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

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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 ammonium phosphate solutions ((NH₄)₂HPO₄), in the presence and absence of four salt solutions (NH₄Cl, NaCl, NH₄F, and NaF) at different ionic strengths, at 200°C and autogenous pressure. The replacement products were analysed 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 NH₄Cl and NaCl and increased significantly with the addition of NaF and NH₄F. The addition of different salts resulted in specific porosity structures resulting from the formation of different phosphate phases. Chlorine-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.

Keywords
Calcite, apatite, fluoride, replacement, pseudomorphism, dissolution-precipitation, porosity

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 behaviour of rocks, an important issue when considering injecting fluids into the upper crust. (Nermoien et al., 2015). Moreover, the relevance of these replacement reactions has been reported in many varying scenarios, such as: CO₂ sequestration (Lackner et al., 2002); the durability of nuclear waste disposal (Geisler et al, 2015); synthesis of new materials (Ben-Nissan et al., 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; Kasioptas et al., 2008, 2010, 2011; Jonas et al., 2013, 2014; Borg et al., 2014).

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:
How does fluid composition influence the evolution of microstructure and porosity generation of the product phase(s)?

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., 2012) 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 (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 μm 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 3mm$^3$, and larger cubes of around 15 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 × 1.5 × 1.5 mm for the small cubes and 3 × 3 × 3 mm for the larger cubes) using a digital caliper.

2.1.2 Fluids

Pure solid ammonium phosphate (NH$_4$)$_2$HPO$_4$(Acrôs Organics powder >99.0 %) was used to make a 2M stock solution from which all other solutions (referred to as phosphate solution) were diluted using deionised water MillQ (resistivity > 18 MΩ cm). Five sets of experiments were carried out. Set 1 were experiments with various concentrations of ammonium
phosphatesolutions (0.1 0.5, 1, 2 M). Set 2 to 5 used 1 M ammonium 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 experiment 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 (without the marble) used in the experiments at 200°C (Table 1) and to define the solution speciation and the saturation states of the solutions relative to all potential phases involved in the reactions at the initial stage when the first layer of marble
dissolves into the fluid. As the supersaturation of the fluid is confined to the dissolving mineral surface for the replacement reaction to take place (Pollok et al., 2011; Ruiz-Agudo et al, 2015) calculations of supersaturation were made for a thin a layer of fluid at the mineral-fluid interface (boundary layer) from which the product phase(s) precipitates. For the purposes of estimating supersaturation at the interface, a 0.3 nm thick monolayer of the marble cube (1.5×1.5×1.5 mm) was considered to be dissolving into a thin boundary layer that contained each of the initial fluids (Table 1) used in the experiments at 200°C. The concentration of dissolved carbonate species is calculated by the program after adding the initial conditions. The choice of width of the boundary layer is somewhat arbitrary, but serves to indicate the evolution of supersaturation at the mineral-fluid interface with respect to likely precipitating phases. Two boundary layer thicknesses were used to check for consistency of results, 0.1 and 1 µm (fluid volumes of $1.35 \times 10^{-9}$ and $1.35 \times 10^{-8} \text{cm}^3$, respectively). The solution boundary layer also included magnesium in the equivalent amount present in the marble (0.3 wt.%).

Saturation state is given as SI (saturation index) where $SI = \log \Omega = \log (\text{IAP}/K_{sp})$, where $\Omega$ is the supersaturation, IAP is the ion activity product and $K_{sp}$ is the solubility product. If $SI = 0$, the mineral and solution are in equilibrium, if $SI < 0$ the solution is undersaturated and if $SI > 0$ the solution is supersaturated. Mineral phases that appear with $SI > 1$ will theoretically be supersaturated and thus possibly precipitate. The simulations are presented in tables S1 and S2 of the supplementary material. From these simulations we find that the solutions are most highly supersaturated with respect to hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) in sets 1, 2 and 3, and fluorapatite in experiments 4 and 5. Tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) is second most supersaturated in set 1 and third in all other sets. Chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) is second in sets 2 and 3, and hydroxyapatite in sets 4 and 5.

2.3.2 X-ray Diffraction

To identify the mineral product phases using powder X-ray diffraction (XRD), the larger reacted samples were dried and powdered in an agate mortar. An X’Pert PW 3040 PANalytical diffractometer and the X’Pert Data Collector software were used to collect the diffraction data in the range $5^\circ$–$75^\circ$ 2 Theta using CuKα1 radiation. The step size was 0.014°2Theta. The primary monochromator used was a Johannson monochromator with a Ge crystal cut on plane (111). The measurement time for each sample was 66 min. An initial analysis of the results was made with the X’Pert High Score and X’Pert Data Viewer. Following the protocol from Jonas et al., (2014),
a beta tricalcium phosphate (TCP) powder (Sigma-Aldrich ≥ 98%) was measured for comparison with the results.

2.3.3 Scanning electron microscopy (SEM)

For qualitative chemical analysis and visualization of the replacement textures and porosity microstructures, the smaller reacted cubes were mounted in epoxy resin, sectioned through the centre, polished and C-coated ready for imaging in a SEM (JEOL JSM-6610LV) equipped with energy-dispersive X-ray analysis (EDX) and an electron back-scattered detector.

2.3.4 Electron microprobe analysis (EMPA)

For quantitative chemical analysis and element mapping, small polished cross-sections of the samples were analysed using an electron microprobe (JEOL JXA 8900 Superprobe), equipped with a wavelength dispersive X-ray spectrometer (WDS) and an energy dispersive X-ray spectrometer (EDS). The point analysis was made using 15 kV accelerating voltage, an electron beam current of 4 nA, and a probe diameter of 3 µm. A minimum of 20 points were analysed in each sample. The mapping was made using 15 kV, a beam current of 50 nA, and 0.5 µm diameter. The major components analysed were those present in the solution that could potentially be incorporated in the replacement product (i.e. CaO, P₂O₅, NaO, MgO, Cl, and F). Molar proportions of the elements analysed were calculated on the basis of 13 oxygens for apatite (Ca₅(PO₄)₃(OH,F,Cl)). The amount of water in apatite (as OH) was calculated assuming ideal mixing of Cl, F, and OH on the anion position.

