UNIVERSIDAD COMPLUTENSE DE MADRID

Facultad de Ciencias Geológicas
DEPARTAMENTO DE MINERALOGÍA Y PETROLOGÍA

Ciudad Universitaria
28040, Madrid (Spain)
Departamento de Mineralogía y Petrología

MSc. Pablo Forjanes
e-mail: *pforjane@ucm.es*

Prof. Dr. Lurdes Fernández-Díaz
e-mail: *lfdiaz@geo.ucm.es*

Madrid, July 9th, 2022:

We express our acknowledgements to the reviewer and the associate editor for the insightful comments, which helped to improve the manuscript.

Below is a detailed reply to all their comments and a description of all the *changes incorporated to the second version of the revised manuscript*. A copy showing all these changes marked in red is attached. We hope that the revised manuscript should now be acceptable for publication in ***Biogeosciences***.

Remarks by Reviewer 3 (Anonymous):

Remark 1: The major concern is with the title. Title addresses the experimental diagenesis but the experimental part talks about the hydrothermal conditions. Kindly change the title accordingly.

The title was chosen because the experimental conditions emulate those that exist in a diagenetic burial environment. A fluid with an average composition from the burial realm (dominated by the Cl anion and the Na and, to a lesser extent, Mg cations; ***Hanor, 1994***) and a temperature consistent with this environment were chosen. The temperature (80°C) corresponds to a depth of about 2 km assuming a normal geothermal gradient of 40°C/km (***Winter, 2013***), consistent with the burial diagenetic realm. This experimental setup contrasts to previous experimental works, which typically used interaction temperatures above 150°C to accelerate the reaction kinetics. Nevertheless, the title has been modified to:

Experimental burial diagenesis of aragonitic biocarbonates: from organic matter loss to abiogenic calcite formation

The following references have been added to the reference list:

Hanor, J. S. (1994). Origin of saline fluids in sedimentary basins. *Geological Society, London, Special Publications*, *78*(1), 151-174.

Winter, J. D. (2013). *Principles of igneous and metamorphic petrology*. Pearson education.

In addition, it has been pointed out in the article that the experimental conditions from this work seek to emulate more closely those that could be found in natural diagenetic environments.

Remark 2: Some comments are made in the pdf itself. kindly reply and make corrections accordingly.

Line 18. Does transformation takes place in all the cases? If not pls mention.

The transformation of aragonite into calcite is one of the most common processes during the early diagenesis of calcium carbonates. However, aragonite is sometimes preserved for different reasons (sedimentary beds protecting it, presence of chemical inhibitors of its transformation into calcite, extremely resistant aragonitic microstructures...) extensively discussed in the manuscript. The sentence has been modified so that it is clear that the aragonite-calcite transformation does not always take place. Furthermore, a sentence pointing out that the experimental conditions used in this work mimic those existing in diagenetic environments has been added to the experimental section of the revised manuscript.

Line 42. deciphering the past climate instead of deciphering past climate. Done

Line 43. Changes instead of change. Done

Line 51. pls rephrase with respect to "and" and commas used in the sentence. Done

Line 78. put "," after work. Done

Line 80. title says 'diagenesis of aragonitic biocarbonates", but the experimental condition says hydrothermal alteration experiment. pls clear the confusion.

See answer to remark 1. The conditions described as hydrothermal mimic those found in digenetic environments. The term “hydrothermal” refers to the presence of an aqueous fluid, which also exists in diagenetic environments. Furthermore, as explained in the answer to Remark 1, the temperature (80°C) at which our experiments were conducted is within the range of temperatures characteristic of burial diagenesis.

Line 306. not so clear. why to compare with 4 months alteration? that to only for Haliotis ovina. What about other species?

The results of 6 month and 4 months long alteration experiments were compared to determine how diagenetic alteration progresses. The reason why we focus on the alteration undergone by *Haliotis ovina* shell is that this is the only biomineral that shows extensive transformation (16 wt.%) of bioaragonite into calcite after 6 months. This is clearly stated in the manuscript. By studying *Haliotis ovina* samples altered for 4 months it can be concluded that even in this most reactive biomineral, calcite formation takes place very late in the alteration process. Thus, the calcite content of 4 moths altered *Haliotis ovina* shells barely reaches 1 wt%. In contrast, the calcite content of all the other 4 moths altered biominerals is negligeable.

Line 310. this comes to 35% for the drop of 0.7 wt% (2 to 1.3 wt%).

We thank the reviewer for pointing out our mistake. The value has been accordingly mended.

Line 406. in methods, it was stated that experiments were done at 80C, here it says 100!

The sentence in line 406 of the manuscript refers to the temperatures at which most other experimental studies of the hydrothermal alteration of aragonitic biocarbonates have been conducted. Indeed, all experiments in the works by Casella et al. (2017 2018), Jonas et al., (2017), Ritter et al. (2017) Pederson et al. (2019a, 2019b, 2020) were conducted at temperatures above 100°C, and most of them above 150°C. Our work is the first one where experiments are conducted at a lower temperature. This is stated in the manuscript.

Remark 3: It would be better to include some lines regarding the applications in the natural settings.

Several sentences highlighting the implications of our results for the interpretation of the processes undergone by aragonitic biocarbonates in natural diagenetic environments have been added to the discussion and conclusion section of the revised manuscript.

Remarks by Editor (*Dr. A . Mazumdar*):

Remark 1: The experiments are carried out specifically to address deep burial diagenesis over a short period of time (6 months). Assuming a geothermal gradient of 40C/km, the experimental temperature shows the possible alteration of aragonite at 2km of burial. So why not state that the paper deals with burial diagenesis including the title?

We thank the editor for the insightful comment. The title of the manuscript has been amended to qualify the diagenetic conditions considered in our work as burial ones. Moreover, a sentence stating that the alteration experiments were conducted at a temperature that would correspond to a burial depth of 2000 m, assuming a geothermal

gradient of 40 °C/km has been added to the experimental section of the revised manuscript (Winter et al., 2013).

Remark 2: The experimental part of the manuscript is robust, however, the implications are not discussed at the required depth!! Geochemists are well aware of burial diagenesis and its influence on isotope ratios and elemental fractionation. In fact, geochemists working on shells study the thin sections in detail and carry out micro-drilling or microprobe to avoid altered micro samples. Keeping in view the elaborate and robustness of the experiments, I suggest you try adding some more muscles to the implication part.

See Remark 3 (Reviewer 3). In the discussion and conclusions section, several sentences have been added emphasizing the implications of the results of this work.