Effects of confinement on reaction-induced fracturing during hydration of periclase

Xiaojiao Zheng¹, Benoît Cordonnier^{1,2}, Wenlu Zhu³, François Renard^{1,4}, and Bjørn Jamtveit¹

¹The Njord Centre, Physics of Geological Processes, Department of Geosciences, University of Oslo, box 1048, Blindern, 0316 Oslo, Norway

²ESRF – The European Synchrotron, CS40220, Grenoble 38043, France

³Department of Geology, University of Maryland, College Park, MD 20742, USA

⁴Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, IFSTTAR, ISTerre, 38000 Grenoble, France

Corresponding author: Xiaojiao Zheng (xiaojiao@geo.uio.no)

Key Points:

- Time- resolved in-situ X-ray microtomography imaging of reaction-induced fracturing
- Reaction-induced fracturing is associated with a transient porosity pulse
- Reaction-induced fracturing slows down considerably when the effective mean stress exceeds a certain threshold

Abstract

Hydration of a nominally dry rock can cause expansion of the solid volume, resulting in reaction-induced fracturing and an associated increase in the porosity and permeability of the rock. We study the effect of confinement on the coupling between stress generation, reaction-induced fracturing and porosity evolution during the hydration of periclase (MgO) into brucite (Mg(OH)₂). Samples of a microporous MgO ceramic were hydrated at 170-210°C, 5-80 MPa confining pressure, 6-95 MPa differential stress, and 5-75 MPa pore fluid pressure in a purpose-designed triaxial load cell. Hydration-induced changes were recorded in-situ by X-ray microtomographic imaging at 5-minute intervals. Below 30 MPa effective mean stress, the fraction of periclase replaced by brucite is a sigmoidal function of time. After a slow start, the replacement rate picks up with concomitant intense fracturing. The porosity increase resulting from the reaction-induced fractures is transient (pulse-like). Following the porosity pulse the rate of replacement declines until the replacement is almost complete. Above 30 MPa, the reaction rate is slow, porosity decreases monotonically without any observable fracturing during the time of the experiment. At these stress conditions, the lack of fracturing cannot be limited by the thermodynamic affinity of the reaction. A possible interpretation is that the stress generated by the reaction may overcome the disjoining pressure at the grain-grain interface, expelling the water film trapped there and thereby dramatically reducing the reaction rate.

1 Introduction

Reaction-induced fracturing is a common phenomenon in both natural and man-made materials. Salt growth in building materials such as rocks and cements is a major problem that causes serious deterioration and weakening of man-made structures (Scherer, 1999). In geological systems, reaction-induced fracturing (MacDonald & Fyfe, 1985; O'Hanley, 1992) occurs in a variety of situations, ranging from weathering to retrograde metamorphism, where volatilization reactions (especially hydration or carbonation) and mineral precipitation result in a local increase in solid volume (Fletcher et al., 2006; Jamtveit et al., 2008; 2009; Kelemen & Matter, 2008; Noiri et al., 2010; Rudge et al., 2010; Kelemen & Hirth, 2012; Kelemen et al., 2011; Gratier et al., 2012; Jamtveit and Hammer, 2012; Ulven et al., 2014a, 2014b; Malvoisin et al., 2017).

Since growth and/or swelling in a porous material will tend to clog initially connected porosity (Hövelmann et al., 2012) and thus reduce the permeability, reaction-induced fracturing (Zhu et al., 2016) is thought to be critical in sustaining fluid-induced reactions in a system that otherwise would become impermeable to the influx of external fluids. Whether reaction-induced fracturing occurs has far-reaching consequence for a number of applications including the feasibility of capturing CO₂ through reactions involving ultramafic rocks (Oelkers et al., 2008; Kelemen et al., 2011).

