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The role of grain boundaries and transient porosity in rocks as fluid pathways for reaction front propagation



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ABSTRACT

The pseudomorphic replacement of Carrara marble by calcium phosphates was used as a model system in order to study the influence of different fluid pathways for reaction front propagation induced by fluid-rock interaction. In this model, grain boundaries present in the rock as well as the transient porosity structures developing throughout the replacement reaction enable the reaction front to progress further into the rock as well as to the center of each single grain until transformation is complete. Hydrothermal treatment of the marble using phosphate bearing solutions led to the formation of hydroxylapatite and β -TCP; the formation of the latter phase was probably promoted by the presence of ~0.6 wt.% Mg in the parent carbonate phase. Completely transformed single grains show a distinctive zoning, both in composition and texture. Whereas areas next to the grain boundary consist of nearly pure hydroxylapatite and show a coarse porosity, areas close to the center of the single grains show a high amount of β -TCP and a very fine porous microstructure. If fluorine was added as an additional solution component, up to 3 wt.% of F were incorporated into the product apatite and the formation of β -TCP was avoided. The use of the isotope ¹⁸O as a chronometer for the replacement reaction makes it possible to reconstruct the chronological development of the calcium phosphate reaction front. Raman analysis revealed that the incorporation of ¹⁸O in the PO₄ tetrahedron of hydroxylapatite results in the development of distinct profiles in the calcium phosphate reaction front perpendicular to the grain boundaries of the marble. Through the use of the ¹⁸O chronometer, it is possible to estimate and compare the time effectiveness of the different fluid pathways in this model system. The results demonstrate that the grain boundaries are an effective pathway enabling the fluid to penetrate the rock more than one order of magnitude faster compared to the newly developing channel-like porosity structures, which act as pathways towards the center of single mineral grains. Thus, after only short reaction durations, it may be possible for the fluid to progress relatively large distances along the grain boundaries without developing broad reaction fronts along the path.

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1. Introduction

Regional-scale alteration or metasomatic transformation of rocks, such as during serpentinization of the ocean floor, albitization of crustal rocks, and eclogitization of subducted rocks (e.g., Austrheim, 1987; Bach and Frueh-Green, 2010; Engvik et al.,

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0012-821X/\$ - see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.epsl.2013.10.050 2011) requires fluid and mass transport through initially low permeability rocks. Such fluid-rock interaction strongly affects the petrophysical properties and chemical composition and has a fundamental impact on the geodynamics and geochemistry of Earth (e.g., Ague, 2003; Jolivet et al., 2005; Yardley, 2009; Jamtveit and Austrheim, 2010). Ore-deposit formation and the development of contact aureoles are prominent phenomena related to fluidmediated heat and mass transport (e.g., Bowman et al., 2009; Jamtveit and Austrheim, 2010).

The most efficient mass transport occurs through channelized fluid flow, but rock transformation and element mobilization require a pervasive interaction between fluid and rock on a mineral scale (e.g., van der Straaten et al., 2008; Holness, 1997; Beinlich et al., 2012). Field evidence indicates that fluid-induced reaction fronts develop from veins, fractures or shear zones (e.g. Austrheim, 1987; Holness, 1997; Bach and Frueh-Green, 2010; Engvik et al.,

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2011), but will ultimately progress through the grain boundary network and the reaction-induced porosity within the crystals that constitute the rock. Accordingly, any pervasive large-scale fluid-rock interaction depends on the development and maintenance of an efficient grain-boundary based porosity–permeability system. The relationship between fluid flow and metamorphism in natural rocks has been the subject of various studies (e.g., Bickle, 1992; Skelton, 1995, 1997a, 1997b; Arghe et al., 2011), emphasizing the importance of determining transport mechanisms.

Fluid infiltration can also alter the isotopic composition of a rock. Isotopic exchange on a mineral scale can result in the development of distinct isotope profiles within the affected grains. Depending on whether the isotopic exchange takes place by diffusion and/or surface reactions involving dissolution and reprecipitation, different types of isotopic profiles may develop. As structures such as grain boundaries and fractures facilitate fluid transport, they also influence the isotopic exchange in the rock (Bowman et al., 2009). Isotopic systems, e.g. lithium or oxygen isotopes, can be used to trace metamorphic fluid–rock interactions and thus provide valuable information about possible sources of the metamorphic fluids and magnitudes and scales of fluid–rock interactions (e.g. Penniston-Dorland et al., 2010; Skelton et al., 2012; Penniston-Dorland et al., 2012).

In the present paper, we used the replacement of Carrara marble by apatite as a model system to investigate the mechanisms of pervasive fluid infiltration, transport and reaction within a massive, low-permeability rock. The experimental replacement of calcium carbonate by apatite by a reaction such as

$$5CaCO_3 + 3HPO_4^{2-} + H_2O \rightarrow Ca_5(PO_4)_3OH + 3CO_3^{2-} + 2H_2CO_3$$
(1)

has been demonstrated in a number of studies using calcite powder (Yoshimura et al., 2004; Tas and Aldinger, 2005; Lemos et al., 2006), single crystals of calcite and aragonite (Eysel and Roy, 1975; Kasioptas et al., 2008, 2011), as well as natural calcite and aragonite materials, e.g., corals, cuttlebone, and sea urchin spine (Roy and Linnehan, 1974; Hu et al., 2001; Xu et al., 2001; Álavrez-Lloret et al., 2010; Kasioptas et al., 2010).