2.3.5 Raman spectroscopy

For better characterization of the crystal phases involved, micro-Raman spectroscopic analysis was performed on one of each of the samples of the five experiment sets, with a high-resolution Horiba Jobin YVON Xplora Raman system equipped with a confocal microscope (Olympus BX51), using an near infra-red 785 nm laser as excitation source. For searching the OH vibrational band, a higher energy laser was necessary (green, 532 nm). The spectrum of the TCP powder used in XRD analysis was also measured for comparison. The Raman light was collected in 180° backscattering geometry and dispersed by a grating of 1200 grooves/mm to allow the recording of the frequency ranges between 100 and 1200 cm⁻¹ (to include the main phosphate vibrational modes), and between at 3000 and 3600 cm⁻¹ (searching for OH stretching vibrations). A x100 objective lens yielded a theoretical spot diameter of 1.1 µm. The spectrometer was calibrated.
against the first order Raman band of silicon located at 520.7 cm\(^{-1}\). Spectra bands were fitted with the Fityk (0.9.8) software (Wojdyr, 2010) using a Lorentzian function.

3. Results

3.1 Replacement products (solids)

3.1.1 X-ray diffraction analysis

The XRD powder patterns of the samples from experiment set 1 (reacted with the phosphate fluid) and experiment sets 2 and 3 (reacted with phosphate plus chlorine-containing fluids) showed the same diffraction peaks. These were compared with the powder patterns of the expected mineral products. Specifically, calcite (CaCO\(_3\)), tricalcium phosphate (TCP - Ca\(_3\)(PO\(_4\))\(_2\)), hydroxyapatite (HAP - Ca\(_5\)(PO\(_4\))\(_3\)OH), chloroapatite (ClAp - Ca\(_5\)(PO\(_4\))\(_3\)Cl), and fluorapatite (FAP - Ca\(_5\)(PO\(_4\))\(_3\)F). All patterns could be found in the (X’Pert) database with the exception of TCP that was measured in this study. In experiment sets 1, 2 and 3 calcite, HAP and TCP peaks are present (e.g. Fig. 1a) and in experiment sets 4 and 5 (reacted with fluoride) only FAP was present (e.g. Fig. 1b).

3.1.2 Extent of replacement and texture

After reaction, the external dimensions (~1.5 × 1.5 × 1.5 mm) and the cubic morphology of all samples were preserved. BSE images and EDX analyses of cross-sections of the reacted samples revealed that after four days of reaction some samples were partially replaced while others were fully replaced (details in Table 1). The BSE images also show that the internal microstructure of the marble was reproduced in the new mineral, including the shape and position of grain boundaries, and many fractures of the original marble. Importantly, the mineral replacement product contained newly formed porosity.

Partially replaced samples included all samples from sets 1, 2 and 3 (e.g. Fig. 2a, b, c). The extent of reaction and the shape of the reaction front was different in each case. Partially replaced samples had sharp compositional reaction interfaces between the parent and the product material that evolved heterogeneously (at different rates) from the surface to the core of the samples, resulting in an irregular and scallop-shaped reaction rim (e.g. Fig. 2a). Inside the reacted rim, sections (up to 10 \(\mu m\)) of unreacted marble were “left behind” by the main reaction front (e.g. Fig. 2a). Even in the samples in which the reaction reached the core, these unreacted pieces of marble were mostly still present (e.g. Fig. 2b). Sometimes these unreacted parts are located at the
centre of individual grains, but there are many areas where these are crossed by grain boundaries and fractures. Moreover, these unreacted parts typically occur closer to the surface of the samples, although in the highly concentrated fluid (2 M of ammonium phosphate) they appear randomly distributed and throughout the sample (Fig. 2b).

The samples reacted with a small amount of Cl-containing fluids (0.01 M) were almost fully reacted, having only a small quantity of unreacted marble near the surface. Increasing concentrations of ammonium chloride and sodium chloride added to the phosphate fluids resulted in a dramatic decrease of the extent of reaction (e.g. Fig. 2c). The reaction rim decreased from an average width of ~500 µm in the samples reacted with 0.1 M NH₄Cl to only ~50 µm width in the samples reacted with 0.5 and 1 M NH₄Cl. With NaCl, the negative impact on the replacement rate was even greater. With 0.1 M NaCl the reaction rim was only ~25 µm thick, with 0.5 M it decreased to ~10 µm, and with 1 M almost no reaction occurred (< 10 µm rims). The thin reaction rims surrounded the edge of the marble grains, even in grains located at the inner part and core of the samples (e.g. Fig. 2c). In sets 4 and 5, almost all samples were fully reacted (e.g. Fig. 2e, f) with the exception of the samples reacted with 0.01 M of F-containing fluids (e.g. Fig. 2d), and one of the samples reacted with 0.25 M NaF that still contained unreacted marble at its core.

3.1.3 Porosity structures

Although the unreacted Carrara marble contained a number of fractures as well as grain boundaries that conferred some initial porosity and permeability to the samples, the porosity described here is that generated by the replacement reactions.

Using BSE images we investigated the porous structure at a submicron scale. To help to interpret the experimental results, the newly formed porosity is classified as:

- Type 1 – Very fine (<1µm) and round pores (examples in Fig. 3)
- Type 2 – Coarser pores, more or less elongated, of 1 to 10 µm diameter (examples in Fig. 3)

A summary of the porosity types found in each reacted sample is shown in Table 1.

In some samples a small gap of less than 1 µm (Fig. 3a) was present at the interface between unreacted and reacted minerals, but in most samples there was no visible gap (from SEM
images). Quenching effects, as the samples were quickly cooled and then exposed to the atmosphere, cannot be ruled out as a cause of slight sample changes.

