

**Supporting information for:**

**Pore-scale controls on calcite dissolution rates from flow-through  
laboratory and numerical experiments**

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SI includes five sections, three tables, fourteen equations and two figures in eight pages

# 1 Pore scale model

## 1.1 Governing equations

The governing equations of the pore scale model are the Navier-Stokes equations for incompressible flow and the advection-diffusion-reaction equations for each component:

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} + \nabla p = \nu \Delta \mathbf{u} \quad (1)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (2)$$

$$\frac{\partial \rho c_i}{\partial t} + \nabla \cdot \rho \mathbf{u} c_i = \nabla \cdot \rho D_i \nabla c_i \quad (3)$$

$$-D_i \nabla c_i \cdot \mathbf{n} = r_i \quad (4)$$

where  $\mathbf{u}$  is the fluid velocity,  $\nabla p$  is the pressure gradient,  $c_i$  is the pore-scale total concentration of component  $i$ ,  $\rho$  is the fluid density,  $\nu$  is the kinematic viscosity,  $D_i$  is the diffusion coefficient of component  $i$  in the fluid, and  $r_i$  is the contribution of the mineral dissolution reaction rate to component  $i$  per unit of surface area, e.g.  $r_{Ca} = r_{CaCO_3(s)}$  (see Eq. 12).

## 1.2 Initial and boundary conditions

The mean inlet velocity was set to  $0.0376 \text{ cm s}^{-1}$ . A fixed pressure ( $p = 0$ ) was used at outlet end of the domain. The simulation is run until steady state is reached.

For transport, a Dirichlet boundary condition was used in the inlet end. The total component concentrations and/or constraints are given in Table 1 below. A free exit boundary condition ( $\partial c_i / \partial \mathbf{n} = 0$ ) was imposed at outlet end (normal vector:  $\mathbf{n}$ ).

	Initial		Inlet boundary	
Component	Value	Constraint/Units	Value	Constraint/Units
H+	3.609	pH	3.609	pH
H2CO3*	4.0 bar	pCO2	4.0 bar	pCO2
Ca2+	0.0	mol/kgw	0.0	mol/kgw
Na+	0.0	mol/kgw	0.01	mol/kgw
Cl-	0.0	mol/kgw	0.01	mol/kgw

**Table 1: Total concentrations and constraints for initial and boundary conditions**

## 2 Continuum scale model

### 2.1 Governing equations

The 1D advection-dispersion equation for each component is solved by the continuum scale model

$$\frac{\partial \theta \rho C_k}{\partial t} + \nabla \cdot \rho q C_k = \nabla \cdot \rho \theta D_k^* \nabla C_k + R_k \quad (5)$$

where  $C_i$  is the continuum-scale total concentration of component  $i$ ;  $\theta$  is the porosity;  $q$  is the Darcy velocity ( $q = \theta \cdot v$ ), with  $v$  being the velocity;  $D_i^*$  is the dispersion coefficient of component ( $D_i^* = \theta \tau D_i + \alpha_L |v|$ ), with  $\alpha_L$  being the longitudinal dispersivity and  $\tau$  the tortuosity coefficient; and  $R_i$  is the contribution of the mineral dissolution reaction rate to component  $i$  per unit volume porous medium, e.g.  $R_{Ca} = A_{Calcite} \cdot r_{CaCO_3(s)}$ , where  $A_{Calcite}$  is the bulk surface area of calcite [ $m^2 m^{-3}$  bulk] and  $r_{CaCO_3(s)}$  is defined in Eq. (12).

## 2.2 Initial and boundary conditions

A uniform Darcy velocity along the 1D domain was set to  $0.0376 \text{ cm s}^{-1}$ . For transport, a Dirichlet boundary condition was used in the inlet end. The total component concentrations and/or constraints are given in Table 1 below. A free exit boundary condition ( $\partial c_i / \partial \mathbf{n} = 0$ ) was imposed at outlet end (normal vector:  $\mathbf{n}$ ).

## 3 Geochemical model

### 3.1 Component definition and aqueous equilibrium

Without loss of generality, the pore-scale concentrations,  $c_i$ , are used in the equations in this section; the same definition applies to the continuum scale concentrations,  $C_i$ . Aqueous complexation reactions (Eq. 6) are assumed in equilibrium and modeled with the mass action law (Eq. 7):

$$\widehat{A}_j = \sum_{i=1}^{N_c} \xi_{ji} A_i \quad (6)$$

$$\log(\gamma_j m_j) = \sum_{i=1}^{N_c} \xi_{ji} \log(\widehat{\gamma}_i \widehat{m}_i) - \log K_j \quad (7)$$

where  $j = 1, N_x$  indicates the reaction index;  $A_i$  and  $\widehat{A}_j$  are the chemical formulas of the primary and secondary species respectively;  $m_i$  and  $\widehat{m}_j$  are the corresponding concentrations and  $\gamma_i$  and  $\widehat{\gamma}_j$  their activity coefficients;  $\xi_{ji}$  are the stoichiometric coefficients; and  $K_j$  is the equilibrium constant of this complexation reaction.

