

## ***Interactive comment on* “Threshold of carbonate saturation state determined by a CO<sub>2</sub> control experiment” by S. Yamamoto et al.**

### **Anonymous Referee #2**

Received and published: 3 November 2011

This manuscript describes the use of a dissolution 'chamber' to determine omega values at which several different carbonate samples (coral, coralline algae, bulk sediment, foraminifera) show net dissolution. The paper is interesting and understanding at what value of omega different carbonate minerals begin to dissolve is important. Research often assumes (incorrectly) that carbonates are grouped simply into calcite and aragonite and corresponding omega values are generated. Dissolution can occur at omega  $\gg 1$  for some biogenic carbonates. Similar work was done in the early 1980's by RS Keir (The dissolution kinetics of biogenic calcium carbonates in seawater). Later, Burke Hale reviewed some of the work of Keir and made corrections to his original measurements. This work should be cited.

Some more specific issues are below. The paper would be much improved by correct-

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ing a range of mistakes with the english. The paper could be streamlined a bunch. Deleting some of the material would improve this manuscript. Condensing certain sections is necessary in places as well.

The entire discussion is problematic. It skips from discussing the results to mentioning the day vs. night dissolution of corals with no logical thread attaching the two. Also, what about bulk sediment and foramifera results. I think the entire discussion should be modified to more specifically discuss all of your results presented here. The discussion should focus on the omega values determined to result in net dissolution of each of the 4 test samples. The coral component is interesting and likely most important, however it is only a piece of your results.

Here are some specifics. Also please see the uploaded pdf with comments written on it.

Line 10 of abstract: “However, the threshold of  $\Delta\delta$  for the dissolution of natural sediments has not been clearly determined, and it is unknown whether these dissolution processes actually occur under natural conditions.”

As written, this is not true. There has been several studies in nearshore terrigenous deposits clearly showing temporal or spatial patterns of biogenic carbonates. In many of these, benthic foraminifera were the dissolving organisms. Some tried to constrain rate constants as well as the reaction order. In addition, there have been numerous studies in carbonate sediments of Florida Bay, USA. These studies go back to the early 1980's, before anyone ever cared. See the references below:

Aller, R. C. 1982. Carbonate dissolution in nearshore terrigenous muds: the role of physical and biological reworking. *J. Geol.* 90: 79-95. Rude, P. D., and R. C. Aller. 1991. Fluorine mobility during early diagenesis of carbonate sediment: An indicator of mineral transformations. *Geochim. Cosmochim. Acta* 55: 2491-2509. Green, M. A., R. C. Aller, and J. Y. Aller. 1993. Carbonate dissolution and temporal abundances of Foraminifera in Long Island Sound sediments. *Limnol. Oceanogr.* 38: 331-345. Green,

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M. A., R. C. Aller, and J. Y. Aller. 1998. The influence of carbonate dissolution on the survival of shell-bearing meiobenthos in nearshore sediments. *Limnol. Oceanogr.* 43: 18-28. Green, M. A., and R. C. Aller. 1998. Seasonal patterns of carbonate diagenesis in nearshore terrigenous muds: relation to spring phytoplankton bloom and temperature. *J. Mar. Res.* 56: 1097-1123. 8620, Line 26: "lowering the pH of surface water and increasing the saturation state". Should be 'decreasing the saturation state'.

8621, Line 21: "The effect of the calcification performed by marine organisms on the decrease in  $\delta^{13}C$  of seawater has been examined by laboratory experiments that control  $\delta^{13}C$ ."

Sentence doesn't read well. . .

8621, Line 26: "This decrease would impact on the calcifiers themselves, as well as on the ecosystems they constructed."

Sentence doesn't read well. . . .

8622, Line 1: "The value of  $\delta^{13}C$  is different among its mineralogy."

Change to something like "The value of  $\delta^{13}C$  varies with carbonate mineralogy"

8622, Line 25: "The difference between (1) and (2) comes from sample treatments. Although previous studies used the same biogenic samples, there are several Mg-calcite solubilities and precise values are not decided.

