

## Reply and revision of bg-2016-355 Casella et al.

REVIEWER 1	SUBMITTED MANUSCRIPT / REVIEWER COMMENTS	AUTHOR COMMENTS / REVISED MANUSCRIPT
Comment 1 / L. 279	“...SEM images on the left hand side of Figs. 5 and 6 are taken from the...”	Changed to: “...SEM images on the left hand side of Figs. 4 and 5 are taken ...”
Comment 2 / L. 303	“...The small changes in MUD values must be attributed to fact that it was impossible ...”	Changed to: “...The small changes in MUD values may be attributed to the fact that it was impossible...”
Comment 3 / L. 343-348	<p>“...Thus, as the replacement reaction proceeds, the percolating diagenetic pore fluid is undersaturated with respect to aragonite but is saturated with respect to calcite....”</p> <p>If the fluid were saturated with respect to calcite this phase would not nucleate in the first place and would not grow after its nucleation. A certain degree of supersaturation is required for the system to overcome the energy barriers associated to both, heterogeneous nucleation of calcite on aragonite and calcite growth. This could be better explained.</p>	<p>As the reviewer requested, we explain the nucleation of calcite even at a low degree of supersaturation. We include an additional Figure (Fig. 12) and include in the text a new chapter (4.1), see below.</p> <p><b>4.1 Driving force in comparison to nucleation barrier</b></p> <p>In sedimentary environments the fate of metastable biogenic aragonite or high-Mg calcite can follow two scenarios: (1) the metastable biogenic matter can be completely dissolved and removed by fluid transport to form molds that are later filled by cement or other neogenic minerals or (2) the metastable minerals may be replaced by stable low-Mg calcite in-situ, by a process which involves dissolution of the metastable phase into a nano- to micro-scale local fluid volume (e.g. a thin fluid film) from which the stable low-Mg calcite precipitates without long-range transport (Brand &amp; Veizer, 1980, 1981; Brand, 1991, 1994; Bathurst, 1994; Maliva 1995, 1998; Maliva et al., 2000; Titschak et al., 2009, Brand et al., 2010).). The latter process may preserve original morphological boundaries and microstructures such as prisms, tablets and fibres in bivalve shells. The replacement reaction from aragonite to stable low-Mg calcite is driven by the higher solubility (free energy) of the the metastable phase compared to the the stable phase. Thus, as the replacement reaction proceeds, the reactive, percolating experimental or diagenetic pore fluid becomes undersaturated with respect to aragonite owing to its relative supersaturation with respect to calcite, the less soluble mineral phase in the system. The maximal</p>

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supersaturation  $\Omega_{\max}$  with respect to calcite, which can be obtained in a fluid, which draws its calcium and carbonate ions from the dissolution of aragonite, can be described as:

$$\Omega_{\max} = \frac{K_{sp}(\text{Aragonite})}{K_{sp}(\text{Calcite})}$$

(1)

, where  $K_{sp}$  stands for the ion activity products of the respective phase in the relevant pore fluid. The free energy difference or thermodynamic driving force is given by  $\Delta G_{\max} = -RT \ln \Omega_{\max}$ . To obtain an estimate we used the data of Plummer & Busenberg (1982) and calculated the solubility products for calcite and aragonite for 25 °C, 100 °C, and 175 °C (Fig. 12). The maximal supersaturations  $\Omega_{\max}$  thus obtained are 1.39 (25 °C), 1.26 (100 °C), and 1.18 (175 °C). The replacement reaction first requires a nucleation step: the formation of the first calcite crystallites larger than the critical size  $r^*$  (Morse et al, 2007). Empirical nucleation theory relates the activation energy  $\Delta G_A(r^*)$  necessary to form a nucleus of critical size to the specific surface energy  $\sigma$  needed to form the interface between the nucleating phase and the matrix phase as

$$\Delta G_A(r^*) \propto \frac{\sigma^3}{(-RT \ln \Omega)^2}$$

(2)

Only supercritical nuclei or pre-existing seed crystals of size  $r > r^*$  of calcite can lower their free energy as their volume free energy gained by growth exceeds the adverse energy contributions of increasing interface area. To obtain a significant number of supercritical nuclei a critical supersaturation needs to be reached (Morse et al., 2007, Gebauer et al., 2008, Nindiyasari et al., 2014, Sun et al. 2015). Reported values for critical supersaturation levels  $\Omega_{\text{crit}}$  required for calcite nucleation in various conditions range from the order of 3.7 (Lebron & Suarez, 1996, Zeppenfeld, 2003) to the order of 30 (Morse et al., 2007; Gebauer et al., 2008) or even several hundreds e.g. in hydrogel matrices (Nindiyasari et al., 2014). The DFT study of Sun et al.

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		<p>(2015) arrives at <math>\Omega_{crit} = 5</math> for systems free of inhibitors such as Mg, and <math>\Omega_{crit} = 35</math> for modern sea-water. Accordingly, the supersaturation produced by the dissolution of aragonite is very small compared to supersaturation levels typically required for the nucleation of calcite. Thus we can expect that nucleation is a critical kinetic step in the replacement reaction of aragonite by calcite.</p>
<p>Comment 4 / L. 420-428</p>	<p>“...However, we find that experiments conducted with the Mg-containing burial solution yield larger calcite crystals (black arrows in Fig. 14B) in comparison to the size of the grains obtained from experiments carried out with meteoric water (Fig. 14A). Grains obtained from alteration experiments with meteoric fluid show a significantly higher degree of mean misorientation (up to 10 degrees, black arrows in Fig. 14A), compared to that in grains that grew in burial solution. We attribute this to the nucleation rate: the crystals growing from each nucleus consume the aragonite educt (the precursor, original aragonite) until they abutted each other. Thus, larger crystals in the experiment with burial solution result from a smaller number of calcite nuclei. Again, this supports the idea that Mg<sup>2+</sup> inhibits calcite nucleation. ...”</p> <p>I basically agree with the authors explanation. However, I would have liked a discussion of the Mg content of the newly formed calcite. If this is magnesian calcite, is higher solubility compared to that of pure calcite would determine a smaller driving force for the transformation. In other words, both nucleation and growth would occur under lower supersaturation, which would further</p>	<p>We included a paragraph (see below, chapter 4.5), a new Table (Table A1) and a Figure showing the Mg distribution in an altered shell measured by electron microprobe analysis (Fig. A13).</p> <p>The newly formed calcite contains only small amounts of magnesium (Table A1) in the order of 0.1 wt % (or 0.006 in the formula unit), while the strontium content of the original aragonite in the order of 0.4 wt.% is retained in the calcite (0,005 in the formula unit). At the rim of the sample, where it was in direct contact with the bulk of the experimental fluid, we observe the local formation of Mg-rich carbonates in some places only (Fig. A13B and Table A1), with measured Mg-contents up to 19.7 wt % (0.716 in the formula unit, encountered in scan field 3 at the outer rim of the sample). The averaged composition in scan fields 4 and 9 may indicate dolomite, but like scan field 3, which has a Mg content exceeding that of dolomite, we more likely have magnesite with some calcite present, as judged from the EPMA map (Fig. A13B).</p>

