The Mechanism of Hydrothermal Replacement of Natural Aragonite Crystals by Calcite

Perdikouri, Christina[1] Kasioptas, Argyrios Putnis, Christine V. Putnis, Andrew
[1]University of Muenster / Institute of Mineralogy / Corrensstrasse 24, 48149, Muenster, Germany

Although aragonite is stable at high pressure it is also commonly formed at ambient conditions, i.e. speleotherms and biogenetic calcium carbonate. Its formation has been related to the combined effect of Mg/Ca and changes to the temperatures. Nevertheless, aragonite is metastable under surface conditions and is expected to be transformed into calcite.

Understanding the mechanism of such a pseudomorphic replacement is important for the study of natural processes. Hydrothermal experiments were carried out in teflon-lined autoclaves in various temperatures and for different periods of time. X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy and Laser ablation inductively coupled mass spectrometry (LA ICPMS) were used to characterize the reaction product. Results indicate that the replacement of aragonite by calcite follows an interface-coupled dissolution-precipitation mechanism. Mineral replacement of one polymorph by another in the presence of a fluid can occur when porosity is generated and fluid transport pathways are available through the product rim. Porosity generation depends on two factors: on the relative molar volumes of the two solid states and on the relative solubilities of the two phases in the fluid. Although the aragonite to calcite transition involves an increase in the molar volume, the reaction proceeds and SEM images show that porosity is generated confirming that the relative solubility of the two phases can outweigh a molar volume increase. Initially the parent crystal is partially replaced by calcite and then non-porous calcite nucleates around the aragonite crystal and the replacement reaction stops.

Taking into consideration the parameters of solubility, molar volumes and structural changes as well as the solutions' concentrations and the experimental conditions, it is understood that the effect of fluids in this replacement is evidently critical.

→