



Experimental evidence for chemo-mechanical coupling during carbon mineralization in ultramafic rocks



H.P. Lisabeth^{a,b,*}, W. Zhu^a, P.B. Kelemen^c, A. Ilgen^d

^a Department of Geology, University of Maryland, College Park, MD, USA

^b Department of Geophysics, Stanford University, Stanford, CA, USA

^c Department of Earth and Environmental Sciences, Columbia University, Lamont–Doherty Earth Observatory, Palisades, NY, USA

^d Geochemistry Department, Sandia National Laboratory, Albuquerque, NM, USA

ARTICLE INFO

Article history:

Received 4 March 2017

Received in revised form 23 June 2017

Accepted 26 June 2017

Available online 20 July 2017

Editor: J. Brodholt

Keywords:

rock deformation

permeability

carbon sequestration, storage and utilization (CSSU)

ultramafic

chemo-mechanical coupling

fluid-rock interaction

ABSTRACT

Storing carbon dioxide in the subsurface as carbonate minerals has the benefit of long-term stability and immobility. Ultramafic rock formations have been suggested as a potential reservoir for this type of storage due to the availability of cations to react with dissolved carbon dioxide and the fast reaction rates associated with minerals common in ultramafic formations; however, the rapid reactions have the potential to couple with the mechanical and hydraulic behavior of the rocks and little is known about the extent and mechanisms of this coupling. In this study, we argue that the dissolution of primary minerals and the precipitation of secondary minerals along pre-existing fractures in samples lead to reductions in both the apparent Young's modulus and shear strength of aggregates, accompanied by reduction in permeability. Hydrostatic and triaxial deformation experiments were run on dunite samples saturated with de-ionized water and carbon dioxide-rich solutions while stress, strain, permeability and pore fluid chemistry were monitored. Sample microstructures were examined after reaction and deformation using scanning electron microscopy (SEM). The results show that channelized dissolution and carbonate mineral precipitation in the samples saturated with carbon dioxide-rich solutions modify the structure of grain boundaries, leading to the observed reductions in stiffness, strength and permeability. A geochemical model was run to help interpret fluid chemical data, and we find that the apparent reaction rates in our experiments are faster than rates calculated from powder reactors, suggesting mechanically enhanced reaction rates. In conclusion, we find that chemo-mechanical coupling during carbon mineralization in dunites leads to substantial modification of mechanical and hydraulic behavior that needs to be accounted for in future modeling efforts of in situ carbon mineralization projects.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

As levels of atmospheric carbon dioxide continue to rise, scientists and engineers search for strategies to mitigate climatic impacts. Carbon capture, storage and utilization (CCSU) has been suggested as a key technology for controlling the near-term carbon budget (IPCC, 2014). Due to its long-term stability, carbon mineralization, or the trapping of carbon dioxide in carbonate minerals, has garnered significant attention (Seifritz, 1990; Lackner et al., 1995). Initial successes at the Carbfix project in Iceland indicate that CO₂ can be rapidly mineralized in a reactive mafic reservoir (Matter et al., 2016), but many questions about the long-term behavior of such projects remain.

Increased awareness of climate change and proposed geoengineering solutions have motivated a number of studies of the carbon dioxide – water – olivine system in the past decades, mostly focused on chemical and mineralogical evolution. Olivine is a commonly occurring mineral, found in many basalts and in great abundance in ultramafic rocks. The dissolution of olivine has one of the fastest rates among Mg-bearing minerals and the magnesium carbonate minerals produced are thermodynamically stable and relatively insoluble in groundwater (Guyot et al., 2011). The olivine carbonation reaction is exothermic, so along with engineered injection tactics, an in-situ reservoir could be maintained at optimal reaction temperature without additional input of energy (Kelemen and Matter, 2008). Alternatively, engineered systems emulating natural processes could capture CO₂ from thermally convecting seawater passing through olivine-rich rocks, and return of carbon depleted water to the surface could draw down atmospheric CO₂ providing a relatively inexpensive method of

* Corresponding author.

E-mail address: hlisabet@stanford.edu (H.P. Lisabeth).

“air capture” (Kelemen and Matter, 2008; Kelemen et al., 2011). The conversion of olivine to magnesite and quartz has a positive change in volume, which has been invoked as both a potential porosity reducing (Xu et al., 2013; Hövelmann et al., 2012) and porosity generating mechanism (Kelemen and Matter, 2008; Kelemen and Hirth, 2012).

There have been a number of studies of powdered olivine in batch reactors seeking to constrain carbonation rates (Chen et al., 2006; King et al., 2010; Daval et al., 2011; Olsson et al., 2012; Gadikota et al., 2014; Johnson et al., 2014), but experiments in aggregates suggest that reaction rates are controlled by grain-scale structure rather than kinetics (van Noort et al., 2013). Flow-through experiments tend to yield dissolution-dominated behavior, with increases in pore space and permeability near injection sites and secondary mineral precipitation at sites of low hydraulic throughput (Andreani et al., 2009; Peuble et al., 2015a). In other experiments, precipitation dominates, yielding reductions in porosity and permeability (Hövelmann et al., 2012; Godard et al., 2013). Recently, experiments have shown that extensional cracks can be formed under confinement by non-uniform volumetric expansion due to precipitation in porous materials (Zhu et al., 2016). It remains unclear under precisely what conditions dissolution and precipitation organize to maintain permeability and facilitate complete carbonation of olivine, but the behavior appears to be related to both thermodynamic factors such as pressure, temperature and reactant fugacities and petrophysical factors such as pore size distribution and microhydrodynamics.

