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Influence of terrestrial weathering on ocean acidification and the next glacial inception
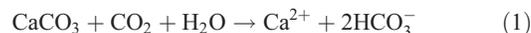
Joji Uchikawa[1] and Richard E. Zeebe[1]

[1] Ocean uptake of anthropogenic CO_2 causes a decline in seawater pH, a process known as ocean acidification, which may adversely affect marine organisms. We investigate whether continental weathering can mitigate future ocean acidification by sequestering atmospheric CO_2. We conducted simulations under a suite of carbon emission scenarios with different weathering parameterizations. The short-term impact of a strong weathering feedback was only notable for large emissions with slow injection. This mitigation by enhanced weathering, however, is an order of magnitude smaller than the expected maximum pH decline based on the default parameterizations. Thus on short timescales, weathering has little effect on future atmospheric CO_2 and ocean acidification, regardless of the assumed weathering feedback strength. But on longer timescales and for large emissions, different weathering parameterizations introduce large uncertainties regarding the time when pCO_2 will return to climatically relevant levels of, say, 400 μatm in the future. **Citation:** Uchikawa, J., and R. E. Zeebe (2008), Influence of terrestrial weathering on ocean acidification and the next glacial inception, *Geophys. Res. Lett.*, *35*, L23608, doi:10.1029/2008GL035963.

1. Introduction

[2] Humans have released over 300 Pg of carbon (1 Pg C = 10^{15} g C) mainly from fossil fuel combustions [*Marland et al.*, 2007], and the emission is still ongoing at accelerating rates [*Archer*, 2005; *Intergovernmental Panel on Climate Change (IPCC)*, 2007]. Much of the anthropogenic CO_2 is absorbed by the ocean, which alleviates rapid climate changes associated with global warming. But this buffering by the ocean unfortunately has its price: ocean acidification. Uptake of atmospheric CO_2 lowers seawater pH and $[CO_3^{2-}]$, and the saturation state of $CaCO_3$ [*Caldeira and Wickett*, 2003; *Orr et al.*, 2005; *Zeebe et al.*, 2008]. After absorbing $\sim$40% of anthropogenic CO_2 over the last 200 years, average surface ocean pH has dropped by 0.1 units [*IPCC*, 2007; *Zeebe et al.*, 2008]. If the world fossil fuel reserves are fully exploited in the future ($\sim$5,000 Pg C of emission [*Sundquist*, 1986; *Rogner*, 1997]), surface ocean pH can drop by $\sim$0.6 to $\sim$0.78 units [*Zeebe et al.*, 2008]. Further ocean acidification may particularly threat marine calcifying organisms [i.e., *Riebesell et al.*, 2000; *Orr et al.*, 2005; *Hoegh-Guldberg et al.*, 2007].

[3] But a future increase in pCO_2 and consequential warming should enhance carbonate and silicate weathering [*Walker et al.*, 1981; *Berner et al.*, 1983; *White and Blum*, 1995], thus removing atmospheric CO_2, followed by $CaCO_3$ burial in sediments:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \qquad (1)$$

$$CaSiO_3 + 2CO_2 + H_2O \rightarrow Ca^{2+} + SiO_2 + 2HCO_3^- \qquad (2)$$

This negative feedback involving weathering of continental materials played a dominant role in regulating pCO_2 on geologic timescales [*Walker et al.*, 1981; *Berner et al.*, 1983; *Zachos et al.*, 2008] and it is likely to remain so in response to future anthropogenic C emissions [*Archer*, 2005; *Lenton and Britton*, 2006]. Then, would this weathering feedback be effective in alleviating future ocean acidification by buffering the decline in ocean pH? This question is largely unresolved because weathering fluxes were typically prescribed as constant [i.e., *Archer et al.*, 1998; *Archer*, 2005; *Ridgwell and Edwards*, 2007] or omitted in previous model simulations [i.e., *Caldeira and Wickett*, 2005; *Montenegro et al.*, 2007; *Tyrrell et al.*, 2007]. Studies by *Walker and Kasting* [1992], *Lenton and Britton* [2006] and *Zeebe et al.* [2008] represent a few model simulations in which weathering fluxes were set to co-vary with pCO_2 (and with plant productivity in *Lenton and Britton* [2006]). *Walker and Kasting* [1992] and *Lenton and Britton* [2006] largely focused on the impact of the weathering feedback on pCO_2; however, less attention was given to ocean acidification. *Zeebe et al.* [2008] modeled future ocean acidification but with a single set of parameterizations to relate carbonate and silicate weathering fluxes to pCO_2.

