

Interactive comment on “Threshold of carbonate saturation state determined by a CO₂ control experiment” by S. Yamamoto et al.

S. Yamamoto et al.

yamamoto-s-@eps.s.u-tokyo.ac.jp

Received and published: 28 December 2011

Interactive comment on “Threshold of carbonate saturation state determined by a CO₂ control experiment” by S. Yamamoto et al. S. Yamamoto et al. yamamoto-s-@eps.s.u-tokyo.ac.jp

Reply to the comments by Referee #1,

We acknowledge you for your valuable and constructive comments on this manuscript. Almost all of the comments and questions have been taken into consideration in the revised manuscript. The points of the revision are explained below. We have revised the manuscript accordingly based on our replies.

Abstract

C5067

Comment#1: I recommend deleting the abstract comment on line 12.

Reply#1: We have deleted line 12.

Introduction

Comment#2: The appropriate references are listed and briefly discussed on page 8622 lines 19 – 29; however some detail on the differences between experiments in the three major categories should be added and should include: the types of samples used and preparation of those samples, basic experimental approach, experimental conditions (i.e. seawater vs. distilled water, pCO₂ conditions and mode of adjusting water chemistry, etc.). An explanation of the difference between the experiments in this study and previous experiments in this section would strengthen the paper significantly.

Reply#2: We appreciate the important suggestion, and we have revised this paragraph to make these points clear. We measured the dissolution rate of biogenic Mg-calcite and aragonite collected from a coral reef by controlling seawater pCO₂.

Comment#3: Page 8621, Lines 21 – 26. The Langdon and Atkinson 2005 study was focused on the coral species *Porites compressa* and *Montipora verucosa*: not on coccolithophorids as stated on line 25. A 40% decline in calcification rate was at the lower end of the range they report.

Reply#3: We have revised this paragraph according to the comment.

Comment#4: Page 8622, Lines 8 – 10, this sentence is very misleading and seems to imply that Mg-calcite spontaneously transforms to dolomite, and that foraminifera et al. are responsible for the production of dolomite. Either clarify the differences in composition and origin between the two mineral phases, or omit any discussion of dolomite.

Reply#4: We have omitted the discussion of dolomite and improved the sentences.

Methods

C5068

Comment#5: In general, the methods are disjointed, need to be organized better, and are lacking detail. Some methods information is buried in the results and discussion sections and needs to be moved to the methods section. An introductory paragraph should be written that includes a brief overview of the experimental approach, nature of samples, target conditions for the experiments and why they were chosen, a brief description of the ranges of carbonate system parameters that naturally occur on the Shiraho reef where the samples were collected, and starting conditions (carbonate system parameters) of un-manipulated seawater used in the experiments. The experimental system description would read more smoothly if the small, individual sections (2.1 through 2.1.4) were combined into paragraph form. . .perhaps one describing the system components and a second describing the procedure. There is much detail missing from the methods and individual points that should be addressed are listed below. It is very difficult to determine how rigorously these experiments were controlled and monitored from the existing description of the procedures. Table 2 should be expanded to include information on the remaining carbonate system parameters for each experimental condition (e.g. total alkalinity, total carbon, carbonate ion concentration, etc.).

Reply#5: We agree that this section needs to be re-written more clearly. We have revised this section and add other carbonate parameters in Table.2 according to the comments.

Comment#6: In previous experiments (e.g. Plummer and Mackenzie 1974 and others), surface area to volume ratio (sample:aqueous solution) has a significant impact on reaction rate for dissolution. Some discussion of the SA/V ratio of the samples in your experiments should be included. Were any of the sediment particles (particularly the forams) identifiable. It would have been helpful to know from what genus and/or species these sediment fractions were derived, or at least a list of potential species contributing to sediment production.

Reply#6: We agree that SA/V has a significant impact, but we didn't measure the sur-
C5069

face area of the samples. In spite of the SA value, we selected the samples with same size because this size fraction (about 1-2mm) consists large portion of the sediments in this coral reef and by selecting all the samples with this grain size, we considered it is possible to measure representative dissolution rates in a real reef environment. The grain composition of sediment sample used is described in Fig.2.

Comment#7: Page 8623, Section 2.1. Is the coiled gas delivery tube porous, and from what is it constructed? Is the experimental system and open or closed-system?

Reply#7: The delivery tube is made of fluorocarbon polymers and this system is closed-system. We have added this information in the revised manuscript.

Comment#8: Page 8624, Line 18 – 20. Re: "The pCO₂ was then checked with a pH electrode. . . "Do you mean the pH and pCO₂ were checked using a pH electrode and NDIR, respectively? With what type of standards was your pH electrode calibrated?

Reply#8: We measured pH by using pH electrode and pCO₂ by NDIR. pH electrode was not calibrated and used just to check if the pH reading (mV) became stable or not. Basically pCO₂ was monitored using NDIR. Our current expression of this part may be misleading, so we have revised this sentence.

Comment#9: Page 8624, Section 2.2 Experimental Procedure. What was the duration of each experiment? How many replicates of each condition did you perform? The authors need to describe in the methods section that analyses were performed both on bulk sediment samples and on individual fractions. You state that carbonate system parameters were measured at the beginning and end of each experiment, yet your data looks like time series experiments with measurement at various intervals throughout the incubation. . . please clarify.

