

Reaction-driven cracking during mineral hydration, carbonation and oxidation

Peter B. Kelemen¹, Heather Savage² and Greg Hirth³

¹Dept. of Earth & Environmental Sciences, Lamont Doherty Earth Observatory, Columbia University, Palisades NY 10964 USA, peterk@ldeo.columbia.edu

²Lamont Doherty Earth Observatory, Columbia University, Palisades NY 10964 USA, hsavage@ldeo.columbia.edu

³Dept. of Geological Sciences, Brown University, 324 Brook Street, Providence RI 02912, USA, Greg_Hirth@brown.edu

ABSTRACT

In this paper we present recent and ongoing results of research on crystallization pressure and the reaction-driven cracking process that can result when hydration, carbonation, and/or oxidation reactions produce large changes in volume, viscosity is high (low temperature) and reaction rates are fast (large chemical potential, catalysts present, etc). Our focus is on natural processes involving reaction of olivine – the primary mineral constituent in the Earth’s upper mantle – with surface waters, and on analogue experiments intended to maximize reaction rates at low temperature (up to ~ 300°C) in a laboratory setting. We show that crystallization pressures can reach 100’s of MPa, enough to fracture rocks in the upper crust. Studies of natural and laboratory systems show that reaction-driven cracking produces fracture spacing down to 10’s or 100’s of microns, less than the diffusion distance on time scales of years, sufficient to produce 100% alteration of mantle rocks.

INTRODUCTION

Mineral hydration, carbonation and oxidation (known as “retrograde metamorphism”, in processes commonly termed “alteration”) are important in controlling the composition and rheology of the Earth’s crust and upper mantle, particularly along tectonic plate margins. Engineered, retrograde metamorphism may be useful in proposed mechanisms for unconventional hydrocarbon extraction, geothermal power generation, in situ mining, and geological carbon storage.

Retrograde processes can lead to an increase in solid mass and volume, or can be balanced by host phase dissolution producing constant or decreasing solid volume. In turn, solid volume changes can reduce permeability and reactive surface area, in a self-limiting negative feedback. Alternatively, volume changes can lead to host rock deformation, via fracture and frictional sliding or viscous flow. Which of these outcomes emerges in specific cases is determined in part by the “crystallization pressure”, which creates local gradients in pressure around growing crystals, and thus a differential stress. When stresses rise high enough to induce “reaction-driven

cracking”, this can maintain or increase permeability and reactive surface area in a positive feedback that can produce 100% hydration, carbonation and/or oxidation.

CRYSTALLIZATION PRESSURE AND FRACTURE DURING HYDRATION AND CARBONATION OF OLIVINE

In recent work (Kelemen et al., 2011; Kelemen & Hirth, 2012), we developed thermodynamic and mineral physics estimates of the crystallization pressure and differential stress resulting from volume changes during hydration and carbonation of the abundant rock forming mineral olivine. Because olivine is so far from equilibrium with fluids near the surface, the stress due to serpentinization and/or carbonation may exceed 300 MPa at temperatures up to 200°C or more, greater than required to fracture rocks and cause frictional failure in the upper 10 km of the Earth (Kelemen et al., 2011; Kelemen & Hirth, 2012; Plümpner et al., 2012).

The “crystallization pressure” is limited by the available chemical potential energy. A variety of approaches developed over the past 100 years (reviews in Scherer, 2004; Stieger, 2005; Kelemen & Hirth, 2012) yield

$$P' = -\frac{\Delta G_r}{\Delta V_s}$$

where P' is the crystallization pressure (a deviatoric stress in excess of confining pressure), ΔG_r is the Gibbs Free Energy of a reaction, and ΔV_s is the change in solid volume resulting from this reaction. Kelemen & Hirth (2012) used but also questioned this traditional approach, which describes potential energy at constant temperature and pressure. Perhaps a better approximation to natural conditions (prior to deformation) would use the Helmholtz Free Energy of reaction, ΔF_r ,

$$P' = -\frac{\Delta F_r}{\Delta V_s} = -\frac{\Delta G_r}{\Delta V_s} + \frac{P\Delta V_r}{\Delta V_s}$$

where P is the confining pressure, to describe potential energy at constant temperature and volume. Note also that these expressions do not incorporate possible energy sinks such as exothermic heating and/or thermal diffusion, implicitly assuming that all chemical potential energy is converted into stress. In any case, these expressions yield crystallization pressures of 100’s of MPa, depending on temperature and pressure.

The thermodynamic expressions in the previous paragraph provide an upper bound on crystallization pressure. We evaluated the actual crystallization pressure for olivine hydration using fractures generated by this reaction. The surface energy density of the new fractures has to be less than or equal to the strain energy density due to volume expansion during the hydration reaction. This yields an estimate of $> 260 \pm 130$ MPa, consistent with the thermodynamic approach.

