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The impact of evolving mineral–water–gas interfacial areas on mineral–fluid reaction rates in unsaturated porous media

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ABSTRACT

The distribution and evolution of mineral–water–gas interfacial areas exert a fundamental yet poorly documented control on mineral–fluid reactions in the unsaturated zone. Here, we explore the impact of changing mineral reactive surface area, water content, and gas distribution on the reaction of brucite [$Mg(OH)_2$] with CO_2 gas to form hydrated Mg-carbonate minerals in partially water saturated meter-scale column experiments. Brucite surface area, which is inferred to exert a direct control on mineral dissolution rates, demonstrates a complex evolution including roughening, fracturing and passivation that is inconsistent with conventional models of geometric evolution. Mineral–fluid reaction in the interior of single brucite grains maintains surface area at near-constant values despite the decreasing volumetric brucite content, until solid carbonate precipitates passivate brucite surfaces. The evolution of reactive surface area during passivation also does not follow simple geometric processes. A porous amorphous carbonate phase permits ready access to brucite surfaces for reaction until recrystallization of the amorphous carbonate into bladed, low-porosity nesquehonite [$MgCO_3 \cdot 3H_2O$] abruptly quenches reaction. The varied water content of the experiments illustrates that the extent of mineral–gas reaction is limited by the abundance of water available to facilitate precipitation of hydrated carbonate minerals. Conversely, at high bulk water saturation, the development of preferential gas flow paths limited the exposure of reactive minerals to CO_2 and reduced the overall extent of reaction. Thus, bulk mineral–fluid reaction rates were reduced at both high and low bulk water contents.

1. Introduction

Mineral weathering in the unsaturated zone, where the pores are only partially water-filled, is an important control on nutrient availability, contaminant transport, and the carbon cycle (e.g., Maher et al., 2009; Manning, 2008; McKinley et al., 2006). The rate at which these reactions occur depends on the available reactive surface area in contact with a reactive fluid (e.g., Brantley and Mellot, 2000; Helgeson et al., 1984), a variable that is dependent on both the physical and chemical properties of the mineral, and environmental conditions such as water saturation (White and Brantley, 2003). In the unsaturated zone, quantification of reactive surface area is complicated by several factors, including heterogeneous water distribution and secondary phase precipitation, which can dictate solution chemistry and passivate reactive surfaces (Brantley, 2008; Maher et al., 2009; Pačes, 1983; Scislewski and Zuddas, 2010; White and Brantley, 2003). Moreover, the reactive surface area may change over time due to consumption of the reactive phase, preferential dissolution of defects and highly reactive sites, alteration of surface morphology, and formation of surface coatings (Daval et al., 2009; Harrison et al., 2015; Helgeson et al., 1984; Maher et al., 2006; Petrovich, 1981; Scislewski and Zuddas, 2010; White and Brantley, 2003). Environmental factors are also highly variable over time in natural systems; water saturation in the shallow subsurface is modified in response to short-term weather events and longer-term climate change that may alter the exposure of mineral surfaces to water, and the development of preferential flow paths may decrease exposure to reactants. At low water contents the extent of reaction of mineral phases may be limited due to a lack of water available to facilitate dissolution–precipitation reactions and incorporate into secondary hydrous minerals (Assima et al., 2013a; Felmy et al., 2012; Harrison et al., 2015; Loring et al., 2011; Miller et al., 2013; Schaef et al., 2013, Bea et al., 2012; Thompson et al., 2013). Here, we aim to assess the evolution of effective (i.e., available) reactive surface area during coupled brucite [$Mg(OH)_2$] dissolution–carbonate precipitation under variably water saturated conditions using meter-scale column reactors. As a follow-up to our previous, smaller scale column experiments that investigated brucite carbonation (Harrison et al., 2015), the much larger experimental scale in the present study provides valuable new insights into processes that operate at a greater length scale, and is an important step towards improved extrapolation of experimental results to the field

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scale. Moreover, the longer flow-path accessed a more dynamic range in experimental variables (e.g., water content) within a single experiment, and allowed for improved spatial and temporal resolution of reaction progress due to the installation of sensors and sampling ports, which were not available in the smaller scale apparatus of Harrison et al. (2015).