In natural systems, it is often difficult to determine to what extent fractures in a hydrated rock are related to the far field external stresses rather than the internal stresses generated by the hydration reaction itself (Rouméjon and Cannat, 2014). Experimental investigations under controlled stress conditions are therefore important to better understand how reactions progress under different stress conditions and under what conditions reaction-induced fracturing occurs. In this study, we conducted dynamic microtomography experiments to investigate the effect of confining pressure on the conversion of chemical potential energy to mechanical work required to produce fractures. We consider a case whereby porous periclase (MgO) is hydrated to form

brucite ($\text{Mg}(\text{OH})_2$). This reaction is believed to represent a relevant analog system similar to many reactions taking place during retrograde metamorphism, including serpentinization. In the oil and gas industry, hydration of cements containing various amounts of calcium or magnesium oxide is often used to efficiently seal boreholes (Wolterbeek et. al., 2017). The real-time microscale structural evolution of the periclase sample at in-situ stress and temperature conditions were obtained using synchrotron X-ray microtomography. We studied the effect of imposed stresses, including the differential and mean stresses, on reaction rate and reaction-induced fracturing.

2 Materials and Methods

The reaction $\text{MgO} + \text{H}_2\text{O} = \text{Mg}(\text{OH})_2$ has an associated solid volume increase of about 110% accompanying a 45% weight increase (Kuleci et al., 2016). The equilibrium temperature of the dehydration reaction of brucite to form periclase is ca. 550°C at 1 atm pressure (Johnson and Walker, 1993). The kinetics of this reaction have been studied experimentally (Liu et al., 2017) and follow an Avrami-type sigmoidal kinetics (Avrami, 1939) at temperatures between 320 to 360°C and pressures ranging from 819 to 1282 MPa. The hydration of periclase into brucite was studied by Kuleci et al. (2016) under a pressure of 200 MPa and temperatures between 350 to 620°C for a duration of between 5 and 40 minutes. In their experiments, a cube of periclase was left in contact with water, and a rim of brucite grew at the surface of the periclase, without fracturing the original periclase crystal.

Here we study the effect of confinement on reaction-induced fracturing during the hydration of periclase (MgO) into brucite ($\text{Mg}(\text{OH})_2$). The cylindrical samples of periclase ceramics with well-connected initial porosities between 0.5 to 1.6 % have a diameter of 5 mm and a height of 10 mm. Each periclase sample was placed in the triaxial deformation apparatus ‘HADES’ (Renard et al., 2016), where the confining pressure, axial stress, pore fluid pressure and temperature can be controlled independently (Fig. 1). A jacket made of Viton fluoropolymer elastomer encased each sample, separating the confining medium (silicon oil) and the pore fluid (distilled water). HADES is transparent to X-rays and was mounted on the rotating stage of the X-ray tomography beamline ID19 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The progress of the periclase hydration reaction can be imaged at the desired conditions of pressure and temperature using synchrotron radiation time-resolved X-ray computed microtomography.

We performed seven experiments at varying confining pressure P_c , temperature T , and axial stress P_a conditions (Table 1, Fig 1b). A pore fluid pressure P_p of 5 MPa was used in all but one experiments, in which the pore pressure was at 75 MPa (sample peri8). A small fluid pressure gradient of 0.5 MPa was imposed between the pore fluid inlet and outlet of the sample to drive fluid flow. In the experiments, the axial and confining pressures were imposed first, then the sample was heated at 2°/min. until the desired temperature, before the pore fluid pressure was increased to the desired value. In all experiments (Table 1), the same procedure was followed. For each sample, 3-dimensional (3D) tomography volumes were acquired every 5 minutes during the progress of reaction. The volumes were then reconstructed as 16-bit gray levels three-dimensional images, with a voxel size of 6.5 micrometers.

All the reconstructed datasets are of excellent quality, with a low level of noise and artefacts. Since X-ray attenuation depends on density and is represented by gray values, the three phases – periclase, brucite and pores – can easily be separated (Fig. 2). The gray value of brucite

is very similar to the jacket around the sample, therefore the background was subtracted with a mask and only the sample was preserved (Figs. 3, 4). For all time steps, we calculated histograms of the gray value frequency distribution from 180 million voxels that constituted a parallelepiped sub-volume just off the center of the sample cylinder (Fig. 2). As the reaction progressed through the parallelepiped, changes in the volume fraction of periclase, brucite and porosity were measured (Fig. 2). By “pore”, we refer to the definition of Sprunt and Brace (1974) for the pore space that includes both the existing pores of the sample and the newly created pores during the experiments. We separated (i.e. segmented) the three phases after reducing the noise in the data through a non-local mean filtering and masking out the sample from the surrounding jacket and background for all the time series.

