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Complex Coupling of Fluid Transport and Geochemical Reaction Rates: Insights from Reactive Transport Models

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Abstract

Geologic heterogeneity can cause spatially variable fluid and solute transport, leading to important implications for geochemical processes. The impact of heterogeneity on spatially variable and averaged, effective geochemical reaction rates is not yet fully described. Two examples of using reactive transport models as a tool to explore the complex connections between fluid transport and geochemical reaction rates are presented. In one case, changes in heterogeneity structure lead to variations in spatial distribution of anorthite dissolution rate in a meter-scale simulation. In areas where fluid flow is fast, reaction products are removed and anorthite dissolution proceeds at far from equilibrium rates. In contrast, in parts of the domain where fluid flow is slow, concentrations of reaction products increase and the fluid approaches chemical equilibrium with respect to anorthite and the dissolution rate slows. The heterogeneity structure and spatial distribution of reaction rates leads to differences in calculated effective reaction rates over the entire domain. In a second case, simulation of biologic reduction of nitrogen at floodplain scale, physical heterogeneity leads to spatial distribution of reaction rates that are up to 5 orders of magnitude lower than the far from equilibrium rate. It is clear from these simulations that heterogeneity in physical structure can impart spatially variable distributions of geochemical reaction rates. More work is still needed to understand how this variation translates to domain averaged reaction rates and whether physical heterogeneity contributes to some of the long-observed differences between laboratory measured and field calculated geochemical reaction rates.

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1. Introduction

Geochemical reactions play an important role in regulating atmospheric CO_2 concentrations over geologic time

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sequestering CO_2 in mineral form, and releaseing rock-bound nutrients into soils for biologic uptake nd to rivers for transport to the oceans. Geochemical models used to describe and investigate these complex, time-dependent systems require kinetic rate data to quantify mineral reactions and their products through time. Mineral reaction rates used in reactive transport simulations are often based on laboratory mineral dissolution experiments performed in well-mixed batch reactors or homogeneous columns. The reproducibility of these laboratory measured reactions rates is high when rates are normalized to a measure of mineral surface area[3,10]; but there persists a difference between laboratory measured rates and apparent rates calculated in field systems that hampers our ability to apply the many carefully measured laboratory rates to larger scale geologic systems.

Geologic systems are highly heterogeneous and rarely approximate the well-mixed conditions in laboratory experiments. Evidence for the importance of heterogeneity in fluid transport on apparent mineral reaction rates can be found in solute transport and runoff relationships in watersheds[4]. Numerical simulations at catchment[6] and pore scale[7] also point to an important coupling of fluid transport and mixing and geochemical reaction rates. Where fluids are not well mixed and fluid velocities cannot remove reaction products at a rate fast enough to keep up with reaction, apparent rates of mineral reaction are lower than rates measured in laboratory conditions. The connection between rates of geochemical reactions and rates of solute or fluid transport, while long recognized as an important facet of understanding Earth systems[2,7], is not yet clearly delineated. Reactive transport models can help bridge the gap between laboratory derived and field calculated weathering rates and their use has elucidated mechanisms and processes responsible for the apparent lab-field discripency[5,8,9]. Two examples of exploration of the impact of physical heterogeneity on geochemical processes are summarized below.

2. Examples

2.1. Mineral Dissolution

We evaluated the impact of heterogeneous fluid flow on anorthite dissolution with reactive transport simulations performed using the software package CrunchFlow. Three permeability fields were generated with geostatistical distribution of permeability in domain 1m x 1m with 50 x 50 grid cells (each grid cell was 0.02 m x 0.02 m). Each of the three fields had the same geometric mean permeability. In the homogeneous case each grid cell was assigned the mean permeability of 10^{-15} m^2. Two heterogeneous cases were generated with random Gaussian distribution with geometric variances of 10^1 (Figure 1). In the isotropic case correlation lengths in x and y were equal to 1 grid cell (0.02m). In the anisotropic case correlation length in the x direction was 10 grid cells (0.2 m) and in the y direction 5 grid cells (0.1 m). Flow was induced in the x-direction across the domain with average velocity in the homogeneous case of 1.577 m yr^{-1}. Preferential flow paths developed in the heterogeneous domains with more preferential flow in the anisotropic domain compared to the isotropic domain (Figure 1).

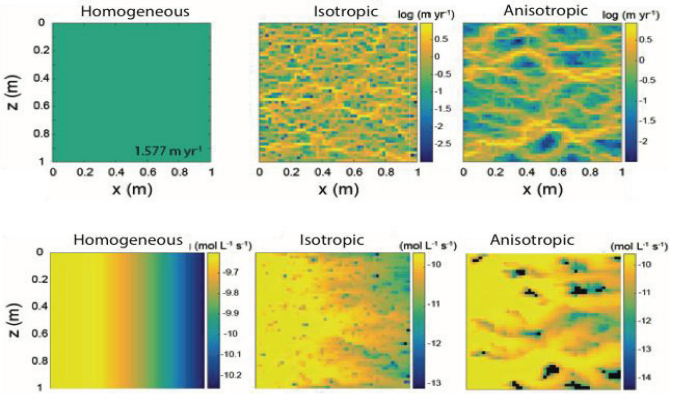

Figure 1. Velocity fields (upper row) and spatially distributed anorthite dissolution rates (lower row) for homogeneous and heterogeneous domains in a reactive transport modeling experiment designed to evaluate the impact of heterogeneity on mineral

The development of preferential flow paths created heterogeneity in saturation sate of the dissolving anorthite (10% by volume in the initial domain with non-reactive quartz comprising the remainder of the solid phase) and induced regions of fast dissolution and slow dissolution that correlate with regions of fast flow and slow flow,