PHYSICAL HETEROGENEITY CONTROL ON MINERAL DISSOLUTION RATES:
FROM PORE TO CONTINUUM SCALE OVER GEOLOGIC TIME

by

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ABSTRACT

Mineral dissolution rates are often determined by laboratory experiments performed in well-mixed conditions for a relatively short time. However, 1) geologic systems are highly heterogeneous that rarely exhibit a well-mixed condition, 2) geologic time scales cannot be reproduced in laboratories, and 3) the hydrologic accessibility of the reactive phases within the pore structure is usually not considered in experiments or continuum scale numerical simulations. These inherent differences lead to the 3~7 orders of magnitude discrepancy between field- and laboratory- measured reaction rates, which prevents direct application of laboratory measured rates to numerical simulations. The objective of this dissertation is to investigate the effect of 1) heterogeneous permeability distribution, 2) time dependent evolution of reactive surface area, and 3) pore geometry on chemical weathering rates. Reactive transport simulations conducted on random permeability fields highlight the importance of variance in permeability distribution and Péclet number in controlling the reduction of reaction rates from the laboratory measured reaction rate. In long-term simulations, highly heterogeneous domains show additional reduction in reaction rates as the remaining surface area of immobile zones over-normalizes the reaction product concentration. For the pore scale investigation, reactive microfluidic devices using silicate minerals, anorthite and albite, were fabricated with a femtosecond laser and HF etching techniques. Fluid flows that are perpendicular to the applied pressure gradient develop in a fabricated microdevice while immobile zones develop in numerical simulations, which indicate reactive microdevices can constrain numerical conditions to better represent the chemical reactions in natural pore system. Overall, the results suggest that physical heterogeneity of natural porous media could reconcile some of the large discrepancy between laboratory- and field- measured chemical weathering rates.
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CHAPTER 1

INTRODUCTION

The rates of mineral dissolution control many important natural processes such as soil fertility (White and Buss, 2013), chemical and physical nature of the landscape (Fortescue, 1992; Anderson et al., 2002; Anderson, 2005), atmospheric CO\textsubscript{2} concentration (Maher and Chamberlain, 2014), evolution of porosity and permeability of geologic porous media (Noiriel et al., 2004; Nogues et al., 2013). Many studies have focused on estimating mineral dissolution rates in laboratories and field systems for several decades to quantitatively evaluate the evolution of natural systems (Stumm, 1997; Zhu, 2005; Maher et al., 2006; Navarre-Sitchler and Thyne, 2007). However, dissolution rates measured in laboratory experiments are typically several orders of magnitude faster than the rates measured in natural field systems. This large discrepancy hampers the applicability of laboratory measured dissolution rates to large field systems and prevents quantitative estimation of natural processes. Therefore, it is necessary to systematically investigate the inherent differences between laboratories and field systems in estimating mineral dissolution rates.

In laboratory experiments, mineral dissolution rates are often measured with the reacting solution in far-from-equilibrium conditions where the effect of reaction affinity can be ignored and thus, laboratory experiments measure the intrinsic reaction rate constant (Amrhein and Suarez, 1992; Gudbrandsson et al., 2014). However, the dependence of mineral dissolution rate on reaction affinity cannot be ignored in natural systems where the fluid is usually in close-to-equilibrium condition (Zhu, 2005; Maher et al., 2009). In addition to uncertainties in the functional relationship between mineral dissolution rates and reaction affinity in close to
equilibrium condition (Hellmann and Tisserand, 2006), development of preferential flow paths in natural porous media complicates the evolution of reaction affinity as it depends on the fluid residence time (Malmström et al., 2008; Wen and Li, 2017). Variation in flow velocity in natural porous media also generates deviation from laboratory experiments where well-mixed conditions eliminate effects of solute transport. Rates measured in well-mixed conditions are controlled only by the physical and chemical nature of the mineral surface (i.e. surface-controlled reaction rates; Li et al., 2008) while rates in field systems with low flow velocities are controlled by the rate of the solute transport (i.e. transport-controlled reaction rate; Molins et al., 2012).

Mineral dissolution rates also decrease through time in laboratory experiments (White and Brantley, 2003; White et al., 2017) and in soil chronosequences (White et al., 1996; Hodson et al., 1998; White et al., 2009) suggesting that some of the discrepancy may be related to time-evolving properties. However, the apparent time scale difference between laboratories and field systems is probably one of the most difficult problems to resolve. The longest experiment for mineral dissolution rate is 13.8 years (White et al., 2017) which is short compared to geologic time scales. Therefore, the time-dependence evolution of mineral dissolution rate observed in laboratory experiments cannot be directly used to represent field systems. Moreover, long-term mineral dissolution reaction accompanies the evolution of mineral surface area which poses additional uncertainties in surface area normalized mineral dissolution rates in heterogeneous porous media (Anbeek, 1992; Anbeek, 1993; Noiriel et al., 2009).

The discrepancy is not only observed in physically heterogeneous media but also observed in homogeneous systems (e.g. Maher et al., 2006). This result indicates that the discrepancy cannot be totally attributed to the large scale physical heterogeneity but highlights the potential role of pore scale heterogeneity (Li et al., 2006; Molins et al., 2012). In both
laboratory and field scale rate measurements, hydrologic accessibility of the reactive surface within the pore network is often ignored. This aspect has been investigated mainly through numerical simulations such as Lattice Boltzmann method (Kang et al., 2006; Hiorth et al., 2013) and pore-scale network modeling (Bijeljic et al., 2004; Li et al., 2006). However, most numerical approaches lack the experimental observations constraining the model parameters for better representation of the natural system.

In this thesis, the effects of physical heterogeneous on mineral dissolution rates are investigated from pore scale to continuum scale over geologic time. In Chapter 2, the effect of physical heterogeneity is investigated at the continuum scale with randomly generated permeability fields. These field are employed in Chapter 3 but the time scale is extended from 3 years to 3,000 years to study the evolution of mineral dissolution rates over geologic time. In Chapter 4, a new experimental method combining laser ablation and chemical etching techniques is developed to create microdevices using reactive substrates for pore scale chemical weathering studies.
CHAPTER 2

PHYSICAL HETEROGENEITY CONTROL ON EFFECTIVE MINERAL DISSOLUTION RATES

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 heterogeneous remain poorly understood. Here, I 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 (1 m or 400 m) effective dissolution rates measured by the flux-weighted average of an ensemble of flow paths. I 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. Dissolution and precipitation rates are calculated according to linear transition state theory with no dependence on pH. 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. Multimodality in permeability distribution is approximated by high permeability variance in large domains. In these simulations, the reduction in effective dissolution rate increases due to the effect of long diffusion length scales through zones with very slow reaction rates.

2.1 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 highly 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 up to 7 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, 1990a; 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, 1990a; 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), saturation state (Kump et al., 2000; Maher et al., 2009), and preferential flow (Velbel, 1993; Malmström et al., 2000; Malmström et al., 2004; Malmström et al., 2008). While the individual influences of each of these factors are relatively well understood, uncertainty still remains when multiple factors are combined in a heterogeneous field system. In this study, I model mineral dissolution in statistically representative heterogeneous domains with laboratory-measured mineral dissolution rate constants to evaluate the combined effects of two extrinsic factors, physical heterogeneity and saturation state, 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, Patrick V., 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 dissolution 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 kinetic-limited 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 can react with minerals for hundreds, if not thousands, of years (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; Porta et al., 2013, 2012; Sanchez-Vila et al., 2007; Werth et al., 2006). This distribution of residence times results in a distribution of saturation state and spatially variable dissolution rates within the system (Li et al., 2008; Dentz et al., 2011a). 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; Malmström et al., 2000; Meile and Tuncay, 2006; Cirpka et al., 2008; Dentz et al., 2011a; Maher and Druhan, 2014). 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 to study the effect of mixing and spreading of reactive plumes on reaction rates. Stochastic studies show, for example, early breakthrough of reactive solutes, larger degree of macro-dispersion in a field than a laboratory, and enhanced local reaction rates of bimolecular reactions as a result of enhanced mixing (Sudicky, 1986; Leblanc et al., 1991; Dagan and Indelman, 1999; Werth et al., 2006).

Heterogeneity can also decrease reaction rates due to dilution, local depletion of reactants, or limited lateral spreading (Cirpka et al., 1999; Atchley et al., 2013). These stochastic approaches have been used to evaluate geochemical reactions in some systems, for example mixing-induced bimolecular or reversible reactions of solutes (Simmons et al., 1995; Cirpka et al., 2008) and precipitation of a single reactive mineral (Tartakovsky et al., 2009).

Multi-component reactive transport models that include geochemical kinetics with a dependence on surface area and saturation state allow for the expansion of this stochastic approach to study the coupling of fluid flow and mineral dissolution rates in heterogeneous systems representative of chemical weathering (e.g. Atchley et al., 2013; Maher and Druhan, 2014; Navarre-Sitchler et al., 2013b; Pandey and Rajaram, 2016; Siirila et al., 2012; Wen and Li, 2017). Chemical weathering reactions are highly nonlinear and involve multi-component
reactions in the dissolved phase and dissolution of primary minerals and precipitation of secondary minerals (White and Brantley, 2003; Hellmann and Tisserand, 2006; Maher et al., 2006). In this study, I use one stochastic approach, Monte-Carlo simulation, to investigate the influence of physical heterogeneity (i.e. preferential flow paths) on kinetically controlled mineral dissolution rates including dissolution and precipitation of primary and secondary minerals and dependence on saturation state.

2.2 Methods

2.2.1 Random Permeability Fields Generation

Latticed domains were constructed with heterogeneous spatial distributions of permeability that induce preferential flow paths. The 2D model domain is 1 m × 1 m, consisting of 100 × 100 cells with \( dx \times dy \) cell discretization where \( dx \) and \( dy \) is the length of a side of a cell \( (dx = dy = 0.01 \text{ m}) \). Heterogeneous permeability fields were generated using sequential Gaussian simulation (SGS) in SGeMS software (Remy et al., 2009). The SGS algorithm generates random values assuming the Gaussian distribution of the unknown variables in the domain and distributes generated values based on the given correlation structure. The correlation structure is an ellipse with the given integral scale of random permeability that was initially aligned horizontally (\( \lambda_{\text{max}} \)) and vertically (\( \lambda_{\text{min}} \)) with respect to x-direction. Isotropic conditions were produced when \( \lambda_{\text{max}} = \lambda_{\text{min}} \) and anisotropic when \( \lambda_{\text{max}} \neq \lambda_{\text{min}} \). The structure is then rotated counter-clockwise with respect to the x-axis to introduce an orientation angle (\( \theta \)) of layered permeability structures for additional domains. The integral scale and orientation angle of correlation structures were varied in a fixed domain size. The ratio of integral scales spanning the domain (domain length (L= 1 m) / integral scale (\( \lambda \)) was limited values > 10 to minimize boundary
effects (e.g. Pandey and Rajaram, 2016). Variation in the degree of heterogeneity introduced by these parameters was compared while honoring the global statistics of permeability.

For this study, permeability was assigned to follow a log-normal distribution with a geometric mean equal to $10^{-13}$ m$^2$ and geometric variances ($\sigma_{\ln K}^2$ ) of 1, 3, and 5. Simple Kriging and exponential semivariogram without a nugget were used to create correlation structures with varying $\lambda_{\text{max}}$, $\lambda_{\text{min}}$, and $\theta$ (Table 2.1). Each case is identified by a unique case name comprised of information about the field generation. A, B, and C indicate low ($\sigma_{\ln K}^2 = 1$), medium ($\sigma_{\ln K}^2 = 3$) and high variance ($\sigma_{\ln K}^2 = 5$), I and N are isotropic and anisotropic distribution, respectively. The lowercase letters a, b, or c refer to $\theta = 0^\circ$, 45°, or 90°, respectively (Table 2.1, Figure 2.1). For medium and high variance of permeability, the number of unique cases was limited to isotropic distributions and anisotropic cases with an orientation angle of 0° (Table 2.1) because these conditions are expected to be most common in geologic systems.

### 2.2.2 Reactive Transport Simulations

The reactive transport code CrunchTope (Steefel and MacQuarrie, 1996; Steefel et al., 2005) was used to investigate the effects of heterogeneous flow and mixing on the spatial distribution of effective mineral dissolution rates across the modeling domain. Single mineral composition was used as a simple geochemical system to isolate the effects of flow on reaction rates. The simulations were performed at 25°C with a diffusion constant of $10^{-9}$ m$^2$ s$^{-1}$. Fixed average Darcy flux conditions in the x-direction ($U_x$) were 1.58, 15.8, and 47.3 m yr$^{-1}$ for slow, medium and fast flow rates, respectively. These fixed average Darcy fluxes produce mean transit times of 81 days, 8.1 days, and 2.7 days, respectively. Flux boundary conditions were used for left and right-side boundaries of the domain with no-flow boundary conditions for top and
bottom boundaries. Simulation times were 3 years, 109.5 days and 36.5 days for slow, medium and fast flow rate simulations, respectively. The simulation times were scaled with flow rate to keep the total number of pore volumes of fluid replaced in the domain (38.7) the same for all simulations. Porosity was updated during the simulation, but the change in porosity was negligible given the short simulation time.

For reactive simulations, domains consisted of 55% Quartz (SiO$_2$) and 10% anorthite (CaAl$_2$Si$_2$O$_8$) by volume with a porosity of 35%. Over the simulated timescales, quartz is represented as an inert mineral (dissolution and precipitation suppressed) to simplify the simulations. Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) was allowed to precipitate as a secondary mineral. Mineral surface areas were 0.68 m$^2$/g for anorthite and 13.2 m$^2$/g for kaolinite (Amrhein and Suarez, 1992; Wieland and Stumm, 1992). Kinetics of anorthite and kaolinite reactions at each grid cell were calculated according to the linear Transition State Theory with log rate constants of -11.79 and -12.37 mol m$^{-2}$ s$^{-1}$, respectively (Amrhein and Suarez, 1992; Wieland and Stumm, 1992). Concentrations of Ca$^{2+}$, Al$^{3+}$, and SiO$_2$(aq) were set to zero and pH was fixed at 4.5 in the input fluid, Cl$^-$ was included in the model for charge balancing purposes. Reaction stoichiometry and parameters (equilibrium constant ($K_{eq}$), reaction rate constant ($k$), and mineral surface area ($A_b$)) used in this study are summarized in Table 2.2.

Simulations are performed on 2D domains to reduce the computational time and maintain fine grid discretization and complex flow fields with multicomponent reactive transport and test various parameters of permeability heterogeneity ($\sigma_{lnK}^2$, $\lambda_{max}$, $\lambda_{min}$, and $\theta$) across many realizations of the permeability field. Reactive transport modeling of mineral dissolution on a 2D domain is consistent with a large body of reactive transport simulations of geochemical weathering (Brantley and White, 2009; Maher et al., 2009; Maher, 2010; Navarre-Stitchler et al.,
Standard deviations of effective dissolution rate converged after fifty realizations of each set of heterogeneous random permeability field conditions (Figure A1). The number of numerical simulations with the 1 m × 1 m domain size is 1551 including a realization for the homogeneous distribution and 502 realizations with different flow rates.

2.2.3 Dissolution Rate Formulations

Two different dissolution rate formulations were defined. The effective dissolution rate ($R_{\text{eff},i}$, mol m$^{-2}$ s$^{-1}$), representing the volume averaged reaction rate over a given part of the domain, was calculated at using the flux weighted Ca$^{2+}$ concentration (Equation 2.1) at different measurement planes ($x = i$) along the main flow direction (Figure 2.2).

\[ R_{\text{eff},i} = \frac{n_z n_{xx} \sum^n_z q_{i,z} \Delta Ca_{i,z}}{V_i \sum^n_z \sum^n_x (A_b)_{x,z}} \]  

where $q_{i,z}$ is Darcy velocity of each cell $z$ (m$^3$ s$^{-1}$) and $\Delta Ca_{i,z}$ is the difference in Ca$^{2+}$ concentration between inlet fluid and each cell at the measurement plane location $x = i$ (mol m$^{-3}$). $V_i$ is the volume (m$^3$) of the domain from $x = 0$ to $x = i$ and $n_{xx}$ is the number of cells in in the domain from $x = 0$ to $x = i$. $A_b$ is the bulk mineral surface area (m$^2$ mineral m$^{-3}$ porous media) calculated using the given specific surface area with Equation 2.2.

\[ A_b = \frac{A_s MW_{m} f}{V_m} \]  

where $A_s$ is the specific surface area (m$^2$ g$^{-1}$), $MW_m$ is the molecular weight of the mineral phase (g mol$^{-1}$), $f$ is the mineral volume fraction, and $V_m$ is the molar volume of the mineral phase (m$^3$).
mol\(^{-1}\)). \(R_{\text{eff}}\) is conceptually the same as reaction rates calculated from mass balance methods in field systems (e.g. Navarre-Sitchler and Thyne, 2007; Pačes, 1983; Plummer, 1977).

Local reaction rates (\(R_{\text{local}}\), mol m\(^{-2}\) s\(^{-1}\)) for each individual grid cell are calculated from linear transition state theory (Equation 2.3),

\[
R_{\text{local}} = k \left(1 - \frac{IAP}{K_{\text{eq}}}\right) \tag{2.3}
\]

where \(k\) is the intrinsic rate constant (mol m\(^{-2}\) s\(^{-1}\)) in the model input, \(IAP/K_{\text{eq}}\) is the saturation state of the fluid with respect to the reacting mineral calculated by CrunchTope for each cell. Initial surface areas (\(A_{s,0}\)) were specified as an initial input (Table 2.2) then the surface area of mineral \(m\) was updated after each time step according Equations 2.4 and 2.5 for dissolution and precipitation reactions, respectively,

Dissolution: \(A_b = A_{b,0} \left(\frac{f_m}{f_{m,0}}\right)^{2/3} \left(\frac{\phi}{\phi_0}\right)^{2/3} \tag{2.4}\)

Precipitation: \(A_b = A_{b,0} \left(\frac{\phi}{\phi_0}\right)^{2/3} \tag{2.5}\)

where \(f_m\) and \(f_{m,0}\) are the mineral volume fraction and the initial mineral volume fraction, respectively.

