

The long-term legacy of fossil fuels

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ABSTRACT

Fossil fuels will have large impacts on ocean chemistry and climate during the period while they are being burnt (and carbon dioxide emitted) in large amounts. It is frequently assumed that these impacts will fade away soon thereafter. Recent model results, by contrast, suggest that significant impacts will persist for hundreds of thousands of years after emissions cease. We present a new analysis that supports these model findings by elucidating the cause of this ‘fossil fuel hangover’ phenomenon. We explain why the carbonate compensation feedback is atypical, compared to other feedbacks, in the sense that convergence is back towards a new steady-state that is distinct from the starting state. We also calculate in greater detail the predicted implications for the future ocean and atmosphere. The post-fossil fuel long-term equilibrium state could differ from the pre-anthropogenic state by as much as 50% for total dissolved inorganic carbon and alkalinity and 100% for atmospheric $p\text{CO}_2$, depending on the total amount of future emissions.

1. Introduction

Anthropogenic emissions of CO_2 into the atmosphere [deriving mostly from burning of coal, oil and gas but also from cement production and land-use change (Prentice et al., 2001)] are causing global warming, and, following diffusion across the sea surface, ocean acidification (Caldeira and Wickett, 2003, 2005; Orr et al., 2005). Impacts will be greatest over the next few centuries but the longer-term behaviour of the carbon cycle is also of interest, for instance in relation to when the next ice age may start and more generally to the quality of the environment we will bequeath to our distant descendants. A recent multinational effort to extract Antarctic ice cores containing much older ice than was previously possible (Siegenthaler et al., 2005) was in part motivated by the desire to examine the interglacial period that ended about 430 000 yr ago, because Earth’s orbital dynamics at that time were similar to today’s and it is thought that the behaviour of the older interglacial may give clues as to when the current interglacial will end (e.g. Loutre, 2003).

The relevance of such a comparison is questioned, however, by recent work that argues that ~8% of fossil fuel CO_2 will remain in the atmosphere for hundreds of thousands of years (Archer et al., 1997, 1998; Archer and Ganopolski, 2005; Archer, 2005), and therefore, even if only 1000 Gt C are eventually emitted, corresponding to about a quarter of recoverable fossil fuels, that the next glaciation is likely to be missed out altogether (Archer

and Ganopolski, 2005). If this result is correct then, because of the residual anthropogenic CO_2 , the future will not resemble past glacial–interglacial cycles and will not be predictable from comparison with them. Here we carry out new model runs aimed at investigating this result, and present a new theoretical explanation.

2. Methods

2.1. Model

The model (Chuck et al., 2005) is an attempt to capture the most significant dynamics of the medium- to long-term behaviour of the ocean carbon cycle in the simplest possible physical structure. It consists of three vertically stacked boxes, the upper one (100 m deep) representing the euphotic zone, the middle one (400 m deep) containing water down to the average depth of maximum annual mixing, and the deep box (3230 m deep) representing all deep ocean water that only connects with the surface via the slower processes of upwelling, ocean circulation and diffusion. Because of the simple physical structure the model does not include any representation of spatial variability such as Atlantic versus Pacific, open ocean versus shelves or high versus low latitudes. For this reason the model does not simulate the solubility pump, which contributes to a lesser degree to the maintenance of vertical gradients in the ocean (Cameron et al., 2005).

The following tracers are transported around the model ocean: inorganic phosphate (PO_4), phytoplankton (surface box only, expressed separately in units of phosphorus, ^{12}C and ^{13}C), DI^{12}C ,

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DI¹³C and alkalinity, giving rise to 15 state variables. The surface ocean exchanges carbon dioxide with coupled atmospheric reservoirs of ¹²CO₂ and ¹³CO₂, the final two state variables. The model code includes mass balance checks to ensure conservation of the summed ocean + atm reservoirs of the different tracers, after taking into account inputs (via rivers and fossil fuels) and outputs (via burial) to the system as a whole. Material can transgress the boundaries; it is an open-system rather than a closed-system model.

Phosphate is assumed to be the ultimate limiting nutrient over these timescales (Tyrrell, 1999), and the representation of phytoplankton and its limitation by phosphate is taken from that model. The strength of the organic carbon pump in the model is therefore dependent on the supply of new phosphate to the surface box.

