Upscaling geochemical reaction rates using pore-scale network modeling

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Abstract

Geochemical reaction rate laws are often measured using crushed minerals in well-mixed laboratory systems that are designed to eliminate mass transport limitations. Such rate laws are often used directly in reactive transport models to predict the reaction and transport of chemical species in consolidated porous media found in subsurface environments. Due to the inherent heterogeneities of porous media, such use of lab-measured rate laws may introduce errors, leading to a need to develop methods for upscaling reaction rates. In this work, we present a methodology for using pore-scale network modeling to investigate scaling effects in geochemical reaction rates. The reactive transport processes are simulated at the pore scale, accounting for heterogeneities of both physical and mineral properties. Mass balance principles are then used to calculate reaction rates at the continuum scale. To examine the scaling behavior of reaction kinetics, these continuum-scale rates from the network model are compared to the rates calculated by directly using laboratory-measured reaction rate laws and ignoring pore-scale heterogeneities. In this work, this methodology is demonstrated by upscaling anorthite and kaolinite reaction rates under simulation conditions relevant to geological CO2 sequestration. Simulation results show that under conditions with CO2 present at high concentrations, pore-scale concentrations of reactive species and reaction rates vary spatially by orders of magnitude, and the scaling effect is significant. With a much smaller CO2 concentration, the scaling effect is relatively small. These results indicate that the increased acidity associated with geological sequestration can generate conditions for which proper scaling tools are yet to be developed. This work demonstrates the use of pore-scale network modeling as a valuable research tool for examining upscaling of geochemical kinetics. The pore-scale model allows the effects of pore-scale heterogeneities to be integrated into system behavior at multiple scales, thereby identifying important factors that contribute to the scaling effect.

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1. Introduction

Geochemical modeling of reactive transport of chemical species in subsurface systems has been widely applied to improve our understanding of the complex processes involved in fluid–rock interactions [1–3], and to solve environmental problems related to groundwater and subsurface contamination [4–7]. Reactive transport modeling is generally classified into forward modeling and inverse modeling [8]. Forward modeling predicts the transport and reaction of chemical species given specified geochemical reactions and reaction rate parameters. Inverse modeling utilizes measured chemical compositions to infer geochemical reactions that have occurred along flow paths. These two types of modeling approaches serve as powerful tools to understand, predict, and interpret reactive transport of chemical species in subsurface environments, and provide insights into possible regulation and management strategies.

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Because reactive transport modeling is typically applied at large scales, it necessarily ignores spatial heterogeneities at scales smaller than the size of model discretization. For mineral dissolution and precipitation, there is a mismatch between the scale at which rate data are needed (the scale of model discretization) and the scale for which rate data are available. Mineral dissolution and precipitation is typically modeled using geochemical reaction kinetics measured in laboratory systems that are very different from natural systems. In the laboratory, geochemical reaction rates are typically measured in well-mixed systems using crushed mineral suspensions [9]. These experiments are intentionally designed to homogenize mineral samples and to eliminate aqueous-phase mass transport limitations. This way the aqueous concentrations reflect reaction progress and can be used to determine the forms and parameters of reaction rate laws. Such rate laws accurately determine the so-called surface-controlled reaction kinetics, but they provide limited information about reaction rates in consolidated porous media.

Natural porous media, such as sedimentary rocks and other geological media encountered in subsurface formations, are inherently heterogeneous [10]. They are mixtures of solid matrix and void space, with the latter consisting of interconnected pores of different shapes, volumes, and surface areas. Furthermore, the mineral composition of surfaces may vary from pore to pore. These pore-to-pore heterogeneities, hereafter referred to as pore-scale heterogeneities, can produce variabilities in the transport and reaction processes that take place within a porous medium, and can result in spatial variations in aqueous concentrations and reaction rates. In such heterogeneous systems, the laboratory-measured geochemical reaction kinetics may not be applicable at the scale of intact porous media. Consequently, spatial heterogeneities at scales smaller than the scale of discretization may be important in determining mineral dissolution and precipitation in reactive transport modeling.

Such scaling effects have been termed “non-classical” behavior as they cannot be predicted by existing theories inferred from laboratory systems [11]. They may be among the potential causes of the oft-cited and discussed field-lab discrepancy, namely, the observed order-of-magnitude differences between lab-measured reaction rates and those derived from field measurements [12–16]. In particular, the scaling effect of geochemical reaction kinetics has been observed in several studies. For example, Szecsody et al. [17] observed that for reactions of Co(II/III)EDTA with Fe oxide-containing sediments, the reaction parameters measured in batch experiments could not be applied directly to describe the reactive transport processes in column experiments, due to the pore-scale heterogeneity in adsorption sites. They found that stochastic modeling efforts that incorporated pore-scale heterogeneity did reproduce the observations. Lichtner and Tartakovsky [18] used volume-averaging methods to upscale the reaction rate constants for quartz dissolution, incorporating the heterogeneity in mineral grain size. They found that, contrary to the usual modeling assumptions, the upscaled effective reaction rate constants varied as a function of time, which is attributed to heterogeneous distribution of grain sizes.