### 2.3 Results

#### 2.3.1 Thermodynamic control on effective dissolution rates (\(R_{\text{eff}}\)) in a homogeneous domain

Homogenous simulations were performed to describe the thermodynamic control on \(R_{\text{eff}}\) at the same domain scale and fluid velocity conditions investigated in the heterogeneous simulations. In a homogeneous domain, fluid enters at far-from equilibrium conditions inducing
mineral dissolution at fast, far-from-equilibrium rates ($R_{\text{local}}$, Figure 2.3a). As these reactions proceed, solute concentrations increase and the saturation state of the fluid moving along the flow path increases, slowing reaction rates further along the flow path (Figure 2.3a and b). As a result of the combined reaction and transport, the lab-derived rate constant $k$ only occurs near the inlet even though reactive mineral is present throughout the domain. $R_{\text{local}} = 6.13 \times 10^{-14}$ mol m$^{-2}$ s$^{-1}$ in the cells at $x = 1$ m with $IAP/K_{eq} = 0.96$. This spatial distribution of reaction rates results in domain averaged $R_{\text{eff}}$ slower than the fast rates that occur at the inlet and the reduction in $R_{\text{eff}}$ is greater as more of the domain is included in the averaged value. At low velocity, this effect is highlighted by a continuous reduction in $R_{\text{eff}}$ with increased distance along the flow path (Figure 2.3c). Additional Ca$^{2+}$ added to the fluid from slow dissolution at near equilibrium conditions is not enough to change the solute chemistry and $\Delta$Ca$^{2+}$ across the domain is approximately invariant as $x$ increases, with a value controlled by the solubility of anorthite. This invariance in Ca$^{2+}$ concentration fixes the numerator in Equation 2.1, however, $V_i$ in the denominator increases with increasing $x$ resulting in decreasing $R_{\text{eff}}$ with increasing $x$ (Figure 2.3).

The degree of reduction in $R_{\text{eff}}$ is controlled by the spatial distribution of $R_{\text{local}}$ and $IAP/K_{eq}$, which are determined by $k$ (the same in all simulations here) and the fluid velocity (Figure 2.3c). $H_{\text{low}}$ ($U_x = 1.58$ m yr$^{-1}$) shows the greatest reduction in $R_{\text{eff}}$ from $1.61 \times 10^{-12}$ mol m$^{-2}$ s$^{-1}$ ($k$) to $2.85 \times 10^{-13}$ mol m$^{-2}$ s$^{-1}$ ($x = 1$ m) along the flow path as $IAP/K_{eq}$ increases to 0.96. Under medium flow rate conditions ($H_{\text{mid}}$, 15.8 m yr$^{-1}$), $R_{\text{eff}}$ decreases to $1.25 \times 10^{-12}$ mol m$^{-2}$ s$^{-1}$ as saturation state increases to 0.53. At high flow rates ($H_{\text{high}}$, 47.3 m yr$^{-1}$) $R_{\text{eff}}$ decreases to $1.58 \times 10^{-12}$ mol m$^{-2}$ s$^{-1}$ with an increase in $IAP/K_{eq}$ to 0.07. This decreasing degree of reduction in $R_{\text{eff}}$ with the increase in flow rate is expected given decreasing fluid residence time with increasing flow rate (0.63, 0.06, and 0.02 year for $H_{\text{low}}$, $H_{\text{mid}}$, and $H_{\text{high}}$, respectively). Even in the $H_{\text{high}}$ case,
fluid accumulates reaction products fast enough to cause some departure of \( IAP/K_{eq} \) from far-from-equilibrium conditions, but the reduction in \( R_{eff} \) from \( k \) is minimal (Figure 2.3c, squares). All values of \( U_x \) tested generate a reduction in \( R_{eff} \) at \( x = 1 \) m indicating that these systems evolve to some degree of transport-limited control over a 1 m length scale. A Darcy flux > 47.3 m yr\(^{-1}\) is necessary to observe the kinetic-limited rate at \( x = 1 \) m, much higher fluxes than expected in field systems and suggesting that field rates are at least partially transport-limited in most cases (e.g. Maher, 2010). Our laboratory scale simulations (1 m × 1 m) show up to an order of magnitude reduction in \( R_{eff} \), but significantly more reduction in \( R_{eff} \) could be expected at field-scale solely due to the averaging over large volumes and low fluid velocities.

### 2.3.2 Local Darcy flow rate \((u)\) and local mineral dissolution rate \((R_{local})\)

Like in the homogeneous simulations, in heterogeneous domains fluids will evolve toward chemical equilibrium along a flow path; however, fluids can take flow paths that have different velocities and residence times through the domain. Preferential flow paths with local velocity \((u)\) higher than the domain average develop around low permeability zones where \( u \) is lower than the domain average (Figure 2.1 and 2.4). The flow path structure is determined by the permeability distribution of the porous media, here defined by the parameters \( \sigma_{lnK}, \lambda, \epsilon, \) and \( \theta \).

In the simulations presented here heterogeneity is introduced as a permeability contrast between high and low permeability zones, which is defined by \( \sigma_{lnK}^2 \). High variance in permeability generates preferential flow paths with \( u \) much faster than \( u \) in zones of low permeability. As a result, simulations with high variance have higher maximum local \( u \) (Figure 2.4g-i) but overall lower mean \( u \) with distributions of \( u \) skewed to low values (Figure 2.5b).
The structure of the permeability heterogeneity in the simulation domains is controlled by integral scales that define the length of correlation in permeability in two directions ($\lambda_{\text{max}}$ and $\lambda_{\text{min}}$). Variation in $\lambda_{\text{max}}$ and $\lambda_{\text{min}}$ both influence mean $u$, but with opposite effects. Flow paths in domains with lower $\lambda_{\text{max}}$ are more tortuous, and thus longer, than those with higher $\lambda_{\text{max}}$ resulting in faster mean $u$. Each simulation has the same mean Darcy flux across the domain, therefore, longer flow paths have higher velocities to maintain the same flux. For example, when $\lambda_{\text{max}}$ is increased from 6 cm (AN1a) to 10 cm (AN2a), mean $u$ decreases from 1.36 m yr$^{-1}$ to 1.30 m yr$^{-1}$ (Figure 2.4b, c, and Figure 2.5). In contrast, when $\lambda_{\text{min}}$ is increased from 3 cm (AN2a) to 5 cm (AN3a) and to 10 cm (AI2) while $\lambda_{\text{max}}$ is fixed to 10 cm, mean $u$ increases from 1.30 m yr$^{-1}$ to 1.34 m yr$^{-1}$ and 1.41 m yr$^{-1}$, respectively because flow paths with high $\lambda_{\text{min}}$ are more tortuous (Figure 2.4a, c, e). When both integral scales, $\lambda_{\text{max}}$ and $\lambda_{\text{min}}$, increase keeping the same aspect ratio ($\epsilon$), less tortuous flow paths develop leading to decreases in mean $u$. For example, case AN1a compared to case AN3a with $u$ values of 1.36 m yr$^{-1}$ to 1.34 m yr$^{-1}$, respectively (Figure 2.5b and e).

The angle that integral scales are oriented relative to the flow direction ($\theta$) also changes the tortuosity of flow paths and impacts the flow velocity. Flow paths are more tortuous with higher mean $u$ when $\theta$ is higher compared to flow path in cases with lower $\theta$ (Figure 2.4c, d, and e). For example, mean $u$ value of AN2a ($\theta = 0^\circ$), AN2b ($\theta = 45^\circ$), and AN2c ($\theta = 90^\circ$) is 1.30 m yr$^{-1}$, 1.46 m yr$^{-1}$, and 1.52 m yr$^{-1}$, respectively (Figure 2.5). These relationships between heterogeneity structure and fluid velocity are the same in high variance cases as low variance cases and consistent with previous research (Gelhar, 1986; Gelhar and Axness, 1983; Tsang and Tsang, 1989; Wang et al., 1999; Zhao and Toksoz, 1991). Given the predictable relationships
between mean $u$ and permeability structure, mean $u$ is employed as a measure of heterogeneity to evaluate the role of permeability heterogeneity in reduction of $R_{\text{eff}}$.

Spatial distributions of velocity within the heterogeneous simulations generate spatial distributions of $R_{\text{local}}$ (Figure 2.6). Like in the homogeneous simulations, $R_{\text{local}}$ is fastest near the inlet where solute concentrations are low. As solute concentrations increase in the fluid, $IAP/K_{eq}$ increases and reaction rates decrease. In simulations where $\sigma_{\ln K}^2 = 1$ (Figure 2.6a-f) the reaction front has some irregularity due to different velocities in each flow path. In contrast, in the homogeneous case the reaction front moves through the domain at the same rate for each flow path. Fingering of fast reaction pathways is more developed in high $\sigma_{\ln K}^2$ cases compared to low $\sigma_{\ln K}^2$ due to enhanced spreading but reduced mixing (Figure 2.6g-i). In the high $\sigma_{\ln K}^2$ cases, fluid moves more restrictively through preferential flow paths with faster velocity. As a result, $R_{\text{local}}$ decreases by $\sim 1$ order of magnitude in these fast flow paths, but decreases more than 1.5 orders of magnitude in the slow flow paths. The maximum values of $R_{\text{local}}$ for all simulated cases including the homogeneous case ($H_{\text{low}}$) is $1.61 \times 10^{-12}$ mol m$^{-2}$ s$^{-1}$ (Figure 2.7), equal to the laboratory-derived rate constant, $k$. In these cells reaction is locally controlled by surface-limited dissolution even though, overall, the average domain exhibits transport-limited conditions (Figure 2.4).

If $R_{\text{local}}$ is controlled only by the local velocity, maximum $R_{\text{local}}$ is expected in grid cells with fast velocity. When $R_{\text{local}}$ values are plotted as a function of log $u$ (Figure 2.8), maximum $R_{\text{local}}$ occurs at log $u$ values $> \sim 1.5$ m yr$^{-1}$ (2 in Figure 2.8), but only for 0.03% of the 10,000 grid cells. At low velocities (log $u < \sim 1.5$ m yr$^{-1}$) only a few points with $IAP/K_{eq} > 0.8$ define transport-controlled conditions (1 in Figure 2.8) where log reaction rates are a linear function of log flow velocity with slope of 1 in a log-log plot. The majority of grid cells (99.3 %) deviate
from strict surface-limited or reaction-limited conditions (3 in Figure 2.8). These grid cells have velocities consistent with surface-limited reaction rates, but also have $IAP/K_{eq}$ values $\gg 0$ due to inheritance of geochemical conditions from previous reactions in the flow path. This region, named here as the saturation-state-limited reaction regime, captures the role of the saturation state in controlling mineral dissolution rates in heterogeneous porous media. As a combined result of the three different reaction regimes developed at the local scale (i.e. each grid cell) with the dominance of the saturation-state-limited control, the fluid composition at the outlet grid cells (marked with thick black outlines in Figure 2.8) is close to the equilibrium ($IAP/K_{eq} \sim 1$). This high $IAP/K_{eq}$ value of outlet grid cells also indicates that reaction rates in the overall domain are transport-limited and the effective dissolution rate ($R_{eff}$) increases with increasing mean flow rate. Therefore, the inheritance of solute concentrations causes the transport-limited behavior of effective mineral dissolution rates in these simulations.

2.3.3 Effective mineral dissolution rates

Domain averaged, or effective, dissolution rates (measured at the domain outlet) are overall positively correlated to the geometric mean of $u$ (Figure 2.9a). This positive correlation between flow rate and effective dissolution rate is expected given that the outflow exhibits transport-limited reaction conditions with high $IAP/K_{eq}$ (Figure 2.8) where dissolution rates increase with flow rate (White and Brantley, 2003; Maher, 2010; Molins et al., 2012). Examining each of the parameters that define the flow field helps elucidate the flow and transport controls on reaction rates in heterogeneous media. The parameter that induces the most variation in $R_{eff}$ is $\sigma_{lnK}^2$. When $\sigma_{lnK}^2$ is increased from 1 (A cases) to 3 (B cases) and 5 (C cases) $R_{eff}$ decreases as mean $u$ decreases (Figure 2.9a). Within each set of cases for a given $\sigma_{lnK}^2$, variation in $R_{eff}$ is induced by changing either the integral scales ($\lambda_{max}$ and $\lambda_{min}$), the ratio of the integral scales ($\epsilon$),
or the orientation of $\lambda_{\text{max}}$ relative to the flow field ($\theta$). When $\theta$ is the only parameter varied (A cases), $R_{\text{eff}}$ increases with increasing $\theta$ as preferential flow paths become more tortuous and velocity increases (Figure 2.9b). While these observations are explained by the overall positive correlation between $R_{\text{eff}}$ and mean $u$, the effect of changing either $\lambda$ or $\epsilon$ on $R_{\text{eff}}$ cannot be explained by variations in velocity.

For simulations where $\lambda_{\text{max}}$ is parallel to the main flow direction ($\theta = 0^\circ$) mean $u$ decreases with increasing $\lambda$ as fast pathways are less tortuous and thus $R_{\text{eff}}$ also decreases. For example, an increase in $\lambda_{\text{max}}$ from 0.06 m (AN1a) to 0.1 m (AN2a) results in a decrease in mean $u$ from 1.42 to 1.41 m yr$^{-1}$ and $R_{\text{eff}}$ from $2.84 \times 10^{-13}$ to $2.83 \times 10^{-13}$ mol m$^{-2}$ s$^{-1}$ (Figure 2.9a). This result is consistent with the expectation with that the domain is under transport limited condition. However, the opposite trend is observed when $\lambda$ that is in perpendicular direction to the main flow direction ($\lambda_{\text{min}}$ for $\theta = 0^\circ$ bur $\lambda_{\text{max}}$ for $\theta = 90^\circ$) is increased. For example, mean $u$ of the cases AN2a, AN3a and AI2 increases from 1.30 to 1.34 and 1.41 m yr$^{-1}$ as $\lambda_{\text{min}}$ increases from 0.03 to 0.05 and 0.1 m while $R_{\text{eff,1m}}$ decreases from 2.837 to 2.834 and $2.832 \times 10^{-13}$ mol m$^{-2}$ s$^{-1}$, respectively (Figure 2.9a). In addition, a relatively large reduction in $R_{\text{eff}}$ is observed when two correlation structures with the same $\epsilon$ but different absolute value of $\lambda$ are compared. For AI1 and AI2 cases, $R_{\text{eff}}$ reduces from 2.841 to 2.832 mol m$^{-2}$ s$^{-1}$ while mean $u$ only decrease from 1.42 to 1.41 m yr$^{-1}$. These unexpected negative correlations between mean $u$ and $R_{\text{eff}}$ (AN2a, AN3a and AI2) and relatively large reduction in $R_{\text{eff}}$ (AI1 and AI2) can be explained by increased length of diffusive transport through low permeability zones generated by the correlation structures. These low permeability zones have low velocity and diffusion becomes an important transport process moving solutes to fast velocity, preferential flow paths. The larger these low permeability zones the longer the diffusion length scales to move solutes to the fast flow paths, and the lower the
contribution to flux-weighted concentrations, leading to slower $R_{\text{eff}}$. In general, physical heterogeneity contributes to decrease $R_{\text{eff}}$ by increasing the diffusion length scales with a large size of the correlation structure (i.e. large $\lambda$) and slow local flow velocity (i.e. large $\sigma_{\text{in,}k}^2$).

In our slow flow rate simulations, the saturation state at the outlet of the domain of all cases has almost reached to equilibrium state ($IAP/K_{eq} > 0.95$) regardless of the degree of heterogeneity. Given the same mean Darcy flux for all cases and small increase in the product concentration ($C_{a^{2+}}$) at slow $R_{\text{local}}$ due to high saturations (Equation 2.3), large differences in $R_{\text{eff}}$ induced by physical heterogeneity are not expected when the fluid is close-to-equilibrium. Thus, while simulations can produce reduced $R_{\text{eff,1m}}$ in heterogeneous domains, an order of magnitude reduction is not expected to close the several orders magnitude gap between $R_{\text{eff}}$ and $k$. However, the simulation results indicate that the effect of physical heterogeneity on the reduction in $R_{\text{eff}}$ may be intensified if the saturation state is low. To investigate the dependence of $R_{\text{eff}}$ to the saturation state, the percent deviation of $R_{\text{eff}}$ in heterogeneous cases from the corresponding homogeneous case is calculated as a function of the location of the measurement plane from $x = 0.1$ m to $x = 1$ m along the main flow direction with 0.05 m spacing (Figure 2.10).

As expected, at lower saturations near closer to the inlet the deviation of $R_{\text{eff}}$ in heterogeneous cases from those in homogeneous cases is greater compared to the outlet (Figure 2.10). However, the absolute degree of reduction in $R_{\text{eff}}$ from $k$ at low saturation state is smaller than the reduction driven by high saturation state. For example, $R_{\text{eff,0.1m}}$ in CI2 is $1.22 \times 10^{-12}$ mol m$^{-2}$ s$^{-1}$ with a saturation state of 0.4, an ~ 8% difference compared to the corresponding location of H$_{\text{low}}$ with an $R_{\text{eff}} = 1.33 \times 10^{-12}$ mol m$^{-2}$ s$^{-1}$ and saturation of ~0.49. However, this $R_{\text{eff}}$ of CI2 case about 4 times higher than the $R_{\text{eff,1m}}$ of H$_{\text{low}}$ ($2.85 \times 10^{-13}$ mol m$^{-2}$ s$^{-1}$) with the saturation state of 0.96. Based on the above simulation results, therefore, it can be concluded that the
reduction in $R_{eff}$ from $k$ is mainly caused by the effect of saturation state (i.e. reaction affinity) while the effect of physical heterogeneity is relatively insignificant in the small domain sizes and with the correlation structures investigated. In addition, if the travel distance is increased beyond 1 m under the conditions simulated, the deviation of heterogeneous cases from homogeneous cases is expected to decrease even further due to the increase in saturation state and all cases will eventually produce the same $R_{eff}$.

