



1 **Experimental diagenesis: Insights into aragonite to calcite**  
2 **transformation of *Arctica islandica* shells by hydrothermal**  
3 **treatment**

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43 **Abstract.** Biomineralised hard parts form the most important physical fossil record of past environmental  
44 conditions. However, living organisms are not in thermodynamic equilibrium with their environment and create  
45 local chemical compartments within their bodies where physiologic processes such as biomineralisation take place.  
46 Generating their mineralized hard parts most marine invertebrates thus produce metastable aragonite rather than  
47 the stable polymorph of  $\text{CaCO}_3$ , calcite. After death of the organism, the physiological conditions which were  
48 present during biomineralisation are not sustained any further and the system moves toward inorganic equilibrium  
49 with the surrounding inorganic geological system. Thus, during diagenesis the original biogenic structure of  
50 aragonitic tissue disappears and is replaced by inorganic structural features.

51 In order to understand the diagenetic replacement of biogenic aragonite to non-biogenic calcite, we subjected  
52 *Arctica islandica* mollusc shells to hydrothermal alteration experiments. Experimental conditions were between  
53 100 °C and 175 °C with reaction durations between one and 84 days, and alteration fluids simulating meteoric and  
54 burial waters, respectively. Detailed microstructural and geochemical data were collected for samples altered at  
55 100 °C (and at 0.1 MPa pressure) for 28 days and for samples altered at 175 °C (and at 0.9 MPa pressure) for 7  
56 and 84 days, respectively. During hydrothermal alteration at 100 °C for 28 days, most but not all of the biopolymer  
57 matrix was destroyed, while shell aragonite and its characteristic microstructure was largely preserved. In all  
58 experiments below 175 °C there are no signs of a replacement reaction of shell aragonite to calcite in X-ray  
59 diffraction bulk analysis. At 175 °C the replacement reaction started after a dormant time of 4 days, and the original  
60 shell microstructure was almost completely overprinted by the aragonite to calcite replacement reaction after 10  
61 days. Newly formed calcite nucleated at locations which were in contact with the fluid, at the shell surface, in the  
62 open pore system, and along growth lines. In the experiments with fluids simulating meteoric water, calcite crystals  
63 reached sizes up to 200 micrometres, while in the experiments with Mg-containing fluids the calcite crystals  
64 reached sizes up to one mm after 7 days of alteration. Aragonite is metastable at all applied conditions. A small  
65 bulk thermodynamic driving force exists for the transition to calcite, which is augmented by stresses induced by  
66 organic matrix and interface energies related to the nanoparticulate architecture of the biogenic aragonite. We  
67 attribute the sluggish replacement reaction to the inhibition of calcite nucleation in the temperature window from  
68 ca. 50°C to ca. 170°C, or, additionally, to the presence of magnesium. Correspondingly, in  $\text{Mg}^{2+}$ -bearing solutions  
69 the newly formed calcite crystals are larger than in  $\text{Mg}^{2+}$ -free solutions. Overall, the aragonite-calcite transition  
70 occurs via an interface-coupled dissolution-precipitation mechanism, which preserves morphologies down to the  
71 sub-micrometre scale and induces porosity in the newly formed phase. The absence of aragonite replacement by  
72 calcite at temperatures lower than 175°C contributes to explain why aragonitic or bimineralic shells and skeletons  
73 have a good potential of preservation and a complete fossil record.

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76 **Key words.** Biominerals, hydrothermal alteration experiments, bivalves, aragonite, calcite, EBSD, EPMA element  
77 maps

78



## 79 1 Introduction

80 The skeletons of marine calcifiers are considered high resolution archives of proxies to understand the evolution  
81 of the Earth system. They are widespread in the fossil record and are sensitive to changes in seawater composition  
82 – which they record with a limited vital effect (e.g. Brand et al., 2003; Parkinson et al., 2005; Schöne & Surge,  
83 2012; Brocas et al., 2013). However, diagenetic alteration of fossil biogenic carbonates is a significant obstacle in  
84 understanding past climate dynamics (Grossmann et al., 1993; Richardson et al., 2001; Immenhauser et al., 2005;  
85 Korte et al., 2005). Despite more than a century of research on carbonate diagenesis, many of the controlling  
86 processes are still only understood in a qualitative manner (Brand and Veizer, 1980, 1981; Swart, 2015). One of  
87 the main problems is that diagenetically altered carbonates occur as the product of a complex alteration pathway  
88 with an unknown number of intermediate steps and controlling factors (Immenhauser et al., 2015; Swart, 2015;  
89 Ullmann and Korte, 2015). Motivated by the lack of quantitative data on rates and products of marine, meteoric,  
90 and burial diagenesis, we performed laboratory-based alteration experiments with *Arctica islandica* shells with the  
91 aim to obtain time series data sets. The bivalve *A. islandica* has been studied in several scientific disciplines, i.e.  
92 biology (Morton, 2011; Oeschger and Storey, 1993; Taylor, 1976; Strahl et al., 2011), ecology (Beal and Kraus,  
93 1989; Kilada et al., 2007; Lewis et al., 2001; Ridgway et al., 2012; Thórarinsdóttir and Einarsson, 1996),  
94 gerontology (Abele, 2002; Ridgway and Richardson, 2011; Strahl, 2007), pollution monitoring (Krause-Nehring  
95 et al., 2012; Palmer and Rand, 1977; Swaileh, 1996) and shellfisheries management (Adelaja et al., 1998; Harding  
96 et al., 2008; Thórarinsdóttir and Jacobson, 2005). *A. islandica* has also gained profound attention in  
97 paleoclimatology due to its long lifespan and its use as a high-resolution long-term archive (e. g. Schöne, 2004;  
98 Schöne, 2005a, 2005b; Wanamaker et al., 2008; Marchitto et al., 2000, Butler et al., 2009, Wanamaker et al., 2011,  
99 Karney et al., 2012 Schöne, 2013, Butler et al., 2013). On the long-term perspective, *A. islandica* plays an  
100 important role in palaeontology, not only as a Neogene palaeoecological and palaeoclimatic archive (e.g. Schöne,  
101 2004; Schöne, 2005a, 2005b; Wanamaker et al., 2008; Marchitto et al., 2000, Butler et al., 2009, Wanamaker et  
102 al., 2011, Karney et al., 2012 Schöne, 2013, Butler et al., 2013, Crippa et al., 2016), but also as a biostratigraphic  
103 tool. Formerly considered a marker for the Pliocene-Pleistocene boundary (Raffi, 1986) in the Mediterranean  
104 region, its first appearance is now regarded as an indicator of the Gelasian-Calabrian (Early Pleistocene) boundary,  
105 around 1.7 Ma (Crippa & Raineri, 2015). The potential of this species for palaeontology is strictly dependent on  
106 its preservation, thus, the dynamics of diagenetic shell alteration.

107 At ambient conditions calcite is the stable and, thus, the least soluble polymorphic phase of  $\text{CaCO}_3$  (Plummer &  
108 Mackenzie, 1974; Plummer & Busenberg, 1982, Sass et al., 1983, Walter & Morse, 1984; Bischoff et al., 1987,  
109 Redfern et al., 1989, Bischoff et al., 1993, Navrotsky, 2004; Morse & Lüttge, 2007; Gebauer et al., 2008, Gebauer  
110 & Cölfen, 2011, Radha & Navrotsky, 2013), while at higher pressures aragonite forms the stable Ca-carbonate  
111 polymorph (Redfern et al., 1989, Radha & Navrotsky, 2013). Accordingly, calcite crystallizes from aqueous  
112 solutions below ca. 50 °C (if no calcite-inhibitors are present). However, even in pure  $\text{Ca}^{2+}/\text{HCO}_3^-$  solutions, at  
113 temperatures above ca. 50 °C metastable aragonite rather than calcite is obtained (Kitano et al. 1962; Taft, 1967,  
114 Ogino et al. 1987). There is no sharp tipping point but rather a gradual change of fraction of the precipitating  
115 phases (Ogino et al., 1987, Balthasar and Cusack, 2015). Further, inhibitors of calcite nucleation and/or growth  
116 decrease the temperature of this regime shift in precipitation even further, where in marine and diagenetic



117 environments the most important inorganic inhibitor is  $Mg^{2+}$  (Kitano et al., 1972; Katz, 1973; Berner, 1975; Morse  
118 et al., 1997; Choudens-Sanchez, 2009; Radha et al. 2010, Balthasar and Cusack, 2015; Sun et al., 2015).

119 The replacement reaction of aragonite to calcite in aqueous systems was investigated by Metzger & Barnard  
120 (1968), Bischoff & Fyfe (1968), Bischoff (1969), Katz (1973), Kitano et al. (1972, Yoshioka et al. (1986), Oomori  
121 et al. (1987), and more recently by Perdikouri et al. (2011, 2013). It was recognized by Fyfe & Bischoff (1965)  
122 that the aragonite to calcite replacement reaction in aqueous environments occurs by dissolution and reprecipitation  
123 reactions. Except for Metzger & Banard (1968) and Perdikouri et al. (2011, 2013), most authors used powdered  
124 samples of natural or powdered synthetic aragonite. For these powdered samples, they claim a rapid replacement  
125 reaction of aragonite to calcite within hours or very few days at temperatures of ca. 100°C or above, depending on  
126 temperature and the Mg-content of the solution.

127 Metzger & Banard (1968) and Perdikouri et al. (2011, 2013) investigated aragonite blocks or single crystals and  
128 report that temperatures IN EXCESS of 160-170 °C are required to transform the aragonite to calcite within a  
129 couple of days, whereas BELOW 160 °C aragonite remains present over many weeks.

130 The present study describes first experimental data of the replacement reaction of BIOGENIC aragonite to non-  
131 biogenic calcite and investigates the kinetics of the replacement reaction of aragonite to calcite in shell material,  
132 geochemistry, nano- and microstructure alteration, and crystallographic texture variation. During  
133 biomineralisation living organisms create local micro-environments for physiological generate of their composite  
134 hard tissues. After the death of the organism all tissues become altered by equilibration with the surrounding  
135 environment - part of the complex set of processes called diagenesis. Thus, as diagenetic alteration proceeds, the  
136 species-specific fingerprint of the biogenic structure disappears and is replaced by inorganic features. Despite the  
137 fact that the evolutionary line of *A. islandica* dates back to the Jurassic (Casey, 1952) only a limited number of  
138 studies have dealt with pre-Neogene *A. islandica* specimens due to the thermodynamically unstable nature of their  
139 aragonitic shells. The aim of the present paper is to describe analysis-based detailed microstructural, geochemical,  
140 phase, and texture data observed in the experimental simulation of diagenesis by hydrothermal treatment of modern  
141 *A. islandica* shell samples. With this study we gain quantitative insight into processes that take place along  
142 pathways from early marine porewater diagenesis to the pervasive recrystallisation under burial conditions. The  
143 targets of the present study are the analysis of microstructural features, the preservation of the organic matrix in  
144 the shell, and the kinetics of the replacement reaction of aragonite to calcite as investigated by X-ray diffraction,  
145 SEM, and crystallographic microanalysis determined by Electron Backscatter Diffraction (EBSD).

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## 147 **2 Materials and Methods**

### 148 **2.1 Test materials**

149 For this study, shells of *A. islandica* were collected from the recent shell middens of a fishing company in northern  
150 Iceland and from Loch Etive waters in Scotland. On average, shells were between 8 and 10 cm in size and represent  
151 adult specimens. Major morphological features of the shell of *Arctica islandica* are displayed in Fig. A1, see also  
152 Schöne (2013).

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154 **2.2 Methods applied**

155 **2.2.1 Organic matrix preparation by selective etching**

156 To image the organic matrix in modern reference shells and hydrothermally altered shell samples as well as the  
157 mineral in reference, geologic, non-biological aragonite, shell or mineral pieces were mounted on 3 mm thick  
158 cylindrical aluminium rods using super glue. The samples were first cut using a Leica Ultracut ultramicrotome  
159 with glass knives to obtain plane surfaces within the material. The cut pieces were then polished with a diamond  
160 knife (Diatome) by stepwise removal of material in a series of 20 sections with successively decreasing thicknesses  
161 (90 nm, 70 nm, 40 nm, 20 nm, 10 nm and 5 nm, each step was repeated 15 times) as reported in Fabritius et al.  
162 (2005). The polished samples were etched for 180 seconds using 0.1 M HEPES (pH = 6.5) containing 2.5 %  
163 glutaraldehyde as a fixation solution. The etching procedure was followed by dehydration in 100 % isopropanol 3  
164 times for 10 seconds each, before the specimens were critical-point-dried in a BAL-TEC CPD 030 (Liechtenstein).  
165 The dried samples were rotary coated with 3 nm platinum and imaged using a Hitachi S5200 Field Emission-  
166 Secondary Electron Microscope (FE-SEM) at 4 kV.

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168 **2.2.2 Hard tissue characterization methods**

169 For FE-SEM and Electron Backscatter Diffraction (EBSD) analyses 5 x 5 mm thick pieces were cut out of the  
170 shell and embedded in epoxy resin. The surface of the embedded samples was subjected to several sequential  
171 mechanical grinding and polishing steps down to a grain size of 1  $\mu\text{m}$ . The final step was etch-polishing with  
172 colloidal alumina (particle size  $\sim 0.06 \mu\text{m}$ ) in a vibratory polisher. For EBSD analysis the samples were coated  
173 with 4-6 nm of carbon, and for SEM visualisation and EPMA analyses with 15 nm, respectively. EBSD  
174 measurements were carried out on JEOL JSM 6400 field emission SEM, equipped with a Nordlys EBSD detector.  
175 The SEM was operated at 20 kV and measurements were indexed with the CHANNEL 5 HKL software (Schmidt  
176 and Olesen, 1989; Randle and Engler, 2000). Information obtained from EBSD measurements is presented as band  
177 contrast images, and as colour-coded crystal orientation maps with corresponding pole figures.

178 The EBSD band contrast the signal strength of the EBSD-Kikuchi diffraction pattern and is displayed as a grey-  
179 scale component of EBSD scanning maps. The strength of the EBSD signal is high when a crystal is detected  
180 (bright), while it is weak or absent when a polymer such as organic matter is scanned (dark/black).

