}\dot{S} = -h_{oc}(p_{\mathrm{CO_2}} - p^s_{\mathrm{CO_2}}) - \left(\frac{A_{\mathrm{E}} - A_{\mathrm{L}}}{A_{\mathrm{E}}}\right)K_{\mathrm{H}}\rho_{\mathrm{H_2O}}Pp_{\mathrm{CO_2}} + w, \tag{3.1}$$

where w represents the net loss of dissolved inorganic carbon (DIC) due to precipitation and calcification minus the supply from weathering. Our estimate of its value in Table 1 is based on a river efflux to the ocean of 3.5×10^{13} m^3 y^{-1} and a river bicarbonate concentration of 0.96 mM (Emerson and Hedges 2008). This gives a net molar flux of carbon of 3.4×10^{13} mol y^{-1}, and we suppose the loss in the ocean is comparable to this. The value we choose for w is determined by assuming the pre-industrial carbon reservoir in the ocean is approximately in a state of balance between input and output (the balance will not be exact due to transient effects associated with recovery from the last ice age, but is not expected to be wildly out of balance, because the variation of atmospheric CO_2 during the ice ages is not enormous). In addition, we have Henry's law and charge conservation from (2.1), (2.4), and (2.9):

$$p_s = \frac{K_2 Q^2}{K_1 K_H S}, \quad Q + 2S = A, \tag{3.2}$$

where A is, approximately, the carbonate alkalinity.

It is helpful, indeed essential, to non-dimensionalise the equations. We do this by writing

$$p_{\mathrm{CO_2}} = p_0 p, \quad p^s_{\mathrm{CO_2}} = p_0 p_s, \quad Q = Aq, \quad S = S_0 s, \quad t \sim t_0, \tag{3.3}$$

where

$$t_0 = \frac{A_{\mathrm{E}}}{M_a g h_{oc}}, \quad p_0 = \frac{K_2 A^2}{K_1 K_H S_0}, \tag{3.4}$$

and

$$A = 2.2 \text{ mM}, \quad S_0 = 0.24 \text{ mM} \tag{3.5}$$

are the current values in Table 2. This leads us to the dimensionless model

$$\dot{p} = \varepsilon(\nu - p) - (p - p_s),$$
$$\dot{s} = \delta\left[-\frac{1}{\varepsilon}(p - p_s) - \{(1-\alpha)p - \Omega\}\right], \tag{3.6}$$
$$p_s = \frac{q^2}{s}, \quad q = 1 - \nu s,$$

where

$$\varepsilon = \frac{w_0}{h_{oc}p_0}, \quad \nu = \frac{I}{w_0}, \quad \delta = \frac{w_0 t_0}{m_{oc}S_0}, \quad \alpha = \frac{A_{\mathrm{L}}}{A_{\mathrm{E}}},$$
$$\Omega = \frac{w}{w_0}, \quad \nu = \frac{2S_0}{A}, \tag{3.7}$$

and where we also define

$$w_0 = K_{\mathrm{H}}\rho_{\mathrm{H_2O}}Pp_0. \tag{3.8}$$

Based on Table 1, typical values of the parameters are given in Table 3.

We are expecting pre-industrial steady values for p and S to be of $O(1)$. It is easy to ascertain steady states of these equations. These are

$$p = \frac{\nu - \Omega}{\alpha}, \tag{3.9}$$

which with the values in Table 3, give $p = 0.86$, corresponding to 30.3 Pa (but this motivated the choice of w), and then from $p_s \approx p$, we have $s \approx 0.79$, correponding to 0.19 mM. Obviously, the

Table 3

Values of scales and parameters

Symbol	Meaning	Typical value
A	Carbonate alkalinity	2.2 mM
p_0	CO_2 scale	35.2 Pa
S_0	Carbonate scale	0.24 mM
t_0	Time scale	100 y
v		0.87 (pre-industrial) 60.3 (anthropogenic)
w_0	Weathering scale	0.81×10^{13} mol y^{-1}
α		0.29
δ		2.48×10^{-3}
ε		1.28×10^{-2}
ν		0.22
Ω		0.62

values do not exactly match, but they indicate self-consistency in the parameter choice.

