

# Supporting Information for “Length and time scales for precipitation during carbon mineralization”

M.A. Chen<sup>1</sup>, W. Yang<sup>1</sup>, H. Peng<sup>1</sup>, P.K. Kang<sup>1,2</sup>, and V.R. Voller<sup>3,2</sup>

<sup>1</sup>Department of Earth and Environmental Sciences, University of Minnesota, Minneapolis, MN, 55455, USA

<sup>2</sup>St. Anthony Falls Laboratory, University of Minnesota, Minneapolis, MN 55455, USA

<sup>3</sup>Department of Civil, Environmental, and Geo- Engineering, University of Minnesota, Minneapolis, MN, 55455

## 1. Introduction

We provide additional discussion of the theoretical choices made for the mineral carbonation scaling model, as well as discussion of various parameter values. All data is sourced from the relevant references as indicated throughout the text.

### 1.1. Derivation of First-Order Reaction Rate Law

There are a few notable cases where a precipitation reaction with two species can result in first-order reaction kinetics with respect to a single concentration. We develop these two cases here to indicate the value of these first-order laws for the purposes of developing the scalings discussed in the main text, which could be extended if additional complexity is needed.

---

Corresponding author: V.R. Voller, Department of Civil, Environmental, and Geo-engineering, University of Minnesota, Minneapolis, MN 55455, USA. (volle001@umn.edu)

Denoting the concentration of species A and B as  $C_A$  and  $C_B$  [mol/m<sup>3</sup>], respectively, we can formally express the reaction rate [mol/m<sup>3</sup>/s] of either reactant per unit volume of the medium (both the solid and liquid phases) as

$$r = k^* S \left( 1 - \left( \frac{C_A C_B}{K_{eq}} \right)^n \right) \quad (1)$$

where  $k^*$  is a rate constant [mol/m<sup>2</sup>/s],  $n$  is the reaction order,  $S$  the solid surface area per unit volume of porous media [1/m] and  $K_{eq}$  is the equilibrium constant for the reaction (Morse et al., 2007; Lasaga, 1995, 1997). In the case of pseudo-first-order reaction as in the main text, there are two cases which we can consider. The first is if  $C_A = C_B$  and the order term,  $n = 0.5$ . In this case, eq. 1 simplifies to

$$r = \frac{k^* S}{C_{eq}} (C_{eq} - C) \quad (2)$$

where  $C = C_A = C_B$ , and  $C_{eq} = \sqrt{K_{eq}}$ .

The second case is where  $C_B(x, t) = C_{B,0} \gg C_A$  (or vice versa), such that the concentration of the abundant species is effectively constant and  $n = 1$ . Eq. (1) can alternatively be simplified to

$$r = \frac{k^* S}{C_{eq,lim}} (C_{eq,lim} - C) \quad (3)$$

where  $C_{eq,lim} = K_{eq}/C_{B,0}$ .

Both equations have the same form, but with a different definition for the  $C_{eq}$  value. To first-order, the specific surface area is given by  $S = S_i g_s \phi$ , thus we can define a first-order rate term  $k = k^* S_i / C_{eq}$  [1/s]. This gives the final rate equation used in the main text:

$$r = k g_s(\phi) (C_{eq} - C). \quad (4)$$

## 1.2. Characteristic Parameter Values for Non-Dimensionalization

Many of the parameters in the equations in the main text are either removed by the non-dimensionalization, or during the simplification of the equations by ignoring terms containing the yield  $Y$ . We consider the values of the relevant parameters here, as a reference.

The equilibrium concentration: This will depend on the main mineralization reactions occurring, which will define  $K_{eq}$ , as well as the initial concentrations of reactants, as discussed in the SI section 1.1.  $K_{eq}$  is thermodynamically defined as a function of temperature, and is well known for many minerals of interest in carbon mineralization. As an example, the equilibrium constant for calcite formation is  $10^{-8.54}$  at 35 °C, and is relatively close to that of other metal carbonates (siderite, magnesite, etc.), though determining an effective equilibrium constant may prove more difficult (Snæbjörnsdóttir et al., 2018; Gysi & Stefánsson, 2011). Uncertainty in the relative concentrations of the reactants (i.e. carbonate and cation) in field conditions, however, will create significant uncertainty in this value should the limiting reactant case apply, as  $C_{eq}$  will also become dependent on initial conditions. Considering calcite equilibria at 35 °C and equal concentrations gives a value around 0.05 mol/m<sup>3</sup>, however, calcite equilibria at 35 °C and an abundant cation concentration of 1 mol/m<sup>3</sup> will give a value of 0.003 mol/m<sup>3</sup>. The key point in exploring these values are not necessarily to derive an exact field concentration, which may vary depending on the mineral, but that the precipitation is defined relative to some equilibrium state, and quantifying a reasonable approximation of that state is necessary to constrain the other parameters, notably  $R$  and  $k$ .