Dissolved inorganic carbon (DIC) in seawater is made up of three different chemical species: dissolved CO₂ gas (CO₂(aq)), bicarbonate ions (HCO₃⁻) and carbonate ions (CO₃²⁻). This system has two degrees of freedom, and so concentrations of all three species can be calculated from knowledge of any two parameters of the system, for instance from DIC and alkalinity in this case. The distribution of DIC between these three forms, the seawater pH, and the calculation of the partial pressure of CO₂ (*p*CO₂) from its concentration ([CO₂(aq)]), were calculated using routines supplied by Zeebe and Wolf-Gladrow (2001), using the constants of Mehrbach et al. (1973) refit by Lueker et al. (2000). [CO₃²⁻] and *p*CO₂ were then used to calculate lysocline depth and air-sea gas exchange. After adding 4000 Gt C, the size of the post-fossil fuel increments to equilibrium values vary a little (by ≤4% for [DIC] and [Alk] and ≤22% for *p*CO₂), depending on the choice of dissociation constants used (see Appendix A), but they are always large and positive. The main findings are therefore robust with respect to the choice of dissociation constants.

Calcium carbonate (CaCO₃) is produced in the model in direct proportion to the magnitude of primary production. This fixed ratio of calcification to photosynthesis also leads to a fixed export ratio (rain ratio, PIC:POC) of 0.15:1. 30% of the calcium carbonate flux falling into the middle box is dissolved there (required in order to reproduce observed vertical gradients in alkalinity). The fate of the remainder of the CaCO₃ particle flux varies according to the value of [CO₃²⁻] in the deep ocean. The model does not include an explicit representation of sediments. The depth of the saturation horizon for calcite is calculated from [CO₃²⁻] deep according to eq. (4) of Jansen et al. (2002): [CO₃²⁻]_c(*z*) = 88.7 exp(0.189[*z* - 3.82]), where *z* is the depth in kilometres and [CO₃²⁻]_c(*z*) is the saturating carbonate ion concentration, for a given depth.

The gradual transition on the ocean floor between the onset of dissolution (at the lysocline) to complete dissolution (at the CCD) is simplified in the model to a simple step boundary between 0 and 100% dissolution. The fractions of the falling CaCO₃ flux which are buried or dissolved are then calculated using the

ocean hypsometry. Once CaCO₃ is buried in the model it is lost from the system and is not made available for later dissolution if bottom waters become more acidic.

An earlier version of this model (without a dynamic lysocline) was used to calculate impacts of different potential anthropogenic changes to the ocean on the rise in atmospheric CO₂ (Chuck et al., 2005, which can be consulted for model equations and parameter values) and for most scenarios gave broadly comparable results to the other models used in that study. While appropriate for the task here, that is, calculating the post-fossil fuel ocean chemical equilibrium, because of its simplicity the model predictions of transient behaviour (as the ocean moves to the new equilibrium) should be treated with caution.

2.2. Graphical calculations

Carbon chemistry calculations for graphs (e.g. isolines of *p*CO₂ and CO₃²⁻ in Figs. 2 and 3) were made using the same routines and constants as for the model runs. Calculations were carried out at a temperature of 17 °C, salinity of 35 and pressure of 1 atmosphere.

3. Results

Most carbon cycle modelling studies are not run far into the future because of the computational costs, but the few model runs of longer duration (Sundquist, 1986, 1990; Archer et al., 1998; Caldeira and Wickett, 2003; Lenton and Britton, 2006) that have been carried out have found extended durations of elevated atmospheric *p*CO₂ and offsets between pre- and post-emissions *p*CO₂ levels (see Table 1). We obtained a similar result (Fig. 1) with our model. The model was forced in the first instance with a single sinusoidal pulse of fossil fuels (cumulative total magnitude 4000 Gt C) imposed between the years 1900 and 2300.

Even after the system settles to a new steady-state subsequent to the fossil fuel transient, neither atmospheric CO₂ (Fig. 1b), nor ocean DIC (Fig. 1c), nor ocean alkalinity (Fig. 1d) return to their pre-anthropogenic values. The system converges to a new equilibrium.