3.1. Pre-Industrial Steady State

More interesting is the transient approach to this steady state, which is easy to read, based on the small values of the parameters ε and δ. On a time scale of $t_0 \sim 100$ y (dimensionlessly $t \sim O(1)$), p approaches an equilibrium in which $p \approx p_s$, but more accurately

$$p - p_s = \varepsilon(v - p) \approx \varepsilon(v - p_s). \tag{3.10}$$

For longer time scales we substitute this into $(3.6)_2$ to obtain (also using $p \approx p_s$)

$$\dot{s} \approx \delta\left[\Omega - v + \frac{\alpha(1-\nu s)^2}{s}\right], \tag{3.11}$$

from which we can see that the carbonate ion approaches equilibrium on the longer time scale $\frac{t_0}{\delta} = \frac{m_{oc}S_0}{w_0} \sim 40{,}000$ y (dimensionlessly $t \sim \frac{1}{\delta}$).

3.2. Anthropogenic Future

Now, consider the nature of the solutions if we use the anthropogenic value of $v = 60.3$ (corresponding as in Table 1 to a 1990s release rate of 6 GtC y^{-1}). We take this initially as a constant, though in practice the value is steadily rising and is unlikely even to level off in the near future. We define

$$v_A = \varepsilon v \approx 0.77, \tag{3.12}$$

and note that it is of $O(1)$. The Eq. (3.6) takes the form

$$\begin{aligned} \dot{p} &= v_A - \varepsilon p - (p - p_s), \\ \dot{s} &= \delta\left[-\frac{1}{\varepsilon}(p - p_s) - \{(1-\alpha)p - \Omega\}\right], \end{aligned} \tag{3.13}$$

and again, it is simple to trace their solutions. On the same atmospheric time scale of 100 y, p reaches an approximate equilibrium

$$p \approx v_A + p_s. \tag{3.14}$$

The meaning of this is that the carbon we are pouring into the atmosphere reaches a quasi-steady state in which the influx is balanced by the efflux to the ocean. With the values in Table 3, this quasi-steady state is (taking p_s as a pre-industrial value 0.8, corresponding to 28 Pa) $p \approx 1.57$, corresponding to 55.2 Pa, or 552 ppmv. This is the good news; on a shortish time scale, the ocean can soak up our anthropogenic excess.

Beyond the century time scale, we have $p - p_s \approx v_A - \varepsilon p$, so that s is given by

$$\dot{s} \approx \delta\left[-\frac{v_A}{\varepsilon} + \alpha\left\{v_A + \frac{(1-\nu s)^2}{s}\right\} + \Omega\right]. \tag{3.15}$$

The behaviour of s is altered dramatically. It decreases almost linearly for a dimensional time

$$\frac{\varepsilon t_0}{\delta v_A} = \frac{m_{oc}S_0}{I} \approx 670 \text{ y}, \tag{3.16}$$

when it fairly abruptly reaches an equilibrium in which

$$s = \frac{\varepsilon\alpha}{v_A}\sigma, \quad p = \frac{v_A}{\varepsilon\alpha}\Pi, \tag{3.17}$$

so that $s \sim 4.8 \times 10^{-3}$ and $p \sim 208$. Thereafter, $\sigma \approx \frac{1}{\Pi}$, and Π increases toward an eventual equilibrium of $\Pi = 1$ on a time scale of $t \sim \frac{1}{\varepsilon\alpha}$, corresponding to 27,000 years. Illustrations of the short-term (millennial) response are shown in Fig. 1.