The difference between $R_{eff}$ in heterogeneous domains and $R_{eff}$ in a homogeneous domains is different for different flow rates (Figure 2.11). The maximum difference between heterogeneous and each corresponding homogeneous case occurs in the medium flow rate condition (15.8 m yr$^{-1}$). For example, $R_{eff,1m}$ in AI2 of high and low flow conditions are $\sim$ 0.6% reduced compared to the corresponding homogeneous case ($H_{high}$ and $H_{low}$, respectively), but reduced by 1.5% compared to the homogeneous case for the medium flow rate condition ($H_{mid}$). The maximum effect of physical heterogeneity on $R_{eff}$ occurs at the medium flow conditions where the fast flow pathways and slow flow pathways generate the biggest difference in solute concentrations. At slow flow conditions, even fluid in the fast flow pathways spends enough time in the domain for the $Ca^{2+}$ concentrations to approach the solubility limit of $C_{eq}$ and the outflow fluid is close to saturation with respect to anorthite. At fast flow conditions the pressure gradient across the domain induces flow through the low permeability zones, reducing $Ca^{2+}$ concentrations and keeping the entire domain at far-from-equilibrium, surface-controlled reaction conditions. At medium flow rate conditions, however, the difference in $Ca^{2+}$ concentrations between the preferential flow paths and low permeability zones is at a maximum leading to the largest deviation of heterogeneous simulations from homogeneous simulations.
2.3.4 Dimensionless analysis

The simulation conditions considered in this study are limited to a small laboratory scale domain size with a given rate constant. However, our limited simulation results can be extrapolated to such cases with different domain size, mean transit time, or rate constant by using the non-dimensional Damköhler ($Da$) and Péclet ($Pe$) number.

$Da_i$ measures the relative importance of characteristic time for advective transport ($\tau_a$) and reaction rates ($\tau_r$)

$$Da_i = \frac{\tau_a}{\tau_r} = \frac{A_b k x}{U_x C_{eq,i}}$$

(2.6)

where $x$ is characteristic length (m), which is the distance from the inlet to the measurement plane here ($x = i$), $U_x$ is the average Darcy flux in x direction (m s$^{-1}$) and $C_{eq,i}$ is the equilibrium concentration of the solute at $x = i$ (mol m$^{-3}$), calculated using thermodynamic data in the datacom.dbs database distributed with CrunchTope. Another commonly used non-dimensional number, Péclet number ($Pe$) describes the relative rates of advection and diffusion.

$$Pe = \frac{U_x L}{D}$$

(2.7)

Péclet numbers for the simulations here are 143, 1430 and 4290 for low, medium, and high flow rate conditions, respectively. The evolution of $Da_i$ and $R_{eff,i}$ along the main flow direction is investigated by moving the measurement plane with 0.01 m spacing from 0.1 m to 1 m for all low flow rate cases. The first 0.09 m of the domain is excluded from the analysis to limit potential boundary effects in the simulations.

Figure 2.12 illustrates the general inverse relationship between $Da$ and $R_{eff}$. This relationship is not surprising as the conditions attributed to larger $Da$ are related to the factors
increasing the fluid saturation state (Equation 2.6). For example, the larger the domain size, the longer the time for fluid to react with minerals (i.e. fluid residence time), thus increasing saturation state. The higher the rate constant, the faster the overall rate, and thus the fluid reaches equilibrium faster given the domain size and flow rate. However, unexpected behavior is observed when $Da$ and $R_{eff}$ are compared at the same location of each domain. The subplot of Figure 2.12 shows the opposite trend between $Da$ and $R_{eff}$ measured at the outlet. Cases with high variance have relatively low $R_{eff}$ and $Da$ with low $IAP/K_{eq}$ while low variance cases have relatively high $R_{eff}$, $Da$, and $IAP/K_{eq}$. As identified in Figure 2.9, 2.10, and 2.11, high variance and large integral scales in permeability distributions reduce $R_{eff}$ by increasing the length of diffusive transport. At a given measurement location $x$, $U_x$, $k$, and mineral surface area ($A_b$) used to calculate $Da$ (Equation 2.6) are the same for different simulations. However, $C_{eq}$, calculated as the equilibrium concentration of Ca$^{2+}$ for the coupled anorthite dissolution – kaolinite precipitation reaction at pH values, varies throughout the domain due to evolving chemical conditions. Thus a range of $R_{eff}$ values are produced for a given $Da$ (Figure 2.12). This range in $R_{eff}$ at a given $Da$ is highest when saturation state is neither far-from-equilibrium or close to saturation (approximately $0.2 < IAP/K_{eq} < 0.6$ at low $Da$ in Figure 2.12). This observation is consistent with the maximum deviation of $R_{eff}$ in heterogeneous cases from homogeneous cases discussed in section 2.3.3 (Figure 2.10 and 2.11).

### 2.3.5 The scale dependence of $R_{eff}$ and the effect of extreme $\sigma_{lnk}^2$

A consistent trend in $R_{eff}$ in domains with varying degrees of heterogeneity ($\sigma_{lnk}^2$, $\lambda$, $\epsilon$, and $\theta$) has been identified in this study with $R_{eff}$ varying with both fluid velocity and the length of diffusive transport through low permeability zones. However, the magnitude of the effect of heterogeneity is too small to explain large discrepancies in dissolution rates between laboratory
and field studies. The simulations here have low Pe values (~143) in order to prevent Da conditions that limit the effect of physical heterogeneity and to observe the impact of physical heterogeneity on $R_{\text{eff}}$ in the 1 m domains. However, low Pe conditions are relatively well-mixed and that should limit the potential for reduction in $R_{\text{eff}}$. Thus, the degree of reduction in $R_{\text{eff}}$ induced by physical heterogeneity was largely negligible compared to the effect of saturation state in the small domains. In larger scale studies, however, Pe conditions can be several orders of magnitude higher without introducing Da conditions that eliminate the effect of physical heterogeneity (e.g. Siirila-Woodburn et al., 2015; Siirila et al., 2012). In high Pe conditions the domain is less well-mixed and the effect of physical heterogeneity on $R_{\text{eff}}$ should be more apparent. A larger domain also allows for increased $\sigma_{\ln K}^2$, a parameter that also generates reductions in $R_{\text{eff}}$ in the 1 m simulations. Here, I investigate the effect of large Pe ($2.3 \times 10^7$) and extreme variance ($\sigma_{\ln K}^2 = 25$) conditions at a large scale (400 m × 400 m) on $R_{\text{eff}}$ with an additional set of simulations (250 total, Table 2.3). Fogg and Zhang (2016) argues that $\sigma_{\ln K}^2$ assuming unimodal distribution should be much higher than the commonly reported values to cover heavy tail behavior in multimodal distributions of hydraulic conductivity in geologic materials. For example, extreme $\sigma_{\ln K}^2$ is necessary to cover the 9 orders of magnitude in fractured bedrock system observed in Pandey and Rajaram, (2016). Lee et al. (2007) used $\sigma_{\ln K}^2 = 25$ for their simulations to represent the multimodality with the domain size of hundreds of meters. Darcy flux ($U_x$) was upscaled proportionally with the size of the domain ($L$) to 631 m yr$^{-1}$ (= 1.7 m day$^{-1}$), thus maintaining the same Da but increasing Pe. While fast, this flow rate is within the range of typical groundwater flow velocity (Driscoll, 1986).

In these high Pe and $\sigma_{\ln K}^2$ conditions, mixing is reduced and non-reactive zones develop in the domain (Figure 2.13). Local velocity ranges over 10 orders of magnitude with preferential
development of low $u$ as a result of high $\sigma_{\ln K}^2$ (Figure A2). In addition, the fast velocity leads to high $Pe$ conditions where the diffusion does not lead to homogenization of the domain solute concentrations. If $\sigma_{\ln K}^2$ or $Pe$ is increased without increasing each other concurrently, non-reactive zones do not develop (Figure A3 and A4). The development of the locally slow or non-reactive zones are more pronounced at high aspect ratio condition (DI2, Figure 2.13a and c) as expected based on results from the 1 m domain simulations.

The development of non-reactive zones and poorly-mixed condition induces further reduction in $R_{\text{eff}}$ compared to the 1 m domain simulations with the same impact of heterogeneous permeability on $R_{\text{eff}}$ (Figure 2.14 and 2.15). The reduction in $R_{\text{eff,1m}}$ between a heterogeneous case (DI2, $2.39 \times 10^{-13}$ mol m$^{-2}$ s$^{-1}$) and the homogeneous case ($H_{\text{low}}$) is $\sim 17$ % even with high $IAP/K_{eq}$ of $\sim 0.9$. This is a significant reduction given that the reduction in $R_{\text{eff}}$ with the similar saturation state for small domain cases was only $< 1$ %. Figure 2.15 also shows the intensified reduction in $R_{\text{eff}}$ compared to Figure 2.12. While the general inverse relationship between $R_{\text{eff}}$ and $Da$ but positive correlation measured at the outlet observed in Figure 2.12 are still maintained, $R_{\text{eff}}$ of the heterogeneous cases with $Pe = 2.3 \times 10^7$ and $\sigma_{\ln K}^2 = 25$ are much smaller than $H_{\text{low}}$. The range of $R_{\text{eff}}$ at the same $Da$ for heterogeneous cases is wider than the range observed with the heterogeneous cases with $\sigma_{\ln K}^2 = 1, 3, \text{or } 5$, which means the uncertainty in $R_{\text{eff}}$ increases along with the increase in $\sigma_{\ln K}^2$. These results demonstrate that the effect of physical heterogeneity is a crucial factor in determining $R_{\text{eff}}$ at large $Pe$ and extreme $\sigma_{\ln K}^2$ conditions.
2.4 Discussion

2.4.1 $R_{\text{eff}}$ in a system with different $Pe$ and $Da$

From the observed behavior of $R_{\text{eff}}$ with respect to $Da$, $Pe$, and $\sigma_{\ln K}^2$ (Figure 2.12 and 1.15), $R_{\text{eff}}$ of systems with $Da$ outside of the investigated range (0.01 ~ 4) can be inferred. Constant values of $R_{\text{eff}}$ are expected regardless of heterogeneity when fluid is at far-from-equilibrium (low $Da$) as $R_{\text{eff}}$ will be determined by the intrinsic dissolution rate ($k$). At high $Da$, where a domain size is large or flow rate is slow, values of $R_{\text{eff}}$ in heterogeneous cases are expected to be the same as $R_{\text{eff}}$ in homogeneous cases as fluids reach equilibrium. In equilibrium conditions, contribution of physical heterogeneity on $R_{\text{eff}}$ would be negligible as $Ca^{2+}$ concentrations are fixed to $C_{eq}$ regardless of the physical heterogeneity of the domain (see section 2.3.3 and 2.3.4). But, $R_{\text{eff}}$ will continuously decrease with increasing $Da$ as the factors increasing $Da$ (high $x$ and low $U_s$, Equation 2.6) are directly decreasing $R_{\text{eff}}$ (high $V_i$ and low $q_i$, Equation 2.1), respectively. The range of $Da$ where $R_{\text{eff}}$ of heterogeneous cases show deviation from the homogeneous case increases when $Pe$ and $\sigma_{\ln K}^2$ are large leading to reductions in $R_{\text{eff}}$ at a given $Da$. These observed and inferred behaviors of variation of $R_{\text{eff}}$ with respect to $Da$ and $Pe$ are consistent with general recognition of uncertainties associated with traditional advection dispersion reaction equation (ADRE) approaches in systems with high $Da$ and $Pe$ conditions (Battiato and Tartakovsky, 2011; Porta et al., 2012).

2.4.2 Implications

The introduction of $\sigma_{\ln K}^2$ up to 25 covers the large range of local velocities expected in multimodal permeability distributions and provides insight into the effect of multimodality on $R_{\text{eff}}$. With the extreme $\sigma_{\ln K}^2$ of 25, the range of local velocities (10 orders of magnitude) is similar...
to those simulated in fractured bedrock (Pandey and Rajaram, 2016). In fractured systems, advective transport is restricted to fractures with diffusive transport in the blocks between fractures. Thus, fast dissolution only occurs along the fracture walls with slow dissolution controlled by diffusion of solutes from the blocks into the fractures. Because of the extreme heterogeneity, like the $\sigma_{\ln K}^2 = 25$ cases, $R_{\text{eff}}$ is reduced by up to an order of magnitude lower than homogeneous simulations of alkali feldspar dissolution (Pandey and Rajaram, 2016). It further supports the observations here that $R_{\text{eff}}$ in heterogeneous systems is reduced when fast flow paths develop around large zones where diffusive transport dominates and consistent with field observations of weathering in systems with high variance in permeability (e.g. Brantley et al., 2011; Fletcher and Brantley, 2010; Navarre-Sitchler et al., 2011, 2013a)

Fast dissolution along preferential flow paths implies the effects of $Pe$ and $\sigma_{\ln K}^2$ on the time dependence of mineral dissolution rates (White and Brantley, 2003). At small $Pe$ and $\sigma_{\ln K}^2$ simulations, all reactive surface of the mineral over the domain participates in reaction and provides more reactants to solution that result in high $R_{\text{eff}}$ at a given time scale (3 years in this study). In contrast, development of non-reactive areas resulted in lower $R_{\text{eff}}$ with extreme $Pe$ and $\sigma_{\ln K}^2$ because of the reduction in effective surface area along with the development of non-reactive zones. However, the order of $R_{\text{eff}}$ in relation to the variance might be reversed at later time (e.g. Pandey and Rajaram, 2016). Depletion of reactive surface area will occur all over the domain for low variance cases while the depletion will only occur preferentially through the preferential flow paths for extreme cases. Therefore, the rate of reduction in $R_{\text{eff}}$ over time will be more gradual because of the remaining surface area which provides dissolution products with slow rate throughout the time.
2.4.3 Effective reactive transport models

This study focused on the effect of physical heterogeneity in macroscale while assuming well-mixed condition within a grid. However, poorly-mixed condition can occur as a result of pore scale heterogeneity that further reduces dissolution rate (Kang et al., 2006; Lichtner and Kang, 2007; Molins et al., 2012; Molins et al., 2014). Complete description of pore scale hydrodynamics would be necessary to correctly reproduce weathering processes but it is not feasible since detailed pore geometry cannot be reconstructed from standard catchment scale information. In this context, application of effective reactive transport models, which have been successfully captured non-Fickian behavior, to weathering studies is expected to better resolve the laboratory and field discrepancy induced by physical heterogeneity. For example, the development of non-reactive immobile zones controls the reduction of $R_{\text{eff}}$ in this study can be represented through non-local in-time formulations such as multirate mass transfer (MRMT) (Lichtner and Kang, 2007; Willmann et al., 2010; Babey et al., 2016). Lagrangian particle tracking and reaction method (PTR) can also provide a better estimate of solute transport and reaction rate by reproducing incomplete mixing conditions without any numerical dispersion (Benson and Meerschaert, 2008; Benson et al., 2017). Although the applicability of PTR still needs validation in chemical weathering context, its ability to reconcile the scale dependence of reaction rate might reduce the large gap of weathering rate (Ding et al., 2017).

2.5 Conclusions

Anorthite dissolution was simulated in the reactive transport code CrunchTope with multiple realizations of permeability distribution to investigate the complex relationship between mineral dissolution reaction rates and fluid flow conditions. All heterogeneous conditions simulated produce preferential flow paths around zones of low permeability that result in a
reduction in $R_{\text{eff}}$ compared to homogeneous domains. The degree of reduction of $R_{\text{eff}}$ is controlled by the structure of the permeability field. In general, effective dissolution rate is higher in domains where local flow velocity is faster. Permeability structure that generates more tortuous paths (high $\theta$, short $\lambda_{\text{max}}$, and long $\lambda_{\text{min}}$) induces fast flow velocity and thus increases dissolution rates. $R_{\text{eff}}$ is lowest when integral scales that define the permeability heterogeneity ($\lambda_{\text{max}}$ and $\lambda_{\text{min}}$) are long creating larger zones of low permeability. These types of distributions would also increase tortuosity, leading to increased $R_{\text{eff}}$. However, as the size of the low permeability zones increases, the length scales of diffusion of solutes out of those zones increases and the contribution of solutes to the flux weighted concentrations from these zones decreases, leading to reduced $R_{\text{eff}}$. We, thus, expect the greatest deviation of mineral weathering rates from laboratory derived rates in conditions with high permeability contrast and large zones of low permeability between zones of high permeability. Fractured bedrock fits this description and simulations of weathering in fractured systems show up to an order of magnitude reduction in overall dissolution rates compared to homogeneous assumptions (Pandey and Rajaram, 2016).