4. Discussion

4.1. Earlier explanation

After encountering the same phenomenon as discussed in Archer's work (Archer et al., 1997, 1998; Archer and Ganopolski, 2005; Archer, 2005), we searched for the underlying explanation. Archer et al. (1997) presented an algebraic derivation of the reason for the phenomenon. However, this calculation included some approximations and also the explicit assumption that, by the time post-fossil fuel equilibrium is reached, every unit of anthropogenic CO₂ added to the Earth system will have induced the dissolution of exactly one unit of calcium carbonate

Table 1. High atmospheric $p\text{CO}_2$ for thousands of years after emissions cease, from various model studies

Source	Total fossil fuels added (Gt C)	Run duration (yr)	Pre-anthropogenic $p\text{CO}_2$ (ppmv)	Final $p\text{CO}_2$ (ppmv)	$\Delta p\text{CO}_2$ (ppmv)
Caldeira and Wickett (2003)	5270	700	~300	~1500	+1200
Walker and Kasting (1992)	4200	2700	~350	~850	+500
Sundquist (1986)	5000	10 000	~300	~550	+250
Archer (1997)	3000	38 000	~280	~420	+140
Lenton and Britton (2006)	4000	1 000 000	~280	~420 ^a	+140 ^a
This study	4000	300 000	282	429	+147

Values from the literature are estimated by eye from the published graphs. Run durations are measured from the time of peak model atmospheric $p\text{CO}_2$, at about year 2300.

^aIn a run without silicate weathering; if silicate weathering is also included then atmospheric $p\text{CO}_2$ eventually returns to pre-industrial levels after hundreds of thousands of years (Lenton and Britton, 2006).

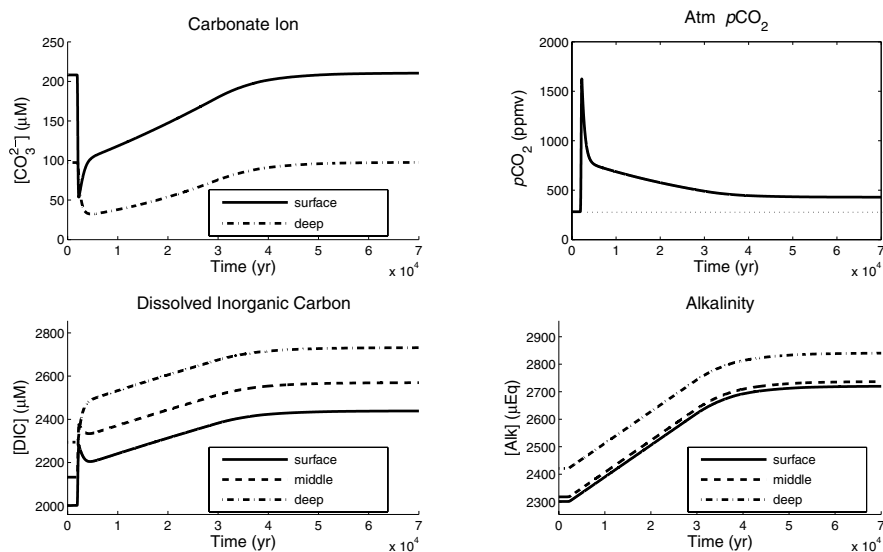


Fig. 1. Response of a simple ocean carbon cycle model to the addition of 4000 Gt C of fossil fuels: (a) recovery of $[\text{CO}_3^{2-}]$ to the same value as before fossil fuel emissions; (b) post-fossil fuel stabilization of atmospheric CO_2 to a higher level than before emissions (dotted line shows pre-industrial $p\text{CO}_2$); (c) dissolved inorganic carbon (DIC) and (d) total alkalinity. μM is micromoles per litre, μEq is micro-equivalents per litre.

in response. Caldeira and Wickett (2005) found instead that, to maintain constant $[\text{CO}_3^{2-}]$, somewhat less than 1 unit of CaCO_3 has to be dissolved per added mol of fossil fuel CO_2 , and we found a ratio of $\sim 0.9:1$ in our model. Archer (2005) notes the lack of attention paid to his earlier work in this area, which may perhaps reflect the rather complex and uncertain derivation. Here we present an alternative explanation that we think provides a more convincing explanation of the phenomenon.