In Fig. 2, we show the results of releasing the estimated reserves of 5,000 GtC (Archer *et al.* 1997; we take 4,800 GtC) in different ways. The different

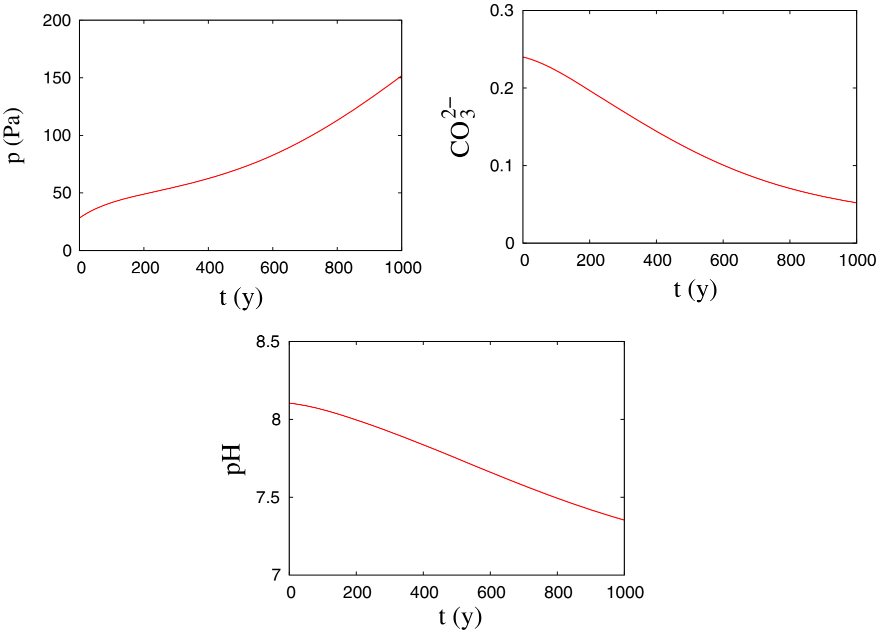

Figure 1
Evolution of CO_2, CO_3^{2-} (mM), and pH over the next millennium under conditions of continuing production of CO_2 at present levels

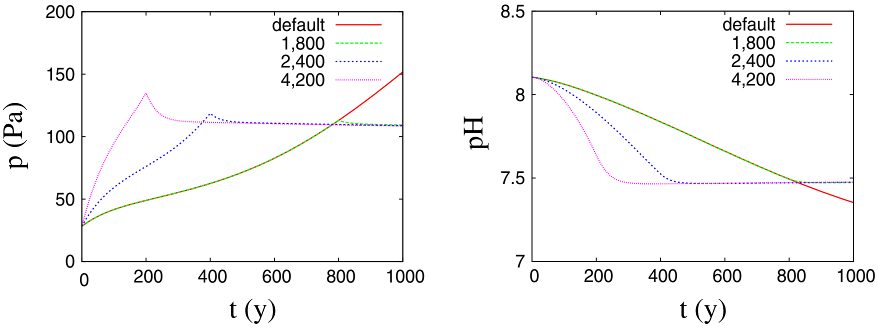

Figure 2
Evolution of p_{CO_2} and pH under different emissions scenarios. The labels have this meaning: 'default' means continued release at 'present' levels (1990s, 6 GtC y^{-1}) indefinitely; 1,800 indicates 6 GtC y^{-1} for 800 years and then zero emissions (switch-off); 2,400 means 12 GtC y^{-1} for 400 years and then a switch-off; 4,200 means 24 GtC y^{-1} for 200 years and then a switch-off. After the switch-off there are a further few decades while the ocean and atmosphere come into quasi-equilibrium, which is then maintained for thousands of years.

release mechanisms yield no ultimate difference, either in atmospheric CO_2 or in ocean pH; the only difference is one of time scale.

