

Reactive transport in discrete fracture networks

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Introduction

The important role of fractures in governing the flow of fluid and the transport of chemical constituents in soils, sediments, and crystalline rocks is increasingly recognized, particularly in near-surface and subsurface environments where fractures account for the bulk of the flow capacity. In Earth systems, fractures are the key that govern the safety and/or the efficiency of energy recovery and storage in the subsurface such as hydrothermal systems, CO₂ sequestration, geothermal exploration, and energy storage (Steefel and Lasaga, 1994; Hu and Rutqvist, 2020, 2021). Fractures also play a crucial role in processes in shallow groundwater systems where their control on transport rates can influence drinking water quality. In this study, we consider the mitigation of atmospheric CO₂ via carbonate mineral sequestration using two-dimensional numerical modeling of reactive flow and transport of a natural intersecting fracture network to investigate the rates and patterns of mineral precipitation in the Earth's critical zone.

Approach

The reactive transport behavior of intersecting fracture networks was investigated in 2D with the software CrunchFlow (Steefel et al., 2015). CrunchFlow (or CrunchTope) is a general purpose multicomponent reactive transport simulator that handles advective, diffusive, and dispersive transport, and an arbitrary number of mixed equilibrium and kinetic reactions. The capability to simulate partially saturated flow based on a predictor-corrector treatment of the Richards equation (Li et al., 2021) has been added recently to the code.

Using a photograph of fractured granite (Figure 1A), we added an additional fracture to increase the interest of the simulation.

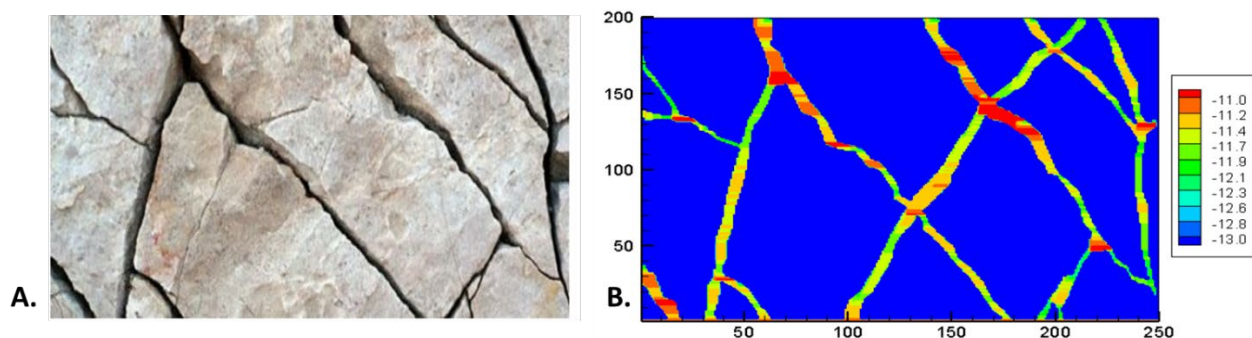
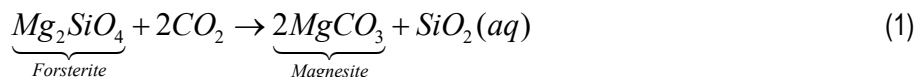


Figure 1. A. Photograph showing intersecting fractures in granite (top). B. Initial log permeability distribution based on a scaled version of the cubic law.

We consider a domain measuring 250 by 200 cm with a 1 cm constant grid spacing in the X and Y direction. In these simulations, we use the cubic law (Witherspoon et al., 1980) to describe the permeability (Figure 1B).

An interest has developed in recent years in simple geochemical and mineralogical systems that could serve as proxies for the mafic and ultramafic rocks. A good example is that of forsterite (Mg-olivine), which reacts with CO₂ to form magnesite (Wang and Giammar, 2013; Xiong and Giammar, 2014; Steefel and Yang, 2021). In the partially saturated (or vadose) zone within the shallow portions of the Earth's critical zone, infiltration of rainwater and snow melt combines with gas diffusion to drive acid-promoted and oxidative reactions that dissolve the primary mafic and ultramafic rock. The overall reaction is thus



mediated by the presence of an aqueous phase. We use the software CrunchFlow (Steeffel et al., 2015) to solve the multicomponent reactive transport equations numerically. For mineral dissolution and precipitation, a TST-type rate law is used to describe both magnesite and forsterite according to $R_m = -A_m k_m \left[1 - Q/K_{eq}\right]$ where A_m is the reactive surface area, k_m is the rate constant, Q is the ion activity product, and K_{eq} is the equilibrium constant. The porosity ϕ is updated according to the evolving mineral volume fractions ϕ_m as a result of reaction according to $\phi = 1 - \sum \phi_m$.

Table 1. Geochemical boundary and initial conditions for the critical zone simulations.

