## Reviewer 1

| Comments of the reviewer | Reviewed manuscript | Author comments / revised manuscript |
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| ”The manuscript “Assessment of hydrothermal alteration on micro- and nanostructures of biocarbonates: quantitative statistical grain-area analysis of diagenetic overprint” by Casella et al. represents a substantial contribution to scientific progress in the field of biomineralization and addresses a very important scientific question, the alteration of biogenic hard tissues, which is within the scope of Biogeosciences. The applied methods are valid and clearly outlined and the interpretation and conclusions are strongly supported by the results. The references are appropriate. The conclusions are fundamental as the authors prove the different steps which ultimately lead to calcite re placement of biogenic carbonates, the possible occurrence of overprinted aragonite and importance of grain size, intergrain surfaces and porosity in controlling timing and extent of alteration.<br><br>However, the overall presentation is not very clear and the language is not always fluent and precise, so I think that the manuscript would benefit of moderate revisions, as discussed below.” | | We accounted for the suggestions of reviewer 1 and rephrased many sections of the manuscript, improved fluency and organization of the text. In addition, the revised version of the manuscript was corrected by two native speaking co-authors (U. Brand and E. M. Harper). |
| “**General comments**<br>In the Introduction, the authors should describe in more details the mineralogy of selected material (i.e. anticipate what it is written at p. 5).” | | The mineralogy, microstructural characteristics and biopolymer content is now described in greater detail for each selected species. See the results section: chapter 3.1 Microstructural |

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| | | characteristics of modern bivalve, gastropod and coral skeletons. |
| "In paragraph 3.1, the authors should describe in greater details the microstructural characteristics of modern bivalve, gastropod and coral skeletons, which at the moment is only briefly addressed. For instance, A. islandica is known to have an outer homogenous/crossed lamellar/crossed acicular layer, an inner fine complex crossed lamellar layer and an irregular simple prismatic pallial myostracum. The brief description reported in 3.1 does not adequately inform the reader about the fabric and does not correspond to what subsequently written at p. 6 line 30 (aragonite prisms, but the microstructure of A. islandica is not prismatic see Dunca et 2009; Schone et al 2013)." | | The microstructure of the shell of *Arctica islandica* is described in the results section (chapter 3.1) in greater detail, according to the suggestion of Reviewer 1. |
| "I do not think that the microstructure of M. edulis can be described as consisting of calcite fibres. What shown in Fig. A2B are calcite prisms not fibers. Other figures may be more questionale, but the microstructures of M. edulis is foliated and prismatic (see for instance Brom & Szopa 2016; Carter et al. 2013). Eventually it is described as fibrous prismatic (Brom & Szopa 2016), a term which I do not agree with, but which is used (Carter et al. 1990) and it is distinct from the typical fibrous fabric of brachiopods." | | To our opinion the mineral units that compose the calcitic shell layer of the bivalve *Mytilus edulis* are fibres and are NOT prisms (e.g. Griesshaber et al. 2013, Acta Biomaterialia). The calcitic fibres in *Mytilus edulis* have a roundish outer morphology and can be few hundred micrometers long. Prisms are significantly shorter, thicker and are bounded at their sides by four to six planes. In order to be called a fibre mineral units in other carbonate biological hard tissues do not need to have the morphology of brachiopod fibres. We definitely want to keep to the term fibre for the mineral units in the calcitic shell layer of *Mytilus edulis*. |
| "An important issue is the time of decay of organic sheaths around the basic mineral units, which is | | Another manuscript focussing on organic contents in pristine and altered hard tissues is currently in |