In experimental sets 1, 2, and 3, Type 1 pores were mainly located in the interior of grains and Type 2 pores were located at the edge of reacted grains adjacent to grain boundaries (Fig. 3b). The structures that contain Type 2 pores seem to have formed at initial stages of the replacement reaction that proceeded from the grain boundaries into the grains. However, in samples reacted with 0.5 and 1.0 M NaCl the opposite was observed: Type 1 pores were at the edge of the grains and Type 2 in the mineral product inside the grain, indicating that the replacement product evolved from the less porous (Type 1) grain surface (right side of Fig. 3c) to a coarser porosity (Type 2 on the left side of Fig. 3c).

In experiments 4 and 5, the type of porosity appears to correlate with fluoride concentrations. In samples reacted with a low F concentration (0.01 M) the replacement at the surface of the sample contains Type 2 porosity and no unreacted marble. This surface replacement is underlain by another replacement microstructure resembling that of experiment set 1 (Fig. 3d). Porosity in the samples reacted with slightly higher F concentrations (between 0.1 and 0.25 M) was quite homogeneous, mostly round-shaped, and of Type 1. With 0.5MF concentration the porosity was of Type 1, but at the core of the samples a geometrically differentiated microstructure of slightly coarser (Type 2) porosity formed (Fig. 3e, f).

3.1.4 Element distribution and its relationship to porosity

The average chemical composition of the replacement products of all samples calculated from EMPA point measurements is presented in supplementary material in Tables S3 and S4. EMPA maps of the element distribution of the samples from sets 1, 2, and 3 show that in a number of samples calcium and phosphorous were not homogeneously distributed in the replaced phase(s), varying as a function of the different porosity structures present.

In sets 1, 2 and 3, the mineral phase with Type 1 porosity contained lower Ca (Fig 4a, d) counts and higher P counts (Fig. 4b, e, g). Conversely, in Type 2 porosity there were higher Ca counts and lower P (same corresponding figures). This indicates the possibility of different mineral phases. This is further supported by Raman analysis. Raman intensity maps (Fig. 5) of a sample from set 1 show that in the same type of porosity (Type 1 or Type 2) located next to grain boundaries (“Y” shape seen in the Raman maps) the hydroxyapatite band at 961 cm\(^{-1}\) is very
intense and loses intensity with increasing distance where Type 1 porosity is seen. These maps also show that the tricalcium phosphate (TCP) band at 405 cm\(^{-1}\) occurs in between the grain boundaries and the unreacted marble characterized by porosity Type 1. Calcite bands (154, 281, 1087 cm\(^{-1}\)) occur where the unreacted marble is located. An example of a spectrum taken at each one of these locations is given in Fig. 6a (unreacted marble), b (porosity Type 1), and d (porosity Type 2). A spectrum of a commercial TCP powder is shown in Fig. 6c for comparison with the spectrum of porosity Type 1 phase. In summary, hydroxyapatite is located at the edge of the grains where the porosity is coarser (Type 2), and TCP (or a very similar mineral) formed in the interior of the grains where the porosity is finer (Type 1). Hydroxyapatite location (next to the grain boundaries) is also marked by the absence of Mg seen in the microprobe map of Fig. 4c. A list of the Raman vibrational bands of the spectra shown in Fig. 6 is presented in Table S5 of supplementary material.

In the three first sets, the OH\(^{-1}\) stretching vibration band was found at 3573(1) cm\(^{-1}\) both in the hydroxyapatite location (next to the grain boundaries) and, unexpectedly, at 3569(1) cm\(^{-1}\) at the interior of grains of porosity Type 1 where the vibrational band of TCP (405 cm\(^{-1}\)) is present (in its pure state OH is not present in this mineral phase). In sets 2 and 3 (reacted in the presence of chlorine salts), EMPA showed that chlorine was present in trace amounts and only in three samples (reacted with 1 M NH\(_4\)Cl, 0.5 M and 1 M NaCl in the fluid) at not more than 0.2(1) wt.%. In set 3 (reacted with NaCl), Na was present in all samples and reached 2.1(2) wt.%, although it is unclear if this Na was present as dried fluid in the grain boundaries or in the pores. Na concentrations are higher at the coarser porosity side (Fig. 4f). Moreover, with an increase of NaCl in the fluids, the total wt.% of elements decreased considerably from 94(3) to 85(5) wt.% probably due to the increasing proximity of the measurement to the grain boundaries. It is worth noting that the increase in NaCl concentration in the fluid inverted the locations of the 2 porosity types compared to all other samples. Here, porosity Type 1 (finer) occurred next to the grain boundaries where Ca counts are lower and P are higher, and the coarser porosity (Type 2) occurred in the interior of grains where opposite Ca and P counts occur (Fig. 4d, e). The two porosity Type locations shown in Fig. 4d and 4e were used for a more detailed EMPA analyses to determine whether they correspond to two different mineral phases (Table 2). In this sample Type 1 porosity has a Ca:P wt.% ratio close to that of tricalcium phosphate (1.95), and Type 2 porosity that developed into the grains approximates the ratio of hydroxyapatite (2.16). The opposite
trend (finer porosity at the centre of core and coarser at the grain boundaries) is seen in all the other samples. The chemical composition of the two distinct porosity areas (Table 2) were recalculated on the basis of a suitable number of anions for both HAP (13 oxygens) and TCP (8 oxygens). Finer porosity resulted in areas containing $\text{Ca}_{2.9}(\text{PO}_4)_2 + 0.2 \text{ Na}$ and the coarser porosity for $\text{Ca}_{5.3}(\text{PO}_4)_3\text{OH} + 0.1 \text{ Mg} + 0.3 \text{ Na}$.