[4] To determine whether enhanced weathering feedback can mitigate the future rise in pCO_2 and ocean acidification, we conducted simulations using the Long-term Ocean-Atmosphere-Sediment CArbon cycle Reservoir (LOSCAR) model [*Zeebe et al.*, 2008; *Zachos et al.*, 2008] under various weathering parameterizations. We also conducted 300,000-year long simulations to test the effect of weathering parameters on predictions of the long-term return to climatically relevant atmospheric CO_2 levels. For example, *Lunt et al.* [2008] suggest that the growth of Northern Hemisphere ice sheets can be triggered if atmospheric CO_2 levels fall below a threshold of $\sim$400 ppmv. Thus, this value could have important implications for the timing of the next glacial inception.

2. Model Descriptions and Weathering Parameterizations

[5] The LOSCAR model is a carbon-cycle reservoir model (modified from *Walker and Kasting* [1992]) coupled

[1]Department of Oceanography, University of Hawaii, Honolulu, Hawaii, USA.
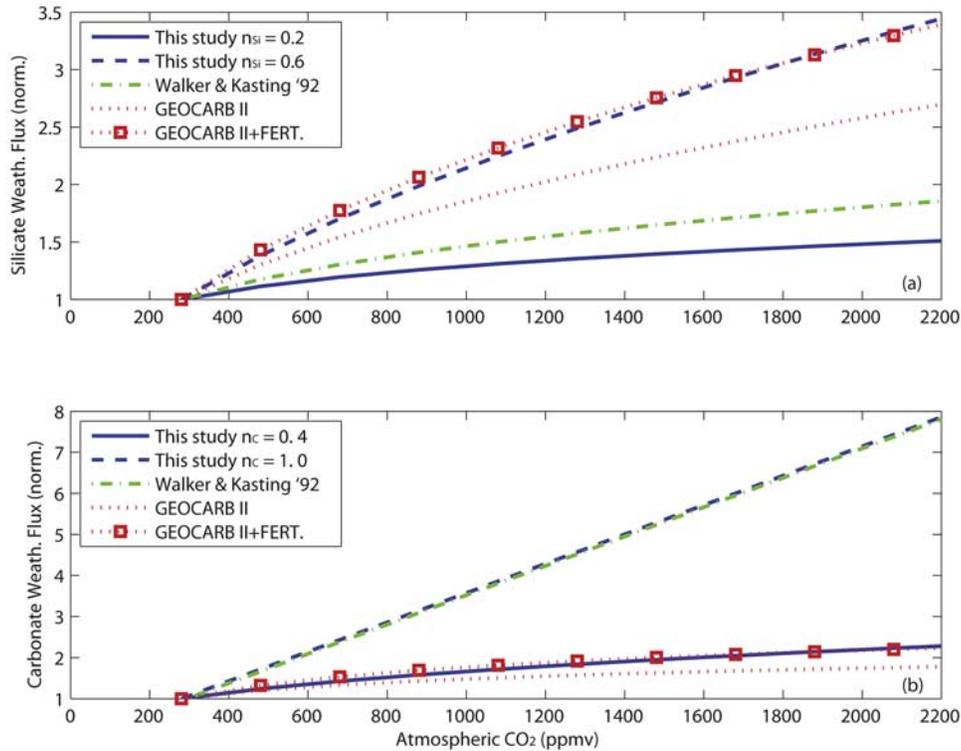
Figure 1. Comparison of (a) silicate and (b) carbonate weathering fluxes as a function of atmospheric CO_2 used in the LOSCAR model (this study), the GEOCARB II and GEOCARB II+FERT model [*Berner*, 2001] and the *Walker and Kasting* [1992] model. The weathering fluxes shown in the plots are normalized to initial weathering fluxes of 1.