The message is simply stated. The carbon that we pour into the atmosphere pours into the ocean, but the maintenance of charge neutrality forces the carbonate ion to decrease dramatically to the level of ≈ 1 µM, a drop of about a factor of 200. Consulting (2.4), we see that the hydrogen ion concentration increases by 200, as does the dissolved CO_2. This causes a drop of pH of about 2.3 to 6.9, while the atmospheric CO_2, which follows ocean CO_2 via Henry's law in (3.14), jumps by about 200 to a dimensionless value of around 166, correspondng to 5,800 Pa, or 58,000 ppmv: 6 % of the atmosphere! Mankind would be long extinct by then. Of course, this assumes unlimited reserves and their continuing use; the more realistic case of finite reserves results in a saturation at 110 Pa, or 1,100 ppmv, and ocean pH levels at 7.5, as seen in Fig. 2.

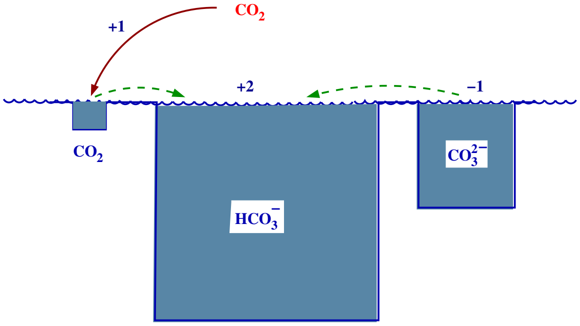

Figure 3
The ocean bicarbonate buffering system

4. *Conclusions*

The main purpose of this article was to make explicit in simple mathematical terms what the consequences of continued anthropogenic CO_2 output will be. Our model is stripped to its essentials, and consists only of two ordinary differential equations, for atmospheric CO_2 and oceanic CO_2. Yet this model yields essentially the same kind of quantitative result as do more complex simulation models, as used for example by Archer *et al.* (1997) and Zeebe *et al.* (2008). Specifically, the same results of rapid CO_2 rise and rapid pH decline are seen, with much slower recovery following the termination of carbon emissions. However, unlike the computational models, the simplicity of our approach enables the mechanisms of warming and acidification to be portrayed more clearly, and the time scales of the responses can be explicitly identified.

In its essence, the message is this. Increasing atmospheric CO_2 causes increased flux to the ocean, until a quasi-equilibrium is reached after a century or two when the ocean uptake balances the discharge to the atmosphere. However, when a mole of CO_2 is dissolved, the bicarbonate buffering system (Fig. 3) immediately empties it into the bicarbonate pool; this would cause charge imbalance, and thus at the same time, a carbonate ion is also transferred to the bicarbonate pool. In effect, the reaction is that described by Archer *et al.* (1997):

$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^- . \tag{4.1}$$

Thus, the flux of CO_2 to the ocean provides also an equivalent flux from the carbonate pool.

Because the acidity is controlled through the buffering relation (2.4)

$$[H^+] \propto \frac{[HCO_3^-]}{[CO_3^{2-}]}, \tag{4.2}$$

$[H^+]$ increases, i. e., pH decreases, resulting in ocean acidification. But at the same time, because

$$[CO_2] \propto \frac{[HCO_3^-]^2}{[CO_3^{2-}]}, \tag{4.3}$$

the dissolved CO_2 increases; not directly because of the flux from the atmosphere, but because of the decrease in carbonate, and the rate of increase is faster than linear. This second consequence of carbonate loss is what causes the accelerated increase of atmospheric CO_2, and its attendant greenhouse effect, following the initial lull.

Our model simulations in Fig. 1 are based on a constant input, while Zeebe *et al.* (2008) consider the input of a fixed quantity corresponding to the total reserves, perhaps 5,000 GtC. It is straightforward to read from (3.15) what happens in this case. The carbonate declines until the ocean has absorbed most of the atmospheric load, but the subsequent recovery of the ocean carbonate takes place over a much longer time scale, that being tens of thousands of years.

As with all models, and particularly this one, the results must be tempered with caution. In particular, the neglect of ocean mixing requires consideration, most notably as regards the vertical profile. With a mixing time on the order of 1,000 years, carbonate changes on shorter time scales than this will be restricted to the upper parts of the ocean. The practical effect is to reduce the effective value of m_{oc} in (3.1), and thus increase δ in (3.6). Consulting (3.16), this suggests that the drawdown in carbonate ion content will be even faster, and further study of this issue is warranted.

