Journal of Structural Geology 94 (2017) 116–135

Contents lists available at ScienceDirect

Journal of Structural Geology

journal homepage: www.elsevier.com/locate/jsg

Reaction-induced fracturing in a hot pressed calcite-periclase aggregate

H. Kuleci [a, *], O.I. Ulven [b], E. Rybacki [c], B. Wunder [c], R. Abart [a]

[a] *University of Vienna, Department of Lithospheric Research, Althanstrasse 14 (UZA 2), 1090, Vienna, Austria*
[b] *University of Oslo, Physics of Geological Processes, Postboks 1048 Blindern, 0316, Oslo, Norway*
[c] *Helmholtz Centre Potsdam, German Research Centre for Geosciences, Telegrafenberg, 14473, Potsdam, Germany*

ARTICLE INFO

Article history:
Received 11 July 2016
Received in revised form
16 November 2016
Accepted 23 November 2016
Available online 28 November 2016

Keywords:
Hot isostatically pressed calcite-periclase aggregate
Hydration of periclase
Swelling particles
Reaction induced fracturing
DEM modelling

ABSTRACT

The chemo-mechanical feedbacks associated with hydration of periclase immersed in a calcite matrix were investigated experimentally. Dense calcite-periclase aggregates with <5% porosity and with a calcite to periclase ratio of 90/10 and 95/5 by volume were prepared by hot isostatic pressing. Subsequent hydration experiments were performed in a hydrothermal apparatus at temperatures of 580–610 °C and a pressure of 200 MPa for run durations of 5–60 min. The rate of the periclase to brucite transformation was primarily controlled by the access of fluid. Where fluid was present, the reaction was too fast for the associated positive volume increase of the solids of about 100% to be accommodated by creep of the calcite matrix, and fracturing was induced. The newly formed cracks greatly enhanced the access of fluid leading to a positive feedback between hydration and fracturing. Mostly the newly formed cracks follow pre-existing grain boundaries in the calcite matrix. Comparison of experimental results with numerical 2D discrete element modelling (DEM) of crack formation revealed that the geometry of the crack pattern around a reacting particle depends on the shape of the original periclase particle, on the mechanical strength of the particle-matrix interface and on the mechanical strength and arrangement of grain boundaries in the calcite matrix in the immediate vicinity of the swelling particle.

1. Introduction

It has long been recognized that mineral reactions and rock deformation are intimately linked. It is a common observation that tectonically induced deformation mediates mineral reactions. Typically, the extent of prograde mineral reactions is enhanced in high-strain zones as compared to the surrounding low-strain domains of a rock. For example, Keller et al. (2004) showed that the extent of an eclogite facies reaction overprinting an amphibolite facies rock was substantially higher in a shear zone than in the surrounding undeformed rock. Similarly, the transformation of a granulite to eclogite in the Norwegian Caledonides was found to be confined to brittle structures and the associated damage zones (Engvik et al., 2001; Austrheim, 2013). Also retrograde phenomena such as hydration or chemical alteration are often localized in domains of intense deformation such as shear zones (Wintsch et al., 1995; Hurzeler and Abart, 2008).

The opposite case, where mineral reactions induce deformation is equally relevant but has received far less attention. In general, the total volume of the product phases of a mineral reaction is different from the volume of the corresponding reactant phases. For example, prograde metamorphic reactions liberate fluid which is expelled from the rock by a combination of reaction enhanced permeability and gravity driven compaction (Connolly and Podladchikov, 1998). On the grain scale, the volume change associated with a mineral reaction causes heterogeneous mechanical stress around the reaction site. Such reaction-induced stress heterogeneity tends to relax towards constant and uniform pressure through plastic yielding of the rock matrix (Carmicheal, 1987). Depending on reaction-rate and the rock's rheology, the stress relaxation may occur by pressure solution, creep or fracturing (Fletcher and Merino, 2001).

The decompression-induced transformation of coesite inclusions in garnet to quartz is an example of the latter scenario. The associated about 8% volume increase typically leads to the formation of radial cracks around such inclusions (Chopin, 1984; Whitney et al., 2000). Another typical example is related to high pore-fluid pressure, which may develop during devolatiliization in rocks with low permeability and which eventually may lead to fracturing (Nishiyama, 1989). Reaction-induced fracturing has also been

---

* Corresponding author.
E-mail address: hakan.kuleci@univie.ac.at (H. Kuleci).

http://dx.doi.org/10.1016/j.jsg.2016.11.009
0191-8141/© 2016 Published by Elsevier Ltd.

reported from replacement of leucite by analcime (Jamtveit et al., 2008) and from cation exchange applied to single-crystal alkali feldspar (Neusser et al., 2012; Scheidl et al., 2013; Schaeffer et al., 2014). Reaction-induced fracturing is also of interest in the context of serpentinization, where large positive volume change is associated with the hydration of olivine (Kelemen and Hirth, 2012). Moreover, fracturing induced by low-temperature hydration of common rock-forming, nominally anhydrous minerals such as feldspar, olivine and pyroxene is an important mechanism in spheroidal weathering (Royne et al., 2008). Finally, the enhancement of permeability due to fracturing induced by swelling particles is of major interest in reservoir engineering (Zhou et al., 2015).