All pores in the above-mentioned parallelepiped were extracted. We used the method of Liu et al. (2009) to label face-connected clusters of pore voxels as individual voids and calculated the position, volume and surface area of each individual pore. We chose pores with volumes bigger than 10 voxels. The sum of periclase, brucite and porosity fractions ranges from 99.24% to 99.98%, and the 0.02%-0.76% difference to 100% would be the contribution from errors on the three phases. So the pores below 10 voxel size contribute 0.01%-0.25% to the overall total volume. Consider the ‘large porosity’ range from 0.5%-1.5%, within our error the small pores (smaller than 10 voxels) neglected here are globally 0.6% to 33% of the total porosity. Because the rates of fluid-mineral interactions are directly controlled by the mineral surface area and not all parts of periclase surface were in contact with fluid, we segmented the reactive surface area as the interface between periclase and pore-fluid at each time step. To do this, we first extracted the surface areas for periclase, brucite and pore phases and labeled them. Then we selected the surface area between periclase and pore fluid, that we consider to represent the reactive surface area.

3 Results

Extensive reaction-produced fracturing is observed in every sample subjected to an effective mean stress $P_{\text{mean}} = (2P_c + P_a)/3 - P_p$ of 30 MPa or less. In contrast, no fracturing was observed in the two experiments with an effective mean stress greater than 30 MPa (P_{mean} 35 & 75 MPa), regardless the level of differential stresses imposed. The control of effective mean stress on fracturing is well illustrated in sample peri6. At a P_{mean} of 35 MPa and a differential stress $P_{\text{diff}} = P_a - P_c$ of 90 MPa (Fig. 1b), sample peri6 exhibited no fracturing. However, when the P_{mean} was decreased to 23 MPa by lowering P_{diff} to 65 MPa, the reaction rate was greatly accelerated and fracturing was observed during the time scale of the experiment. In the following we describe the evolution in porosity and phase content for the various experiments.

3.1 Experiments without reaction-induced fracturing

The hydration progress in sample peri4 at $P_{\text{mean}} = 75$ MPa and $P_{\text{diff}} = 1$ MPa (Fig. 3) is very similar to that in sample peri6 at $P_{\text{mean}} = 35$ MPa and $P_{\text{diff}} = 90$ MPa despite the large difference in differential stress. Reaction-induced fracturing was not observed in either experiment. The evolution of porosity in a sub-volume composed of $250 \times 250 \times 250$ voxels (or $1625 \mu\text{m} \times 1625 \mu\text{m} \times 1625 \mu\text{m}$) is shown in Fig. 3b.

Over the first 40 minutes, the total porosity in peri4 decreased from an initial value of 1.3% to a constant value of 0.5%. Large pores are preferentially filled by brucite (Fig. 5). After 110 minutes about 3.5 vol.% of brucite was formed, and more than 3 vol.% appeared during the

first 30 minutes. This suggests that the existing pores were clogged and without reaction-induced fracturing the reaction progress is very slow.

3.2 Experiments with reaction-induced fracturing

Six experiments were conducted at a mean stress below 30 MPa, (Fig. 1b, Table 1). Three of them (peri7, peri8, perisp1) were performed to check reproducibility of results and confirm the fracturing limit of effective mean stress at 30 MPa. Most experiments were conducted at a confining pressure of 10MPa and differential stresses of 6 MPa (peri1, Fig. 4), 15 MPa (peri5, Fig. S1) and 60 MPa (peri6, Fig.7). One experiment (peri8) was conducted at high confining pressure (80 MPa) and high pore fluid pressure (75 MPa). Detailed analyses show that in all these experiments, the replacement of periclase to brucite is a sigmoid function of time. After a slow start (stage 1), the rate of replacement picks up accompanied by intense fracturing and a pulse-like porosity increase (stage 2). In stage 3, the rate gradually declines till the replacement is complete (Fig. 4).

