

## A kinetic study of the replacement of calcite marble by fluorite

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Replacement reactions are relevant in any situation that involves the reequilibration between a solid and an aqueous fluid phase and are commonly controlled by an interface-coupled dissolution-precipitation mechanism (Putnis and Putnis, 2007). These reactions control many large-scale Earth processes whenever aqueous fluids are available, such as during metamorphism, metasomatism, and weathering. An important consequence of coupled dissolution-precipitation is the generation of porosity in the product phase that then allows the infiltration of the fluid within the mineral being replaced.

Understanding the mechanism and kinetics of the replacement of carbonates by fluorite has application in earth sciences and engineering. Fluorite ( $\text{CaF}_2$ ) occurs in all kinds of rocks (igneous, sedimentary, and metamorphic) and its origin is commonly associated with hydrothermal fluids. Moreover, calcium carbonate has been suggested as a successful seed material for the sequestration of fluoride from contaminated waters (Waghmare and Arfin, 2015). The aim of the present work is to investigate aspects of the replacement of calcium carbonate by fluorite to better understand the mechanism and kinetics of this reaction.

Small cubes ( $\sim 3 \times 3 \times 3$  mm) of Carrara marble ( $\text{CaCO}_3 > 99\%$ ) were cut and reacted with a 4 M ammonium fluoride ( $\text{NH}_4\text{F}$ ) solution for different times (1 to 48 hours) and temperatures (60, 80, 100, and 140 °C). The microstructure of the product phases was analysed using SEM. The kinetics of replacement was monitored from the Rietveld analysis of X-ray powder diffraction patterns of the products as a function of temperature and reaction time.

After reaction, all samples preserved their size and external morphology (a pseudomorphic replacement) and the product phase (fluorite) was highly porous. The activation energy  $E_a$  (kJ/mol) of the replacement reaction was empirically 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. This is consistent with ion diffusion through the fluid phase. These results suggest that the replacement reaction is dependent on the fluid migration rate through the newly formed porosity.

Putnis, A., Putnis C.V., 2007. The mechanism of reequilibration of solids in the presence of a fluid phase. *Journal of Solid State Chemistry*, 180, 1783-1786.

Waghmare, S.S., Arfin, T. (2015). Fluoride removal from water by calcium materials: A state-of-the-art review. *Int. J. Innov. Res. Sci. Eng. Technol.* 4, 8090–8102.