An upscaled rate law for magnesite dissolution in heterogeneous porous media

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Abstract

Spatial heterogeneity in natural subsurface systems governs water fluxes and residence time in reactive zones and therefore determines effective rates of mineral dissolution. Extensive studies have documented mineral dissolution rates in natural systems, although a general rate law has remain elusive. Here we fill this gap by answering two questions: (1) how and to what extent does spatial heterogeneity affect water residence time and effectively-dissolving surface area? (2) what is the upscaled rate law that quantifies effective dissolution rates in natural, heterogeneous media? With data constraints from experimental work, 240 Monte-Carlo numerical experiments of magnesite dissolution within quartz matrix were run with spatial distributions characterized by a range of permeability variance $\sigma^2_{\ln\kappa}$ (0.5–6.0) and correlation length (2–50 cm). Although the total surface area and global residence time (τ_a) are the same in all experiments, the water fluxes through reactive magnesite zones varies between 0.7 and 72.8% of the total water fluxes. Highly heterogeneous media with large $\sigma^2_{\ln\kappa}$ and long λ divert water mostly into non-reactive preferential flow paths, therefore bypassing and minimizing flow in low permeability magnesite zones. As a result, the water residence time in magnesite zones (i.e., reactive residence time $\tau_{a,r}$) is long and magnesite dissolution quickly reaches local equilibrium, which leads to small effective surface area and low dissolution rates. Magnesite dissolution rates in heterogeneous media vary from 2.7 to 100% of the rates in the equivalent homogeneous media, with effectively-dissolving surface area varying from 0.18 to 6.83 m^2 (out of 51.71 m^2 total magnesite surface area). Based on 240 numerical experiments and 45 column experiments, a general upscaled rate law in heterogeneous media, $R_{MgCO_3,ht} = kA_{e,\mathrm{hm}}\left(1 - \exp\left(-\frac{\tau_a}{\tau_{a,r}}\right)\right)^{\alpha}$, was derived to quantify effective dissolution rates. The dissolution rates in heterogeneous media are a function of the rate constants k being those measured under well-mixed conditions, effective surface area in equivalent homogeneous media $A_{e,hm}$, and the heterogeneity factor $\left(1 - \exp\left(-\frac{\tau_a}{\tau_{a,r}}\right)\right)^{\alpha}$. The heterogeneity factor quantify heterogeneity effects and depends on the relative magnitude of global residence time (τ_a) and reactive residence time ($\tau_{a,r}$), as well as the shape factor $\alpha\left(= \frac{5}{\sigma^2_{\ln\kappa}}\right)$ of the gamma distribution for reactive residence times. Exponential forms of rate laws have been used at the micro-scale describing direct interactions among water and mineral surface, and at the catchment scale describing weathering rates and concentration-discharge relationships. These observations highlight the key role of mineral-water contact time in determining dissolution rates at different scales. This work also emphasizes the importance of critical interfaces between reactive and non-reactive zones as determined by the details of spatial patterns and effective surface area as a scaling factor that quantifies dissolution rates in heterogeneous media across scales.

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1. INTRODUCTION

Mineral dissolution plays an important role in determining water chemistry, soil formation, biogeochemical cycling, and global climate. Mineral dissolution rates measured in natural systems via field studies have long been observed to be lower than those measured in well-mixed batch reactors by 3–6 orders of magnitude (Paces, 1983; White and Brantley, 2003; Navarre-Sitchler and Brantley, 2007). A large body of literature has documented contributing factors including reaction affinity, surface roughness, temperature, water saturation, microorganisms, secondary mineral precipitation, and flow conditions (Gadd, 2010; Bonneville et al., 2011; Luttge et al., 2013; Hattanji et al., 2014; Putnis, 2014; Kirstein et al., 2016).

Natural subsurface systems are spatially heterogeneous with large variations in subsurface properties arising from distinct soil horizons, macropores, fractures, and lithofacies (Binley et al., 2015). Such spatial heterogeneity governs water flow pathways, extent of mixing, and contact time between reactants, therefore profoundly influencing mineral dissolution rates. Spatial heterogeneity of permeability, often characterized by geostatistical measures including variance ($\sigma_{\ln\kappa}^2$) and correlation length (λ) (Freeze, 1975; Gelhar, 1986; Jussel et al., 1994), have been documented to significantly affect flow and solute transport (Dagan, 1984; Gotovac et al., 2009; Beaudoin et al., 2010). Low $\sigma_{\ln\kappa}^2$ leads to Gaussian distributions of local flow velocities while high $\sigma_{\ln\kappa}^2$ causes flow channeling and non-Gaussian distributions with heavy tailing (Moreno and Tsang, 1994; Englert et al., 2006; Nowak et al., 2008). Longitudinal macrodispersion coefficients depend linearly and quadratically on $\sigma_{\ln\kappa}^2$ under low ($\sigma_{\ln\kappa}^2 < 1.0$) and high heterogeneity conditions ($\sigma_{\ln\kappa}^2 > 1.0$), respectively (Gelhar and Axness, 1983; de Dreuzy et al., 2007; Dentz and Tartakovsky, 2008). Longitudinal dispersivity also increases linearly with λ when $\sigma_{\ln\kappa}^2$ is larger than 1.0 (Moreno and Tsang, 1994). Long λ in low permeability zones increases longitudinal dispersivity more significantly compared to those in high permeability zones (Fiori et al., 2010).