Based on these estimates, provided that fluid access is initiated, for example along pre-existing fractures, the volume change due to hydration and carbonation can

Downloaded from ascelibrary.org by COLUMBIA UNIVERSITY on 07/17/13. Copyright ASCE. For personal use only; all rights reserved.

cause fracture formation and dilation, maintaining or increasing permeability and reactive surface energy in a positive feedback mechanism.

ROLE OF “DISJOINING PRESSURE”

The crystallization pressure recorded in natural rocks that underwent olivine hydration, ca 300 MPa, may be substantially larger than likely “disjoining pressures” (G. Scherer pers. comm. 2012), though as yet there are no quantitative estimates for disjoining pressure in geological systems (Espinosa_Marzal & Scherer, 2010). The disjoining pressure is a repulsive force between growing crystals and their solid host phase, which permits the persistence of a fluid-filled nano film that, in turn, facilitates continued crystal growth by diffusion, increasing the stress on the surrounding host phase. In principle, if the compressive stress on the crystal-host interface exceeds the disjoining pressure, then a nano film would not be present, and crystal growth would cease. Thus, the disjoining pressure has been invoked as a maximum bound on the crystallization pressure (e.g., Espinosa_Marzal & Scherer, 2010). We speculate that, in some geological systems, the three dimensional contact between a growing crystal and the host phase is not smooth, with “pillars” of solid-solid contact surrounded by fluid-filled nano pores. The pillars are sufficiently small that solid diffusion over short distances feeds continued crystal growth, generating stresses higher than could be supported by the nano film alone.

ANALOGUE EXPERIMENTS

A remarkable benchtop example of reaction-driven cracking is the action of “demolition mortar”. This commercially available material, composed mainly of CaO, undergoes hydration in an aqueous slurry poured into an open borehole. In work on geological systems we commonly assume that the instantaneous fluid fraction is small, with large time integrated amounts of H₂O, CO₂ and/or O₂ supplied via fluid flow through an open system. In contrast, demolition mortar in a borehole approximates a closed system (ignoring evaporation) with a large fluid fraction (ca 50% by weight). Thus, the volume change of the slurry in the borehole is negative, involving condensation of H₂O via hydration of CaO to form portlandite, Ca(OH)₂. However, the material expands, creating compressive stresses on the borehole wall and fracturing the host rock, despite the fact that the slurry is not confined at the top of the borehole. The initial density of the slurry is ~ 2000 kg/m³, and the final density of the crystallized material is ~ 1000 kg/m³, due to ~ 50% air-filled porosity within the crystallized material. The structure of the demolition mortar is such that it adheres to the pore walls, causing stresses of about 100 MPa, sufficient to fracture the host rock, rather than cataclastically compressing into the air-filled pores. Efforts to experimentally measure the stresses in this system are underway.

FUTURE PLANS

Though there has been extensive work on reaction-driven cracking in the context of salt weathering (reviews in Steiger REF, Scherer REF), there are few or no quantitative measures of the effect of confining pressure on crystallization pressure and resulting fracture. We plan a series of increasingly complex experiments on analogue systems, such as hydration of lime (CaO) to produce portlandite (Ca(OH)₂), starting with cylinders of lime produced by decarbonation of limestone (CaCO₃) confined in customized molds, and continuing with experiments in a flow-through, triaxial deformation apparatus at constant temperature and confining pressure, while monitoring stress, strain, and – in the more complex setup – fluid composition.

ACKNOWLEDGEMENTS

We would like to thank many friends and colleagues, especially Bernard Evans, Jake Eichenbaum-Pikser, Ray Fletcher, Bjørn Jamtveit, Ted Koczyński, Yanick Ricard, John Rudge, George Scherer, Marc Spiegelman and Cian Wilson, for their continuing advice and criticism of our developing research on crystallization pressure and reaction-driven cracking.

REFERENCES

- Espinosa-Marzal, R. M. and Scherer, G. W. (2010). “Mechanisms of damage by salt.” *Geol. Soc. London, Spec. Pub.*, 331, 61-77.
- Kelemen, P. B., Matter, J., Streit, E. E., Rudge, J. F., Curry, W. B., and Bluztajn, J., (2011). “Rates and mechanisms of mineral carbonation in peridotite: Natural processes and recipes for enhanced, in situ CO₂ capture and storage.” *Ann. Rev. Earth Planet. Sci.* 39, 545-576.
- Kelemen, P. B. and Hirth, G. (2012). “Reaction-driven cracking during retrograde metamorphism: Olivine hydration and carbonation.” *Earth Planet. Sci. Lett* 345–348, 81–89.
- Plümper, O., Røyne, A., Magrasó, A., and Jamtveit, B. (2012). “The interface-scale mechanism of reaction-induced fracturing during serpentinization.” *Geology*, 40, 1103–1106.
- Scherer, G.W. (2004). “Stress from crystallization of salt.” *Cement Concrete Res.*, 34, 1613-1624.
- Steiger, M. (2005). “Crystal growth in porous materials – I: The crystallization pressure of large crystals.” *J. Crystal Growth*, 282, 455-469.