The samples reacted in the presence of fluoride gave homogeneous distributions of Ca, P, Mg and Na (when present), with two exceptions - samples reacted with very high F concentration (0.5 M), and samples reacted with very low F concentration (0.01 M). The former (high F) showed a high deviation of results at the centre of the cube, registering standard deviations up to 50%, probably due to residue from dried fluid inside this sample because the porosity was slightly coarser at the centre of these samples (Fig. 3e and 3f). In both sets, fluoride average content increased linearly ($R^2 = 99\%$) in the product samples with increasing F used in the fluids. The second (reacted in very low F concentration) shows that the coarser porosity structure (Type 2) that formed at the surface of the sample is a fluoride-containing replacement rim (Fig. 4h), confirmed by Raman analysis to be fluorapatite (Fig. 6e). In the fluoride-free part, element distribution (comparing Fig. 4b, g, h) and Raman spectra are the same as in the samples reacted with the ammonium phosphate alone. The main interface between the F-containing and F-free phases is marked by a Mg peak (Fig. 4i), and similar to the samples of set 1, is absent around the grain boundary (the location of the grain boundary is marked with a black line in Fig. 8g). In all other samples reacted with fluoride, Mg was homogeneously distributed, but appeared as spots of higher intensity in the replaced areas. In these samples the OH band was not detected in the Raman spectrum.

The average chemical formula of fluorapatite samples calculated from the EMPA results were:

- Set 4: $\text{Ca}_{10.1(1)}(\text{PO}_4)_{5.9(2)}F_{1.8(4)}\text{OH}_{0.2(4)} + 0.1(0)\text{ Mg}$
- Set 5: $\text{Ca}_{10.1(2)}(\text{PO}_4)_{5.9(1)}F_{1.6(5)}\text{OH}_{0.4(5)} + 0.2(1)\text{ Mg} + 0.3(1)\text{ Na}$

3.1.5 Mass changes

The relative mass changes before and after each experiment (Table 1) were used to infer the extent of reaction, and in fully reacted samples the mass changes were used to estimate the total porosity. All experimental samples (except the samples reacted in 1 M (NH$_4$)$_2$HPO$_4 + 0.5$ M NH$_4$F) had higher densities (positive weight changes) after reaction. In experiment set 1 the
relative mass of the samples increased with increasing ammonium phosphate concentration in accordance with the higher degree of replacement. In experiment sets 2 and 3, adding increasing amounts of ammonium chloride resulted in a slight decrease of the relative mass in accordance to the lower degree of replacement. However, the mass of samples reacted with fluoride-containing fluids was not consistent with the degree of replacement. Samples reacted with 0.1 M F (fully replaced samples) were heavier than those reacted with 0.01 M F (partially replaced), but the samples reacted with 0.25 M F (also fully reacted) were lighter than the previous (reacted with 0.1 M F), and with 0.5 M F even lighter (the relative wt.% change is lower, Table 1). This is most likely due to the variations in the porosity in each case.

3.2 Replacement products (fluids)

To identify if some of the parent material (calcium and trace magnesium present in the marble) was transferred to the bulk fluid, the chemical compositions of the initial and final fluids were analysed. The initial fluids contained neither calcium (Ca) nor magnesium (Mg). Parent material losses into the bulk fluid contribute to solid weight losses. In the final fluids very small quantities of Mg and Ca were found. The chemical analyses (ICP-OES) of the fluids after reaction and the respective mass loss, due to element release, are shown in Table 3. There was a slightly higher concentration of Ca and Mg in the fluids after reaction with higher salt concentrations. The highest Ca loss was from the sample reacted with 2 M ammonium phosphate and the minimum with 0.1 M. The highest Mg loss was from the sample reacted with 0.25 M NH₄F. The maximum Mg loss from sets 1, 2, and 3 was from the sample reacted with 1 M NaCl. The pH of the bulk fluids did not change during the experiments; initial and final pH of all fluids averaged 7.8(1).

3.2.1 Fluid pathways and replacement rates

BSE images of the reacted samples showed that the fluid transport pathways depended on the fluid composition. With ammonium phosphate the aqueous fluid moved arbitrarily both through grain boundaries and through the newly formed porosity (Fig. 2a). With the addition of chlorine in the fluids and decreasing replacement rates, fluid transport through grain boundaries was highly preferred (Fig. 2c). With fluoride-containing fluids the replacement rates were very high and transport through the newly formed porosity was preferred. Evidence of this can be seen in almost fully replaced samples that show no replacement around grain boundaries ahead of the
main reaction front, also evidenced by the lack of any relict unreacted marble within the reaction rims (Figures 2e and 2f).

4. Discussion

All experiments involved the reaction of a calcium carbonate rock (Carrara marble) with different concentrations of phosphate fluids (with and without the addition of chloride and fluoride salts) and resulted in the pseudomorphic replacement of the rock by new phosphate product phases while retaining the external dimensions of the marble parent phase. The conservation of volume results from the high degree of coupling between the dissolution and the precipitation processes within a fluid boundary layer at the parent solid-fluid interface (Putnis and Putnis, 2007). All products were porous, thus allowing progress of the phosphate-bearing solution to the reaction interface within the marble. Such pseudomorphic replacement reactions have been previously reported and described as an interface-coupled dissolution-precipitation mechanism (see Putnis, 2009, and references therein).

4.1 End products

The end products of the experiments performed here resulted in calcium phosphate phases with variable composition. This is not surprising, given the variability of fluid composition and the wide range of element substitutions possible within the apatite crystal structure (Hughes and Rakovan, 2015).

Geochemical modeling performed with PHREEQC (Parkhurst and Appelo, 1999) has proven to some extent to be successful for predicting the end products of the reaction of the marble with the five phosphate bearing solutions (adding the two chloride and the two fluoride salts). For set 1, PHREEQC predicted that at initial conditions the mineral with the highest saturation index was hydroxyapatite (HAP) followed by tricalcium phosphate (TCP), and both minerals were found in the reacted samples. For set 2 and 3, the prediction was not as accurate. The SI of chlorapatite (ClAP) was predicted to be the second highly saturated mineral after HAP and followed by TCP, however no measurable ClAP occurred in the reacted samples and only HAP and TCP were present. For sets 3 and 4, the model predicted fluorapatite as being the most highly supersaturated phase and it was indeed the only phase found in the reacted samples of these sets.

