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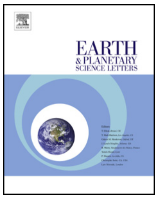

The role of grain boundaries and transient porosity in rocks as fluid pathways for reaction front propagation

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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 ^{18}O 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 ^{18}O in the PO_4 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 ^{18}O 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., 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 fluid-mediated 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., 2000; Skelton, 2011; John 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

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

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 ^{18}O-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 ^{18}O-labeled water is similar to the time scale for the replacement process (Kasioptas et al., 2011). The ^{18}O composition of the apatite at any point in the sample reflects the ^{18}O 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 $CaCO_3$, with only trace amounts of incorporated Mg (∼0.6 wt.%). The marble was cut into cubes of two different side lengths, $\sim 1.5 \times 1.5 \times 1.5\ mm^3$ and $\sim 5.0 \times 5.0 \times 5.0\ mm^3$. 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 $(NH_4)_2HPO_4$ (Acrōs Organics, >99%) solution prepared with MilliQ water (referred to here as the "standard phosphate solution").

(II) A solution enriched with ^{18}O by diluting a 4.0 M $(NH_4)_2HPO_4$ solution with the same amount of ^{18}O-enriched water (Campro Scientific, 97% ^{18}O) (referred to as the "^{18}O 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 ^{18}O were prepared ("fluorine-containing phosphate solution" and "fluorine-containing ^{18}O phosphate solution") by diluting different stock solutions of $(NH_4)_2HPO_4$ and NaF with $H_2{}^{18}O$ (Campro Scientific, 97% ^{18}O).

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 ^{18}O 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

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

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

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