181 Co-orientation statistics are derived from pole figures obtained by EBSD scans and are given by the MUD  
182 (multiple of uniform (random) distribution) value. The MUD value is a measure of crystal co-orientation (texture  
183 sharpness) in the scanned area. A high MUD values indicate a high crystal co-orientation (in this study calcite),  
184 whereas low MUD values reflect a low to random co-orientation, respectively.

185 In order to trace the infiltration and percolation of fluids into and through the shells, pristine and hydrothermally  
186 altered shell samples were scanned with EPMA (Goetz et al., 2014). Chemical data were obtained by using a  
187 CAMECA SX100 EPMA system equipped with a  $\text{LaB}_6$  cathode. An accelerating voltage of 15 keV at a current of  
188 40 nA were used as operative settings. All elements were analysed with wavelength-dispersive X-ray  
189 spectrometers. The Sr-K $\alpha$ , Mg-K $\alpha$ , and Na-K $\alpha$  were measured on a TAP crystal. Ca-K $\alpha$ , and Ba-La were measured  
190 on a PET crystal, whereas K $\alpha$  emission lines of P, and Cl were measured on a LPET crystal. La emission lines of  
191 Mn, and Fe were detected with a LLIF crystal. A step size in the range of 1-2  $\mu\text{m}$  with a dwell time of 150 ms was



192 chosen for the element mappings. Celestine (Sr), dolomite (Ca, Mg), ilmenite (Mn), apatite (P), albite (Na),  
193 benitoite (Ba), vanadinite (Cl), and hematite (Fe), and were used as standard materials. Matrix correction was  
194 carried out using the PAP procedure (Pouchou and Pichoir, 1984).

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### 197 **2.2.3 Alteration experiments**

198 Hydrothermal alteration experiments mimicked burial diagenetic (and meteoric) alteration of recent *A. islandica*  
199 under controlled laboratory conditions. Chemical and isotopic compositions of experimental fluids are given in  
200 Table 1. All fluids for this were spiked with  $^{18}\text{O}$ -depleted oxygen in order to trace fluid-solid exchange reactions.

201

202 Pieces (2 x 1 cm) of recent *A. islandica* specimens were placed in a PTFE liner together with 25 mL of either the  
203 meteoric (10 mM NaCl aqueous solution) or burial fluid (100 mM NaCl + 10 mM  $\text{MgCl}_2$  aqueous solution) and  
204 sealed with a PTFE lid. Each of the PTFE liners was placed in a stainless steel autoclave, sealed and kept in the  
205 oven at temperatures between 100 °C and 175 °C for different periods of time between one day and 84 days (see  
206 Table 2). Obviously, this temperature regime is far beyond natural meteoric diagenetic environments but are typical  
207 for the burial realm. Nevertheless, elevated fluid temperatures were applied to meteoric experiments, too, as  
208 reaction rates under surface conditions are too slow for experimental approaches. After the selected time period,  
209 an autoclave was removed from the oven, cooled down to room temperature and then opened. The aqueous fluid  
210 that had passed through a 0.2  $\mu\text{m}$  cellulose acetate filter was subjected to further chemical and isotopic analyses.  
211 Recovered solids were dried at 40 °C overnight.

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### 214 **2.2.4 Chemical analysis of experimental fluids**

215 Aqueous fluid concentrations were measured before and after the experiment by Inductive-Coupled Plasma  
216 Optical Emission Spectrometry (ICP-OES) using a Perkin Elmer Optima ICP-OES 4300 at TU Graz (Austria)  
217 with an uncertainty of  $\pm 3\%$ . The total fluid alkalinities were determined by a Schott TitroLine alpha plus titrator  
218 with an uncertainty of  $\pm 2\%$ . The detection limit of this apparatus lies in the range of  $5 \times 10^{-6}$  M. The pH  
219 measurements were performed with a Schott BlueLine 28 combined electrode, calibrated with NIST standard  
220 buffers at pH of 4.01, 7.00, and 10.00 with an uncertainty of  $\pm 0.07$  units at room temperature.

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### 223 **2.2.5 X-ray diffraction analysis**

224 X-ray diffraction analysis of pristine and hydrothermally treated samples was performed with  $\text{Mo-K}\alpha_1$ -radiation  
225 in transmission geometry and with  $\text{Cu-K}\alpha_1$ -radiation in reflection geometry on a General Electric Inspection  
226 Technologies XRD3003 X-ray diffractometer with an incident-beam Ge111 focussing monochromator and a  
227 Meteor position-sensitive detector. The diffractograms were analysed by Rietveld analysis with the software  
228 package FULLPROF (Rodríguez-Caravajal, 2001) using the aragonite structure data of Jarosch & Heger (1986)  
229 and calcite structure data of Markgraf & Reeder (1985).



## 230 3 Results

### 231 3.1 The shell ultrastructure of modern *Arctica islandica*

232 Figures 1 to 5 show characteristic ultrastructural features of the shell of modern *A. islandica*. Images of the pristine  
233 shell are given in Figs. 1-3, while Figs. 4 and 5 present structural features of the hydrothermally altered shells. The  
234 valve of *A. islandica* is layered, with various shell parts showing different internal structural features (Fig. 1). The  
235 distribution patterns of porosity, pore sizes and the dimensions of basic aragonitic crystal units vary significantly  
236 along the cross-section of the shell. The shell portion facing seawater, indicated with yellow stars in Figs. 1A and  
237 1B, consists of aragonite crystal units in the 5  $\mu\text{m}$  size range (Fig. 2A). This shell portion is highly porous (Fig.  
238 1B) with pore diameters in the range of a few ( $< 5$ ) micrometres. The inner shell portion, i.e., the part very close  
239 to the soft tissue of the animal (indicated with white rectangles in Figs. 1A, 1C), is dense and is composed of very  
240 small aragonite crystallites with sizes of less than 1  $\mu\text{m}$  (Fig. 2B) and contains very few pores. The dimension of  
241 pores in this shell region is in the 1 to 2  $\mu\text{m}$  range. However, the innermost shell layer, the layer that is in contact  
242 with the mantle tissue of the animal (white stars in Figs. 1A, 1C) contains large (up to 12 micrometre diameter)  
243 and elongated pores that are oriented perpendicular to the rim of the shell (see white arrows in Fig. 1C). Growth  
244 lines are clearly visible in the cross-section through the shell (white arrows in Fig. 1A) as thin layers characterised  
245 by higher accumulations of organic material (this study and Richardson, 2001).

246 Figures 2, and 3 show, at increasing magnification, structural features of modern *A. islandica* shells that were made  
247 visible by slight etching of the mineral and simultaneous chemical fixation of the organic matrix. Structural  
248 characteristics of the reference material (non-biologic aragonite grown from solution), treated chemically in a  
249 similar way as the biogenic aragonite samples, are shown in the appendix, in Fig. A2. Fig. 2A shows features that  
250 are characteristic of the seawater-adjacent side of the shell, whereas Fig. 2B depicts internal characteristics of the  
251 tissue-adjacent side of the shell (the region marked by white rectangles in Fig. 1). Etching brings out the outlines  
252 of the aragonite grains, revealing the fabric of the biopolymer matrix within the hard tissue and its interlinkage  
253 with the mineral. The mineral units (crystals) in the outer shell layer are highly irregular in shape with dimensions  
254 in the 1-5  $\mu\text{m}$  range (Fig. 2A). In contrast, although the mineral units (crystals) in the dense layer of the shell also  
255 have irregular morphologies, they are of significantly smaller dimensions, mainly in the 1-2 micrometre range and  
256 below (Fig. 2B). The predominant fabric of the organic matrix in the shell of *A. islandica* is a network of  
257 intracrystalline fibrils (Fig. 3, yellow arrows in Figs. 3A, 3B) that interconnect the mineral units across the grain  
258 boundaries. However, organic membranes are occasionally also present and surround the mineral units (white  
259 arrows in Fig. 3A). Like all other biological carbonate hard tissues, at the finest scale, the shell of *A. islandica* is  
260 composed of nanoparticles that are a few tens of nanometres in diameter (white arrows in Fig. 3C). These are co-  
261 aligned to form mesocrystals - here in the 1-5  $\mu\text{m}$  size range.

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### 265 3.2 The ultra-, and microstructure of experimentally altered *A. islandica* shells

266 In order to trace fluid infiltration into and their percolation through the shell we performed major and minor  
267 element chemical analyses by EPMA. The distribution patterns of sodium, chlorine and strontium are shown as



268 characteristic examples (Figs. A3, A4, A5). Fluids enter the shell through pores and along growth lines, as  
269 demonstrated by the perfect correspondence between increased Na, Cl contents and the outlines of annual growth  
270 lines, indicated by elevated Sr contents (Fig. A3). These growth lines are readily detected by an increase in Sr  
271 contents in pristine (Figs. A3A) as well as in hydrothermally altered shell samples (Figs. A4, A5, see also Shirai  
272 et al. 2014). However, neither the temperature of hydrothermal alteration, nor the chemistry of the alteration fluid  
273 has an influence on the amount of Sr present along growth lines. Relative to neighbouring shell increments, the Sr  
274 content along the growth lines is always higher. Maximal concentrations (along annual growth lines) in pristine  
275 and altered shells vary between 0.4 and 0.6 wt% Sr (Figs. A3, A4, A5).

276 FE-SEM images of Figs. 4 and 5 highlight the grain structure and remnants of the organic matrix in hydrothermally  
277 altered *A. islandica* shells. In the case of the samples shown in Figs. 4 and 5, burial water was used as alteration  
278 solution; the hydrothermal treatment conditions were 100 °C for 28 days (Figs. 4A, 4B, 5A, 5B) and 175 °C for 7  
279 days (Figs. 4C, 4D, 5C, 5D), respectively. SEM images on the left hand side of Figs. 5 and 6 are taken from the  
280 shell section adjacent to seawater, while SEM images on the right hand side of Figs. 4 and 5 are taken from the  
281 dense layer of the shell very close to the soft tissue of the animal. Alteration at 100 °C for 28 days did not change  
282 the internal ultrastructure of the shell significantly. The shape and size of the mineral units are retained and they  
283 are still interconnected with a few organic fibres (Figs. 4A, 4B, 5B). However, at 175 °C for 7 days, the formerly  
284 present network of biopolymer fibres and membranes has vanished completely (Figs. 4C, 4D, 5C, 5D). At higher  
285 magnification a multitude of tiny holes (indicated with yellow arrows in Figs. 5C, 5D) become readily visible. In  
286 the unaltered shell these holes were filled with the network of biopolymer fibrils interconnecting the mineral units  
287 (e.g. Fig. 3B). The tiny holes in the mineral units start to become visible even in the samples altered at 100 °C  
288 (yellow arrows in Fig. 5B). Although at 175 °C shell aragonite has transformed to large calcite crystals (see  
289 following the description of results), etching still outlines a grain fabric on the size-scale of the former bioaragonite  
290 crystal units (Figs. 4C, D). The newly formed fabric resembles that of a fine-grained inorganic ceramic material.  
291 Aragonite crystal orientation patterns of modern *A. islandica* shells and those altered at 100 °C are presented in  
292 Figs. 6, A6, A7 with EBSD grey-scale band contrast images (upper images of Figs. 6A, 6B, 6C, A6), EBSD colour-  
293 coded orientation maps (lower images of Figs. 6A, 6B, 6C), and corresponding pole figures. Fig. 6E gives grain  
294 area information deduced from the EBSD measurements that are shown in Figs. 6A to 6C. Alteration occurred at  
295 100 °C, over a period of 28 days, and took place in meteoric (Fig. 6B) and burial fluid (Figs. 6C, A6), respectively.  
296 The microstructure and texture of pristine *A. islandica* shell material is shown in Fig. 6A. The crystallographic co-  
297 orientation in pristine and altered *A. islandica* shells is axial with the c-axes (setting  $a = 4.96 \text{ \AA}$ ,  $b = 7.97 \text{ \AA}$ ,  $c =$   
298  $5.74 \text{ \AA}$ , space group  $Pm\bar{c}n$ ) pointing approximately perpendicular to the growth lines. Co-orientation of the  
299 aragonite crystallites in the shell portion adjacent to seawater, even in the modern *A. islandica*, is very low with  
300 Multiple of Uniform Random Distribution (MUD) values of 12 (Fig. 6A) and 32 (Fig. A7A). Hydrothermal  
301 treatment of *A. islandica* at 100 °C does not produce a significant change in aragonite co-orientation pattern,  
302 texture, grain fabrics, and grain size distributions. The pristine and the hydrothermally treated shell materials  
303 appear to be quite similar. The small changes in MUD values must be attributed to fact that it was impossible to  
304 locate the EBSD scan fields on the different samples in exactly corresponding spots with respect to the outer shell  
305 margin and to the patterns of growth lines. The shell is not uniformly textured. In particular, the slight preferred  
306 crystallographic orientation of the a\*-axes (the (100) plane normal) in Fig. 6C is a singular case, while c-axis



307 preferred orientation is otherwise dominant (Fig. 6C). Figs. 7, A6B, A6C show microstructure and texture  
308 characteristics deeper within the shell (Figs. 7A, A6, A7) and at the innermost margins next to the soft tissue of  
309 the animal (Figs. 7C, 7D; alteration in meteoric fluid: Figs. 7A to 7D; alteration in burial fluid: Figs. 7E, 7F). In  
310 the EBSD band contrast map of Fig. 7A we clearly see the change in microstructure from the distal (seawater  
311 adjacent) shell layer with the larger aragonite crystals (yellow star in Fig. 7A) to the inward shell portion where  
312 aragonite crystals become small to minute (white star in Figs. 7A, A6B, A6C). As the pole figures and MUD  
313 values demonstrate, the axial c- and a-axes co-orientation increases gradually towards the inner shell layer (the  
314 layer close to the soft tissue of the animal) where MUD values of almost 100 are reached (Figs. 7D, 7F, A6, A7).  
315 Using X-ray diffraction (XRD) we obtained an overview of the kinetics of the *A. islandica* biogenic aragonite to  
316 calcite transition under hydrothermal conditions up to 175 °C in artificial burial solution (Figs. 8A, 8B, A8). A  
317 representative Rietveld-plot of the analysis of the XRD data obtained for the six days alteration is given in Fig.  
318 A9. As Fig. A6 demonstrates, experiments below 175 °C show no signs of a replacement reaction of bioaragonite  
319 to calcite in the XRD bulk measurements. At 175 °C in burial solution, calcite formation starts after a passive  
320 period of about 4 days (Figs. 8A, 8B A8) and then proceeds rapidly. After 7 days only a few patches of aragonite  
321 in the dense shell layer are not yet completely transformed to calcite (as seen in the EBSD investigations, unaltered  
322 shell portions are indicated with white rectangles in Fig. 1A). After 8 days the transition to calcite is complete.