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| not clearly indicated but just discussed as short." | | preparation. |
| "In paragraph 4.3, the authors should add the stratigraphic age of the described fossil material in order to support their conclusions." | | Paragraph 4.3 describes similarities between microstructural features that we observe in our hydrothermally altered specimens and microstrcutural/geochemical characteristics that we find in diagenetically overprinted fossil samples. For each example that we describe we state clearly a reference, where additional details such as stratigraphic age, sedimentological context, lithologies are stated. Our intention with paragraph 4.3 is to show that some microstructural features that we observe in our altered skeletons can also be observed in fossil samples. The intention of the paragraph is clearly stated at ist beginning. |
| "In the conclusions, the authors should report and give more enphasis to the important statement: "even though nacreous aragonite is still preserved as aragonite, it is an overprinted aragonite that, most probably, holds little of the original microstructural or geochemical signature"." | | This is corrected according to the suggestion of the reviewer. We added an additional point in the conclusions. |
| "Technical corrections<br>p. 1 line 34: sentence unclear" | "...The latter analysis enables an unequivocal determination of the degree of diagenetic overprint and discloses information especially about low degrees of hydrothermal alteration...." | "...The used statistical analysis derived from EBSD measurements enables an unequivocal determination of the degree of diagenetic overprint of biogenic carbonates, and discloses information especially on low degrees of hydrothermal alteration...." |
| "p. 2 line 9-10: long and complex sentence" | "...In particular, deciphering the sequence of those processes with many steps of alteration and unknown intermediate stages poses one of the major problems in understanding carbonate diagenesis (Immenhauser et al., 2015a; Swart, 2015; Ullmann and Korte, 2015)...." | "...In particular, deciphering the sequence of diagenetic evolution poses one of the major problems in understanding carbonate diagenesis (Immenhauser et al., 2015a; Swart, 2015; Ullmann and Korte, 2015)...." |

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| "p. 2 line 16 (and below in the text): sp. not italics" | "...*Porites sp.*..." | "...*Porites* sp...." |
| "p. 2 line 25-30: I would describe before all the molluscs and only after the corals or viceversa." | "...As long-lived organisms, stony corals attract great interest for the reconstruction of palaeoclimates derived from skeletal oxygen isotopic compositions and major element abundances, as these geochemical signals vary in response to changes in seawater temperature (e.g., Meibom et al., 2007). It is assumed that $\delta^{234}U$ in sea water has remained constant in the past, thus, the comparison between present-day and decay-corrected $\delta^{234}U$ in sea water and in coral skeletons is a major tool for the detection of diagenetically altered corals. $\delta^{234}U$ values of the latter are higher relative to present day sea water (Hamelin et al., 1991; Stirling et al., 1995; Delanghe et al., 2002), while pristine corals exhibit a $^{234}U/^{238}U$ activity ratio similar to modern sea water (Henderson et al., 1993; Blanchon et al., 2009)…." | The order of the described specimens is based on their mineralogy and not on their animal class. To avoid repetitive descriptions of similar microstructures and to keep the manuscript as short as possible we keep to this order.<br><br>Order:<br>- *Arctica islandica* – aragonite<br>- *Porites* sp. – aragonite<br>- *Haliotis ovina* – aragonite (prisms & nacre)<br>- *Mytilus edulis* – calcite (fibres) & aragonite (nacre) |
| "p.3 line 2: correct M s edulis to M edulis test material: it would be better to indicate the dimension for the size (length, width, height?)" | "...In *H. ovina* the two layers are composed of aragonite, whereas the shell of *M.s edulis* consists of an outer calcite and inner aragonite layer…." | Changed accordingly<br><br>Dimensions of used specimens are given in subchapter 2.1 (Test materials) |
| "p. 4, line 24: the critical misorientation value. Sentence not finished" | "...A grain is defined as a region completely surrounded by boundaries across by which the misorientation angle relative to the neighbouring grains is larger than a critical value; the critical misorientation value...." | Wrong punctuation<br>"...A grain is defined as a region completely surrounded by boundaries across by which the misorientation angle relative to the neighbouring grains is larger than a critical value, the critical misorientation value...." |
| "p.5 line 19: correct H s ovina to H ovina" | "...Skeletons of *A. islandica*, *H.s ovina*, and *Porites* sp. consist entirely of aragonite, whereas *M. edulis* contains both carbonate phases, calcite and aragonite...." | Changed accordingly |
| "p. 5 line 20: add the type of fabric for A. | "...The shell of *A. islandica* is comprised of an | The fabric is given within this sentence: |