Another cause of reduction of $R_{\text{eff}}$ compared to laboratory rates is over-averaging in systems where fluids reach equilibrium prior to an outlet. In these cases large parts of the domain that are at equilibrium and non-reactive can be included in the averaging or normalization. In field systems this may be an important contribution to the laboratory-field discrepancy because even in the small 1 m domains simulated here fluids approached equilibrium at Darcy Flux values appropriate for field systems. In addition, reactive surface area will be depleted along preferential flow paths prior to large reductions of mineral surface area in in low permeability, slow reacting zones. For surface area normalization of dissolution rates, this change in surface area distribution through time should be considered as to properly evaluate $R_{\text{eff}}$. 
The set of simulations presented here do not include any correlation between physical heterogeneity and chemical heterogeneity, such as distributions of mineralogy or mineral surface area as a function of physical parameters. Previous work has shown that such correlations can also introduce variations in effective reaction rates (Li et al., 2006; Atchley et al., 2014; Beisman et al., 2015). Further studies exploring the functional relationship between chemical reaction and physical heterogeneity (i.e. aspect ratio and the variance of permeability distribution) and correlation between physical and chemical heterogeneity will provide additional information regarding bridging the gap between lab and field measured reaction rates.
Figure 2.1. One example of 50 generated realizations of permeability fields with $\sigma_{ln.K}^2 = 1$ and varying orientation angles as given in Table 2.1.
Figure 2.2. Definitions for each dissolution rate calculation ($R_{\text{local}}$ and $R_{\text{eff},i}$) and schematic description of the measurement planes.
Figure 2.3. Spatial maps of $H_{low}$ are shown with the color code representing (a) local dissolution rate ($R_{local}$) and (b) saturation state ($IAP/K_{eq}$). (c) Evolution of effective dissolution rate ($R_{eff}$) along the main flow direction in a homogeneous domain at different Darcy flow rate ($H_{low} = 1.58 \text{ m yr}^{-1}$, $H_{mid} = 15.8 \text{ m yr}^{-1}$, and $H_{high} = 47.3 \text{ m yr}^{-1}$). Color code represents the saturation state ($IAP/K_{eq}$).
Figure 2.4. Selected log-transformed local Darcy velocity (log $u$) fields with (a ~ f) $\sigma_{\ln K}^2 = 1$ developed from the corresponding permeability field in Figure 2.1, and (g ~ i) $\sigma_{\ln K}^2 = 5$. 
Figure 2.5. Distribution plot of log transformed local Darcy flow rate ($u$, m yr$^{-1}$) of random permeability distribution with (a) $\sigma_{\ln K}^2 = 1$ and (b) $\sigma_{\ln K}^2 = 3$ and 5. The color scale represents the number of cells with a given log $u$ normalized by the number of cells with the most abundant log $u$, in other words the color scale is the histogram of the data with the data in each bin normalized to the count in the bin with the maximum number of occurrences. Mean (white line) of each heterogeneous case is given with the mean of homogeneous case with low flow rate ($H_{low}$, red line).
Figure 2.6. Selected log-transformed local dissolution rate (log $R_{local}$) fields developed from the corresponding local flow field (log $u$) in Figure 2.4.
Figure 2.7. Distribution plot of log transformed local dissolution rate ($R_{local}$, mol m$^{-2}$ s$^{-1}$) of random permeability distribution with (a) $\sigma_{ln K}^2 = 1$ and (b) $\sigma_{ln K}^2 = 3$ and 5, where the color scale represents the number of cells with a given $R_{local}$ normalized by the number of cells with the most abundant $R_{local}$. Mean (white line) of each heterogeneous case and lab-derived rate constant ($k$, red line) are plotted.
Figure 2.8. Scatter plot of local Darcy velocity ($u$) vs. local dissolution rate ($R_{local}$) illustrates three distinctive processes that determine mineral dissolution rates. 1) Surface-limited reaction (dashed-line), 2) transport-limited reaction (solid line), and 3) saturation-state-limited reaction (region below two lines). This is one simulation result of the case CN3a. The outlet grid cells are marked with thick black outlines.
Figure 2.9. Scatter plot of the geometric mean of local Darcy flow rate \( (u) \) vs. effective mineral dissolution rate \( (R_{\text{eff,1m}}) \) for the cases with (a) all low flow rate cases and (b) \( \sigma_{lnK}^2 = 1 \). \( R_{\text{eff,1m}} \) of the homogeneous case (H_{low}) is plotted as a purple cross-line in each figure. Error bar represents 1 standard deviation of each \( R_{\text{eff,1m}} \).
Figure 2.10. Difference in $R_{\text{eff},i}$ (%) compared to the homogeneous case $[(1 - \frac{R_{\text{eff},i}^{\text{hetero}}}{R_{\text{eff},i}^{H_{\text{low}}}}) \times 100]$ with low flow rate in Figure 2.3 (H$_{\text{low}}$) along with the main flow direction.
Figure 2.11. Scatter plot of the geometric mean of local Darcy flow rate ($u$) vs. effective mineral dissolution rate ($R_{eff,1m}$) with (a) all cases (see Figure 2.9 for low flow rate), (b) medium flow rate (15.8 m yr$^{-1}$) and (c) high flow rate (47.3 m yr$^{-1}$). $R_{eff,1m}$ of the corresponding homogeneous case (b. $H_{mid}$ and c. $H_{high}$) is plotted as a purple cross-line in each figure. Error bar represents 1 standard deviation of each $R_{eff}$. 
Figure 2.12. Scatter plot showing the relationship between $R_{\text{eff}}$ and $Da$. Homogeneous case is plotted as a red-dotted line. Subplot shows $R_{\text{eff,1m}}$ and $Da$ of the fluid measured at the outlet (1 m). Note that a different color scale is used for the subplot.
Figure 2.13. Local velocity (a and b) and dissolution rate ($R_{local}$, c and d) fields of selected cases with $\sigma_{lnK}^2 = 25$. The grid cells reached equilibrium ($IAP/K_{eq} = 1$) where $R_{local} = 0$ are marked with black color.
Figure 2.14. Scatter plot showing the relationship between normalized geometric mean of local Darcy flow rate vs. effective mineral dissolution rate ($R_{eff,1m}$). Mean $u$ in is normalized by the domain size (400 m for case ID starting with D and 1 m for others).
Figure 2.15. Scatter plot showing the relationship between $R_{\text{eff}}$ and $Da$. Homogeneous case is plotted as a red-dotted line. Subplot shows $R_{\text{eff,1m}}$ and $Da$ of the fluid measured at the outlet (1 m). Note that a different color scale is used for the subplot.
Table 2.1. Permeability field conditions with the mean of $10^{-13}$ m$^2$ and varying variance ($\sigma^2_{lnK}$), integral scales ($\lambda_{max}$ and $\lambda_{min}$), aspect ratio ($\epsilon = \lambda_{min} / \lambda_{max}$) and orientation angle ($\theta$).

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<td>0.5</td>
<td>0°</td>
<td>CN1a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1 m</td>
<td>0.03 m</td>
<td>0.3</td>
<td>0°</td>
<td>CN2a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1 m</td>
<td>0.05 m</td>
<td>0.5</td>
<td>0°</td>
<td>CN3a</td>
</tr>
</tbody>
</table>
Table 2.2. Reaction stoichiometry and parameters for the minerals considered in dissolution (anorthite) and precipitation (kaolinite) reactions. Equilibrium constants ($K_{eq}$) and reaction rate constants ($k$) are given in mol m$^{-2}$ s$^{-1}$ and mineral surface area ($A_b$) is given in m$^2$ g$^{-1}$.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Reaction Stoichiometry</th>
<th>$K_{eq}$</th>
<th>$k$</th>
<th>$A_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anorthite</td>
<td>CaAl$_2$Si$_2$O$_8$ + 8H$^+$ → Ca$^{2+}$ + 2Al$^{3+}$ + 2SiO$_2$(aq) + 4H$_2$O</td>
<td>$10^{26.5780}$</td>
<td>$10^{-11.79b}$</td>
<td>0.68$^b$</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al$_2$Si$_2$O$_5$(OH)$_4$ + 6H$^+$ ↔ 2Al$^{3+}$ + 2SiO$_2$(aq) + 5H$_2$O</td>
<td>$10^{6.8101}$</td>
<td>$10^{-12.37c}$</td>
<td>13.2$^c$</td>
</tr>
</tbody>
</table>

$^a$ datacom.dbs distributed with CrunchTope

$^b$ Amrhein and Suarez [1992]

$^c$ Wieland and Stumm [1992]

Table 2.3. Permeability field conditions with the mean of 10$^{-13}$ m$^2$, the extreme variance ($\sigma_{ln,K}^2 = 25$), and varying degree of integral scales ($\lambda_{max}$ and $\lambda_{min}$), aspect ratio ($\epsilon = \lambda_{min} / \lambda_{max}$).

<table>
<thead>
<tr>
<th>Geometric mean</th>
<th>$\sigma_{ln,K}^2$</th>
<th>Distribution</th>
<th>$\lambda_{max}$</th>
<th>$\lambda_{min}$</th>
<th>$\epsilon$</th>
<th>$\theta$</th>
<th>Case Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>10$^{-13}$ m$^2$</td>
<td>25</td>
<td>isotropic</td>
<td>20 m</td>
<td>20 m</td>
<td>1</td>
<td>-</td>
<td>DI1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40 m</td>
<td>40 m</td>
<td>1</td>
<td>-</td>
<td>DI2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>anisotropic</td>
<td>24 m</td>
<td>12 m</td>
<td>0.5</td>
<td>0°</td>
<td>DN1a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40 m</td>
<td>12 m</td>
<td>0.3</td>
<td>0°</td>
<td>DN2a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40 m</td>
<td>20 m</td>
<td>0.5</td>
<td>0°</td>
<td>DN3a</td>
</tr>
</tbody>
</table>
CHAPTER 3

ON MINERAL SURFACE AREA NORMALIZATION: THE EFFECT OF PHYSICAL HETEROGENEITY ON THE TIME DEPENDENCE OF MINERAL DISSOLUTION RATES

Hydrologic heterogeneity complicates the time dependent behavior of mineral dissolution rate and introduces large uncertainty in effective surface area estimation. In order to resolve the coupled evolution of mineral dissolution rate and mineral surface area over time in various fluid flow conditions, this study presents multiple reactive transport simulations of anorthite dissolution over 3,000 years with 2D latticed random permeability fields. Physical heterogeneity is controlled by varying integral scales ($\lambda_{min}$ and $\lambda_{max}$) and variance in permeability distribution ($\sigma_{ln k}^2$) conditions. Chemistry is simplified to a single dissolving primary mineral (anorthite) distributed homogeneous throughout the domain and a single secondary mineral (kaolinite) that is allowed to dissolve or precipitate. It is shown that large $\lambda$ and $\sigma_{ln k}^2$ contribute to develop low-reactive zones and reduce effective dissolution rates in early time period. However, the remaining mineral surface area that has been preserved in low-reactive zones provides reactive surface in late time period resulting in gradual decrease of non-normalized effective mineral dissolution rate. These remaining surface areas over-normalize effective dissolution rates resulting in $\sim 1.5$ orders of magnitude reduction from the homogeneous case when domain-averaged reactive surface area is used for normalization. In cases with low $\lambda$ and $\sigma_{ln k}^2$, reactive surface area normalized dissolution rate shows increasing trend over time which is the opposite from most field and experimental observations. This is because reactive surface area is assumed to decrease while BET surface area, which is used for most natural weathering studies, increases.
with time. When surface area is assumed to linearly increase with time and employed for normalization of the homogeneous case, effective dissolution rates roughly reproduce power law decay during the early period of time.

3.1 Introduction

Understanding long-term behavior of mineral dissolution reaction rates that underpin geochemical weathering processes is crucial for analyzing feedbacks between geochemical, tectonic, and ocean processes over geologic history (Bluth and Kump, 1994; Kump et al., 2000; Brantley, 2010; Maher and Chamberlain, 2014) and predicting future changes in mineral dissolution rates with, for example, perturbation of atmospheric CO$_2$ concentrations (Gaillardet et al., 1999; Navarre-Sitchler and Thyne, 2007; Brantley et al., 2013). While experimental studies provide detailed understanding of how mineral dissolution rates respond to changes in physical and chemical conditions, our ability to link these laboratory measured dissolution rates to weathering rates in field systems is limited due to a long-observed difference between laboratory measured mineral dissolution rates and rates derived from field data that is several orders of magnitude (Pačes, 1983; White and Brantley, 2003; Zhu, 2005; Navarre-Sitchler and Thyne, 2007). Various factors contribute to this discrepancy, including secondary mineral precipitation, heterogeneity in flow paths, aging of reacting minerals, and saturation state of reactive fluids (Anbeek, 1993; Maher et al., 2006; Maher et al., 2009; Reeves and Rothman, 2013). Mineral dissolution rates also decrease through time in laboratory experiments (White and Brantley, 2003; White et al., 2017) and in soil chronosequences (White et al., 1996; Hodson et al., 1998; White et al., 2009) suggesting that some of the discrepancy may be related to time-evolving properties. Recent reactive transport simulation results demonstrate a ~1.5 orders of magnitude reduction in weathering rate to the depletion of reactive mineral surface with time.
along preferential flow paths provide compelling evidence that heterogeneity in field systems produces spatial distribution of reaction rates that evolve through time (Pandey and Rajaram, 2016).

Physical heterogeneity complicates the estimation of field scale chemical weathering processes because fluids take pathways with varying velocity and residence times (Dagan and Indelman, 1999; Werth et al., 2006; Sanchez-Vila et al., 2007; Li et al., 2008; Dentz et al., 2011b; Porta et al., 2012; Porta et al., 2013) and determining properties such as surface area and volume of reactive rock is difficult (Velbel, 1993; Navarre-Sitchler and Brantley, 2007). While mineral dissolution rates are typically reported after specific surface area normalization (Anbeek et al., 1994; White and Brantley, 2003; Zhu, 2005; Navarre-Sitchler and Thyne, 2007); specific surface area tends to increase during the course of chemical weathering with the development of etch pits and micropores (Anbeek, 1992; Anbeek, 1993; White and Brantley, 2003), total reactive surface area often decreases (Noiriel et al., 2004; Luquot and Gouze, 2009; Gouze and Luquot, 2011) contributing to uncertainties in surface area normalization. In addition, heterogeneity can create zones of low reactivity where reactive mineral surface area does not dissolve because fluid in immobile zones reaches equilibrium (Lichtner and Tartakovsky, 2003; Dentz et al., 2011; Li et al., 2014; Jung and Navarre-Sitchler, in review; Wen and Li, 2017). Thus, specific surface area estimated in heterogeneous media might be higher than the effective surface area leading to artificial reduction in mineral dissolution rates due to over-normalization (Jung and Navarre-Sitchler, in review).

The combination of heterogeneity in porous rocks and the time scales of weathering in field systems produces the largest unresolved uncertainties in scaling mineral reaction rates from laboratory studies to field systems. It is impossible to reproduce both the time scale of natural
mineral dissolution in laboratory experiments, even with some experiments running 13.8 years (White et al., 2017), and represent field scale heterogeneity in laboratory systems. Systematic investigations of the relationship between time and mineral dissolution rate in heterogeneous porous media can help resolve the contribution of surface area normalization to variation in dissolution rates. In this study I present results from multi-component reactive transport models used to investigate time-dependent evolution of mineral dissolution rates in heterogeneous domains. Dissolution rates estimated via flux-weighed concentration are normalized either with local or domain-averaged surface areas and compared with non-normalized rates. The effect of normalization with the assumption of linearly increasing surface area over time in the homogenous domain condition is also investigated and the implications for heterogeneous systems are discussed.

3.2 Method

3.2.1 Random Permeability Fields Generation

Latticed domains were constructed with heterogeneous spatial distributions of permeability that induce preferential flow paths. The 2D model domain is either 1 m × 1 m or 400 m × 400 m consisting of 100 × 100 cells with \( dx \times dy \) cell discretization where \( dx \) and \( dy \) is the length of a side of a cell (\( dx = dy = 0.01 \) m or 4 m). Heterogeneous permeability fields were generated using sequential Gaussian simulation (SGS) in SGeMS software (Remy et al., 2009). For this study, the permeability was assigned to follow a log-normal distribution with the geometric mean equal to \( 10^{-13} \) m² and the geometric variances (\( \sigma_{lnK}^2 \)) of 1 and 5 for a small domain (1 m × 1 m) and 25 for a large domain (400 m × 400 m). Generated permeability values were spatially distributed according to the predefined correlation structure with the given integral scales (\( \lambda_{\text{max}} \) and \( \lambda_{\text{min}} \)). The correlation structure is an ellipse that was aligned horizontally (\( \lambda_{\text{max}} \))
and vertically ($\lambda_{\text{min}}$) with respect to x-direction. The integral scale was varied while the domain size remains fixed (Figure 3.1, Table 3.1, and Figure A5). Each case is identified by a unique case name comprised of information about the field generation following Jung and Navarre-Sitchler (2017). A, C, and D indicate low ($\sigma_{\text{inK}}^2 = 1$), high ($\sigma_{\text{inK}}^2 = 5$) and extreme variance ($\sigma_{\text{inK}}^2 = 25$), I and N is isotropic and anisotropic distribution, respectively.

### 3.2.2 Reactive Transport Simulations

The reactive transport code CrunchTope (Steefel and MacQuarrie, 1996; Steefel et al., 2005) was used to investigate the effects of heterogeneous flow and mixing on the evolution of weathering rates over time. Single mineral composition was used as a simple geochemical system to isolate the effects of flow on reaction rates. The simulations were performed at 25°C with a diffusion constant of $10^{-9}$ m$^2$ s$^{-1}$. Average Darcy flux in the x-direction ($U_x$) was fixed to 1.58 m yr$^{-1}$ for a small domain and upscaled proportionally with the domain length to 631 m yr$^{-1}$ (=1.73 m day$^{-1}$) for a large domain. These two fixed Darcy fluxes for different domain sizes result in the same mean transit time of 81 days for all simulations. Flux boundary conditions were used for left and right boundaries of the domain with no-flow boundary conditions for top and bottom boundaries. Data were reported at 18 times during the simulation (0.5, 1, 3, 5, 7, 10, 25, 50, 75, 100, 250, 500, 750, 1000, 1500, 2000, 2500, and 3000 years) with a total simulation time of 3,000 years for all simulations. Porosity was updated as minerals dissolved and precipitated in the domains.

For reactive simulations, initial domains consisted of 55% Quartz (SiO$_2$) and 10% anorthite (CaAl$_2$Si$_2$O$_8$) by volume with a porosity of 35%. Over the simulated timescales, quartz is represented as an inert mineral (dissolution and precipitation suppressed) to simplify the chemistry and kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) was allowed to precipitate as a secondary mineral.
Mineral surface areas were 0.68 m$^2$ g$^{-1}$ for anorthite and 13.2 m$^2$ g$^{-1}$ for kaolinite (Amrhein and Suarez, 1992; Wieland and Stumm, 1992). Kinetics of anorthite and kaolinite reactions at each grid cell were calculated according to linear Transition State Theory with log rate constants of -11.79 and -12.37 mol m$^{-2}$ s$^{-1}$, respectively (Amrhein and Suarez, 1992; Wieland and Stumm, 1992). Concentrations of Ca$^{2+}$, Al$^{3+}$, and SiO$_2$(aq) were set to zero and pH was fixed at 4.5 in the input fluid, Cl$^-$ was included in the model for charge balancing purposes. Reaction stoichiometry and parameters (equilibrium constant ($K_{eq}$), reaction rate constant ($k$), and mineral surface area ($A_b$)) used in this study are summarized in Table 3.2.

Fifty realizations of each simulation condition resulted in a total of 451 numerical simulations including a realization for the homogeneous distribution.

### 3.2.3 Dissolution Rate Formulations

Dissolution in each individual grid cell was investigated using two different formulations calculated from linear transition state theory; non-normalized local dissolution rate ($R_{local}$, mol L$^{-1}$ s$^{-1}$, Equation 3.1), and reactive surface area normalized local dissolution rate ($\bar{R}_{local}$, mol m$^{-2}$ s$^{-1}$, Equation 3.2, Figure 3.2).

\[
R_{local} = \frac{kA_b}{1000\phi} \left(1 - \frac{IAP}{K_{eq}}\right) \tag{3.1}
\]

\[
\bar{R}_{local} = k \left(1 - \frac{IAP}{K_{eq}}\right) \tag{3.2}
\]

where $k$ is the intrinsic rate constant (mol m$^{-2}$ s$^{-1}$) defined in the model input, $\phi$ is porosity, $IAP/K_{eq}$ is the saturation state of the fluid with respect to the reacting mineral calculated by
CrunchTope for each cell at each time step, and \( A_b \) is the bulk mineral surface area (m\(^2\) mineral m\(^{-3}\) porous media) calculated using the given specific surface area with Equation 3.3,

\[
A_b = \frac{A_s MW_m f}{V_m} \tag{3.3}
\]

where \( A_s \) is the specific surface area (m\(^2\) g\(^{-1}\)) given in Table 3.2, \( MW_m \) is the molecular weight of the mineral phase (g mol\(^{-1}\)), \( f \) is the mineral volume fraction, and \( V_m \) is the molar volume of the mineral phase (m\(^3\) mol\(^{-1}\)).