In this work, we present a methodology to explore upsampling of geochemical reaction kinetics using pore-scale network modeling. A pore-scale network model is one that discretizes the void space of a porous medium into a collection of pores within an interconnected network. Such models have been widely used to explore a variety of phenomena related to multiphase flow in porous media [19–21], including, for example, drying processes [22–25], moisture transport [26], and bubble transport [27]. In recent years, pore-scale network models have also been applied to examine problems concerning chemical and biological processes, such as dissolution of organic liquids [28–32], biomass growth [33–38], adsorption [39,40], and the formation of wormholes in porous media [41]. However, this approach has never been used to address scaling questions associated with geochemical reaction kinetics. As such, this work presents a novel application of pore-scale network modeling.

Within the pore network constructed for this work, the individual pores are considered to be homogeneous systems. Reactive transport processes are simulated at the pore scale, incorporating variations in chemical and physical properties from pore to pore. Using mass balance principles, the continuum-scale reaction rates are obtained from the network model and are compared to continuum-scale rates calculated by ignoring pore-scale details and using laboratory-measured reaction kinetics directly. In addition, we use volume-averaging principles to quantify the errors that may occur when field measured concentrations are used in inverse modeling. The differences between these continuum-scale rates quantify the scaling effect of geochemical reaction kinetics.

This work focuses on the reaction kinetics of minerals that are considered to be important in the context of geological sequestration of CO2. In geological sequestration, CO2 is injected into deep subsurface formations and trapped by a variety of mechanisms [42–44]. Studies have found that, for both geological sequestration and natural long-term regulation of atmospheric CO2 levels, Ca- and Mg-rich feldspars provide the primary sinks for the net consumption of CO2 [45–51]. In this work, we focus on a Ca-rich feldspar, anorthite, as the model mineral, with kaolinite as the coexisting reactive mineral. The reactions of interest are those that would occur under the acidic conditions created when CO2 dissolves in formation waters under high pressures. The reaction
2. The reaction rate laws

2.1. Theory of reaction rate laws

Reaction rate laws are functions that relate mineral dissolution and precipitation rates to the concentrations of aqueous species involved in the reactions (although some rate laws have been described as functions of concentrations of sorbed species [52,53]). Based on transition state theory and the principle of detailed balancing, reaction rate laws take the following general nonlinear form [9]:

\[ r = k \prod_s \{s\}^{n_s} f(\Delta G), \]

where \( r \) is the reaction rate (mol cm\(^{-2}\) s\(^{-1}\)); \( k \) is the reaction rate constant; \( s \) represents a chemical species that has catalytic or prohibitory effects on the reaction; \( \{s\} \) denotes the activity of species \( s \), the product of the activity coefficient and the aqueous concentration \( [s] \); and \( n_s \) is a constant that describes the degree of rate dependence on \( s \). The saturation state function \( f(\Delta G) \) captures the dependence on the activities of chemical species that directly participate in the reaction.

For the expression of \( f(\Delta G) \), the following practical form is used in this work [9]:

\[ f(\Delta G) = 1 - \Omega^m, \]

where \( \Omega \) is the saturation state, and \( m \) is a constant that describes the dependence of rate on saturation state. The magnitude of the saturation state \( \Omega \) is an indicator of how far away the reaction is from equilibrium. Theoretically, it is equal to the ratio of the ionic activity product, IAP, to the equilibrium constant, \( K_{eq} \). As the value of \( \Omega \) usually covers orders of magnitude, the saturation index, \( SI = \log \Omega \), is often used to quantify the magnitude of the saturation state. If \( \Omega < 1 \), then \( SI < 0 \), and the net reaction is dissolution; otherwise, the net reaction is precipitation. If \( \Omega = 1 \) and \( SI = 0 \), the reaction is at equilibrium.