For sample peri1 (Fig. 4, Video S1), brucite is barely visible after 20 minutes (stage 1) and becomes obvious after 30 mins (onset of stage 2). At about 35 minutes, the reaction rate accelerates at the onset of global fracturing. At 45 minutes a maximum porosity of ca. 2.5% is reached. After that the reaction slows down gradually and the pore space is quickly reduced to less than 1% (stage 3). After 85 minutes, the reaction is about 95% complete in terms of periclase consumption. The pore size distribution (Fig. 6) shows an evolution where the porosity pulse corresponds to an increasing and then decreasing number of pores. The reduction in porosity is associated with interconnection of previously isolated pores.

In sample peri5 (Fig. S1, S2, Video S2), fracturing and brucite formation can be observed after 25 mins (onset of stage 2), then it follows a reaction pattern similar to the one in peri1. Again, the porosity increase is pulse-like, first increasing to ca. 2.1% and then decreasing. The microstructure that formed during the intermediate stages of reaction progress (stage 3) is remarkably similar to the so-called mesh textures that often develop during serpentinisation of olivine-rich rocks (Wicks & Whittaker, 1977; O'Hanley, 1992; Jamtveit et al., 2009). Again, the reaction is nearly complete after 90 minutes.

At P_{mean} of 23MPa and P_{diff} of 65MPa, sample peri6 was subjected to higher stresses than samples peri1 and peri5 (Fig. 1b). The initial porosity of peri6 was also higher ($\phi=1.65\%$). In this case, the transition between stage 1 and 2 took only 10 minutes. In stage 2 both the progress of the reaction and the development of a porosity pulse are slower in peri6 than in the previous cases (Fig. 7). The porosity does however reach a much higher value ($\sim 12.5\%$) at around 90 minutes. After 140 minutes, there is still 20% periclase left and the reaction rate is still significant. For peri8 which was conducted at high confining pressure (80 MPa) and high pore fluid pressure (75 MPa), fracturing started from around 120min and the reaction was approximately 80% complete after 250min.

The experimental results suggest that the brucite growth in the pore space of the porous periclase produces reaction-induced fracturing only if the effective mean stress is less than 30 MPa either at low confining pressures or at high confining pressures but with a pore fluid pressure close to the confining pressure. When the hydration reaction takes place under higher effective mean stresses, brucite growth clogs the existing pores and causes a substantial

reduction of the global reaction rate. Detailed inspection of the pore size statistics (Figs. 5, 6 and S2) shows that the reaction product (i.e., brucite) preferentially fills the largest pores.

4 Discussion and Conclusions

Brucite growth clearly produces fracturing during experiments conducted at low effective mean stress, and the volume increase of brucite is an approximately sigmoidal function of time. After a slow start, the brucite growth rate accelerates at the onset of fracturing, and slows down as the system is running out of reacting periclase (Figs. 4, 7 and S1). This behavior resembles an Avrami type kinetics where the initial stage is slow due to slow nucleation and the reaction rate follows a bell-shaped curve when plotted versus time. The Avrami kinetics model (Avrami 1939) describes the relationship between the transformed volume fraction $X(t)$ and time t according to the equation $X(t) = 1 - \exp(-kt^n)$, where k is the reaction rate in s^{-n} and n is a time exponent that depends on the reaction mechanism. This equation can be linearized after taking the logarithm two times, to give $\ln(-\ln[1 - X(t)]) = \ln k + n \ln t$ which produces a sigmoidal reaction progress, as observed in our experiments.

We define the reaction rate as $R = \Delta V / \Delta t$ where ΔV represents for the increase in brucite volume or the decrease in periclase volume. Our data do not follow a simple Avrami model due to the large volume increase involved. However, the bell-shaped Avrami rate has in many respects an analog in the ‘porosity pulse’ observed in these experiments. This pulse reflects the evolution of reactive surface area largely generated by the fracturing process and thus also reflects the evolution in reaction rate. The reduction in porosity observed during the last stages of the experiments results from clogging of cracks and pores when the rate of the fracture generating reaction ($MgO + H_2O = Mg(OH)_2$) decreases. Zhang et al. (1994) proposed that the pore closure could be related to plastic deformation (i.e. pore collapse) due to stress concentration at the pore walls. Because our dynamic microtomography data show no evidence of pore collapsing, we conclude that porosity reduction observed in our experiments is mainly due to pore clogging.