The effective dissolution rate, representing the volume averaged reaction rate over the domain, was formulated in three different ways: 1) non-normalized effective dissolution rate \((R_{eff},\) mol L\(^{-1}\) s\(^{-1}\), Equation 3.4) using the flux weighted Ca\(^{2+}\) concentration at the domain outlet, 2) locally-normalized effective dissolution rate \((\bar{R}_{eff},\) mol L\(^{-1}\) s\(^{-1}\), Equation 3.5) taking the arithmetic average of \( \bar{R}_{local} (< \bar{R}_{local} >) \), and 3) domain normalized effective dissolution rate \((\bar{\bar{R}}_{eff},\) mol m\(^{-2}\) s\(^{-1}\), Equation 3.6) using the domain-averaged \( A_b (< A_b >) \).

\[
R_{eff} = \frac{\sum^n_z (q \Delta Ca)_z}{1000 \phi V} 
\tag{3.4}
\]

\[
\bar{R}_{eff} = < \bar{R}_{local} > 
\tag{3.5}
\]

\[
\bar{\bar{R}}_{eff} = \frac{1000 \phi R_{eff}}{< A_b >} 
\tag{3.6}
\]

where \( q \) is Darcy flux of each cell (m\(^3\) s\(^{-1}\)) and \( \Delta Ca \) (mol m\(^{-3}\)) is the difference in Ca\(^{2+}\) concentration between inlet fluid and each cell at the outlet. \( V \) is the volume (m\(^3\)) of the domain, 1000 is a unit conversion factor from m\(^3\) to L, and \( \phi \) is porosity. Initial surface areas \((A_{s,0}) \) were
specified as an initial input (Table 3.2) then the surface area of mineral \( m \) was updated after each time step according Equations 3.7 and 3.8 for dissolution and precipitation reactions, respectively.

\[
\text{Dissolution: } A_b = A_{b,0} \left( \frac{f_m}{f_{m,0}} \right)^{2/3} \left( \frac{\phi}{\phi_0} \right)^{2/3}
\]

\[
\text{Precipitation: } A_b = A_{b,0} \left( \frac{\phi}{\phi_0} \right)^{2/3}
\]

where \( f_m \) and \( f_{m,0} \) are the mineral volume fraction and the initial mineral volume fraction, respectively.

### 3.3 Results

#### 3.3.1 Local Darcy velocity and local dissolution rate

Depending on the preassigned geostatistical parameters, flow paths with different velocities and residence times developed in heterogeneous domains. In this study, heterogeneous flow fields are defined by the parameters \( \sigma_{ink}^2 \) and integral scales \( \lambda_{\text{min}} \) and \( \lambda_{\text{max}} \). Figure 3.3a reveals that the range of local velocity \( (u) \) is largely determined by \( \sigma_{ink}^2 \). Low (\( \sigma_{ink}^2 = 1 \)), high (\( \sigma_{ink}^2 = 5 \)), and extreme (\( \sigma_{ink}^2 = 25 \)) variances in permeability field lead \( u \) to range about 2, 6, and 11 orders of magnitude, respectively. This increasing range with increasing \( \sigma_{ink}^2 \) is largely caused by the favorable development \( u \) toward low values that leads to decrease in ensemble average of \( u \). For example, after normalization of \( u \) by the domain size, DI2 has only \( \sim 1 \) order of magnitude higher maximum \( u \) while the minimum \( u \) is \( \sim 8 \) orders of magnitude lower than AI2 (Figure 3.3a). The domain-size normalized ensemble average of \( u \) for AI2 and DI2 are 1.41 yr\(^{-1} \) (= 1.41 m yr\(^{-1} \)) and 0.20 yr\(^{-1} \) (= 79.3 m yr\(^{-1} \)), respectively. The effect of \( \lambda \) on \( u \) is relatively insignificant compared to \( \sigma_{ink}^2 \) but the general opposite effects between \( \lambda_{\text{min}} \) and \( \lambda_{\text{max}} \) exist. Flow
paths in domains with low $\lambda_{\text{max}}$ and high $\lambda_{\text{min}}$ are more tortuous and longer than in domains with high $\lambda_{\text{max}}$ and low $\lambda_{\text{min}}$ (Figure 3.4 and Figure A6). Because each simulation has the same mean Darcy flux across the domain, longer flow paths result in higher velocities to maintain the same flux. For example, mean $u$ of AN3a is 1.34 m yr$^{-1}$ with $\lambda_{\text{max}}$ and $\lambda_{\text{max}}$ of 0.1 m and 0.05 m, respectively. This mean $u$ increases to 1.36 m yr$^{-1}$ and 1.41 m yr$^{-1}$ when $\lambda_{\text{max}}$ decreases to 0.06 m (AN1a) and $\lambda_{\text{min}}$ increases to 0.1 m (AI2), respectively.

As a result of heterogeneous flow paths, nonuniform spatial fields of $R_{\text{local}}$ develops in the domains where chemical constraints (initial mineral surface area and rate constant) were uniformly distributed initially. Figure 3.5 show the spatial distribution of non-normalized mineral dissolution rate ($R_{\text{local}}$) after 3 years of simulation. Fingers of high reactivity develop near the inlet (Figure 3.5). In A cases (first column in Figure 3.5), $R_{\text{eff}}$ decreases ~1.5 orders of magnitude across the length of the domain with a corresponding increase in solute concentration and IAP/K$_{eq}$ relatively homogeneously. The decrease in $R_{\text{local}}$ along the preferential flow paths is approximately the same, however, large blocks of slow $R_{\text{local}}$ (~ 4.5 order of magnitude reduction) appear in D cases (second column in Figure 3.5). The spatial locations of these less reactive blocks correspond to immobile (i.e. low $u$) zones in Figure 3.4 where solute transport occurs mainly through diffusion. Since diffusion is a slow process, residence times of a fluid in the immobile zones are long and decrease $R_{\text{local}}$ by increasing IAP/K$_{eq}$. The favorable development of low $u$ with high $\sigma_{\text{lnK}}^2$ also corresponds to preferential development of low $R_{\text{local}}$ (Figure 3.3b). However, increased $u$ with high $\sigma_{\text{lnK}}^2$ does not necessarily result in the increase in $R_{\text{local}}$ as the maximum $R_{\text{local}}$ is limited by the predefined rate constant, $k$, which is known as the surface-limited reaction rate (Maher, 2010; Molins et al., 2012). Moreover, $R_{\text{local}}$ of grid cells located downgradient with high $u$ may not have the maximum $R_{\text{local}}$ due to the inheritance of the
fluid that receive high $IAP/K_{eq}$ condition from upgradient grid cells (Jung and Navarre-Sitchler, in review). Therefore, physical forcing acting toward increasing the dissolution rate is chemically inhibited but the forcing to the opposite direction always induce the reduction in $R_{local}$.

In D cases, high $Pe$ conditions (i.e. large domain size and high $U_x$) also contribute to decreased $R_{local}$ by increasing the diffusion length scale while large $\sigma_{\text{lnK}}^2$ intensifies the relative importance of diffusive transport due to decreased $u$. When either $\sigma_{\text{lnK}}^2$ or $Pe$ is increased holding the other parameter constant, reduction in $R_{local}$ is not as apparent as D cases (Figure A7). In D cases, the size of the immobile zones is larger than A cases due to the increased $\lambda_{\text{min}}$ and $\lambda_{\text{max}}$ from 0.1 m (AI2) to 40 m (DI2). The increased length scale of the immobile zones increases fluid residence time in the immobile zones and $IAP/K_{eq}$ reducing $R_{local}$. Some portions of the immobile zones reach equilibrium and $R_{local}$ becomes 0 as a combined result of low $u$ and long diffusion length scale (3 out of 10,000 grid cells in DN3a case, not included in Figure 3.3b). The effect of diffusion length scale, although the impact is less significant, also appears for different integral scales in the domains with same $Pe$. For example, $R_{local}$ of DN1a, DN3a, and DI2 cases decrease to 1.33, 1.30, and $1.28 \times 10^{-10}$ mol L$^{-1}$ s$^{-1}$, respectively, as $\lambda_{\text{max}}$ increase to 24 m to 40 m and $\lambda_{\text{min}}$ from 12 m to 20 m and 40 m.

### 3.3.2 Time dependence of local dissolution rate and mineral surface area

The general influence of physical heterogeneity on mineral dissolution rate was investigated after 3 years of simulation time. In this short time period, the dissolving mineral has not depleted throughout the domain. At later times depletion of reactive surface area induces time dependence of mineral dissolution rates (White and Brantley, 2003; Pandey and Rajaram, 2016; White et al., 2017). Chemical weathering in natural system involves geologic time scales, therefore, weathering rates estimated in natural systems are expected to be different than the short-term
simulations. A grid scale behavior of dissolution rate is investigated using two different local dissolution rate formulations ($R_{local}$ and $\bar{R}_{local}$) in order to identify time dependent behavior of local dissolution rates.

Figure 3.6 and 3.7 show the non-normalized ($R_{local}$, mol L$^{-1}$ s$^{-1}$, Equation 3.1) and locally normalized ($\bar{R}_{local}$, mol m$^{-2}$ s$^{-1}$, Equation 3.2) dissolution rates and the ratio of remaining surface area ($A_b$) to the initial surface area ($A_{b,0}$) at simulation times of 10, 100 and 500 years. One example from each of AI2 (Figure 3.6) and DI2 (Figure 3.7) that corresponds to the permeability field in Figure 3.1 is shown here and other cases are provided in Supplementary materials (Figure A8 ~ A14). In the first column of Figure 3.6, the location of the active reaction front with fast $R_{local}$ has moved from $\sim$ 0.1 m at 10 years (Figure 3.6a) to $\sim$ 0.25 m at 100 years (Figure 3.6b) and exited the domain by 500 years (Figure 3.6c) leaving slow $R_{local}$ at times after 500 years. This spatial evolution of $R_{local}$ distributions corresponds to the evolution of $A_b/A_{b,0}$ (third column of Figure 3.6). In early time period, fast dissolution occurs mostly near the inlet and produces high Ca$^{2+}$ concentration. This process hinders fast reaction in downstream grid cells by increasing $IAP/K_{eq}$ and preserves the dissolving mineral, anorthite, during early time periods. Once the dissolution depletes the mineral at upstream locations, however, downstream fluid no longer inherits high $IAP/K_{eq}$. As a result, propagation of the active reaction front leaves reduced $R_{local}$ and depleted mineral (i.e. low $A_b/A_{b,0}$) behind and starts to dissolve downstream mineral at fast rates, a condition referred to as quasi-steady state (Lichtner, 1988).

Depletion of reactive surface area in the domain produces different trends of spatial distribution of the overall mass transfer rate, $R_{local}$, and the surface area normalized rate, $\bar{R}_{local}$, through time. While the actual rates are different, the spatial distribution of fast and slow $R_{local}$ (Figure 3.6a) after 10 years of dissolution is similar to $\bar{R}_{local}$ (Figure 3.6d). After 100 years, $R_{local}$
behind the initial reaction front that propagates through the domain are slower compared to those in the reaction front (Figure 3.6b). In contrast, $\bar{R}_{local}$ are faster behind the initial reaction front compared to those in the reaction front (Figure 3.6e). As the reaction front propagates through the domain, surface area is reduced reducing the overall rates of mass transfer (represented by $R_{local}$), which leads to lower solute concentrations and $IAP/K_{eq}$ behind the reaction front producing the fast values of $\bar{R}_{local}$ (Equation 3.2). After 500 years the initial reaction front has moved through the domain, but some surface area remains (Figure 3.6i). Overall mass transfer rates in the entire domain are low because the surface area is low (Figure 3.6i) and the fluid chemistry is far from equilibrium with respect to anorthite dissolution producing $\bar{R}_{local}$ close to $k$ (Figure 3.6f). The opposite trends of $R_{local}$ and $\bar{R}_{local}$ are produced by the dependence on $IAP/K_{eq}$ after surface area normalization (Equation 3.2). $IAP/K_{eq}$ behind the front is very low as the depleted mineral can no longer supply reaction products to solution fast enough to increase concentrations. Thus, when the reaction rate is surface area normalized it is close to $k$.

The general trends in spatial and temporal distribution of $R_{local}$ and $\bar{R}_{local}$ observed in AI2 (Figure 3.6) are also observed in DI2 (Figure 3.7). However, fast dissolution is limited to preferential flow paths and low-reactivity zones develop in DI2 domains where diffusion length scales are increased in the large $\sigma_{\ln K}^2$ and $Pe$ conditions. These low-reactivity zones persist for the full simulation time scale and fluid in the low-reactivity zones reaches equilibrium ($R_{local} = \bar{R}_{local} = 0$). However, the size of low-reactivity zones decreases with time. In Figure 3.7b and c, the active reaction front propagates into the low-reactive zones slowly through diffusion as the mineral along the preferential flow paths gets depleted. This slow propagation of reaction front allows the domain to maintain reactivity by preserving the reactive mineral and prevents
homogenization of spatial distribution of rates in the domain for the total simulation time of 3,000 years.

### 3.3.3 Time dependence of effective dissolution rate

The transference of local scale mineral dissolution behaviors to effective dissolution rates, which are equivalent to field determined weathering rates through mass-balance approaches, is investigated through three different effective dissolution rate formulations (Equation 3.4-3.6). The reaction product, Ca\(^{2+}\), does not experience any other reactions in this study so Equation 3.4 is equivalent to the domain average of \( R_{\text{local}} \) (i.e. \( R_{\text{eff}} = \langle R_{\text{local}} \rangle \)) (Jung and Navarre-Sitchler, n.d.; Pandey and Rajaram, 2016). This condition makes \( R_{\text{eff}} \), the mass balance estimation of dissolution rate averaged by the volume of the domain, comparable with \( \bar{R}_{\text{eff}} \), the arithmetic average of surface area normalized local dissolution rate over the domain.

The spatial distributions of \( R_{\text{eff}} \) and \( A_{b}/A_{b,0} \) through time are similar (Figure 3.8), indicating the strong dependence of \( R_{\text{eff}} \) on available mineral surface area (White et al., 1996; White and Brantley, 2003). In early time, \( R_{\text{eff}} \) and \( A_{b}/A_{b,0} \) of all cases are constant with \( IAP/K_{eq} > 0.9 \) and \( R_{\text{eff}} \approx 1 \) order of magnitude smaller than \( k \) (in mol L\(^{-1}\) s\(^{-1}\)) due to the reduction in dissolution rate induced by high \( IAP/K_{eq} \) (Jung and Navarre-Sitchler, 2017). After 100 years, \( R_{\text{eff}} \) and \( IAP/K_{eq} \) of D cases (DI2, DN1a, and DN3a) start to decrease first while A and C cases remain constant at initial values. As time proceeds, \( R_{\text{eff}} \) of D cases decreases gradually and \( R_{\text{eff}} \) begins to decrease in A and C cases. The decrease in \( R_{\text{eff}} \) of A and C is more rapid compared to D cases resulting in higher \( R_{\text{eff}} \) in D cases than A and C cases after 600 ~ 700 years.

The earlier reduction of \( R_{\text{eff}} \) from the initial state in D cases than A and C cases can be explained by preferential depletion of reacting mineral surface along the fast flow paths (Figure
3.6 and 3.7). At 100 years in AI2, mineral surface area is depleted in the first ~0.25 m of the domain and the reaction front moves through the domain at similar rates without the development of strong preferential flow paths (Figure 3.6h). While the active reaction front remains in the domain, fluid exiting the domain is close to equilibrium and $R_{\text{eff}}$ is high due to high concentrations of $\text{Ca}^{2+}$ in the fluid. In contrast, in DI2 the reaction front moves along strong preferential flow paths and at 100 years the reaction front is no longer in the domain in these flow paths due to the preferential depletion of reacting mineral (Figure 3.7h). Thus, $IAP/K_{\text{eq}}$ and $R_{\text{eff}}$ of the fluid exiting the domain decreases due to lower $\text{Ca}^{2+}$ concentration contribution from the fast flow paths (Equation 3.4). At 500 years simulation time, reactive mineral volume in AI2 has decreased to ~1% from the initial volume fraction of 10 % (Figure 3.6i and 3.8b). In A cases, this low remaining surface area after 500 years of dissolution decreases $R_{\text{eff}}$. In contrast, reactive mineral percentages remain high in immobile zones in DI2 (Fig. 3.7i and 3.8b) and active reaction ($R_{\text{eff}} \sim k$) still occurs within the domain (Figure 3.7c). This condition produces comparatively higher values of $R_{\text{eff}}$ at later times as the reaction front propagates and $\text{Ca}^{2+}$ slowly diffuses from the immobile zones. $R_{\text{eff}}$ in D cases then gradually decreases over time as mineral surface area depletes in the low-reactivity zones.

Within each domain heterogeneity structure, different values of $\lambda$ produce different trends in reduced $R_{\text{eff}}$ through time. These differences are small, but provide insight into the control of heterogeneity on time dependence of $R_{\text{eff}}$. The ensemble average of $R_{\text{eff}}$ ($<R_{\text{eff}}>$) after three years of simulation time is highest in DN1a with $<R_{\text{eff}}>$ = $1.33 \times 10^{-10}$ mol L$^{-1}$ s$^{-1}$, followed by DN3a ($1.30 \times 10^{-10}$ mol L$^{-1}$ s$^{-1}$) > DI2 ($1.28 \times 10^{-10}$ mol L$^{-1}$ s$^{-1}$). However, after 1000 years of simulation time the fastest $<R_{\text{eff}}>$ is from DI2 ($1.36 \times 10^{-11}$ mol L$^{-1}$ s$^{-1}$) followed by DN3a ($1.34 \times 10^{-11}$ mol L$^{-1}$ s$^{-1}$) > DN1a ($1.24 \times 10^{-11}$ mol L$^{-1}$ s$^{-1}$); thus, reversing the order. At early times, the
amount of available mineral surface is approximately the same for all cases so the fastest domain averaged reaction occurs where low-reactivity zones are small (i.e. the order of $R_{eff}$ at early time is $H > AN1a > AN3a > AI2 > CN1a > CN3a > CI2 > DN1a > DN3a > DI2$). However, this fast reaction also depletes available mineral surface area through time and at later time periods heterogeneity structures that produce larger areas of low-reactivity zones have faster domain averaged reaction rates with $DI2 > DN3a > DN1a > CI2 > CN3a > CN1a > AI2 > AN3a > AN1a > H$ (Figure 3.8a). Thus, when the effect of reactive surface area on dissolution rate is removed in local normalization ($\bar{R}_{eff}$), the early time order stays throughout the simulation time (Figure 3.9) and $\bar{R}_{eff}$ increases over time instead of decreasing like $R_{eff}$. These trends are consistent with observed trends in $\bar{R}_{local}$ (section 3.3.2). As dissolution depletes the reactive surface area over the domain, $\bar{R}_{eff}$ approaches $k$ as $IAP/K_{eq}$ decreases like the behavior observed in trends in $R_{local}$ (Figure 3.6 and 3.7). This similarity is not surprising because $\bar{R}_{eff}$ is effectively the mean of $\bar{R}_{local}$ ($<\bar{R}_{local}>$, Equation 3.5). The time it takes $\bar{R}_{eff}$ to reach values approximating $k$ is longer for D cases due to the development of non-reactive zones that take longer for the mineral surface area to deplete. Complete depletion is not observed within the simulation time scale of this study, but values of $\bar{R}_{eff}$ in D cases are also expected to reach $k$ in later time.