323

324 EBSD data clearly show that after a hydrothermal treatment at 175 °C, with either, meteoric or burial fluid, shell  
325 aragonite is transformed to calcite (Figs. 9, 10 and 11). In the outer shell layer the replacement reaction to calcite  
326 is complete with the development of large crystal grains, some reaching sizes of hundreds of micrometres (see  
327 EBSD maps in Figs. 9 and 10). In contrast, dense shell regions devoid of pores still retain patches of the original  
328 aragonitic microstructure and texture (coloured EBSD maps in Figs. 11A, 11B). The MUD values for the newly  
329 formed calcite material are high (Figs. 9, 10), but this is related to the fact that within the range of the EBSD scan  
330 just a small number of large, newly formed, individual crystals is encountered. Figure 11 shows shell regions  
331 where patches of aragonite have survived which contain first-formed calcite. Calcite nucleation sites are the  
332 locations where the hydrothermal fluid has access to the shell: at its outer and inner surfaces (yellow stars in Fig.  
333 11B) and at growth lines (yellow arrows in Fig. 11A). Fig. 11A demonstrates how calcite crystals form strings  
334 along linear features, which correspond to growth lines in the pristine shell material.

335

336

#### 337 4 Discussion

338 In sedimentary environments replacement reaction of metastable biogenic aragonite and high-Mg calcite to  
339 inorganic low Mg-calcite occurs mainly through the following processes: (1) shell dissolution followed by  
340 subsequent low Mg-calcite formation and/or (2) micro- to nanoscale recrystallization to low Mg-calcite with  
341 preservation of some specific boundaries such as prisms, tablets and fibres in bivalves (Swart, 2015). The  
342 replacement reaction from metastable carbonate phases to a stable low-Mg calcite phase is driven by the difference  
343 in solubility (free energy) between aragonite and calcite (Plummer & Busenberg, 1982). Thus, as the replacement



344 reaction proceeds, the percolating diagenetic pore fluid is undersaturated with respect to aragonite but is saturated  
345 with respect to calcite. However, the replacement reaction first requires a nucleation step, the formation of the first  
346 calcite crystallites larger than the critical size (Morse & Lüttge, 2007), where the bulk energy gained by further  
347 growth exceeds adverse energy contributions such as increasing interface energies and strain energies arising from  
348 increasing the size of the calcite crystals.

349

350

#### 351 **4.1 Characteristics of the grains obtained by reaction at 100 °C and 175 °C**

352 Our laboratory-based hydrothermal alteration experiments were carried out at 100 °C in both meteoric and burial  
353 fluids. At 100 °C, both, the aragonite mineral as well as the characteristic biological microstructure, survive the  
354 hydrothermal treatment up to at least 28 days. This is consistent with the findings of Ritter et al. (2016) who  
355 analysed the light stable isotope signatures ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ) of our hydrothermally treated samples. In the 100 °C  
356 alteration experiments using isotope-doped hydrothermal fluids, Ritter et al. (2016) found that the carbon and  
357 oxygen isotope ratios of the treated shells are within the same range as those measured in the pristine samples.  
358 Furthermore, no obvious patterns emerge from the comparison of sub-samples exposed to seawater, meteoric, and  
359 burial fluids. Most of the extensive literature on aragonite precipitation from aqueous solutions and aragonite-  
360 calcite replacement reactions in aqueous environments, as reviewed in the introduction, makes clear that both  
361 temperatures around the boiling point of water and the presence of  $\text{Mg}^{2+}$  inhibit calcite nucleation. Thus, the  
362 inhibition of calcite nucleation favours the growth of aragonite if the solution is supersaturated with respect to the  
363 Ca-carbonate phases. If supersaturation is exceedingly high and rapidly generated, vaterite or even amorphous  
364 calcium carbonate will precipitate and reduce the supersaturation below the levels required for aragonite or calcite  
365 nucleation (Gebauer et al., 2008, 2012; Navrotsky, 2004; Radha et al., 2010). However, it is unlikely that these  
366 levels of supersaturation are reached in our case, as aragonite is already present. We, thus, conclude that the  
367 absence of aragonite to calcite replacement reaction in our 100 °C treatments is related to inhibition of calcite  
368 nucleation (Sun et al., 2015), a mechanism that has rarely been rigorously explored.

369 At 175 °C the replacement reaction of biological aragonite to coarse-grained calcite occurs rapidly; it starts after  
370 a dormant period of about 4 days and proceeds rapidly almost to completion after 3 more days (Figs. A3, 13A).  
371 Calcite nucleation occurs (and replacement reaction proceeds) where the hydrothermal fluid is in contact with the  
372 bio-aragonite: at the surfaces of the shell, in pores and along growth lines (Figs. 7, 8, 9).

373

374

#### 375 **4.2 The time lag of aragonite to calcite replacement reaction at 175 °C**

376 The several-day dormant period followed by the rapid growth of calcite indicates that the nucleation of calcite is  
377 inhibited, at least initially. Inhibition of calcite nucleation occurs by the presence of magnesium in the solution  
378 and/or by temperatures between 70 °C and 160 °C even without Mg (Kitano et al., 1962; Taft, 1967; Kitano et al.,  
379 1972; Katz, 1973; Berner, 1975; Morse et al., 1997; Choudens-Sanchez, 2009; Radha et al. 2010, Balthasar &  
380 Cusack, 2015; Sun et al., 2015). A possible scenario explaining the dormant period could be that, despite inhibition,  
381 there is still a small, but non-zero nucleation rate of calcite, which permits the formation of individual nuclei after  
382 4 days, which then grow rapidly. Another, perhaps more likely scenario is the initial, rapid formation of a



383 passivation layer on the surface of the aragonite or on the surface of any calcite nuclei; the dormant period is then  
384 the time that is needed to dissolve this passivation layer, at least in some places, where subsequently calcite nuclei  
385 of critical size can form.

386 In meteoric solutions the grain size of the newly formed calcite reaches 200 micrometres (e.g. Figs. 9C) while in  
387 the Mg-bearing burial solution newly formed calcite crystals reach sizes in the 1 mm range, in both, the 7- and 84-  
388 day treatments (e.g. Figs. 10B, 10C). The large grains exceeding 200 micrometres suggest an Ostwald-ripening or  
389 strain-driven grain growth. The latter is potentially due to the 8.44 % volume increase when the denser aragonite  
390 transforms to calcite. The determination of *local misorientation* from an EBSD data set gives small orientation  
391 changes and visualizes regions of deformation of the crystal structure, thus, the local misorientation parameter is  
392 an indication of internal strain or stress in the material. Figure 12 depicts the distribution pattern of local  
393 misorientation within five selected EBSD maps (Fig. 12B, 12E, 12H, 12K, 12N). Legends accompany all local  
394 misorientation maps (Figs. 12C, 12F, 12I, 12L, 12O). A high degree of internal strain is indicated by blue colours,  
395 while light green to yellow colours highlight shell portions where local misorientation is low. Grains in Fig. 12 are  
396 defined by a *critical misorientation* value set at 5° (i.e. tilts smaller than 5° are counted as mosaic block  
397 boundaries), thus, a tilt of five degrees has to be present for the distinction between two adjacent grains rather than  
398 a single grain with small angle grain boundaries < 5° misorientation. For the better visualization of individual  
399 grains we outlined these with white lines and show them in random colours (Figs. 12A, 12D, 12G, 12J, 12M). As  
400 it is well visible from the white 'dots' in Figs. 12A, 12D, 12G, 12J, 12M, all calcite grains contain numerous small  
401 calcite crystallites, a clear cause for the occurrence of internal strains. In all five investigated data sets local  
402 misorientation goes up to 2 degrees, thus, neither alteration time, nor the chemical composition of the used  
403 alteration solution exerts a major impact to the degree of strain accumulation within the EBSD maps (and grains).  
404 Figure 13 shows in color-coded maps the pattern of strain/stress accumulation distribution in two large calcite  
405 grains that grew at 175 °C in Mg-bearing burial solution. Corresponding legends are given below the grains. In  
406 the case of the grain shown in Fig. 13A, obtained at an alteration that lasted for 7 days, (see also Figs. 12J and  
407 12K, the white star in 12K indicates the location of the grain within the map) some portions of the crystal are  
408 strain/stress-free (portions with the blue to dark green colours in the map shown in 13A). In contrast, the grain  
409 marked by a yellow star in Figure 13C (and Figs. 12M and 12N), shows high stress/strain accumulations  
410 everywhere within the grain and no strain/stress-free regions. We find that the local misorientations are mainly  
411 curvilinear structures in the cross section (white arrows in Figs. 13A, 13B) and correspond to subgrain boundaries  
412 within the newly formed calcite crystals. These boundaries do not appear to heal or to disappear with an increased  
413 alteration time, an indication again of the little effect of alteration duration on the fabric and internal structure of  
414 calcite grains crystallized from *Arctica islandica* shell bioaragonite.

415 To investigate grain growth patterns further, we took a statistical approach based on the EBSD measurements  
416 shown in Figs. 9 and 10 (alterations experiments carried out for 7 and 84 days at 175°C in meteoric and burial  
417 solution, respectively). Figs. 14A and 14B show the statistics of grain area (we define a grain by a critical  
418 misorientation of 5 °) versus degree of *mean* misorientation within a grain. On the basis of our measurements and  
419 observations, we do not see major evidence for a specific calcite grain growth phenomenon with an increase in  
420 alteration time, as we expected for the 7 and 84 days alteration series. However, we find that experiments  
421 conducted with the Mg-containing burial solution yield larger calcite crystals (black arrows in Fig. 14B) in



422 comparison to the size of the grains obtained from experiments carried out with meteoric water (Fig. 14A). Grains  
423 obtained from alteration experiments with meteoric fluid show a significantly higher degree of mean  
424 misorientation (up to 10 degrees, black arrows in Fig. 14A), compared to that in grains that grew in burial solution.  
425 We attribute this to the nucleation rate: the crystals growing from each nucleus consume the aragonite educt (the  
426 precursor, original aragonite) until they abutted each other. Thus, larger crystals in the experiment with burial  
427 solution result from a smaller number of calcite nuclei. Again, this supports the idea that  $Mg^{2+}$  inhibits calcite  
428 nucleation.

429

430

#### 431 **4.3 The calcite to aragonite replacement reaction kinetics**

432 Inorganic experiments on aragonite to calcite transition at 108 °C in hydrothermal conditions were reported by  
433 Bischoff & Fyfe (1968) and by Bischoff (1969). These authors used fine-grained powders as educts (the precursor,  
434 original material) and observed a comparatively rapid transition to calcite that was complete within 48 hours,  
435 depending on the composition of the fluid. For example, larger  $CO_2$  partial pressure (leading to lower pH and thus  
436 larger solubility of the carbonates) accelerated, while the presence of Mg-ions retarded the process. This rapid  
437 reaction kinetics as reported by Bischoff & Fyfe (1968) and by Bischoff (1969) is discrepant to our observations.  
438 We do not see a replacement reaction of the biogenic aragonite to calcite at 100 °C even within 28 days.  
439 Hydrothermal experiments by Metzger & Barnard (1968) and by Perdikouri and co-workers (2011, 2013),  
440 however, who used aragonite single crystals in their experiments, report reaction kinetics which correspond to our  
441 observations. They do not observe any evidence of the replacement reaction at 160 °C even within 1 month, but a  
442 partial replacement of their aragonite crystals by calcite within 4 weeks at 180 °C. Setting kinetic control aside, it  
443 appears that aragonite loses its metastability between 160 °C and 180 °C, just like the tipping point between 50 to  
444 60 °C (Kitano et al. 1962, Balthasar & Cusack, 2015) above which aragonite precipitates from a solution rather  
445 than the stable calcite phase. We observed that the fluids used (artificial meteoric and/or burial fluids) cause only  
446 a minor difference in replacement reaction kinetics in our experiments, with the  $MgCl_2$ -bearing artificial burial  
447 fluid reducing the nucleation rate of calcite, thus, leading to the observed significantly larger calcite crystals in the  
448 recrystallised product. As compared to the work of Perdikouri et al. (2011, 2013) on aragonite single crystals,  
449 shell-aragonite does not crack during the replacement of the aragonite by calcite. The reason for this difference  
450 may be ascribed to the porosity of the bioaragonite which results from the loss of its organic component. Figs. 5C  
451 - D and 6C - D illustrate that the (newly formed) calcite product reveals an internal structure that is very reminiscent  
452 of the original bioaragonite/biopolymer composite. The structure arises as the solution penetrates along former  
453 sites of organic matrix (former aragonite grain boundaries), such that the structural features obtained after  
454 alteration still outline the former aragonite grains. Thus, limited grain size of the bioaragonite together with the  
455 formerly biopolymer-filled spaces reduce any stresses that may be built up by the specific volume change of the  
456  $CaCO_3$  during the replacement reaction. The replacement process preserves original morphological features.  
457 Several studies (Putnis & Putnis, 2007, Xia et al., 2009, Putnis and Austrheim, 2010, Kasiotas et al., 2010, Pollok  
458 et al., 2011) experimentally investigated mineral replacement reactions creating pseudomorphs, even reproducing  
459 exquisite structures such as the cuttlebone of *Sepia officinalis*. These studies conclude that the essential factor in



460 producing pseudomorphs is the dissolution of the replaced parent material as the rate-limiting step, while the  
461 precipitation of the product phase and the transport of solution to the interface must be comparatively fast. The  
462 preservation of morphology - even as observed on the nano- to microscale - is ensured if nucleation and growth of  
463 the product immediately take place at the surface of the replaced material when the interfacial fluid film between  
464 the dissolving and the precipitating phase becomes supersaturated in the product after dissolution of the educt: an  
465 interface-coupled dissolution-precipitation mechanism (Putnis & Putnis, 2007). If dissolution of the educt is fast  
466 and precipitation of product is slow, more material is dissolved than precipitated, and the solutes can be transported  
467 elsewhere. This would create not only an increased pore space which potentially collapses under pressure, but the  
468 dissolved material would eventually precipitate elsewhere with its own characteristic (inorganic) morphology.