In a closed system (such as in batch experiments) the replacement reaction results in local changes in the composition of the bulk fluid, but most importantly, inside the newly-formed pores
of the sample itself. An evolving solution composition as the reaction interface moves through the reacting crystal, allowing for diffusion of elements within the fluid phase, may also be responsible for the heterogeneity of end-products (such as in experiment sets 1, 2, and 3). Similar examples of compositional and phase variability resulting from replacement reaction has been reported for the replacement of calcite by both dolomite and magnesite (Etschmann et al., 2014) as well as in apatite replacement in the presence of As in solution (Borg et al., 2014). In both cases this was ascribed to variations in composition and hence local equilibrium at a reaction interface. From EMPA point analyses it was seen that none of the samples matched the stoichiometric Ca:P atomic ratio of apatite (1.67), and the maps showed different distributions of calcium and phosphate, but also the presence of F, and minor Mg, Na, and Cl in the replacement products (dependent on original fluid composition), that suggests possible incorporation of these elements in the apatite structure during replacement. The possibility of incorporating CO$_3^{2-}$ in the apatite structure is discussed later.

Considering our results, the general chemical equations of the replacement reactions can be written for sets 1, 2, and 3 as,

$$5 \text{CaCO}_3 (s) + 3 \text{HPO}_4^{2-} (aq) + \text{H}_2\text{O} \rightarrow \text{Ca}_5(\text{PO}_4)_3\text{OH} (s) + 5 \text{CO}_3^{2-} (aq) + 4 \text{H}^+ (aq),$$

and

$$3 \text{CaCO}_3 (s) + 2 \text{HPO}_4^{2-} (aq) \rightarrow \text{Ca}_3(\text{PO}_4)_2 (s) + 3 \text{CO}_3^{2-} (aq) + 2 \text{H}^+ (aq),$$

with trace amounts of Mg$^{2+}$ and Na$^+$ (when present) substituting for Ca$^{2+}$, and possible CO$_3^{2-}$ substitution for OH$^-$ and/or PO$_4^{3-}$.

For sets 4 and 5 as,

$$5 \text{CaCO}_3 (s) + 3 \text{HPO}_4^{2-} (aq) + \text{F}^- \rightarrow \text{Ca}_5(\text{PO}_4)_3\text{F} (s) + 5 \text{CO}_3^{2-} (aq) + 3 \text{H}^+ (aq),$$

With possible minor trace amounts of Na$^+$ substituting for Ca$^{2+}$, and CO$_3^{2-}$ substituting for OH$^-$ and/or PO$_4^{3-}$.

4.2 Porosity generation

Results showed that the different porosity microstructures are directly linked to the chemical and mineralogical changes in the reacted samples. The precipitation of different phases depends on the saturation state of the fluid, and the different solubilities, molar volumes and morphologies of the precipitating phases will determine the porosity (Pollok et al., 2011). Thus ultimately fluid
chemistry determines porosity and the composition of the fluid at the reaction interface depends on the fluid and element transport through the reaction rims. A more homogeneous porosity distribution was associated with a homogeneous distribution of elements (Ca, P, F, Mg), such as in samples reacted with moderate F contents (0.1 and 0.25 M). The distinct porosity Type 2 that was present at the edge of replaced grains was identified as being a magnesium-depleted area (from EMPA maps) and Raman analysis showed that the product was hydroxyapatite. Where the porosity was finer (Type 1) Raman spectra significantly changed, identifying other mineral phase(s) present (TCP, or a hydroxyapatite solid solution).

Assuming that the end product of the first three experiment sets was a mixture of tricalcium phosphate (TCP) and hydroxyapatite (HAP), and in the last two sets fluorapatite (FAP), the theoretical molar volume changes that would result from these replacement reactions is -8.7% for TCP, -13.8% for HA, and -14.7% for FAP. On this basis alone, it is expected that the replacement of calcite by FAP results in the highest porosity, followed by HAP and TCP. However, the solubility differences between parent and product phases in the solution at the interface are not known precisely. Furthermore as the fluid composition evolves during the replacement reaction, so do the relative solubilities of the associated phases in the evolving fluid at the reaction interface. As fluorapatite is the least soluble of the apatite phases this would also add to an increased volume deficit and hence higher porosity for the case of FAP. Although a more detailed measurement of total porosity would be needed (such as by use of microtomography), results showed, as expected, that samples replaced by FAP effectively contained larger pores than the product mixture of TCP and HAP.

From SEM observations, the samples reacted with NaF have coarser porosity than those reacted with NH₄F although, Table 4 shows that the samples reacted with the same concentration of NH₄F have higher total porosity. The different scale of the porosity in each case may reflect the effect of fluid composition on the nucleation density of the apatite, with the presence of NaF resulting in lower nucleation density, larger crystals and coarser porosity while the presence of NH₄F results in high nucleation density, finer crystals and porosity on a much finer scale. Such results have implications for the design of porous apatite materials using the replacement route. For example, for the conservation of cultural heritage (Sassoni et al., 2011), the replacement of limestone by a less soluble material such as apatite might be more durable, however, due to high porosity it might break easily losing its suitability. The replacement of calcite by apatite could
represent a route for the development of a ceramic for medical application (Vallet-Regí, 2001). There is a clinical need for new bone replacement materials that combine long implant life with compatibility and appropriate mechanical properties. Dissolution-precipitation is a process that has been proposed for the synthesis of porous biocompatible material (apatite) for bone implants (Heness and Ben-Nissan, 2004).

4.2.1 Estimating porosity by examining weight changes

The weight percentage (wt.%) change between unreacted and reacted samples depends not only on the progression of the reaction, but also on the density differences between the parent and product phase(s), and on the total porosity formed. Moreover, the total porosity depends on the molar volume changes and the solubility differences between the parent and product (Pollok et al., 2011). The generation of porosity is a key factor for the progression of reaction because it creates the pathway for fluid infiltration towards an ongoing reaction front. The simple fact that we obtained fully reacted samples indicates that this pathway (or permeability) existed at least until full replacement of the samples occurred.

