

***Interactive comment on “Linking the lithogenic, atmospheric, and biogenic cycles of silicate, carbonate, and organic carbon in the ocean” by S. V. Smith and J.-P. Gattuso***

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Review of Linking the lithogenic, atmospheric, and biogenic cycles of silicate, carbonate, and organic carbon in the ocean S. V. Smith and J.-P. Gattuso Biogeosciences Discuss., 6, 6579-6599, 2009

Reviewer: Christoph Heinze

At the beginning of this review, I would like to state that I potentially misunderstand the authors, and will be happy to discuss with them.

Major concern:

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The authors describe the ocean as functioning in the following way: Obviously on long time scales of millions of years the calcium carbonate weathering on land is balanced by calcium carbonate precipitation in the oceans rendering approximate constant  $p\text{CO}_2$  in the atmosphere. Looking at the ratio of gaseous  $\text{CO}_2$  set free by (mostly) biogenic  $\text{CaCO}_3$  precipitation in the surface ocean to moles  $\text{CaCO}_3$  removed from the ocean, they arrive at a “too small”  $\text{CO}_2$  release. From this they argue the atmosphere could be stripped of  $\text{CO}_2$  on a 10,000 years timescale if not other processes take place. They then invoke organic carbon reactions (production and release of organic matter) in order to remove the apparent contradiction.

I think the way the problem is posed is misleading as the concentrations in the ocean (and linked to this the  $\text{CO}_2$  in the atmosphere) as well as the output of matter through sedimentation are kinetically controlled. Carbon can cycle many times in the ocean between surface and deep waters before leaving the ocean either to the atmosphere or the lithosphere at the ocean floor. Also the  $\text{CaCO}_3$  export production at the sea surface exceeds the  $\text{CaCO}_3$  output through burial (or the input through rivers). Therefore, the (a) ratio of  $\text{CO}_2$  produced by biogenic precipitation and  $\text{CaCO}_3$  biologically precipitated at the sea surface at a specific region and the (b) global net removal of  $\text{CO}_2$  through calcium carbonate through sediment burial have no direct relationship. Atmospheric  $\text{CO}_2$  and ocean pH are kept relatively constant through carbonate compensation (if alkalinity is getting too low in the ocean,  $p\text{CO}_2$  goes up, more weathering results, and alkalinity is brought back to the ocean; likewise if the ocean gets less alkaline – e.g. through uptake of anthropogenic  $\text{CO}_2$  – less  $\text{CaCO}_3$  gets buried and alkalinity gets slowly built up again) while the  $\text{CaCO}_3$  lysocline oscillates slowly around a mean value. This kinetic controlling of atmospheric  $\text{CO}_2$  and ocean pH is not mentioned in the paper, but needs taken into account. However, when doing this, the “conundrum” that the authors describe vanishes. Perhaps the authors could rather use their considerations plus a more thorough study of input/burial estimates for  $\text{CaCO}_3$  for a deconvolution of oceanic  $\text{CaCO}_3$  export (assuming a steady state ocean and using their  $\Psi$  values from the sea surface)? This could be an interesting approach.

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Further comments:

Abstract, l. 10-14: The term “buffer effect” for the CO<sub>2</sub> release per CaCO<sub>3</sub> produced may be misleading. It is not clear what the buffer system would be.

Abstract l. 17 and p. 6592 l. 4: “couplet” is mostly used in literature and in music has a further meaning.

Abstract l. 19-20 and p. 6592, l. 11-15: The conclusive sentence is not clear. Why can there be dramatic changes in the oceanic carbon reservoir without changes in the small atmosphere reservoir (if we believe in the Revelle factor, a 1% change in DIC induces a 10% in pCO<sub>2</sub>)? Perhaps this just needs to be better described with a vertical differentiating into provinces.

p. 6581, eqs. (1) and (2) and l. 12-14: The production of free CO<sub>2</sub> during CaCO<sub>3</sub> is a consequence of the changing ability of seawater to dissociate weak acids such as CO<sub>2</sub> if carbonate ions (or calcium ions) are removed. I cannot see such an explanation from eqs. (1) and (2).

p. 6581, l. 21: “can form” should read “can be formed?”

p. 6582, first paragraph: The authors list two fairly special oceanic domains to back up their “conundrum”. I think the conundrum does not exist, if the ocean as a global system is taken into account in an integrated view.

p. 6582, l. 19: What is meant by “produce more rapidly”?

p. 6582, l. 26-27: This general statement may be omitted.

p. 6583, l. 11-12: Many regions of the world ocean are not in equilibrium with atmospheric pCO<sub>2</sub>, otherwise we would not need the pCO<sub>2</sub> maps from Takahashi and others.

p. 6583, l. 12-15: This section is a bit awkward concerning the language. You probably want to say, that the marine inorganic carbon system is fixed by two out of six carbon

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state variables and that often those two variables are chosen which are easily derived from measurements (see the section “From 2 to 6” in the annex of the book by Zeebe and Wolf-Gladrow, “CO<sub>2</sub> in seawater: Equilibrium, Kinetics, Isotopes”, Elsevier).

p. 6583, l. 21-22: The sentence is incomplete (missing subject).

p. 6583, l. 27-28: I do not see this from the equation.

p. 6583, l. 26 – p. 6584, l. 3: How can you link an isolated chemical reaction equation for only one reservoir with the physical equation of air-sea gas transfer including two reservoirs? I do not understand your statement.

p. 6586, l. 19: The open ocean water column is not an isolated system as at each location the system is open on top to the atmosphere, at the sea floor open to the sediment, and laterally open to advective fluxes.

p. 6588, l. 9-17: The terms “above” and “below” the lysocline are used not according to normal convention. “Above” usually means “shallower than...” and “below” means “deeper than...”. This needs to be clarified in order to avoid confusion.

Section 4, p. 6588-6589: This section is very difficult to follow. It is not clear how the results are achieved. I think a prognostic dynamic model needs to be used. What are the equations used leading to the conclusions?

Generally: I think the pressure dependence of the CaCO<sub>3</sub> solubility product should be mentioned more clearly.

The manuscript should be checked by a native English speaker. I expect that some issues could already be clarified by better formulations.

I think the paper needs at least a fundamental revision and may have to be thought over as a whole.

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