



# The pseudomorphic replacement of marble by apatite: The role of fluid composition



Elisabete Trindade Pedrosa <sup>a,\*</sup>, Christine V. Putnis <sup>a,b</sup>, Andrew Putnis <sup>a,c</sup>

<sup>a</sup> Institut für Mineralogie, University of Münster, Corrensstrasse 24, 48149 Münster, Germany

<sup>b</sup> Nanochemistry Research Institute, Department of Chemistry, Curtin University, Perth 6845, Australia

<sup>c</sup> The Institute for Geoscience Research (TIGeR), Curtin University, Perth 6845, Australia

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## ABSTRACT

The replacement of a natural carbonate rock (Carrara marble) by apatite was used as a model to study the role of fluid chemistry in replacement reactions, focusing on the mineralogy, chemical composition, and porosity of the replacement product. Carrara marble was reacted with diammonium phosphate solutions ((NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>), in the presence and absence of four salt solutions (NH<sub>4</sub>Cl, NaCl, NH<sub>4</sub>F, and NaF) at different ionic strengths, at 200 °C and autogenous pressure. The replacement products were analyzed using powder X-ray diffraction, Scanning electron microscopy (SEM), electron microprobe analysis (EMPA), and Raman spectroscopy. The reaction in all samples resulted in pseudomorphic replacements and shared the characteristics of an interface-coupled dissolution–precipitation mechanism. Increasing the ionic strength of the phosphate fluid increased the replacement rates. With a fixed concentration of phosphate, replacement rates were reduced with the addition of NH<sub>4</sub>Cl and NaCl and increased significantly with the addition of NaF and NH<sub>4</sub>F. The addition of different salts resulted in specific porosity structures resulting from the formation of different phosphate phases. Chloride-containing fluids showed a higher degree of fluid percolation through grain boundaries. This study illustrates the significant impact that small differences in solvent composition can have in the progress of replacement reactions, the nature of the products and the resultant porosity.

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## 1. Introduction

Fluid mediated re-equilibration of solids is of great importance in many geological systems (e.g. Putnis, 2002, 2009 and references therein), and industrial processes (e.g. Xia et al., 2008, 2009a). Of particular interest are mineral replacement reactions that result in the formation of pseudomorphs of the parent phase (preservation of the external shape and total volume). In the presence of fluids, the mechanism of pseudomorphic replacement has been explained as the re-equilibration process between fluid and minerals involving an interface-coupled dissolution–precipitation mechanism occurring at the mineral–fluid interface (Putnis and Putnis, 2007; Ruiz-Agudo et al., 2014). In this mechanism the solid–fluid interface is of most importance because as soon as a small amount of solid material dissolves, it generates a boundary layer of fluid that may become supersaturated with a new solid phase that immediately precipitates (Ruiz-Agudo et al., 2012). These reactions are characterized by sharp reaction fronts between parent and product phases, and the development of intracrystalline porosity in the product phase (Putnis and Mezger, 2004; Putnis et al., 2005).

The formation of porosity is critical because it allows continuous percolation of fluid to the reaction front and ultimately the complete replacement of one phase by another. Porosity generation also has a significant impact on the mechanical behavior of rocks, an important issue when considering injecting fluids into the upper crust (Nermoen et al., 2015). Moreover, the relevance of these replacement reactions has been reported in many varying scenarios, such as: CO<sub>2</sub> sequestration (Lackner, 2002); the durability of nuclear waste disposal (Geisler et al., 2015); synthesis of new materials (Ben-Nissan, 2003; Xia et al., 2008, 2009a); remediation of contaminated soil (Wang et al., 2012) and groundwater (Turner et al., 2005); new wastewater treatments (Yang et al., 1999); and the preservation of monument surfaces (Sassoni et al., 2011).

In this work, we investigate in detail the role of the bulk fluid composition on fluid–mineral reactions using as a model system, the reaction of a calcium carbonate rock (Carrara marble) with various phosphate-containing fluids. Carrara marble is an ideal experimental material because it is a relatively pure calcium carbonate (calcite) rock with regular grain size (average 200 μm), and the pseudomorphic replacement of calcite by apatite has been previously demonstrated (e.g. Ames, 1959, 1961; Kasiotas et al., 2008, 2010, 2011; Jonas et al., 2013, 2014; Borg et al., 2014).

\* Corresponding author.

Of particular interest is to understand the role of the composition of fluids in controlling the progress of reactive fluid flow. In this work, two main questions were posed:

- (i) How does fluid composition influence the evolution of micro-structure and porosity generation of the product phase(s)?
- (ii) How does fluid chemistry influence the chemical composition of the product phase(s), and overall mass transfer?

These questions are relevant to natural Earth environments whenever aqueous fluids are in contact with crustal rocks. When rocks are out of equilibrium with the surrounding fluids reactions continuously take place in order to reach a more stable thermodynamic state. The volume of fluid can be quite small for mineral replacement reactions to occur (Milke et al., 2013) and the results of the re-equilibration processes are the formation of new minerals (reaction product phases) as well as a fluid charged with new elements released from the mineral–fluid reaction. In this way elements may be sequestered or released to solution and carried away in the fluid phase (Xia et al., 2008).