In the case of hydrothermal replacement of single crystals of calcite or aragonite by apatite a reaction front propagates through the crystals due to the generation of porosity resulting from the change in the molar volume and the difference in the solubilities of the parent and product phase in the fluid (Putnis, 2009). The pore structure and its interconnectivity (Raufaste et al., 2011) is of great importance to the progress of the replacement as it provides the necessary permeability for further replacement and the progression of the reaction front towards the unreacted core of the crystals.

By using Carrara marble as the starting material for the pervasive replacement reaction we can compare the extent and rate of fluid infiltration and reaction along grain boundaries and through individual calcite crystals. Ferry et al. (2010) demonstrated the importance of in situ sub-grain-scale isotope analysis for an improved understanding of reactive fluid flow, reaction kinetics, and thermal history during metamorphism. By using an ¹⁸O-enriched phosphate solution as the reactant we are able to chronologically reconstruct the development of the reaction fronts inside the marble. This method relies on the fact that the time scale for the isotopic equilibration of aqueous phosphate species (in our case HPO_4^{2-}) with ¹⁸O-labeled water is similar to the time scale for the replacement process (Kasioptas et al., 2011). The ¹⁸O composition of the apatite at any point in the sample reflects the ¹⁸O composition in the phosphate in solution, thereby providing an internal chronometer for the replacement reaction.

2. Materials and methods

2.1. Starting material

White Carrara marble was used as a starting material for the hydrothermal experiments. It has a uniform grain size of ~200 µm. Electron microprobe analysis showed that it is almost pure CaCO₃, with only trace amounts of incorporated Mg (~0.6 wt.%). The marble was cut into cubes of two different side lengths, ~1.5 × 1.5 × 1.5 mm³ and ~5.0 × 5.0 × 5.0 mm³. The exact size and weight of each cube was measured individually. The weight of the cubes varied between 0.0080 and 0.0088 [g] for the smaller cubes and between 0.3315 and 0.4495 [g] for the larger cubes. The marble cubes were washed with acetone before each experiment to remove impurities from the reaction surface.

We used four different aqueous solutions for the reactions:

- (I) 2.0 M (NH₄)₂HPO₄ (Acros Organics, >99%) solution prepared with MilliQ water (referred to here as the "standard phosphate solution").
- (II) A solution enriched with ¹⁸O by diluting a 4.0 M (NH₄)₂HPO₄ solution with the same amount of ¹⁸O-enriched water (Campro Scientific, 97% ¹⁸O) (referred to as the "¹⁸O phosphate solution").
- (III–IV) To check whether any fluorine is incorporated into the structure of the apatite at the reaction front, additional solutions with 1.5 M of $(NH_4)_2HPO_4$ and 0.5 M of NaF (Merck, >99%) with and without ¹⁸O were prepared ("fluorine-containing phosphate solution" and "fluorine-containing ¹⁸O phosphate solution") by diluting different stock solutions of $(NH_4)_2HPO_4$ and NaF with H_2 ¹⁸O (Campro Scientific, 97% ¹⁸O).

2.2. Hydrothermal experiments

For each experiment, one marble cube was put into a Teflon reactor together with 2.0 ml of solution for experiments with large cubes or 1.0 ml of liquid for experiments with small cubes. The solutions were prepared by diluting stock solutions to achieve the different concentrations of $(NH_4)_2HPO_4$ and NaF described in Section 2.1 immediately before the start of each experiment. The Teflon reactors were placed into a steel autoclave and sealed, then heated in a furnace at either 150 °C or 200 °C for different periods of time. After the reaction, the autoclaves were removed from the furnace and cooled to room temperature using an electric fan. Each autoclave was weighed after cooling to ensure that no fluid loss had taken place. The marble cubes were removed from the reactors, washed with distilled water to remove the remaining solution from the surface, and left to dry at ~60 °C in a drying cabinet. After drying, the marble cubes were weighed again.

To characterize the run products and study the extent of reaction the marble cubes were either crushed for X-ray diffraction analysis or mounted in epoxy resin and polished to half of their size to obtain a cross section of the sample for further investigations.

2.3. Equilibration of the phosphate in solution with $H_2^{18}O$

The use of ¹⁸O as a chronological tracer for the replacement relies on the rate of oxygen isotope exchange between the phosphate ions in solution and the enriched water according to the reaction

$$HP^{16}O_4^{2-} + H_2^{18}O \to HP^{18}O_4^{2-} + H_2^{16}O$$
⁽²⁾

The time scale of this exchange reaction is very slow at room temperature (the conditions at which the solutions were prepared),



Fig. 1. BSE image of a partly transformed marble cube after five days of reaction at 200 °C. The calcium phosphate reaction front (pale) progresses from the outer edge of the cube towards the unreacted calcite core (gray). The reaction front advances along the grain boundaries of the marble surrounding the single grains.

but at the run temperatures for the calcite–apatite replacement experiments the exchange rate in the fluid is comparable to the rate of the replacement reaction (Kasioptas et al., 2011).

Experiments with ¹⁸O as a tracer were carried out at $150 \degree C$ for five days, with the ¹⁸O phosphate solution and with the fluorine-containing ¹⁸O phosphate solution using the small marble cubes and 1.0 ml of liquid.

2.4. Analytical methods

An X'Pert PW 3040 PANalytical diffractometer with the X'Pert Data Collector software was used to identify the different phases in the reacted samples.

The structure of the calcium phosphate reaction front was studied by scanning electron microscopy (SEM) using a JEOL 840 scanning electron microscope and a JEOL JSM-3600F high resolution field emission scanning electron microscope with an energydispersive X-ray detector.