The formation of *Predazzite* is an example of the relaxation of reaction-induced stress by creep. Predazzite is a calcite-brucite rock, which forms from dolomite, when its upper thermal stability limit is exceeded, and dolomite decomposes into calcite + periclase (Rogers, 1913, 1928; Watanabe, 1935; Mueller et al., 2009). Periclase (MgO) is strongly hygroscopic and is thus prone to transformation to brucite ($Mg(OH)_2$) by hydration. The transformation of periclase to brucite after the reaction

$$MgO + H_2O = Mg(OH)_2$$

involves a substantial volume increase of the solids from 11.25 cm^3/mol to 24.63 cm^3/mol. Thus, the volume of the solids increases by more than 100% relative to the initial value. As a consequence, considerable excess pressure is developed, if the reaction occurs in confined space (Ostapenko, 1976). No cracks are visible in natural predazzite indicating that stress-relaxation occurs by creep of the calcite matrix.

Several questions arise in this context: Consider a calcite-periclase aggregate as a model example for the more general case of reactive swelling particles dispersed in a non-reacting matrix. What are the factors that decide whether the associated stress-heterogeneity is relaxed by fracturing or by creep? What are the factors that control the crack pattern around the swelling particles? Unlike creep and pressure solution, fracturing creates new fluid pathways possibly leading to a positive feedback between reaction and fracturing (Ulven et al., 2014b). It has been argued that porosity generated by a mineral reaction with negative volume change of the solids may enhance fluid access, whereas a positive volume change tends to close porosity and prevent further access of fluid (Putnis, 2002). Can a positive feedback between fracturing and a hydration reaction be documented, or does the volume increase during reaction close potential fluid passageways and suppress further reaction?

We present the results of hydration experiments on synthetic calcite-periclase aggregates. During hydration, the periclase grains act as swelling particles and the calcite behaves as a non-reactive matrix. At the conditions of our experiments, the periclase to brucite transformation is extremely fast (see Kuleci et al., 2016 and references therein), and the rate-limiting process during the hydration of dense calcite-periclase aggregates is the supply of H_2O. Wherever hydration occurs, the associated volume increase leads to fracturing. We characterize the spatial distribution of reaction progress and the crack patterns around the swelling particles by scanning electron microscopy. In addition, we present results from 2D discrete element modelling (DEM). Some general inferences with respect to the factors controlling fracturing, crack patterns and reaction progress are made from a comparison of experimental and modelling results.

2. Experimental details

2.1. Starting material

Synthetic periclase and Carrara marble were used as starting materials. Periclase single crystals and tablets of sintered periclase, a highly porous (>10% porosity) aggregate of less than 10 μm sized periclase particles, were purchased from MaTeck (Germany). The periclase single crystals and Carrara marble were crushed and sieved to obtain 400, 200, 100 and 63 μm sieve fractions. The tablets of sintered polycrystalline periclase were just crushed and sieved. This procedure mainly yielded fragments <63 μm, which were then used for preparing calcite-periclase aggregates.

2.2. Experimental assemblies

Three different types of calcite-periclase aggregates were prepared by hot isostatic pressing (HIP). The first two types, which had unrestricted water access, are represented by conventional HIP aggregates with two different calcite to periclase ratios of 90/10 and 95/5 by volume, respectively. A third type of assembly, which was designed to only allow for restricted access of water, was prepared in thin (1.8 mm inner diameter) platinum tubes.

For all assemblies calcite powder of the sieve fraction <63 μm was used. Single crystal periclase fragments with grain sizes <63 μm (HIP-3), 63–100 μm (HIP-4, HIP-7) and 100–200 μm (HIP-8) were used for different HIP experiments. In one experiment fragments of sintered periclase were used (HIP-5) (see Table 1). Calcite and periclase powders were carefully mixed, homogenized and finally dried for more than 24 h at 120 °C. For conventional HIP experiments, the mixes were cold-pressed into thin-walled cylindrical steel sleeves of 15 mm diameter and 30 mm length.

The samples were then hot isostatically pressed (HIPed) in a Paterson type gas medium apparatus at the Helmholtz Centre Potsdam, German Research Centre for Geosciences. A temperature of 700 °C and a confining pressure of 300 MPa – this is within the stability field of calcite and periclase – were applied for 2 h (Milsch et al., 2003). The HIPed aggregates were then cut into 1 × 1 × 1 mm and 1 × 1 × 0.5 mm sized cuboids using a Logitech Model 15 Diamond & Wire Disc Saw. These cubes were then used for hydration experiments.

In addition, calcite-periclase aggregates were prepared in thin, 1.8 mm inner diameter platinum tubes. To this end calcite-periclase mixes with a calcite to periclase proportion of 90/10 by volume and 100–200 μm fraction of the periclase single crystals were cold pressed into 25 mm long platinum tubes which had been sealed on one end. Nine such tubes were inserted into a thin-walled cylindrical steel sleeve of 15 mm diameter and 30 mm length and fixed using calcite to fill the space between the platinum tubes. The entire assembly was cold pressed and then HIPed like the conventional HIP samples. After HIPing the whole assembly was cut in the middle, so that one half of the Pt tubes was open at both ends and the other half was closed at one end and open on the other end. In this manner, the accessibility of reactive sites for water was substantially reduced.

2.3. Hydration experiments

Hydration experiments were done at the Helmholtz Centre

Table 1
Starting assemblies prepared by hot isostatic pressing (HIP). Periclase single-crystals were used for HIP-3, HIP-4 and HIP-8, and sintered periclase aggregates were used for HIP-5; Pt-tubes were used for preparing HIP-7.

Sample	Size fraction of $CaCO_3$ (Cc)	Size fraction of MgO (Per)	Volume ratio (Cc/Per)
HIP-3	<63 μm	<63 μm	90/10
HIP-4	<63 μm	63–100 μm	90/10
HIP-5	<63 μm	powder (~<20 μm)	90/10
HIP-7	<63 μm	63–100 μm	90/10
HIP-8	<63 μm	100–200 μm	95/5