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Comment

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

Anonymous Referee #1

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General comments

Dissolution of carbonate sediments in natural reef systems has long been recognized and documented despite the fact that mineral saturation states in these ecosystems are generally much greater than 1. The ability of reefs to keep up with rising sea level depends upon the balance between carbonate production, dissolution, and transport of sediments from the reef. Ocean acidification causes a decrease in seawater pH, carbonate ion concentrations, and carbonate mineral saturation states that may enhance dissolution of carbonate sediments and decrease calcification rates. Carbonate dissolution serves as a natural buffer for increasing pCO₂ and pH; and this process may provide some relief for calcifying organisms from the effects of ocean acidification at local scales.

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There is a very large body of literature that examines carbonate mineral solubility, and, more recently, the potential impacts of elevated $p\text{CO}_2$ and ocean acidification on biogenic carbonate dissolution. Early laboratory investigations were performed under conditions that do not simulate natural conditions. Recently, attention has been focused on examining mineral solubility and thresholds of biogenic carbonates using experiments that simulate natural and predicted future environmental conditions. Biogenic carbonates exhibit very different solubilities from abiotic carbonates and among different types of biogenic carbonates with similar Mg content. Quantifying their thermodynamic solubility necessitates experiments on a variety of different biogenic carbonates from different origins and locations to fully understand the dissolution process.

This study used a custom experimental system to expose natural carbonate sediments (Mg-calcite and aragonite) collected from the Shiraho Reef to controlled $p\text{CO}_2$ and mineral saturation states that simulate $p\text{CO}_2$ conditions out to the year 2100+. Results of these experiments are consistent with previous laboratory experiments and field observations of dissolution rates in reef settings and higher rates of dissolution for Mg-calcite (as opposed to aragonite) in seawater that is saturated with respect to carbonate minerals. The results of this study are significant in that they help to further constrain the chemical conditions under which dissolution of natural carbonates occurs. However, the presentation of the work does not do justice to the experimental scope and the significance of the results. There is lack of detail in the methods section that makes it difficult to determine the rigor and control of the experiments. The description of previous work on Mg-calcites in the introduction needs improvement; and a better explanation of why and how these experiments differ from previous work would help clarify the significance of the results. There are numerous grammatical errors and the manuscript needs to be carefully proofread and edited. These presentation issues can be easily remedied (and I've included specific comments below). The paper is appropriate for Biogeosciences, but should be revised and improved before publication.

Abstract

Page 8620, Line 12 – In the abstract the authors state “it is unknown whether these dissolution processes actually occur under natural conditions.” This contradicts background information that the authors provide in the introduction section (lines 4-7) where reference is made to field observations of dissolution and the statement is made that “net dissolution under conditions of $\Omega_a > 1$ has been observed at several coral reef sites” (line 4 and 5). Carbonate dissolution in natural systems has long been observed and documented in many field studies dating back to at least the 1970’s (e.g. Kinsey 1978, Barnes & Devereux 1984, Gattuso et al. 1993, Conand et al. 1977, Boucher et al. 1998, Yates and Halley 2003, 2006, Nakamora and Nakamuri 2009) and has demonstrated in recent modeling work by Silverman et al. 2009 to name a few. I recommend deleting the abstract comment on line 12.

Introduction

The introduction needs a better explanation of previous work. 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. There are a couple of incorrect statements that need to be corrected, and some slightly confusing sections that should be reworded (see below).

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. In their discussion, they indicate declines in coral and coral reef calcification ranging from 40 to 83% based on their experimental data. However, they point out that data from Gattuso et al. 1998, Leclercq et al. 2000, Marubini et al. 2001,

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2002, and Reynaud et al. 2003 predict a decline of only 1 to 18%.

Page 8622, Lines 5 – 7. These statements directly contradict line 12 in the abstract, see item 1 above.

Page 8622, Lines 8 – 10. Re: “Mg-calcite is a carbonate in which some of the Ca is replaced by Mg, giving rise to the mineral dolomite. It is formed by foraminifera, coralline algae, and sea urchins. . .”. 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.

Methods

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.). In previous

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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.

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?

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?

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.

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.

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

Page 8627, Lines 7- 8. This information should be included in the results section.

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Page 8627, Lines 23 – 27. This information should be included in the results section.

Results

Results of the salinity calibration experiments should be discussed in this section.

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 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. 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

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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 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.

Discussion

The discussion is generally well organized and touches on comparison to other key laboratory experiments that have quantified solubilities of carbonate sediments and comparison of laboratory dissolution rates to rates observed in the natural environment. One of the most important issues that seems to be absent from many lab experiment manuscripts is a word of caution on use of lab derived solubilities to predict dissolution rates in natural reef systems. There are numerous other environmental factors that affect in situ mineral dissolution of “live sediments” that have not been replicated in laboratory solubility experiments including surface organics on minerals that are likely removed during drying and ultrasonic treatment steps, grain size effects, physical effects such as water residence time, bacterially induced dissolution (e.g. see recent work by A. Tribollet 2008. *Microb. Ecology* 55:569-580), and modification of seawater carbon chemistry by surrounding biological processes on the local scale (e.g. see Anthony et al. 2011. *Global Change Biology* 17:3655-3666). Future experiments and application of lab derived solubility data to natural systems should also consider the potential influence of these types of factors.

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

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

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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.

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 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.

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