Mineral dissolution and precipitation reactions are generally driven by several different parallel mechanisms, with each catalyzed by a different chemical species, for instance, \( H^+, H_2O, \) and \( OH^- \). The rate law for each mechanism takes the same general form as in Eq. (1):

\[ r_H = k_H[H^+]^{n_H}(1 - \Omega^m), \]
\[ r_{H,O} = k_{H,O}(1 - \Omega^m), \]
\[ r_{OH} = k_{OH}[OH^-]^{n_{OH}}(1 - \Omega^m). \]

The total reaction rate is the sum of these three:

\[ r = r_H + r_{H,O} + r_{OH}. \]

The value of \( r_H \) dominates under acidic conditions, and \( r_{OH} \) dominates under alkaline conditions. There may or may not be neutral conditions where the rate is dominated by \( r_{H,O} \), depending on the relative magnitude of these rates. The full reaction rate law requires the following kinetic parameters: the reaction rate constants, \( k_H, k_{H,O} \) and \( k_{OH} \); the degrees of rate dependence on \( pH, n_H \) and \( n_{OH} \); and the degree of dependence on saturation state, \( m \).

2.2. Anorthite and kaolinite reactions

In this section, we review the literature on anorthite and kaolinite reaction rates and establish the rate laws used in the present work. The anorthite reaction is as follows:

\[ \text{CaAl}_2\text{Si}_2\text{O}_6(s) + 8H^+ \rightarrow \text{Ca}^{2+} + 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4. \]

It is well known that under conditions far from equilibrium (i.e., \( \Omega \ll 1 \)), the anorthite dissolution rate depends on proton activity in acidic conditions [54]. Examination of published experimental data of anorthite dissolution kinetics suggests that the degree of dependence, \( n_H \), varies from 1 to 3 [55–57]. In this work, we use kinetic parameters measured by Oelkers and Schott [57], who observed that at 25 \( ^\circ \text{C} \) the reaction order of anorthite dissolution with respect to \( [H^+] \) is 1.5 under acidic conditions. For neutral conditions, we use the reported value for \( k_{H,O} \) of \( 10^{-15.6} \) mol cm\(^{-2}\) s\(^{-1}\) [55]; this value is nearly identical to that reported by Helgeson et al. [58]. For alkaline conditions, we use data from Brady and Walther [56], who observed that the exponent describing rate dependence on \( [OH^-] \) is 0.33. As anorthite dissolution is thermodynamically favorable in most environments and almost never reaches equilibrium, there are no data on the form of its saturation state function. For completeness we include a saturation state on
function, and use Eq. (2), assuming \( m = 1 \). Combining all these parameters (summarized in Table 1), the anorthite reaction rate law takes the following form:

\[
r_A = (k_H\{H^+\}^{1.5} + k_{H_2O} + k_{OH} \{OH^-\}^{0.33})(1 - \Omega_A),
\]

with the expression for the saturation state for the anorthite reaction as follows:

\[
\Omega_A = \frac{(Ca^{2+})\{Al^{3+}\}^2\{H_2SiO_4\}^2}{\{H^+\}^6 K_{eq,A}},
\]

where \( K_{eq,A} \) is the equilibrium constant of anorthite reaction.

The kaolinite reaction is

\[
Al_2Si_2O_5(OH)_4(s) + 6H^+ = 2Al^{3+} + 2H_2SiO_4 + H_2O.
\]

Examination of kinetics for kaolinite dissolution far from equilibrium reveals that the kaolinite reaction rate does not have an obvious pH-independent region [60]. Under acidic conditions, the kaolinite dissolution rate is reported to be proportional to \( \{H^+\} \) raised to the power of 0.35–0.40 [59,60]. In this work, a value of 0.4 is used, based on data from Ganor et al. [59]. The literature on the kaolinite dissolution rate under alkaline conditions suggests that the rate dependence on \( \{OH^-\} \) is approximately 0.3 [60], which is the value used in this work. Using the saturation state function from Nagy et al. [61] and assuming that the principle of detailed balancing applies, the overall reaction rate law of kaolinite is as follows:

\[
r_K = (k_H\{H^+\}^{0.4} + k_{OH} \{OH^-\}^{0.1})(1 - \Omega_K^{0.9}),
\]

with the following expression for the saturation state for kaolinite reaction:

\[
\Omega_K = \frac{\{Al^{3+}\}^2\{H_2SiO_4\}^2}{\{H^+\}^6 K_{eq,K}},
\]

where \( K_{eq,K} \) is the kaolinite dissolution reaction equilibrium constant. The values of all the kinetic parameters are listed in Table 1. The thermodynamic parameters are discussed in Section 5.

The dissolution rates of both minerals as a function of pH at conditions far from equilibrium are shown in Fig. 1.

**Fig. 1.** Dissolution rates of anorthite and kaolinite as a function of pH under conditions far from equilibrium using the parameters summarized in Table 1.

