Reaction-Induced Fracturing: When Chemistry Breaks Rocks

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Abstract  Reaction-induced fracturing occurs when fluid-rock interactions lead to the growth of a mineral phase that produces a volume increase, which perturbs the stress field and can cause fracturing in the surrounding rock. This process may occur with a positive feedback loop because, as more fractures are formed, more water can infiltrate the pore space, enhancing the kinetics of reaction. Yoshida et al. (2020, https://doi.org/10.1029/2020JB020268) have studied and modeled reaction-induced fracturing in oceanic rocks collected during the Oman Drilling Project. These rocks have been intensively hydrated by a process called serpentinitization, which has profound geodynamic implications. The authors couple detailed microstructural observations and numerical modeling of reaction-induced fracturing that incorporates permeability evolution. Building on the outcomes of their study, I discuss here the current knowledge of the reaction-induced fracturing process, in which chemical forces control rock fracture in various geological environments. Based on recent experimental results and molecular dynamics simulations, I discuss the conditions under which reaction-induced fracturing may either self-amplify or slow down and even stop.

Plain Language Summary  In the oceanic crust, rocks may interact with oceanic fluids and become hydrated, producing a new class of minerals called serpentine. These minerals have a larger specific volume (+50%) and smaller density (−25%) than the original rock. Two main hypothesis have been proposed to explain how this volume and mass difference may be accommodated: (1) either the transport of dissolved elements by intense fluid circulation removes significant mass from the original rock and thus keeps a constant volume, or (2) the volume of the initial rock increases by the opening of fractures that accommodate the volume increase of the new minerals. Rocks collected during the Oman Drilling Project have recorded microstructures that demonstrate that this second hypothesis better matches the observations. Both detailed observations of oceanic rocks and mechano-chemical numerical simulations demonstrate that as mineral transformation occurs, the generated stresses are high enough to fracture the surrounding rock, and accommodate volume expansion. This mechanism, called reaction-induced fracturing, involves an intricate coupling between chemical and mechanical forces that could self-amplify or self-stop the overall rock transformation process.

1. Introduction

Reaction-induced fracturing occurs in various geological environments and engineering settings. This process controls the transformations of rocks during serpentinitization and carbonation of oceanic lithosphere (e.g., P. B. Kelemen and Matter, 2008; MacDonald & Fyfe, 1985; Martin & Fyfe, 1970), eclogitization of lower continental crust (e.g., Jamtveit et al., 2019), rock weathering (Røyne et al., 2008), formation of travertine deposits (Gratier et al., 2012), damage due to salt precipitation in cultural heritage monuments and in cement (e.g., Scherer, 2004), fracturing of shale during maturation of organic matter, leading to primary migration of hydrocarbons (e.g., Chauve et al., 2020), hydration of cement in boreholes (Wolterbeek et al., 2018), and frost heave and freeze-thaw cycles in cold regions (e.g., Walder & Hallet, 1985).

Reaction-induced fracturing occurs when a mineral reaction involves a volume increase that increases stress. This process may fracture the rock and increase the porosity such that water can continuously access the reacting mineral surfaces. A crystallization pressure indicates the maximum confining pressure that would be necessary to stop the reaction. This pressure, also called swelling pressure, can be calculated from first principles of thermodynamics. The theoretical effective swelling pressure for the serpentiniza-
tion process was calculated in the range 60 MPa at 260°C to 238 MPa at 180°C (Table 3 in MacDonald & Fyfe, 1985). This range led to the conclusion that swelling pressure may induce pervasive microfractures propagation that allows water to access the mineral surface and the reaction to proceed further because new reactive surfaces are created. These microfractures lengthen and widen with increasing reaction and accommodate the dilation of the rock (O’Hanley, 1992). However, negative feedbacks may cause reaction-induced fracturing to be self-limiting because fluid-rock reactions that increase the solid volume may (i) fill the pore space and thus reduce permeability (Aharonov et al., 1998), (ii) passivate the solid-fluid interface with reaction rims, (iii) close existing fracture and prevent fracture propagation due to the local increase of confining pressure, and (iv) reduce the access of water to grain-grain boundaries by squeezing out the confined water film (Guren et al., 2021).