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	explain the smaller number of crystals and their larger sizes.	
Comment 5 / L. 472	“...in palaeontology as it a prerequisite to taxonomic,...”	Changed to: “...in palaeontology as it is a prerequisite to taxonomic, ,...”
Comment 6 / L. 489-492	<p>“...In particular, the resistance of biogenic aragonite to replacement by calcite up to temperature of 175 °C during hydrothermal alteration offers an additional explanation for the preservation of aragonitic shells/skeletons, besides the taphonomic windows envisaged by Cherns et al. (2008). ...”</p> <p>The authors conduct experiments at two temperatures, 100 and 175 °C. In my opinion, the fact that at 100 °C the aragonite-calcite transformation does not occur after 28 days does not qualify them to state that there is a resistance of biogenic aragonite to be replaced by calcite at temperatures below 175 °C. The window temperature between 100 and 175 °C is too large and 28 days is not such a large time, not for an experiment and more so when compared to geological times.</p>	<p>We have conducted the following alteration experiments: at 100 °C, 125 °C, 150 °C and 175 °C, ranging for time periods between one and 84 days. Details are given in Table 1, Fig. A11 and all experiments are described in the method (2.2.3) as well as in the results (3.2) sections. Thus, we investigated in this study shell samples that were not only altered at 100 °C and 175 °C but also between these two temperatures. In addition we conducted experiments that lasted up to three months, and not only for 28 days. During the time span of a Ph. D. study (3 years) we could not conduct experiments with geologic time scales.</p>
Comment 7 / L. 522-524	<p>“...7. Between two tipping points, one between 50 and 60 °C, the other between 160 and 180 °C, aragonite appears to precipitate from supersaturated aqueous solutions rather than calcite, such that the hydrothermal treatments of aragonite within this temperature bracket do not yield calcite. ...”</p> <p>This is not a conclusion of this work. I understand that it must correspond to the paper by Balthasar and Cusack</p>	<p>Taking results from the literature and from our experiments conducted at additional temperatures, we can state that between the two tipping points, one between 50 and 60 °C (Kitano et al. 1962; Taft, 1967, Ogino et al. 1987, Balthasar and Cusack, 2015), the other between 160 and 180 °C (Perdikouri et al, 2011, 2013, this paper), aragonite appears to precipitate from supersaturated aqueous solutions rather than calcite, such that the hydrothermal treatments of aragonite within this temperature bracket do not yield calcite....”</p>

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	(2015), but it is not supported by results in this manuscript.	
Comment 8 / L. 525-527	<p>“... 8. The absence of aragonite replacement by calcite at temperatures lower than 175°C contributes to explain why aragonitic or bimineralic shells and skeletons have a good potential of preservation and a complete fossil record. ...”</p> <p>See comment 6.</p>	<p>See reply to comment 6.</p> <p>During the time span of a Ph. D. study (3 years) we could not conduct experiments with geologic time scales.</p> <p>Our experiments record the short term answer which may be different from the the possible change through geological times. However, within the applied time and temperature range we find very interesting results that help to understand microstructural and mineralogical findings generated from diagenesis taking place in nature. There is evidence that our results may explain some patterns of the geological record and if this is true for the 100 °C experiments it is also true for the 175 °C ones. There is no reason to expect a different behavior in 28 days in the window between 100 and 175 °C. So our assumptions and conclusions are valid and should be kept. The important point is that they help to explain and discuss several patterns of aragonitic preservation which were left unsolved up to now. Of course these are preliminary data, but they help to identify an experimental procedure to follow to understand diagenetic processes.</p> <p>We will never be able to experiment with geological time, but we can get observations that help to explain patterns.</p>
Comment 9 / L. 1019-1020	“...shown in Fig. 5. 10 mM NaCl + 10 mM...”	<p>Changed to:</p> <p>“...shown in Fig. 4. 10 mM...”</p>
Comment 10 / L. 1108-1113	<p>“... <b>Fig. 14.</b> Grain area versus mean misorientation within individual grains obtained for newly formed calcite at alteration of <i>Arctica islandica</i> aragonite in artificial meteoric (A) and in burial (B) solutions at 175 °C and for 7 and 84 days, respectively. The Mg-containing (burial) alteration fluid induces the formation of large calcite grains that show a low degree of misorientation within</p>	<p>We briefly discussed this point in sub chapter 4.5 (see below).</p> <p>Grains obtained from alteration experiments with meteoric fluid show a significantly higher degree of mean misorientation (up to 10 degrees, black arrows in Fig. 15A), compared to the grains that grew in burial solution. Large mean misorientation of &gt;4 ° occur notably in the grains grown in the 7 days treatment in meteoric solution, while the corresponding 84 days</p>

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	<p>the grains (B), while with artificial meteoric solution, the solution that is devoid of Mg, significantly smaller grains are obtained. However, the latter occur with a high mean misorientation within the individual, newly formed grains. ...”</p> <p>I miss a discussion of why the mean misorientation within the individual, newly formed grains in contact with burial solutions. I guess that this points to Mg incorporating into the newly formed calcite.</p>	<p>treatment does not show a significant increase in grain area compared to the 7 days treatment.</p>
<b>REVIEWER 2</b>		
Comment 1	<p>The main result of this study is that below 175 °C there are no signs of aragonite to calcite trans-formation. At 175 °C the authors found a period of 4 days where the systems seems “dormant”. After this period the transformation reaction becomes detectable and runs to completion within a remark-able short time of just 6 days. It would be of great interest for future studies to elucidate the processes that occur during the 4 day dormant period. This seems to be a likely analog to cement hydration reactions, in which an induction period of low heat production is followed by an “acceleration period”, during which significant nucleation and growth advances the overall extent of reaction.</p>	<p>We thank for the comment and fully agree with the reviewer. Accompanying experiments are conducted right now.</p>
Comment 2	<p>For the community, it is an interesting question as to whether (micro)organisms simply passively modify local environmental conditions, thus rendering metastable what would otherwise be thermodynamically unstable</p>	<p>The question of the production of metastable aragonite by organisms was not an issue in this study.</p>