4.2. Our explanation

This explanation hinges on the nature of the carbonate compensation process, which is a negative feedback process that plays a

major role in controlling ocean carbon chemistry (Broecker and Peng, 1987; Sundquist, 1990; Walker and Kasting, 1992; Archer et al., 1997; Zeebe and Westbroek, 2003). The term refers to the negative feedback provided by the adjustment of the calcite and aragonite lysoclines in the ocean so as to regulate carbonate ion concentration ($[\text{CO}_3^{2-}]$). It acts as follows. If the ocean becomes more acid (as is happening at present (Caldeira and Wickett, 2003), as anthropogenic carbon dioxide diffuses into the ocean) then carbonate ion concentration drops (Orr et al., 2005). This causes a shallowing of the calcite and aragonite lysoclines (Caldeira and Wickett, 2005). These lysoclines define the depths at which the two forms of calcium carbonate

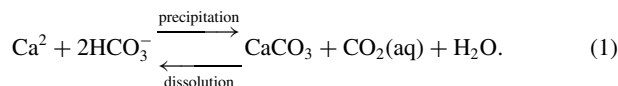
dissolve in the ocean. Above the calcite lysocline, nearly all of the calcite that falls to the sea floor accumulates in the sediments. Below the calcite lysocline the waters become corrosive, leading to dissolution of calcite in sea floor sediments which releases calcium and carbonate ions back into the sediment pore waters and thence, by diffusion, into the overlying ocean. Shallowing of the lysoclines increases global dissolution and decreases burial. This brings about an imbalance between the riverine input of dissolved calcium and carbon and their removal in buried calcium carbonate, such that ocean carbonate ion concentration increases, which will continue until the original, steady-state carbonate ion concentration is re-attained. The e-folding response time for carbonate compensation is variously estimated at between 6 and 14 ky (Sundquist, 1986; Archer et al., 1997, 1998; Zeebe and Westbroek, 2003).

It is the unusual properties of the carbonate compensation response that will, it appears, cause extra CO_2 to remain in the atmosphere following recovery from fossil fuels. The reason that the system returns to a new steady-state that is different from before is that carbonate compensation is a negative feedback on $[\text{CO}_3^{2-}]$ only. It is not a negative feedback on [DIC] or [Alk] or atmospheric $p\text{CO}_2$. It affects them only indirectly. In the process of stabilizing $[\text{CO}_3^{2-}]$ the feedback will drive other dissolved carbon system variables to novel values.

The reasons for the predicted system behaviour become clearer when several fossil fuel perturbations and associated carbonate compensation responses are drawn on a dual contour plot of $p\text{CO}_2$ and $[\text{CO}_3^{2-}]$ against DIC and alkalinity (Fig. 2). We calculated the responses to three different emissions scenarios: (1) 1000 Gt C [optimistic assumption, equivalent to most fossil fuel reserves staying untapped and no release of methane clathrates;

about 300 Gt C have been released so far (Marland et al., 2005)], (2) 4000 Gt C (equivalent to virtually all recoverable fossil fuel reserves eventually being tapped, but with no release of methane clathrates) and (3) 8000 Gt C (pessimistic assumption, in which the burning of all fossil fuels is accompanied by the exploitation and/or warming-induced release of a fraction of methane clathrates).

Burning of fossil fuels extracted from underground is a source of carbon but not of alkalinity, leading to a horizontal shift to the right in Fig. 2. The carbonate compensation response (reduction in calcium carbonate burial), on the other hand, results in an accumulation of both DIC and alkalinity. The equation for calcification/dissolution is:

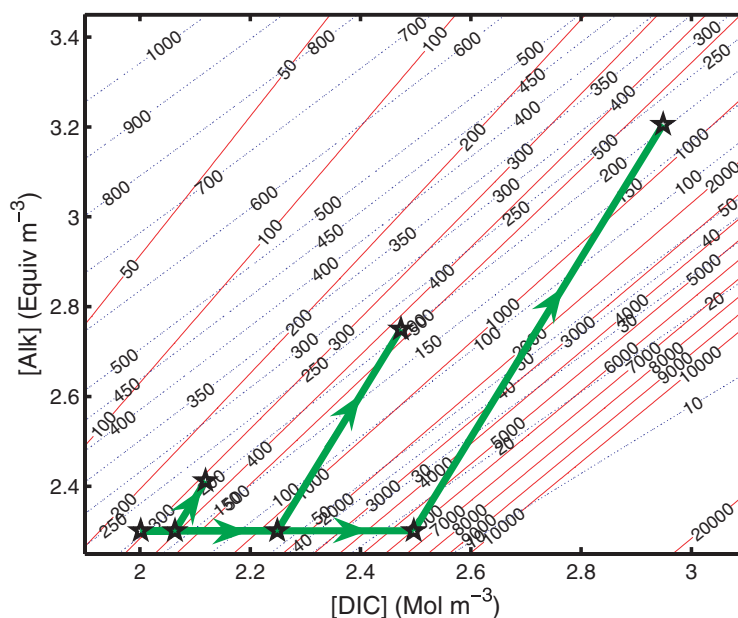


For every mole of DIC added to the ocean by dissolution of CaCO_3 that would otherwise have been buried, two moles of alkalinity are simultaneously added, because solid CaCO_3 contains a doubly charged positive Ca^{2+} atom but only a single carbon atom. There is therefore a 2:1 positive slope on the feedback line in Fig. 2. The lysocline will stay shallow and the ocean relatively undersaturated with respect to CaCO_3 until the deep ocean carbonate ion returns to its original concentration of about $90 \mu\text{M}$ (Jansen et al., 2002).

4.3. Unusual feedback

A straightforward negative feedback is directly antagonistic to the perturbation. Here the induced feedback follows a trajectory which is far from opposite to the original; in fact, instead of being at an angle of 180° it is at an angle of less than 90° to the

Fig. 2. Fossil fuel perturbation and carbonate compensation response in DIC-Alk space. The carbon chemistry of seawater has two degrees of freedom, allowing calculation of isolines of $p\text{CO}_2(\text{aq})$ (red solid lines) and $[\text{CO}_3^{2-}]$ (blue dashed lines) as a function of [DIC] and [Alk]. Superimposed on these are three scenarios (1000, 4000 and 8000 Gt C) for total fossil fuel emissions over the next few centuries (the 'perturbations', shown as horizontal solid green lines starting from an initial pre-industrial state of $\text{DIC} = 2000 \mu\text{M}$ and alkalinity = $2300 \mu\text{Eq}$) and the three corresponding feedbacks by which the system returns to $[\text{CO}_3^{2-}]$ equilibrium (diagonal solid green lines).



