

Review of the article „*Experimental diagenesis: Insights into aragonite to calcite transformation of *Arctica islandica* shells by hydrothermal treatment*“ by Casella et al. – Contributing to an interesting discussion

Andreas Luttge, Cornelius Fischer & Rolf S. Arvidson
MARUM, Department of Earth Science (FB5), University of Bremen, Germany

The paper by Casella et al. tackles an interesting and important topic, i.e., the kinetics of the transition from biomineralized aragonite to inorganic calcite. The authors present an impressive data pool and some extensive observations from long-term laboratory experiments (up to 84 days!) at temperatures ranging from 100 to 175 °C, and two different Na-, and Mg-concentrations. These settings mimic burial and meteoric fluid conditions.

The main result of this study is that below 175 °C there are no signs of aragonite to calcite transformation. 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 remarkable 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.

The authors present SEM images of their starting material, the shells of modern *Arctica islandica*. This material is characterized by heterogeneous distribution of porosity pattern and pore sizes. There is an interesting structural difference between the inner side of the shell, the center section, and the outer side that has originally faced the sea water. It is certainly a complication that there is also organic material interspersed with the solid shell material.

Discussion: 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 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?

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].

Reference:

- [1] A Luttge, L Zhang, KH Nealson (2005) Mineral surfaces and their implications for microbial attachment: results from Monte Carlo simulations and direct surface observations. *American Journal of Science* 305 (6-8), 766-790
- [2] KJ Davis, KH Nealson, A Luttge (2007) Calcite and dolomite dissolution rates in the context of microbe–mineral surface interactions. *Geobiology* 5 (2), 191-205

[3] C Fischer & A Luttge (2016) Beyond the conventional understanding of water–rock reactivity. Earth and Planetary Science Letters, <http://dx.doi.org/10.1016/j.epsl.2016.10.019>