469

#### 470 **4.4. A paleontological perspective of our laboratory-based hydrothermal alteration experiments**

471 The understanding of the diagenetic processes which control organism hard tissue preservation is very important  
472 in palaeontology as it a prerequisite to taxonomic, taphonomic, palaeoecological, and biostratigraphic studies (e.g.  
473 Tucker, 1990). Most organisms have hard tissues composed of calcium carbonate, and its metastable form,  
474 aragonite, is one of the first biominerals produced at the Precambrian-Cambrian boundary (Runnegar & Bengtson,  
475 1990), as well as one of the most widely used skeleton-forming mineral in the Phanerozoic record and today; in  
476 fact, aragonitic shells/skeletons are characteristic of hyolithids, cnidarians, algae, and the widespread and  
477 diversified molluscs.

478 Several studies (Cherns & Wright, 2000; Wright et al., 2003; Wright & Cherns, 2004; James et al., 2005) have  
479 underscored that Phanerozoic marine faunas seem to be dominated by calcite-shelled taxa, the aragonitic or  
480 bimineralic groups being lost during early diagenesis (in the soft sediment, before lithification), potentially causing  
481 a serious taphonomic loss. Considering that most molluscs are aragonitic or bimineralic, this loss could be  
482 particularly detrimental both for palaeoecological and biostratigraphic studies. However, it has been shown that  
483 the mollusc fossil record is not so biased as expected (Harper, 1998; Cherns et al., 2008). This is due to high  
484 frequency taphonomic processes (early lithification/hardgrounds, storm plasters, anoxic bottoms, high  
485 sedimentation rates) that produce taphonomic windows allowing molluscs preservation (James et al. 2005; Cherns  
486 et al., 2008).

487 In this perspective, the laboratory-based hydrothermal alteration experiments performed here offer very interesting  
488 insights into the fate of the aragonitic or bimineralic hard tissues that escape early dissolution during shallow burial  
489 and have the potential to enter the fossil record, a matter relatively neglected so far. In particular, the resistance of  
490 biogenic aragonite to replacement by calcite up to temperature of 175 °C during hydrothermal alteration offers an  
491 additional explanation for the preservation of aragonitic shells/skeletons, besides the taphonomic windows  
492 envisaged by Cherns et al. (2008). The results of our experiments neatly explain the observation that the mollusc  
493 fossil record is good and allows restoration of evolutionary patterns.

494

495

496 **5 Conclusions**

- 497 1. Aragonite crystallite size, porosity, and pore size varies across the cross-section of the valve of modern *Arctica*  
498 *islandica*. While the outer shell layer is highly porous, with pore sizes in the range of a few micrometres, and  
499 contains mineral units in the 1-5  $\mu\text{m}$  size range, the inner shell layers (which are closer to the soft tissue of the  
500 animal) are characterised by a dense shell structure with small (1  $\mu\text{m}$ ) mineral units and a very low porosity.  
501 The innermost section of the shell is penetrated by elongated pores oriented perpendicular to the shell inner  
502 surface. At annual growth lines Sr contents are always high, relative to shell increments between the growth  
503 lines in both pristine and experimentally altered shell samples. The chemistry of the alteration fluid and the  
504 duration of the alteration experiment do not exert a major effect on the concentration of Sr along the growth  
505 lines.
- 506 2. During hydrothermal alteration at 100 °C for 28 days, most but not all of the biopolymer matrix is destroyed,  
507 while shell aragonite and its microstructure are largely preserved.
- 508 3. During hydrothermal alteration at 175 °C for 7 days or more, the biopolymer shell fraction is destroyed, such  
509 that pathways for fluid penetration are created. At this temperature shell aragonite is almost completely  
510 transformed to calcite.
- 511 4. When meteoric solution is used for alteration, newly formed calcite crystal units reach sizes up to 200  
512 micrometres, while alteration in burial solution induces the formation of calcite crystals that grow up to 1 mm  
513 in 7 days. We attribute the latter, larger grains to the Mg-content of the burial solution, which inhibits calcite  
514 nucleation. The formation of fewer nuclei leads to the growth of larger calcite crystals.
- 515 5. Geochemical results show that calcite nucleates and replacement reaction proceeds where the hydrothermal  
516 fluid is in contact with the aragonite: at the two shell surfaces, in pores, and at growth lines, which are thin,  
517 formerly organic-filled layers.
- 518 6. The replacement reaction of bioaragonite to calcite does not proceed at temperatures much lower than 175 °C.  
519 At 175 °C we observe a dormant time of about 4 days during which no XRD-detectable calcite is formed. The  
520 replacement reaction then proceeds within 2-3 days to virtually complete replacement reaction, with small  
521 amounts of aragonite still prevailing in the dense, proximal layer of the shell.
- 522 7. Between two tipping points, one between 50 and 60 °C, the other between 160 and 180 °C, aragonite appears  
523 to precipitate from supersaturated aqueous solutions rather than calcite, such that the hydrothermal treatments  
524 of aragonite within this temperature bracket do not yield calcite.
- 525 8. The absence of aragonite replacement by calcite at temperatures lower than 175°C contributes to explain why  
526 aragonitic or bimineralic shells and skeletons have a good potential of preservation and a complete fossil  
527 record.

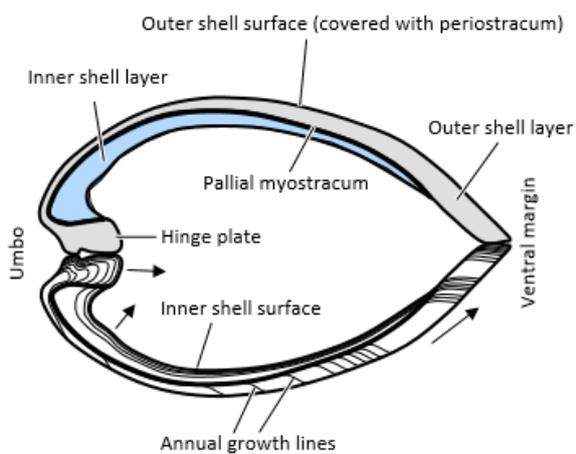
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531 6 Appendix A



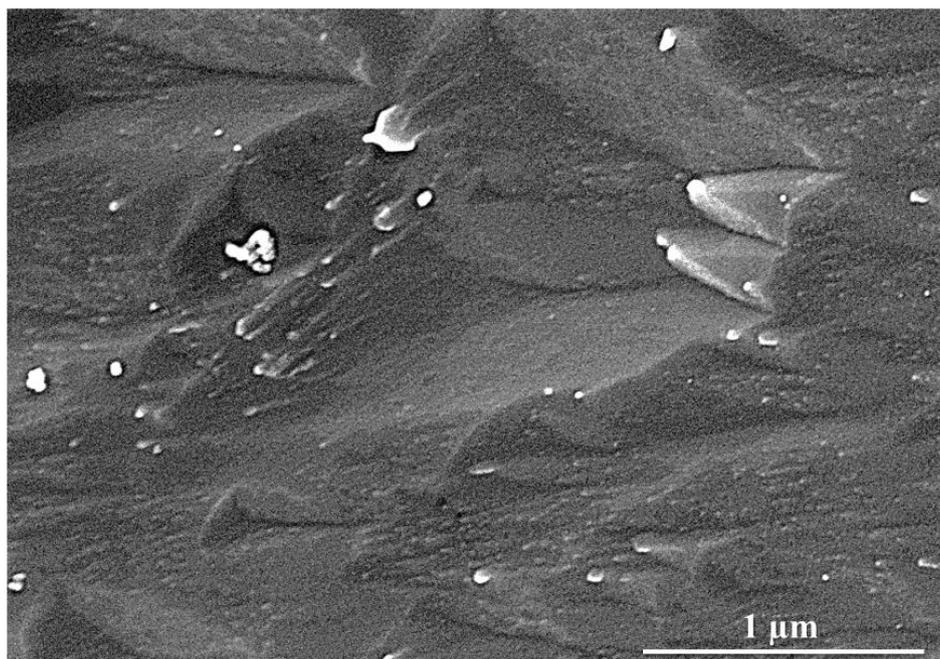
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533 **Appendix Fig. A1.** Morphological characteristics of the shell of the bivalve *Arctica islandica*. A detailed  
534 description is given in Schöne (2013).

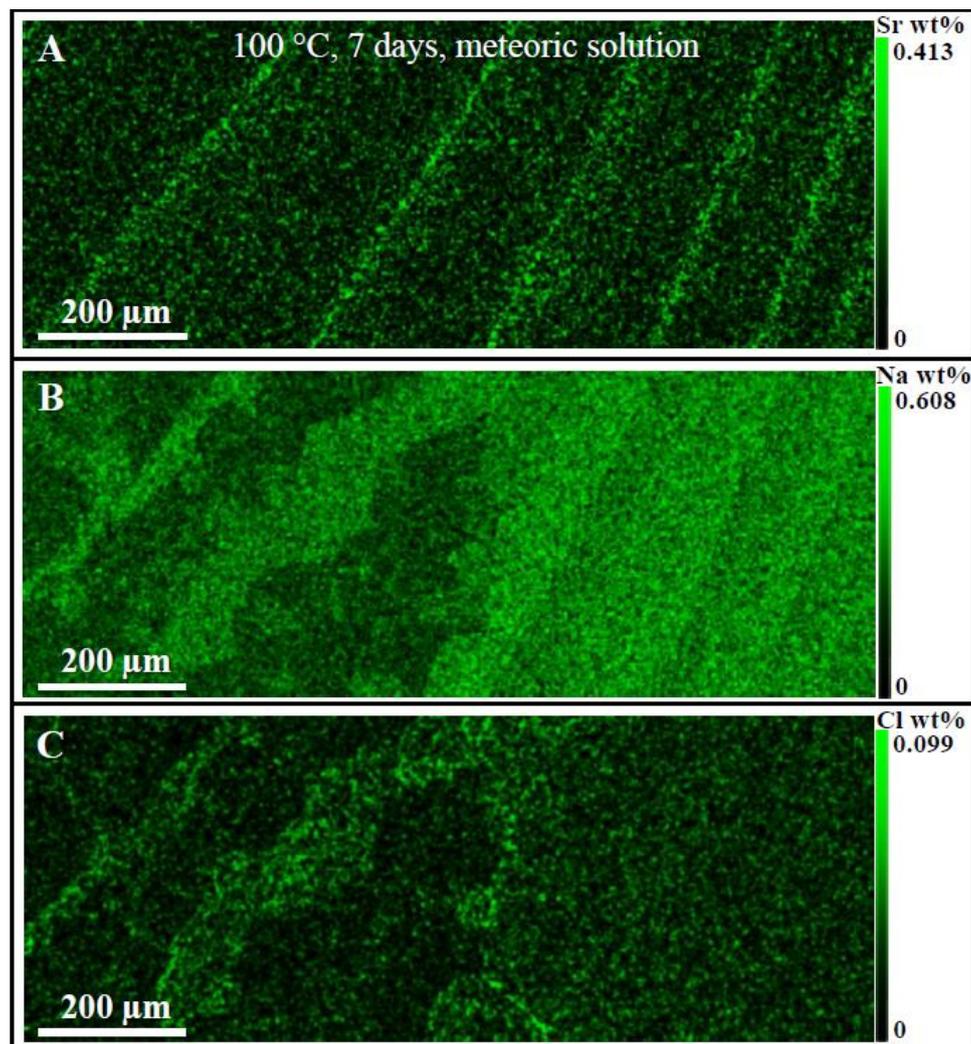
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539 **Appendix Fig. A2.** FE-SEM image of microtome cut, polished, etched and critical-point-dried surface of non-  
540 biologic aragonite grown from solution.  
541  
542



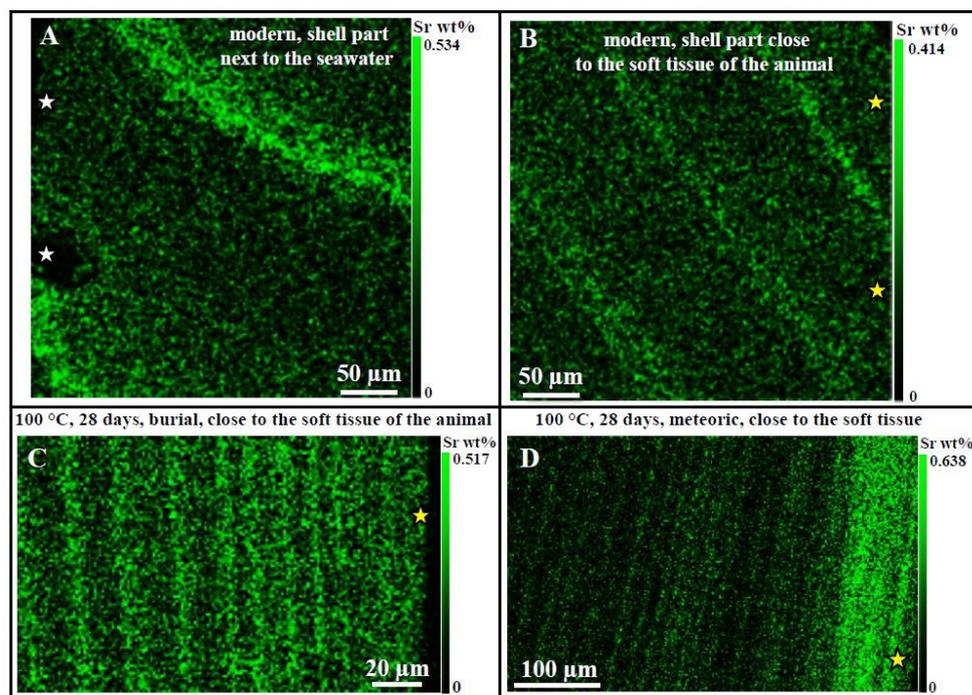
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544 **Appendix Fig. A3.** Sr<sup>2+</sup>, Na<sup>+</sup>, and Cl<sup>-</sup> concentrations along annual growth lines in a hydrothermally altered shell545 portion of *Arctica islandica*. The alteration fluid is NaCl-rich, i. e., simulating meteoric waters. The degree of fluid546 infiltration into and through the shell is well traceable with Na<sup>+</sup> and Cl<sup>-</sup> concentrations. Infiltration occurs, in

547 addition through pores, along growth lines that act as conduits for fluid circulation.