Reply#9: We admit that our explanation for the experimental procedure is not enough. We measure A_T and C_T every several hours, not only at the beginning but also at the end of each experiment. We have added Table.3 which shows the experimental

condition of each run precisely.

Comment#10: Page 8625, Section 2.3 Samples. Why did you use deep (500m) water for the experimental manipulations instead of water from the Shiraho reef where samples were collected? How was the bulk sediment collected and from what parts of the reef? Storage, treatment, and cleaning of sediment samples also needs to be discussed in the methods.

Reply#10: Ideally, Shiraho seawater should be used, but it was difficult to get a large amount of Shiraho seawater and sterilize it because of cost. This deep (500m) seawater is filtered and sterilized by ultraviolet rays and is commercially available relatively cheap, so we used this seawater instead. We collected surface layer of bulk sediment by using a scoop. Sampling point was 600m from shoreline, which is middle of a moat (shallow lagoon) and where typical coral zonation can be seen in Shiraho reef. Samples were cleaned by ultrasonic bath and dried at 40°C for about 12 hours. We have added these descriptions for the method section.

Comment#11: Page 8226, Line 19. What pH scale was used (seawater scale, total pH, etc.)?

Reply#11: Total pH scale was used. We have added this information.

Comment#12: Page 8627, Lines 7- 8. This information should be included in the results section. Page 8627, Lines 23 – 27. This information should be included in the results section. Results of the salinity calibration experiments should be discussed in this section.

Reply#12: According to Referee#1's and Referee#2's comments, we have moved both 3.1 and 3.2 sub-sections to method section and made it compact.

Result

Comment#13: Page 8628, Line 2. Re: "The results of the experiments are listed in Table 2." Table 2 lists the experimental conditions, and does not contain results from any

C5071

of the experiments. This table would be better placed in the methods section. A data table listing average dissolution rates and standard deviations for each experimental set would be helpful for comparison to previous work summarized in Table 3. It is very difficult to determine in the figures which data points represent individual experiments, and which data points represent average values from sets of experiments. Page 8628, Line 4. Re: "The experiments were performed for 6.0 to 11.5 hours." This information should be in the methods section Page 8628, Line 3. From the results in Figure 5, it looks as if these experiments were performed as a time series and the C_T and A_T were analyzed periodically through the duration of the experiment (as opposed to the beginning and end of each experiment as stated in the methods)? Please clarify in the methods whether these were time series incubation, or if each data point represents an individual experiment.

Reply#13: We agree that the result section contains the description for methods and needs a table which compiles the results of each run. We have moved the description part for the method section, and added a new table which compiles the result of each run. The data plots in the figures have been detailed in this new table.

Comment#14: Also in figure 5, it appears as if the dissolution trends over time for incubations at 590 to 1290 are not significantly different, and that there may be three distinct dissolution rate trends: the first for samples incubated at 420ppm, the second for samples incubated between 590 to 1290 ppm, and the third for samples incubated at 2030 ppm. Perhaps this is an indication of some critical thresholds between 420 and 590ppm and between 1290 and 2030ppm? Page 8628, Lines 10-14. From figure 7, it appears that the coralline algae threshold is slightly lower (2.8) than the foraminifera threshold. Also, it is curious that your bulk sediment threshold is so much higher than the individual fractions given that care was taken to use similar grain sizes for all sediments. It appears that there is something [unidentified] in the minor fractions that is much more soluble than the Mg-calcite from the forams and coralline algae. These small amounts of dissolution at very high Omega (3.7 to 3.8) may be more significant

C5072

in different locations on the Shiraho reef (or other reefs) where the minor fractions represent a larger component of the bulk sample. It seems that a closer look at the “other” fraction (22% of the bulk sample) including XRD analysis of this fraction is warranted.

Reply#14: We do not know what “other minerals” are, but we consider they are calcite or Mg-calcite because they do not color with dyeing (aragonite colors red-purple). In this study, we did not measure XRD of “other minerals”, so we could not distinguish “other minerals” from foraminifera or coralline algae or something unknown. We have added discussion part about possibility of underestimating net dissolution and difference of dissolution rate of each sample.

Discussion

Comment#15: Page 8629, Line 2. The Plummer and Mackenzie 1977 reference should actually be 1974.

Reply#15: We have corrected the year.

Comment#16: Page 8629, Lines 12 – 14. Discussion of sample treatment should be in the methods section.

Reply#16: We have moved these lines to Methods section.

Comment#17: Page 8631, Section 5.4. Some discussion of more recent work than (Andersson et al. 2003) on the future impacts of ocean acidification on Mg-calcite should be discussed in context with the results of this study. The appropriate references are included in the paper (e.g. Andersson et al. 2007, 2009, Morse et al. 2006) and results in these previous studies are relevant to (and should be included in) this section of the discussion.

Reply#17: We have added and correct the references.

Comment#18: Page 8631, Line 19. Re: “Mg-calcite dissolution occurs only during night at present, but it will occur during all day in the near future.” This statement needs to be

C5073

qualified. There is likely precipitation and dissolution during both day and night, with net calcification dominating the signature during the day, and net dissolution dominating during the night. On the Shiraho reef, calcification rates show net dissolution only during the night.

Reply#18: We agree the statement needs to be qualified. We have made clear the net and gross dissolution.

Interactive comment on Biogeosciences Discuss., 8, 8619, 2011.

C5074