The role of magnesite spatial distribution patterns in determining dissolution rates: When do they matter?

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Abstract

We systematically explore the role of magnesite distribution patterns in dictating its dissolution rates under an array of flow velocity and permeability contrast conditions using flow-through column experiments and reactive transport modeling. Columns were packed with magnesite distributed within quartz matrix in different spatial patterns: the Mixed column has uniformly distributed magnesite while the zonation columns contain magnesite in different number of zones parallel to the main flow. Dissolution rates are highest under conditions that maximize water flowing through the magnesite zone. This occurs under fast flow and high-permeability or uniformly distributed magnesite zones. Under high flow and low permeability magnesite conditions, dissolution only occurs at the magnesite–quartz interface, leading to rates an order of magnitude lower in the One-zone columns than those in the Mixed columns. Spatial patterns do not make a difference under low flow conditions when the system approaches equilibrium ($v < 0.36$ m/d) or under conditions where magnesite zones have higher permeability than quartz zone. The bulk column-scale rate depends on A_e through $R_{MgCO_3,B} \text{(mol/s)} = 10^{-9.60} A_e$, where A_e is the surface area that effectively dissolves with $IAP/K_{eq} < 0.1$. The rate constant of $10^{-9.60}$ is very close to $10^{-10.0}$ mol/m^2/s under well-mixed conditions, suggesting the potential resolution of laboratory-field rate discrepancy when A_e, instead of the total BET surface area A_T, is used. The A_e values are 1–3 orders of magnitude lower than A_T. The effectively-dissolving magnesite–quartz interface areas vary between 60% and 100% of A_e, pointing the importance of "reactive interfaces" in heterogeneous porous media. This work quantifies the significance of magnesite spatial distribution patterns. It has important implications in understanding biogeochemical processes in the Critical Zone and in the deep subsurface, where spatial variations in mineral properties prevail.
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1. INTRODUCTION

Mineral dissolution reactions occur ubiquitously and are important in understanding earth system formation and functioning in applications relevant to water, energy, and environment. Different minerals exhibits orders of magnitude variations in permeability and are distributed in patterns varying from uniform distribution in one extreme to layered or clustered patterns at the other end of the spectrum. For example, clays typically are present as low permeability "lenses", while carbonates are commonly distributed as scattered cementation in sandstones of much higher permeability (Koltermann and Gorelick, 1996; Peters, 2009). Preferential flow paths and interfaces abound in the Critical Zone, defined as the zone from the top of the tree canopy to the top of the bedrock (Brantley and Lebedeva, 2011; Chorover et al., 2011), due to the presence of roots, macro pores, and different soil horizons (Beven and

Germann, 1982; Zhang et al., 2014). Spatial heterogeneities in conductive properties regulate water distribution and local flow velocities, while those in geochemical properties and mineral reactivity determine where and how much reactions occur. The combination of the two types of heterogeneities controls the extent and rates of water–rock interactions.

The role of spatial variations in porosity and permeability has been studied for decades (Sudicky, 1986; Adams and Gelhar, 1992; Fiori et al., 2010; Sudicky et al., 2010; Dagan et al., 2013; Pedretti et al., 2013) and has been known to be pivotal in determining flow and non-reactive solute transport (Zinn et al., 2004; Willingham et al., 2008; Willmann et al., 2008; Rolle et al., 2009; Heidari and Li, 2014). Extensive work has been done to capture the anomalous, non-Fickian solute transport commonly observed in heterogeneous porous media using effective models including the dual porosity model (Gerke and Vangenuchten, 1993), multi-rate mass transfer model (Haggerty and Gorelick, 1995), as well as non-local methods such as Continuous Time Random Walk (Berkowitz et al., 2006) and Fractional Advection Dispersion Equation (fADE) (Benson et al., 2000a, b).

The collective wisdoms on physical heterogeneities, however, have not been incorporated in understanding the role of spatial patterns in determining mineral reactions. Chemical weathering rates inferred from soil profiles measured in field studies are a natural result of spatial heterogeneities and have been extensively documented to be 2–6 orders of magnitude lower than laboratory-derived rates (Swoboda-Colberg and Drever, 1993; White and Brantley, 2003; Maher et al., 2006; Zhu et al., 2010). Water chemistry and organic carbon content have exhibited close tie to the spatial distribution of different zones with distinct physical and biogeochemical characteristics (Andrews et al., 2011; Jin et al., 2011). Quantification of the effects of mineral spatial patterns, however, is challenging due to the complex process coupling.