This result where dissolution rates only depend on $IAP/K_{eq}$ ($\bar{R}_{local}$ and $\bar{R}_{eff}$) indicates laboratory measured reaction rate constants, $k$, can be extrapolated to other heterogeneous field scale weathering studies without fully resolving reaction time or heterogeneous flow paths if the effect of surface area is completely removed. However, this would be rarely the case because measuring mineral surface area with high enough resolution to calculate $\bar{R}_{local}$ and $\bar{R}_{eff}$ is likely impossible. Instead, the entire domain is usually represented by a single surface area measurement or an average of a few measurement points (Anbeek, 1992; Anbeek, 1993; Zhu,
This practical limitation introduces uncertainties in estimating the effective dissolution rate normalized by the domain averaged surface area ($\bar{R}_{\text{eff}}$). $\bar{R}_{\text{eff}}$ might be a good approximation if the domain is homogeneous. However, estimated $\bar{R}_{\text{eff}}$ can be problematic if the domain is highly heterogeneous.

$\bar{R}_{\text{eff}}$ evolves through time as surface area changes. $\bar{R}_{\text{eff}}$ initially increases for all cases, up to ~250 years. After ~250 years, $\bar{R}_{\text{eff}}$ continues to increase and approaches $k$ in A and C cases. In contrast, in D cases $\bar{R}_{\text{eff}}$ decreases after ~250 years (Figure 3.10). These opposing trends for different heterogeneity structures illustrate the problem of using domain averaged surface area in normalizing mineral dissolution rates for comparison to laboratory-derived rates. For instance, in case AI2 distribution of $A_b$ is generally uniform perpendicular to the flow path and $A_b$ continually decreases with time at any given point in the domain as mineral dissolves (Figure 3.6). However, in case DI2 mineral surface area is depleted in fast fluid pathways throughout the domain but is not depleted in low-reactivity zones (Figure 3.7). The different distributions of surface area relative to initial surface area leads to high domain-averaged surface area $<A_b>$ in DI2 cases but low $<A_b>$ in AI2 cases. Thus, when rates are normalized to domain-averaged surface area there is an artificial reduction in $\bar{R}_{\text{eff}}$ of ~ 1.7 orders of magnitude after 3000 years of dissolution for the DI2 case. This result indicates effective dissolution rate estimation based on the domain averaged surface area normalization may not be adequate in heterogeneity conditions that lead to development of immobile or low-reactivity zones (i.e. high $Pe$ and $\sigma_{\text{HK}}^2$). It is not shown in the time scale of the simulations presented here but $\bar{R}_{\text{eff}}$ of D cases is expected to increase to $k$ once $A_b$ in the immobile zones is depleted.
3.4 Discussion

In field systems, it is difficult to estimate mineral surface area for comparison to laboratory-derived rates; leaving uncertainty in the sources of discrepancies the laboratory-derived rates and field rates (e.g. Navarre-Sitchler and Brantley, 2007). The evolution of mineral surface with reaction, both specific surface area and reactive surface area, with time adds additional uncertainty to the discussion of comparing laboratory and field mineral reaction rates. As dissolution proceeds, minerals dissolve often reducing reactive surface area (Noiriel et al., 2004; Luquot and Gouze, 2009; Gouze and Luquot, 2011) while increasing specific surface area as mineral surfaces develop etch pits and roughness (e.g. Anbeek, 1992; Anbeek, 1993; Zhu, 2005; Navarre-Sitchler and Brantley, 2007; White et al., 2017). Flow paths can develop as a result of dissolution reactions that increase accessible reactive surface area accompanies with increased specific surface area (Noiriel et al., 2009; Ibarra et al., 2016). The numerical simulations presented here help elucidate the effects of decreasing reactive surface area on mineral dissolution rates over time scale up to thousands of years, much longer than any experimental approach can approximate. However, simulations based on the shrinking sphere model (Equation 3.7) do not account for increasing surface area. The normalization approaches with the decreasing surface area in section 3.3.3 are likely to represent minimum estimates of reduction in mineral dissolution rates because increased surface area would lead to slower surface area normalized rates than those presented here. For example, normalizing the constant mass transfer with linearly increasing specific surface area showed decreasing weathering rates with time which is the opposite from the increasing trend of this study (e.g. White and Brantley, 2003). The relationship between the evolution of weathering rate and mineral surface area can be more complicated in natural systems if the increased specific surface area accompanies the
increase in reactive surface area increases. Higher reactive surface area leads to faster total mass transfer rate while the rate is normalized with increasing specific surface area, so the relationship may not linearly related to evolving specific and reactive surface area. Further experimental studies investigating the evolution of mineral surface area and mass flux through time are necessary to model the complex effects of evolving surface area on time-dependence of mineral reaction rates.

Besides the effects of evolving surface area, the chemical weathering rate is assumed to follow simple linear dependence on saturation state and not to depend on pH change or Al concentration in this study. The observed deviation from these assumptions (e.g., Oelkers et al., 1994) can be another source of laboratory-field discrepancy given the crucial role of non-reactive zones in controlling effective mineral dissolution rate. In addition, correlations between physical heterogeneity and chemical heterogeneity can introduce additional variation in effective mineral dissolution rates (Li et al., 2006; Atchley et al., 2014; Beisman et al., 2015). Further studies exploring the coupled influence of physical and chemical heterogeneity to time dependence of mineral dissolution rate will provide additional information regarding bridging the gap between lab and field measured reaction rates.

3.5 Conclusion

Anorthite dissolution was simulated in the reactive transport code CrunchTope with multiple realizations of permeability distribution over 3,000 years to investigate the role of heterogeneous flow in observed time dependence of mineral dissolution rates. In simulations with large $\lambda$, $\sigma_{ln,k}^2$, and $Pe$, mineral dissolution rates initially decrease through time (Figure 3.4 and 3.5). This reduction in dissolution rate is attributed to slow diffusive transport in immobile zones that allows the fluid to maintain high $IAP/K_{eq}$ and preserves the reacting mineral. For these
cases, \( \sigma^2_{\ln k} \) exerts more influence on reduced effective mineral dissolution rates than \( \lambda \) within the tested range of parameters. When the scale of both \( \sigma^2_{\ln k} \) and \( \lambda \) is enhanced in a large domain (i.e. large \( Pe \)), the degree of reduction in mineral dissolution rate is significantly intensified.

Therefore, the order of non-normalized effective dissolution rate (\( R_{eff} \)) is as follows from fast to slow: \( H > AN1a > AN3a > AI2 > CN1a > CN3a > CI2 > DN1a > DN3a > DI2 \) (Figure 3.6 and 3.8). However, this order of \( R_{eff} \) is reversed to \( DI2 > DN3a > DN1a > CI2 > CN3a > CN1a > AI2 > AN3a > AN1a > H \) in late time with the depletion of the dissolving mineral. In relatively well-mixed conditions (A and C cases), depletion of reacting mineral occurs throughout the domain and \( R_{eff} \) decreases rapidly. However, the dissolving mineral is preserved in a poorly mixed condition (D cases) with the development of immobile and low-reactivity zones. These zones provide reactive surfaces through slow diffusive transport throughout the 3,000 years of simulation time and thus decrease in \( R_{eff} \) is much more gradual than the other cases (Figure 3.7 and 3.8).

Yet, the reversal is not observed when the rate is normalized by the remaining local mineral surface area (Figure 3.6, 3.7 and 3.9). Instead, the time dependent evolution of \( \bar{R}_{local} \) and \( \bar{R}_{eff} \) show increasing rates through time. When the effect of reactive surface area is completely eliminated, dissolution rates only depend on the preassigned rate constant, \( k \), and saturation state of fluid, \( IAP/K_{eq} \) (Equation 3.2 and 3.5). As the reactive mineral gets depleted with dissolution, \( IAP/K_{eq} \) decrease as there is no more mineral to react and the rate approaches to \( k \). This would be the ideal condition where dissolution rates only depend on \( IAP/K_{eq} \) which can be measured relatively easily. However, a large domain is usually represented by a single domain-averaged surface area in most studies and used to normalize the measured flux-weighted solute concentration (\( \bar{R}_{eff} \), Equation 3.6). \( \bar{R}_{eff} \) reproduces the observed behavior of \( \bar{R}_{eff} \) when the domain
is relatively homogeneous (A and C cases, Figure 3.10). In poorly mixed domain (D cases), however, remaining surface area in immobile zones over-normalize the dissolution rate and $\bar{R}_{\text{eff}}$ shows decreasing trend in late time simulations. This over-normalization leads to $\sim 1.5$ orders of magnitude artificial reduction in $\bar{R}_{\text{eff}}$.

This simulation study does not account for the effect of increasing surface area through time commonly observed in experimental studies. Increasing surface area may intensify the reduction of weathering rate than the observation of this study. Further study resolving the functional relationship between the evolution of specific surface area and mass flux can provide a model to be employed for a long-term weathering simulation.
Figure 3.1. One example of 50 generated realizations of permeability fields with (a - c) $\sigma_{lnK}^2 = 1$ and (e - f) $\sigma_{lnK}^2 = 25$ as given in Table 3.1.
Figure 3.2. Definitions for each dissolution rate calculation ($R_{local}$ and $R_{eff,i}$) and schematic description of the measurement planes.
Figure 3.3. Distribution plot of log transformed (a) local Darcy flow rate normalized by the length of each domain \((u, \text{yr}^{-1})\) and (b) local dissolution rate \((R_{\text{local}}, \text{mol L}^{-1}\text{s}^{-1})\). The color scale represents the number of cells with a given log \(u\) (or log \(R_{\text{local}}\)) normalized by the number of cells with the most abundant log \(u\) (or log \(R_{\text{local}}\)), in other words the color scale is the histogram of the data with the data in each bin normalized to the count in the bin with the maximum number of occurrences.
Figure 3.4. Selected log-transformed local Darcy velocity (log $u$) fields with (a ~ c) $Pe = 143$ and $\sigma_{ln,K}^2 = 1$, and (d ~ f) $Pe = 2.3 \times 10^7$ and $\sigma_{ln,K}^2 = 25$ developed from the corresponding permeability field in Figure 3.1.
Figure 3.5. Selected log-transformed local dissolution rate ($\log R_{local}$) fields with (a ~ c) $Pe = 143$ and $\sigma_{ln,k}^2 = 1$, and (d ~ f) $Pe = 2.3 \times 10^7$ and $\sigma_{ln,k}^2 = 25$ developed from the corresponding local flow field ($\log u$) in Figure 3.4.
Figure 3.6. Anorthite dissolution rate fields of (a-c) Non-normalized rate ($R_{\text{local}}$) and (d-f) normalized rate ($\bar{R}_{\text{local}}$), and (g-h) corresponding ratio of remaining mineral surface area to the initial surface area ($A_b/A_{b,0}$) for one realization of A12 at 3 different times (10, 100, and 500 years).
Figure 3.7. Anorthite dissolution rate fields of (a-c) Non-normalized rate ($R_{local}$) and (d-f) normalized rate ($\bar{R}_{local}$), and (g-h) corresponding ratio of remaining mineral surface area to the initial surface area ($A_b/A_{b,0}$) for one realization of DI2 at 3 different times (10, 100, and 500 years).
Figure 3.8. Evolution of log-transformed ensemble average and ±σ of (a) non-normalized effective dissolution rate ($R_{eff}$) and (b) ratio of remaining to initial surface area ($A_{b}/A_{b,0}$) with time in 50 realizations. Subplots are provided to show the order of each case.
Figure 3.9. Evolution of log-transformed ensemble average and ±σ of locally normalized effective dissolution rate ($\bar{R}_{eff}$) with time in 50 realizations. Subplot is provided to show the order of each case.
Figure 3.10. Evolution of log-transformed ensemble average and ±σ of effective dissolution rate normalized by domain-averaged surface area ($\bar{R}_{\text{eff}}$) with time in 50 realizations. Subplot is provided to show the order of each case.
Table 3.1. Permeability field conditions with the mean of $10^{-13}$ m$^2$ and varying variance ($\sigma_{ink}^2$), integral scales ($\lambda_{max}$ and $\lambda_{min}$), and aspect ratio ($\epsilon = \lambda_{min} / \lambda_{max}$).

<table>
<thead>
<tr>
<th>Geometric mean</th>
<th>$\sigma_{ink}^2$</th>
<th>Distribution</th>
<th>$\lambda_{max}$</th>
<th>$\lambda_{min}$</th>
<th>$\epsilon$</th>
<th>Case Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-15}$ m$^2$</td>
<td>-</td>
<td>homogeneous</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>isotropic</td>
<td>0.1 m</td>
<td>0.1 m</td>
<td>1</td>
<td>AI2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>anisotropic</td>
<td>0.06 m</td>
<td>0.03 m</td>
<td>0.5</td>
<td>AN1a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1 m</td>
<td>0.05 m</td>
<td>0.5</td>
<td>AN3a</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>isotropic</td>
<td>0.1 m</td>
<td>0.1 m</td>
<td>1</td>
<td>CI2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>anisotropic</td>
<td>0.06 m</td>
<td>0.03 m</td>
<td>0.5</td>
<td>CN1a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1 m</td>
<td>0.05 m</td>
<td>0.5</td>
<td>CN3a</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>isotropic</td>
<td>40 m</td>
<td>40 m</td>
<td>1</td>
<td>DI2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>anisotropic</td>
<td>24 m</td>
<td>12 m</td>
<td>0.5</td>
<td>DN1a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40 m</td>
<td>20 m</td>
<td>0.5</td>
<td>DN3a</td>
</tr>
</tbody>
</table>

Table 3.2. Reaction stoichiometry and parameters for the minerals considered in dissolution (anorthite) and precipitation (kaolinite) reactions. Equilibrium constants ($K_{eq}$) and reaction rate constants ($k$) are given in mol m$^{-2}$ s$^{-1}$ and mineral surface area ($A_s$) is given in m$^2$ g$^{-1}$.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Reaction Stoichiometry</th>
<th>$K_{eq}$</th>
<th>$k$</th>
<th>$A_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anorthite</td>
<td>$\text{CaAl}_2\text{Si}_2\text{O}_8 + 8\text{H}^+ \rightarrow \text{Ca}^{2+} + 2\text{Al}^{3+} + 2\text{SiO}_2(\text{aq}) + 4\text{H}_2\text{O}$</td>
<td>$10^{26.5780}$</td>
<td>$10^{11.79 , b}$</td>
<td>0.68$^b$</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \leftrightarrow 2\text{Al}^{3+} + 2\text{SiO}_2(\text{aq}) + 5\text{H}_2\text{O}$</td>
<td>$10^{6.8101}$</td>
<td>$10^{12.37 , c}$</td>
<td>13.2$^c$</td>
</tr>
</tbody>
</table>

$^a$ datacom.dbs distributed with CrunchTope  
$^b$ Amrhein and Suarez [1992]  
$^c$ Wieland and Stumm [1992]
CHAPTER 4

THE FABRICATION OF PLAGIOCLASE FELDSPAR MICRODEVICES:
AN EXPERIMENTAL TOOL FOR PORE SCALE
CHEMICAL WEATHERING STUDIES

Pore scale chemical weathering reactions and solute transport are fundamental building
blocks of the life sustaining system on Earth. However, investigating pore scale phenomena has
relied mainly on numerical simulation due to difficulties in experimental approaches at the
micron-scale of pore networks. Here, I present an experimental method using both femtosecond
laser ablation and HF etching techniques to fabricate reactive microdevices in natural silicate
minerals, anorthite and albite. The femtosecond laser minimizes heat affected zones in the
mineral and HF etching successfully removes a thin amorphous layer induced by laser ablation.
The flow field observed in an anorthite microdevice has components both parallel and
perpendicular to the applied pressure gradient in a rectangular pore geometry. This experimental
observation results from the imperfect symmetry (i.e. surface roughness) of the experimental
device while the flow field in an idealized, symmetric simulation domain develops immobile
zones channels perpendicular to the applied pressure gradient. Anorthite dissolution rates,
quantified by total calcium mass transfer rates, in the experimental domain are higher than the
idealized simulation domain due to the differences in flow dynamics. These results demonstrate
that the reactive microfluidics approach can constrain numerical simulations to better represent
the natural pore system.
4.1 Introduction

Chemical weathering is an important natural process that sustains life on earth by releasing dissolved ions as nutrients (Brantley, 2010; Graham et al., 2010), regulating atmospheric CO$_2$ concentrations over geologic time scales (Kump et al., 2000; Navarre-Sitchler and Thyne, 2007; Maher and Chamberlain, 2014), and contributing to the evolution of the chemical and physical nature of landscapes (Anderson et al., 2002; Anderson, 2005). Despite the importance, quantitative estimation and prediction of chemical weathering in natural systems remains elusive due to the long-observed discrepancy between laboratory- and field-measured reaction rates (White and Brantley, 2003; Maher et al., 2004; Navarre-Sitchler and Brantley, 2007). Some portion of this discrepancy has been attributed to heterogeneous nature of geologic materials (Dagan, 1984; Sanchez-Vila et al., 2007; Dentz et al., 2011a; Rubin et al., 2012).

