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Reaction fronts, permeability and fluid pressure development during dehydration reactions

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ABSTRACT

Fluids released by prograde metamorphism are often invoked to explain a range of crustal processes from earthquake triggering to metasomatism. These fluids can be either trapped and overpressured or released and channelized depending on the interplay between permeability, reaction rate and compaction. Experimental data are presented, measuring permeability, porosity and microstructural evolution throughout the dehydration of gypsum to form bassanite. Reaction fronts, regions over which the reaction largely occurs, are used as a framework to explain the results. Experiments were conducted under hydrostatic conditions at a constant temperature of 115 °C at two effective pressures of 60 MPa and 110 MPa and three pore-fluid pressures of 20, 40 and 60 MPa. At high effective pressure, creep of the gypsum solid framework results in low porosity and permeability, producing high pore-fluid pressure build-up that slows the reaction rate. A clearly defined narrow reaction front migrates along the sample and the average permeability remains low until the front sweeps across the entire sample. Conversely, at low effective pressure the reaction front is wide producing a permeable, drained network. Average permeability is enhanced significantly after only a small fraction of the reaction has completed, by the interconnection of open pores. This study shows that the width of reaction fronts and hence the permeability development is strongly controlled by compaction. The reaction front velocity is broadly dependent on permeability and the reaction driving force. A simple quantitative model for these relationships is developed.

1. Introduction

Dehydration and devolatilization reactions are fundamental processes controlling fluid movement in the Earth. Dehydration reactions occur during prograde metamorphism when the increase of temperature causes hydrous minerals to become progressively unstable, break down and release water. Fluids released during reactions have been inferred to play an important role in key processes such as earthquake triggering and crustal melting in volcanic arc settings (Hacker et al., 2003; Miller et al., 2004; Abers et al., 2013; John et al., 2012). For instance, at intermediate depths in subduction zones (70–200 km), the development of locally high pore-fluid pressure during dehydration has been proposed as a mechanism to allow embrittlement at depths where the lithostatic pressure is typically considered to be too high to allow brittle deformation to occur (Raleigh and Paterson, 1965; Okazaki and Hirth, 2016). It has also been proposed that fluids from dehydration reactions can be channelized for long distances along the subduction interface, providing a route for water to be recycled back to the surface (Plümper et al., 2017; Angiboust et al., 2014; Scambelluri et al., 2015). The fate of fluids released by dehydration reactions, whether they become trapped and overpressured or drained and channelized, is strongly controlled by the permeability of the dehydrating rock which continuously evolves during reaction due to pore volume changes (Milsch et al., 2011; Tenthorey and Cox, 2003; Wang and Wong, 2003; Bedford et al., 2017). Changes of permeability and pore-fluid pressure have been shown previously to be key in controlling mechanical weakening during dehydration by changing the effective confining pressure (Milsch and Scholz, 2005; Proctor and Hirth, 2015; Brantut et al., 2012; Okazaki and Hirth, 2016; Leclère et al., 2016). Understanding how key physical properties such as permeability evolve during dehydration reactions is therefore fundamental for deciphering how high pore-fluid pressure can build up and also how trapped fluids in dehydrating rocks can be dissipated.

It has been shown that metamorphic devolatilization reactions can progress via a reaction front (Padrón-Navarta et al., 2011; Blattner, 2005). Reaction fronts may be defined as a region between

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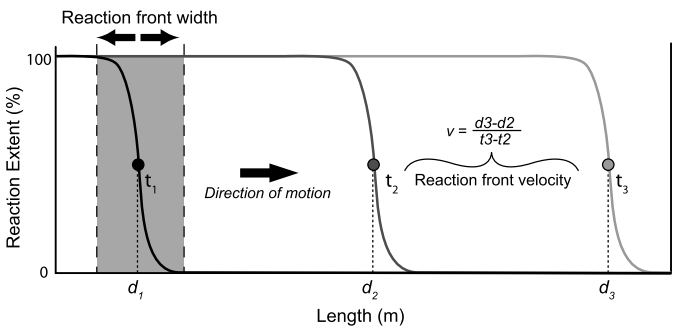

Fig. 1. Schematic drawing explaining reaction front development.

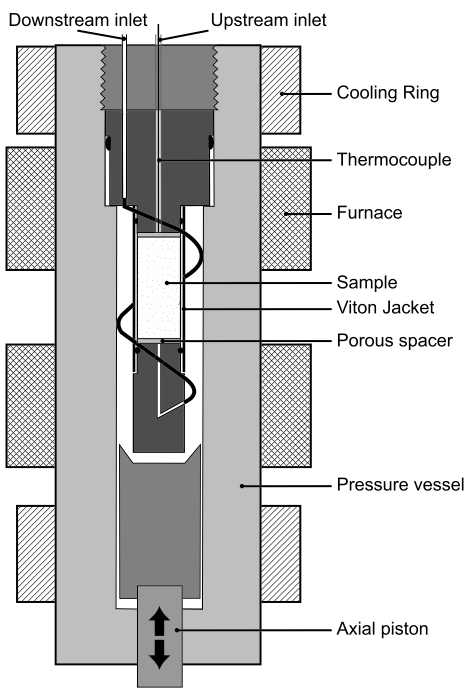

Fig. 2. Schematic drawing of the pressure vessel and the sample assembly used in this study. All tests conducted in this study are hydrostatic (*i.e.* axial loading is not applied by the piston).