to a sediment module [*Zeebe and Zachos*, 2007]. The model runs were performed from year 1,700 (pre-industrial condition) to 10,000 (or 300,000) under a suite of C emission scenarios based on historic total emissions of 315 Pg C until year 2004 [*Marland et al.*, 2007] and projected future emissions ranging from 600 to 5,000 Gt C total emissions released over 200 to 1,000 years. Simulations over the next few centuries by the LOSCAR model [*Zeebe et al.*, 2008; *Zachos et al.*, 2008] are in good agreement with the results of previous carbon-cycle model studies [*Caldeira and Wickett*, 2003; *Orr et al.*, 2005; *Montenegro et al.*, 2007]. However, our estimates of atmospheric CO_2 rise and seawater pH decline for a given emission scenario are more conservative because the model incorporates dissolution of sedimentary $CaCO_3$ and a weathering feedback.

[6] In the model, silicate and carbonate weathering fluxes (F_{Si} and F_C) are expressed as:

$$F_{Si} = F_{Si}^0 \times (pCO_2/pCO_2^0)^{nSi} \qquad (3)$$

$$F_C = F_C^0 \times (pCO_2/pCO_2^0)^{nC} \qquad (4)$$

where F_{Si}^0 and F_C^0 (initial silicate and carbonate weathering flux) values are 5×10^{12} mol C/yr [*Walker and Kasting*, 1992] and 12×10^{12} mol C/yr [*Morse and Mackenzie*, 1990]. The default silicate and carbonate weathering parameters (n_{Si} and n_C) were set at 0.2 and 0.4 [*Zeebe et al.*, 2008; *Zachos et al.*, 2008]. For the simulations under the assumption of strong weathering feedbacks, n_{Si} and n_C

were raised to 0.6 and 1.0. We assessed the effects of weathering on pCO_2 and ocean pH with four sets of settings: (1) default (n_{Si} = 0.2, n_C = 0.4), (2) enhanced silicate weathering (n_{Si} = 0.6, n_C = 0.4), (3) enhanced carbonate weathering (n_{Si} = 0.2, n_C = 1.0) and (4) enhanced silicate and carbonate weathering (n_{Si} = 0.6, n_C = 1.0). The parameterizations used in this study cover the range of weathering fluxes as a function of pCO_2 prescribed in the GEOCARB II and GEOCARB II+FERT model [*Berner*, 2001] and the *Walker and Kasting* [1992] model (Figure 1). The abbreviation 'FERT' here refers to a feedback that includes a possible CO_2 effect on weathering by plants [*Berner*, 2001].

3. Results

[7] On the timescale of our simulations (10,000 years) the individual effect of enhanced carbonate (n_{Si} = 0.2, n_C = 1.0) and enhanced silicate weathering (n_{Si} = 0.6, n_C = 0.4) on CO_2 drawdown was small and barely distinguishable from each other, although carbonate weathering is slightly more effective. Thus, we will only present the results of the simulations in which silicate and carbonate weathering fluxes were simultaneously increased (n_{Si} = 0.6, n_C = 1.0) (Figure 2).