## 2. Materials and methods

### 2.1. Starting material

#### 2.1.1. Solids

Carrara marble (from Carrara, Italy) was chosen as the parent material due to its high purity of calcium carbonate ( $\text{CaCO}_3 > 99.7\%$ ), confirmed from X-ray diffraction (XRD) and Raman spectroscopy analyses, and its facility to be replaced by calcium phosphate when reacted with phosphate-bearing solutions (Kasioptas et al., 2008, 2011). The rock is polycrystalline, composed of equant grains of approximately 200  $\mu\text{m}$  in size, and contains 0.3(1) wt.% of Mg, homogeneously distributed. Two sets of small marble cubes were cut from the white parent rock: small cubes of around 3  $\text{mm}^3$ , and larger cubes of around 15  $\text{mm}^3$ . The initial weight of the samples was on average 8(1) mg and 40(1) mg, respectively. The individual cubes were cut and then polished to the desired sizes (1.5  $\times$  1.5  $\times$  1.5 mm for the small cubes and 3  $\times$  3  $\times$  3 mm for the larger cubes) using a digital caliper.

#### 2.1.2. Fluids

Pure solid diammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$  (Acrös Organics powder >99.0%) was used to make a 2 M stock solution from which all other solutions (referred to as phosphate solution) were diluted

using deionized water MillQ (resistivity >18  $\text{M}\Omega\text{ cm}$ ). Five sets of experiments were carried out. Set 1 were experiments with various concentrations of ammonium phosphate solutions (0.1, 0.5, 1, 2 M). Set 2 to 5 used 1 M diammonium phosphate to which varying concentrations of other salts were added. The preparation of these stock solutions was made by dissolving ammonium chloride (T.H. Geyer GmbH 99.8%), sodium chloride (E. Merck 99.5%), ammonium fluoride (Alfa Aesar GmbH 98.0%), and sodium fluoride (E. Merck 99.0%) powders with MillQ water. The molar concentration of each solution used in the experiments is shown in Table 1.

### 2.2. Hydrothermal experiments

For the hydrothermal replacement experiments each marble cube was placed into a Teflon®-lined reactor together with 2 mL of the corresponding fluid. The Teflon® reactor was placed into a steel autoclave and tightly sealed to avoid any fluid loss during reaction. The temperature for all experiments was 200 °C, at autogenous pressure. After reaction, the autoclaves were removed from the furnace and quickly cooled to room temperature (22 °C) in a stream of compressed air. The samples were washed with distilled water, left to dry overnight at 40 °C, and then weighed. The pH of the fluids was also measured before and after reaction. Magnesium and calcium contents in the final fluids were measured using inductively-coupled plasma optical emission spectrometry (ICP-OES).

The smaller cube samples were reacted for 4 days, in which the only parameter changed was the composition of the fluid. One small Carrara marble cube was used for each experiment, and five sets of experiments were made. Each set was composed of four experiments (see Table 1). Because these experiments used natural samples, it is possible that each one differed slightly in terms of grain boundary distribution. To estimate the potential variation that this difference could have on the results, at least two replicas of each experiment were made.

To be able to better identify the product phases (for XRD analysis), the larger marble cubes were reacted with the five different types of fluids for 8 days.

### 2.3. Analytical methods

#### 2.3.1. PHREEQC simulations

The computer program PHREEQC (Parkhurst and Appelo, 1999) was used to determine the ionic strength (IS) of each of the bulk fluids

**Table 1**  
Summary of experimental and calculated results.

Experiment	Fluid solution	Fluid solution		Solid samples			
		n (M)	IS (200 °C)	Initial mass (mg)	Mass change (%)	Replacement extent	Porosity Type (code)
Set 1	$(\text{NH}_4)_2\text{HPO}_4$	0.1	0.2	8.8 ± 0.5	0.9 ± 0.2	Partial	1,2
		0.5	0.9	9.3 ± 0.0	2.7 ± 0.7	Partial	1,2
		1	2.1	8.7 ± 0.8	4.2 ± 0.2	Partial	1,2
		2	4.7	8.5 ± 0.9	4.5 ± 0.3	Partial	1,2
Set 2	$(\text{NH}_4)_2\text{HPO}_4 + n \text{NH}_4\text{Cl}$	0.01	2.1	8.4 ± 1.2	3.7 ± 0.0	Partial	1,2
		0.1	2.2	8.8 ± 0.7	3.3 ± 0.4	Partial	1,2
		0.5	2.3	8.9 ± 0.7	2.8 ± 0.7	Partial	1,2
		1	2.6	7.9 ± 2.1	3.0 ± 0.2	Partial	1
Set 3	$(\text{NH}_4)_2\text{HPO}_4 + n \text{NaCl}$	0.01	2.1	9.1 ± 0.0	3.8 ± 0.8	Partial	1,2
		0.1	2.2	9.2 ± 0.3	4.0 ± 1.3	Partial	1,2
		0.5	2.6	9.2 ± 0.3	2.2 ± 1.4	Partial	1,2
		1	3.0	7.6 ± 1.8	0.7 ± 0.8	Partial	1
Set 4	$(\text{NH}_4)_2\text{HPO}_4 + n \text{NH}_4\text{F}$	0.01	2.1	9.2 ± 0.0	3.1 ± 0.7	Partial	2 (surface); 1, 2 (core)
		0.1	2.2	9.5 ± 0.4	3.1 ± 0.5	Complete	1
		0.25	2.3	8.8 ± 0.6	1.8 ± 0.3	Complete	1
		0.5	2.6	8.8 ± 0.8	−0.2 ± 0.1	Complete	1 (surface), 2
Set 5	$(\text{NH}_4)_2\text{HPO}_4 + n \text{NaF}$	0.01	2.1	9.4 ± 0.0	4.0 ± 0.0	Partial	2 (surface), 1, 2 (core)
		0.1	2.2	8.2 ± 0.2	5.6 ± 0.3	Complete	1
		0.25	2.3	6.9 ± 1.1	4.0 ± 0.6	Complete	1
		0.5	2.6	8.7 ± 0.7	0.8 ± 0.1	Complete	2 (1, inside the crystal)

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