The total component concentration ( $c_i$ ) is defined as the sum of the concentration of a primary species and a set of the secondary species in equilibrium with the primary species:

$$c_i = m_i + \sum_{j=1}^{N_x} \xi_{ji} \widehat{m}_j \quad (8)$$

### 3.2 Geochemical system

<i>Primary species</i>
$H^+$
$H_2CO_3(aq)$
$Ca^{2+}$
$Na^+$
$Cl^-$

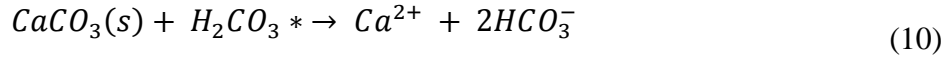
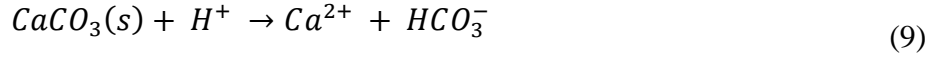
Table 2. List of primary species

<i>Aqueous reaction (secondary species <math>\rightleftharpoons</math> reactants)</i>	$\log K_{eq}$
$OH^- \rightleftharpoons -H^+ + H_2O$	13.9951
$HCO_3^- \rightleftharpoons -H^+ + H_2CO_3(aq)$	6.34143
$CO_3^{2-} \rightleftharpoons -2H^+ + H_2CO_3(aq)$	15.959
$CaCO_3(aq) \rightleftharpoons -H^+ + H_2CO_3(aq) + Ca^{2+}$	13.3502
$CaHCO_3^+ \rightleftharpoons -H^+ + H_2CO_3(aq) + Ca^{2+}$	5.29856
$CaOH^+ \rightleftharpoons -H^+ + Ca^{2+}$	12.85
$HCl(aq) \rightleftharpoons H^+ + Cl^-$	-0.69993
$CaCl^+ \rightleftharpoons Ca^{2+} + Cl^-$	0.70039
$CaCl_2(aq) \rightleftharpoons Ca^{2+} + 2Cl^-$	0.65346

Table 3. List of aqueous complexation reactions and equilibrium constants

### 3.3 Calcite reaction rate

Calcite dissolution occurs via three parallel pathways



The rate of calcite dissolution is described by the Transition State Theory (TST) as the product of a far-from-equilibrium term and an affinity (or  $\Delta G$ ) term that goes to zero at equilibrium <sup>1,2</sup>.

$$r_{CaCO_3} = (k_1 a_{H^+} + k_2 a_{H_2CO_3^*} + k_3) \left( 1 - \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_s} \right) \quad (12)$$

where  $k_1$ ,  $k_2$  and  $k_3$  are the rate constants [ $\text{mol m}^{-2} \text{ mineral s}^{-1}$ ] associated with Eq. (9), (10), (11), respectively;  $K_s$  is the equilibrium constant of the reaction; and  $a_{Ca^{2+}}$ ,  $a_{H_2CO_3^*}$ , and  $a_{CO_3^{2-}}$  are the activities of  $H^+$ ,  $H_2CO_3^*$ ,  $CO_3^{2-}$ , and  $Ca^{2+}$  [dimensionless] respectively.

The saturation index of calcite is defined as the ratio of ion activity product to the equilibrium constant or solubility product of calcite:

$$SI = \log \left( \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_s} \right) \quad (13)$$

## 4 Effluent geochemistry

The effluent concentrations from the pore scale model are averaged at the outlet end ( $S^{out}$ ) to obtain a single value that can be compared to experimentally measured concentration or the simulated continuum model value:

$$c_k^{out} = \frac{\int c_k \mathbf{u} \cdot d\mathbf{S}}{Q^{tot}} \quad (14)$$

where  $Q^{out}$  is the volumetric flow rate ( $4.9 \mu\text{L min}^{-1}$ ).