[8] Under the default condition, predicted maximum pCO_2 (pCO_2^{Max}) and maximum surface ocean pH decline (ΔpH) range from ~400 to ~2,300 μatm and 0.14 to 0.78 units (Figures 3a and 3b). The magnitude of both pCO_2^{Max} and ΔpH is dependent on the amount of total C emissions as well as the release time. In contrast, predicted atmo-
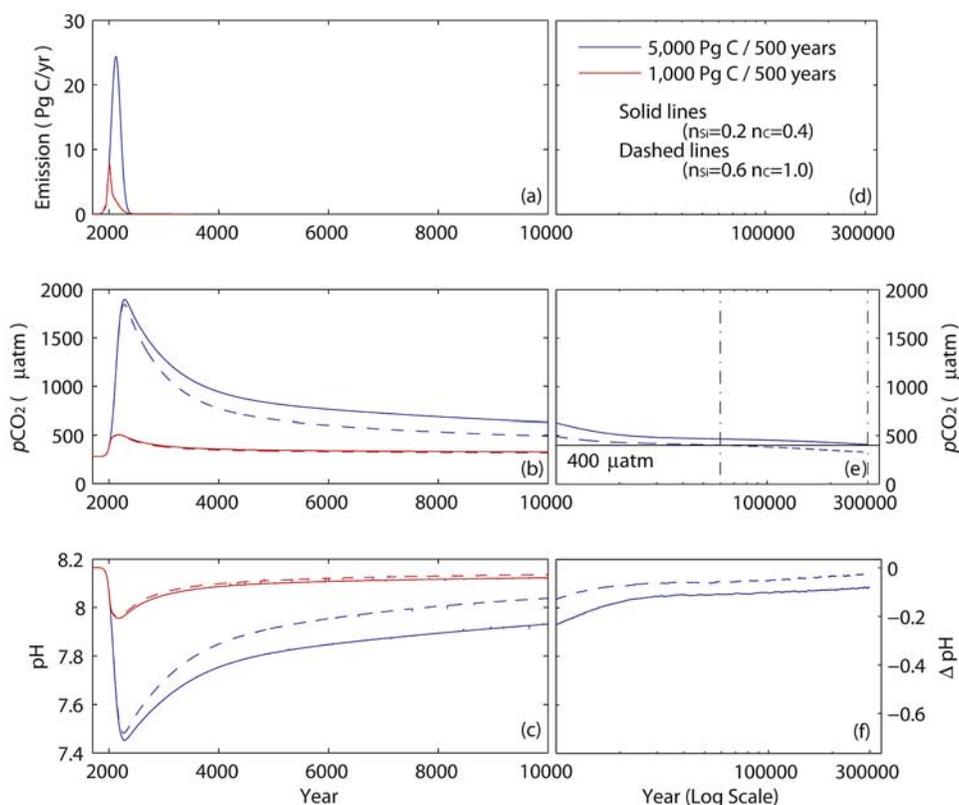
Figure 2. Simulated response of anthropogenic C emissions. Color coding by blue and red, respectively, indicates the model results under the emission scenario of 5,000 Pg C and 1,000 Pg C released over 500 years. (a and d) C emission scenarios and response of (b and e) atmospheric pCO_2 (μatm) and (c and f) surface ocean pH and pH decline from a pre-industrial value of 8.16 (denoted as ΔpH). Note that, in Figures 2e and 2f, the time axis (from year 10,000 to 300,000) is logarithmic and only the results under the emission scenario of 5,000 Pg C released over 500 years are shown. Solid and dashed trajectories represent simulations under default ($n_{Si} = 0.2$ and $n_C = 0.4$) and enhanced ($n_{Si} = 0.6$ and $n_C = 1.0$) weathering feedback. Two vertical dash-dot-lines in Figure 2e indicate the timing when pCO_2 simulated under default and enhanced weathering parameterizations returns to 400 μatm (roughly year 300,000 and 60,000).

spheric CO_2 in year 10,000 (pCO_2^{10K}), ranging from ~300 to ~630 μatm, showed dependency only on the amount of total C emissions (Figure 3c). The reason for this is that the total C input affects the quasi-steady state established in the carbon cycle after 10,000 year, while the release time does not (if much shorter than 10,000 years).

[9] Enhanced weathering generally has a minor effect on CO_2 drawdown (Figure 3d). Reductions in pCO_2^{Max} are less than 40 μatm unless large amounts of C (> 3,500 Pg C) are released over relatively long periods of time (> 500 years). The maximum drawdown of atmospheric CO_2 before it equilibrates with the ocean by enhanced weathering is only of the order of 5% (under a scenario of 5,000 Pg C total emissions released over 1,000 years). Concomitantly ocean acidification was mitigated by 0.04 pH units under this emission scenario. This reduction is, however, negligible relative to ~0.65 units of pH decline under the default weathering fluxes (Figures 3b–3e).

