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 (NH₄F) 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

INTRODUCTION

Mineral replacement reactions may occur in any situation that involves the reequilibration between a solid and a fluid phase and are commonly controlled by an interface-coupled dissolution-precipitation mechanism (Putnis 2002, 2009; Putnis and Putnis 2007). Such reactions occur commonly in the crust of the Earth, where aqueous fluids are ubiquitous, for example, during metamorphism, metasomatism, and weathering. These large-scale processes are often characterized by pseudomorphic mineral replacements as seen in albitization, where Ca- or K-rich feldspars are progressively replaced by the Na-rich plagioclase, albite (Hövelmann et al. 2010; Niedermeier et al. 2009; Engvik et al. 2011). During albitization many elements are mobilized and removed into the fluid phase that may migrate through the rock and ultimately be associated with large-scale ore deposition. Replacement reactions also occur quite commonly in carbonate rocks, promoted by the higher solubility of carbonates compared to other rock-forming minerals. For example, calcite (CaCO₃) may be replaced by other carbonates such as dolomite or siderite (Pearce et al. 2013) or may form other calcium compounds when in contact with appropriate solutions. For example, calcite in contact with PO₄-bearing solutions is easily replaced by apatite or other Ca-phosphate (Yoshimura et al. 2004; Kasiptas et al. 2011; Jonas et al. 2013, 2014; Pedrosa et al. 2016).

Replacement reactions are complex reactions controlled by at least three reaction steps: dissolution, mass transfer (including fluid migration through a porous solid phase and element diffusion through a fluid phase), and precipitation (including nucleation and growth). The kinetics of replacement reactions depends on the contribution of each of these steps and these may vary during the progression of the reaction. The overall reaction rate generally depends on the slowest of these reaction steps. The temperature dependence of the reaction rate is referred to as the empirical activation energy ($E_a$), without specific reference to the overall rate-controlling step.

A study by Xia et al. (2009) has shown that during mineral replacement reactions, when the rate-controlling step is dissolution, there may be perfect preservation of the mineral microstructure inherited from the parent phase (micro- and nano-scale pseudomorphism). The relevance of coupled dissolution-precipitation reactions to a wide range of fluid-solid reactions has been recently reviewed by Ruiz-Agudo et al. (2014) and Altree-Williams et al. (2015). As well as describing reequilibration reactions occurring in the Earth, these reactions may be used to design new materials with specific engineered and functionalized properties. Examples of compositional control and designed products include the use of apatite formed from the replacement of a carbonate such as calcite or aragonite (Kasiptas et al. 2010). New bone replacement materials (apatite) need to combine long implant life with compatibility and appropriate mechanical properties and dissolution-precipitation is a process that has been proposed for the synthesis of porous biocompatible material for bone implants (Heness and Ben-Nissan 2004).

In this paper we describe the replacement of calcite (Carrara marble) by fluorite (CaF₂). Understanding the mechanism and kinetics of the replacement of carbonates by fluorite has applications in both Earth sciences and engineering. Fluorite (CaF₂) occurs naturally in many types of rocks (igneous, sedimentary,