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| islandica." | assemblage of irregularly-shaped and micrometre sized aragonitic basic mineral units (white stars in Fig. 1A), that are larger in the outer shell layer compared to basic mineral units of the inner shell layer (this study and Casella et al., 2017)...." | "...assemblage of irregularly-shaped and micrometre sized aragonitic basic mineral units..." |
| "p. 6 line 5: I do not think that the shell of M. edulis can be described as consisting of fibres, but prisms. Please check carefully also in the literature (Carter et al. 1990)." | | We do not agree with the comment of the referee and follow the definition for the calcite microstructure found in *M. edulis* as is described by Griesshaber et al. (2013) and Checa et al. (2014) in detail. Reference added.<br><br>Checa, A.G., Pina, C.M., Osuna-Mascaró, A.J., Rodrígues-Navarro, A.B. & Harper, E.M. (2014). Crystalline organization of the fibrous prismatic calcitic layer of the Mediterranean mussel *Mytilus galloprovincialis*. European Journal of Mineralogy 26: 495-505. |
| "p. 6 line 13-14: explain better this statement. The examples that follows are not strictly related to it." | | Inorganic calcite contents were determined in altered specimens using XRD. Those initially aragonitic specimens differed in their microstructure (nacreous, prisms, needle-like, fine-grained). It was observed that calcite formation in fine-grained *A. islandica* was fastest compared to the needle-like *Porites* sp. coral skeleton. Slowest replacement kinetics was observed for *H. ovina* containing aragonite prisms and nacre. The latter is most resistant to dissolution-reprecipitation reactions. |
| "p. 6 line 29: How long does it take for organic fibrils to be destroyed? What is the relationship between this processdecay and the "dormant" interval reported at p. 7?" | | The degradation of organic matrix is depending on the temperature applied, and its chemical components. In a previous study, our experiments showed that the organic matrix of brachiopds was destroyed after 2 days of thermal alteration at 400 |

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| | | °C (cf. Casella et al., 2018a-b). |
| "p. 6 line 30 and p. 14: the microstructure of A islandica is not prismatic (Dunca et 2009; Schone et al 2013)" | "...At these conditions aragonite prisms in the shell..." | Schöne et al. (2013) describe the microstructure as „simple prismatic crystal fabric". We changed the text passage as follows according to our previous publication (Casella et al., 2017).<br>"...At these conditions aragonite mineral units in the shell...." |
| "p. 7 line 25: again it is very important for this statement that the microstructure of the two taxa is described in great details, which is not at the moment." | "...However, it should be noted that even though there is a resemblance in basic mineral unit morphology and size, the existence of primary porosity, and the fabric of occluded biopolymers between the prismatic shell parts of *H. ovina* and *A. islandica*, the kinetics of carbonate phase replacement is distinct for the two microstructures (Figs. 2A, 2C). While in *A. islandica* shell replacement between carbonate phases is 25 rapid and extensive, it is slow and patchy in the prismatic shell layer of *H. ovina*...." | "...In the *A. islandica* shell, in which small irregularly shaped aragonite mineral units comprise the shell microstructure, replacement between carbonate phases is rapid and extensive, while replacement in the outer shell layer of *H. ovina,* which microstructure consists of aragonite prisms, is slow and patchy...." |
| "p. 8 line 13: "for both microstructures", is it true also for both mineralogical phases in M edulis?" | | Yes, calcite fibres and nacreous aragonite increase in grain size due to amalgamation. |
| "p. 8 line 22-25: the description of the "rise in porosity" is very important but it is not described enough clearly. It should be stated more clearly that pores are present in the biogenic carbonates." | "...A further characteristic caused by hydrothermal alteration is the significant rise in porosity within individual basic mineral units (Fig. 6). Even though the latter grow together at their perimeters (Fig. 7) a multitude of nanopores develop within them due to decomposition of biopolymer fibrils, which were present in the pristine hard tissue (e.g., Griesshaber et al., 2013; Casella et al., 2018a, 2018b)...." | "...A further characteristic caused by hydrothermal alteration is the significant rise in porosity within individual basic mineral units (Fig. 6). that grew together at their perimeters (Fig. 7). A multitude of nanopores developed within each biocarbonate crystal due to decomposition of biopolymer fibrils. The latter were located in primary pores within each crystallite of the pristine hard tissue (e.g., Griesshaber et al., 2013; Casella et al., 2018a, 2018b)...." |
| "p. 9 line 12-14. Sentence not clear." | "...Based on Mg-contents, in addition to the 'final' calcite, two high-Mg-calcite phases can be distinguished (Figs. 10, 11, A15), which seperate | "...In addition to secondary calcite, , two high-Mg-calcite phases can be distinguished (Figs. 10, 11, A15) based on Mg-content measurements. Both |