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References

Archer, D. 1999 Modeling CO_2 in the ocean: a review. In: Scaling of trace gas fluxes between terrestrial and aquatic ecosystems and the atmosphere, ed. A., F. Bouwman. Developments in Atmospheric Science, Vol. **24**, pp. 169–184, Elsevier Sciences, Amsterdam.

Archer, D. and V. Brovkin 2008 The millennial atmospheric lifetime of anthropogenic CO_2. Climate Change **90**, 283–297.

Archer, D., H. Kheshgi and E. Maier-Reimer 1997 Multiple timescales for neutralization of fossil fuel CO_2. Geophys. Res. Letts. **24**, 405–408.

Bijl, P.K., J.A.P. Bendle, S.M. Bohaty, J. Pross, S. Schouten, L. Tauxeg, C. E. Stickley, R.M. McKay, U. Röhl, M. Olney, A. Sluijs, C. Escutia, H. Brinkhuis, and Expedition 318 Scientists 2013 Eocene cooling linked to early flow across the Tasmanian Gateway. Proc. Nat. Acad. Sci. **110**, 9,645–9,650.

Budyko, M.,I. 1969 The effect of solar radiation variations on the climate of the Earth. Tellus **21**, 611–619.

Caldeira, K. 1992 Enhanced Cenozoic chemical weathering and the subduction of pelagic carbonate. Nature **357**, 578–581.

Denman, K.L., G. Brasseur, A. Chidthaisong, P. Ciais, P.M. Cox, R.E. Dickinson, D. Hauglustaine, C. Heinze, E. Holland, D. Jacob, U. Lohmann, S. Ramachandran, P.L. da Silva Dias, S.C. Wofsy and X. Zhang 2007 Couplings between changes in the climate system and biogeochemistry. *In: Climate change 2007: the physical science basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, eds. S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller. C.U.P., Cambridge.

Eby, M., K. Zickfeld, A. Montenegro, D. Archer, K.J. Meissner and A.J. Weaver 2009 Lifetime of anthropogenic climate change: millennial time scales of potential CO_2 and surface temperature perturbations. J. Climate **22**, 2,501–2,511.

Emerson, S.R. and J.I. Hedges 2008 Chemical oceanography and the marine carbon cycle. C.U.P., Cambridge.

Fowler, A.C., R.E.M. Rickaby and E.W. Wolff 2013 A simple model of ice ages. Int. J. Geomath. **4**, 227–297.

Ganopolski, A., R. Calov and M. Claussen 2010 Simulation of the last glacial cycle with a coupled climate ice-sheet model of intermediate complexity. Clim. Past **6**, 229–244.

Gillett, N.P., V.K. Arora, K. Zickfeld, S.J. Marshall and W.J. Merryfield 2011 Ongoing climate change following a complete cessation of carbon dioxide emissions. Nature Geosci. **4**, 83–87.

Holland, D.M, R.H. Thomas, B. de Young and M.H. Ribergaard 2008 Acceleration of Jakobshavn Isbrae triggered by warm subsurface ocean waters. Nature Geoscience **1**, 659–664.

Houghton, J.T. 2009 Global warming: the complete briefing, 4th ed. C.U.P., Cambridge.

Johnson, H .L., D.P. Marshall and D.A.J. Sproson 2007 Reconciling theories of a mechanically driven meridional overturning circulation with thermohaline forcing and multiple equilibria. Clim. Dyn. **29**, 821–836.

Palmer, T.N. 2001 A nonlinear dynamical perspective on model error: a proposal for non-local stochastic-dynamic parametrization in weather and climate prediction models. Quart. J. R. Met. Soc. **127**, 279–304.

Pearson, P.N. and M.R. Palmer 2000 Atmospheric carbon dioxide concentrations over the past 60 million years. Nature **406**, 695–699.