A JEOL JXA 8900 Superprobe electron microprobe was used for quantitative analysis and element mapping.

The amount of ¹⁸O incorporated into the newly-formed apatite was determined by Raman spectroscopy. The incorporation of ¹⁸O results in the appearance of new bands in the Raman spectrum of hydroxylapatite and makes it possible to determine the amount of ¹⁸O incorporated into the phosphate group in the apatite structure.

Raman spectroscopic measurements were performed using the 785 nm laser of a confocal Jobin Yvon XPlora Microraman system with a 50 µm slit width and 1800 lines/mm grating to obtain a high spectral resolution. Fitting of the Raman bands was performed by using the freeware fitting program Fityk (Wojdyr, 2010).

(For detailed description of the analytical parameters, please refer to the supplementary material.)

3. Results

3.1. Microstructure of the reaction front

Back scattered electron (BSE) images of reacted marble cubes reveal a sharp reaction front progressing along the grain boundaries towards the unreacted core of the marble cubes (Fig. 1). Single grains of calcite are rimmed by a porous reaction product. With increasing duration, the reaction front migrates further towards the core of each grain until it is completely replaced. The shape of the cubes as well as the distribution of the grain boundaries is preserved during the reaction. High magnification BSE images of the reaction front inside a single grain that has



Fig. 2. BSE images of partly transformed marble grains after five days (A) and ten days (B) of reaction at 200 °C. Parts of the reaction front located close to the grain boundary ("exterior") show a coarser porosity than parts located close to the calcite interface ("interior").

developed after relatively short reaction times reveal microtextural differences between the areas located at the grain boundary and those located closer to the unreacted grain core (referred to as "exterior" and "interior" respectively in the following). The exterior regions have a coarser porosity with larger pore diameters between ~0.4 and ~2.6 μ m, whereas the interior part has much finer porosity of ~0.2 to 0.4 μ m (Fig. 2). With increasing duration and almost complete transformation of the grains, the coarser pore structure migrates towards the center of the grain. Completely transformed single grains show an overall coarse porosity resembling that of the exterior part described before. This suggests that the fine-textured parts are themselves replaced by the coarsertextured phase during the course of the reaction.

3.2. Replacement products

XRD analyses revealed that the reaction products consist of hydroxylapatite [Ca₅(PO₄)₃OH] and a second calcium phosphate phase. However, XRD results alone cannot distinguish whether this second phase is whitlockite [Ca₁₈(Mg, Fe)₂H₂(PO₄)₁₄] or the H⁺-free form β -tricalcium phosphate (β -TCP) [β -Ca₃(PO₄)₂]. Since it is difficult to distinguish the two phases by XRD analysis, the names "whitlockite" and " β -TCP" have been used interchangeably in the past (Gopal and Calvo, 1972; Gopal et al., 1974; Wopenka and Pasteris, 2005). In this study, the term "whitlockite" will refer to the phase with the chemical formula Ca₁₈(Mg, Fe)₂H₂(PO₄)₁₄, whereas the H⁺-free form with the formula β -Ca₃(PO₄)₂ will be called " β -TCP".

Raman spectroscopic measurements confirmed the presence of hydroxylapatite in the reaction rim and clarified that the second calcium phosphate phase present in the samples of this study is actually β -TCP, as no distinct peak at 925 cm⁻¹ corresponding to the v_1 mode of HPO₄²⁻ in whitlockite (Wopenka and Pasteris, 2005; Jolliff et al., 2006) could be identified in the Raman spectra. Raman spectroscopy indicated that most parts of the product phase at the reaction front consist of a mixture of both hydroxylapatite and β -TCP. These two calcium phosphate phases can also be distinguished by differences in their Raman spectra (see De Aza

Table 1
Chemical composition of the unreacted Carrara marble as well as the calcium phos-
phate reaction front formed in solutions with and without fluorine.

	Composition (wt.%)				
	CaO	CO ₂	MgO	P_2O_5	F
Marble	55.5	43.9	0.6	n.d.	n.d.
Reaction front	53.2	n.d.	0.5	46.3	n.d.
Reaction front (with F)	57.0	n.d.	0.6	39.4	3.0

et al., 1997; Cuscó et al., 1998). One difference is that in the spectrum of hydroxylapatite, a single main band corresponding to the v_1 mode of PO_4^{3-} can be detected at 961 cm⁻¹, whereas β -TCP shows a main band at 971 cm⁻¹, a shoulder band near 961 cm⁻¹ and a broad band near 946–949 cm⁻¹. Another important difference is the frequency gap in the spectrum separating the Raman bands that arise from the v_1 and v_2 modes. Whereas the bands are separated by a relatively large gap in the spectrum of hydroxylapatite (~120 cm⁻¹), the gap in the spectrum of β -TCP is much smaller (~55 cm⁻¹).

Parts of the reaction rim located next to the grain boundary in the exterior part of each grain consist of a relatively high amount of apatite and only a minor amount of β -TCP or even no β -TCP at all, as indicated by high intensity of the apatite bands in the Raman spectrum. In some spectra close to the grain boundary, the apatite band near \sim 961 cm⁻¹ becomes narrower, no band or shoulder can be detected near 971 cm⁻¹ and no broad band appears near 946–949 cm⁻¹, indicating that no β -TCP is present in these parts of the reaction rim. Closer to the calcite interface in the interior part of the grain, the bands of β -TCP in the spectrum become more dominant, indicating relatively high amounts of β -TCP close to the reaction interface. In these spectra, the band splitting between 961 cm⁻¹ and 971 cm⁻¹ and the development of a broad shoulder near 946–949 cm⁻¹ are clearly visible. Additionally, the change in the size of the frequency gap can be observed as described by Cuscó et al. (1998). From these observations we conclude that the phase with coarser porosity in Fig. 2 is hydroxylapatite, whereas the phase with fine porosity is β -TCP. However, due to the overlap of the Raman bands of each phase small amounts of the minor phase may still be present in any specific area of the reaction rim.

