

Response to review of:

Effects of increased $p\text{CO}_2$ and geographic origin on purple sea urchin (*Strongylocentrotus purpuratus*) calcite elemental composition.

M. LaVigne, T.M. Hill, E. Sanford, B. Gaylord, A.D. Russell, E.A. Lenz, J.D. Hoffelt, and M.K. Young

Biogeosciences Discuss., 9,1-34 (2013).

Author response in bold italics:

*We would like to thank Anonymous Reviewer 2 for his/her constructive review of our manuscript. The comments, questions, and suggestions raised in the interactive discussion have greatly improved the manuscript. In this study we examined (1) the geochemical composition of purple sea urchin (*Strongylocentrotus purpuratus*) skeleton precipitated during both adult and early life history stages; (2) potential differences in geochemical composition among individuals originating from regions spanning a broad latitudinal range encompassing a spectrum of oceanographic regimes; and (3) the impact of ocean acidification on Mg and Sr incorporation into larval and juvenile *S. purpuratus* skeleton in culture. Both reviewers identified the strengths of the manuscript as being (1) and (2) above, and raised important questions that have strengthened our interpretation of (3) in the revised manuscript.*

Below are our point by point responses (in bold italics) to all issues raised by Reviewer 2. The manuscript has been revised accordingly.

Anonymous Referee #2

Received and published: 18 March 2013

This study firstly provides useful information on the mineralogy and uptake of strontium of tests and spines of echinoderms from separate geographical regions, and second, provides experimental results demonstrating that source region can influence geochemical responses of offspring to enriched $p\text{CO}_2$ treatment. Their finding that the skeletal mineralogy in adult and juveniles stages is relatively robust to enriched CO_2 whereas it is during the early life stages that a response is apparent, is an important contribution to the growing body of evidence that ocean acidification can have different affects depending on the life stage of the organism. For this reason I endorse publication of this paper subject to revisions as detailed below. I note the published comments and review by J.P. Gattuso and Maria Byrne and restrict my comments to areas not already commented on. My main concerns are with their discussions on strontium and solubility.

Specifically P 17943 paragraph starting line 3. This paragraph starts off being about utilization of different carbonate polymorphs at different life stages but none of the subsequent discussion links back to the mineralogy of different life stages. Either link this paragraph to the life stages or shift the intro sentence to relevant paragraphs on page 17944.

We have moved the topic sentence mentioned above to the appropriate paragraph on page 17944 of the original manuscript.

In this paragraph authors refer to solubility being dependent on mineral structure and elemental composition. However much of this understanding on biomineral solubility has come from a combination of experiments on abiotic precipitation/ dissolution and dissolution experiments using powdered dead skeletal material whereas the authors are experimenting with a living growing organism, that have apparently strong control over mineralization processes that proceeds within an organic matrix (as discussed by authors on p17945). Experiments have demonstrated that living organisms and intact skeletons do not always respond to higher CO₂ as would be expected if their response was as per these earlier experiments on abiotic or powdered material (e.g. (Ries et al., 2009;Ries, 2011;Nash et al., 2012;Henrich and Wefer, 1986). Also there is literature showing that dissolution is also dependent on crystal size and other structural characteristics (reviewed in (Morse et al., 2007;Walter and Morse, 1985) and that studies on synthetic calcites may not be appropriate for interpreting biogenic material stability (Bischoff et al., 1987). Can the authors refine their discussion to delineate clearly between references to results that were from non-living experiments and those from living / intact skeletons and role of organic coverings so that the possible drivers of variations in response are more obvious to the reader. This delineation will help with later interpretation of results.

We acknowledge that the degree to which the observed changes in elemental composition will impact skeletal solubility cannot necessarily be predicted by abiotic experiments or even dissolution experiments on other biogenic material. Thus, we have referenced several of the studies mentioned in the review and added detail to the introduction to clarify that biogenical calcite does not always follow the geochemical behavior predicted by abiotic calcite experiments. The results and discussion section has also been edited to specify that dissolution experiments on urchin calcite would be required to confirm our conclusions on skeletal solubility.

Same paragraph- sentence starting line 7. This sentence is misleading. The authors should separate comments on incorporation of Mg being known to increase solubility from Strontium. The references cited do not support a role for the incorporation of strontium leading to higher solubility. These references refer to magnesium increasing solubility and in Morse strontium has been noted to have a correlation with MgCO₃- but it is the Mg content that has been confirmed experimentally to influence solubility, not Sr.

We have removed any potentially misleading text that would imply Sr incorporation affects skeletal solubility. Instead we have added statements to clarify that dissolution experiments on urchin calcite would be required to quantify impacts on skeletal stability/solubility.

Also, two of the references cited are missing from the reference list (Morse et al. 2007- Walter and Morse 1983- I cannot find a reference for Walter and Morse 1983 , only 1984). Check all references in the document are included in the reference list.

The reference list has been edited and updated appropriately.

line 21 'For example, effects of: : : quotes Ries 2011 experiment on CO₂ however previous two sentences were talking about temperature effects, this is a bit confusing, edit appropriately.

We have edited this sentences as per Reviewer #2's suggestions for the introduction of the work by Ries.

P17946 line 17 – typo- Ries, not Reis

Typo has been corrected.

