Porosity generated during the replacement of calcite by fluorite

ELISABETE TRINDADE PEDROSA[1], ALEJANDRO BURGOS-CARA[1,2], CHRISTINE V. PUTNIS[1,3], ANDREW PUTNIS[1,4]

[1]Institute of Mineralogy, University of Münster, Münster, Germany (e.trindade.pedrosa@uni-muenster.de)

[2] Department of Mineralogy and Petrology, University of Granada, Granada, Spain (aburgoscara@live.com)

[3]Department of Chemistry, Curtin University, Perth, Australia (putnisc@uni-muenster.de)

[4]The Institute of Geoscience Research (TIGeR), Curtin University, Perth, Australia (putnis@uni-muenster.de)

In natural rocks, fluids can infiltrate through grain boundaries and/or pre-existing fractures, playing an important role on the rate at which chemical alteration occurs. In the presence of fluids, pseudomorphic mineral replacement reactions are typically characterized by the generation of porosity. To the best of our knowledge, no attempt was made before to quantitatively measure the porosity that is generated during such reactions. We used the replacement of calcite by fluorite as a model system to study the porosity generation during such reactions.

Calcite single crystals were reacted with sodium fluoride solutions at 40 °C for different reaction times (2, 4, 8, 16, 22, 32 days). The surface area and porosity of the samples were determined through nitrogen adsorption measures. The quantification of the phases was made using powder XRD, and SEM was used to study the microstructure of the product phase.

After reaction, all samples had been either partially or fully replaced by fluorite. The replacement was pseudomorphic, preserving the original shape and size of the original calcite crystals. The fluorite crystals have a needle-like shape. At the reaction front the needles are oriented perpendicular to the reaction interface, and as the reaction interface moves forward into the crystal, the needles heal or recrystallize forming sheets of fluorite parallel to the reaction front.

The diameter of the pores ranged between 3.1 and 31.0 nm. Samples reacted for higher reaction times have bigger pores. The concentration of pores was higher for three specific pore diameters in each sample: at the lowest diameter (~3.1 nm); at a middle diameter (between 10.0 and 16.0 nm, depending on the sample); and at the higher diameters (for samples reacted for more than 2 days, ranging from 21.6 to 31.0 nm).

The surface area of the samples increased as well as the permeability. There is a linear relationship correlation between porosity and the fraction of fluorite transformed, and a power law correlation of each with the reaction time.