

Towards the kinetics of diagenetic overprint processes deduced from laboratory-based hydrothermal alteration of modern *Arctica islandica* shell material

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Benthic and nektonic marine biogenic carbonate archives represent the foundation of numerous studies aiming at paleo-environment reconstructions. However, living organisms are not in thermodynamic equilibrium as they form local chemical environments for physiologic processes such as biological mineralization of their hard tissues. This disequilibrium is not sustained after death and all biological tissues are altered by equilibration with the surrounding environment: diagenesis. To understand transformation during diagenesis we performed laboratory-based hydrothermal alteration experiments on *Arctica islandica* shells at four different temperatures between 100 °C and 175 °C treated in simulated meteoric and burial waters, respectively. We investigated, relative to unaltered shells, the kinetics of *Arctica islandica* bioaragonite to calcite transition as well as microstructural- and nanostructural characteristics of the altered shells with X-ray diffraction, micro-Raman, high-resolution SEM and EBSD.

At hydrothermal treatment at 100 °C bioaragonite - although metastable at 1 bar - does not transform to calcite, even in meteoric fluids and over a time period of 28 days. We noted a drastic recrystallization from the initial fine-grained fractal microstructure and pronounced axial texture to a new and still fine-grained microstructure with an almost randomized orientation distribution. At 175 °C the transformation to coarse-grained calcite is complete after 8 days. Calcite formation starts after a passive incubation period of 4 days; after 6 days the aragonite is almost completely transformed. In solutions simulating meteoric water the grain size of the newly formed calcite reaches 100-150 μm , while in burial fluids the calcite reaches sizes in the 1mm range during 28 days of alteration. Phase transformation proceeds where the hydrothermal fluid is in contact with the aragonite: at shell surfaces, around pores and in growth lines.

Our observations lead us to the following conclusions: Surprisingly, we do not only observe transformation of nominally metastable bioaragonite to calcite, we also observe recrystallization of bioaragonite to aragonite and biocalcite to calcite. All these types of recrystallization significantly reduce the crystallographic preferred orientation, which is characteristic for the original biological hard tissue. The newly formed crystals do not nucleate epitaxially on the original material, and this causes the randomized crystallographic orientation after diagenetic overprinting. The driving force for recrystallization is due to internal stresses caused by organic matrices and interface energies related to the nanoscale fabric of the biomineral. The pores left behind by decomposed organic matrix apparently serve as nucleation sites for newly formed mineral.