The reaction transforms periclase into brucite with a volume expansion of 110%. This expansion increases the pore volume by fracturing. At the same time, some pores become clogged because of the precipitation of brucite. The volume of the sample, V_{sample} , evolves as a function of time according to:

$$(1 - \phi(t))V_{sample}(t) = n_{pe}(t)\bar{V}_{pe} + n_{br}(t)\bar{V}_{br} \quad (1)$$

where n_{pe} and n_{br} are the number of moles of periclase and brucite, respectively, $\bar{V}$ ($m^3 \cdot mol^{-1}$) is a molar volume and ϕ is the porosity. As a consequence, porosity varies according to a partial differential equation:

$$(1 - \phi(t)) \frac{dV_{sample}(t)}{dt} - V_{sample}(t) \frac{d\phi(t)}{dt} = \frac{dn_{pe}(t)}{dt} \bar{V}_{pe} + \frac{dn_{br}(t)}{dt} \bar{V}_{br} \quad (2)$$

The net porosity change is determined by two mechanically coupled processes, the formation of fracture and the clogging of pores:

$$\frac{d\phi}{dt} = \frac{d\phi_{frac}}{dt} + \frac{d\phi_{clogging}}{dt} \quad (3)$$

where $d\phi_{frac}$ is the porosity change due to the formation of fractures and $d\phi_{clogging}$ is the porosity change due to precipitation of brucite that clog the pores because of its higher molar volume than periclase. The resolution of the system of equations (2) and (3) requires numerical modelling of the coupling between the Avrami kinetics of the periclase to brucite reaction that

controls volume expansion and mechanical modelling of fracture formation. Such modelling could be performed using, for example, a discrete element modelling approach (Ulven et al., 2014), but is out of the scope of the present study. Aharonov et al. (1997) simulated crystallization during reactive fluid flow into porous rock. They demonstrated that crystallization preferentially took place within fluid pathways with high permeability, gradually changing a well-connected channelized network to a disconnected, more random, distribution of pores. In our experiments a similar effect can be expected, in addition to the deformation due to volume expansion of the transformation of periclase into brucite.

The reaction in sample peri6 was carried out at high mean and differential stress (23 and 65 MPa, respectively) and this experiment shows a different evolution than the ones described above. An initial period of gradual increase in the reaction rate and associated porosity growth, to a very high porosity of 12.5%, is followed by a reduction in reaction rate. This reduction in reaction rate takes place while the porosity is still increasing and the progress of reaction has reached only about 20% periclase consumption. The reaction and fracturing in sample peri6 (Fig. 7a) proceeded slower than for samples peri1 (Fig. 4a) and peri5 (Fig. S1a). Because sample peri6 has a higher porosity than other samples, the slower reaction rate cannot be due to limited fluid supply or low reactive surface area. A possible explanation could be that the rate of brucite growth in the periclase pores or fractures is slower in this case. Since, all experiments are conducted at broadly similar temperature and pressure conditions, this effect is not due to differences in the thermodynamic affinity of the brucite-forming reaction which is very high in all cases. A ‘force of crystallization’ σ_{foc} , equivalent to the pressure required to stop the reaction by pushing it towards equilibrium, can be calculated from Eq. 13 of Kelemen and Hirth (2012) and also derived in Wolterbeek et al. (2017):

$$\sigma_{\text{foc}} = \frac{\Delta_f G_{\text{MgO}}^{P,T} + \Delta_f G_{\text{H}_2\text{O}}^{P,T} - \Delta_f G_{\text{Mg}(\text{OH})_2}^{P,T}}{V_{\text{m,Mg}(\text{OH})_2}^{P,T} - V_{\text{m,MgO}}^{P,T}}. \quad (4)$$