The reaction of brucite and other alkaline earth metal-bearing hydroxide and silicate minerals with CO_2 to form carbonate minerals is known as mineral carbonation (e.g., Lackner et al., 1995). Mineral carbonation reactions are ideal for studying reactive surface area evolution because of the coupled nature of the reaction and relatively high extent of reaction that can be achieved on experimental time scales (Harrison et al., 2015). As a natural weathering reaction, mineral carbonation is an important part of the global carbon cycle and regulates atmospheric CO_2 concentrations over geologic time (Berner et al., 1983). These reactions may also be harnessed as engineered CO_2 sequestration strategies, for instance by injection of CO_2-rich gases or fluids in the subsurface or alkaline waste stockpiles (Bobicki et al., 2012; Gislason et al., 2010; Kelemen and Matter, 2008; McGrail et al., 2006; Power et al., 2013b), or direct air capture via enhanced weathering of pulverized rock or wastes (Assima et al., 2012, 2013a, 2013b; Pronost et al., 2011; Renforth et al., 2009, 2011; Schuiling and de Boer, 2010; Washbourne et al., 2012; Wilson et al., 2006, 2009, 2014). Brucite carbonation is of specific interest for CO_2 sequestration (e.g., Fricker and Park, 2013; Hövelmann et al., 2012b; Li et al., 2014; Nduagu et al., 2013; Zhao et al., 2010), particularly as a component of ultramafic mine wastes that can be exploited for its high reactivity (Assima et al., 2012, 2013a,b; Bea et al., 2012; Beinlich and Austrheim, 2012; Harrison et al., 2013a, 2013b, 2015; Pronost et al., 2011; Wilson et al., 2014). Reactions in these environments tend to occur under variably water saturated conditions (e.g., Bea et al., 2012; Wilson et al., 2014). The study of brucite carbonation therefore allows assessment of fundamental controls on reactivity during coupled dissolution–precipitation reactions in the unsaturated zone, with important implications for offsetting anthropogenic greenhouse gas emissions responsible for global climate change.

The objectives of this study were to 1) investigate the evolution of reactive surface area during coupled brucite dissolution–carbonate mineral precipitation, 2) evaluate the influence of water saturation on extent of reaction in variably water-saturated conditions, and 3) elucidate key processes controlling the rate and extent of CO_2 sequestration that may be achieved by engineered CO_2 sequestration strategies in the shallow subsurface.

2. Methods

2.1. Experimental setup

Column experiments were used to investigate the evolution of reactive surface area during dissolution–precipitation reactions in the unsaturated zone (Fig. 1). In order to examine the impacts of water saturation on rates, extent, and distribution of reaction, experiments with heterogeneous water content and different initial water saturation profiles were performed. A total of three experiments were conducted in 25 cm diameter × 90 cm tall acrylic columns that contained 10 wt.% pulverized brucite ore and 90 wt.% quartz sand (Fig. 1). Of these, two were duplicates with 35% bulk water saturation and one had 60% bulk water saturation. The duplicate experiments are henceforth referred to as "35% 1 and 2." The 60% saturated column provided a greater total water volume and allowed a greater portion of the column to be at or near 100% pore water saturation in the otherwise identical columns. The brucite ore was pulverized to between 250 and 500 μm in diameter (mass weighted median ≈ 188 μm as estimated based on sieving; refer to the Supplementary Material (SM) for details; SM Fig. S1). The quartz sand was a product of Lane Mountain Materials ("LM 50") that had been sieved to between 53 and 425 μm.

