

## ***Interactive comment on “Assessment of hydrothermal alteration on micro- and nanostructures of biocarbonates: quantitative statistical grain-area analysis of diagenetic overprint” by Laura A. Casella et al.***

**Anonymous Referee #3**

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Through a series of well planned experiments followed by analyses at the micrometer and nanometer scale, the authors have documented the effect of medium-temperature hydrothermal solutions on the calcium carbonate shells of six different species displaying five different types of microstructural units. They have demonstrated the (expected) importance of the amount of time the materials spend in the hydrothermal solutions on the degree of shell alteration. What may be less expected, however, are the documented differences in degree of alteration under the same experimental conditions, but in different species and in different microstructures. The authors focused on observ-

C1

able structural changes, but also investigated some aspects of compositional changes due to interaction between the calcite/aragonite shells and the Mg-Na-Cl solutions at 175 C. Changes in grain size and orientation within selected areas of the shells were monitored through EBSD and FE-SEM. Changes in grain size were found to be the most sensitive indicators of hydrothermal alteration. The paper is replete with excellent photomicrographs and EBSD color-coded images showing grain orientation and phase identification. The results of this extensive work have important implications for our ability to recognize which biocarbonate fossil materials are most pristine and therefore most appropriate for chemical and isotopic analysis that may be used to reconstruct the details of past environments.

In summary, this is a very good paper that provides well-documented, quantitative experimental observations on the species-specific, microstructure-specific aqueous alteration of biocarbonate shells. I believe that this work marks a large step forward in the understanding of the preservation/fossilization process of shells. As the authors point out, their work also sheds light on how differential alteration effects can account for differential preservation of shell material. The implications of this result alone are extremely important for the interpretation of the fossil record. The results of this study also will guide the evaluation of fossil materials for isotopic and geochemical analysis with the goal of environmental reconstruction.

The current document requires some minor re-writing, as well as the addition of materials indicated in the comments below and on the attached annotated copy of the manuscript. I believe this paper will be of strong interest to the readership of this journal.

There are some improvements that could be made in the paper. Immediately below are more general suggestions. Below them are more specific comments, questions, and suggestions keyed to identified lines in the manuscript. A scanned copy of the annotated manuscript is also provided with additional detailed suggestions.

C2

The abstract is not appropriate as written. The first paragraph provides too much background information that instead should be in the introduction. The abstract, however, does not include necessary details about the experimental procedure and the types of analyses performed.

This paper covers a huge amount of information on several morphologically different parts of the shells of six species, undergoing alteration for up to 35 days. The authors have included some figures and tables to guide the reader through this information so that the discussion and conclusions will be convincing. Any additional techniques to help the reader keep track of, organize, and compare these data/observations would further enhance the impact of this work.

As much as I appreciate the level of detail presented on the individual samples and their respective microstructures, I suggest that the authors take a fresh look at the paper to determine if they reasonably can condense it further. At times, the density of information approaches overwhelming.

A distinction that should be addressed in the paper is the difference intended by the authors between the terms "overprinted" and "replaced." This is an important distinction especially for (future?) work on chemical and isotopic signatures that may or may not be transferred to the "new" solids formed after hydrothermal alteration.

The tracking of Mg and its importance in the alteration products are not well explained; nor is the addition of only that one element to the NaCl hydrothermal solution. Given the so-called "Mg-poisoning" of calcite, some more discussion is needed. Does all the Mg that occurs in the secondary Mg-calcites come from that introduced by the hydrothermal solutions, or is there Mg in the pristine aragonite?

Question that is more appropriate for on-line discussion:

What should be the next steps in experimental and analytical studies to evaluate how well texturally altered samples (as shown by changes in grain-area evaluation) of bio-

C3

genic carbonate hard tissues retain their chemical (incl. trace-element) and isotopic signatures?

Attached here is a scanned copy of the annotated manuscript, which has numerous detailed suggested changes. In the right-hand margins are circled numbers that are linked to comments and questions below.

Point 1, page 2: The information in the first paragraph of the abstract would be better placed in the introduction. One usually avoids including reference citations in an abstract.

Point 2, page 2: The second paragraph in the abstract is a good overview of the results and implications of the work. However, more detail is needed on the experimental procedure and analytical techniques used.

Point 3, page 4, line 111: The term "basic mineral unit" should be defined here, where it is first introduced, or the placement of the definition should be stated here.

Point 4, page 4, lines 115-117: The parts of this statement that are not currently in the abstract would be very useful there.

Point 5, page 6, lines 169-171: It would seem that the authors wish to provide an overview for or give a "heads-up" to the reader regarding the upcoming experiments and their results. However, this sentence is very compact and uses several not-yet-defined terms, making it unsuccessful in this inferred purpose.

Point 6, page 6, lines 175-176: The term "burial fluid" should be explained and its chosen composition justified, especially given the importance of the Mg component, as revealed by the experimental results.

Point 7, page 9, line 232: Although the term "microstructure" was defined earlier, it would be useful to remind the reader how that term is being applied in this paper. It is not a general term, but rather a stand-in for several types of mineralogical-structural morphologies focused on in the paper. Perhaps the parenthetical interjection "(e.g.,

C4

calcite fibers, prismatic aragonite, nacreous aragonite)” would be useful here.

Point 8, page 10, lines 261-262: It would helpful to the reader to be told how long these intervals of time are that give rise to the changes observed.

Point 9a, page 10, line 278: Does “other shell regions” refer to other parts of the prismatic area or to regions other than in the prismatic area?

Point 9b, page 13, lines 355-356: The excellent question is posed here of what determines the preservation potential of a fossil archive. This question should be re-stated and succinctly answered toward the end of the paper.

Point 10, page 15, lines 408-410: This is an important discussion of a complicated set of experiments. It is difficult for the uninitiated reader to understand what the focal points are. Perhaps some additional details about the original experiments would clarify the discussion.

Point 11, page 16, lines 446-447: I agree with this statement. At some point in the paper, though, it should be acknowledged that the present work does not directly address the issue of the geochemical fidelity of the recognizably/quantifiably altered carbonates.

Point 12, pages 20 and 21, lines 563 and 566: There seems to be a self-contradiction between these two lines with regard to the (lack of) fidelity in the geochemical signature.

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2018-249/bg-2018-249-RC3-supplement.pdf>

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Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2018-249>, 2018.