For bimolecular reactions ($A + B \rightarrow C$) in the aqueous phase, spatial heterogeneity has been shown to enhance transverse mixing and increase rates through both modeling (Dentz et al., 2011; Chiogna et al., 2012) and experimental work (Thornton et al., 2001; Bauer et al., 2009). Werth et al. (2006) shows that inclusion of high permeability zones enhances reaction rates by a factor of 1.8–11.9. Increasing spatial heterogeneity ($\sigma_{\ln\kappa}^2$ from 0 to 1.0) elongates reactive plumes by 58.1% (Cirpka et al., 2012) and the extent of reaction by over 15.0% (Luo and Cirpka, 2011).

Mineral dissolution occurs at the critical interfaces of zones with contrasting reactivity and permeability (Li et al., 2017). Spatial heterogeneity has been shown to dictate flow paths, mineral-water contact time, and the occurrence of biogeochemical "hot spots" (Scheibe et al., 2006; Li et al., 2011; Bao et al., 2014; Molins et al., 2017). The concept of mineral-water contact time is similar to groundwater age in hydrogeology (Bethke and Johnson, 2008) and fluid residence time in watershed hydrology (McGuire et al., 2005; Rademacher et al., 2005; McGuire and McDonnell, 2006). At the catchment scale, the distribution of residence time reflects soil properties, topography, flow paths, and landscape characteristics (McGuire et al., 2005; McGuire and McDonnell, 2006). Fluid residence time has been demonstrated to play a key role in determining the extent of disequilibrium and therefore weathering rates (Rademacher et al., 2005; Maher, 2010; Zapata-Rios et al., 2015; Pandey and Rajaram, 2016; Jin et al., 2011). The classical residence times reflect the times in both non-reactive and reactive zones and therefore differ from mineral-water contact time in heterogeneous media. Previous studies proposed the concept of exposure time as reflecting interacting times between water and solid phase reactants, which differs from fluid residence time (Ginn, 1999; Seeboonruang and Ginn, 2006; Sanz-Prat et al., 2016). Glassley et al. (2002) noticed negligible difference in reaction rates of heterogeneously and homogeneously distributed minerals, as long as the water residence time in reactive zones remains relatively similar.

Spatial heterogeneity has also been found to determine mineral-water contact area, i.e., the surface area that controls reaction rates. Mineral Total Surface Area (TSA) is typically measured using the Brunauer-Emmett-Teller (BET) approach. Recent studies have documented "accessible" mineral surface area in heterogeneous media through advanced imaging techniques (Noiriel et al., 2009; Peters, 2009; Landrot et al., 2012; Al-Khulaifi et al., 2017; Beckingham et al., 2016). Another concept is the Effective Surface Area (ESA), defined as mineral surface area bathed in far-from-equilibrium water and is therefore effectively dissolving (Li et al., 2014; Salehikhoo and Li, 2015). Using a series of heterogeneously packed column experiments and reactive transport modeling, our previous studies have shown that magnesite dissolution rates depend on ESA instead of TSA. The ESA differs from the static surface area measured through BET, imaging techniques, and neutron scattering. It is dynamic and emergent, depending on flow, mineral-water contact time, as well as spatial heterogeneity. It can be orders of magnitude lower than measured surface areas using experimental approaches. These studies also show that reaction rate constants measured in well-mixed reactors can be used directly to estimate reaction rates in heterogeneous media if ESA is used, indicating ESA as a scaling parameter to connect reaction rates across scales.

Although these studies suggest key connections between spatial heterogeneity, residence time, effective surface area, and dissolution rates, a general rate law of mineral dissolution in heterogeneous porous media remains elusive. This work aims to fill this knowledge gap by answering two questions: (1) how and to what extent does spatial heterogeneity affect water residence time in reactive zones, effective surface area, and ultimately dissolution rates? (2) Can we predict dissolution rates via mineral-water contact time and geostatistical measures of spatial heterogeneity? We hypothesize that highly heterogeneous media with large $\sigma_{\ln\kappa}^2$ and long λ prolong reactive residence times leading to reaction equilibrium, therefore reducing effectively-dissolving surface area and dissolution rates. We answer these questions using Monte-Carlo simulations of magnesite dissolution in heterogeneous domains with a range of