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

Anonymous Referee #1

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The manuscript entitled "Identifying vital effects in Halimeda algae with Ca isotopes" by Blattler and coauthors presents new results of measurements of stable Ca isotope ratios in Halimeda discoidea collected and grown in the laboratory (basal pre-lab and terminal 'experimental' samples) and "wild" Bahamas Halimeda samples. The mineralogy was quantitatively determined on these samples using a calibrated XRD technique. All of the 8 experimental samples were mostly aragonite (<9% calcite) except one sample that was 88% calcite. The mineralogy of the "wild" samples was mentioned in the text (p. 3567, Line 3) but not shown in the data Table. The Ca isotopic signature of the experimental samples (and thus fractionation from the experimental seawater) is related to the mineralogy of the biologically induced mineral precipitated similar to inorganic precipitates. However the carbonate from Halimeda is offset (isotopically heavier) than the inorganic forms (previously published data). The authors suggest

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that this is a result of specific vital effects due to Rayleigh distillation within the algal intercellular space. These results suggest that mineralogy has a first-order control on this carbonate sink and therefore they suggest mineralogy has a first-order control for the Ca isotopic composition of seawater.

These novel results are of broad interest to the scientific community, which is actively trying to understand biomineralization processes during carbonate precipitation and the controls on calcium isotopic fractionation in the global carbonate sink. The techniques employed seem appropriate and the discussion and conclusions are well founded in the given data. It would be nice to include mention of the few previously measured Halimeda samples from Holmden et al. 2012 (Geochim. Cosmochim. Acta) – all of which were identified as aragonite and seem to fit these new observations. Presentation of the data should be improved with a new figure 3, which does not include a mixing line that is arguably poorly defined (see discussion below). Additional clarifications should be made on the XRD calculations and the authors should address the specific comments below.

Specific comments: p. 3561, Line 14: I would suggest replacing 'biogenic aragonite' with 'biologically induced aragonite" following your discussion in this paragraph. p. 3562, Lines 2-3: It is stated that these experiments were done "to reproduce the unusual case of aragonite and calcite grown simultaneously under the same conditions" – is this what Stanley et al. (2010) saw? It was previously stated here that the mineralogy changed from aragonite to calcite – not that both precipitated in the experiments of Stanley et al. (2010). I found these two statements unclear. p. 3562, Line 5: I suggest inserting "relatively" before "simple algal biology". p. 3562, Lines 9-11: References are needed for this statement (they don't appear until much later in the paragraph). p. 3562, Line 19: I suggest give the range of isotopic fractionations that were observed in the laboratory speleothem-like calcite growth. p. 3562, Line 25: I suggest adding the temperature for the vaterite isotopic fractionation given here. p. 3563, Lines 17-20: I suggest adding references for this statement (they appear later

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in the paragraph but would give more credence to this statement upfront). p. 3563, Line 21: I suggest inserting “marine” before “organisms” as all the examples given are marine organisms. p. 3564: Lines 8-20: In this paragraph several different species are given without specific indication of what they are. . . i.e., planktonic foraminifera, coccolithophore. I suggest specifying the organism each time an organism is mentioned for the benefit of the reader. p. 3566: Lines 24-26: The authors state that they converted d44/42Ca to d44/40Ca relative to modern seawater but do not give the equation for the conversion, just the result in the table. Did the authors measure seawater? What value was assumed for seawater in order to make the conversion, since their lab standard was NIST SRM915a and not seawater. This should be very clear in order to compare these results precisely with other previous work. p. 3567: Lines 10-12: How was the skeletal mass fraction of the total sample mass determined? This was not described in the methods (or here in the results). p. 3567: Lines 12-16: If there was no identifiable aragonite peak in the sample, how was the 88% calcite determined? Wouldn’t it be 100% if no other carbonate mineral was identified? This statement makes me question what the “calcite %” truly represents in the experimental samples (data in Table 1). Further explanation is required. Supplemental data including all the XRD spectra for the experimental and natural samples would be appreciated and should be referred to here. p. 3567: Lines 26-28: Was there a change in concentration (along with the measured change in isotopic signature) of the experimental solution? This seems like a large change and if caused by removal of light Ca isotopes then you should see a change in concentration because these isotopic fractionations are not large. Discussion of how this would affect your measured isotopic composition of the carbonate should be included. I’m just suggested a sentence that states how much this change in solution could affect the fractionation you calculated from the measured isotopic ratios. p. 3569: Lines 5-7: The ‘mixing line’ in figure 3 in reality is just connecting two points of data – one with high calcite concentration and the other 7 samples with aragonite composition. I would agree that you’ve identified your endmembers based on your measurements rather than the other way around. The y-intercept or aragonite

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endmember is dictated by a line that is essentially created with two points, such that the one sample has a large influence on the slope (and intercept) of the line. I don't ultimately think this is important as you've identified samples with different mineralogy with different fractionations and these differences mirror the inorganic data – just offset. Your following discussion is based on this and I agree with this interpretation. It would be better to have more than one calcite sample, but it seems that was not available. Figure 3 needs to be removed an replaced with a figure that shows the measured data and the differences in fractionation between the minerals and that compared to inorganic measurements – but not relate it to % calcite and show a 'mixing' line. A box plot or something along those lines. p. 3570, Lines 13-16: This observation seems fine, but it would have been great to get an actual measure of growth rate – so that you know for certain that the one calcite sample was not controlled by growth rate isotope effects over mineralogy as you've described. Table 1: How was the error for %cc of +/- 5% and 15% for HAL-6 determined? This should be explained in the methods or results section. Furthermore, if these errors are included in constructing the mixing line – how could one be sure of the slope of that line? See comments above that suggest replacing Figure 3 and removing the idea of constructing a 'mixing' line with the data presented here. How was the wt % carbonate determined? Does that indicate calcification rate? See comments on p. 3570. Figure 3: See comments above suggesting replacing Figure 3 and removing the idea of constructing a mixing line with the data presented here.

Technical corrections: p. 3562, Line 15: Insert "per degree C" after 0.015 permil in order to indicate a temperature sensitivity.

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