	Top Boundary	Initial Condition
pH	6.78	7.5
pCO ₂ (bars)	0.02	00003
Mg ⁺⁺	0.001	0.0005
Na ⁺	0.001	0.1
Cl ⁻	0.001	0.1
Forsterite Saturation	-11.962	-11.150
Magnesite Saturation	-1.359	-2.282

Rate constants) for both forsterite and magnesite are set to 10^{-8} mol m⁻² s⁻¹ and reactive surface areas are assumed equal to 100 m² m⁻³ for both minerals. The land surface and infiltration are along the top boundary and the system drains downward in the Z direction as a result of gravity.

Results

The land surface and infiltration are along the top boundary and the system drains downward in the Z direction as a result of gravity. Results of the simulations with infiltration rates ranging from 315 cm/yr to 3.15 cm/yr are shown in Figure 2. Only with a relatively high infiltration rate of 315 cm/yr does the domain remain mostly saturated—the others develop a water table at about 1 meter above the lower boundary. The very minor change in magnesite rates over 3 orders of magnitude change in infiltration indicates that forsterite dissolution and magnesite precipitation are largely diffusion-controlled. Only at the highest infiltration rate of 315 cm/yr is magnesite precipitation suppressed, and this is evidently due to the increase in liquid saturation that limits CO₂ gas diffusion.

The rates for precipitation of metal carbonates sequestering atmospheric CO₂ are relatively low based on the simulations here. This is due to the limited reactive surface area available for dissolution of primary minerals, but also to the limitation of transport of reactive CO₂ in partially saturated fracture network. To the highly local and selective dissolution and precipitation occurring in the fractures, we add the effect of drainage within the fracture network that contributes to a heterogeneous liquid saturation distribution, and thus variable gas diffusion rates. It is noteworthy that in the partially saturated fractured CZ, the system is largely diffusion-controlled as the precipitation of carbonate phases depends on the ability of reactive gases to diffuse through the fracture network system.

Conclusions

We considered the problem of natural weathering of fractured mafic and ultramafic rocks and how this could contribute to mitigation of atmospheric CO₂. It is apparent that the strong heterogeneity associated with intersecting fracture networks raises the possibility of substantial reorganization of the near surface and subsurface fracture flow system in the Earth's critical zone where mineral precipitation can clog the fractures. However, the rates for precipitation of metal carbonates sequestering atmospheric CO₂ are relatively low based on the simulations presented here. This is due to the limited reactive surface area available for dissolution of primary minerals, but also to the limitation of transport of reactive CO₂ in partially saturated fracture network. To the highly local and selective dissolution and precipitation occurring in the fractures, we add the effect of drainage within the fracture network that contributes to a heterogeneous liquid saturation distribution, and thus variable gas diffusion rates. It is noteworthy that in the partially saturated fractured CZ, the system is largely diffusion-controlled as the precipitation of carbonate phases depends on the ability of reactive gases to diffuse through the fracture network system.

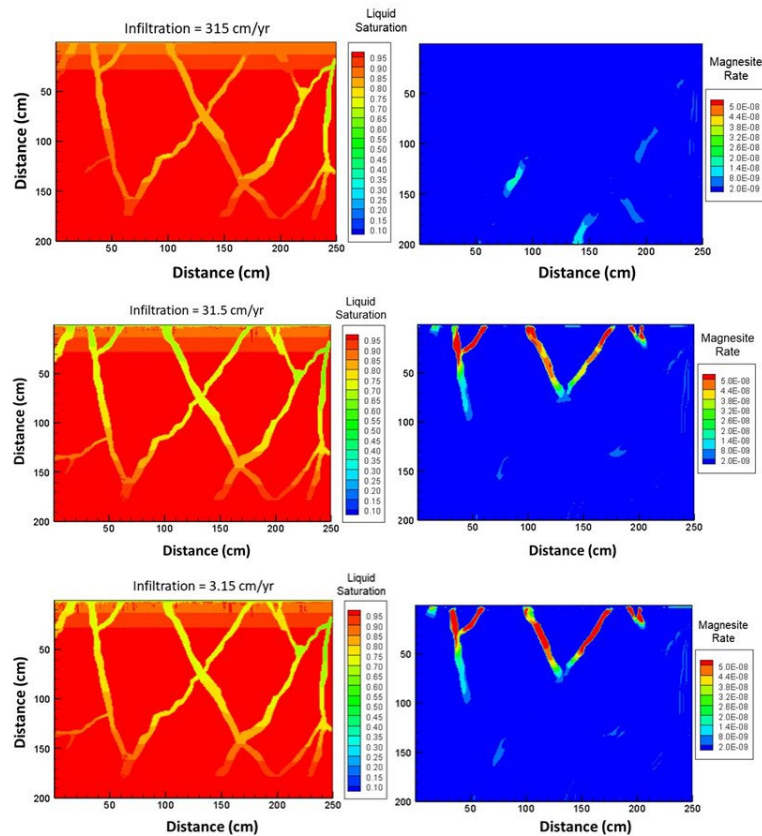


Figure 2. Liquid saturations and magnesite precipitation rates for infiltration rates ranging from 3.15 to 315 cm/year.

Acknowledgments

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