



Experimental replacement of calcium carbonates by fluorite: high volume changes and porosity generation

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Pseudomorphic mineral replacement reactions are a common phenomena in nature, and often described as interface-coupled dissolution-precipitation processes. The generation of porosity is a key factor for its progression since it creates the pathway for fluid infiltration towards an ongoing reaction front. The generation of porosity depends on two key factors: the molar volume differences between parent and product phase, and the relative solubilities of the parent and product in the fluid at the mineral-fluid interface (Pollok et al., 2011). Jamtveit et al., (2009) demonstrated that the permeability of the parent rock may also be enhanced by the development of fractures as a response to stresses generated by local volume changes at the reaction interface, which in turn increases the reaction rate. The replacement of calcite (CaCO_3) by fluorite (CaF_2) involves a molar volume decrease of 33.5 %. If indeed high volume changes generate high local stresses, a fragmentation process is expected to be driven by this replacement reaction. To test this hypothesis, a number of hydrothermal experiments were performed.

Small cubes of calcite rock (Carrara marble), and single crystals of calcite were used as parent materials. Two fluoride solutions (ammonium fluoride and sodium fluoride) were used as reactants. Samples were reacted at temperatures up to 200°C for various times and quenched to room temperature. After drying, samples were mounted in epoxy holders, cross sections through the centre of the samples were cut and polished, and analysed using scanning electron microscopy (SEM), X-ray diffraction (XRD), and electron microprobe analysis (EMP). The replacement end product of all experiments was confirmed to be fluorite. In every case the external shape of the samples was perfectly maintained. No reaction induced fracturing was visible in any of the samples (rock or single crystals) although the texture of the replaced material was quite complex, often with a 'V' shaped reaction front. The main difference between single crystals and rock was that in the former, grain boundaries were rapid transport pathways for fluid infiltration resulting in the precipitation of fluorite within the sample at locations further from the main reaction front. The porosity formed was very high and complex, its texture depending on the shape and orientation of the replaced material. Very large hollow spaces with diameter $>30 \mu\text{m}$ formed in several samples. In this system the large volume decrease is accommodated by a high porosity rather than fracturing.

Jamtveit B., Putnis C.V. & Malthe-Sørenssen A. (2009). Reaction induced fracturing during replacement processes. *Contrib. Min. Pet.*, 157 127–133

Pollok K., Putnis C.V. & Putnis A. (2011) Mineral replacement reactions in solid solution-aqueous solution systems: Volume changes, reaction paths and end points using the example of model salt systems. *Am. J. Sci.*, 311, 211-236