Heterogeneous physical and chemical properties of geologic porous media are often simplified in laboratory experiments in order to assume well-mixed, homogeneous conditions (Gudbrandsson et al., 2008; Gudbrandsson et al., 2014). However, heterogeneous and poorly-mixed conditions are common in natural systems (Malmström et al., 2000; Meile and Tuncay, 2006; Dentz et al., 2011b). Accounting for this heterogeneity in high resolution numerical approaches can bridge the gap between laboratory and field derived rates (Ding et al., 2017). However, the discrepancy cannot be entirely attributed to macroscopic heterogeneity since variation still exists in homogeneous conditions (Maher et al., 2006).

In traditional laboratory experiments and macroscopic numerical simulations, small scale properties that range from several nanometers to microns have been represented by averaged parameters such as porosity, permeability and specific surface area (White and Peterson, 1990b; Gautier et al., 2001; Zhu, 2005). This approach is scale-dependent and induces large deviations.
as the reactive phases within the pore structure are ignored (Meile and Tuncay, 2006; Navarre-
Sitchler and Brantley, 2007). A number of studies have shown the necessity of pore scale
consideration for a proper estimation of chemical reaction and solute transport in a continuum
scale continuum porous media (Li et al., 2006; Noiriel et al., 2009; Battiato and Tartakovsky,
2011; Molins et al., 2014). Therefore, investigating chemical weathering coupled to solute
transport with pore scale resolution in experiments is necessary to constrain pore-scale models
and better explain the long-observed mineral dissolution rate conundrum.

Microfluidics provide a unique opportunity to study pore scale reactive transport
phenomena and help constrain pore-scale numerical simulations. For example, the dependence of
mixing induced bimolecular reaction on grain orientations of micro grains was shown in a silicon
microdevice (Willingham et al., 2008). If chemical reactions change physical properties of pore
geometry, such as a mineral precipitation blocking pores, numerical simulation might fail to
capture the chemical behavior (Yoon et al., 2012). In a microdevice with a realistic pore
structure, multi-continuum formulation based on the pore size distribution of a microdevice was
necessary to effectively upscale small-scale heterogeneity (Zhang et al., 2013; Liu et al., 2015).
In these studies microfluidics approaches have been used in studies of fluid dynamics, mineral
precipitation, and reductive iron dissolution (Zhang et al., 2013), but to our knowledge
microfluidics approaches have not yet been developed to experimentally evaluate pore-scale
silicate mineral weathering. Reactive properties of silicate minerals cannot be approximated with
engineered substrates commonly used for microdevices, including PDMS, silicon, or glass. In
one study a microfluidics device in a calcite substrate was created by laser ablating a 2D pore
structure in a wax mask and selectively dissolving the calcite with nitric acid (Song et al., 2014).
A real-rock micromodel fabricated on shale used a femtosecond laser ablation to carve fluid
pathways into the alumino-silicate clay minerals that comprise the rock. This study highlighted the importance roughness of the pore surfaces and channels on fluid flow that is usually ignored in pore scale studies (Porter et al., 2015). Previous work on laser ablation of materials shows that damage to the substrate can occur with laser ablation, including change in chemistry and crystallinity (Mendez et al., 2006; Gamaly, 2011). In order to use laser ablation techniques to fabricate microfluidic devices in silicate mineral substrate with the intention of using the devices to study dissolution of the silicate mineral, damage to substrate needs to be evaluated and minimized.

Here, I present a femtosecond laser ablation method combined with a chemical etching technique to fabricate microfluidic devices in reactive geologic substrates (anorthite and albite) for pore scale chemical weathering experiments. These devices can be used to investigate geochemical processes, such as sorption, dissolution and precipitation, and provide direct observation of reactive transport at the pore scale in a geologic material; providing important experimental data that can constrain pore scale numerical simulations.

4.2 Methods

4.2.1 Femtosecond laser ablation

Reactive microfluidic devices were fabricated with two silicate mineral substrates, anorthite (An; CaAl$_2$Si$_2$O$_8$) and albite (Al; NaAlSi$_3$O$_8$), with a femtosecond laser system at Colorado School of Mines. A wafer of each silicate mineral (purchased from Ward's Science) was sectioned into 4 cm × 2.5 cm using Hillquist thin section machine (Model 1005) with a HCR-100 diamond blade and polished (Hillquist thin section grinder, Model 800) to a thickness of ~ 3 mm. The simplified pore network with reservoirs at the left- and right- side of the pattern was ablated using a femtosecond laser (Figure 4.1). Detailed description of the laser system used
in this study is available in Squier et al., (2014) and references there in. Here I present a brief
description of the femtosecond laser system.

The laser system combined a Yb fiber oscillator (KM Labs Y-Fi fiber laser) with a
Yb:CaF\(_2\) CPA (chirped pulse amplification) amplifier (KM Labs Zylant). The system outputs
185 fs pulses at a central wavelength of 1035 nm with a bandwidth of ~5 nm. The amplifier runs
at a repetition rate of 10 kHz. In order to minimize dispersion and beam aberrations resulting
from refractive optics, the amplified beam is directed along an all reflective beam path to a 3-
axis stage setup and where it is focused by a 25.4 mm focal length, aluminum plated, 90° off-axis
parabola (OAP) to the sample. The 3-axis machining stages are made by Aerotech (X-Y Axis:
ANT130-XY Series Two-Axis XY Direct-Drive Nanopositioning Stage, Z-Axis: ANT130-L-Z
Series Single-Axis Z Direct-Drive Nanopositioning Stage). The X-Y stage has 1 nm resolution,
75 nm repeatability, accuracy of 250 nm, and an in-position stability of < 1 nm with a quoted
maximum speed of 350 mm/s. The Z stage has a resolution of 2 nm, repeatability of 75 nm,
accuracy of 300 nm, and an in-position stability of < 2 nm, with a quoted maximum speed of 200
mm/s. The laser system was run at an average power of 200 mW, which led to a pulse energy of
20 µJ and the energy fluence of 17.85 J cm\(^{-2}\). The pore network was ablated by passing the laser
over the sample at a scanning speed of 5 mm/s 6 times with a lateral spacing of 5 µm per pass.
These laser parameters resulted in a trapezoidal channel with top width, bottom width, and depth
of ~ 40 µm, ~ 19 µm, and ~ 31 µm for an anorthite wafer and ~ 37 µm, ~15 µm, and ~ 26 µm for
an albite wafer, respectively (Figure 4.2).

4.2.2 Transmission electron microscopy (TEM)

After laser fabrication, the right-side edge of each anorthite and albite mineral wafer
including 10 individual ablated channels (Figure 4.1b) was sectioned for transmission electron
microscope (TEM) foil preparation using focused ion beam (FIB, FEI Helios Nanolab 600i) milling. The foil preparation protocol used in this study was 1) sputter coating of gold on the sectioned mineral including laser ablated channels, 2) deposition of a thin protection layer (~ 2 µm) of Pt on the area of interest (i.e. the bottom of a channel) prior to any Ga ion beam milling, 3) FIB milling vertical to the laser ablated channel surface, 4) placement of foil on a copper TEM grid, and 5) thinning of an electron transparent TEM foil. More details on this FIB milling technique for TEM foil preparation can be found in other studies (Wirth, 2004; Wirth, 2009).

TEM analysis for anorthite and albite foils was conducted using FEI Talos F200X operated at 200 kV accelerating voltage. The TEM foil mounted on a double-tilt holder was tilted to align its low-order zone axis to the direction of the electron beam to evaluate structural damage to the mineral crystal induced by laser ablation. Maps of energy dispersive spectra (EDS) were collected using a Bruker EDS system to capture any changes in chemistry induced by the laser ablation.

4.2.3 Microfluidics experimental setup

The mineral wafers with the microfluidic network model were sonicated in a series of baths (acetone, ethanol, and DI water for 3 minutes each) to clean any ejected material from the surface of the device. Cleaned wafers were oven dried for an hour at 80°C. A PDMS cover (poly-(dimethylsiloxane), Sylgard 185 – Dow Corning, of 8:1 polymer:curing agent ratio cured for 4 hours at 80°C) was plasma bonded to the surface of the microdevice. Inlet and outlet holes, made in the PDMS cover using a 0.5 mm punch prior to bonding, were aligned with the reservoirs on either end of the device. The PDMS sealed microdevices were put in an 80°C oven for 30 minutes after plasma bonding to improve the bonding quality.
The experimental setup for pore scale silicate mineral dissolution reactions with the fabricated reactive microdevices is illustrated in Figure 4.3. The injection fluid (acidified DI water of pH 3.05 by HCl) was pressurized with N\textsubscript{2} gas and average flow rate of 1 μl/min was maintained using Elveflow OB 1 flow controller connected to an Elveflow FLOW-03-07 regulator. The first set of experiments was performed with an anorthite wafer for 24 hours, sampling outlet fluids every 2 hours to obtain sample volumes of 0.12 ml. An additional 0.45 ml sample was collected at 31.5 hours. pH was measured right after the collection of each sample using a micro pH probe (Orion PerpHeT Ross combination pH Micro Electrode, 8220BNWP). Ca\textsuperscript{2+} concentration of the last sample (No. 13) was measured using Ion Chromatography (IC; Dionex ICS-1100). Fluid flow within the fabricated pore structure was visualized using fluorescent beads with diameter of 2 μm (Fluo-ro-Max Red – Thermo Scientific, R0200) with an Olympus BX51 fluorescence microscope with TRITC filter and INFINITY3-6URM camera (Lumenera). The velocity of the fluorescent beads was estimated by measuring the trajectory of the fluorescent beads in a time-lapse image and dividing the length of the illuminated trajectory by the exposure time. The velocity of the beads was considered to represent the flow velocity within the channel. The drag force acting on the fluorescent beads and flow instability that might be caused by the presence of the beads were not considered here. In addition, the three-dimensional flow component that changes the fluorescence intensity along the flow paths was not considered.

4.2.4 Pore scale flow and reactive transport simulations

Fluid flow was modeled using the Lattice Boltzmann method (LBM) in the open-source code, OpenLB (Kang et al., 2006; Mohamad, 2011; Hiorth et al., 2013). LBM simulates the
pore-scale flow of a single aqueous phase by solving the discrete Boltzmann equation with the BGK collision model across a limited number of particles (Equation 4.1)

\[ f_\alpha(x + e_\alpha \delta t, t + \delta t) = f_\alpha(x, t) + \frac{f_\alpha(x, t) - f_\alpha^{eq}(\rho, \mathbf{u})}{\tau} \]  

(4.1)

where \( f_\alpha \) is the particle velocity distribution function to the \( \alpha \) direction, \( e_\alpha \) is the discrete velocity vector, \( \mathbf{u} \) is the fluid velocity vector, \( \delta t \) is the time increment, \( \rho \) is the fluid density, \( \tau \) and \( \tau \) is the relaxation time related to the kinematic viscosity by \( \nu = (\tau - 0.5)RT\delta t \). The equilibrium distribution function is

\[ f_\alpha^{eq}(\rho, \mathbf{u}) = \omega_\alpha \rho \left( 1 + \frac{e_\alpha \cdot \mathbf{u}}{RT} + \frac{(e_\alpha \cdot \mathbf{u})^2}{2(\rho T)^2} - \frac{\mathbf{u}^2}{2\rho T} \right) \]  

(4.2)

where \( R \) is the gas constant, \( T \) is the temperature, \( \omega_\alpha \) is the weight coefficient associated to the direction \( \alpha \). In a D2Q9 lattice (Figure 4.4a), the discrete velocity \( e_\alpha \) is given as

\[ e_\alpha = \begin{cases} 0 & \alpha = 0, \\ \left( \cos \frac{(\alpha - 1)\pi}{2}, \sin \frac{(\alpha - 1)\pi}{2} \right) & \alpha = 1 - 4, \\ \sqrt{2} \left( \cos \left[ \frac{(\alpha - 5)\pi}{2} + \frac{\pi}{4} \right], \sin \left[ \frac{(\alpha - 5)\pi}{2} + \frac{\pi}{4} \right] \right) & \alpha = 5 - 8, \end{cases} \]  

(4.3)

with the corresponding weight coefficients of \( \omega_0 = 4/9, \omega_{1-4} = 1/9, \) and \( \omega_{5-8} = 1/36. \) The Chapman-Enskog expansion proves that Equation 4.1 recovers the Navier-Stokes equation (Chen et al., 1992; Qian et al., 1992)

\[ \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} = -\nabla p + \nu \Delta \mathbf{u} \]  

(4.4)

where \( \nabla p \) is pressure gradient. Once the LBM flow fields converge to steady-state, the flow fields were imported into the reactive transport code, CrunchTope (Steefel et al., 2005) solves the macroscopic advection dispersion equation with chemical reactions.
\[
\frac{\partial (\phi c)}{\partial t} + (u \phi \cdot \nabla) c = \nabla \cdot D \nabla c + R_t
\]  \hspace{1cm} (4.5)

where \( \phi \) is porosity, \( c \) is concentration, \( D \) is the dispersion-diffusion tensor, and \( R_t \) is the total reaction source term of homogeneous \( (R_{hm}) \) and heterogeneous \( (R_{ht}) \) reactions \( (R_t = R_{hm} + R_{ht}) \).

One intersection of the laser ablated pore network consisting of a horizontal and a vertical channel was numerically reconstructed in 2D Cartesian domain (Figure 4.4b). The 2D domain was discretized to 200 × 200 grid cells with a 1 \( \mu \)m resolution and the width of each channel is 40 \( \mu \)m. Mineral dissolution reactions and transport of reactive solutes were coupled through the operator splitting approach. Time steps of reactive transport were constrained to 0.5 of the Courant-Friedrich-Levy criterion. Anorthite was considered as a dissolving mineral with the reaction stoichiometry (Equation 4.6) and the dissolution rate following linear Transition State Theory (Equation 4.7).

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + 8\text{H}^+ \rightarrow \text{Ca}^{2+} + 2\text{Al}^{3+} + 2\text{SiO}_2(\text{aq}) + 4\text{H}_2\text{O}
\]  \hspace{1cm} (4.6)

\[
R_{ht} = \frac{k A_b}{1000 \phi} \left( 1 - \frac{\text{IAP}}{K_{eq}} \right)
\]  \hspace{1cm} (4.7)

where \( k \) is the intrinsic rate constant (mol m\(^{-2}\) s\(^{-1}\)), \( A_b \) (m\(^{-1}\)) is the mineral surface area, \( \phi \) is porosity, and \( \text{IAP}/K_{eq} \) is the saturation state of the fluid with respect to anorthite. The heterogeneous reaction occurring at the mineral-fluid interface was converted to pseudo-homogeneous reaction by assigning \( A_b = \Delta s/\Delta V (= \Delta x^{-1}) \) at the discretized fluid cells that are in contact with the solid cell (Patel et al., 2014). Injecting solution concentrations of \( \text{Ca}^{2+}, \text{Al}^{3+}, \) and \( \text{SiO}_2(\text{aq}) \) were set to zero and pH was fixed at 3.05 to mimic the experimental condition, and Cl\(^-\) was included in the model for charge balancing purposes.
4.3 Results and Discussion

4.3.1 TEM result

Laser ablated microdevices would not properly represent the original reactivity of natural minerals if laser ablation induces any changes in physical or chemical properties of minerals. In this regard, using a short pulse laser, which is known to induce less damage, is favored over long pulse or continuous wave lasers (Gamaly et al., 2002; Sudrie et al., 2002; Sugioka and Cheng, 2014). Irradiation of a continuous wave laser, such as CO$_2$ laser, heats the reacting material at a focal point that initiates the thermal decomposition and volatilizes the material surface (Snakenborg et al., 2004; Mendez et al., 2006). The surrounding zone of the focal point also gets melted due to the thermal diffusion but the temperature is not high enough for volatilization. This molten zone (i.e. heat affected zone; HAF) is re-solidified after the removal of laser irradiation yielding an amorphous material (Chung et al., 2005; Dahotre and Harimkar, 2008). ESEM images of the microchannels fabricated with CO$_2$ laser show significant thermal damage distorting and amorphizing the channel surface (Figure 4.5a and b). Unlike a continuous wave laser, an ultra-short laser (e.g. femtosecond laser) eliminates the thermal diffusion as the efficient energy transfer from a laser pulse to the material occurs within hundreds of femtoseconds while the time scale of thermalization is 1~100 picoseconds (Sugioka and Cheng, 2014; Phillips et al., 2015). This ultrafast laser processing suppresses the development of HAF and results in improvement of the laser ablated channel morphology (Figure 4.5c and d).

Despite the apparent improvement, TEM analysis reveals the development of an ~ 500 nm thick amorphous layer underneath the laser ablated microfluidics channels of both minerals (Figure 4.6). Amorphous materials tend to exhibit higher reaction rates than the crystalline phase due to the lower bonding strength (Oelkers and Gislason, 2001; Gislason and Oelkers, 2003;
Clow and Mast, 2010). In addition, the preexistence of amorphous layer complicates investigating the behavior of mineral dissolution reactions with a solid sample as the incongruent dissolution of silicate minerals accompanies the development of the amorphous layer (Hellmann et al., 2012; Daval et al., 2013; Yang et al., 2014; Maher et al., 2016). Therefore, the laser induced amorphous layer should be removed prior to microfluidic experiments. Different laser parameters including lower laser powers and longer pulse intervals were tested to prevent the accumulation of heat energy but they didn’t reduce the thickness of the observed amorphous layer. Therefore, a chemical etching technique using HF was chosen to remove the amorphous layer.

The etchant of 0.05 % HF buffered by 2 % NH₄F was used for chemical etching of laser ablated wafers. Putting a mask prior to HF etching was not necessary since the main pattern was already prepared and low HF concentration prevents uncontrollably fast oxidation reaction (Saito et al., 2009). TEM images show successful removal of amorphous layers after 1 and 2 hours of HF etching for anorthite and albite, respectively (Figure 4.7). Longer reaction time required for albite than anorthite is likely due to the stronger bonding strength in the albite. EDS maps of each mineral (Figure 4.8 and 4.9) also illustrates that the chemistry of mineral surfaces after HF treatment is not different from the deeper part of the mineral that is not affected by laser irradiation.