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| | the 'final' calcite (calcite with a low Mg-contents) from the overprinted aragonite that was not yet replaced by calcite (Figs. 11, A15)...." | high-Mg calcites seperate the secondary calcite (calcite with low Mg-content) from the altered aragonite that was not yet replaced by calcite (Figs. 11, A15)...." |
| "p. 12, lines 3-4 and p. 15, line 3-4. Prismatic and nacre microstructures are among the shell microstructures, the ones having the higher amount of organic content, more than the homogeneous/fine complex crossed lamellar fabric in A. islandica. Having a high organic content they should have also a high primary porosity. Or is it a matter of pore size?" | "...Stacks of calcite fibres in *Mytilus edulis* and the nacreous tablet arrangements in *M. edulis* and *H. ovina* are the most compact microstructures investigated in this study. These materials lack primary porosities. Nonetheless, when the shells are altered, the extent of alteration-induced secondary porosity is high in the nacreous tablets, as the occluded intra-tablet membranes and inter-tablet fibrils decompose and create space for fluid circulation....."<br>"...Our study clearly shows that of the investigated aragonite microstructures the nacreous tablets are the most resistant to replacement by calcite, irrespective of the assembly pattern of the tablets in columns or sheets. Porosity closure and basic mineral unit (nacre tablet), amalgamation recasts at first completely the original microstructure, however, with the 5 preservation of the original phase (Figs. 9A, A17A, A17B)...." | In the pristine shells, biopolymer matrices are surrounding each mineral unit and may also be located within each crystal as fibrils or network located within primary pores. Due to decomposition of the organic matter caused by alteration these pores become visible. Additionally, secondary porosity concomitantly is formed during dissolution-reprecipitation reactions when alteration is applied.<br><br>Changed to:<br>"...These materials scarcely contain primary porosities...." |
| "p. 12, line 11 Regenberg et al. 2007, comma missing after et al." | | Changed accordingly |
| "p. 12, line 29-35. This part is not very clear and not very well fitted into the paragraph.<br>Also should not it be placed in the results?" | "...The least difference in grain area change between pristine and most altered states was observed for *A. islandica* aragonite (Fig. 12A), while the most significant difference occurred for *M. edulis* fibrous calcite (Fig. 12E). For *Porites* sp. acicular aragonite and *H. ovina* prismatic and nacreous aragonite, we find a perceivable, but small difference in grain area size between the | "...The least difference in grain-areas between the pristine and most altered states was observed for *A. islandica* aragonite (Fig. 12A), while the most significant difference occurred for *M. edulis* fibrous calcite (Fig. 12E). For *Porites* sp. acicular aragonite. and *H. ovina* prismatic and nacreous aragonite we find a perceivable, but small difference in grain areas between the pristine and the most altered |