P17950 line 13 This may be beyond the scope of this paper to answer, but is there any evidence that this mid-range MgCO₃ is the ultimate source of the Mg for both the LMC and HMC for the adult spines and tests?

There is no evidence of this to our knowledge, but this would be an interesting idea to explore.

P17952 Dsr regressions- nice work, clear discussion separates the factors influencing uptake of Mg v Sr. Figs 2 and 3 tell the data story clearly.

P17953 line 25 'As a consequence: : :.' The authors start by talking about geochemical attributes of the northern skeletons, then the predicted shift in saturation but do not go back to link this shift to possible changes in geochemical attributes. Edit appropriately.

Text has been edited to link the discussion back to geochemical attributes.

Also, Anderssons (Andersson, 2008) model starts at 12 mol% MgCO₃, whereas the authors echinoderms are 2-6mol%, a composition comparable to aragonite in solubility according to Chave 1962 cited by the authors. Can the authors link their work the aragonite saturation state, undersaturation of which is more likely to be the threshold for dissolution than for 12 mol%MgCO₃.

We agree with this point, and note that the figures in Andersson (2008) suggest that the timing of the predicted shift in aragonite undersaturation is actually the same as that of high magnesium calcite (12%) (based on the Plummer and Mackenzie solubility curve). Therefore, the sentence will be edited to clarify that the timing of both aragonite and high magnesium calcite (>12% MgCO₃) undersaturation will impact the high latitude *S. purpuratus* populations by the end of this century.

P17955 line 25 on. The authors provide no evidence that their echinoderms had faster precipitation rates under the higher CO₂, and indeed, much experimental work shows a decline in calcification rates of many calcifying organisms- this underpins the concerns regarding OA impacts. Based on their discussion, extrapolating the greater variance of Sr to physiological stress response does not seem warranted – suggest further explanation as to how this is evidence of stress. P17956 line 13 pm. Authors claim that results suggest a trend indicating faster mineral precipitation rates for the southern echinoderms this presumption of rate increase is based on the incorporation of more Sr, - however according to the literature cited throughout the paper, more Sr, while accepted to have a correlation with Mg, can be independent of precipitation rates, eg Mucci and Morse

1983- recognizing Lorenz 1981 found a correlation with rate. Thus the authors statement here is not unequivocally supported. Edit appropriately.

We acknowledge that the link between Sr/Ca and calcification would require further work in order to draw conclusions regarding changes in calcification rate in this section of the paper. Therefore, conclusions and statements previously interpreting Sr/Ca trends as a function of calcification rate were removed. Instead, a speculative tone was taken in the section entitled “Possible controls on Mg/Ca and Sr/Ca in *S. purpuratus*” to suggest future work to explore this possibility.

Conclusion line 7 as per previous comment, without proof that your echinoderms had a faster calcification rate, this claim is unsupported. It does not follow that because there is more Sr, rates are faster, the cited literature is not in agreement on this point.

As noted above, we have removed this statement from the conclusion, and instead suggest further study.

L13 There are some logic flaws here - How would increased precipitation rates be negative? Surely this would be good? Could faster rates offset any negative influence of higher solubility due to more Mg? Also, there is no evidence as per your cited literature that more Sr, per se, leads to increased solubility, and the increased Mg was not found to be statistically significant. Thus increased rates would not necessarily lead to increased solubility. The authors claim that increased precipitation rates would likely have a negative effect on skeletal stability and solubility is not supported by their results. A contrary argument could be put forward that the faster rates (if the extra Sr is evidence of this) would instead be a positive outcome for the southern echinoderms under future CO₂ scenarios as faster calcification rates may / could compensate for increased dissolution (or other physiological costs) due to lower saturation state. Furthermore, at line 20 on page 17956, the authors refer to the Sr incorporation as being an adaptive response (presumably for the southern echinoderms), which suggests a response that improves the chances of survival rather than a negative outcome. However, the authors have shown through cited literature that Sr incorporation seems not to be linked directly to biological activities, rather is an associated mineralization which suggests it is not a controlled adaptive response.

Based on this comment, and given that the connections to growth rates and skeletal solubility require future research, we have edited any text that seemed to overstate the data by inferring a “positive” or “negative” adaptive response that would affect survival.

The manuscript does not depend on demonstrating that there will be a negative outcome for the southern echinoderms under higher CO₂, rather, the data shows a level of geochemical resilience for echinoderms in higher CO₂ but a distinctly different response for the juvenile stage for echinoderms from a geographically distinct region. This is the most interesting outcome of the experiment and should be the highlight of the conclusion. It will be fascinating to see in future work whether the driver for this difference can be identified. Suggest edits to the conclusion.

We agree with this statement and have highlighted this point throughout the text of the revised manuscript (including the Abstract, Results and Discussion, and Conclusion sections).

Other notes Abstract- include information on temperature and pH for collection sites. *While we agree with the importance of these data, the variable nature of temperature and chemistry within each of these sites would make annual mean pH or temperature comparisons misleading in the abstract. Rather, we have edited the abstract in the revised manuscript to mention this variable coastal range. In addition, as per the suggestion of Maria Byrne, have included a description of new timeseries pH data collected from each of the collection sites in the text of the methods section.*

Supplementary information- Very good to see this thorough testing of preparation methods.