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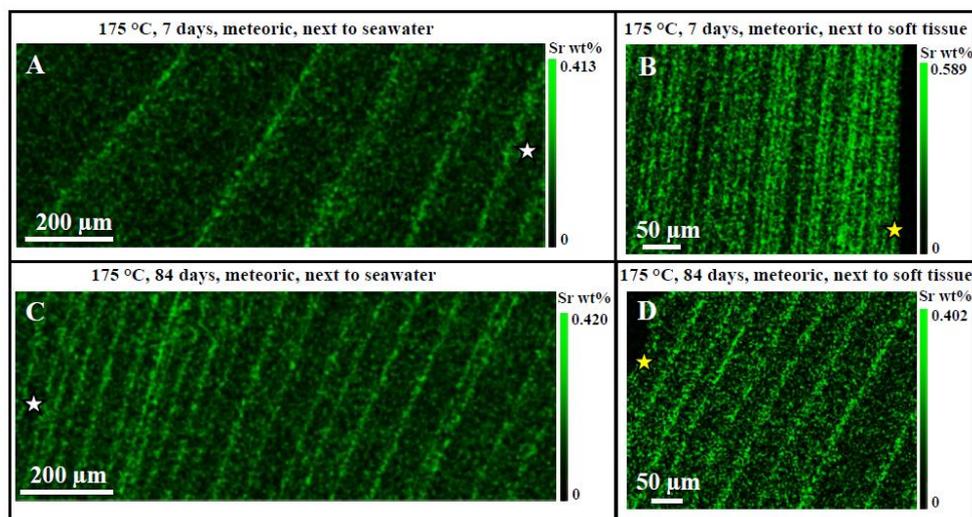


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551 **Appendix Fig. A4.**  $\text{Sr}^{2+}$  concentrations along annual growth lines in pristine (A, B) and hydrothermally altered  
 552 (C, D) *Arctica islandica* shell portions. White stars indicate shell regions next or close to seawater, while yellow  
 553 stars point to the shell parts that are next or close to the soft tissue of the animal. Fluids enter the shell at its two  
 554 surfaces (see enrichment in  $\text{Sr}^{2+}$  in Fig. 8D) and, especially along growth lines. Neither the degree of hydrothermal  
 555 alteration, nor the chemistry of the alteration fluid changes significantly the  $\text{Sr}^{2+}$  contents along the growth lines.  
 556 Maximal values for both, pristine and altered samples, range between 0.4 and 0.6 wt% Sr.

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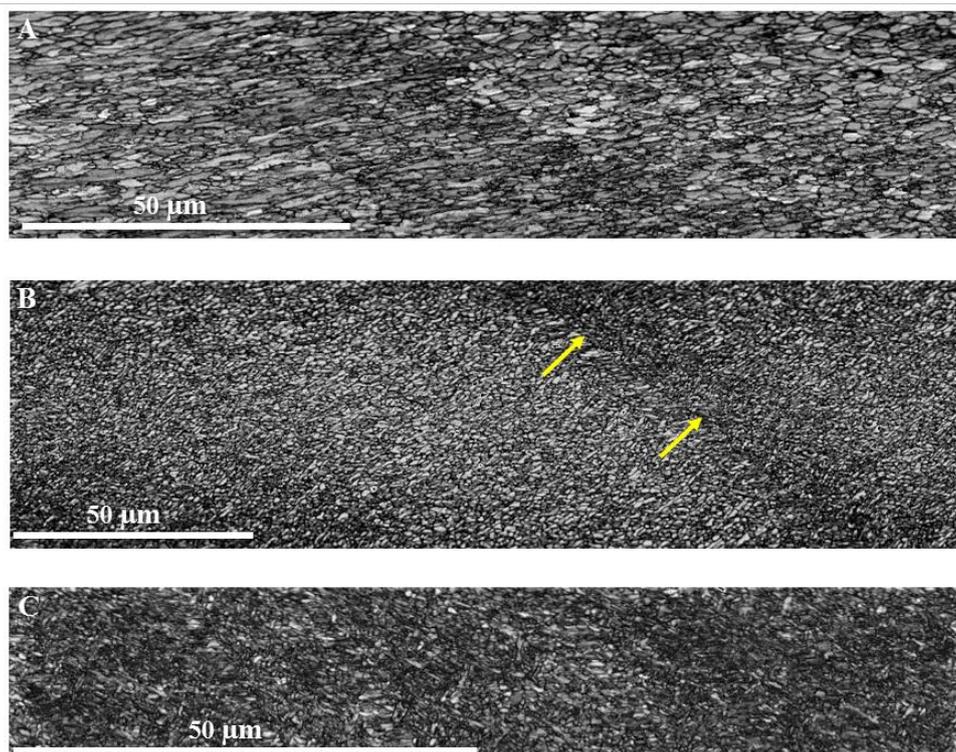


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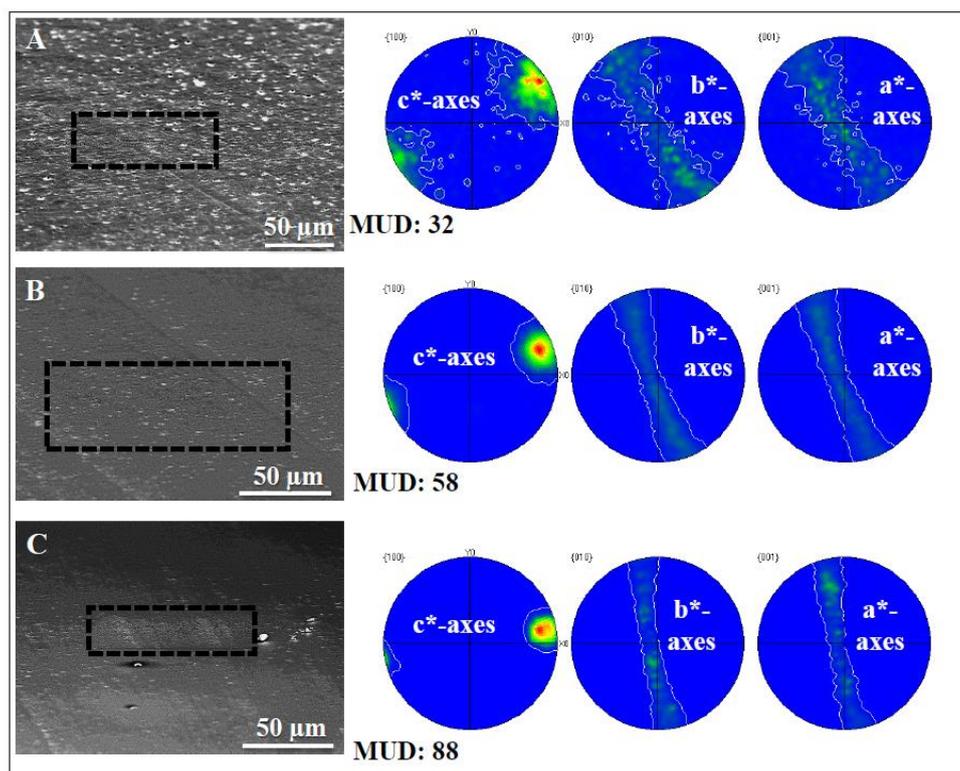
560 **Appendix Fig. A5.**  $\text{Sr}^{2+}$  concentrations along annual growth lines in hydrothermally altered *Arctica islandica* shell  
561 portions. Alteration temperature was 175 °C; meteoric water was used as alteration fluid; the alteration experiments  
562 lasted for 7 and 84 days.  $\text{Sr}^{2+}$  concentration scatters for both alteration times around 0.4 wt%  $\text{Sr}^{2+}$  and is similar to  
563 the value measured in the pristine *Arctica islandica* reference samples (see Figs. 8A, 8B).

564

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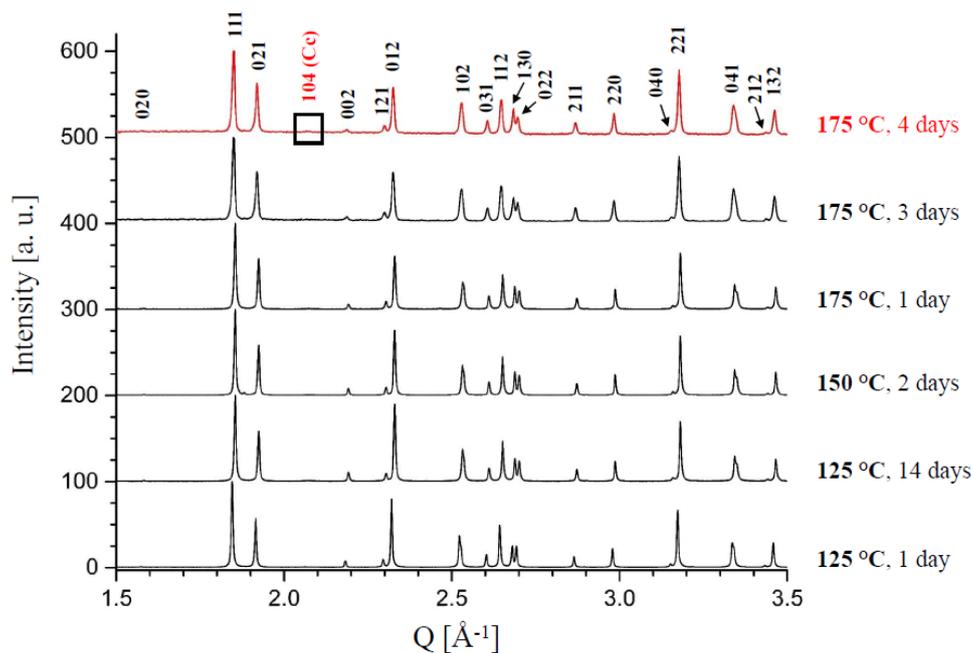
566  
567 **Appendix Fig. A6.** EBSD band contrast images taken along a cross section from different parts of the shell of  
568 pristine *Arctica islandica*. (A) Shell region next to seawater, (B) central shell section, (C) shell layer next to the  
569 soft tissue of the animal. Well visible is the difference in crystallite size. In contrast to the shell layer close to  
570 seawater (A), the innermost shell section, the section close to the soft tissue of the animal, is highly dense and  
571 consists of minute aragonite crystals.  
572



573

574 **Appendix Fig. A7.** Pole figures obtained from EBSD measurements shown in Figure A6. Measurements are done  
575 on pristine *Arctica islandica*. SEM images on the left hand side indicate the location of EBSD maps; (A) shell  
576 layer facing seawater, (B) central shell portion, (C) shell part close to the soft tissue of the animal. The pole figures  
577 and MUD values indicate clearly that aragonite co-orientation increases significantly towards innermost shell  
578 sections.

579



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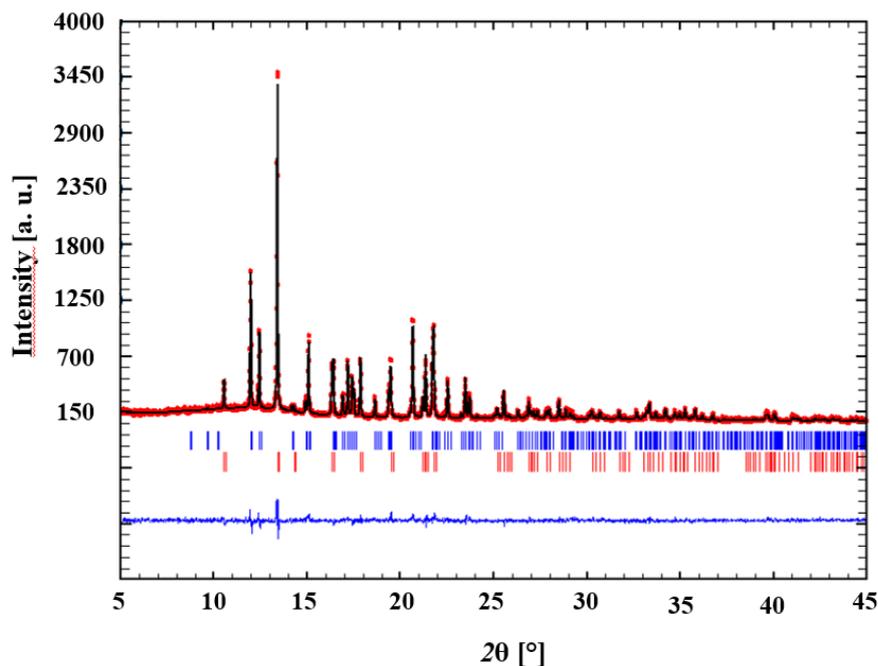
581 **Fig. A8.** XRD measurements of experimentally altered *Arctica islandica* samples subjected to alteration

582 temperatures between 125 °C and 175 °C for various lengths of time (1, 2, 3, 4 and 14 days). Calcite formation

583 starts at 175 °C and an alteration time of four days. Red Miller indices (Cc): calcite and black Miller indices:

584 aragonite.

585



586

587 **Appendix Fig. A9.** A representative Rietveld plot for the product of the alteration experiment at 175 °C for 6 days  
588 in artificial burial solution.