## 5 Details of transport control on rates

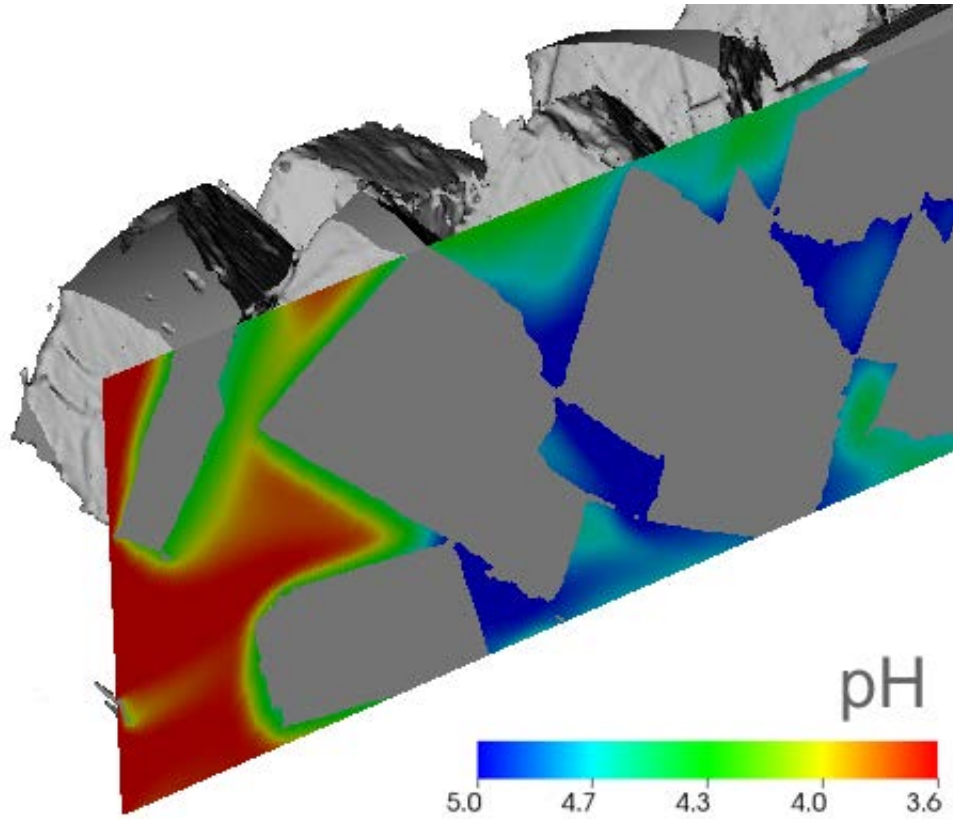


Figure A. Detail of pH boundary layer at 16 s around the mineral grains near the inlet boundary

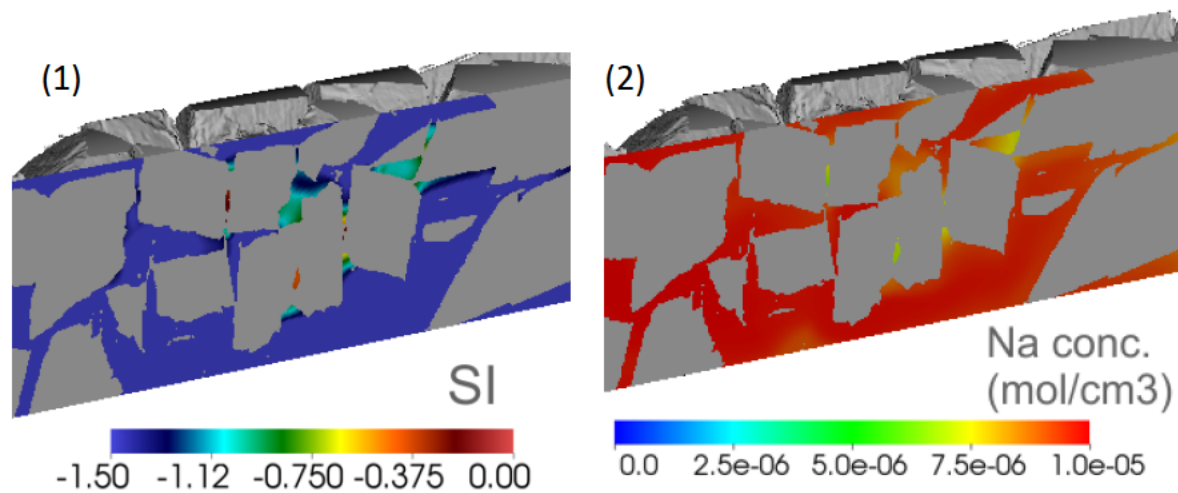


Figure B. Detail of slow-flowing pore spaces where (1) near-equilibrium conditions are observed at 16 sec and (2) slow convergence to inlet values is observed at 4.6 s for concentrations of sodium, a conservative tracer.

## References

- (1) Plummer, L.; Wigley, T.; Parkhurst, D., Kinetics of calcite dissolution in CO<sub>2</sub>-Water systems at 5°C to 60°C and 0.0 to 1.0 atm CO<sub>2</sub>, *Am. J. Sci.* **1978**, 278 (2), 179–216.
- (2) Chou, L.; Garrels, R.; Wollast, R., Comparative-study of the kinetics and mechanisms of dissolution of carbonate minerals, *Chem. Geol.* **1989**, 78 (3-4), 269–282.