For fully-reacted cubes that did not change size after reaction (pseudomorphed), the total volume of the pores formed can be determined from the difference in expected weight (if there was no porosity) and the actual weight measured after the sample is dried. Using the initial sample (Carrara marble microprobe analysis, calcite 99.7%) density calculated as pure calcite (2.71 g/cm$^3$) and the density of fluorapatite (FAP) as 3.20 g/cm$^3$, the porosity of most of the samples replaced by fluorapatite could be calculated (Table 4). The relative molar volume difference between calcite and fluorapatite is -14.7%. This matched the amount of porosity formed in the samples reacted with 0.5 M NaF in the phosphate fluid (Table 4). Samples reacted with higher F-content in the fluid had higher porosity (Table 4) and higher but more variable F counts in the EMPA data. This suggests that samples reacted with fluids containing a higher F content approximate to end-member fluorapatite, while samples reacted with lower F content are possibly replaced by hydroxyfluorapatite (Ca$_{10}$(PO$_4$)$_6$OH$_x$F$_{2-x}$) which would be slightly less porous because the relative volume difference between calcite and HAP (-13.4%) is lower than between calcite and FAP (-14.7%).

4.3 The role of fluoride in the replacement reaction
Fluoride salts were added to the phosphate fluids in experiment sets 4 and 5. Fluorapatite is the least soluble compound among the three common calcium orthophosphates (Ca$_5$(PO$_4$)$_3$(OH,Cl,F), (Dorozhkin, 2007). This was also the main replacement product in our experiments when F was added to the fluids, as was confirmed by EDX and Raman analyses. F-containing fluids also significantly enhanced replacement rates. Fluoride added as NH$_4$F resulted in even higher replacement rates than with NaF. The replacement products contained overall homogeneous porosity structures, no unreacted marble, and less chemical variability in the fluorapatite.

During the replacement of calcite by fluorapatite the “preferred” fluid migration pathway was through the newly-formed porosity rather than along the pre-existing grain boundaries and fractures in the marble. The replacement reaction evolved from the surface into the core of the sample with almost no observable influence of the presence of grain boundaries. This was different from the case for the samples reacted with chloride salts where the reaction took place first along grain boundaries. This suggests different wetting properties of fluids of different composition may influence the preferred reaction path taken, but may also be related to the much faster reaction rate in F-bearing fluids and the formation of fluorapatite.

4.4 The role of carbonates in the replacement reaction

During the replacement of the calcite by calcium phosphates the carbonate may be released to the fluid phase or reincorporated in the new phases. The fact that the pH of the fluids at the end of the experiments did not increase, as would be expected if significant carbonate ions were present, suggests that carbonate released during the dissolution of calcite may have been incorporated into the structure of the product phases. To some extent, this is supported by Raman analysis.

Carbonate apatites are classified in three different types depending on the crystal lattice position of CO$_3^{2-}$: A-type, when it occupies the OH$^-$ site; B-type, when it occupies the PO$_4^{3-}$ site; and AB-type, when it occupies both PO$_4^{3-}$ and OH$^-$ sites. In a Raman study by Awonusi et al., (2007) for heavily carbonated apatites (up to 10%) of B-type, a combination of the $v_1$ vibrational mode of carbonate with the $v_3$ phosphate mode was assigned to a broad band at the region between 1070-1076 cm$^{-1}$. For the same type of substitution, Penel et al., (1998) assigned the band at 1070 cm$^{-1}$, and Antonakos et al., (2007) assigned the bands 1072, 1074, 1075, and 1080 cm$^{-1}$. Besides this
band, all three studies reported two more bands present: one at the $v_3$ mode of $\text{PO}_4^{3-}$ between 1026 cm$^{-1}$ (highly carbonated) and 1030 cm$^{-1}$ (less carbonated); and the other between 1045 and 1047 cm$^{-1}$, also from lower to highly carbonated apatite. In the previously cited studies the $v_1$-$\text{PO}_4^{3-}$ band position of B-type carbonate apatites was located between 959 and 961 cm$^{-1}$.

The Raman signal of the samples from our experiments may have similarities to those in previous studies, specifically, the $v_1$-$\text{PO}_4^{3-}$ band position at around 961-962 cm$^{-1}$, and the variable $v_1$-$\text{PO}_4^{3-}$ bands at around 1028(1), 1044(2), and 1075(1) cm$^{-1}$ (Table S5 supplementary material). Hence, the replacement of calcite by a carbonated apatite seems probable.

4.5 The role of magnesium in the replacement reaction

Magnesium was transported out of the calcite during the replacement reactions. In the F-free fluids the transport of magnesium was localized specifically to the edge of replaced grains and corresponded to the location of hydroxyapatite. The Raman detection of the OH group in the Mg-containing areas might be an indicator that instead of TCP, a hydroxyapatite that incorporated minor Mg and carbonate, such as $(\text{Ca,Mg})_5(\text{PO}_4)_3(\text{OH,CO}_3)$ may be present.

The amount of magnesium in the product fluids of samples replaced by fluorapatite was only slightly higher than in the free-fluorine fluids, but the fact that it appears as spots in the samples might indicate that it was trapped in the pores and the reaction time was not enough to permit its full escape into the bulk fluid. Magnesium is most probably not incorporated into the fluorapatite.