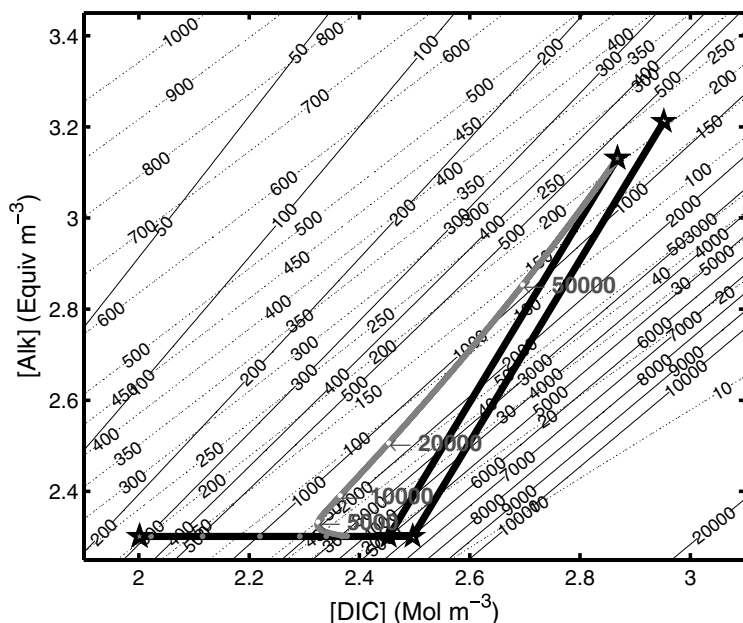


Fig. 3. Comparison of model- and graphically calculated response to addition of 8000 Gt C. The same isolines of $p\text{CO}_2(\text{aq})$ (thin solid lines) and $[\text{CO}_3^{2-}]$ (thin dotted lines) as shown in Fig. 2 are also shown here, as is the 8000 Gt C perturbation and response (thick black lines). The additional perturbation and response represents the equivalent calculation for 7294 Gt C of fossil fuels, corresponding to the final amount of fossil fuel carbon that ends up residing in the ocean following the addition of 8000 Gt C to the atmosphere. Grey dots (every 500 yr) show the trajectory of ocean surface DIC and alkalinity through the course of the 300 ky model run, with arrows indicating the surface ocean chemistry at 5, 10, 20 and 50 ky (fossil fuels were added around year 2000). The model converges to the analytically predicted end-point.

original (in DIC-Alk space). The combination of: (1) the feedback response being far from the direct opposite of the perturbation and (2) contours of $p\text{CO}_2$ and $[\text{CO}_3^{2-}]$ not being quite parallel, explains why the post-fossil fuel equilibrium will be different from the pre-industrial equilibrium state.

4.4. Including airborne fraction

The feedback lines in Fig. 2 assume that all of the fossil fuel carbon dioxide emitted to the atmosphere ends up in the ocean, which is not completely realistic; in our model 8–10% remains permanently in the atmosphere and hence does not instigate carbonate compensation. A very close fit to model results is obtained if the airborne fraction is kept out of the ocean (see Fig. 3 and Table 2), suggesting that the graphical analysis successfully explains the reason for the model results.

4.5. Predicted changes to ocean chemistry

The major likely after-effects of the three different scenarios are summarized in Table 3. Atmospheric CO_2 could plateau at up to 600 ppm, more than double pre-industrial values, and remain at that level for several hundred thousand years. DIC and alkalinity could plateau at values nearly 50% higher than pre-industrial (for the most extreme scenario), which is much higher than might naively be expected since the inventory of DIC is originally perturbed by only ~20%.

The implications for a wider range of chemical parameters are shown in Table 4.

The simple ocean model used here includes changes in lysocline depth as a function of time-varying $[\text{CO}_3^{2-}]$. Other feedbacks are also likely or possible but have not been included here.

Some of these feedbacks will act in concert with carbonate compensation to return $[\text{CO}_3^{2-}]$ towards equilibrium. For example, (1) acidification of the ocean may well considerably reduce the rate of formation of CaCO_3 in the surface ocean over the next few centuries (Raven et al., 2005) and (2) a more acidic ocean is likely to cause dissolution and erosion of calcium carbonate previously deposited in the sediments (Sundquist, 1990; Archer et al., 1997, 1998). These two feedbacks will not alter the new steady-state that is attained, they will only hasten the rate at which the new steady-state is reached. Regrowth of terrestrial vegetation and other processes could mitigate the rise in ocean DIC considered here, or Amazon die-off and increased respiration of soil microbes (Cox et al., 2000) could exacerbate it. Purposeful disposal of CO_2 in the deep ocean would affect the transient behaviour but not the long-term equilibrium considered here. Over even longer timescales weathering-related feedbacks may, by altering the rate of flow of carbon and alkalinity to the ocean, eventually bring the system back towards the pre-industrial equilibrium. The residence time of ocean DIC with respect to silicate weathering is, however, of order 1 Myr (Kump et al., 2004).

