

Reply to comment by K. Caldeira et al. on “Modern-age buildup of CO₂ and its effects on seawater acidity and salinity”

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1. Introduction

[1] This reply corrects several misstatements and omissions in *Caldeira et al.*’s [2007] comment and provides additional results pertinent to ascertaining the effect of atmospheric CO₂ buildup during the Holocene on average seawater salinity, density, and acidity. *Loáiciga* [2006] used atmospheric CO₂ values for the 18th century (280 ppmv), for 2006 (380 ppmv), and equal to twice the current concentration, or $2 \times \text{CO}_2 (= 760 \text{ ppmv})$ in his analysis. This $2 \times \text{CO}_2$ scenario value may or may not materialize in the next few centuries depending on future anthropogenic emissions of CO₂ and on natural processes affecting its uptake and release on Earth. The buildup of atmospheric CO₂ should not be construed to be a post-Industrial Revolution (that is, post 18th century) phenomenon. It has been estimated that the atmospheric CO₂ concentration reached a minimum of approximately 190 ppmv during the last (Wisconsinan) ice age (see *Fedorov et al.* [2006, Figure 1b] for a recent account). Ever since, the CO₂ atmospheric concentration has increased unabated to its present value of approximately 380 ppmv, which, coincidentally, is twice the ice-age minimum. The rise in atmospheric CO₂ accelerated since the mid 1700’s from approximately 280 ppmv to its present value (380 ppmv).

[2] A long-term, post last-ice age, view of atmospheric CO₂ increase and synchronous biogeochemical and climate-change processes was implicit in the work of *Loáiciga* [2006] because it is essential in interpreting current trends observed in the terrestrial ice-oceanic water balance, sea level, average seawater salinity, density, and acidity. This key point was missed by *Caldeira et al.* [2007]. Among the causes of seawater quality changes in the Holocene one must not overlook the effects of post-ice age ocean warming, to which the heightened concentrations of greenhouse gases by human action are contributors. Moreover, large human settlements and the associated disposal of vast amounts of untreated or poorly treated sewage and other harmful chemicals into coastal waters have taken a toll on marine ecosystems. So has the overfishing of various marine species. Evidently, there are multiple, interrelated,

factors currently affecting marine organisms as claimed by *Caldeira et al.* [2007]. To complicate matters, organisms are not passive targets of seawater-quality changes. They modify their behavior, morphology, physiology, and undergo genetic changes in their struggle to adapt to altered environmental conditions caused by rapid climatic shifts (taking place over decades) or anthropogenic impacts [*Bradshaw and Holzapfel*, 2006]. *Caldeira et al.* [2007] failed to provide convincing evidence that the rapid rise in atmospheric CO₂ over the last few decades has played a role in deleterious impacts to marine organisms through purported changes in seawater pH, and overlooked the more plausible effects of ocean warming, ocean pollution in its many forms, sea-level rise, and overfishing. The authors instead, speculated that changes of 0.20 pH units by rising atmospheric CO₂ could have substantial adverse effects on marine biota without addressing adaptation and evolution on the part of marine organisms.

[3] This reply makes the case for a recognition that the long-term view—that is, post-last ice age—to the problem of seawater acidification is the correct one, and for the use of models of seawater acidification that consider the dissolution of carbonate rocks and mixing of seawater over periods of centuries to thousands of years, as implied in the paper by *Loáiciga* [2006]. The constant-alkalinity model of seawater-acidification advocated by *Caldeira et al.* [2007], this reply argues, overestimates the plausible reduction in seawater pH likely to occur as atmospheric CO₂ continues to rise in the coming centuries.

2. Time Scale of Changes in Average Seawater Acidity

[4] *Loáiciga* [2006] proposed an approximate model to calculate the concentrations of carbonate species in seawater induced by the dissolution of atmospheric CO₂. The model was written to calculate the total hydrogen ion concentration $[\text{H}_{\text{SWS}}^+] = [\text{H}^+] + [\text{HSO}_4^-] + [\text{HF}^-]$ based on the total concentrations of carbonate species [*Stumm and Morgan*, 1996]. Following *Millero* [1995], *Loáiciga*’s [2006] model applied equilibrium constants, solubility products, and Henry’s constants calibrated to the total hydrogen and total carbonate concentrations. *Caldeira et al.* [2007] challenged the use of the carbonate solubility product in *Loáiciga*’s [2006] model [see *Loáiciga*, 2006, equation 5]. Their challenge centered about the argument that the equilibration of seawater with carbonate minerals takes five to ten thousand years, in which case the average seawater alkalinity would undergo changes. Yet, ocean alkalinity increases are not substantiated by recent measurements according to *Caldeira et al.* [2007]. Therefore, these authors claimed, there hasn’t been sufficient time to produce a