3.3. Chemical composition of the reaction front

Quantitative electron microprobe analysis (Table 1) reveals that small amounts of MgO present in the calcite were incorporated into the calcium phosphate at the reaction front. However, depletions in the Mg content were detected next to the grain boundaries in the outermost grains along the edge of the cube, i.e. the part of the sample exposed to the solution for the longest reaction time (Fig. 3E). Thus, the exterior parts of the single grains described in Section 3.1 are separated from the interior parts not only by different porosity structures, but also by a difference in the Mg content, at least in the outermost grains of the cubes. It is further remarkable that the interface separating the "low Mg" zone along the grain boundaries from the interior of the grain is marked by a thin zone of Mg enrichment relative to both parts of the grain (Fig. 3E).

The reaction product within cubes that reacted with the fluorine-containing phosphate solution showed a fluorine content of up to 3 wt.%. Simultaneously, the phosphate content in these samples was ~6 wt.% lower, leading to a higher Ca/P ratio in the reaction rim. The Mg distribution in these samples appears to be homogeneous. None of the bands typical for β -TCP can be observed in the Raman spectra of the fluorine-containing reaction rims, even close to the calcite interface. The Raman spectra, as

well as the higher Ca/P ratio, are all consistent with the reaction product being apatite.

3.4. Incorporation of ¹⁸O into the reaction front

The incorporation of ¹⁸O into hydroxylapatite leads to the generation of four new Raman bands in the Raman spectrum of hydroxylapatite (Kasioptas et al., 2011), in addition to the "normal" v_1 (P¹⁶O₄) stretching mode near ~962 cm⁻¹. These bands result from the mass-related isotope splitting associated with the substitution ¹⁶O by ¹⁸O in the PO₄ group, resulting in four individual stretching modes related to the isotopologues P¹⁶O_{4-i}¹⁸O_i ($1 \le i \le 4$) (see also Geisler et al., 2012). The positions of the additional Raman bands agree well with those theoretically calculated and observed by Kasioptas et al. (2011). Only a minor shift difference in the band position is observed in the samples that reacted with the fluorine-containing ¹⁸O phosphate solution (Table 2).

Although the positions and intensities of these newly developed bands can be identified in samples that reacted with the ¹⁸O phosphate solution, the bands are very broad with considerable overlap (Fig. 4A), especially from the β -TCP in the interior part of the reaction rim. In the exterior part, near the original grain boundaries where the phase is predominantly apatite, the four isotopologue bands are better resolved (Fig. 4B). Samples that reacted with the fluorine-containing ¹⁸O solution, show clearly distinguishable narrow bands with limited overlap

The amount of ¹⁸O incorporated into different parts of the reaction front was calculated using the equation

$$f^{18}O(\%) = \left(\sum_{i=1}^{4} \left[\frac{5-i}{4} \times a_i\right] / \sum_{i=1}^{5} a_i\right) \times 100$$
(3)

with a_1 , a_2 , a_3 , a_4 and a_5 representing the integral intensities of the Raman bands at 909, 919.9, 931.4, 945 and 962 cm⁻¹, respectively (Kasioptas et al., 2011).

Raman profiles perpendicular to reaction fronts across grain boundaries (Fig. 5A; Table 3) reveal variations in the amount of ¹⁸O incorporated into the PO₄ group of the calcium phosphate phases (Fig. 5B). Line profiles across parts of the reaction rim located close to the outer edge of the marble cubes show an increasing ¹⁸O content as a function of the distance from the grain boundary, resulting in a v-shaped oxygen isotope profile (Fig. 5B). The minimum ¹⁸O content in these parts of the reaction rim is \sim 8 wt.% next to the grain boundary in the scan closest to the edge of the marble cube (scan A). With increasing distance from the grain boundary, the amount of 18 O increases to a maximum of \sim 45 wt.%. As the reaction front progresses further into the marble cube, the minimum content of ¹⁸O next to the grain boundary increases, resulting in a "flattening" of the v-shaped oxygen isotope profile closer to the center of the cube. After a certain point, the oxygen isotope data define a horizontal rather than a v-shaped curve with an almost constant amount of 18 O of \sim 45 wt.% (Fig. 5B, scan D).

3.5. Uncertainties in the ¹⁸O content

Uncertainties in the determination of the ¹⁸O content in PO₄ arise from the relatively broad bands in the wavenumber range between 900 and 1000 cm⁻¹. Bands developed due to the incorporation of ¹⁸O in the PO₄ tetrahedron of β -TCP may partially overlap the apatite bands and thus influence the intensities of these bands. During data fitting, all points in the spectrum >962 cm⁻¹ were deactivated to exclude the influence of the β -TCP main band near 971 cm⁻¹ on the intensity of the ν_1 (PO₄) band of hydroxylapatite. To obtain the most accurate results for the Raman intensities, the band positions were fixed at the positions calculated through Eq. (3). Additionally, the same half width was chosen for each peak



Fig. 3. BSE image (A) as well as element maps showing the distribution of Ca (B), P (C), O (D), and Mg (E) in different parts in the partially transformed marble sample.