During serpentinization, the transformation of olivine and pyroxene into several polymorph serpentine and carbonate minerals occurs with a decrease of density of up to 25%, from an initial density of 3,300 kg/m³ to a density of 2,500 kg/m³ (O’Hanley, 1992) and a volume increase of up to 50% (McDonald, 1985). In this system, the matrix supplies reactive components via dissolution that can precipitate within the pore space. Such reactions are commonly referred to as replacement reactions (Putnis & Putnis, 2007). Because of their low static friction coefficient close to 0.3, serpentine minerals can reduce the strength of the oceanic lithosphere by up to 30% and this in turn controls the faulting style in spreading ridges (Escartín et al., 1997). Therefore, reaction-induced fracturing has long-term geodynamic consequences because it affects both the density and mechanical properties of tectonic plates, and helps recycling water, hydrogen and carbon dioxide in the oceanic lithosphere (e.g., Guillot et al., 2015).

Serpentinization may initiate through both very small microfractures and large scale faults produced by tectonic forces, earthquakes, and thermal fracturing of rocks due to the cooling of the oceanic crust (e.g., Boudier & Coleman, 1981; Rouméjon & Cannat, 2014). These processes promote serpentinization by providing the water access to fresh mineral surfaces. Reaction-induced fracturing then amplifies this initial stage through a positive feedback loop, leading to a complete transformation of the rock.

Here, I present the results of the compelling study of Yoshida et al. (2020) who combined both microstructural observations of ophiolite rocks and numerical mechano-chemical modeling. The authors reproduce and quantify the fracture patterns observed in serpentinized oceanic lithosphere rocks collected during the Oman Drilling Project. Their study is complementary to recent studies where laboratory experiments (Zheng et al., 2019; Zhu et al., 2016) and numerical modeling (Guren et al., 2021; Zhang et al., 2019) have identified key parameters that control the rate of reaction-induced fracturing and identified under which conditions this rate may increase or decrease. These parameters include the temperature, the amount of available water, the effective pressure, and the strength and initial porosity of the rock.

2. Results

In their study, Yoshida et al. (2020) use field microstructural observations (Figure 1a-b) and mechano-chemical numerical modeling (Figure 1d-e) to demonstrate that the hydration of oceanic rocks into serpentine is the main mechanism of rock transformation in samples collected in a borehole of the Oman Drilling Project (P. B. Kelemen et al., 2020). Yoshida et al. (2020) demonstrate how the coupling between chemical and mechanical forces leads to pervasive rock fragmentation. The results show that reaction-induced fracturing produces new fluid pathways and increases permeability. The numerical model proposes quantitative predictions of how the opening of fractures pumps the fluid into the rock and how porosity and permeability evolve. The fracture patterns in the model appear remarkably similar to the fracture patterns observed in the Oman rocks, as shown in the Figures 4 and 8 in Yoshida et al. (2020), and to laboratory experiments (Figure 1c).

The overall reaction-induced fracturing process occurs as a series of steps (Figure 2). (1) Water accesses olivine and pyroxene surfaces (mineral A in Figure 2), promoting reactions that produce hydrated minerals (mineral B in Figure 2). (2) The hydrated minerals have a larger specific volume and exert a swelling pressure on their surroundings. (3) This additional pressure modifies locally the stress field and may either induce fracturing and hence increase porosity, or promote clogging and hence decrease porosity. (4) The formation of new fractures increases porosity and permeability, allowing more fluid to reach the reactive
mineral surfaces in a positive feedback loop. In a system with sequential steps, the slowest step controls the overall kinetics. The dissolution rates of olivine and pyroxene under hydrothermal conditions in laboratory experiments are fast, and the reactions occur over days. Thus it has been proposed that the rate-controlling step is the transport of water to the mineral surfaces (Martin & Fyfe, 1970), a process controlled by the opening of microfractures. There is therefore a competition between processes that increase porosity and permeability (Figure 2, plus signs) and processes that clog pores and fractures and decrease permeability (Figure 2, minus signs).

