The role of grain boundaries and transient porosity as fluid pathways for reaction front propagation

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The pseudomorphic replacement of Carrara marble by hydroxylapatite is a model system to study the influence of different fluid pathways for reaction front propagation induced by fluid-rock interaction. Grain boundaries present in the rock as well as the transient porosity which forms as a result of the replacement reaction enable the reaction front to progress into the rock as well as to the center of each single grain until transformation is complete. Hydrothermal experiments with calcite marble cubes using phosphate bearing solutions result in its replacement by hydroxylapatite.

Using $H_2{}^{18}O$ as a tracer in the phosphate solution, and knowing the equilibration rate of $^{18}O/^{16}O$ with the phosphate ions, provides an internal chronometer for the replacement reaction, assuming that the ^{18}O in the apatite measured by Raman spectroscopy reflects the ^{18}O in the phosphate solution at the time of replacement. By measuring the ^{18}O in the apatite at various points along the replacement front it is possible to estimate and compare the time effectiveness of the different fluid pathways in this model system. The results demonstrate that the grain boundaries are an effective pathway enabling the fluid to penetrate the rock more than one order of magnitude faster than through the newly developing porosity, which provides pathways towards the center of single calcite grains.