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	<p>phases, or if, conversely, such organisms actively form unstable phases by pumping electrons or redox-sensitive molecules against gradients [1,2]. In any case, we would expect that the deviation from thermodynamic equilibrium would be relatively small. In other words, one would expect that energetically expensive reactions would also be “expensive” for the organism involved. Casella et al.’s findings seem to nicely support this hypothesis. It takes a significant increase in temperature to convert the aragonite into thermodynamically stable calcite. However, this insight does not answer the important question: why do organisms produce metastable aragonite and not the stable phase calcite?</p>	
Comment 3	<p>Another interesting point is the potential occurrence of spatial patterns in the distribution of replacement reaction rates. The existence of a characteristic porosity distribution within the shell material is able to foster heterogeneous material fluxes. Thus, in future studies we expect direct mapping of the reaction rate in order to identify rate components that form the heterogeneous overall reaction rate. Such rate components provide important input values for the simulation of fluid-solid reactions [3].</p>	<p>We thank the reviewer for his highly valuable suggestions and will perform future experiments and simulation studies accordingly.</p>
<b>REVIEWER 3</b>		
Comment 1	<p>Does the paper address relevant scientific questions within the scope of BG? YES, particularly taphonomy of shells.</p>	----
Comment 2	<p>Does the paper present novel concepts, ideas, tools, or data? YES, particularly, the focus is highly innovative.</p>	---

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Comment 3	Are substantial conclusions reached? YES, it adds substantial knowledge to the particular process studied.	---
Comment 4	Are the scientific methods and assumptions valid and clearly outlined? YES, in general, although I find that some conceptual aspects should be explained more in length (see detailed comments).	---
Comment 5	Are the results sufficient to support the interpretations and conclusions? YES, in general (but see detailed comments).	---
Comment 6	Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? YES, in general, although additional data on the composition of the fluids (Table 1) are needed	Chemical and experimental information on hydrothermal experiments utilised in the present study are given in Table 1.
Comment 7	Do the authors give proper credit to related work and clearly indicate their own new/original contribution? YES, in general (but see detailed comments).	---
Comment 8	Does the title clearly reflect the contents of the paper? YES.	---
Comment 9	Does the abstract provide a concise and complete summary? YES.	---
Comment 10	Is the overall presentation well-structured and clear? YES.	---
Comment 11	Is the language fluent and precise? YES	---
Comment 12	Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Some technical abbreviations (EPMA, TAP, PET, LPET, LLIF: : :) should be defined for non-specialists. L. 173: "...SEM visualization and EPMA..."	Following abbreviations, which are not common, were defined: "...SEM visualization and electron Probe Micro Analysis (EPMA)..." "...TAP (thallium acid pthalate) crystal..." "...PET (pentaerythritol) crystal..." "...LPET (large pentaerythritol) crystal...LLIF (large lithium flouride) crystal..."



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	L. 190: "...TAP crystal..." L. 191: "...PET crystal..." L. 192: "...LPET...LLIF..."	
Comment 13	Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? NO.	---
Comment 14	Are the number and quality of references appropriate? YES.	---
Comment 15	Is the amount and quality of supplementary material appropriate? YES.	---
Comment 16 / L. 133	"...create local micro-environments for physiological generate of their composite..."  'for physiological generate', this is an odd expression	Changed to: "... living organisms create local micro-environments for physiological generation of their composite..."
Comment 17 / L. 138	"...dealt with pre-Neogene <i>A. islandica</i> specimens..."  'pre-Neogene <i>A. islandica</i> ', certainly not this species.	Changed to: "...dealt with <i>A. islandica</i> specimens..."
Comment 18 / L. 157	"...samples as well as the mineral in reference, geologic,..."	Changed to: "...samples as well as the mineral part in the reference specimens, i.e. geologic, and non-biological aragonite, ..."
Comment 19 / L. 159	"...with glass knives to..."	Changed to: "...with glass knives to..."
Comment 20 / L. 193	"...and hematite (Fe), and were used..."	Changed to: "...and hematite (Fe), were used..."
Comment 21 / L. 198-199	"... Hydrothermal alteration experiments mimicked burial diagenetic (and meteoric) alteration of recent <i>A. islandica</i> under controlled laboratory conditions. Chemical and isotopic compositions of experimental fluids are given in Table 1...."	The used fluid compositions are empirical values and may differ from those which can be found in nature. Nevertheless, we decided to use 10 mM of NaCl for the simulated meteoric fluid and 100 mM of NaCl and 10 mM of MgCl <sub>2</sub> for the simulated burial fluid due to the fact that burial waters have more Na compared to meteoric fluids but also some Mg.