[10] The effect of enhanced weathering is comparatively more important on timescales of thousands of years. The trajectories shown in Figure 2 indicate that the effectiveness of enhanced CO_2 drawdown increases after year ~2,300. The magnitude of CO_2 drawdown by weathering is enhanced under large C emissions, because weathering fluxes increase

at higher atmospheric CO_2 levels (Figure 1). Enhanced weathering under the emission of 5,000 Pg C results in a decrease of pCO_2^{10K} values by as much as 140 μatm, representing a ~22% reduction relative to pCO_2^{10K} values under the default condition (Figures 3c–3f). The return of seawater pH toward pre-perturbation state is also facilitated by enhanced weathering on millennial timescales. Seawater pH under the default condition rebounds to 7.93 units in year 10,000 (Figure 2c). When a strong weathering feedback is assumed, however, the same pH is reached in year 5,250. The range of weathering parameterizations yields about 0.1 units of difference in ocean pH after year ~3,000.

[11] We also conducted 300,000-year long simulations to characterize the uncertainties due to weathering parameterizations in determining 'restoring time', the time when pCO_2 will subside to climatically relevant levels after the anthropogenic perturbation (Figures 2d–2f). Under total emissions of 5,000 Pg C released over 500 years with default weathering fluxes, it takes ~300,000 years for pCO_2 to return to 400 μatm. However, under the assumption of a strong weathering feedback, the 400 μatm level is reestablished in ~60,000 years. Thus the range of weathering parameters used in this study (Figure 1) can produce
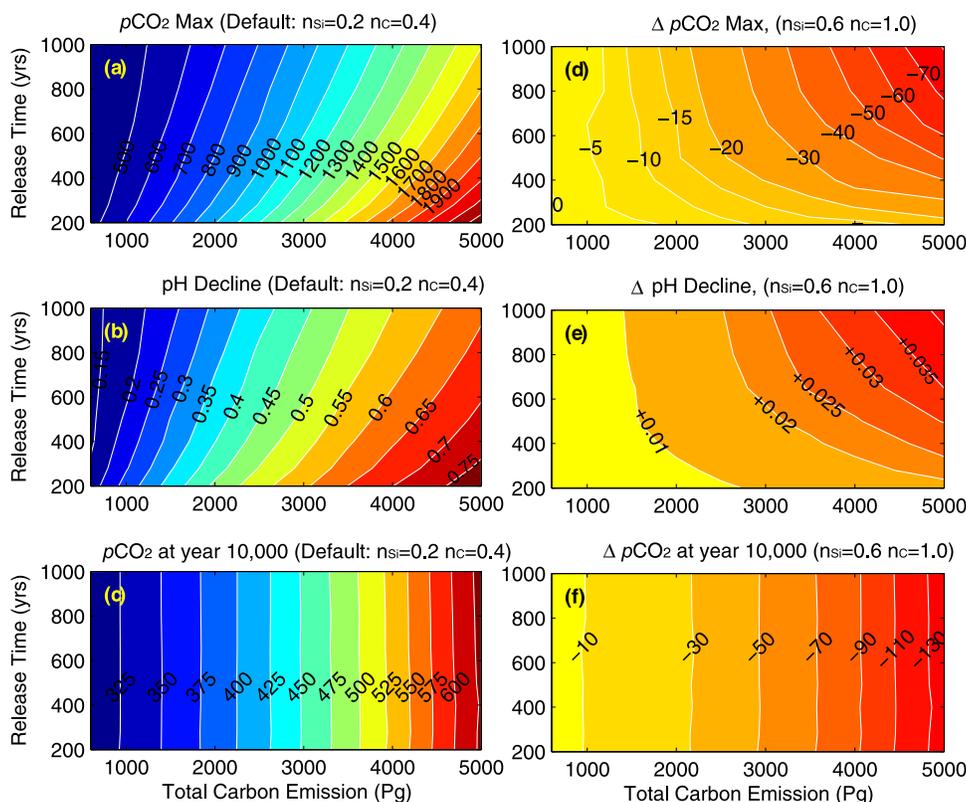
Figure 3. (left) Expected (a) maximum pCO_2 (μatm), (b) maximum pH decline of average surface seawater and (c) pCO_2 in year 10,000 as a function of total C emissions (Pg C) and release time (years) under default weathering parameterization ($n_{Si} = 0.2$ and $n_C = 0.4$). (right) Differences in (d) maximum pCO_2, (e) maximum pH decline and (f) pCO_2 in year 10,000 between model runs under the default and enhanced weathering parameterizations ($n_{Si} = 0.6$ and $n_C = 1.0$).

uncertainties up to ~240,000 years in the restoring time under the same emission scenario.