One of the least well-understood aspects of geological carbon sequestration is the mechanical response of reservoir rocks to injection of carbon dioxide. The olivine dissolution process is sensitive to flow rate, pore geometry and crystallographic orientation (Peuble et al., 2015b), suggesting that deformation may couple with this process. Most of the research on geomechanical effects of carbon dioxide injection has focused on injection into saline aquifers (e.g. Hawkes et al., 2005; Lucier and Zoback, 2008; Rutqvist, 2012), and neglects chemo-mechanical feedbacks that may be relevant in more reactive reservoirs such as mafic or ultramafic-hosted reservoirs. Tests monitoring the evolution of pore geometry and of fractures in carbonate rocks saturated with carbon dioxide rich solutions flowing through them indicate substantial changes that have hydraulic and mechanical consequences (Elkhoury et al., 2013). The chemical alteration of wellbore cement by carbon dioxide has been investigated with the motivation of better understanding borehole stability (Kutchko et al., 2007; Mason et al., 2013; Huerta et al., 2012) and seal integrity (Wolterbeek et al., 2016), but there is a dearth of data regarding the chemo-mechanical response of ultramafic reservoir rocks themselves to carbon dioxide injection.

How does the carbonation reaction affect the shear strength and deformation behaviors of the host rock? If there are significant effects, what are the key micromechanisms responsible? Does stress-induced cracking and dilatancy alter the permeability and thus affect carbonation rates? To answer these questions, we conducted a series of hydrostatic and triaxial deformation experiments on dunite samples undergoing carbonation reactions. These experiments were conducted at two temperatures and 3 different pore fluids were used to elucidate the coupling between mechanical and chemical load. We measured stress, strain, permeability and fluid chemistry during the carbonation reaction.

2. Materials and methods

Two suites of experiments were designed to test the mechanical response of ultramafic rocks to carbonation reactions, (1) long duration (~168 h) hydrostatic pressing tests with continuous permeability, strain and fluid chemistry measurement, and (2) triaxial

deformation tests, in which shorter hydrostatic pressing (~72 h) is followed by triaxial loading. The first set of tests was conducted on samples saturated with either de-ionized water or CO₂-rich 0.6 M NaHCO₃ solution. For the second set of tests, CO₂-rich 1.5 M NaHCO₃ solution was also used as pore fluid in addition to the aforementioned two, to test the effect of bicarbonate concentration in the pore fluid. The addition of NaHCO₃ is both to buffer the pH of the pore fluid, to avoid undue stress on instrumentation, and also to provide an optimal rate of reaction (O'Connor et al., 2002).

2.1. Sample material

Experiments were run on thermally cracked Twin Sisters dunite, a uniform and nearly monomineralic pristine olivine rock from the Cascade Range near Bellingham, Washington, USA. Grains were equant and range from 0.2 to 2 mm in size. The mineralogy of the block from which samples were cored is approximately 99% olivine with trace chromite, enstatite and chromium diopside. The composition of the olivine is Fo₉₀ (Ragan, 1963).

Right cylinders 18.4 mm in diameter and 38.1 mm long were cored and ground out of dunite slabs. The initial permeability of the material was too low to be measured on a bench-top system ($<10^{-18}$ m²), and was not suitable for flow-through experiments, so samples were thermally cracked to induce sufficient permeability. Thermal cracking was accomplished by heating samples to 1250 °C in a gas-mixing furnace with a 3:1 CO–CO₂ atmosphere to prevent oxidation, then rapidly cooled. Samples were ramped to temperature in 4 h, held at temperature for 2 h, and then cooled in 6 h. Cracks result from stresses induced by anisotropic thermal expansion in olivine grains (Demartin et al., 2004). After thermal treatment samples had an average permeability of 10⁻¹⁵ m² and average porosity of 1%. Thermal cracks were largely along grain boundaries and had high aspect ratios. The large increase in permeability attests to the interconnectivity of the new pore space.

2.2. Pore fluid preparation

Three compositions of pore fluid were used for experiments, de-ionized water, CO₂-rich 0.6 M NaHCO₃ solution and CO₂-rich 1.5 M NaHCO₃ solution. The CO₂-rich solutions were prepared by mixing the desired amount of NaHCO₃ with de-ionized water, then pressurizing an external fluid-mixing vessel with 3.6 MPa of CO₂ (see Supplementary Figure S1). The fluid is allowed to equilibrate for at least 48 h before the sample is flushed. Using the online tool GEOPIG (Johnson et al., 1992) to calculate equilibrium constants for CO₂ dissolution reactions at experimental conditions, we calculate the pCO₂ at experimental conditions to be 0.8 MPa. The fluid-mixing vessel is plumbed into the pore pressure system of the triaxial deformation apparatus, and the pressure controlled by upstream and downstream intensifiers in order to move the fluid through the system without depressurizing and degassing CO₂. According to the equation of state of Duan and Sun (2003), the amount of dissolved CO₂ in the system remains below the solvus for the duration of the experimental procedure, so we expect the pore fluid remained a single phase.

2.3. Experimental procedure

Thermally cracked dunite cylinders were jacketed in 127 μm thick copper foil and outfitted with foil strain gages, then vacuum saturated with de-ionized water. Instrumented samples were loaded into a triaxial deformation apparatus with a confining pressure of 15 MPa and a pore fluid pressure of 10 MPa, resulting in an effective confining pressure of 5 MPa. Once at pressure, the sample and vessel were heated to 150 °C using an external heater, with a

Download English Version:

<https://daneshyari.com/en/article/5779745>

Download Persian Version:

<https://daneshyari.com/article/5779745>

[Daneshyari.com](https://daneshyari.com)