Taking the Gibbs free energies of formation of periclase, brucite, and water at 200°C equal to -550 kJ·mol⁻¹, -785 kJ·mol⁻¹ and -210 kJ·mol⁻¹, respectively, and the molar volumes of periclase and brucite (11.248 and 24.630 cm³·mol⁻¹, respectively) the expected force of crystallization is ca. 1.9 GPa. The variation of Gibbs free energy due to the creation of surface area is defined as $\gamma \left(\frac{\partial G}{\partial A} \right)_{T,P}$, where γ is the surface energy, and A is the surface area. Surface tension of MgO has been measured by Jura and Garland (1952) who found values of the order of 1.05 J/m². For brucite we did not find surface tension data, and we assume a value of the same order as for periclase. The contribution of the surface energy to the Gibbs free energy for particles of radius $r = 1$ micrometer size, and given the molar volume of periclase $\bar{V}_{\text{pe}} = 11.62 \cdot 10^{-6}$ m³/mol is $\Delta G_{\gamma} = \frac{2\gamma}{r} \bar{V}_{\text{pe}} = 23$ J/mol. Compared to the driving force related to the phase transformation from periclase to brucite, of the order of 25 kJ/mol, the effect of surface tension is small and we neglected it in the calculation of the force of crystallization.

However, our experimental results show that an effective mean stress of only 30 MPa, less than 2% of the theoretical ‘force of crystallization’, may be sufficient to prevent reaction-induced fracturing during the course of our experiments and slow down the reaction rate. A similar lack of reaction produced fractures is also observed during serpentinization and carbonation of single grains of olivine (Hövelmann et al., 2012), another system in which the ‘force of crystallization’ is expected to be hundreds of MPa (e.g., Kelemen and Hirth, 2012). One

possible explanation for this observation is that the reduction in the rate of the brucite-forming reaction is due to a change in the structure of the reactive periclase-water-brucite interface itself.

For the brucite forming reaction to progress where brucite simultaneously exerts a pressure on the confining periclase, a fluid film must be able to remain stable at the periclase-brucite interface even when subject to significant normal stress (Renard and Ortoleva, 1997; Scherer, 2004). This requires that the close range hydration forces between the brucite and periclase interface in the presence of a fluid film are repulsive, as is observed in a number of other systems such as the calcite-calcite interfaces (Røyne et al., 2011). If, however, the normal stress exceeds the repulsion forces, the fluid film thickness will be reduced down to one or two layers of water molecules (Renard and Ortoleva, 1997). As a consequence, transport of water along grain boundaries will slow down, the reaction will slow down as well. This level of normal stress is often referred to as the disjoining pressure (Derjaguin and Churaev, 1974; De Gennes, 1985).

The disjoining pressure describes the physics of wetting or dewetting of a liquid film on a solid surface. It is the negative derivative of the free energy with respect to film thickness (Derjaguin and Churaev, 1974). The disjoining pressure arises from the interaction energies of molecules in a film being different from that in the bulk. The energy contributions to the energy of thin films could have different origins: surface curvature (Steiger, 2005); osmotic effect due to surface charges at the mineral surfaces (Renard and Ortoleva, 1997), van der Waals forces acting between the film and the mineral surface, or polar interactions between water molecules near the mineral surface that are different from bulk water. Because several effects are involved, parameters that are likely to control the disjoining pressure are mineral surface charge, salinity of the fluid, curvature of the solid surface, and temperature. Despite a variety of processes involved, the net effect of disjoining pressure is that it induces an excess fluid pressure within a grain contact, compared to the pore fluid (Scherer, 2004). If the stress loading two grains increases, the resulting effect is to squeeze out the film at the contact. When the total pressure in the thin film overcomes the pore pressure plus the disjoining pressure, water should be expelled, producing a dry contact. The rate of a fluid-consuming reaction will be reduced in a system where the local normal stress at the reactive interfaces approaches the relevant disjoining pressure. We thus infer that at an effective mean stress of 30 MPa, the periclase-brucite system is approaching a situation where the normal stresses at the reacting interfaces approach the disjoining pressure, and the rate of reaction will slow down, even if the porosity in the system is still high. It is the interfacial forces at the reactive surface that dictate the behavior of the system, and not the theoretical thermodynamic pressure required to push the reaction towards equilibrium.

