

Biogeosciences Discuss., referee comment RC1 https://doi.org/10.5194/bg-2021-222-RC1, 2022 © Author(s) 2022. This work is distributed under the Creative Commons Attribution 4.0 License.

Comment on bg-2021-222

Anonymous Referee #1

Referee comment on "Experimental burial diagenesis of aragonitic biocarbonates: from organic matter loss to abiogenic calcite formation" by Pablo Forjanes et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2021-222-RC1, 2022

The paper by Pablo Forjanes and co-authors entitled "Long-term experimental diagenesis of aragonitic biocarbonates: from organic matter loss to abiogenic calcite formation" is one of the most comprehensive to date structural and mineralogical analysis of biomineral samples that underwent long term hydrothermal alteration experiments at 80°C using burial-like fluids. The samples consisted of outer and inner shell layers of Arctica islandica bivalve, the prismatic and nacreous shell layers of Haliotis ovina gastropod, and the "fibrous" skeleton of Porites sp. scleractinian coral. Noteworthy, the skeleton fragments selected for alteration were taken from the same skeletal regions to avoid differences in the alteration caused by metabolic effects. Since it was expected by the authors that in contrast to short term experiments at high temperatures ($T > 160^{\circ}C$) conducted previously by Casella et al. 2018, the diagenetic changes will be more subtle, various high resolution analytical tools were employed such as: X-ray diffraction, thermogravimetry analysis, laser confocal microscopy, scanning electron microscopy, electron backscatter diffraction and atomic force microscopy. The authors recognized 3 main phases of diagenetic alteration: (1) biopolymer decomposition which generates secondary porosity, (2) abiogenic aragonite precipitation that obliterates the secondary porosity, and (3) transformation of aragonite into calcite. Although these steps are common to all examined aragonite biominerals, the kinetics of the alteration is highly dependent on primary microstructural features. In comparison to aragonite skeleton of scleractinian coral Porites sp. which remains almost unaltered during the experiment, the aragonite skeleton (nacre) of the gastropod Haliotis underwent extensive secondary aragonite precipitation, whereas aragonite layers of Arctica bivalve shell were extensively transformed into calcite.

Remarks:

1. The paper provides very important, massive analytical documentation of more or less subtle alteration of biogenic aragonites in experimental diagenetic conditions. It provides direct comparison between short-term, high-temperature diagenetic experiments (Casella et al. 2017) and long-term, low-temperature experiments described in reviewed paper. The methods to assess some of these tiny structural modifications of the skeleton are very appropriate, especially the EBSD measurements and grain size statistical evaluation (combined with other characterization methods). However, diagenetic experiments at 90°C (Bernard et al. 2017 Nat. Commun. 8: 1–10; Cisneros-Lazaro et al. 2022 Nat.

Communications 13:113) suggest that even such theoretically stable biominerals like low-Mg calcite are subject of rapid diagenetic geochemical alteration which is not expressed in any structural changes. From this view point the structural stability is not a proof of lack of diagenetic imprint. This perspective should be outlined in the revised version of the paper (it will additionally append the authors conclusion that "during the diagenesis, most fossil carbonate hard tissues are probably overprinted, even if they do not show clear signs of carbonate phase change" (line 705).

2. Figures 6 and A13 shows comparison between pristine vs. 6 month altered skeleton of Porites sp.. The authors conclude in the caption (Fig. 6) that "No major changes can be observed between the pristine and the altered skeletal elements". However, in contrast to elongated aragonite biocrystals in "6a" that form the fibrous skeletal region (not the microcrystalline centers of calcification), it is clear that crystals in '6b" form domains that are larger than diameters of pristine aragonite biocrystals. These domains are also visible in EBSD band contrast maps (Fig. A13). As mentioned by the authors [line 580] "Pristine and altered samples of Porites sp. consist of aragonite crystals that are poorly cooriented: EBSD scans show identical MUD values: 10 (Fig. 6).", but the coarse domains that suggest some incipient? alteration may escape from being detected by this method; the quality of optical images is too low to assess this (Fig. A11). It is possible that in the Mg2+-rich burial-mimicking diagenetic waters such as used in authors' experiments (Mg2+ may also derive from local dissolution of biogenic aragonite) the secondary mineral phase may be the same as original one; in contrast to mollusks whose nacre aragonite tablets have unique morphology, aragonite fibers of corals are morphologically not so distinct from acicular aragonite cements thus distinguishing these two phases can be troublesome (see distinct difference between primary and secondary aragonite in bivalves: Webb et al. 2007 Geology 35: 803–806). Noteworthy, the coral skeleton described by the authors as "pristine" e.g., Fig. A12 is full of bioerosion traces (compare Nothdurft et al. 2007: Geochimica et Cosmochimica Acta 71, 5423-5438) which may create additional migration routes of the diagenetic fluids. These problems should be addressed in the text.

3. AFM images of pristine skeleton of Arctica islandica shell suggest that "aragonite has a slightly rough surface made up of spherical aragonite subunits down to 0.1 µm in diameter (yellow star in Fig. 2)". Similar AFM observations of Haliotis ovina shell suggest that "aragonite prisms have a rough surface composed of up to 0.3 µm aragonite subunits" whereas the aragonitic acicular crystals of Porites sp. are "composed of aragonitic subunits" of up to 1 µm". Why there is such significant discrepancy in sizes of observed subunits in comparison to dimensions of subunits documented e.g., by Cuif el al. 2011 "Biominerals and Fossils Through Time"? In mollusks (including different species of Haliotis) the "evidence also suggests that, provided that the presence of irregular rounded nanograins is a feature common to all microstructural units known thus far, this uniformity of morphology of the 10 nm "building block"" (ibidem p. 130). In scleractinian corals, the "skeletal aragonite appears formed of nodular grains with their long axis approximately 100 nm" (ibidem p. 122; see also Benzerara et al. 2011, Ultramicroscopy 111: 1268–1275). In fact, the units illustrated by the authors in Fig. 7 (especially in b and d) are very different from what is typically described as coral skeleton nanostructural organization (moreover these larger subunits e.g., in Fig. 7b are smooth and do not suggest nanogranular organization). Lack of such nanostructural organization is particularly intriguing in experimental samples: removal of organics should result in enhancement of nanograin presence that are thought to be outlined by some organic-rich material. These aspects should be explained in the text.

4. The scale bars should be normalized in all figures: [Figure 1] Magnifications of all items i.e., a, b, c, d should be the same to be comparable e.g., 50 μ m; [Figure 2] Magnifications of all items i.e., a-h (note "f") should be the same to be comparable e.g., 1 μ m and 500 nm. Explain magnified region in "f" and provide scale-bar; explain in the caption the yellow star mark, [Figure 3] Magnifications of all items i.e., a, b, c, d should be the same

to be comparable e.g., 50 μ m [magnification should be the same as in Fig. 1]; [Figure 4] Magnifications of all items i.e., a-h should be the same to be comparable e.g., 1 μ m and 500 nm; explain in the caption the yellow star mark ("0.3 μ m aragonite subunits (yellow star in Fig. 4b" - found in the main text).