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carbonate speciation of the type implied by *Loáiciga's* [2006] model. The answer to the issue of the time scale required to induce carbonate dissolution by oceanic mixing of atmospheric CO₂ is found in the Introduction to this reply: the atmospheric concentration of CO₂ has been increasing unabated since the last ice age. The trend has lasted through the Holocene, and certainly longer than 10,000 years. Therefore, there has been ample time for carbonate dissolution to neutralize acidity increases caused by Holocene CO₂ rise beyond what will be expected if the seawater alkalinity had remained constant through time. Furthermore, average seawater pH is about 8.2 at present, and it has been near that level for several decades, in spite of the rapid increase of atmospheric CO₂ in that period. This near constancy of the observed seawater pH is inconsistent with *Caldeira et al.'s* [2007] hypothesis of a stable seawater alkalinity. Given the ever changing nature of factors that drive the oceanic aqueous carbonate system, the feasibility of constant alkalinity claimed by *Caldeira et al.* [2007] is untenable, at least over sufficiently long periods such as those relevant to *Loáiciga's* [2006] model.

[5] The question of what has kept seawater pH from falling to biologically catastrophic levels over geologic time has received the attention it deserves from geochemists. *Krauskopf* [1979, p. 534] wrote the following in regards to changes of seawater acidity: "Seawater today is protected from major changes in pH by reactions involving carbonic acid and its ions, and to a lesser extent by boric acid and borate ion. This is certainly sufficient to counteract minor additions of acid or alkali, but would it be effective as a long-term control if acid or alkali were added in large quantities? To make the question specific, suppose that the acid gases mentioned in the last section –especially CO₂, HCl, and SO₂ were added to the modern sea continuously and in large amounts from volcanic emanations. The carbonate buffer could take up a great deal of these gases; solid carbonates would be dissolved, CO₃²⁻ would be changed to HCO₃⁻, and HCO₃⁻ eventually to H₂CO₃. The pH would fall slowly as these reactions took place, but even when it dropped to 6.5 or 7, the buffer would still be able to take up H⁺."

[6] What *Krauskopf* [1979] was referring to was the buffering of seawater by carbonate dissolution, a concept applied by *Loáiciga* [2006]. The former author cited large CO₂ input from volcanic eruptions, but he could have as well chosen natural and anthropogenic CO₂ emissions during the Holocene as example. Moreover, in discussing carbonate equilibria and the dissolution of calcium carbonate as a seawater buffer, *Krauskopf* [1979, p. 48] stated: "These various processes serve to hold the pH of seawater in the neighborhood of 8 and probably have so held it for a long time in the geologic past. The ultimate controls, it should be noted, are CO₂ in the atmosphere and CaCO₃ in the bottom sediments."

3. A Comparison of Two Competing Predictors of Average Seawater Acidity

[7] This section presents a comparison of the calculated changes in average seawater pH corresponding to several levels of atmospheric CO₂. Two models are used to obtain results. The first is that of *Loáiciga* [2006]. The second is a

carbonate-speciation model that sets the alkalinity (Alk) of seawater constant, and equal to 2.47×10^{-3} eq/L [*Stumm and Morgan*, 1996]. The second model uses the concentration of the H⁺ ion in the calculation of pH, instead of the total hydrogen ion concentration [H_{SWS}⁺] used by *Loáiciga* [2006]. This introduces an inter-model discrepancy that is of secondary importance to the comparison of calculated pHs. Constant-alkalinity of seawater was advocated by *Caldeira et al.* [2007] in the calculation of pH changes in seawater caused by rising atmospheric CO₂ concentrations. For the sake of specificity, the calculations were carried assuming a seawater temperature equal to 15°C. The entertained atmospheric CO₂ concentrations are: 190 ppmv (minimum during the last ice age, partial pressure P_{CO2} = 190×10^{-6} atm), 280 ppmv (mid 18th century, P_{CO2} = 280×10^{-6} atm), 380 ppmv (current value equals to twice the last ice-age minimum, P_{CO2} = 380×10^{-6} atm), and 760 (the 2 × CO₂ scenario, P_{CO2} = 760×10^{-6} atm). Both models assume equilibrium conditions of the involved reactions for a given concentration of atmospheric CO₂. This is an approximation because of the ever changing concentration of CO₂ prevents full achievement of chemical equilibrium.

[8] The equations of the constant-alkalinity model are as follows (all concentrations and equilibrium constants are molar, seawater temperature equals 15°C):

$$\text{Ion product of water: } K_W = [\text{H}^+][\text{OH}^-] \quad (K_W = 2.0 \cdot 10^{-14}) \quad (1)$$

$$\text{Aqueous CO}_2 \text{ system: } K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \cdot (K_1 = 8.8 \cdot 10^{-7}) \quad (2)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (K_2 = 5.6 \cdot 10^{-10}) \quad (3)$$

$$\text{Boric acid – borate reaction: } K' = \frac{[\text{H}^+] \cdot [\text{B}(\text{OH})_4^-]}{[\text{H}_3\text{BO}_3]} \cdot (K' = 1.6 \cdot 10^{-9}) \quad (4)$$