589

590

#### 591 **7 Competing interests**

592 The authors declare that they have no conflict of interest.

593

594

#### 595 **8 Acknowledgements**

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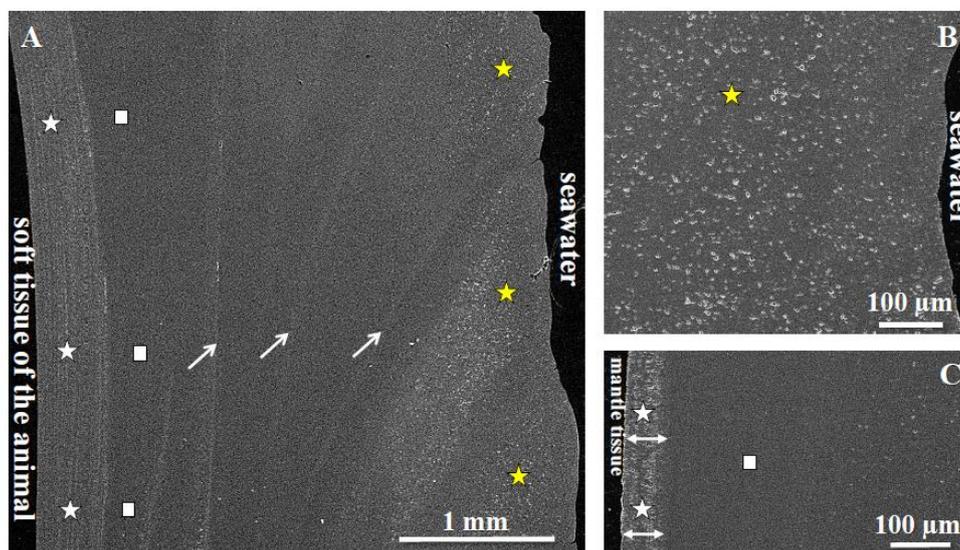
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977 **Figure captions**

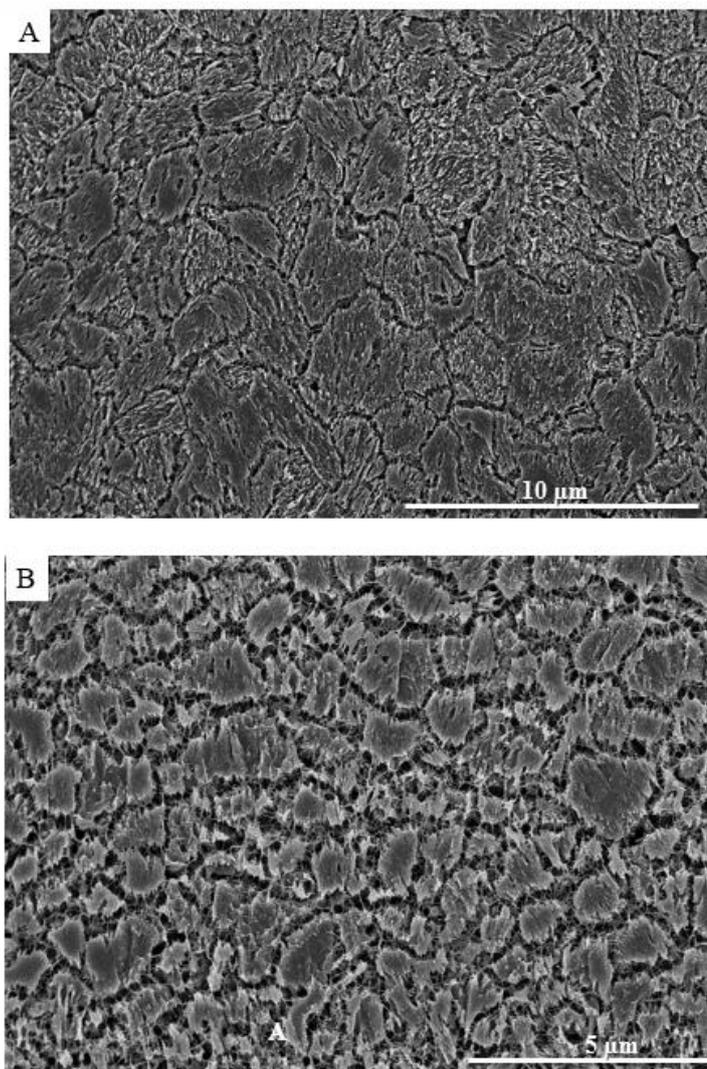
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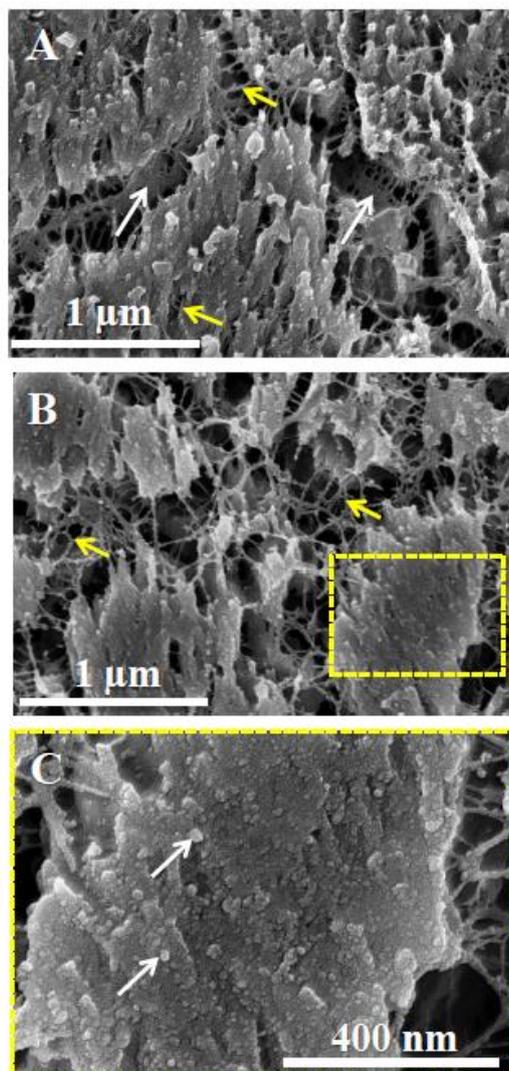
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983 **Fig. 1.** SEM image showing ultrastructure characteristics of the shell of modern *Arctica islandica* (A), its high  
984 porosity in shell layers facing seawater (yellow stars in A, B) and the dense shell portions (white stars in A, C)  
985 close to the soft tissue of the animal. The innermost shell portions contain elongated pores (white star in C) with  
986 the long axis of the pores oriented perpendicular to the inner surface of the shell (white arrows in C). Dense shell  
987 parts are also present (white rectangles in A, C), in which pore density and size is very low and minute aragonite  
988 crystals are closely packed. White arrows in A indicate the location of growth lines.

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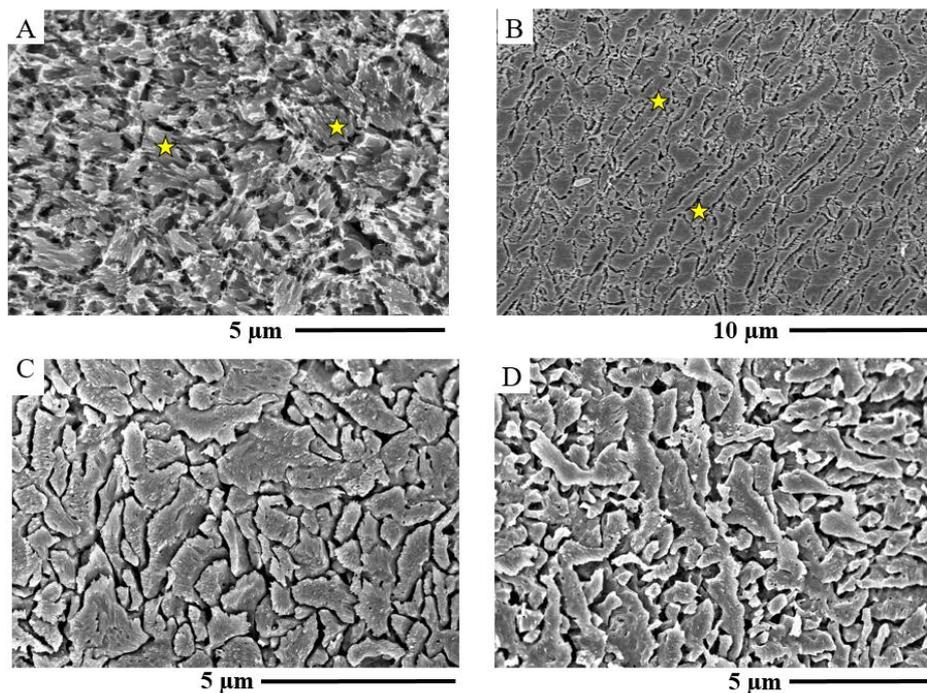


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991 **Fig. 2.** FE-SEM micrograph of microtome cut, microtome polished, etched, and critical-point-dried surface of the  
992 shell of modern *Arctica islandica*. (A) the shell portion next to seawater, (B) shell layer close to the soft tissue of  
993 the animal. Etching occurred for 180 seconds and was applied to remove aragonite in order to visualise the spatial  
994 distribution of (glutaraldehyde-stabilised) biopolymers within the shell. The portion of the shell facing seawater  
995 consists of large and irregular mineral units, connected to each other and infiltrated by a network of organic fibrils.  
996 In the layers next to soft tissue of the animal consists of significantly smaller mineral units. These are also  
997 interconnected by organic fibrils.  
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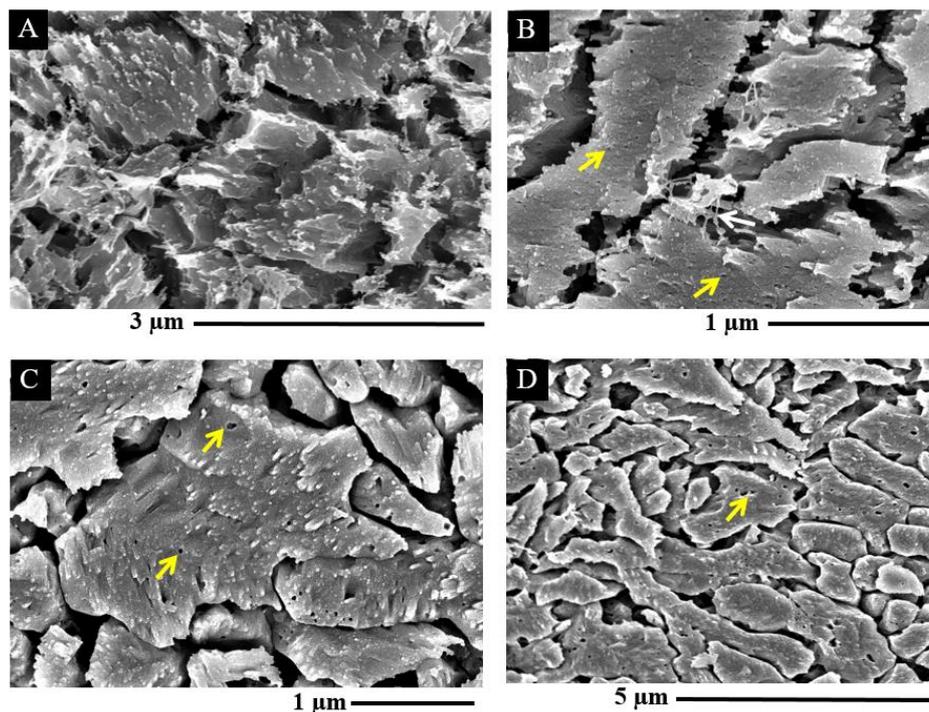
**Fig. 3.** FE-SEM micrographs of cut, microtome polished, etched, and critical-point-dried surfaces of of modern *Arctica islandica* next to seawater (A) and close to the soft tissue of the animal (B, C). Etching occurred for 180 seconds and removed aragonite in order to visualise the spatial distribution of (glutaraldehyde-stabilised) biopolymers within the shell. Readily visible is the nano-particulate consistency of the aragonitic hard tissue (white arrows in C) and the presence of biopolymer membranes (white arrows in A) and fibrils (yellow arrows in A, B) between the mineral units as well as between the aragonitic nanoparticles.



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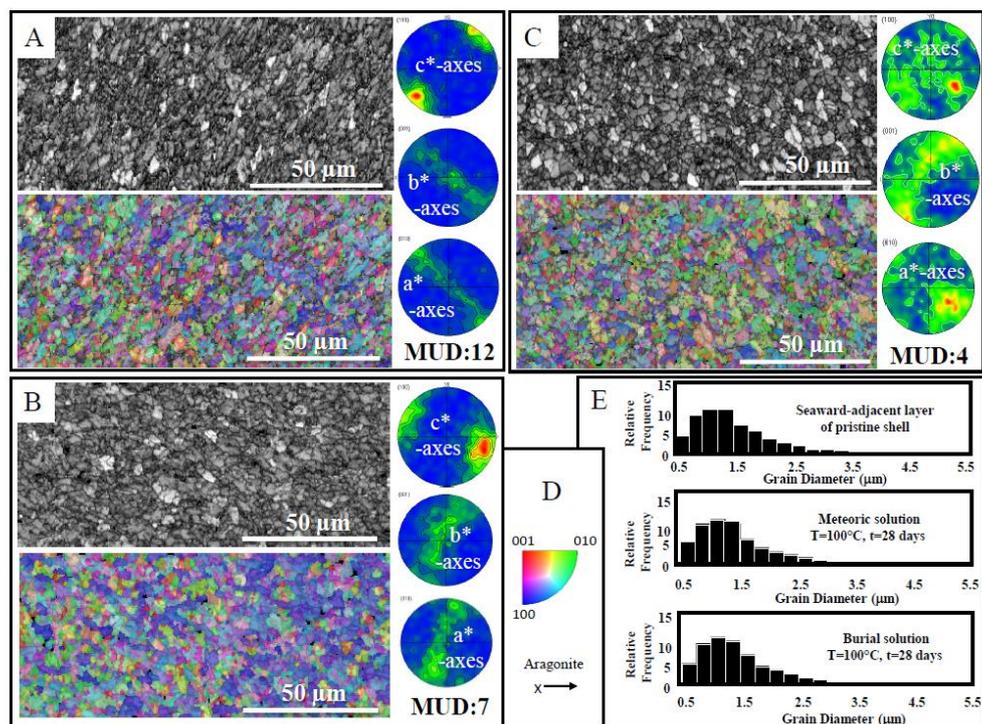
1011 **Fig. 4.** SEM micrographs of cut, microtome polished, etched, and critical-point-dried surfaces of the of  
1012 experimentally altered *Arctica islandica* shell materials: (A, C) sweater-adjacent layer, and (B, D) shell layer close  
1013 to the soft tissue of the animal. Etching occurred for 180 seconds and was applied for visualisation of the spatial  
1014 distribution of (glutaraldehyde-stabilised) biopolymers within the shell. 10 mM NaCl + 10 mM MgCl<sub>2</sub> aqueous  
1015 solution (burial fluid) was used for alteration at 100 °C for 28 days (A, B) and at 175 °C for 7 days (C, D). Mineral  
1016 units are indicated by yellow stars in A and B.