Table 2

Observed frequencies (ν_{obs}) of the isotopic species of PO₄ with different amounts of ¹⁸O incorporated for samples that reacted with and without fluorine in solution. The values for ν_{obs} coincide with those observed by Kasioptas et al. (2011).

Isotopic	$\nu(PO_4)_{obs}$ (cm ⁻	$\nu(\mathrm{PO}_4)_{\mathrm{obs}}~(\mathrm{cm}^{-1})$				
species	without F	with F	Kasioptas et al. (2011)			
P ¹⁶ O ₄	962.0	965.0	962.0			
P ¹⁶ O ₃ ¹⁸ O	945.0	948.9	945.5			
P ¹⁶ O ₂ ¹⁸ O ₂	931.4	935.0	932.0			
P ¹⁶ O ¹⁸ O ₃	919.9	923.0	919.7			
P ¹⁸ O ₄	909.0	911.9	908.8			



Fig. 4. Raman spectra showing the effect of the incorporation of 18 O into the PO₄ tetrahedron of hydroxylapatite in samples that reacted with the standard 18 O phosphate solution (A: "interior" part; B: "exterior" part of the reaction front) and the fluorine-containing 18 O phosphate solution (C).

in all the spectra, to ensure that the changes in the intensities of the single Raman bands obtained from different scans are comparable. Nevertheless, an influence of peaks corresponding to the β -TCP phase cannot be ruled out completely. In general, the error of the ¹⁸O content in PO₄ varies between ~1.5% for small amounts (e.g. 10%) to ~3.5% for high amounts (e.g. 40%) of ¹⁸O in PO₄.



Fig. 5. (A) BSE image of a partially transformed marble cube that reacted with the ¹⁸O phosphate solution at 150 °C for five days. The ¹⁸O composition across four linescans perpendicular to the grain boundary were measured using Raman spectroscopy at the positions marked on the image. (B) ¹⁸O content (%) incorporated into the PO₄ tetrahedron of hydroxylapatite determined from Raman line profiles A–D measured on different positions of the reaction front oriented perpendicular to the grain boundary as indicated on (A). The position of the grain boundary is marked by the gray line on position 0 on the *x*-axis. With increasing distance from the grain boundary, the amount of ¹⁸O in the PO₄ tetrahedron increases with increasing distance from the outer edge of the marble cube (see also Table 3).

0

Distance [µm]

5

10

15

20

Table 3

0 -20

-15

-10

-5

Distances measured between the outer edge of the marble cube and the linescans measured at the different positions marked on Fig. 5 as well as the minimum and maximum content of $^{18}O~(\%)$ incorporated in the PO₄ tetrahedron calculated for the different linescans.

Position	Distance from edge (µm)	f ¹⁸ 0 (%)	
		min.	max.
1	21.7	7.3	45.3
2	96.9	18.1	44.0
3	153.7	32.0	45.7
4	204.4	42.2	49.0

4. Discussion

4.1. Replacement of marble by calcium phosphates

The reaction of Carrara marble with a 2.0 M $(NH_4)_2HPO_4$ solution at 150 °C and 200 °C partly transforms the calcite to hy-

droxylapatite as described by Eq. (1). β -TCP is formed as a second product phase as given by the reaction

$$3CaCO_3 + 2HPO_4^{2-} \rightarrow Ca_3(PO_4)_2 + 2CO_3^{2-} + H_2CO_3,$$
 (4)

with minor amounts of Mg^{2+} substituting for Ca^{2+} .

Both the external shape and grain distribution of the marble cubes are preserved in this pseudomorphic replacement reaction. Pseudomorphic replacement of CaCO₃ by apatite has been reported previously (e.g. Eysel and Roy, 1975; Kasioptas et al., 2008, 2011) and is explained by an interface-coupled dissolutionreprecipitation mechanism (Putnis and Putnis, 2007). In case of the replacement of marble by apatite and β -TCP, as calcite begins to dissolve stoichiometrically at the reaction interface in the presence of the phosphate solution, a boundary layer supersaturated with respect to hydroxylapatite and β -TCP develops, leading to immediate reprecipitation of these product phases. Thus, the original morphology of the parent phase is maintained after the reaction. The progress of the reaction front into the calcite is dependent on the generation and maintenance of porosity in the calcium phosphate since aqueous phosphate has to reach the reaction interface (Fig. 2).

Raman spectroscopy revealed that the relative amounts of the two product phases change in different parts of the reacted material. Since the reaction front consists of higher amounts of β -TCP, it is likely that the calcite is first replaced by β -TCP, which is later transformed to apatite through ongoing dissolution and reprecipitation. The formation of β -TCP as an intermediate step has been described for the hydrothermal conversion of coral into hydroxy-lapatite (Xu et al., 2001). Furthermore, the reaction of β -TCP with water or ammonium fluoride in water-1-octanol biphase to form apatite has been reported (Sakamoto et al., 2001; Brunner et al., 2007).

4.2. The distribution of β -TCP and hydroxylapatite and the role of Mg

The specific distribution of the product phases in different areas in the sample may also explain the variance in the Mg content. Whereas β -TCP is stabilized by the incorporation of magnesium (e.g. Hayek and Newesely, 1958; Tardei et al., 2006), the presence of magnesium ions may actually inhibit the precipitation and growth of apatite (e.g. Martens and Harriss, 1970; Salimi et al., 1985; Johnsson and Nancollas, 1992). According to Schroeder et al. (1977), β -TCP containing Mg has a lower free energy and is more stable than the pure phase since the Mg–O distances are smaller than the Ca–O distances, and the electrostatic energy is proportional to 1/r (with *r* as the radius), leading to a lower internal energy of the Mg-containing β -TCP.