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	<p>This initial bit needs to be expanded further. More data on the composition of fluids and why their compositions have been chosen are necessary.</p>	<p>Moreover, both simulated diagenetic fluids were spiked with <math>^{18}\text{O}</math>-depleted oxygen in order to trace fluid-solid exchange reactions. The isotopic aspect of the performed hydrothermal alterations were analysed by other project members (see Ritter et al., 20016, accepted manuscript in Sedimentology) in order to trace fluid-solid exchange reactions. Due to the fact that the present manuscript does neither focus, nor deal with isotopic changes, we deleted the mentioned isotopic fluid compositions.</p>
Comment 22 / L. 207	<p>“... this temperature regime is far beyond natural meteoric diagenetic environments but are typical for the burial realm....”</p> <p>At least a reference is needed before the period.</p>	<p>References added, see below:  “...Obviously, this temperature regime is far beyond natural meteoric diagenetic environments (Lavoie and Bourque, 1993) but are typical for the burial realm (Heydari, 1997). ...”</p>
Comment 23 / L. 237-238	<p>“... The shell portion facing seawater, indicated with yellow stars in Figs. 1A and 1B, consists of aragonite crystal units in the 5 <math>\mu\text{m}</math> size range (Fig. 2A). This shell portion is highly porous (Fig. 1B) with pore diameters in the range of a few (&lt; 5) micrometres...”</p> <p>This feature is not visible at the magnification of Fig. 1B.</p>	<p>Changed to:  “... This shell portion is highly porous (see the white dotted features in Fig. 1B), pore diameters range within a few micrometers...”</p> <p>See Fig.A2</p>
Comment 24 / L. 240	<p>“... dense and is composed of very small aragonite crystallites with sizes of less than 1 <math>\mu\text{m}</math> (Fig. 2B) and contains very few pores....”</p> <p>Fig. 2B is heavily etched. Accordingly, any conclusion about the density of pores is doubtful.</p>	<p>Changed to:  “... is dense and is composed of very few small aragonite crystallites with pore sizes of less than 1 <math>\mu\text{m}</math> (Fig. 2B)....”</p>
Comment 25 / L. 260	<p>“... shell of <i>A. islandica</i> is composed of nanoparticles that are a few tens of nanometres in diameter...”</p> <p>Again, the nanogranules I Fig. 3C are etching and not original features.</p>	<p>Changed to:  “... In order to check the validity of nanoscale structural features observed in pristine <i>Arctica islandica</i> shells, we prepared non-biological aragonite grown from solution in a similar way (microtome cut, polished, etched slightly, only for 180 seconds, critical point dried). As it is well visible in</p>

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		Fig. A3 etch pits develop, the presence in aragonite grown from solution and assembly of nanoparticles is not evident....”
Comment 26 / L. 260-261	<p>“...the shell of <i>A. islandica</i> is composed of nanoparticles that are a few tens of nanometres in diameter (white arrows in Fig. 3C). These are co-aligned to form mesocrystals - here in the 1-5 <math>\mu\text{m}</math> size range....”</p> <p>‘These are co-aligned to form mesocrystals’, probably true, but not demonstrated here. I advise deletion.</p>	<p>These are co-aligned to form mesocrystals – probably true but not demonstrated here.</p> <p>The term mesocrystal was deleted.</p>
Comment 27 / L. 284-287	<p>“...At higher magnification a multitude of tiny holes (indicated with yellow arrows in Figs. 5C, 5D) become readily visible. In the unaltered shell these holes were filled with the network of biopolymer fibrils interconnecting the mineral units (e.g. Fig. 3B)....”</p> <p>‘holes’, do the authors refer to the membranes between mineral units? Please, be precise.</p>	<p>“... At higher magnification a multitude of tiny holes (indicated with yellow arrows in Figs. 5C, 5D and enlarged in Figs. A7A and A8B) become readily visible ...”</p> <p>We changed the text accordingly and included two new Figures in the appendix.</p>
Comment 28 / L. 302-303	<p>“... Hydrothermal treatment of <i>A. islandica</i> at 100 °C does not produce a significant change in aragonite co-orientation pattern, texture, grain fabrics, and grain size distributions. The pristine and the hydrothermally treated shell materials appear to be quite similar....”</p> <p>the coincidence in the orientations of the c-axes of aragonite and calcite, before and after alteration, is remarkable. I would like the authors to comment on this. Could there be some kind of epitaxial growth of calcite on the aragonite?</p>	<p>In the first few days of alteration the pristine aragonite microstructure predetermines to some degree the microstructure of the newly formed product.</p>
Comment 29 / L. 303	<p>“...values must be attributed to fact...”</p>	<p>Changed to: “...values must be attributed to the fact...”</p>

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<p>Comment 30 / L. 304-305</p>	<p>“...EBSD scan fields on the different samples in exactly corresponding spots with respect to the outer shell margin and to the patterns of growth lines...”</p> <p>‘and to the patterns of growth lines’, what is meant with this exactly? please reword.</p>	<p>“...EBSD scan fields on the different samples in exactly corresponding spots with respect to the outer shell margin and to the patterns of annual growth lines...”</p>
<p>Comment 31 / L. 305-306</p>	<p>“...The shell is not uniformly textured. In particular, the slight preferred crystallographic orientation of the a*-axes (the (100) plane normal) in Fig. 6C is a singular case, while c-axis preferred orientation is otherwise dominant (Fig. 6C)....”</p> <p>There is something wrong here. The maximum for a* is more or less coincident with the maximum of c*, and does not conform with the orientations of b*. The authors should review their data to make sure that the a* pole figure is the correct one.</p>	<p>We checked our data shown in Fig. 6 amended the text accordingly to the reviewers comment.</p>
<p>Comment 32 / L. 306</p>	<p>“...while c-axis preferred....”</p>	<p>Changed to: “...while the c-axis preferred...”</p>
<p>Comment 33 / L. 329-330</p>	<p>“...The MUD values for the newly formed calcite material are high (Figs. 9, 10), but this is related to the fact that within the range of the EBSD scan just a small number of large, newly formed, individual crystals is encountered. ...”</p> <p>The explanation based on the small number of crystals mapped is not enough. Again, as above, is there the possibility of epitaxial growth?</p>	<p>We cannot change the number of newly formed crystals. The investigation of epitaxial growth of the product on the educt was not the major point of investigation in our study.</p>
<p>Comment 34 / L. 351</p>	<p>“...Characteristics of the grains obtained by reaction at 100 °C and 175 °C...”</p>	<p>We changed the title according to the comment of the reviewer.</p>

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	<p>Subsection 4.1.- I do not think that the title (particularly 'Characteristics of the grains') actually conforms to the contents.</p>	
<p>Comment 35 / L. 372</p>	<p>"...Calcite nucleation occurs (and replacement reaction proceeds) where the hydrothermal fluid is in contact with the bio-aragonite: at the surfaces of the shell, in pores and along growth lines (Figs. 7, 8, 9). ..."</p> <p>'Figs. 7, 8, 9', I find that only Fig. 9b is relevant in the context.</p>	<p>We changed the text accordingly.</p>
<p>Comment 36 / L. 394-395</p>	<p>"...). A high degree of internal strain is indicated by blue colours, while light green to yellow colours highlight shell portions where local misorientation is low..."</p> <p>May be I do not understand properly, but in the scale of misorientations, blue colors imply very low values, whereas green, yellow and red are increasing values. Isn't it the other way round?</p>	<p>We agree with the reviewer and the text was changed (see below):</p> <p>Blue colours indicate the absence of measurable internal strain, while light green to yellow colours highlight areas where local misorientation is larger than experimental resolution.</p>
<p>Comment 37 / L. 400-401</p>	<p>"...all calcite grains contain numerous small calcite crystallites, a clear cause for the occurrence of internal strains..."</p> <p>'numerous small 400 calcite crystallites, a clear cause for the occurrence of internal strains'. Something is inconsistent here. Crystallite boundaries are defined by misorientations values above 5°, but this is not real, just a convenience. At the positions of 'crystallites' (defined in this way) misorientations values just peak. Therefore, they are not real and cannot be the origin of</p>	<p>We revised the statement in the text.</p>

