Physical heterogeneity control on effective mineral dissolution rates

Heewon Jung [a,*], Alexis Navarre-Sitchler [a,b]

[a] *Hydrologic Sciences and Engineering, Colorado School of Mines, United States*
[b] *Department of Geology and Geological Engineering, Colorado School of Mines, United States*

Abstract

Hydrologic heterogeneity may be an important factor contributing to the discrepancy in laboratory and field measured dissolution rates, but the governing factors influencing mineral dissolution rates among various representations of physical heterogeneity remain poorly understood. Here, we present multiple reactive transport simulations of anorthite dissolution in 2D latticed random permeability fields and link the information from local grid scale (1 cm or 4 m) dissolution rates to domain-scale (1m or 400 m) effective dissolution rates measured by the flux-weighted average of an ensemble of flow paths. We compare results of homogeneous models to heterogeneous models with different structure and layered permeability distributions within the model domain. Chemistry is simplified to a single dissolving primary mineral (anorthite) distributed homogeneously throughout the domain and a single secondary mineral (kaolinite) that is allowed to dissolve or precipitate. Results show that increasing size in correlation structure (i.e. long integral scales) and high variance in permeability distribution are two important factors inducing a reduction in effective mineral dissolution rates compared to homogeneous permeability domains. Larger correlation structures produce larger zones of low permeability where diffusion is an important transport mechanism. Due to the increased residence time under slow diffusive transport, the saturation state of a solute with respect to a reacting mineral approaches equilibrium and reduces the reaction rate. High variance in permeability distribution favorably develops large low permeability zones that intensifies the reduction in mixing and effective dissolution rate. However, the degree of reduction in effective dissolution rate observed in 1 m × 1 m domains is too small (<1% reduction from the corresponding homogeneous case) to explain several orders of magnitude reduction observed in many field studies. When multimodality in permeability distribution is approximated by high permeability variance in 400 m × 400 m domains, the reduction in effective dissolution rate increases due to the effect of long diffusion length scales through zones with very slow reaction rates. The observed scale dependence becomes complicated when pH dependent kinetics are compared to the results from pH independent rate constants. In small domains where the entire domain is reactive, faster anorthite dissolution rates and slower kaolinite precipitation rates relative to pH independent rates at far-from-equilibrium conditions reduce the effective dissolution rate by increasing the saturation state. However, in large domains where less- or non-reactive zones develop, higher kaolinite precipitation rates in less reactive zones increase the effective anorthite dissolution rates relative to the rates observed in pH independent cases.
© 2018 Elsevier Ltd. All rights reserved.

* Corresponding author.
  E-mail addresses: hjung@mines.edu (H. Jung), asitchle@mines.edu (A. Navarre-Sitchler).

1. INTRODUCTION

Mineral dissolution plays an important role in many complex Earth processes; for example regulation of

atmospheric CO_2 concentration over geologic time (Berner, 1994; Kump et al., 2000; Navarre-Sitchler and Thyne, 2007; Maher and Chamberlain, 2014), chemical and physical nature of the landscape (Fortescue, 1992; Anderson et al., 2002; Anderson, 2005), fate of geologically sequestered CO_2 (Xu, 2003; Benson and Cole, 2008; Choi et al., 2012), and quality of potable water (Welch et al., 2000; Saxena and Ahmed, 2001; Siirila and Maxwell, 2012; Navarre-Sitchler et al., 2013b; Jung et al., 2014). Reactive transport models (RTMs) allow for evaluation of geochemical processes in these systems and may provide predictive capabilities for system response to perturbation. Rate constants used to calculate dissolution for each mineral in RTM simulations are determined from laboratory experiments and then adjusted in simulations to account for factors that inhibit or catalyze dissolution, such as pH, saturation state, and mineral surface area. While laboratory dissolution rates for given minerals are reproducible when normalized to a measure of mineral surface area (Cama et al., 2002; Gislason and Oelkers, 2003; White and Brantley, 2003; Gudbrandsson et al., 2008; Gudbrandsson et al., 2014; White et al., 2017), there remains uncertainty in the application of laboratory rates to field systems because of the long-standing observation of 4–5 orders of magnitude difference in laboratory-derived rates and effective reaction rates in field systems often calculated from differences in flux weighted concentrations (Pačes, 1983; White and Peterson, 1990; Anbeek, 1992; Anbeek, 1993; Gislason and Arnórsson, 1993; Velbel, 1993; White and Brantley, 2003; Zhu, 2005; Navarre-Sitchler and Brantley, 2007; Maher, 2010; Maher, 2011). This discrepancy between laboratory- and field-measured rates complicates the interpretation of geochemical processes in field systems using knowledge gained from laboratory experiments.