Petit, J.R., J. Jouzel, D. Raynaud, N.I. Barkov, J.-M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V.M. Kotlyakov, M. Legrand, V.Y. Lipenkov, C. Lorius, L. Pépin, C. Ritz, E. Saltzman and M. Stievenard 1999 Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. Nature **399**, 429–436.

Pierrehumbert, R.T. 2010 Principles of planetary climate. C.U.P., Cambridge.

Pollard, D. and R.M. DeConto 2005 Hysteresis in Cenozoic Antarctic ice-sheet variations. Global Planet. Change **45**, 9–21.

Pross, J., L. Contreras, P.K. Bijl, D.R. Greenwood, S.M. Bohaty, S. Schouten, J.A. Bendle, U. Röhl, L. Tauxe, J.I. Raine, C.E. Huck, T. van de Flierdt, S.,S.R. Jamieson, C.E. Stickley, B. van de Schootbrugge, C. Escutia, H. Brinkhuis and Integrated Ocean Drilling Program Expedition 318 Scientists 2012 Persistent near-tropical warmth on the Antarctic continent during the early Eocene epoch. Nature **488**, 73–77.

Ridgewell, A. and R.E. Zeebe 2005 The role of the global carbonate cycle in the regulation and evolution of the Earth system. Earth Planet. Sci. Letts. **234**, 299–315.

Rignot, E., D.G. Vaughan, M. Schmeltz, T. Dupont and D. MacAyeal 2002 Acceleration of Pine Island and Thwaites Glaciers, West Antarctica. Ann. Glaciol. **34**, 189–194.

Rott, H., P. Skvarca and T. Nagler 1996 Rapid collapse of Northern Larsen Ice Shelf, Antarctica. Science **271**, 788–792.

Sellers, W.D. 1969 A climate model based on the energy balance of the earth-atmosphere system. J. Appl. Meteorol. **8**, 392–400.

Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.) 2007 Climate Change 2007: The Physical Science Basis. C.U.P., Cambridge.

Solomon, S., G.-K. Plattner, R. Knutti and P. Friedlingstein 2009 Irreversible climate change due to carbon dioxide emissions. Proc. Nat. Acad. Sci. **106**, 1,704–1,709.

Tiedtke, M. 1993 Representation of clouds in large-scale models. Month. Weath. Rev. **121**, 3.040–3.061.

Toggweiler, J.R. 2008 Origin of the 100,000–year timescale in Antarctic temperatures and atmospheric CO_2. Paleoceanogr. **23**, PA2211, doi:10.1029/2006PA001405.

Walker, J.C.G., P.B. Hays and J.F. Kasting 1981 A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. J. Geophys. Res. **86** (C10), 9,776–9,782.

Zachos, J.C., J.R. Breza and S.W. Wise 1992 Early Oligocene ice-sheet expansion on Antarctica: stable isotope and sedimentological evidence from Kerguelen Plateau, southern Indian Ocean. Geology **20**, 569–573.

Zeebe, R.E. 2012a History of seawater carbonate chemistry, atmospheric CO_2, and ocean acidification. Ann. Rev. Earth Planet. Sci. **40**, 141–65.

Zeebe, R.E. 2012b 'LOSCAR': Long-term Ocean-atmosphere-Sediment CArbon cycle Reservoir model v2.0.4. Geosci. Model Dev. **5**, 149–166.

Zeebe, R.E. and D. Wolf-Gladrow 2001 CO_2 in seawater: equilibrium, kinetics, isotopes. Elsevier, Amsterdam.

Zeebe, R.E., J.C. Zachos, K. Caldeira and T. Tyrell 2008 Carbon Emissions and Acidification. Science **321**, 51–52.

Zeebe, R.E. and J.C. Zachos 2013 Long-term legacy of massive carbon input to the Earth system: Anthropocene vs. Eocene. Phil. Trans. R. Soc. A, in press.

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