Roy and Linnehan (1974) showed that hydrothermal treatment of calcite spines of Acanthaster planci using a (NH₄)₂HPO₄ solution resulted in the formation of Ca₃(PO₄)₂ ("whitlockite"), whereas slices of the scleractinian coral Porites treated under the same conditions were replaced by hydroxylapatite. The relatively high Mg content in the calcite spines of Acanthaster planci was considered a possible reason for the formation of Ca₃(PO₄)₂. Eanes and Rattner (1981) proposed that the adsorption of Mg at active surface sites may temporarily block these sites, delaying apatite growth and hydrolysis of precursor phases such as octocalcium phosphate to hydroxylapatite. Posner et al. (1984) suggested that magnesium ions entering into hydroxylapatite prenuclei structures may distort these structures and create a mismatch in epitaxial development; thus, further hydroxylapatite growth and transformation of amorphous calcium phosphate into hydroxylapatite will be inhibited. Furthermore, magnesium ions not only destabilize the hydroxylapatite structure, but high concentrations of magnesium ions may even lead to the conversion of hydroxylapatite into β -TCP at high temperatures (Bigi et al., 1988, 1992, 1993, 1997).

It is conceivable that most of the Mg initially incorporated into β -TCP in the exterior part of the grain is not incorporated into the later-formed hydroxylapatite. If recrystallization and the progression of the reaction front is faster than the transport of the Mg ions from the interface towards the grain boundary and from there to the bulk solution, Mg will be enriched on the reaction interface between the interior and exterior parts of the grain.

Another reason explaining the distribution of Mg (Fig. 3E) could be that at an early stage of the replacement process, most of the Mg incorporated in the marble diffuses into the bulk solution. As long as the reaction front has not progressed very far into the single grains, effective fluid-mediated diffusive transport of Mg from the reaction interface into the bulk solution is still possible. At a certain point, the reaction front advances so far into the grains that diffusion pathways through the porous channel-like structures become too long. The diffusion time increases with the square of the diffusion distance and the diffusion distance, in turn, increases due to complex geometry of the micropores of the reaction front (i.e. tortuosity), which may lead to anomalous diffusion where the diffusion distance no longer increases with the square root of time. Thus, the transport of Mg becomes inefficient or even stops (cf. van der Straaten et al., 2008), leading to an enrichment of the element in the interfacial solution located at the boundary between the interior and exterior parts of the grains. One could further argue that the diffusive transport of Mg through the pore solution is actually the factor controlling whether the parent phase is replaced by apatite or β -TCP. In that case, parts of the grains located next to the grain boundary would be replaced by apatite (low Mg at the interface) at the beginning of the reaction. As soon as the diffusion of Mg becomes less efficient, the calcite is replaced by β -TCP (high Mg at the interface) with further progression of the reaction front. Thus, no replacement of β -TCP by apatite would occur during the ongoing progression of the reaction front. At this stage the replacement reaction becomes controlled by diffusion of solute species through the porous product phase(s). A similar observation has been reported in experiments with radiation-damaged, natural rare earth element (REE)-containing pyrochlore (Pöml et al., 2007). Here aeschynite, a REE-bearing niobate, started to replace the pyrochlore once a certain thickness of a rutile/anatase reaction rim had formed. The authors attributed the formation of aeschynite to an ineffective transport of solute species (e.g., the REE) through the growing rutile/anatase reaction rim.

4.3. Influence of fluorine on the replacement reaction

The presence of fluorine in the solution leads to the incorporation of significant amounts of F into the apatite crystal structure, where the anion F⁻ substitutes for OH⁻. Because of the small ionic radius of F⁻, F is preferred over the incorporation of OH⁻ into the apatite structure. Fluorine substitution in apatite leads to strong variations in the ν_3 (PO₄) phosphate mode in the Raman spectrum (Penel et al., 1997). The results of this study confirm the observations by Penel et al. (1997) that the number of Raman bands in the 900–1100 cm⁻¹ region decreases from seven to five with the incorporation of fluorine into apatite.

The smaller amount of phosphate determined by electron microprobe in samples that reacted with the fluorine bearing phosphate solution leads to a higher Ca/P ratio in the reaction rim, which is connected to the absence of β -TCP and thus the higher amount of apatite formed. LeGeros et al. (1988) suggested that the presence of F in solution may even lead to an increase in the Ca/P ratio because of the higher crystallinity of the apatite formed and simultaneously suppresses the formation of Mg-substituted β -TCP, thus minimizing the negative effects caused by the presence of cations such as Mg²⁺ in solution.