A number of factors intrinsic and extrinsic to the dissolving mineral are responsible for some of the discrepancy (e.g. Lüttge and Arvidson, 2008). Intrinsic factors include reduction of reactive surface area in fresh rock as weathering progresses (White and Peterson, 1990; Anbeek, 1993), slow secondary mineral precipitation and armoring by secondary precipitates (Nugent et al., 1998; White and Brantley, 2003; Maher et al., 2006; Zhu and Lu, 2009; Maher et al., 2009), and aging of reacting minerals (White and Brantley, 2003; Maher et al., 2004; Reeves and Rothman, 2013). Extrinsic factors include climate and biology (Drever, 1994; White and Blum, 1995), and preferential flow (Velbel, 1993; Malmström et al., 2000; Malmström et al., 2004; Malmström et al., 2008). In this study, we model mineral dissolution in statistically representative heterogeneous domains with laboratory-measured mineral dissolution rate constants to evaluate the effects of physical heterogeneity on effective mineral dissolution rates at column scales.

Laboratory experiments measuring mineral dissolution rates are generally conducted under well-mixed, far-from-equilibrium conditions (Chou and Wollast, 1984; Chou and Wollast, 1985; Brady and Walther, 1990; Amrhein and Suarez, 1992; Huertas et al., 1999; Cama et al., 2002; Zhu and Lu, 2009; Gudbrandsson et al., 2014; Zhu et al., 2016). Under far-from-equilibrium conditions mineral dis-

solution proceeds at a rate equivalent to the intrinsic rate constant, k, which is a function of the chemistry and structure of the mineral surface. This far-from-equilibrium rate is often described as the surface-controlled reaction rate (e.g. Molins et al., 2012; Brantley et al., 2013). However, far-from-equilibrium conditions are not common in natural systems where the fluid collects reaction products over long flow paths (e.g. Gislason and Arnórsson, 1993; Maher, 2010). In field systems, as the fluid reacts with minerals and evolves toward chemical equilibrium, mineral dissolution rates decrease and are no longer comparable to laboratory measured rates (Garrels and Mackenzie, 1967; Anbeek, 1993; Gislason and Arnórsson, 1993; Bluth and Kump, 1994; Zhu, 2005; Navarre-Sitchler and Thyne, 2007; White et al., 2009; Maher et al., 2009). Transition state theory accounts for the reduction of mineral dissolution rates as a function of saturation state, however, this factor does not explain all of the observed discrepancy between laboratory and field rates.

In heterogeneous porous media, additional complexity in evaluating the role of fluid saturation state on mineral dissolution rates is introduced as fluids take pathways with different velocities and residence times (e.g. Dagan and Indelman, 1999; Werth et al., 2006; Sanchez-Vila et al., 2007; Steefel, 2008; Steefel and Maher, 2009; Porta et al., 2012; Porta et al., 2013). This distribution of residence times results in a distribution of saturation state and spatially variable dissolution rates within the system (Li et al., 2008; Steefel and Maher, 2009). Complex hydrology of natural systems, thus, imparts complexity in mineral dissolution rates not captured in homogeneous and well-mixed laboratory experiments or in RTM simulations of field systems that assume homogenous fluid flow (Swoboda-Colberg and Drever, 1993; Velbel, 1993; Murphy et al., 1998; Navarre-Sitchler et al., 2009; Salehikhoo and Li, 2015). Hydrological heterogeneity is generally known to reduce weathering rates by inducing transport-controlled reaction rates (Li et al., 2008; Steefel and Maher, 2009; Molins et al., 2012) and reducing effective mineral surface area physically (Beckingham et al., 2016) or chemically (Li et al., 2014; Salehikhoo and Li, 2015; Wen and Li, 2017). In addition, the volume averaging approach for rate calculations (e.g. mass-balance based effective dissolution rate estimation) is likely to increase the uncertainty in estimated parameters and contributes to the scale dependence of mineral dissolution rates (Malmström et al., 2000; Meile and Tuncay, 2006; Navarre-Sitchler and Brantley, 2007). In order to accurately represent effective dissolution rates in heterogeneous field systems it is necessary to define all flow paths and fully resolve the spatial distribution of reaction rates, which is not possible for most field systems. Therefore, it is crucial to understand how local behavior of mineral dissolution is transferred to an effective dissolution rate systematically under various heterogeneous conditions.

Stochastic reactive transport approaches, which estimate the probability of a dependent variable as a result of independent variables with uncertainties, provide a method to rigorously investigate variation in mineral dissolution rates in physically heterogeneous porous media. This approach has been successfully employed in the field of hydrology