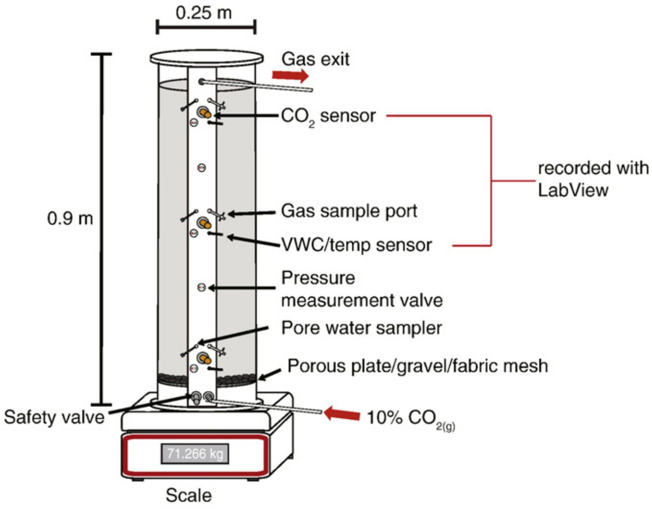

Fig. 1. Schematic of experimental setup.

The initial major oxide composition of the brucite ore and quartz sand was determined using X-ray fluorescence spectroscopy (XRF; refer to SM). XRF measurements indicated that the oxides present in the brucite ore at ≥1.00% ± 1σ abundance were: MgO (60.16 ± 0.43%), SiO_2 (2.71 ± 0.04%), and CaO (2.04 ± 0.03%), with 34.29 ± 0.43% loss on ignition. The quartz sand was 99.10 ± 0.28% SiO_2, with the remainder consisting primarily of Al_2O_3. Rietveld refinement of X-ray diffraction (XRD) data from analysis of the quartz sand indicated it was nearly 100% pure with trace mica (biotite or muscovite at ≤1.0 wt.% abundance). Analysis of triplicate samples of the brucite ore indicated it contained 78.8 ± 3.8 wt.% brucite, 5.5 ± 0.4 wt.% dolomite, 1.9 ± 0.3 wt.% magnesite, 7.4 ± 1.0 wt.% hydromagnesite, and <0.5 wt.% lizardite and pyroaurite. The remainder was amorphous content. The surface area of the brucite ore was determined on duplicate samples using BET with N_2 adsorption, with the average equal to 2.4 $m^2\ g^{-1}$.

Mixtures of 10 wt.% brucite ore and 90 wt.% quartz were prepared by mechanically mixing 4.5 kg of brucite ore, and 40.5 kg of quartz sand (total mass = 45.0 kg). The mixtures were wetted with approximately half of the total desired water volume prior to being loaded into the column. The added solution had 0.1 M $MgCl_2$ and $<1.7 \times 10^{-4}$ M dissolved inorganic carbon (DIC). The partially wetted mixtures were loaded into the columns and compacted by manual compression, with the final height of the porous medium equal to 72 cm in all experiments. After loading, additional $MgCl_2$ solution was applied to the top of the column in order to reach the desired saturation using a watering can to minimize surface disturbance. The solution was allowed to infiltrate under the force of gravity. The porosity was approximately 0.52–0.54 for all columns, as estimated based on the bulk density of the solids and the height of the porous medium, for a total porous medium volume of 35.4 L.

The columns were continuously flushed with N_2 gas at ~220 ± 25 mL min^{-1} overnight to remove laboratory air from the pore space prior to initiating the supply of CO_2, and to allow time for the water distribution to equilibrate. The CO_2 supply was begun without interrupting the flow of N_2, such that the total gas flow rate was ~250 ± 25 mL min^{-1} and the supplied gas was 10 vol.% CO_2. The gas entered through a hose barb into the base of the column, and through a porous ceramic plate overlain by a 2 cm thick gravel layer and a sheet of fabric mesh to promote homogeneous distribution of the gas into the brucite/quartz medium (Fig. 1). The top of the column was sealed with a gas-tight acrylic lid, and the gas effluent exited through an outlet at the top of the column (Fig. 1). The flow rate of the gas effluent was measured at least twice a day using a Cole-Parmer® direct reading flow meter.