4.6 Fluid composition and replacement kinetics

In this study, higher concentrations of $(\text{NH}_4)_2\text{HPO}_4$ resulted in faster replacement rates. The coupling between dissolution and precipitation that results in pseudomorphic replacement suggests that the rate controlling step is dissolution (Xia et al., 2009b) and that whatever influences the dissolution step would have a similar effect on the replacement kinetics. However, atomic force microscopy (AFM) experiments by Klasa et al. (2013) showed that the dissolution rate of calcite ($\text{CaCO}_3$) is significantly reduced in the presence of $(\text{NH}_4)_2\text{HPO}_4$ in solution, but not in the presence of $\text{Na}_2\text{HPO}_4$ (both solutions pH ~ 8) compared to that observed in pure deionized water, suggesting that the $\text{NH}_4^+$ group may inhibit calcite dissolution. Moreover, the experiments performed here showed that phosphate fluids containing Cl had a negative kinetic effect on the replacement rates, both when adding Cl as NaCl and NH$_4$Cl, with the addition of NaCl having a more significant effect in decreasing the reaction rate than NH$_4$Cl. An AFM study
by Ruiz-Agudo et al., (2010) showed that in the presence of small amounts of NaCl (1 mM), calcite dissolution is slightly higher than in deionized water, and at higher concentrations of NaCl the dissolution rate is enhanced. A further AFM study by Wang et al., (2012) on the replacement of calcite by apatite showed that in the presence of high concentrations (0.5 M) of NaCl, the calcite surface displayed a greater density of calcium phosphate nuclei, indicating that the precipitation of apatite was enhanced in the presence of NaCl. Both studies suggest that the presence of NaCl would increase the replacement rates, because it increases both dissolution of calcite and precipitation of calcium phosphates. However, in this study the presence of NaCl did not increase the replacement rates suggesting that some factors other than dissolution rate and precipitation rate may affect the overall reaction rate. On the other hand, the AFM experiments were carried out under quite different conditions of fluid flow over a free cleaved calcite surface and so the chemical composition of the fluid was maintained constant, not allowing for fluid re-equilibration. In our experiments it is possible that the higher NaCl concentrations together with PO$_4^{2-}$ in solution effectively increased the threshold for supersaturation of the precipitating phase within the boundary layer.

4.7 Fluid transport

During a replacement process, natural porosity of rocks, such as grain boundaries and fractures, play an important role in allowing fluid access within the rock. This enhances the available internal surfaces where replacement reactions are initiated. Fluid movement through newly formed pores plays an important role in the advancement of a reaction front. If fluid movement was limited, the reaction front may be arrested. In this case the replacement process would stop. Fluid movement could also be limited by the loss of permeability. Permeability depends on the interconnection of pores formed in the product phase. When a sample is fully replaced, such as occurred in several samples of sets 3 and 4, this indicates that it was, at least temporarily, permeable. The importance that interfacial fluid composition plays on replacement reactions is extensively reported in Putnis (2009).

Our results indicate that there are two types of fluid preferred pathways: along grain boundaries and fractures and through newly-formed connected pores. We hypothesize that when replacement rates are very low, the absence of newly formed porosity results in the motion of fluid along the grain boundaries, resulting in the replacement of interior grains (both surface and interior grains contained very small replacement rims), as seen with the samples reacted with high chloride.
content solutions. On the other hand, when replacement rates are high, the fluid moves through
the newly formed pores seen in the samples reacted in the presence of fluoride. The movement
of the fluid preferentially through newly-formed pores rather than fractures and grain boundaries
may be related to wettability. The product and parent phases have different critical surface
tensions that are determined by the chemistry of each solid phase, and therefore have different
surface tension or wetting properties. However, in the absence of data on the wetting properties
of different fluid compositions on calcite at the temperature of the experiments this hypothesis
could not be tested.

Conclusions

This study demonstrates that fluid composition of a reacting fluid controls the chemical
composition, mineralogy, and porosity generated in a product during a pseudomorphic
replacement reaction. All experiments on the replacement of calcite by Ca-phosphate shared the
typical characteristics of an interface-coupled dissolution-reprecipitation mechanism.

Carrara marble (calcite) can be replaced by hydroxyapatite and another phase that shares many
similarities to tricalcium phosphate upon reaction with a phosphate solution (\((\text{NH}_4)_2\text{HPO}_4\)). The
addition of NH\(_4\)Cl and NaCl to this solution resulted in the same product phases. However, in the
presence of fluoride as dissolved NH\(_4\)F and NaF, the mineral product was fluorapatite.

Reaction rates were affected by both the composition and ionic strength of the bulk fluids. An
increase in the phosphate concentrations in the fluid increased the replacement rates. For the same
concentration of phosphate, the addition of increased amounts of chloride (Cl) lowered the
replacement rates. The inhibitory effect of chloride added as NaCl was higher than when added
as NH\(_4\)Cl, indicating that the cations Na\(^+\) and NH\(_4\)^+ may play an important role in the kinetics of
this replacement reaction. In the presence of fluoride the reaction rates were greatly increased and
the product phases were uniform in composition. All samples reacted with 0.1 M or more of
fluoride ions were fully reacted within the reaction time. In the presence of a small amount of
fluoride (0.1M) the reaction resulted first in the generation of a fluorapatite rim and proceeded
inwards from the surface to the core of the marble cube.

Porosity within the replacement products varied with the chemical composition of the fluids, and
depended mostly on the mineral phase that was precipitating. Porosity conferred permeability to
the rock during replacement, permitting mass transfer between the bulk fluid and the reaction
interface. The presence of grain boundaries also conferred permeability to the rock samples. Both mass transfer pathways were significant for the replacement using phosphate fluids alone, but with the addition of chloride salts the replacement rates decreased significantly and the mass transfer through grain boundaries became increasingly dominant. With fluoride-containing fluids grain boundary mass transfer was not as important because the rapid advance of the reaction front resulted in preferred mass transfer through the newly formed porosity.

This study demonstrates the important impact that small differences in fluid composition can have on the progression of solid-liquid reactions. Small fluid compositional changes can change the nature of the products, the microstructure and texture of rocks and the resultant porosity and permeability. This is significant for the interpretation of microstructures in rocks as well as for the synthesis of new materials.

Acknowledgements

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References


Figure captions

Figure 1 Example of an XRD powder pattern representative of: (a) samples from experiment sets 1, 2 and 3 (reacted with ammonium phosphate and with chloride salts). The peaks matching calcite (CaCO$_3$), hydroxyapatite (HAP), and tricalcium phosphate (TCP) patterns are indicated; (b) samples from experiment sets 4 and 5 (reacted with ammonium phosphate plus fluoride salts) that matched fluorapatite.

