



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 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 Mg^{2+} -bearing solutions
69 the newly formed calcite crystals are larger than in 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

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