The total boron concentration B_T = [H₃BO₃] + [B(OH)₄⁻] is constant and equal to 4.1×10^{-4} M [*Stumm and Morgan*, 1996]. The dissolution of atmospheric CO₂ in seawater proceeds according to Henry's law:

$$K_H = \frac{[\text{H}_2\text{CO}_3^*]}{P_{\text{CO}_2}} \quad K_H = 4.0 \cdot 10^{-2} \text{ M/atm at } 15^\circ\text{C} \quad (5)$$

[9] The equation for alkalinity is Alk = [HCO₃⁻] + 2[CO₃²⁻] + [B(OH)₄⁻] + [OH⁻] – [H⁺] equal to 2.47×10^{-3} eq/L. Equations (1)–(5) are used in the equation for alkalinity to yield the following expression in terms of the equilibrium constants, [H⁺], P_{CO2}, and the total boron concentration B_T:

$$\text{Alk} = \frac{K_H \cdot P_{\text{CO}_2}}{\alpha_0} (\alpha_1 + 2\alpha_2) + \frac{B_T \cdot K'}{[\text{H}^+] + K'} + \frac{K_W}{[\text{H}^+]} - [\text{H}^+] \quad (6)$$

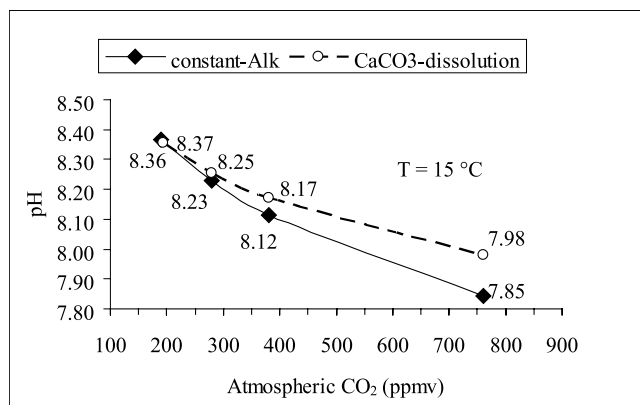


Figure 1. Changes in the average pH of seawater calculated with a constant-alkalinity (constant-Alk) model and Loáiciga's [2006] CaCO₃-dissolution influenced model for atmospheric CO₂ concentrations equal to 190, 280, 380, and 750 ppmv. The temperature of seawater was set to 15°C.

in which the coefficients α_0 , α_1 , α_2 are: $\alpha_0 = 1/\{1 + (K_1/[H^+]) + (K_1K_2/[H^+]^2)\}$, $\alpha_1 = 1/\{1 + ([H^+]/K_1) + (K_2/[H^+])\}$, $\alpha_2 = 1/\{1 + ([H^+]/K_2) + ([H^+]^2/K_1K_2)\}$.

[10] Equation (6) was solved numerically to produce $[H^+]$ for a specified P_{CO_2} .

4. Results and Conclusions

[11] Figure 1 shows the calculated pH values as a function of P_{CO_2} ($= 190, 280, 380$, and 760×10^{-6} atm). The constant-alkalinity pH (constant-Alk in Figure 1) is generally less than the CaCO₃-dissolution influenced pH (from Loáiciga's [2006] model). Both models yield a pH of about 8.36 for $P_{CO_2} = 190 \times 10^{-6}$ atm. The doubling of atmospheric CO₂ to $P_{CO_2} = 380 \times 10^{-6}$ atm (year 2006 value) lowered the constant-alkalinity pH by 0.24 pH units to 8.12, while the CaCO₃-dissolution influenced pH dropped 0.19 pH units to 8.17. Could the 0.24 pH-unit decline through the Holocene estimated with the constant-alkalinity model explain some of Caldeira et al.'s [2007] claimed impacts on marine organisms? This is unlikely. First, it has been argued in this reply that the constant-alkalinity model overestimates the seawater pH reduction.

Secondly, Caldeira et al. [2007] failed to provide factual evidence that purported pH changes in seawater during the 20th century had any adverse impacts on marine biota. A second doubling of P_{CO_2} to 760×10^{-6} atm produced an additional 0.27 pH-unit drop by the constant-alkalinity pH to 7.85, while the CaCO₃-dissolution influenced pH drops another 0.19 pH units to 7.98. Again, the constant-alkalinity drop in pH exceeds the U.S. Environmental Protection Agency's [1976] criterion of maximum 0.20 pH-units change, although this is an artifice of ignoring carbonate buffering.

[12] What are the implications of these results? First, the constant-alkalinity model overestimates seawater pH reductions by rising atmospheric CO₂. On the other hand, if future CO₂ buildup is sufficiently fast, the carbonate-buffered model would underestimate pH reductions. It is conceivable that the actual future evolution of seawater pH is somewhere between the values predicted in this reply with the constant-alkalinity and carbonate-buffered models. Secondly, time might hold the key to assessing the impacts of the future rise in atmospheric CO₂ on marine biota. That is, the time over which pH changes in seawater occur and is available for evolution and adaptation of affected marine organisms.

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