4.4. Importance of fluid pathways

The development of porosity in the reaction product has been observed in other studies on the hydrothermal replacement of single crystals of calcite and aragonite by calcium phosphate (e.g. Kasioptas et al., 2008, 2011). Porosity generation enables the continuation of the transformation towards the center of the single grains by providing fluid pathways (Putnis et al., 2005; Perdikouri et al., 2011; Raufaste et al., 2011). The generation of porosity in the product phase is due to a combination of molar volume change and the relative solubility (Putnis and Putnis, 2007; Pollok et al., 2011). In this case, three formula units of calcite are replaced by one formula unit of β -TCP and five formula units of calcite are replaced by one formula unit of hydroxylapatite. The replacement of calcite by β -TCP results in a molar volume decrease of \sim 9.63 cm³/mol (-9%), whereas the change in molar volume is even larger (\sim 25.68 cm³/mol or -14%) for the replacement of calcite by apatite. Furthermore, calcite is more soluble than hydroxylapatite and β -TCP, and thus more calcite will be dissolved than apatite and β -TCP reprecipitated. However, a negative volume change is not always necessary to ensure further replacement of the parent phase. Intracrystalline porosity may develop even though the fluid-mediated reactions would result isochemically in a constant or increased bulk reaction volume if mass is efficiently removed via transport through the fluid (van der Straaten et al., 2008; Parsons and Lee, 2009). Large-scale replacement may also be supported by perpetuation of initial porosity structures of the parent rock (Beinlich et al., 2012).

As described in Section 3.1, the porosity undergoes a textural change with further replacement of a single grain. A change in the porous microstructure with ongoing replacement of the precursor has been reported for other mineral replacement reactions (Putnis et al., 2005; Pollok et al., 2011; Rausfaste et al., 2011) and may be connected to the fact that the system is moving towards attaining chemical and textural equilibrium (Putnis et al., 2005). Another reason why the exterior parts of the grains show a coarser porosity may be that these parts consist mainly of hydroxylapatite. The molar volume change is larger when calcite is replaced by hydroxylapatite rather than by β -TCP. Thus, a greater change in molar volume in the exterior part of the grains may contribute to the development of a coarser porosity. The coarsening of the porosity towards the grain boundary cannot be clearly observed in every single grain. However, this may be due to the irregular three-dimensional shape of the grains, which is difficult to estimate from two-dimensional cross sections.

Another important feature of the replacement of marble is that grain boundaries are an important part of the internal texture of the marble and provide pathways for the fluid. If the fluid passes through the grain boundaries, the first replacement takes place at the outer parts of the single grains. After that, porosity generation providing additional pathways enables further progress of the reaction front towards the center of the grains until the complete transformation. The recrystallization of minerals with new compositions along grain boundaries accompanied by the migration of sharp reaction fronts from the grain boundaries concentrically into the grains is a phenomenon that has been observed in natural rocks and has been attributed to large-scale pervasive fluid flux along the grain boundaries (Konrad-Schmolke et al., 2011).

4.5. Use of ¹⁸O as a chronometer

Raman spectroscopy revealed that different amounts of ¹⁸O are incorporated in different parts of the reaction rim resulting in the development of four additional peaks corresponding to the $v_1(PO_4)$

mode (Table 2). In the exterior parts of the grains that reacted with the ¹⁸O phosphate solution, these peaks are more clearly resolved (Fig. 4B) than in the interior parts (Fig. 4A). In samples that reacted with the fluorine-containing ¹⁸O solution, the individual bands are even better resolved, i.e. narrower (Fig. 4C). One possible reason for these differences could be that in the marble samples that reacted with the fluorine-containing solutions less or even no β -TCP is present in the exterior part of the grains, since additional bands may develop in the same spectral range due to the incorporation of ¹⁸O into the β -TCP. It is also conceivable, however, that this observation reflects the higher crystallinity of the fluorine-bearing hydroxylapatite (LeGeros et al., 1988).

Fig. 5B shows four oxygen isotope line profiles across a single grain boundary. The profiles are ordered along the grain boundary from the outer surface of the marble cube towards the interior (Fig. 5A). In parts of the reaction rim located close to the outer edge of the cubes, the ¹⁸O content shows a minimum value right next to the grain boundary (Fig. 5B). These parts of the reaction front must have formed early during the reaction when very little O-O exchange between water and phosphate species in the solution had taken place, resulting in only a small amount of ¹⁸O being incorporated into the phosphate group of the precipitating calcium phosphate phase. Through the formation of intracrystalline porosity, the reaction front proceeds from the grain boundary towards the center of the grain. As the reaction front progresses with time, more O-O exchange has taken place in the solution, leading to an increase in the amount of ¹⁸O in the aqueous phosphate phase and thus also in calcium phosphate phase(s) that precipitated further away from the grain boundary (Fig. 5B). Since it takes time for the phosphate solution to penetrate further into the marble along the grain boundaries, the minimum value of ¹⁸O in the calcium phosphate phase(s) next to the grain boundary increases with further distance from the outer edge of the cube.

At a certain point, the ¹⁸O content next to the grain boundary is close to the maximum value that can possibly be incorporated (Fig. 5B), showing that the phosphate solution was almost completely equilibrated when it reached this point. Thus, the oxygen isotope composition of different parts of the reaction rim represents the oxygen isotope composition of the aqueous phosphate (ignoring minor isotope fractionation effects) at the time when the actual replacement took place (Kasioptas et al., 2011).

If, for example, the amount of 18 O is \sim 42 wt.% in different parts of the sample, these different parts of the reaction front must have been developed at the same time. In line profile A the amount of \sim 42 wt.% ¹⁸O was measured at a distance of \sim 12 µm away from the grain boundary (Fig. 5B). In profile D, the same amount can be found right next to the grain boundary (Fig. 5B). The measurements show that during the same time period the fluid penetrated about \sim 204 µm along the grain boundary, but the reaction front only penetrated about 12 µm towards the core of the grain. These results clearly show that the fluid is able to infiltrate the marble more than an order of magnitude faster along the grain boundaries compared to the progression of the reaction front towards the center of the grains through porosity formation. Note, however, that we ignore in the following the O-O exchange between water and aqueous carbonate that increases in concentration in solution with increasing calcite dissolution.