Because brucite is a mechanically weak phyllosilicate mineral, the lack of reaction-induced fracturing at effective stress >35 MPa could also result from relaxation of crystallization pressure via viscous creep and via frictional sliding along existing fractures or cleavage planes. Taking the flow law derived by Mariani et al. (2006) at 200°C and 30 MPa of effective stress, the viscous creep during the time scale of our experiments would be insignificant so we can rule it out. Relaxation of crystallization pressure via frictional sliding is not consistent with our experimental results. Here we compared the two experiments PERI1 and PERI4 conducted at the same different stress of 1 MPa (Table 1).

Frictional sliding along the preexisting fractures or cleavages obeys the Coulomb-Mohr failure criterion. In PERI1, the maximum effective principal stress is 6 MPa, and the intermediate and minimum effective principal stresses are 5 MPa, which give the mean effective

stress of ~5.5MPa. Given the frictional coefficient of ~0.3 (Moore and Lockner, 2004, 2005, 2007) the yield strength is roughly ~1.6 MPa for PERI1. With a differential stress of 1MPa applied on sample PERI1, it is conceivable that frictional sliding could contribute to the relaxation of crystallization pressure.

In comparison, in PERI4, the maximum effective principal stress is 76 MPa, and the intermediate and minimum effective principal stresses are 75MPa, which give the mean effective stress of ~75.5MPa. Thus the yield strength of PERI4 is ~22.6 MPa. With a differential stress of 1 MPa for PERI4, relaxation via frictional sliding in PERI4 is unlikely. If relaxation via frictional sliding is the mechanisms that inhibit fracturing then more fracturing is expected in PERI4 than in PERI1, which is opposite to the observation. Therefore, we conclude that the low shear strength of the brucite cannot explain the difference in kinetics of periclase transformation we observe.

In the case of a higher differential stress, the formation of brucite along well-defined planes could induce shear faulting because of the small friction of this mineral. This mechanism has been proposed to explain the weakness of large continental faults (Moore et al. 2007). However, we did not observe shear faulting in our experiments conducted with a differential stress of 45 or 55 MPa (see Table 1). We cannot rule out, however, that experiments performed at high differential stress, while keeping a confining pressure below 30 MPa, could produce shear faulting where the low shear strength of brucite would play a role in controlling the kinetics of periclase transformation.

These results are relevant to common geological systems, such as the hydration of olivine-rich rocks to form variably serpentinized product rocks. The microstructures produced during serpentinization are often strikingly similar to those observed in the experiments described above (Figs. 4b, 7b) and may reflect a similar reaction driven fracturing mechanism as serpentinization is associated with a solid volume increase of 30-55% (MacDonald & Fyfe, 1985; O'Hanley). At temperatures around 200°C, thermodynamic consideration suggests that serpentinization should be able to produce stresses exceeding 300 MPa (Kelemen and Hirth, 2012), and thus be able to crack rocks to a depth of several kilometers in the Earth's lithosphere. However, complete serpentinization is uncommon in rocks that have not been subject to penetrative shear deformation. This observation is usually ascribed to clogging of the pore space due to the solid volume increase, which would limit fluid supply, like observed in samples peri4 and peri6 in this study. Whether such clogging effects are effected by interface properties such as the disjoining pressure for the olivine-serpentine couple, or merely is an effect of the bulk transport properties of the partly serpentinized peridotite is not known and would be an interesting topic of further field and laboratory studies.

Acknowledgments

The deformation apparatus was built by Sanchez Technology. This study received funding from the Norwegian Research Council (project HADES, grant 250661 to FR), the European Union (H2020 ERC Advanced Grant Agreement n°669972, 'Disequilibrium Metamorphism' to BJ), beamtime was allocated at the European Synchrotron Radiation Facility (Long Term Proposal ES-295) Data storage was provided by UNINETT Sigma2 - the National Infrastructure for High Performance Computing and Data Storage in Norway (project NS9073K). WZ was partially supported by the US National Science Foundation through EAR-1551300. Maya Kobchenko is

thanked for the help provided to analyze the tomography data. We thank Peter Kelemen and one anonymous referee who provided constructive reviews that helped improving the article.