Figure 2 BSE images of cross sections of Carrara marble cubes reacted for 4 days at 200°C, using different solutions: (a) 0.5 M (NH$_4$)$_2$HPO$_4$; (b) 2 M (NH$_4$)$_2$HPO$_4$; (c) 1 M (NH$_4$)$_2$HPO$_4$ + 0.5 M NaCl (d); 1 M (NH$_4$)$_2$HPO$_4$ + 0.01 M NaF (similar result with 0.01 M NH$_4$F); (e) 1 M (NH$_4$)$_2$HPO$_4$ + 0.5 M NH$_4$F; (f) 1 M (NH$_4$)$_2$HPO$_4$ + 0.5 M NaF. Darker grey areas correspond to the unreacted marble and brighter grey areas to the replacement product. The squares indicate the sites of the zoom areas as shown in Figure 3.

Figure 3 Detail BSE images of the mineral and porosity textures of areas assigned in Figure 2a, b, c, d, e and f, respectively. Darker grey areas correspond to the unreacted marble and brighter grey areas to the replacement product. Black areas correspond to pores.

Figure 4 Electron microprobe element maps (100×100 µm) of samples reacted with: (a), (b), and (c) 1 M (NH$_4$)$_2$HPO$_4$; (d), (e) and (f) 1 M (NH$_4$)$_2$HPO$_4$ plus 0.5 M NaCl; (g), (h), and (i) 1 M (NH$_4$)$_2$HPO$_4$ plus 0.01 NaF.

Figure 5 Example of a Raman spectra measured at: (a) unreacted marble (b) core of a fully replaced grain of set 1 (reacted with ammonium phosphate and finer porosity - Type 1) (c) commercial (beta) tricalcium phosphate powder; (d) surface of a replaced grain right next to the grain boundary (reacted with ammonium phosphate and coarser porosity - Type 2); (e) samples reacted with fluoride-containing fluids (sets 4 and 5).

Figure 6 Intensity maps (85 × 85 µm) of Raman vibrational bands in the area assigned in Fig. 2b (the maps are mirror images of Fig. 3b). The sample was reacted with 2 M (NH$_4$)$_2$HPO$_4$ at 200°C for 4 days. Each map corresponds to one vibrational band.
Table 1 Summary of experimental and calculated results

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Fluid solution</th>
<th>Solid samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n (NH$_4$)$_2$HPO$_4$</td>
<td></td>
</tr>
<tr>
<td>Set 1</td>
<td>n (NH$_4$)$_2$HPO$_4$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1 2.0</td>
<td>8.8 ± 0.5</td>
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<tr>
<td></td>
<td>0.5 0.9</td>
<td>9.3 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>1 2.1</td>
<td>8.7 ± 0.8</td>
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<tr>
<td></td>
<td>2 4.7</td>
<td>8.5 ± 0.9</td>
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<td>(NH$_4$)$_2$HPO$_4$ + n NH$_4$Cl</td>
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</tr>
<tr>
<td></td>
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<td>8.4 ± 1.2</td>
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<tr>
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<td>8.8 ± 0.7</td>
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<td>1 2.6</td>
<td>7.9 ± 2.1</td>
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<td>Set 3</td>
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<td>Set 4</td>
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<tr>
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<td>Set 5</td>
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<td></td>
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<td>8.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>0.25 2.3</td>
<td>6.9 ± 1.1</td>
</tr>
</tbody>
</table>

Table 2 Electron microprobe results of the replacement product of a sample reacted with 1 M ammonium phosphate plus 0.5 M sodium chloride, showing the contrast between areas of finer and coarser porosity. Values normalized to 100 wt.%.

<table>
<thead>
<tr>
<th>wt.%</th>
<th>Na$_2$O</th>
<th>CaO</th>
<th>Cl</th>
<th>MgO</th>
<th>P$_2$O$_5$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1 porosity (Ca/P = 1.86)</td>
<td>1.78 ± 0.22</td>
<td>52.49 ± 1.32</td>
<td>0.04 ± 0.03</td>
<td>0.6 ± 0.1</td>
<td>46.1 ± 1.5</td>
<td>100.01 ± 0.01</td>
</tr>
<tr>
<td>Type 2 porosity (Ca/P =</td>
<td>2.31 ± 0.11</td>
<td>56.39 ± 0.6</td>
<td>0.6 ± 40.6</td>
<td>100.01 ± 0.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3 Ca and Mg concentrations (measured by ICP-OES) in the bulk fluid after reaction and the respective mass lost by the samples. Both Ca and Mg were measured using a minimum of two wavelengths, and standard deviations were lower than 0.06 ppm for Ca and 0.02 ppm for Mg.

<table>
<thead>
<tr>
<th></th>
<th>sets 1, 2, 3</th>
<th>sets 4, 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca</td>
<td>Mg</td>
</tr>
<tr>
<td>Min (mg/L)</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Max (mg/L)</td>
<td>3.6</td>
<td>2.7</td>
</tr>
<tr>
<td>Average (mg/L)</td>
<td>1.1 ± 0.5</td>
<td>0.9 ± 0.8</td>
</tr>
<tr>
<td>Mass loss (wt.%)</td>
<td>0.02 ± 0.01</td>
<td>0.02 ± 0.02</td>
</tr>
</tbody>
</table>

Table 4 Average porosity (%) of samples fully replaced by fluorapatite.

<table>
<thead>
<tr>
<th>Fluid composition</th>
<th>NH₄F</th>
<th>NaF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M (NH₄)$_2$HPO₄ + 0.1 M</td>
<td>12.7 ± 0.4</td>
<td>10.6 ± 0.3</td>
</tr>
<tr>
<td>1 M (NH₄)$_2$HPO₄ + 0.25 M</td>
<td>13.8 ± 0.2</td>
<td>12.3</td>
</tr>
<tr>
<td>1 M (NH₄)$_2$HPO₄ + 0.5 M</td>
<td>15.5 ± 0.1</td>
<td>14.7 ± 0.0</td>
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