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	<p>misorientations. To demonstrate that they are real, other techniques (e.g., TEM) are necessary.</p>	
Comment 38 / L. 411	<p>“...curvilinear structures in the cross section (white arrows in Figs. 13A, 13B) and ...”</p>	<p>Changed to: “...curvilinear structures in the cross section (white arrows in Figs. 13A, 13C) and ...”</p>
Comment 39 / L. 412	<p>“...correspond to subgrain boundaries within the newly formed calcite crystals. These boundaries do not appear to heal or to disappear with an increased alteration time, an indication again of the little effect of alteration duration on the fabric and internal structure of calcite grains crystallized from <i>Arctica islandica</i> shell bioaragonite...”</p> <p>The linear structures in 13C at consistent angles argue for crystalline structures ({104} faces of calcite?).</p>	<p>We do not understand the comment of the reviewer and did not change our text. We think that what we state in the text is right.</p>
Comment 40 / L. 422-424	<p>“...Grains obtained from alteration experiments with meteoric fluid show a significantly higher degree of mean misorientation (up to 10 degrees, black arrows in Fig. 14A), compared to that in grains that grew in burial solution....”</p> <p>This conclusion does not seem significant in the absence of a statistical analysis, and in view of the low number of data which deviate from the trend in 14B.</p>	<p>We do observe this feature in duplicate samples.</p>
Comment 41 / L. 426-428	<p>“...Thus, larger crystals in the experiment with burial solution result from a smaller number of calcite nuclei. Again, this supports the idea that Mg<sup>2+</sup> inhibits calcite nucleation....”</p>	<p>We expanded this statement in subchapter 4.5 (see also below):</p> <p>We attribute the large calcite grains to the nucleation rate: The crystals growing from each nucleus consume the aragonite educt (the precursor, original aragonite) until they abutted each other. Thus, larger crystals in the experiment with burial solution result from a smaller number of</p>

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	I cannot follow the statements contained in the two sentences.	calcite nuclei, which may be attributed to the presence of aqueous Mg in the experimental fluid. Note here, that both the reduction of Mg concentration in the reactive fluid, compare to that in the initial burial fluid (see Table 1), as well as speciation calculations, suggest that the formation of Mg-bearing carbonate minerals (magnesite and/or dolomite) is likely possible to occur at the experimental conditions. Indeed, we observe small patches of newly formed Mg-rich carbonates (Fig. A13). The formation of such minerals occurs at lower rates compared to pure Ca-bearing carbonates owing to the slow dehydration of aqueous Mg that is required prior to its incorporation in the crystal (e.g. Mavromatis et al., 2013) even at temperature as high as 200 °C (Saldi et al., 2009; 2012).
Comment 42 / L. 431	Subsection 4.3.- In my opinion, the paragraph immediately above could be included within this subsection.	The subsections of the discussion were changed.
Comment 43 / L. 451	<p>“...6C - D illustrate that the (newly formed) calcite product reveals an internal structure that is very reminiscent of the original bioaragonite/biopolymer composite...”</p> <p>Fig. 6C-D is not relevant within the context. The images supporting this statement have to be referred unequivocally.</p>	<p>We changed the sentence as follows:  “...As the band contrast and orientation maps of Figs. 6A-C illustrate...”</p>
Comment 44 / L. 472	“...as it a ...”	<p>Changed to:  “...as it is a ...”</p>
Comment 45 / L. 475	“...skeleton-forming mineral in...”	<p>Changed to:  “...skeleton-forming minerals in...”</p>
Comment 46 / L. 485	“...allowing molluscs preservation...”	<p>Changed to:  “...allowing mollusc preservation...”</p>
Comment 47/ L. 487-493	“...In this perspective, the laboratory-based hydrothermal alteration experiments performed here	The text has been changed according to the suggestions of the reviewer.

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	<p>offer very interesting insights into the fate of the aragonitic or bimineralic hard tissues that escape early dissolution during shallow burial and have the potential to enter the fossil record, a matter relatively neglected so far. In particular, the resistance of biogenic aragonite to replacement by calcite up to temperature of 175 °C during hydrothermal alteration offers an additional explanation for the preservation of aragonitic shells/skeletons, besides the taphonomic windows envisaged by Cherns et al. (2008). The results of our experiments neatly explain the observation that the mollusc fossil record is good and allows restoration of evolutionary patterns...”</p> <p>Somewhere around here, the authors should state that the change from aragonite to calcite does not always proceed in this way. For instance, there is also the possibility that total dissolution followed by precipitation by calcite (or other minerals, gypsum, pyrite) takes place.</p>	
<p>Comment 48 / L. 522-524</p>	<p>“...Between two tipping points, one between 50 and 60 °C, the other between 160 and 180 °C, aragonite appears to precipitate from supersaturated aqueous solutions rather than calcite, such that the hydrothermal treatments of aragonite within this temperature bracket do not yield calcite...”</p> <p>Please, state clearly that the recognition of the first tipping point (50 °C to 60 °C) is not derived from the present study.</p>	<p>The text has been changed accordingly.</p>