I don't understand exactly what you mean. Consider changing the sentences to something more clear.

8623, Line 2: "to set  $\delta^{13}C$  in", do you mean 'to determine  $\delta^{13}C$  in'? Hard to tell what you mean here. Last line, "Dissolution samples were set in this chamber, which", Worded poorly. How about "Carbonate samples for dissolution experiments were placed in this chamber, which"

8625, Line 25: "The A T of seawater increases by 2 moles for every 1 mole of carbonate

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dissolution.” Should be “for every 1 mole of calcium carbonate dissolution.”

8625 and 8626: Bottle gas is very dry. If you had bubbled the gas prior to introduction into your experimental system you likely would have minimized evaporation.

8626: Evaluation of the experiment system: Is this entire section even necessary? Could the paragraph on salinity variation over the course of the experiment be omitted and the following sentence inserted? “Small salinity changes that occurred due to evaporation over the course of the experiment were corrected for using pre-determined relationships between gas flow and salinity change rate.” Similarly, the section on Evaluation for remaining seawater seems like it could be shortened. The volume remaining is small relative to the total volume, correct (is it only 1.7% of total volume)? Can a simple sentence such as “A small amount of seawater (10mL or 1.7% of total volume) remained in the pump at the end of each experiment and was corrected for when determining mass balance of AT”?

8628, Line 16: “From Fig. 7, the dissolution rate was highest for coralline algae, followed by foraminifera and then coral.” Is this true based on some statistical comparisons of slopes? It certainly isn’t that clear to me. I would at least write something along the lines of “At any given value of  $\Delta\phi$ , relative dissolution rate is generally coralline algae>foraminifera>bulk sediment>coral.”

8628, Line 17–: Combine these into a short sentence “Consistent with previous work (Morse et al., 2006, 2007; Bischoff et al., 1993), the results show that higher dissolution rates were observed for samples with higher Mg-calcite contents. 20 Because the grain size and other properties of the samples were as consistent as possible, the differences in dissolution rates between samples were probably caused by differences in the instability (i.e., solubility) of the minerals.

How about “Consistent with earlier work (e.g. Morse et al., 2006, 2007; Bischoff et al., 1993) the differences in dissolution rates between samples presumably resulted from the solubility differences of minerals with varying Mg content”

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8630, Line 1: Sentence is wordy. Also, isn't it 'net' dissolution and not 'bulk'? How about something like "According to Eqs. (5)–(7), net dissolution of bulk sediment was zero at  $3.7 < \alpha < 3.8$  and  $3.0 < \alpha < 3.2$  for foraminifera and coralline algae." Line 3: I don't know what this means? 'Difference of these values comes from "other minerals".' 8630, Section 5.3:lines 13-17 could be written more clearly. I suggest: We compared results of bulk sediment dissolution rate vs.  $\alpha$  from this study with previous research.

I don't think is relative: 'Because our laboratory result is described by  $[\% \text{ h}^{-1}]$ , we have to convert the units to  $[\text{mmol m}^{-2} \text{ h}^{-1}]$ .'

Line 16: "If upper 1 cm sand sediment dissolves, and without considering pore water (i.e., Mgcalcite is influenced only by column seawater), dissolution rate  $R[\text{mmol m}^{-2} \text{ h}^{-1}]$  is described as follows:" can be simplified to:

"Assuming a density of calcium carbonate of  $2700 \text{ kg m}^{-3}$  and a porosity of coral reef sediment = 0.45 (Morse and Mackenzie, 1990), dissolution rate (R) was converted from  $\% \text{ h}^{-1}$  to  $\text{mmol m}^{-2} \text{ h}^{-1}$  according to equation (8):

8630-8631: Line 24 until end of document. The sentence structure all needs work.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/8/C4104/2011/bgd-8-C4104-2011-supplement.pdf>

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