mostly unreacted material and mostly reacted material. The permeability development in a dehydrating system must therefore be related in some way to the properties of these reaction fronts. Reaction fronts migrate from reacted material towards unreacted material (Fig. 1). They may be zones of measurable width, or narrow quasi 2D surfaces. In general, reaction fronts migrate according to how fluid overpressures generated by the reaction are able to dissipate. As dehydration reactions typically involve solid volume reductions, porosity is generated as reaction proceeds and thus the permeability of the reacting rocks is enhanced. Reaction fronts presumably migrate when fluids, moving perpendicular to the front, are able to drain from the unreacted material into the enhanced drainage architecture of the reacted rocks. Reaction front velocity is presumably dependent on how quickly fluids can escape and linked to permeability increase. In experiments described here, reaction fronts can be generated when excess pore-fluid pressure from a dehydrating sample is drained to an externally controlled reservoir at one end of the sample (upstream reservoir) and is semi-undrained to an isolated reservoir on the other end (downstream reservoir) (Fig. 2).

Field studies of dehydrating systems, from exhumed fossil subduction zones, have shown two distinct dehydration structures: (1) narrow reaction fronts (Padrón-Navarta et al., 2011; Blattner, 2005), and (2) wide reaction fronts forming an anastomosing network of merging veins comprised of dehydration products having a distributed net-like structure (Taetz et al., 2016; Plümper et al., 2017). However, the current state of understanding does not include any detailed explanation of what influences reaction front width or velocity. A knowledge of the controlling factors would enable interpretation of preserved reaction fronts in terms of those factors, and prediction of velocities and hence large scale reaction and fluid flow rates. In this contribution compaction and reaction rate are shown to be key parameters controlling reaction front width and velocity. Reaction rate must be linked to front development, and compaction must have an effect in terms of reducing porosity and increasing fluid pressure. These effects were discussed by Wang and Wong (2003), although in their experiments reaction fronts were in most cases deduced indirectly from fluid expulsion behavior. Many dehydration reactions are characterized by a solid volume decrease but a net volume increase if fluid pressure is kept fixed (*e.g.* serpentinite breakdown). Such reactions run faster when pore-fluid pressure is low; they can create their own porosity and permeability but evolving pore-fluid pressure will feedback on evolving reaction rate (Brantut et al., 2017; Connolly and Podladchikov, 1998). Compaction will also alter pore-fluid pressure and thus indirectly affect reaction rate. Here experiments are used to show how reaction and compaction interact to control reaction front behavior, going beyond previous work by monitoring average permeability, separating and measuring effects of reaction and compaction, and characterizing microstructures at multiple stages.

In this paper, the links between fluid pressure, permeability, deformation and reaction are explored during the development of wide/narrow and fast/slow reaction fronts. Reaction front width is shown to be controlled by the effective confining pressure (defined as confining pressure minus the fluid pressure). At high effective confining pressures narrow fronts are promoted, as low permeability is maintained in the sample, allowing high pore-fluid pressure build-up which slows down the reaction rate. Reaction front velocity is broadly dependent on effective confining pressure and the reaction driving force with a slow reaction front for a high effective confining pressure and a slow reaction rate while for a low effective confining pressure and a fast reaction rate, a fast reaction front will develop. This study therefore provides a framework for characterizing the width and the velocity of reaction fronts and understanding how fluid pressure builds up and is dissipated during dehydration and devolatilization reactions.

2. Experimental methods

The reaction of gypsum ($CaSO_4$) to bassanite ($CaSO_4 0.5H_2O$) is utilized in this study, as it acts as an analogue material for other hydrous minerals (*e.g.* serpentine, mica, lawsonite) with the advantage that its reaction can be closely controlled allowing for a wide range of parameters to be explored. The reaction is associated with a solid volume reduction of 29% (mineral products only) and a net volume increase of 8% (mineral and fluid products) leading to fluid pressure build-up in an undrained system.

All tests are conducted under hydrostatic conditions at a constant temperature of 115 °C and are designed to investigate how effective confining pressure (*i.e.* affecting compaction) and pore-fluid pressure (*i.e.* the driving force affecting reaction rate) combine to control permeability and fluid overpressure evolution during reaction front propagation. Two different constant effective confining pressures named hereafter HP_{eff} (effective confining pressure 110 MPa) and LP_{eff} (effective confining pressure 60 MPa) and three pore-fluid pressures named hereafter $PP20$, $PP40$ and $PP60$ for 20, 40 and 60 MPa respectively are analyzed. Fluid pressure is known to play a key role on the reaction rate while effective confining pressure effects pore compaction (Llana-Fúnez et al., 2012).