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Comment 49 / L. 598	<p>“...Dr. E. M. Harper, Prof. U. Brand...”</p> <p>Dr. E.M. Harper is also a coauthor; please remove</p>	<p>Request was removed.</p> <p>“..., Prof. U. Brand...”</p>
Comment 50 / L. 654	<p>“..., and Ramirez...”</p>	<p>Changed to:</p> <p>“...Ramírez...”</p>
Comment 51 / L. 657	<p>“...Ramirez-Rico, J., Gonzalez-Segura, and Sanchez-Navas...”</p>	<p>Changed to:</p> <p>“...Ramirez-Rico, J., González-Segura, and Sánchez-Navas...”</p>
Comment 52 / L. 666	<p>“...Choudens-Sanchez, V., and Gonzales, L. A...”</p>	<p>Changed to:</p> <p>“...Choudens-Sánchez, V., and Gonzáles, L. A...”</p>
Comment 53 / L. 670	<p>“...genera Glycymeris, Aequipecten and Arctica...”</p>	<p>Changed to:</p> <p>“...genera <i>Glycymeris</i>, <i>Aequipecten</i> and <i>Arctica</i>,...”</p>
Comment 54 / L. 677	<p>“...Perez-Huerta...”</p>	<p>Changed to:</p> <p>“...Pérez-Huerta...”</p>
Comment 55 / L. 718	<p>“...of bivalvemolluscs...”</p>	<p>Changed to:</p> <p>“...of bivalve molluscs...”</p>
Comment 56 / L. 775	<p>“...Arctica islandica...”</p>	<p>Changed to:</p> <p>“...<i>Arctica islandica</i>...”</p>
Comment 57 / L. 826	<p>“...Zetterstrom...”</p>	<p>Changed to:</p> <p>“...Zetterström...”</p>
Comment 58 / L. 1023-1024	<p>“...Readily observable are minute round holes within the mineral units (yellow arrows in B, C, D) that were filled in the pristine shell, prior to alteration, by biopolymer fibrils...”</p> <p>How do the authors know that the minute holes were filled with biopolymer fibrils. I do not think the statement can be drawn with the techniques used in this study. I will remove it.</p>	<p>“...For further details concerning the interlinkage between mineral units and nanoparticles with organic matrices, see Figs. A7 and A8....”</p>
<b>REVIEWER 4</b>		

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Comment 1	First paragraph of 'Abstract' may be moved to 'Introduction'.	We do not agree.
Comment 2 / L. 52	<p>"... Experimental conditions were between 100 °C and 175 °C..."</p> <p>I understand from the text that experimental conditions were at 100°C and 175°C, and not 'between' these temperatures.</p>	<p>Changed to:          "...Experimental conditions were between 100 °C and 175 °C with the main focus on 100 °C and 175 °C,..."</p>
Comment 3 / L. 58	<p>"... In all experiments below 175 °C there are no signs..."</p> <p>'...in all experiments below 175 °C. . .' This implies that the described observation occurs at, e.g., 174 °C. Be precise.</p>	<p>The text has been changed accordingly (see below):</p> <p>"... In all experiments up to 174 °C there are no signs of a replacement reaction of shell aragonite to calcite in X-ray diffraction bulk analysis. At 175 °C the replacement reaction started after a dormant time of 4 days ..."</p>
Comment 4 / L. 72	<p>"...The absence of aragonite replacement by calcite at temperatures lower than 175°C contributes to explain why aragonitic or bimineralic shells and skeletons have a good potential of preservation..."</p> <p>Again, this statement implies that 175 °C is a critical threshold temperature, while it is simply the temperature at which many of the experiments were run.</p>	<p>This finding has been explained in the text in great detail. The alteration temperature of 175 °C corresponds to temperatures that are present at shallow burial diagenesis.</p>
Comment 5 / L. 83	<p>"... They are widespread in the fossil record and are sensitive to changes in seawater composition -which they record with a limited vital effect (e.g. Brand et al., 2003; Parkinson et al., 2005; Schöne &amp; Surge, 2012; Brocas et al., 2013) ..."</p>	<p>We follow the suggestion of the reviewer and changed that sentence accordingly.</p> <p>"...They are widespread in the fossil record and are sensitive to changes in seawater composition (e.g. Brand et al., 2003; Parkinson et al., 2005; Schöne &amp; Surge, 2012; Brocas et al., 2013) ..."</p>

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	<p>'...limited vital effect. . .' This is certainly an over-simplification, as 'vital effects' depend on the complexity of the biomineralisation process of the organism, the element or isotope system considered; and can be negligible or significant.</p>	
<p>Comment 6 / L. 91-106</p>	<p>"... we performed laboratory-based alteration experiments with <i>Arctica islandica</i> shells with the aim to obtain time series data sets. The bivalve <i>A. islandica</i> has been studied in several scientific disciplines, i.e. biology (Morton, 2011; Oeschger and Storey, 1993; Taylor, 1976; Strahl et al., 2011), ecology (Beal and Kraus, 1989; Kilada et al., 2007; Lewis et al., 2001; Ridgway et al., 2012; Thórarinsdóttir and Einarsson, 1996), gerontology (Abele, 2002; Ridgway and Richardson, 2011; Strahl, 2007), pollution monitoring (Krause-Nehring et al., 2012; Palmer and Rand, 1977; Swaileh, 1996) and shellfisheries management (Adelaja et al., 1998; Harding et al., 2008; Thórarinsdóttir and Jacobson, 2005). <i>A. islandica</i> has also gained profound attention in paleoclimatology due to its long lifespan and its use as a high-resolution long-term archive (e. g. Schöne, 2004; Schöne, 2005a, 2005b; Wanamaker et al., 2008; Marchitto et al., 2000, Butler et al., 2009, Wanamaker et al., 2011, Karney et al., 2012 Schöne, 2013, Butler et al., 2013). On the long-term perspective, <i>A. islandica</i> plays an important role in palaeontology, not only as a Neogene palaeoecological and palaeoclimatic archive (e.g. Schöne, 2004; Schöne, 2005a, 2005b; Wanamaker et al., 2008; Marchitto et al., 2000, Butler et al., 2009, Wanamaker et al., 2011, Karney et al., 2012 Schöne, 2013, Butler et al., 2013, Crippa et</p>	<p>We shortened the text according to the suggestion of the reviewer.</p>

