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The replacement of a carbonate rock by fluorite: Kinetics and microstructure

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Abstract

Understanding the mechanism and kinetics of the replacement of carbonates by fluorite has applications in Earth sciences and engineering. Samples of Carrara marble were reacted with an ammonium fluoride (NH_4F) solution for different reaction times and temperatures. The microstructure of the product phase (fluorite) was analyzed using SEM. The kinetics of replacement was monitored using Rietveld refinements of X-ray powder diffraction patterns of the products. After reaction, all samples preserved their size and external morphology (a pseudomorphic replacement). The grain boundaries of the original marble were preserved although each calcite grain was replaced by multiple fine crystals of fluorite creating inter-crystal porosity. The empirical activation energy E_a (kJ/mol) of the replacement reaction was determined by both model-fitting and model-free methods. The isoconversional method yielded an empirical activation energy of 41 kJ/mol, and a statistical approach applied to the model-fitting method revealed that the replacement of Carrara marble by fluorite is better fitted to a diffusion-controlled process. These results suggest that the replacement reaction depends on the ion diffusion rate in the fluid phase through the newly formed porosity.

Keywords: Calcite, fluorite, replacement, dissolution-precipitation, kinetics, porosity