The initial supersaturation: For precipitation to occur,  $R > 1$ , however, more practically, the specific value of  $R$  will depend on both  $C_{eq}$  and  $C_0$ . As is emphasized in the main text, it is worthwhile to reiterate that the initial concentration when precipitation initiates,  $C_0$ , is not necessarily the concentration at the injection well. This is because the injected waters are significantly acidic, and precipitation will be preceded by a region where the injected water dissolves the rock and liberates cations. The result is that the amount of cation and carbonate driving the reaction may be significantly smaller than the injected value, depending on the ambient water conditions. This will also be affected by mixing of the injected waters with the formation waters, which will further reduce the concentration from the injected value. The result is that the concentration when precipitation initiates (i.e.  $t = 0$  in the model) may be significantly lower than the concentration injected. Snæbjörnsdóttir et al. (2018) state that CarbFix 1, for example, had an injected  $\text{CO}_2$  of  $840 \text{ mol/m}^3$ , and the authors note significant dilution of the injected water with the formation waters. The maximum divalent cation concentration observed, in contrast, was around  $0.5 \text{ mol/m}^3$ , though these values are after some precipitation has occurred. Relative to calcite equilibria (see  $C_{eq}$  discussion above), these value ranges give  $R < 10$ , the value limit considered in the main text.

The porosity yield: This factor comprises the product of the initial concentrations of solute, as well as the molar volume of the precipitate  $Y = \nu_s C_0$ . The molar volume for minerals is strictly defined, and are typically  $O(10^{-5})$  for carbonate minerals such as calcite, siderite, magnesite, etc. (Parkhurst & Appelo, 2013). As discussed for  $R$ , the value of  $C_0$  depends on the actual concentration of the reactants when precipitation

initiates. The values considered above,  $0.5 < C_0 < 840 \text{ mol/m}^3$ , give, therefore,  $Y < 0.01$ , with the possibility of  $Y \ll 0.01$ .

The initial porosity: Here we focus on higher permeability mafic rocks (as opposed to much lower porosity olivines), similar in nature to those used in the CarbFix project, though we note that the host rock need not strictly be basalt (Snæbjörnsdóttir et al., 2020, 2018; Clark et al., 2020). In this setting a reasonable initial porosity value is  $0.1 < \phi_i < 0.3$ . In general, larger porosities will favor longer operation times, and likely larger storage capacities.

The dispersivity coefficient: This term typically scales with the domain length  $\alpha_L = \beta_L L$ . In the analysis of multiple field sites, Gelhar, Welty, and Rehfeldt (1992) noted that dimensionless longitudinal dispersivity ranged from  $10^{-2}$  to  $10^4$  m for domain scales ranging from  $10^{-1}$  to  $10^5$  m. Thus, in the absence of any specific information on a given potential reservoir, a reasonable range is to set  $0 < \beta_L < 0.1$ , with the  $\beta_L = 0$  case specifically considered as a limiting case with no dispersion.

The ratio of the precipitate to liquid density: We would expect the precipitate to be denser than the liquid, for precipitates of interest somewhere in the range  $1 < \rho_r < 3$ . As an example, for calcite and water at  $25^\circ\text{C}$ ,  $\rho_r \approx 2.71$  (Parkhurst & Appelo, 2013). Hence, it is reasonable to presume that  $\rho_r \approx O(1)$ .

## References

- Clark, D. E., Oelkers, E. H., Gunnarsson, I., Sigfússon, B., Snæbjörnsdóttir, S. Ó., Aradóttir, E. S., & Gíslason, S. R. (2020, June). CarbFix2: CO<sub>2</sub> and H<sub>2</sub>S mineralization during 3.5 years of continuous injection into basaltic rocks at more than 250 °C. *Geochimica et Cosmochimica Acta*, 279, 45–66. doi: 10.1016/j.gca.2020.03.039

- Gelhar, L. W., Welty, C., & Rehfeldt, K. R. (1992). A critical review of data on field-scale dispersion in aquifers. *Water Resources Research*, 28(7), 1955–1974. doi: 10.1029/92WR00607
- Gysi, A. P., & Stefánsson, A. (2011, September). CO<sub>2</sub>-water-basalt interaction. Numerical simulation of low temperature CO<sub>2</sub> sequestration into basalts. *Geochimica et Cosmochimica Acta*, 75(17), 4728–4751. doi: 10.1016/j.gca.2011.05.037
- Lasaga, A. C. (1995, January). Fundamental approaches in describing mineral dissolution and precipitation rates. *Reviews in Mineralogy and Geochemistry*, 31(1), 23–86.
- Lasaga, A. C. (1997). *Kinetic Theory in the Earth Sciences* (1st ed.). Princeton University Press.
- Morse, J. W., Arvidson, R. S., & Lüttge, A. (2007, February). Calcium Carbonate Formation and Dissolution. *Chemical Reviews*, 107(2), 342–381. doi: 10.1021/cr050358j
- Parkhurst, D., & Appelo, C. (2013). Description of Input and Examples for PHREEQC Version 3 — A Computer Program for Speciation , Batch-Reaction , One-Dimensional Transport , and Inverse Geochemical Calculations. In *book 6, ch. a43* (p. 497). United States Geological Survey. (Available only at <https://pubs.usgs.gov/tm/06/a43/>.)
- Snæbjörnsdóttir, S. Ó., Gislason, S. R., Galeczka, I. M., & Oelkers, E. H. (2018, January). Reaction path modelling of in-situ mineralisation of CO<sub>2</sub> at the CarbFix site at Hellisheidi, SW-Iceland. *Geochimica et Cosmochimica Acta*, 220, 348–366. doi: 10.1016/j.gca.2017.09.053
- Snæbjörnsdóttir, S. Ó., Sigfússon, B., Marieni, C., Goldberg, D., Gislason, S. R., & Oelkers, E. H. (2020, February). Carbon dioxide storage through mineral carbonation. *Na-*

*ture Reviews Earth & Environment*, 1(2), 90–102. doi: 10.1038/s43017-019-0011-8