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Figure 1. a) Schematic diagram of the HADES triaxial rig. b) Stress states (effective mean stress vs. differential stress) for all samples (see Table 1). Dashed arrows represent changes of stress states in a sample during reaction. Samples subjected to effective mean stresses less than 30MPa show intense reaction-induced fracturing.

Table 1. Summary of Experiment Conditions.

Test no.	P_a (MPa)	P_c (MPa)	P_p (MPa)	P_{mean} (MPa)	$P_{diff.}$ (MPa)	T (°C)	t (min.)	No.	Φ_0 %
Peri1	11	10	5	5	1	210	120	30	0.53
Peri4	81	80	5	75	1	200	180	68	1.29
Peri5	20	10	5	8	10	180	90	27	0.63
Peri6	100→65	10	5	35→23	90→55	180	150→180	130	1.65
Peri7	40	10	5	15	30	170	300	65	1.31
Perisp1	30→25→50	10→5	5	12→10→15	20→15→45	180	210	93	0.81
Peri8	81	80	75	5	1	180	250	40	1.56

P_a = axial stress P_c = confining pressure, P_p = pore-fluid pressure, $P_{mean} = (P_a + 2P_c)/3 - P_p$ effective mean pressure, $P_{diff} = P_a - P_c$ differential stress, T = temperature, t = duration of experiment after temperature was stable and water was injected. No. = number of tomography scans per experiment. Φ_0 = initial porosity.

Figure 2. Histograms of gray scale values of the microtomography images of sample peri1 undergoing the periclase to brucite transformation. The histograms (solid curves, different colors represent different reaction time) can be divided into three slightly overlapping bell-shaped curves (dashed lines), which are interpreted as pore space, brucite and periclase, from left to right. Periclase volume fraction decreased while brucite increases with time as reaction progressed.

Figure 3. a) Evolution of porosity (green), volume fractions of brucite (red) and periclase (blue) in sample peri4 at an effective mean stress of 75 MPa. b) Microstructures of sample peri4 A) 5 and B) 28 minutes after reaction started. In the cross-section view of the whole sample, the initial periclase (per) is dark blue, porosity (pore) is green and brucite (brc) is red. 3D and 2D images of sub-volumes are shown

as insets where periclase (per) is light grey, porosity (pore) is dark grey and brucite (brc) is intermediate grey. Filling of the existing pores with brucite can be observed.

Figure 4. a) Reaction progress for sample peri1 showing a sigmoidal evolution of brucite-for-periclase replacement. A porosity pulse was observed between 65 to 80 minutes. b) Time evolution of peri1 with a 3D view (top) and 2D cross-section view (bottom) at the middle of the sample (locations marked by dashed curves). 3D views show the X-ray adsorption data in gray scale. The segmented phases are colored (per: periclase, blue; brc: brucite, red; porosity: green).

Figure 5. Pore size distribution in a sub-volume of sample peri4. a) Probability that a pore X has a size (i.e. volume) larger than x. b) Histogram of pore volume. c) Evolution of total pore volume with time. d) Total number of pores detected as reaction progresses. All these data show that initial pores

488 become filled with brucite and both their number, size, and total volume decrease. The cyan to magenta
489 color transition represents the increasing reaction time.

490

491 **Figure 6.** Pore size distribution of sample peri1. A: Probability that a pore X has a size (i.e.
492 volume) larger than x. B: Histogram of pore volume. C: Evolution of total pore volume with time. D:
493 Total number of pores detected as reaction progresses. All these data show that initial pores become filled

with brucite and both their number, size, and total volume decreases. The cyan to magenta color transition represents the increasing reaction time.

Figure 7. a) Reaction progress for sample peri6 showing a sigmoidal evolution of brucite-for-periclase replacement. A porosity pulse was observed between 45 to 120 minutes. b) Time evolution of peri6 with a 3D view (top) and 2D cross-section view (bottom) at the middle of the sample (locations marked by dashed curves). 3D views show the X-ray adsorption data in gray scale. The segmented phases are colored (per: periclase, blue; brc: brucite, red; porosity: green).