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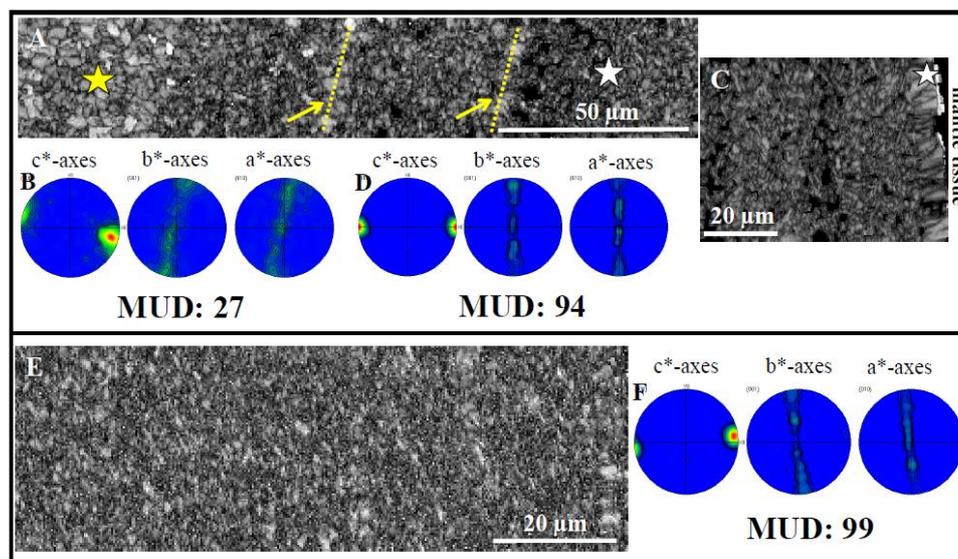
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1019 **Fig. 5.** FE-SEM micrographs that zoom into experimentally altered *Arctica islandica* shell material shown in Fig.  
1020 5. 10 mM NaCl + 10 mM MgCl<sub>2</sub> aqueous solution (burial fluid) was used for alteration at 100 °C for 28 days (A,  
1021 B) and at 175 °C for 7 days (C, D). Figs. A and C show material from the seawater-adjacent shell layers; B and D  
1022 depict material from shell layers at the soft tissue of the animal. For the material treated at 175 °C (C and D) the  
1023 biopolymers have decomposed and dissolved. Readily observable are minute round holes within the mineral units  
1024 (yellow arrows in B, C, D) that were filled in the pristine shell, prior to alteration, by biopolymer fibrils.



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1026 **Fig. 6.** EBSD band contrast images (grey scale) and orientation maps (colored, color code given in D) with  
 1027 corresponding pole figures of pristine (A) and experimentally altered (B, C) *Arctica islandica* shell material. In  
 1028 the pole figure colour codes for pole density, with the maximum in red corresponding to the given MUD value for  
 1029 each set of pole figures, respectively. All EBSD measurements were taken at the seawater side of the shell.  
 1030 Alteration temperature was 100 °C and was applied for 28 days. The solutions used were artificial meteoric fluid  
 1031 in (B) and artificial burial fluid in (C). As the pole figures show, in comparison to the microstructure of pristine  
 1032 *Arctica islandica* (A), the crystal orientation pattern in the skeleton is not affected by treatment with the solutions.  
 1033 (E) Grain diameter statistics for pristine and experimentally altered *Arctica islandica* shell material obtained from  
 1034 the EBSD measurements that are shown in Figures A to C. There is no significant difference in grain size between  
 1035 pristine and hydrothermally altered *Arctica islandica* shells.



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1037 **Fig. 7.** EBSD band contrast images (grey scale) and corresponding pole figures of hydrothermally altered (100 °C  
1038 for 28 days) *Arctica islandica* shell material with artificial meteoric fluid (A, B, C, D) and artificial burial fluid (E,  
1039 F). In Fig. A the change in shell microstructure is visible from the seawater-adjacent shell layer that contains large  
1040 aragonite crystals (yellow star in 7A) and many pores, to shell portions close to the soft tissue of the animal, which  
1041 consist of densely packed small aragonite crystallites (white star in 7A). In C and E band contrast maps and pole  
1042 figures are shown that were taken at the shell portion next to the soft tissue of the animal. As the pole figures and  
1043 the high MUD values in D and F highlight, this part of the shell remains almost unaltered and the pristine *Arctica*  
1044 *islandica* microstructure is kept. In (A) the two yellow arrows and the two dashed lines indicate the location of  
1045 former growth lines where, in pristine shells, an increased amount of organic material is present. As the latter is  
1046 destroyed during hydrothermal alteration space becomes available for infiltration of fluids.

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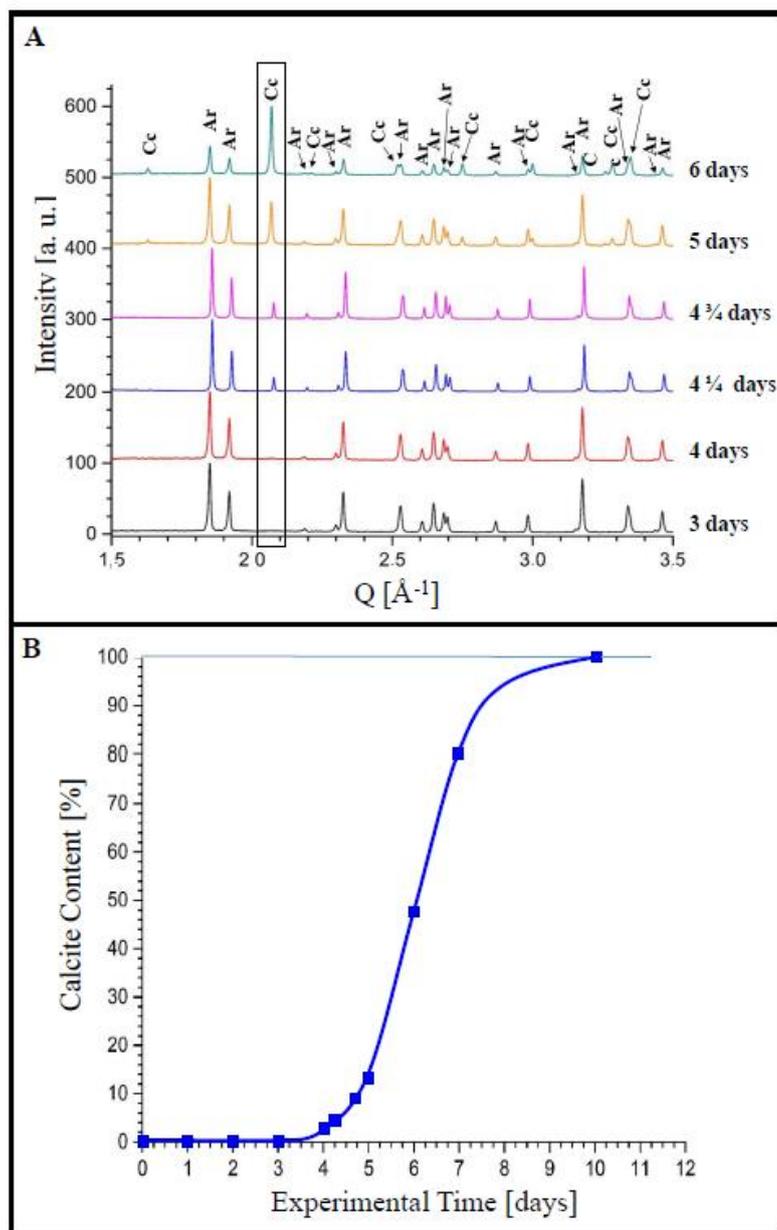
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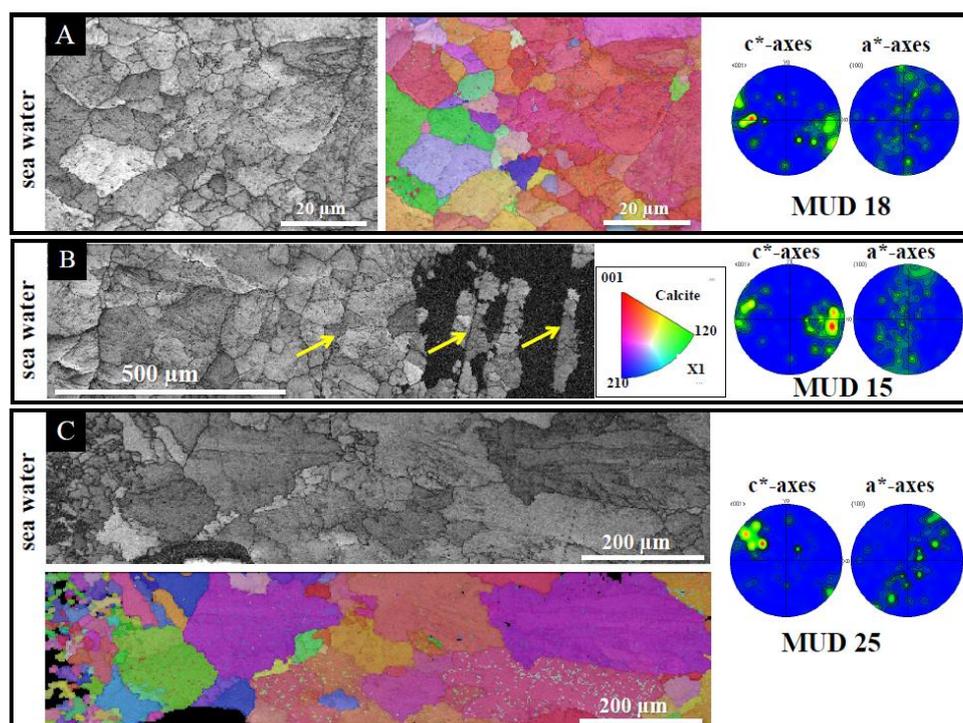


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1058 **Fig. 8.** (A) Selected x-ray diffractograms for three to six days of alteration of *Arctica islandica* shell material.  
1059 Alteration took place in artificial burial solution at 175 °C. (B) Newly formed calcite content relative to alteration  
1060 time (days) calculated from Rietveld analyses of the XRD measurements.



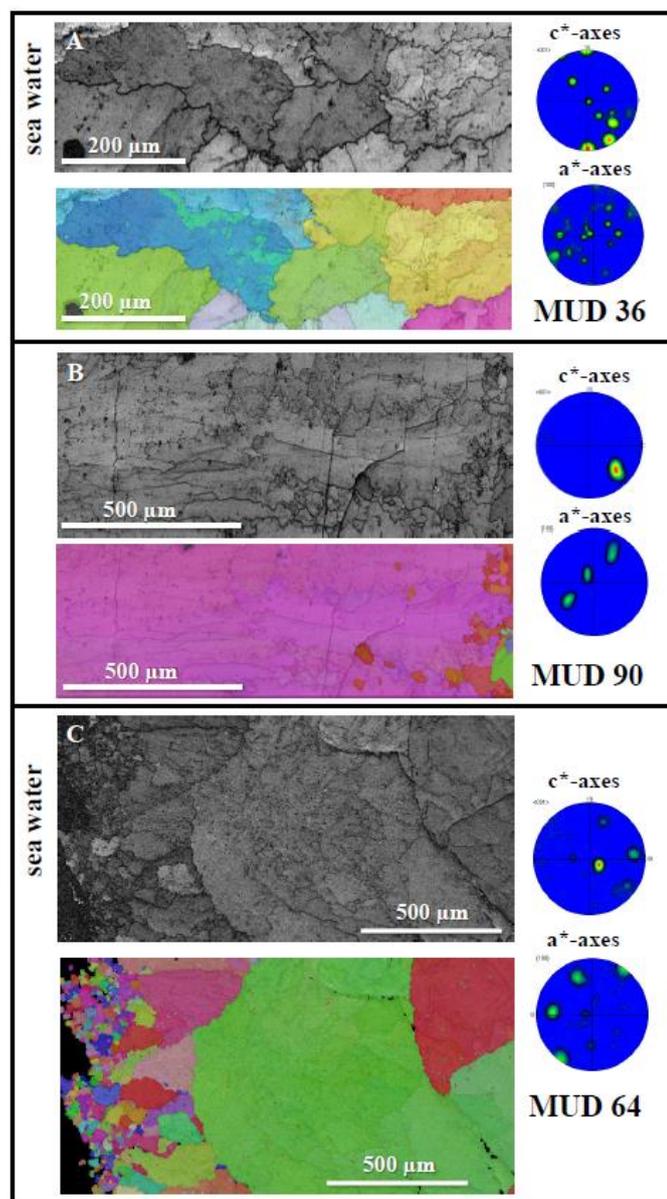
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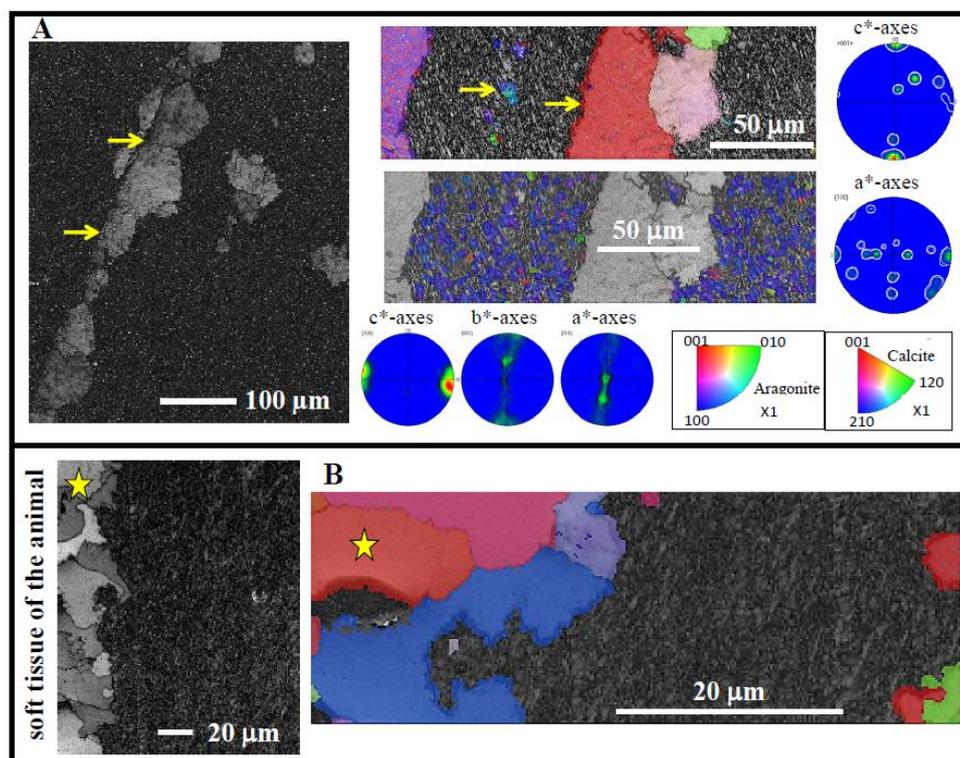
1063 **Fig. 9.** EBSD band contrast maps, colour-coded orientation maps, and corresponding pole figures highlight the  
1064 microstructure and texture of altered *Arctica islandica* shells at 175 °C in artificial meteoric solution. EBSD  
1065 measurements shown in (A, B) were taken on shells that were subject to hydrothermal alteration for 7 days.  
1066 Measurements shown in image C refer to shells where alteration lasted for 84 days. At 175 °C for both alteration  
1067 times aragonite has transformed almost completely to calcite, and the shell microstructure is characterised by large  
1068 and randomly oriented calcite crystals. The initial growth of calcite is visible at the location of former growth lines  
1069 (yellow arrows in B).