4.3.2 Microfluidic experiments

Anorthite mineral dissolution reaction consumes H⁺ and produces Ca²⁺ (Equation 4.6) thus pH and Ca²⁺ concentration of outflow are expected to be higher than the injected fluid with pH = 3.05 and Ca²⁺ = 0. However, outflows are not showing the increased pH for the duration of the dissolution experiment (Figure 4.10). Ca²⁺ concentration of the sample collected at the last
stage of the experiment was estimated only as 6 ppb. This measured Ca\(^{2+}\) concentration is higher than the injected solution, where Ca\(^{2+}\) was not detectable with IC. These results indicate that the fabricated microdevice is reactive, but the fluid residence time under the experimental conditions is too low to effectively capture the dissolution reaction within the microdevice using the outflow concentrations. The albite microdevice was not tested but it is expected to be less reactive than anorthite (Lüttge et al., 1999; Gudbrandsson et al., 2014; Zhu et al., 2016). Increasing the size of the microfluidic pore network which increases fluid residence time is likely to help measuring the changes in reaction product concentrations of outflow.

Although the results are not decisive, they provide information worthy to consider. Given the volume of the pore network (~ 1.9 mm\(^3\)) and fluid injection rate (1 µl/min), the mean fluid residence time is ~ 1.9 minutes. If the dissolution rate of anorthite follows linear transition state theory with a surface area \((A_b)\) ~ 54 mm\(^2\) and dissolve congruently ignoring the effect of saturation state (Equation 4.7), the effective rate constant resulting in Ca\(^{2+}\) = 6 ppb is \(4.62 \times 10^{-11}\) mol m\(^{-2}\) s\(^{-1}\) (log \(k_{eff} = -10.3354\)). This estimated value is within the range of rate constants measured from other studies (Palandri and Kharaka, 2004; Brantley et al., 2008). However, the intrinsic rate constant, \(k\), can be higher than the estimated effective rate constant, \(k_{eff}\), if heterogeneous fluid field creates transport-limited rate condition (Dentz et al., 2011b; Dentz et al., 2011a; Ding et al., 2017). In a perfectly symmetric system, fluid cannot flow across a vertical channel because the equivalent force acts on both side of a vertical channel to the opposite directions. Therefore, immobile zones develop in the middle of vertical channels where solute transport occurs only via diffusion (i.e. transport-limited).

However, achieving a perfectly symmetric pore geometry is not plausible because of the heterogeneous nature of geologic material. Therefore, the laser ablated pattern is not perfectly
symmetric due to the roughness created by the laser and flow along the channels perpendicular to flow occurs in the microfluidic experiment (Figure 4.11). Fluid flows fast horizontally from right to left along the direction of the applied pressure gradient in the supplemental movie (Movie B1). The estimated flow velocities with the trajectory of the beads are 3.65 mm s\(^{-1}\), \(\sim 4.53\) mm s\(^{-1}\), and 2.19 mm/s at the right- and left- side of the intersection, respectively (Figure 4.11). The reduction in flow velocity in the left side of the horizontal channel occurs as the fluid diverges to the vertical channel at the intersection. Fluid velocities are estimated as 0.49-0.66 mm/s and 0.34 mm/s at the top and bottom of the vertical channel, respectively. The vertical flow is \(< \sim 1\) order of magnitude than the horizontal flow velocities but advection carries solutes across the perpendicular channel without developing immobile zones. Although immobile zones developed at some other perpendicular channels (Movie B2), the development of vertical flow suggests that the reduction of effective rate from intrinsic constant is likely not significant.

### 4.3.3 Numerical simulations

The difference in fluid flow conditions between perfectly symmetric and not symmetric channels on elemental flux was evaluated through numerical simulations. Here, the effective rate constant is assumed to be equal to the intrinsic rate constant, \(k\). Flow field from the experiment (Figure 4.11) was reproduced by assigning the flux boundary on the top and bottom boundary and pressure boundary on the left and right side of the simulation domain. For a symmetric case, the pressure gradient was adjusted to match the total flux of the experimental domain.

Figure 4.12 and Figure 4.13 show the distribution of fluid velocity within the channel intersection and corresponding Ca\(^{2+}\) concentration of both symmetric and experimental field, respectively. In a symmetric domain (Figure 4.12a), flow field develops primarily along the direction of the main pressure gradient. Vertical flow also develops only near the intersection
and does not flow across the perpendicular channel. Fluid in the vertical channel is immobile, therefore, the initial solution with high Ca\textsuperscript{2+} concentration remains in the vertical channel after 0.5 seconds (Figure 4.13a) while the initial fluid was already flushed out from the experimental domain (Figure 4.13b). This low vertical flux in the symmetric domain contributes to low elemental flux. After 20 seconds of simulation, total Ca\textsuperscript{2+} flux out of the symmetric domain is $1.07 \times 10^{-21}$ mol s\textsuperscript{-1} (Figure 4.13c) which is slightly lower than the flux from the experimental domain ($1.22 \times 10^{-21}$ mol s\textsuperscript{-1}, Figure 4.13d).

### 4.4 Implications

Upscaled behavior of mineral dissolution reactions can be inferred from the simulation results. In a larger domain, fluid collects more reaction products with increased fluid residence time leading to high saturation state and reduces dissolution rate (Li et al., 2006; Navarre-Sitchler and Brantley, 2007). However, the degree of saturation state is likely to be different because of the difference in mass transfer rate. Ca\textsuperscript{2+} flux transported to downstream would be lower for the symmetric domain than the experiment domain due to the development of immobile zones in vertical channels. Therefore, for a symmetric system, effective dissolution rate would be lower and the length required for the fluid to reach equilibrium would be longer than an asymmetric system (Maher, 2010).

In this study, depletion of the reacting mineral is not considered given the slow dissolution reaction rate and relatively short reaction time. However, initial pore geometry will change as a result of dissolution/precipitation reactions over geologic time scale (White and Brantley, 2003; Molins et al., 2014; Pandey and Rajaram, 2016; White et al., 2017). Mineral dissolution occurs predominantly along the fluid-mineral interface of the horizontal channel in the symmetric domain while all mineral interfaces dissolve in the experiment domain. Another
factor that needs to be considered is the change in flow velocity along with the change in pore size induced by dissolution reaction (Noiriel et al., 2004; Song et al., 2014). If the pressure gradient is maintained, increased channel width due to the mineral dissolved away will decrease the flow velocity and increase the fluid residence time and saturation state. However, drastic change in saturation state is not plausible considering the small scale of interest (~ μm). Therefore, the mineral is expected to be depleted faster in asymmetric pore networks.

### 4.5 Conclusions

Reactive microdevice using two silicate minerals, anorthite and albite, are fabricated through a combined method of femtosecond laser ablation and chemical etching. A femtosecond laser minimizes laser induced damage (Figure 4.5) but it still creates a thin amorphous layer (Figure 4.6). The amorphous layer was successfully removed by HF etching without altering the chemistry of both mineral (Figure 4.7 ~ 4.9). The microfluidic experiment with an anorthite mineral shows effective mineral dissolution rate constant of $4.62 \times 10^{-11}$ mol m$^{-2}$ s$^{-1}$ ($\log k_{\text{eff}} = -10.3354$) assuming well-mixed and far-from-equilibrium conditions. The effective rate constant might have reduced from the intrinsic rate constant due to the possible development of immobile zones in vertical channels. However, the flow field visualized with fluorescent beads shows the flow crossing the vertical channel without developing immobile zones (Figure 4.11). The vertical flow develops because of the imperfect symmetry (i.e. roughness) of the fabricated microdevice even though it was designed to be symmetric. As a result, the channel intersections having the vertical flow transport more solute by transferring Ca$^{2+}$ dissolving out from the mineral-fluid interface in the vertical channel ($1.22 \times 10^{-21}$ mol s$^{-1}$, Figure 4.13d) while the perfectly symmetric condition isolates the reactive mineral surface in vertical channels from dissolution reactions ($1.07 \times 10^{-21}$ mol s$^{-1}$, Figure 4.13c). Therefore, the effective rate constant from a
symmetric system will deviate more from the intrinsic constant than an asymmetric system. This reactive microfluidics approach can be applied to reveal coupled physical-chemical behavior in porous media. In addition, it can constrain numerical simulations to better represent the natural system and to improve predictability over long time scale.
Figure 4.1. (a) A picture and (b) a schematic diagram of the anorthite microdevice.

Figure 4.2. Cross-section of a laser ablated channel of (a) anorthite and (b) albite mineral.
Figure 4.3. Experimental setup for chemical weathering with the injection of acidified DI water to pH of 3.05 and the mean flow rate of 1 μm min\(^{-1}\). The flow was visualized with the injected fluorescent beads and recorded with the fluorescence microscope.

Figure 4.4. (a) A lattice grid with D2Q9 model for a lattice Boltzmann method with (b) the simulation domain of a channel intersection.
Figure 4.5. ESEM images of laser ablated silicate minerals, (a and c) anorthite and (b and d) albite. Heat affected zone appears in (a and b) CO₂ laser ablated minerals while they don’t show up in (c and d) femtosecond laser cuts.
Figure 4.6. TEM images for (a) anorthite and (b) albite minerals after femtosecond laser ablation. The amorphous layer develops at the top of the TEM foil (i.e. bottom of the laser ablated flow channel) with the thickness of ~ 500 nm for both mineral.

Figure 4.7. TEM images for (a) anorthite and (b) albite minerals after 1 and 2 hours of HF etching, respectively. The laser-induced amorphous layer in Figure 4.6 is no longer observed.
Figure 4.8. The map of energy dispersive spectra (EDS) of the anorthite TEM foil in Figure 4.7a.
Figure 4.9. The map of energy dispersive spectra (EDS) of the anorthite TEM foil in Figure 4.7b.
Figure 4.10. The pH of each sample collected over time. pH of injecting solution (pH = 3.05) is plotted as a red line.
Figure 4.11. Flow field in an intersection of a horizontal and a vertical channel visualized with the injection of fluorescent beads. Flow velocities are estimated by dividing the length of the beads’ trajectory with the exposure time (0.02 s). Fast flow (~ 4.53 mm s\(^{-1}\)) develops along the main pressure gradient (from right to left) and reduced to ~ 2.19 mm s\(^{-1}\) after the divergence to the vertical channel where the velocities are ~ 1 order of magnitude slower than the horizontal flow.

Figure 4.12. Flow fields simulated with lattice Boltzmann method in (a) the ideal symmetric domain and (b) the experiment domain reproducing the velocity field of Figure 4.11. Pressure gradient applied for the symmetric domain was adjusted to match the total flux out from the experiment domain.
Figure 4.13. Ca\(^{2+}\) concentration (mol kg\(^{-1}\)) fields of (a and b) the symmetric domain and (c and d) the experiment domain. (a) The initial fluid with high Ca\(^{2+}\) concentration remains in the vertical channel of the symmetric domain while (c) it was flushed out in the experiment domain after 0.5 seconds. (b) The initial fluid is flushed out by diffusion after 20 seconds in the initial domain and shows similar concentration field with (d) the experiment domain.
CHAPTER 5

CONCLUSIONS

This study presents the effects of physical heterogeneity on mineral dissolution rates from the pore scale to the continuum scale over geologic time. Continuum scale heterogeneities were investigated with random permeability fields created through a sequential Gaussian simulation algorithm. Simulation time scale was varied from 3 years to 3,000 years and the evolution of mineral dissolution rates and mineral surface area were investigated. For an experimental observation of pore scale mineral dissolution, reactive microdevices using anorthite and albite were created through the combination of laser ablation and a chemical etching.

Physical heterogeneity contributes reducing the effective mineral dissolution rates by developing non-reactive zones that are spatially corresponding to immobile zones where the mass transfer is controlled mainly by diffusion. The degree of reduction depends on the size of the correlation structures (i.e. integral scales), which contributes to the length scale of diffusive transport, and the variance in permeability distribution, which controls the intensify of diffusive transport. As the size of the correlation increases, diffusive length scale increases and leads to increased fluid residence time and reduction of mineral dissolution rates. Large variance in permeability distribution contributes to reduce local flow velocities that intensifies the relative importance of diffusion over advection. Therefore, large variance and large correlation structures contribute reducing mineral dissolution rates. The degree of reduction can be intensified in a large domain given the large size and multimodality of geologic porous media.

However, the development of non-reactive zones resulting in reduced mineral dissolution rate in early time preserves reactive mineral phases for long-term mineral dissolution reactions.
In general, mass-balance based (i.e. before the surface area normalization) effective mineral dissolution rates show decreasing trends with time along with the depletion of the dissolving mineral. In the case with the preservation of mineral, however, the preserved mineral provides reaction products to the domain outflow thus contribute higher non-normalized effective mineral dissolution rates than the cases where the mineral is depleted throughout the domain (i.e. reversal in orders). This reversal does not occur when the effect of mineral surface area is completely removed by local surface area normalization and shows increasing trends with time instead. However, local surface area normalization is impossible in large field scale studies. Using domain-averaged surface area to normalize the measured reaction product concentration shows similar temporal trends with the local normalization result for a domain without the development of non-reactive zones. However, the preserved minerals in a domain with the non-reactive zones result in over-normalization and artificial reduction in mineral dissolution rate.

Microdevices using silicate minerals, anorthite and albite, were fabricated through a combined use of a femtosecond laser and HF etching. The femtosecond laser ablation minimizes the laser damaged surfaces and HF etching removes the laser-induced amorphous layer with the thickness of ~ 500 nm. The reactive flow experiment conducted with an anorthite microdevice showed the development of vertical flows as a result of rough pattern (i.e. imperfect symmetry) created by heterogeneous nature of geologic materials. Pore scale reactive transport simulations comparing idealized symmetric domain and the experimental domain show higher mass-flux in the experimental domain than the symmetric domain. This result indicates the reactive microdevices can be used to constrain numerical conditions for better representation of natural systems.
Overall, the results suggest that physical heterogeneity of natural porous media could reconcile some of the large discrepancy between laboratory- and field- measured mineral dissolution rates, especially for long-time scales in highly heterogeneous systems.
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Figure A1. The standard deviation of $R_{\text{eff}}$ with the number of realizations. The change in standard deviation of all simulation conditions converges after 40 realizations.
Figure A2. Distribution plot of local Darcy flow rate normalized by the length of the domain \((u, \text{yr}^{-1})\) with random permeability distribution with (a) \(\sigma_{ln,K}^2 = 25\). The color scale represents the number of cells with a given \(\log u\) normalized by the number of cells with the most abundant \(\log u\), in other words the color scale is the histogram of the data with the data in each bin normalized to the count in the bin with the maximum number of occurrences. Mean (white line) of each heterogeneous case is given with the mean of homogeneous case with low flow rate \((H_{\text{low}}, \text{red line})\).
Figure A3. Log-transformed local dissolution rate ($\log R_{local}$) fields developed from the domain with $\sigma_{in,K}^2 = 25$ and $Pe = 143$. Due to the short diffusion length scale in a small domain (i.e. low $Pe$), the development of non-reactive zones is less apparent and the reduction in $R_{local}$ is less compared to the large domain case (Figure 1.13).
Figure A4. Log-transformed local dissolution rate (log $R_{\text{local}}$) fields developed from the domain with $\sigma_{\text{in}K}^2 = 1$ and $Pe = 2.3 \times 10^7$. Due to the short diffusion length scale in a relatively homogeneous domain (i.e. low $\sigma_{\text{in}K}^2$), the development of non-reactive zones is less apparent and the reduction in $R_{\text{local}}$ is less compared to the large domain case (Figure 1.13).
Figure A5. One example of 50 generated realizations of permeability fields with $\sigma_{\ln K}^2 = 5$ and varying integral scales as given in Table 2.1.
Figure A6. Selected log-transformed local Darcy velocity (log $u$) fields with $\sigma^2_{ln K} = 3$ developed from the corresponding permeability field in Figure A5.
Figure A7. Log-transformed local dissolution rate ($\log R_{\text{local}}$) fields developed from the domain with (a) $\sigma_{\ln K}^2 = 1$ and $Pe = 2.3 \times 10^7$ and (b) $\sigma_{\ln K}^2 = 25$ and $Pe = 143$. 

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Figure A8. Anorthite dissolution rate fields of (a-c) Non-normalized rate ($R_{\text{local}}$) and (d-f) normalized rate ($\bar{R}_{\text{local}}$), and (g-h) corresponding ratio of remaining mineral surface area to the initial surface area ($A_b/A_{b,0}$) for one realization of AN1a at 3 different times (10, 100, and 500 years).
Figure A9. Anorthite dissolution rate fields of (a-c) Non-normalized rate ($R_{\text{local}}$) and (d-f) normalized rate ($\bar{R}_{\text{local}}$), and (g-h) corresponding ratio of remaining mineral surface area to the initial surface area ($A_b/A_{b,0}$) for one realization of AN3a at 3 different times (10, 100, and 500 years).
Figure A10. Anorthite dissolution rate fields of (a-c) Non-normalized rate ($R_{local}$) and (d-f) normalized rate ($\bar{R}_{local}$), and (g-h) corresponding ratio of remaining mineral surface area to the initial surface area ($A_b/A_{b,0}$) for one realization of CI2 at 3 different times (10, 100, and 500 years).
Figure A11. Anorthite dissolution rate fields of (a-c) Non-normalized rate ($R_{local}$) and (d-f) normalized rate ($\overline{R}_{local}$), and (g-h) corresponding ratio of remaining mineral surface area to the initial surface area ($A_b/A_{b,0}$) for one realization of CN1a at 3 different times (10, 100, and 500 years).
Figure A12. Anorthite dissolution rate fields of (a-c) Non-normalized rate ($R_{local}$) and (d-f) normalized rate ($\bar{R}_{local}$), and (g-h) corresponding ratio of remaining mineral surface area to the initial surface area ($A_b/A_{b,0}$) for one realization of CN3a at 3 different times (10, 100, and 500 years).
Figure A13. Anorthite dissolution rate fields of (a-c) Non-normalized rate ($R_{local}$) and (d-f) normalized rate ($\bar{R}_{local}$), and (g-h) corresponding ratio of remaining mineral surface area to the initial surface area ($A_b/A_{b,0}$) for one realization of DN1a at 3 different times (10, 100, and 500 years).
Figure A14. Anorthite dissolution rate fields of (a-c) Non-normalized rate ($R_{local}$) and (d-f) normalized rate ($\bar{R}_{local}$), and (g-h) corresponding ratio of remaining mineral surface area to the initial surface area ($\frac{A_b}{A_{b,0}}$) for one realization of DN3a at 3 different times (10, 100, and 500 years).
Appendix B
Supplementary Movies

Movie B1. https://drive.google.com/open?id=0B1v1FXxZGTgQV1FEZGNSR255Ym8

Movie B2. https://drive.google.com/open?id=0B1v1FXxZGTgQOUNVcm9BZzFzNkk