The effects of physico-chemical heterogeneities on biogeochemical reactions have started to be addressed for microbe-mediated redox reactions (Zhang et al., 2010b; Li et al., 2011; Scheibe et al., 2011; Bao et al., 2014), adsorption–desorption (Liu et al., 2008, 2013; Deng et al., 2012; Sassen et al., 2012; Wang and Li, 2015), and mineral dissolution and precipitation (Willingham et al., 2008; Werth et al., 2010; Zhang et al., 2010a; Navarre-Sitchler et al., 2013; Atchley et al., 2014; Salehikhoo et al., 2013). Mineral spatial distribution has been observed to cause unstable dissolution fronts and wormhole development (Smith et al., 2013). Liu et al. (2013) concluded that spatial patterns of sediment grains that led to preferential flow paths result in much slower uranium desorption compared to those in relatively homogeneous columns. Existing work mostly documents the observation of impacts through numerical experiments and to a lesser degree, flow-through pore-scale or column experiments.

Despite of recent advances, there is a significant lack of data and mechanistic understanding on the role of spatial heterogeneities in determining mineral reaction rates. As a result, predicting (bio)geochemical processes in heterogeneous porous media, whether they are shallow Critical Zone or deep subsurface, has continued to present a major challenge for earth and environmental systems. The objective here is to understand and quantify how and to what extent the spatial patterns of magnesite, a representative carbonate mineral, in controlling its dissolution under an array of flow velocity and permeability contrast conditions. Using columns packed with the same total amount of magnesite however distributed in different spatial patterns, this work expands Li et al. (2014) by investigating a large variable space, with the ultimate goal of understanding general principles that underlie the dependence of mineral dissolution on spatial patterns. All measured data, including those from this work and those from our previous work (Salehikhoo et al., 2013; Li et al., 2014), are available in
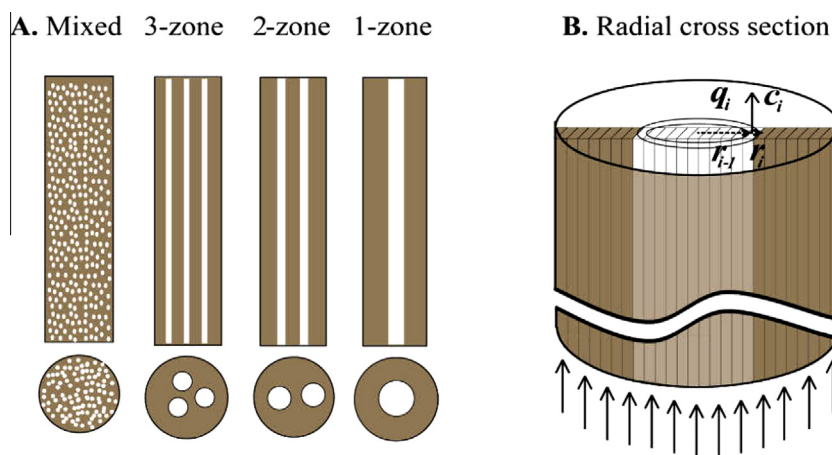

Fig. 1. (A) Schematic figures of columns with four spatial patterns of magnesite (white) and sand (sand color): Mixed, Three-zone, Two-zone, and One-zone. A total of seven columns were packed into two sets of columns with different permeability contrasts. The MgHigh columns were packed with the same grain sizes of magnesite and quartz (354–500 μm) and have higher permeability magnesite zone with a $\kappa_{ratio,Mg/Qtz}$ of 1.2. The MgLow columns have smaller magnesite grains (297–354 μm) and lower permeability magnesite zone with a $\kappa_{ratio,Mg/Qtz}$ of 0.74. (B) A 3D schematic of the One-zone column and its radial cross-section representation. The symbol q_i and c_i represent the flow rates and concentrations from the annulus between radius r_i and r_{i-1}.