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1072 **Fig. 10.** EBSD band contrast maps and colour-coded orientation maps with corresponding pole figures for  
1073 hydrothermally altered *Arctica islandica* shells at 175 °C in water simulating burial diagenesis. EBSD  
1074 measurements shown in A and B were taken on shells that were subject to hydrothermal alteration for 7 days,  
1075 while the measurement shown in C was performed on shells where alteration lasted for 84 days. At 175 °C for  
1076 both alteration times most of the aragonite has transformed to calcite.



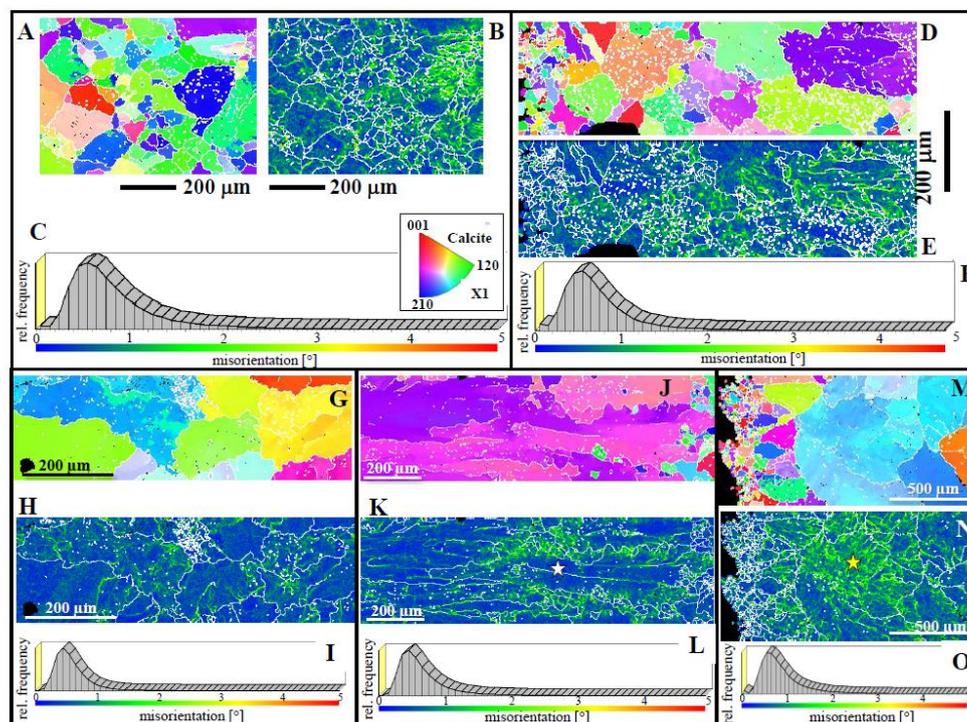
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1079 **Fig. 11.** EBSD band contrast (in grey), crystal orientation (colour-coded for orientation) maps, and corresponding  
1080 pole figures of altered *Arctica islandica* shells at 175 °C in artificial meteoric (A) and burial (B) solution,  
1081 respectively. Clearly visible is the initial formation of calcite at the location of former growth lines (yellow arrows  
1082 in A) and the growth of large calcite crystals (yellow stars in B) that formed at the shell portion that is in direct  
1083 contact with the alteration solution. Note that some pristine aragonite in the dense shell portion is still present.

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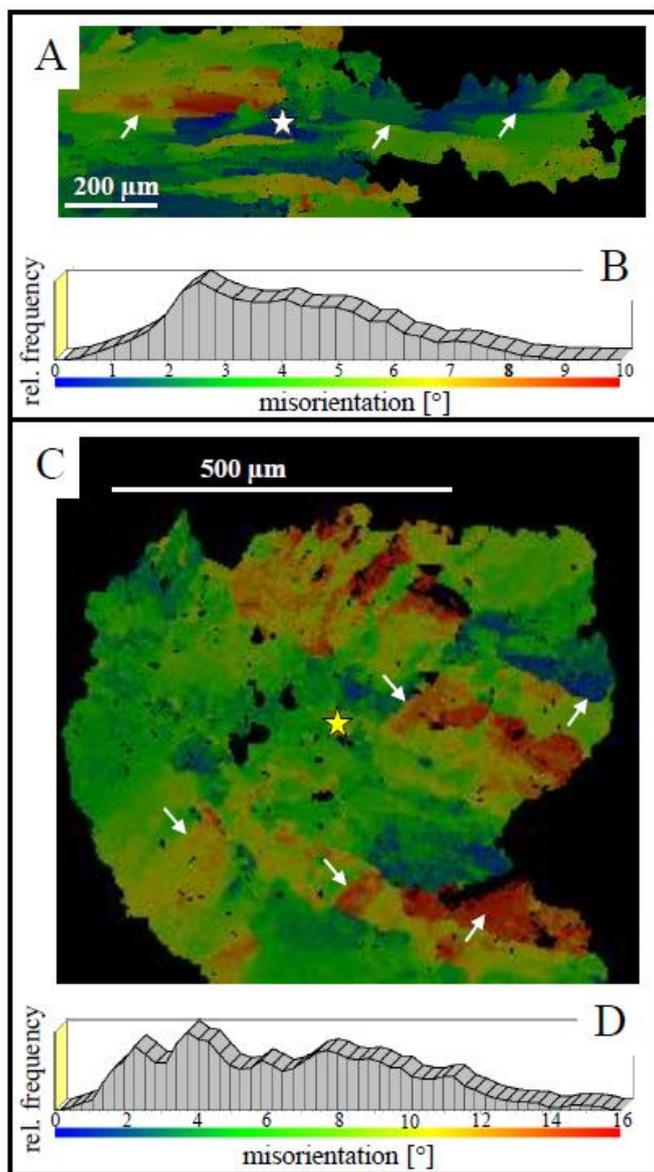
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1088 **Fig. 12.** Presentation of grain size (A, D, G, J, M), pattern of local misorientation distribution (indication of internal  
 1089 stress/strain) (B, E, H, K, N), and degree of local misorientation (C, F, I, L, O) for experimentally altered shells of  
 1090 *A. islandica* carried out in simulated meteoric solution at 175 °C for 7 (A to C) and for 84 days (D, E, F), and in  
 1091 burial solution at 175 °C for 7 (G to L) and 84 days (M to O), respectively. Grains are defined by using a critical  
 1092 misorientation of 5°. The outer perimeter of each grain is outlined with white lines and, for a better visualisation  
 1093 of individual grains, the grain map is shown in random colours (thus the colour-coding in A, D, G, J, M does not  
 1094 show orientation differences). At an alteration temperature of 175 °C, large calcite grains form. Local  
 1095 misorientation is about 2 degrees (see legends in C, F, I, L, O), irrespective of alteration duration and solution. The  
 1096 white star in K marks stress-free shell portions, while the yellow star in N indicates the location of an increased  
 1097 stress accumulation.

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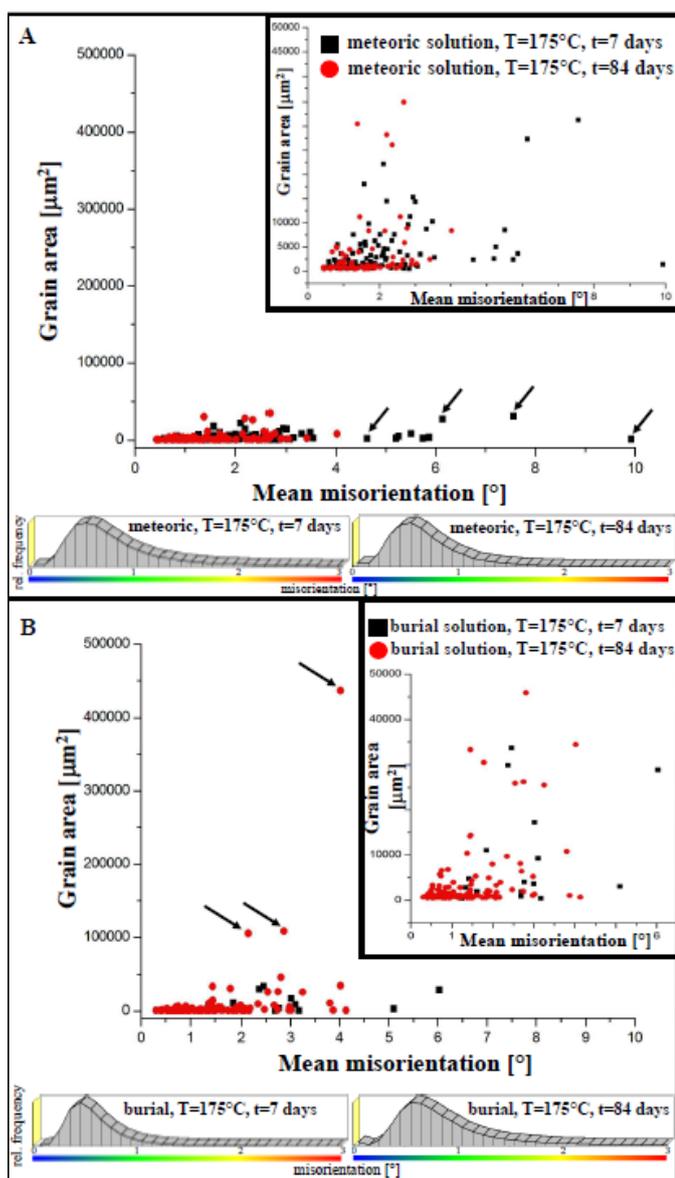
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1101 **Fig. 13.** Colour-coded visualisation (A, C) and degree of internal misorientation (B, D) within two large, mm-  
1102 sized grains that grew in simulated burial solution at 175 °C for 7 (A) and 84 (C) days. The grain shown in A  
1103 contains some stress-free portions within its centre (indicated by blue colours and the white star in A), while  
1104 internal misorientation in the grain shown in C is highly increased and occurs everywhere within the grain (D).  
1105 The yellow star in C points to the region where, in this grain, stress accumulation is highest.

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1108 **Fig. 14.** Grain area versus mean misorientation within individual grains obtained for newly formed calcite at  
1109 alteration of *Arctica islandica* aragonite in artificial meteoric (A) and in burial (B) solutions at 175 °C and for 7  
1110 and 84 days, respectively. The Mg-containing (burial) alteration fluid induces the formation of large calcite grains  
1111 that show a low degree of misorientation within the grains (B), while with artificial meteoric solution, the solution  
1112 that is devoid of Mg, significantly smaller grains are obtained. However, the latter occur with a high mean  
1113 misorientation within the individual, newly formed grains.

1114 **Tables**

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1120 **Table 1.** Detailed conditions used in hydrothermal alteration experiments of modern *Arctica islandica*.1121 Major and minor element chemical data of pristine *Arctica islandica* were obtained by EPMA using a

1122 CAMECA SX100 system (Goetz et al., 2014) and amounts to: 0.11 wt% Sr, 38.06 wt% Ca, 0.05 wt% Mn,

1123 0.54 wt% Na, 0.01 wt% P, 0.01 wt% Mg, 0.09 wt% Ba, 0.05 wt% Fe(III) and, 0.02 wt% Cl.

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Sample name	Fluid type	NaCl content [mM]	MgCl <sub>2</sub> content [mM]	Temperature [°C]	Experimental time	Alkalinity [mM]	pH	Mg-content of fluid after experiment [mg/L]
CHA-M-040 AI21 B2	meteoric	10	-	100	28 days	1.69	7.91	3
CHA-M-042 AI 23 B2	meteoric	10	-	175	7 days	7.72	-	0
CHA-M-046 AI27 B1	meteoric	10	-	175	84 days	10.75	7.78	1
CHA-M-043 AI24 B2	burial	100	10	100	28 days	2.02	8.39	112
CHA-M-041 AI22 B2	burial	100	10	175	7 days	9.96	-	84
CHA-M-046 AI 27 B2	burial	100	10	175	84 days	6.99	7.51	165

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1139 **Table 2.** Crystal co-orientation (texture) strength expressed as multiple of uniform (random)  
 1140 distribution (MUD) of modern and experimentally altered *Arctica islandica* shells. Ar: aragonite, Cc:  
 1141 calcite.  
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Sample name	Fluid type	Temperature [°C]	Experimental time	MUD value of the outermost shell part	MUD value of the central shell part	MUD value of the innermost shell part
modern reference	-	-	-	12 Ar/32 Ar	58 Ar	88 Ar
altered specimen <i>CHA-M-040 AI21 B2</i>	meteoric	100	28 days	7 Ar	27 Ar	94 Ar
altered specimen <i>CHA-M-043 AI24 B2</i>	burial	100	28 days	4 Ar	-	99 Ar
altered specimen <i>CHA-M-042 AI23 B2</i>	meteoric	175	7 days	18 Cc	15 Cc	-
altered specimen <i>CHA-M-046 AI27 B1</i>	meteoric	175	84 days	25 Cc	32 Cc	-
altered specimen <i>CHA-M-041 AI22 B2</i>	burial	175	7 days	36 Cc	90 Cc	80/81 Cc
altered specimen <i>CHA-M-046 AI27 B2</i>	burial	175	84 days	64 Cc	62 Cc	-

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