From both Figs. 1 and 2, it is clear that the greater the amount of fossil fuels eventually burnt, the larger will be the difference between the pre- and post-fossil fuel atmospheric CO_2 and climate. It has recently been predicted that the relic atmospheric CO_2 could delay glaciation for as long as 500 000 yr (Archer and Ganopolski, 2005). Emission of fossil fuels may continue for a few hundreds of years, but it appears that the after-effects will continue to affect climate for hundreds of thousands of years. Our results support Archer's work and additionally demonstrate the likelihood of large future excursions in the levels of DIC and alkalinity in the oceans. These are in addition to the shorter-term effects on pH, which may have pervasive consequences

Table 2. Comparison between model- and graph-derived impacts

Fossil fuel scenario	From model results				From graphical calculations			
	Chemical changes		Carbon inventories		Chemical changes			
	$\Delta[\text{DIC}]$ (μM)	$\Delta[\text{Alk}]$ (μM)	$\Delta p\text{CO}_2$ (ppmv)	Total ^a (Gt C)	Extra C in ocean CaCO_3 dissolution ^b (Gt C)	Emissions ^c (Gt C)	Extra C in atm. Emissions ^d (Gt C)	Most added C in ocean, some in atm. ^e
1000 Gt C	+111	+106	+33	1790	862	928	72	$\Delta[\text{DIC}]$ (μM) $\Delta[\text{Alk}]$ (μM) $\Delta p\text{CO}_2$ (ppmv) $\Delta[\text{DIC}]$ (μM) $\Delta[\text{Alk}]$ (μM) $\Delta p\text{CO}_2$ (ppmv) $\Delta[\text{DIC}]$ (μM) $\Delta[\text{Alk}]$ (μM) $\Delta p\text{CO}_2$ (ppmv)
4000 Gt C	+438	+419	+147	7073	3391	3682	318	$\Delta[\text{DIC}]$ (μM) $\Delta[\text{Alk}]$ (μM) $\Delta p\text{CO}_2$ (ppmv) $\Delta[\text{DIC}]$ (μM) $\Delta[\text{Alk}]$ (μM) $\Delta p\text{CO}_2$ (ppmv) $\Delta[\text{DIC}]$ (μM) $\Delta[\text{Alk}]$ (μM) $\Delta p\text{CO}_2$ (ppmv)
8000 Gt C	+867	+830	+327	14003	6709	7294	706	$\Delta[\text{DIC}]$ (μM) $\Delta[\text{Alk}]$ (μM) $\Delta p\text{CO}_2$ (ppmv) $\Delta[\text{DIC}]$ (μM) $\Delta[\text{Alk}]$ (μM) $\Delta p\text{CO}_2$ (ppmv) $\Delta[\text{DIC}]$ (μM) $\Delta[\text{Alk}]$ (μM) $\Delta p\text{CO}_2$ (ppmv)

By comparing columns 2–4 with columns 12–14 it can be seen that there is good agreement between the two approaches, when the airborne fraction is taken into account. The values in columns 2–8 are the final values after running the model scenarios out to 300 000 yr in the future, at which point the post-fossil fuel steady-state has been reached (deep ocean $[\text{CO}_3^{2-}]$ has returned to the pre-fossil fuel value). Square brackets denote concentrations. Δ denotes the difference between the pre-industrial values (surface ocean: $[\text{DIC}] = 2000 \mu\text{M}$, $[\text{Alk}] = 2300 \mu\text{Eq}$; atmospheric $p\text{CO}_2 = 282 \text{ ppmv}$) and the post-fossil fuel equilibrium values.

^aCalculated by multiplying the difference between pre- and post-fossil fuel $[\text{DIC}]$'s by the box volumes.

^bCalculated by multiplying the increment to the ocean's alkalinity content (not shown) by 0.5, because calcification and dissolution impact $[\text{DIC}]$ and $[\text{Alk}]$ in a 1:2 ratio.

^cCalculated as the difference between the numbers in the two previous columns.

^dCalculated by multiplying the difference between pre- and post-fossil fuel atmospheric $p\text{CO}_2$ by the atmospheric volume.

^eValues of 928, 3682 and 7294 Gt C are taken from column 7.