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	<p>al., 2016), but also as a biostratigraphic tool. Formerly considered a marker for the Pliocene-Pleistocene boundary (Raffi, 1986) in the Mediterranean region, its first appearance is now regarded as an indicator of the Gelasian-Calabrian (Early Pleistocene) boundary, around 1.7 Ma (Crippa &amp; Raineri, 2015). ...”</p> <p>Do we need to know that much about <i>A. islandica</i> in order to understand the significance of this paper, which is more concerned about general aspects of biological aragonite diagenesis? I suggest shortening this paragraph as it distracts from the main focus of the paper.</p>	
Comment 7 / L. 124	“ . . .natural or synthetic aragonite. . .“	<p>Changed to: “ . . .geological or synthetic aragonite. . .“</p>
Comment 8 / L. 128-130	<p>“... Metzger &amp; Banard (1968) and Perdikouri et al. (2011, 2013) investigated aragonite blocks or single crystals and report that temperatures IN EXCESS of 160-170 °C are required to transform the aragonite to calcite within a couple of days, whereas BELOW 160 °C aragonite remains present over many weeks. ...”</p> <p>edit capitalized words</p>	<p>Changed to: “... Metzger &amp; Banard (1968) and Perdikouri et al. (2011, 2013) investigated aragonite blocks or single crystals and report that temperatures <i>in excess</i> of 160-170 °C are required to transform the aragonite to calcite within a couple of days, whereas <i>below</i> 160 °C aragonite remains present over many weeks. ...”</p>
Comment 9 / L. 132-140	<p>“... During biomineralisation living organisms create local micro-environments for physiological generate of their composite hard tissues. After the death of the organism all tissues become altered by equilibration with the surrounding environment - part of the complex set of processes called diagenesis. Thus, as diagenetic alteration proceeds, the species-specific fingerprint of</p>	<p>We do not agree with the reviewer.</p>

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	<p>the biogenic structure disappears and is replaced by inorganic features. Despite the fact that the evolutionary line of <i>A. islandica</i> dates back to the Jurassic (Casey, 1952) only a limited number of studies have dealt with <i>A. islandica</i> specimens due to the thermodynamically unstable nature of their aragonitic shells....”</p> <p>These statements should be at the beginning of the ‘Introduction’.</p>	
Comment 10 / L. 199-200	No isotope data are reported in table 1.	All fluids were spiked with <sup>18</sup> O-depleted oxygen in order to trace fluid-solid exchange reactions and isotopic studies investigated by Ritter et al., 2016.
Comment 11 / L. 200	<p>“... All fluids for this were spiked with <sup>18</sup>O-depleted oxygen in order to trace fluid-solid exchange reactions....”</p> <p>Something wrong with this sentence; as no isotope data are reported or discussed, sentence could be omitted.</p>	See comment above
Comment 12 / L. 205	<p>“...oven at temperatures between 100 °C and 175 °C for different periods of time between one day and 84 days (see Table 2)...”</p> <p>According to table 2, samples were experimentally altered during 7, 28, and 84 days at temperatures of 100 or 175°C. Be precise.</p>	<p>Changed to:</p> <p>“...oven at temperatures between 100 °C and 175 °C for different periods of time ranging between one day and 84 days ( see Table 1, Fig. A11 and Table 2 for experiments focussing on 100 °C and 175 °C)...”</p>
Comment 13 / L. 232	“...Figures 1 to 5 show characteristic ultrastructural features of the shell of modern <i>A. islandica</i> . Images of the pristine shell are given in Figs. 1-3, while Figs. 4 and 5 present structural features of the hydrothermally...”	We changed the text accordingly.

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	It may be advisable to refer to inner and outer shell layers, consistent with the terminology in Fig. A1. 'Shell portion facing seawater' is somewhat misleading, as only the surface of the shell may be in contact with seawater, and is additionally protected by the periostracum (see Fig. A1).	
Comment 14 / L. 273-275	<p>"...Relative to neighbouring shell increments, the Sr content along the growth lines is always higher. Maximal concentrations (along annual growth lines) in pristine and altered shells vary between 0.4 and 0.6 wt% Sr (Figs. A3, A4, A5)...."</p> <p>No explanation is offered for the high Sr-concentrations along growth lines throughout the text. Is Sr part of the organic matrix, or the mineral aragonite?</p>	<p>"... Relative to neighbouring shell increments, the Sr content along the growth lines is always higher (Shirai et al., 2014)...."</p> <p>According to Shirai et al. (2014) Sr is contained in the mineral part of the shell.</p>
Comment 15 / L. 288	I suggest reporting the EBSD results in a separate section with its own subheading.	We do not agree with the reviewer, and need to present data from all methods together in one major results section.
Comment 16 / L. 315	<p>"...Using X-ray diffraction (XRD) we obtained an overview of the kinetics of the <i>A. islandica</i> biogenic aragonite to calcite transition ..."</p> <p>The observation of calcite formation is a very fundamental result that should be higher up in the 'Result' section, not at its end, hidden in the description of aragonite microfabrics.</p>	We do not agree with the reviewer, and need to present data from all methods together in one major results section.
Comment 17 / L. 368	"...reaction in our 100 °C treatments is related to inhibition of calcite nucleation (Sun et al., 2015), a mechanism that has rarely been rigorously explored..."	Possibly, this issue was not a major point of investigation in our study.

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	<p>Is there evidence that supersaturation was reached in the 100°C experiments? The experimental fluids should be initially undersaturated, no aragonite dissolution is reported from the experiments, and the data in Table 1 are not sufficient to estimate saturation states.</p>	
Comment 18 / L. 370	<p>“... At 175 °C the replacement reaction of biological aragonite to coarse-grained calcite occurs rapidly; it starts after a dormant period of about 4 days and proceeds rapidly almost to completion after 3 more days (Figs. A3, 13A)...”</p> <p>Fig. A3 shows alteration at 100°C, and not at 175°C.</p>	<p>Changed to:  “... At 175 °C the replacement reaction of biological aragonite to coarse-grained calcite occurs rapidly; it starts after a dormant period of about 4 days and proceeds rapidly almost to completion after 3 more days (Figs. A11, 8)...”</p>
Comment 19 / L. 375	<p><b>“...4.2 The time lag of aragonite to calcite replacement reaction at 175 °C... The several-day dormant.... critical size can form...”</b></p> <p>Only the first paragraph of this section is about the time lag of calcite replacement, while 4/5 of the section are about orientation of newly formed calcite crystals. The latter discussion is very important, and certainly deserves its own subheading.</p>	<p>We changed the title of the subparagraph 4.2.</p>
Comment 20 / L. 445	<p>“...We observed that the fluids used (artificial meteoric and/or burial fluids) cause only a minor difference in replacement reaction kinetics in our experiments, with the MgCl<sub>2</sub>-bearing artificial burial fluid reducing the nucleation rate of calcite, thus, leading to the observed significantly larger calcite crystals in the recrystallised product...”</p>	<p>We do not have any data on the partial pressure of CO<sub>2</sub>. Concerning the further comments of the reviewer, we slightly modified the discussion.</p>