Further, if, as suggested above, the first phase to replace the calcite is β -TCP, which is, in turn, replaced by hydroxylapatite by recrystallization, the ¹⁸O content calculated from the Raman spectra would only represent the phosphate composition of the fluid at the time the first replacement took place if dissolution of the β -TCP and reprecipitation of the hydroxylapatite is more or less instantaneous, i.e., faster than the O–O exchange between the phosphate, released into solution during the dissolution of β -TCP, and water.



Fig. 6. A schematic figure to illustrate the possible effect of the timing of the replacement of β -TCP by apatite by dissolution-reprecipitation. A non-instantaneous dissolution of β -TCP and reprecipitation of apatite (t_1) would result in the incorporation of additional ¹⁸O into apatite and in a shift of the original ¹⁸O content (black line) towards higher values (black dotted line) in a certain area of the reaction front (left side of gray dotted line) in which hydroxylapatite is the main calcium phosphate phase. However, the original ¹⁸O content would still be preserved in the parts of the reaction front (right side of gray dotted line) containing mainly β -TCP. In the case of instantaneous recrystallization, however, the original ¹⁸O content (incorporated at t_0) would be preserved throughout the whole profile (black line).

If the replacement of β -TCP by hydroxylapatite is, however, somewhat delayed in time, further exchange of oxygen ions in the solution may take place before the apatite recrystallizes. If so, the amount of ¹⁸O in PO₄ in the hydroxylapatite presented in Fig. 5B represents a higher f^{18} O than the original value when calcite was first (at t_0 in Fig. 6) replaced by β -TCP, resulting in a shift of the plot on the *y*-axis towards higher values for f^{18} O (at t_1 in Fig. 6).

Considering the possibility that the fluid-mediated diffusive transport of Mg is the factor controlling whether the calcite is replaced by apatite or by β -TCP (see Section 4.1), no change in the amount of ¹⁸O incorporated due to dissolution of β -TCP and reprecipitation of hydroxylapatite during ongoing progression of the reaction front would occur. However, recrystallization of the calcium phosphate material cannot be fully excluded, since the coarsening of the porosity in the reaction front extending even to the center of completely reacted single grains is observed.

4.6. Implications for fluid flow in natural rocks

Fluid-rock interactions affect the petrophysical properties of a rock along with its chemical or isotopic composition (Jamtveit and Austrheim, 2010; Beinlich et al., 2012). The transient porosity-permeability, developing during reaction, controls its efficiency. To effectively alter large-scale rock units, e.g., during contact aure-ole formation, grain-boundary assisted pervasive mass transport is necessary (Holness, 1997; Bowman et al., 2009).

Studies on marble samples from Naxos, Greece, have shown that a change in the oxygen isotopic composition of the rock was caused by infiltration of a fluid phase (Bickle and Baker, 1990; Graham et al., 1998; Lewis et al., 1998). Textural features significant for fluid transport, including grain boundaries and fractures, were identified (Graham et al., 1998). The combination of all pathways represents a complex and interconnected three-dimensional network allowing fluid flow throughout the marble, hence providing the effective flow porosity, i.e. permeability (Norton and Knapp, 1977). Equilibration between the infiltrating fluid depleted in ¹⁸O and the marble along the fluid pathways as well as fluid-mediated transport of oxygen and trace elements spreading from these pathways resulted in the development of δ^{18} O gradients and trace-element distributions in the marble. Similarly, in the retro-

grade Dalradian rocks of the SW Scottish Highlands, fluid infiltration caused an alteration of calcite-rich marble bands to dolomite and the development of distinctive isotope fronts perpendicular to the dolomite veins (Fein et al., 1994). Such distinct isotope fronts are often used to model fluid-rock interaction processes (e.g., Bickle, 1992; Penniston-Dorland et al., 2010, 2012). However, understanding the reactive, grain-boundary related permeability (Figs. 2 and 4) is crucial in gaining further quantitative information on rates and mass action of fluid-rock interaction. If reactive grainboundaries provide efficient, though transient, fluid pathways that allow the progress of reaction fronts and their connection with the source of the infiltrating fluid (e.g., Konrad-Schmolke et al., 2011), rates of replacement reactions as well as overall flux of mass might be higher than otherwise expected (John et al., 2012; Zhao and Skelton, 2013).

5. Conclusions

Carrara marble was pseudomorphically replaced by calcium phosphates through an interface-coupled dissolution-reprecipitation process in the presence of phosphate-bearing solutions. The reaction front penetrates along the grain boundaries, surrounds single grains, and progresses towards the center of individual grains through the development of intracrystalline porosity. The presence of small amounts of Mg in the starting material leads to the formation of β -TCP as an additional phase alongside hydroxylapatite. The presence of F in solution, however, suppresses the formation of β -TCP and results in the transformation of calcite to fluorine-bearing hydroxylapatite. The incorporation of the ¹⁸O into the phosphate reaction front produced distinct isotope profiles perpendicular to the grain boundaries of the marble. The use of ¹⁸O as a chronometer for the reaction showed that grain boundaries represent an effective fluid pathway allowing relatively fast fluid transport compared to the pores acting as channel-like pathways in the reaction front. To determine the actual reaction rates for the replacement process, further study including in situ observation of the ¹⁸O equilibration in the phosphate solution is necessary.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2013.10.050.

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