Table 3. Long-term impacts of various magnitudes of total emissions on the ocean and atmosphere

Scenario	Equilibrium after fossil fuel emissions have ceased		
	$\Delta[\text{DIC}]$ (μM)	$\Delta[\text{Alk}]$ (μEq)	$\Delta p\text{CO}_2$ (ppm)
(pre-industrial)	0	0	0
1: 1000 Gt C (1/4 of fossil fuel reserves)	+111	+106	+33
2: 4000 Gt C (all reserves)	+438	+419	+147
3: 8000 Gt C (all reserves plus most clathrates)	+867	+830	+327

ΔDIC , ΔAlk and $\Delta p\text{CO}_2$ are the differences between pre-industrial values ($[\text{DIC}] = 2000 \mu\text{M}$, $[\text{Alk}] = 2300 \mu\text{Eq}$, $p\text{CO}_2 = 282 \text{ ppm}$) and those of the new steady-state in the future, after carbonate compensation has restored deep $[\text{CO}_3^{2-}]$ to its equilibrium value. These were calculated by running the model out to 300 000 yr into the future. By way of comparison, ice core records show that the amount of CO_2 in the atmosphere naturally varies between about 180 ppm (depths of ice ages) and 280 ppm (interglacials), i.e. a natural range of about 100 ppm.

Table 4. Model-calculated impacts in greater detail. All values are the differences between pre-industrial values (surface ocean: $[\text{DIC}] = 2000 \mu\text{M}$, $[\text{HCO}_3^-] = 1780 \mu\text{M}$, $[\text{CO}_3^{2-}] = 210 \mu\text{M}$, $[\text{CO}_2(\text{aq})] = 10 \mu\text{M}$, $\text{pH} = 8.16$, $[\text{Alk}] = 2300 \mu\text{Eq}$; atmospheric $p\text{CO}_2 = 282 \text{ ppmv}$) and those of the future steady-state, after carbonate compensation has restored deep ocean $[\text{CO}_3^{2-}]$ to its equilibrium value.

Fossil Fuel Total (Gt C)	Surface ocean						Atmosphere
	$\Delta[\text{DIC}]$ (μM)	$\Delta[\text{HCO}_3^-]$ (μM)	$\Delta[\text{CO}_3^{2-}]$ (μM)	$\Delta[\text{CO}_2(\text{aq})]$ (μM)	ΔpH Total scale	$\Delta[\text{Alk}]$ (μEq)	$\Delta p\text{CO}_2$ (ppmv)
1000	+111	+109	+1	+1	−0.02	+106	+33
4000	+438	+429	+3	+5	−0.09	+419	+147
8000	+867	+852	+3	+12	−0.16	+830	+327

(Raven et al., 2005). We are not currently aware of any reason to believe that these long-term changes to DIC and alkalinity will impact negatively on ocean life, but in light of the magnitude of the changes appropriate experiments should be conducted.

5. Conclusions

Our new analysis supports earlier work by David Archer (Archer et al., 1997, 1998; Archer and Ganopolski, 2005; Archer, 2005) and confirms that the carbonate compensation feedback induced by ocean acidification will, as a side-effect, cause a remnant of fossil fuel CO_2 emissions to remain in the atmosphere for many thousands of years, possibly many hundreds of thousands of years. Our analysis clarifies how the carbonate compensation feedback should return the ocean to the pre-perturbation (pre-industrial) CaCO_3 saturation state, but in the process of so doing will shift the ocean to a new state with respect to other chemical parameters such as atmospheric CO_2 .

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Appendix A: Robustness of results to choice of constants

As shown in Table A1, there is some quantitative sensitivity to the choice of dissociation constants, but large positive increments to [DIC], [Alk] and pCO₂ (of approximately the same magnitude) are seen in all cases. Sensitivity to the first two sets of constants was calculated by running the model out for 300 000 yr, using the carbon chemistry calculations supplied by Zeebe and Wolf-Gladrow (2001); all others were estimated graphically using Lewis and Wallace's (1998) CO₂SYS code.

Table A1. Sensitivity of impacts on carbonate chemistry to the choice of dissociation constants

Constants	Difference between pre- and post-fossil fuel (at equilibrium, after adding 4000 Gt C to the ocean)		
	ΔDIC (μM)	ΔAlk (μEq)	$\Delta p\text{CO}_2$ (ppmv)
Mehrbach et al. (1973) (refit by Lueker et al., 2000)	+438	+419	+147
Roy et al. (1993)	+434	+414	+159
Hansson (1973)	+423	+402	+179
Dickson and Millero (1987)	+424	+404	+153
Goyet and Poisson (1989)	+427	+409	+165
Millero (1995)	+427	+410	+164