Several numerical models have reproduced systems where mineral transformation is coeval with microfracturing, and producing hierarchical fracturing as reactions progress (e.g., Fletcher et al., 2006; Rudge et al., 2010; Røyne et al., 2008; Malvoisin et al., 2017). These models consider a one way coupling between chemical reaction, volume increase and the formation of tensile microfractures that allow fluid to penetrate close to the reacting surfaces. A more recent model (Zhang et al., 2019) has reproduced the volume increase, the nonlinear evolution of the reaction with time, the formation of microfractures, and the existence of a transient porosity pulse observed in experiments by Zheng et al. (2019). This porosity pulse occurs because of a competition between processes that generate microfractures, due to volume increase, and processes that clog the existing porosity, due to mineral precipitation. In all these models above, the mineral transformation can occur because of the presence of a nanometre-thick liquid film trapped along the grain boundaries. This confined water film supplies ions for mineral growth. It also sustains a normal stress along grain boundaries, allowing the growing mineral to perform work to its surrounding volume (Røyne et al., 2011).

Laboratory experiments have demonstrated that, under specific conditions, a swelling pressure could build-up and break the surrounding rocks. This happens when sodium sulphate precipitates into cement (Scherer, 2004), calcium oxide hydrates into borehole cement (Wolterbeek et al., 2018), and sodium chloride precipitates into a porous sandstone (Noiriel et al., 2010). Recently, three experimental studies have imaged reaction-induced fracturing in rocks using dynamic in situ synchrotron X-ray microtomography (Zheng et al., 2019; Zhu et al., 2016). In these experiments a mineral (olivine or periclase) is reacted under constant effective pressure (3–75 MPa), 180–200°C, and in the presence of water, such that a new hydrated mineral with larger volume (magnesite or brucite, respectively) forms and fractures the surrounding rock (Figure 1b). The results demonstrate a positive feedback between the hydration reaction, volume increase and fracturing. They also reproduce a complex three-dimensional fracturing pattern often referred to as a mesh structure in serpentines. However, Zheng et al. (2019) showed that when the effective pressure applied to the sample exceeds about 30 MPa, the periclase (MgO) to brucite (Mg(OH)2) reaction-induced fracturing process slows dramatically. Such slowing with increasing the confining pressure has also been observed in the hydration of CaO into Ca(OH)2 (Wolterbeek et al., 2018). These results demonstrate that, as outlined in Figure 2, the coupling between mineral reaction and volume increase could also lead to a slow-down of the overall reaction when the confining of effective pressure increases.

One possible explanation of such slowdown is that, under higher confining pressure, the water film confined along the grain boundaries may...
be squeezed out. This effect would then reduce the access of water to mineral surfaces and decrease the overall kinetics of reaction. Molecular dynamics simulations demonstrate that increasing normal stress can squeeze out the water between periclase surfaces (Guren et al., 2021). These simulations, motivated by the experimental results of Zheng et al. (2019), indicate that above 30 MPa effective pressure only one water layer is confined between periclase surfaces, over a range of temperatures from ambient to 250°C. In such thin water layers, diffusion of the magnesium ions, which have a broad hydration shell of water molecules, is slowed down, thereby slowing down the reaction. These positive and negative feedback loops occur in a system where the external stress and transient perturbations also control the overall kinetics of reaction-induced fracturing.

This result suggests that the theoretical swelling pressure, which corresponds to the confining pressure under which the reaction would stop based on thermodynamic considerations, is a maximum value (i.e., above this theoretical thermodynamic limit, swelling cannot occur). Other effects may therefore cancel swelling at pressures much lower than the theoretical limit. For example, the squeezing of the water film at grain contacts, could reduce the actual swelling pressure by stopping the chemical reaction along grain boundaries (Guren et al., 2021). One consequence of this effect would be that complete serpentinization of oceanic crust may be reached only in the first kilometers near the surface, where the confining pressure is low enough to allow a positive feedback between volume increase and fracturing, unless external perturbations such as earthquakes or thermal cooling continue to fragment the rock and produce new reactive surfaces.

3. Conclusion

Reaction-induced fracturing controls rock transformation in a wide range of geological environments, including the serpentinization of oceanic lithosphere (Yoshida et al., 2020). Figure 2 summarizes the current knowledge, where positive and negative feedback loops coexist, explaining why in some geological situations the serpentinization process could be almost complete while in some other situations it would be only partial. New studies are necessary to characterize the competition between these positive and negative feedback loops.
feedbacks of porosity evolution. For example laboratory experiments that reproduce and image the entire rock transformation process in 4D provide valuable information on the transition between the two regimes of porosity evolution where either new fractures are produced or the existing pore space is clogged (Zheng et al., 2019; Zhu et al., 2016).

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