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| | pristine and the most altered states. For *M. edulis* nacre the majority of grain area data overlap for this microstructure, as well for some large grains formed in the altered shell (Fig. A16). …“ | states. For pristine *M. edulis* nacre the majority of grain-area data overlap for this microstructure, as well for amalgamated nacre after applied hydrothermal alteration (Fig. A16). …“ |
| “p. 14 line 5-13. Very important process, to be described more clearly. It is nor clear why “Carbonate phase alteration kinetics in A. islandica shell is sluggish at first” and why porosity “explains the little difference in mineral grain area”.” | “...The large number of small basic mineral units gives rise to exceedingly large surface areas where the fluid can get into contact with the mineral. Carbonate phase alteration kinetics in *A. islandica* shell is sluggish at first. However, once the nucleation barrier is overcome and the alteration process is started, it proceeds very rapidly (Figs. 2A, A4A; Casella et al., 2017). Thus, overgrowth of inorganic aragonite in voids and basic mineral unit amalgamation might well be masked by the almost instantaneous replacement of biogenic aragonite by inorganic calcite in the microstructure of *A. islandica* shells. The high volume of interconnected porosity in *A. islandica* explains why alteration becomes active after only a short time in contact with diagenetic fluids. Moreover, the topological characteristics of porosity facilitate the coupling between the rate of aragonite dissolution and calcite reprecipitation. This, in turn, explains the little difference in mineral grain-area found in the hard tissue of *A. islandica* between the pristine and the most altered states. ...” | The sluggish alteration kinetics is described in detail by Casella et al. (2017).<br>In the present manuscript we refer to the publication above as data on *A. islandica* completes the presented research on hydrothermal alteration of mainly biogenic aragonites.<br>“...The large number of small basic mineral units gives rise to exceedingly large surface areas where the fluid can get into contact with the mineral at grain boundaries and nanopores found within each mineral unit. Carbonate phase alteration kinetics in *A. islandica* shell is sluggish at first. However, once the nucleation barrier is overcome and the alteration process is started, it proceeds very rapidly (Figs. 2A, A4A; Casella et al., 2017). Thus, overgrowth of inorganic aragonite in voids and basic mineral unit amalgamation might well be masked by the almost instantaneous replacement of biogenic aragonite by inorganic calcite in the microstructure of *A. islandica* shells. The high volume of interconnected porosity in *A. islandica* and the presence of thermodynamically less stable biogenic aragonite explain why alteration becomes active after only a short time in contact with diagenetic fluids. Moreover, the topological characteristics of porosity facilitate the coupling between the rate of aragonite dissolution and calcite reprecipitation. This, in turn, explains the |

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| | | little difference in mineral grain-area found in the hard tissue of *A. islandica* between the pristine and the most altered states....” |
| “p. 14 line 22-23. “the increased prevalence of the nacreous shell layer of M. edulis relative to calcitic shell layers in seashore sediments”. This statement should be better<br>explaned and supported.“ | “...The nacreous shell part grows into a compact entity and becomes sealed and protected against fluid infiltration. This explains the observation of remnants of nacreous shell areas surrounded by calcite (Brand, 1994) as well as the increased prevalence of the nacreous shell layer of *M. edulis* relative to calcitic shell layers in seashore sediments....” | We explain the statement in more detail. |
| “p. 15 line 5-6: sentence not clear” | “...Porosity closure and basic mineral unit (nacre tablet) amalgamation at first completely recasts the original microstructure, but with the retention of the original phase (Figs. 9A, A17A, A17B)....” | “...Reprecipitation processes and amalgamation of neighbouring nacre tablets at first completely recasts the original microstructure, but with the retention of the original phase (Figs. 9A, A17A, A17B)....” |
| “p. 15, “It has been further demonstrated that in Palaeozoic marine faunae taxa with calcitic skeletons prevail”. The authors have to add fossil before marine fauna” | | Changed accordingly |
| “p. 16 line 26: tissue forms or tissues form” | “...Biogenic carbonate hard tissue form the basis of studies of past climate and environmental change....” | “...Biogenic carbonate hard tissues form the basis of studies of past climate and environmental change....” |
| “p. 17 line 26: “Thus, in the case of aragonitic tissue the survival of biogenic aragonite” better to correct into “Thus, in the case of aragonitic tissue the survival of biogenic aragonite”?“ | “...Thus, in the case of aragonitic tissue the survival of biogenic aragonite cannot be used as a distinct indicator for pristine elemental and isotope signals....” | The comment of the reviewer corresponds to the text passage given in our manuscript. → no further changes needed |
| “References: Crippa & Raineri (2015) is in the text but it missing from the ref list” | “...to mark the former Pliocene–Pleistocene boundary (e.g., Crippa and Raineri, 2015;...” | Reference added<br>Crippa, G. and Raineri, G.: The genera Glycymeris, Aequipecten and Arctica, and associated mollusk fauna of the Lower Pleistocene Arda River section (Northern Italy), Riv. Ital. Paleontol. Stratigr., 121, 61-101, 2015. |