4. Discussions and Conclusions

[12] Our simulations suggest that CO_2 drawdown by enhanced weathering becomes significant only on millennial timescales in response to large C emissions. But on centurial timescales, the CO_2 drawdown by weathering is small regardless of the magnitude of C emissions. Because CO_2 drawdown by weathering proceeds on millennial or longer timescales, this negative feedback mechanism can only remove negligible amounts of atmospheric CO_2 before the equilibration between the atmosphere and the ocean, which occurs within a few centuries [*Archer et al.*, 1998; *Archer*, 2005]. Thus, continental weathering has little control on the immediate pCO_2 rise and ocean acidification due to future C emissions. Under the assumption of a weak weathering feedback, we predict average surface ocean pH to be lowered anywhere from 0.64 to 0.78 units for total emissions of 5,000 Pg C, depending on the release time. Under the assumption of a strong weathering feedback, the corresponding decline is estimated to be 0.60 to 0.77 units (Figures 3b–3e).

[13] The effectiveness of continental weathering on CO_2 drawdown over centurial to millennial timescales demonstrated by our simulations agrees with previous studies by *Lenton and Britton* [2006]. Their simulations under ~4,000 Gt C of emissions show that effect of carbonate and silicate weathering on CO_2 drawdown, although small (up to ~3% and ~9% enhancement for carbonate and silicate weathering), is best highlighted on timescales of 10^3–10^4 and 10^5–10^6 years, respectively. Dual enhancement of carbonate and silicate weathering further improved CO_2 sequestration capability (by ~3% at most) on 10^3–10^4 year timescales. *Archer et al.* [2005] also suggests that carbonate weathering is important on timescales of thousands of years, whereas effect of silicate weathering is dominant on timescales over hundreds of thousands of years.

[14] The selection of weathering feedback strength is expected to be important for the simulations over long timescales. Our long-term simulations (Figures 2d–2f) show huge uncertainties caused by weathering parameters in determining the restoring time. The most important variables controlling the restoring time are, for example, the total anthropogenic C input and variations in Earth's orbital parameters. But, for a given emission scenario, the weathering parameters are critical for the predicted restoring time. A recent study by *Lunt et al.* [2008] suggests that below a threshold pCO_2 value of 400 μatm, Northern Hemisphere glaciations can be successfully triggered. In our simulations, the different weathering parameters lead to uncertainties of up to ~240,000 years in the predicted restoring time for pCO_2 to drop below 400 μatm (Figure 2e).

[15] *Archer and Ganopolski* [2005] predicted that the onset of the next glacial period can be suppressed for the upcoming 500,000 years if 5,000 Gt of C are released to the atmosphere, based on an atmosphere-ocean-vegetation model

coupled to an ice sheet model. We believe that their overall timescale ($\sim$500,000 years) is probably more realistic than ours (60,000 to 300,000 years) because their results are based on the combined influence of elevated pCO$_2$ as well as low insolation variability due to weak orbital forcing expected in the future [*Loutre and Berger*, 2000]. In contrast, our model does not include orbital forcing and is less complex. Nonetheless, our results show that weathering parameters can result in significant uncertainties in long-term predictions of atmospheric CO$_2$ levels in response to massive anthropogenic C emissions.

[16] In summary, continental weathering has a minor effect on future pCO$_2$ and ocean acidification on timescales of centuries, regardless of the assumed weathering feedback strength. This implies that uncertainties in predicting immediate atmosphere-ocean response to future C emissions due to continental weathering are small. Weathering processes are too slow to effectively alleviate short-term consequences of anthropogenic C emissions. Avoiding such consequences requires establishment of emission targets via policy protocols. On longer timescales, different parameterizations introduce huge uncertainties (up to hundreds of thousands of years) in the predicted timing when pCO$_2$ will return to climatically relevant threshold values. In order to reduce these uncertainties, a better understanding of weathering processes is required to improve parameterizations.

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J. Uchikawa and R. E. Zeebe, Department of Oceanography, University of Hawaii, 1000 Pope Road, Honolulu, HI 96822, USA. (uchikawa@hawaii.edu; zeebe@hawaii.edu)