Autoclave experiments on the aragonite-calcite transformation of coral, shell and single-crystal samples

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To understand the diagenetic replacement of biogenic aragonite (Arg) by abiogenic calcite (Cc) in nature and to specifically constrain transformation kinetics associated with dissolution-precipitation processes, we subjected samples of several cubic-millimeter in volume prepared from a coral (*Porites* sp.), a bivalve shell (*Arctica islandica*), and Arg single crystals to hydrothermal alteration by distilled water, artificial burial fluid (100 mM NaCl and 10 mM $MgCl_2$), and artificial meteoric water (10 mM NaCl). The samples were placed in stainless-steel autoclaves with Teflon insets together with the fluid (water rock ratio=20) and exposed to 150, 170 or 200 °C for periods of 4, 16, 64, 256 and 1024 hours. After the experiments, X-Ray diffraction analysis as well as X-ray tomographic analysis were performed to characterize the phase content. Scanning electron microscopy images document the samples' surface topography and composition, and back-scattered electron images of single crystal cross-sections help to identify newly-grown phases and the width of the reaction rims. Analysis of the fluid by atomic absorption spectroscopy quantifies the species concentrations in the solutions. Weighing of all components of the setup before and after a run constrains the extent of dissolution, decomposition of organics, and combined water and carbon dioxide loss from the autoclave. In experiments with single crystals and burial fluid we observed brucite after 16 h, which is together with Arg subsequently converted to Mg-rich carbonates and Cc forming a layered structure. For coral and shell samples immersed in burial fluid and distilled water we only identified Cc as reaction product. For example X-ray diffraction measurements of the outer regions show that 46 % and 84 % of a coral sample and 18 % and 26 % of a shell sample are replaced by Cc when hydrothermally treated in distilled water at 200 °C for 64 and 256 hours, respectively. In addition, we found that the density contrast of Cc and Arg suffices to distinguish the two phases in X-ray tomographic images and thus this method provides the spatial characteristics of the transformation in the sample volume. We inferred removal of organic material from coral and shell samples by mass balance; the decomposition of organic constituents likely increases porosity and thus may increase reaction rate due to the increased reaction surface.