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	<p>The pH of the solution and/or CO<sub>2</sub> partial pressure must be considered important, as they control the solubility of the original phase. Experiments of the current study were run with fluids with relatively high pH values and presumably very low pCO<sub>2</sub> (no data provided). This should be discussed when comparing the present result with older studies that observed more rapid reactions with low-pH solutions (lines 435-436).</p>	
<p>Comment 21 / L. 470-493</p>	<p><b>“...4.4. A paleontological perspective of our laboratory-based hydrothermal alteration experiments...”, complete part</b></p> <p>I disagree with many statements in this section. Aragonite dissolution is known from many near-surface environments and occurs essentially at surface temperatures, e.g. in the vadose environment. Factors other than temperature, e.g. pH of vadose fluids, anoxic diagenetic environments with sulfate reduction etc., have to be considered. Much has been written about a taphonomic bias related to shell mineralogy as well as about carbonate diagenesis, and these complex issues cannot be adequately addressed in such a short paragraph. It is not strictly relevant to the main topic addressed in this paper and I suggest omitting it.</p>	<p>The focus of this paragraph is to underscore the significance of the experiments for understanding the palaeontological record and not to discuss the factors that control aragonite dissolution, which, as the reviewer says represent, a very complex and debated subject. We think that it is very important to link the results of these experiments on extant bivalves to the possible fate of the main aragonite biomineralisers, which are vulnerable to early dissolution and yet can be found in the fossil record. This paragraph can raise the attention of palaeontologists and fill the gap, which is invariably present, between those who study recent taxa or recent processes and the researchers who study the fossil record, widening the audience of the readers of this paper and providing new ideas for future collaboration. So the message contained in this paragraph is different to what inferred by the reviewer. More than discussing aragonite dissolution, this paragraph seeks to offer an additional explanation for the preservation of aragonitic shells/skeletons and thus their rather complete fossil record. We have slightly changed the text to make our message clearer.</p> <p>We modified chapter 4.4 (see below and revised manuscript).</p> <p>The alteration experiments of recent <i>A. islandica</i> under controlled laboratory conditions are very important from a palaeontological perspective as they reproduce burial diagenetic conditions. The</p>



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understanding of the diagenetic processes which control organism hard tissue preservation in fact a fundamental prerequisite to taxonomic, taphonomic, palaeoecological, and biostratigraphic studies (e.g. Tucker, 1990). Most organisms have hard tissues composed of calcium carbonate, and its metastable form, aragonite, is one of the first biominerals produced at the Precambrian-Cambrian boundary (Runnegar & Bengtson, 1990), as well as one of the most widely used skeleton-forming minerals in the Phanerozoic record and today; in fact, aragonitic shells/skeletons are produced by hyolithids, cnidarians, algae, and by the widespread and diversified molluscs.

Several studies (Cherns & Wright, 2000; Wright et al., 2003; Wright & Cherns, 2004; James et al., 2005) have underscored that Phanerozoic marine faunas seem to be dominated by calcite-shelled taxa, the labile aragonitic or bimineralic groups being lost during early diagenesis (in the soft sediment, before lithification), potentially causing a serious taphonomic loss. Considering that most molluscs are aragonitic or bimineralic, this loss could be particularly detrimental both for palaeoecological and biostratigraphic studies. However, it has been shown that the mollusc fossil record is not so biased as expected (Harper, 1998; Cherns et al., 2008). This is due to high frequency taphonomic processes (early lithification/hardgrounds, storm plasters, anoxic bottoms, high sedimentation rates) that, throughout the control of organic matter content and residence time in the taphonomically active zone, produce taphonomic windows allowing mollusc preservation (James et al. 2005; Cherns et al., 2008). Even if the factors that control aragonite dissolution are multiple and their interpretation is complex.

The laboratory-based hydrothermal alteration experiments performed here offer very interesting insights into the fate of the aragonitic or bimineralic hard tissues that escape early dissolution during shallow burial and have the potential to enter the fossil record. In particular, the

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		resistance of biogenic aragonite to replacement by calcite up to temperature of 175 °C during hydrothermal alteration offers an additional explanation for the preservation of aragonitic shells/skeletons once they have escaped early dissolution. The results of our experiments neatly explain the observation that the mollusc fossil record is good and allows restoration of evolutionary patterns.
Comment 22 / L. 499	<p>“... and contains mineral units in the 1-5 µm size range, the inner shell layers (which are closer to the soft tissue of the animal) are characterised by a dense shell structure...”</p> <p>While it is correct that the inner shell layer is closer to the soft body of the bivalve, this is probably quite irrelevant for the observed differences in shell structure and porosity. Inner and outer shell layers are precipitated from the extrapallial fluid, i.e. at about the same distance from the tissue of the mantle margin where the shell is formed.</p>	<p>Changed to:            Next to the soft tissue of the animal → inner shell layer / portion            Next to the seawater → outer shell layer / portion / section</p>
Comment 23 / Table 1	Please clarify that all data (except Mg) are referring to fluids before the experiment. Did changes of any of the tabulated items occur during the experiment, or was this not analyzed?	All given values are valid for the fluids after the experiments as the stock fluids prior to the experiment were not analysed.
Comment 24	‘hydrothermal’: rephrase to ‘solution’, ‘diagenetic fluid’, or ‘experimental’ fluid. ‘Hydrothermal’ is not synonymous with ‘hot water’.	<p>Changed to:            “experimental fluid(s)”</p>
Comment 25	What about the importance of the organic matrix, its decay, and its role of providing pathways for fluids and in changing the chemistry of fluids? The time lag observed before nucleation of calcite crystals could be related to the time required for disintegration of the organic	The disintegration of the organic matrix is not mainly responsible for the time lag before nucleation of new calcite crystals, as the organic matrix disintegrates very quickly and well below 100 °C.

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	matrix, formation of local acidic conditions due to the addition of CO <sub>2</sub> from the inorganic breakdown of organic molecules, and the permeability created in the process.	
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