

Interactive comment on “Identifying vital effects in Halimeda algae with Ca isotopes” by C. L. Blättler et al.

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We appreciate the detailed comments from the two reviewers.

In response to reviewer 1:

We do have XRD data on natural (wild) Halimeda samples and will show these in the data table as well.

We will also include mention of the wild Halimeda samples whose Ca isotopes were measured by Holmden et al., 2012. It is puzzling to us why their values are significantly heavier (-1.22 to -1.11) than the samples that we measured (-1.52 to -1.28). With no quantitative XRD performed on Holmden et al.'s study, one possibility for the difference is ingrowth of calcite in the heavier samples. We will clarify this outstanding question

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within the text.

We would like to clarify that Stanley et al. (2010) also observed both aragonite and calcite grown in Halimeda under their previous experimental conditions, which we can make clear by describing their results as a 'partial change in carbonate mineralogy'.

The conversion to seawater values will be clarified. This was performed with a $\delta^{44}/^{40}\text{Ca}$ value of seawater relative to SRM915a of 1.88‰ (after Hippler et al., 2003) and by converting $\delta^{44}/^{42}\text{Ca}$ to $\delta^{44}/^{40}\text{Ca}$ values by multiplication by 2. The multiplication factor is rougher than the precise conversion factor for either theoretical equilibrium or kinetic fractionations, but given the uncertainty about the type of isotopic effect (equilibrium vs kinetic) and the limits of analytical precision, we find that this conversion method is sufficient within error.

Skeletal mass fraction was determined by weighing the dried sample before carbonate dissolution, and calculating the amount of carbonate that was dissolved using Ca concentrations of the dissolved solution. This will be clarified in the methods section. Wt% carbonate has no direct relation to calcification rate of the Halimeda, although we speculate that slower growth rate would result in lower calcification and lower wt% carbonate.

XRD errors of 5% are determined by the scatter on standards to create the standard calibration curve. This will be clarified in the methods section. The value of 88% calcite (as a minimum) for sample #6 was the result of applying the formula to calculate % calcite from peak areas under the characteristic aragonite and calcite peaks, and despite no visible aragonite peak, the result must have been influenced by the background noise on the spectrum. We therefore treat the value of 88% calcite as a minimum. We will provide XRD spectra in a revised version of the manuscript.

We unfortunately do not have Ca concentration data on the experimental waters, but we agree that a 0.1‰ shift would imply a significant removal of Ca from the growth aquarium. We suggest that the difference of 0.1‰ between the pre-experimental and

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post-experiment waters is possibly due to analytical error, or to precipitation of significant amounts of carbonate on other surface of the tank (not just from Halimeda growth). This degree of enrichment would imply 90% of the original Ca remained in solution, and would not have a great effect on the fractionation of carbonate precipitation.

We unfortunately have no information on growth rate, however, we will describe the possible effects of growth rate in the discussion section, as an alternative to the difference in fractionation being wholly caused by mineralogy.

We share your disappointment that the 'mixing line' is unfortunately defined by only one calcite-rich sample, but the experimental samples were all we had to work with. We disagree that we should entirely remove the x-axis (% calcite) in Figure 3 – in our opinion, the most interesting aspect of the data was that the one calcite-rich sample indeed looked isotopically like calcite. We can reduce the emphasis on the 'mixing line' by instead demonstrating this relationship with arrows pointing up from the inorganic line, however, we believe that the 2-dimensional nature of the data (Ca isotopes and mineralogical composition) merits plotting it on the axes as given in Figure 3. We can show the data in an additional figure in the manner suggested – with a single quantitative axis, and showing the fluid and carbonate data populations, along with the inferred fractionations.

All other specific comments will be incorporated in the text.

In response to reviewer 2:

Again, we share your disappointment that the main results of this work are strongly dependent on just one 'malformed' sample, but the data from this sample is nonetheless quite suggestive and, we believe, warrants publication. We are unable at this time to reproduce the results, but can re-write the discussion to emphasize the suggestive nature of this single analysis, and draw more attention to the other elements of the work (e.g. the marine Ca isotope budget and inferred vital effects).

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We describe the experiments as precipitating two different polymorphs from the same bulk fluid, since there are surely small changes in the boundary region/microenvironment that are driving different precipitation regimes.

We will incorporate more details about the sampling, preparation, and analytical methods, when available. We did perform bleaching and washing tests for their effects on both XRD and Ca isotope data, and will include the results (which showed no effect).

We choose to keep elements of Figure 3 (see above), but we will incorporate an additional figure showing the raw Ca-isotope data (not just the Δ Ca data) of solutions and samples. We hope this will clarify the data in a better way.

See above for responses concerning the reference to Stanley et al., 2010, the errors on XRD analyses, and the definition of skeletal mass fraction.

The difference between basal samples and natural samples is explained in the text as a mixture of skeletal material grown in seawater with skeletal material grown in the experimental fluid (which has a lower Ca isotope composition). For this reason, we expect them to differ from the natural Bahamas samples, and the data support this interpretation. Our experiments neither agree nor conflict with the results of Steuber and Buhl (2006), who suggest that Cretaceous seawater was 0.3-0.4‰ lower than modern seawater. The experiments were designed to obtain Δ 44/40Ca values, by subtracting sample composition from fluid composition, and thus the Ca isotopic composition of seawater does not need to be matched in the growth solution for the purposes of our experiments.

We disagree that significant changes in Cenozoic δ 44/40Ca can be observed in the records of Griffith et al., 2008, Schmitt et al., 2003, Heuser et al., 2005, and Fantle and DePaolo, 2005/2007. In combination, these records and others (e.g. Sime et al., 2007), do not show similar trends, and thus the majority of the variation can best be explained by natural and analytical scatter.

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All other suggestions for additions and clarifications to the text will be incorporated. We will organize the methods, results, and discussion sections further, which we agree will make the presentation of this work more clear.

Interactive comment on Biogeosciences Discuss., 11, 3559, 2014.

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