**Table 1.** Reaction kinetic parameters at 25 °C

<table>
<thead>
<tr>
<th></th>
<th>( \log k ) (mol cm(^{-2}) s(^{-1}))</th>
<th>( n_H )</th>
<th>( n_{OH} )</th>
<th>( m )</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anorthite</td>
<td>-7.32(^a)</td>
<td>-15.6(^b)</td>
<td>-17.5(^c)</td>
<td>1.5(^a)</td>
<td>0.33(^c)</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-14.8(^d)</td>
<td>-19.7(^e)</td>
<td>0.4(^d)</td>
<td>0.3(^e)</td>
<td>0.9(^f)</td>
</tr>
</tbody>
</table>

\(^a\) Data from Oelkers and Schott [57], based on measurements for pH 2.4–3.2.

\(^b\) Data from Amrhein and Suarez [55] and Helgeson et al. [58], based on measurements for pH 5–9.

\(^c\) Data from Brady and Walther [56], based on compiled data from various measurements for pH 7–12.

\(^d\) Data from Ganor et al. [59], based on measurements for pH 2–4.2.

\(^e\) Data from Carrol and Walther [60], based on measurements for pH 7–12.

\(^f\) Data from Nagy et al. [61], based on measurements for pH around 3.

3. Pore-scale network modeling

In pore-scale network modeling, the processes of interest are simulated in individual pores, and information at the pore scale is summed up and averaged over the network to obtain descriptions of processes at the continuum scale. In this way a pore-scale network model serves as a computational tool to upscale processes from the pore scale to the continuum scale. This section presents (i) the equations for reaction and transport at the pore scale, (ii) the construction of the pore network, including parameter specification for porous medium properties, and (iii) the method for flow field calculation.
3.1. Reactive transport processes at the pore scale

Within each pore, the mass of each species in the aqueous phase changes due to transport (advection and diffusion) and reaction processes. The relevant reactions include aqueous reactions, which are considered to be instantaneous, and mineral dissolution and precipitation reactions, which are described kinetically. Examination of different aqueous reactions have shown that there are nine important instantaneous reactions, including the water dissociation reaction, and the precipitation reactions of carbon-bearing species, silica-bearing species, and aluminum-bearing species. The two kinetic reactions include the dissolution and precipitation of anorthite and kaolinite. All reactions and their equilibrium constants are listed in Table 2. In total 14 aqueous species are involved in these reactions: Ca$^{2+}$, H$^+$, OH$^-$, H$_2$CO$_3$, HCO$_3^-$, CO$_3^{2-}$, H$_4$SiO$_4$, H$_2$SiO$_3^-$, H$_2$SiO$_4^-$, Si$_2$O$_5$(OH)$_4$(s); and the aluminum-containing species Al$^{3+}$, Al(OH)$_3^-$, Al(OH)$. This assumption is justified by the calculation of a Damkohler number, a dimensionless number which compares the reaction rate to the molecular diffusion rate in an average pore. The diffusion rate is estimated using the expression $D_{ij} = \frac{\lambda_{ij}}{A_i \times \frac{l^2}{2}}$, with $D$ being the diffusion coefficient (approximately $10^{-4}$ cm$^2$ s$^{-1}$ for hydrogen ion [9]), $l$ being the length of the pore (0.017 cm), $A_i$ being the characteristic cross-sectional area for diffusion in a pore, conservatively estimated as $\tilde{P}$, and $\Delta C$ (mol cm$^{-3}$) being the difference in concentrations at the center of the pore and at locations close to the mineral surface. For hydrogen ion, $\Delta C$ is approximately $10^{-5.9}$ mol cm$^{-3}$ at pH of 2.9, which leads to the diffusion rate of $10^{-11.6}$ mol s$^{-1}$. This rate is approximately 1.7 orders of magnitude larger than the reaction rate. This relatively fast diffusion rate, combined with the much faster advection rate, is sufficient to eliminate the concentration gradient within the fluid in individual pores.

The mass balance equations describing the mass change of chemical species within individual pores were developed following Lichtner’s systematic formulation for multicomponent systems that involve both kinetically controlled and instantaneous reactions [63,64]. We chose to develop the mass balance equations for five key components: Ca$^{2+}$, C$_T$, Si$_T$, Al$_T$, and H$_T$, with C$_T$ collectively representing all carbon-bearing species, Si$_T$ collectively representing all silica-bearing species, Al$_T$ collectively representing all aluminum-bearing species, and H$_T$ representing the total aqueous proton. The concentration of H$_T$ is computed as $[H_T] = -\frac{[Al(OH)]}{2\times[Al(OH)]} - 3\times[Al(OH)] - 4\times[Al(OH)] + [H_2SiO_4] - [H_2SiO_4] + [H_2CO_3] - [CO_3^{2-}] + [H^+] - [OH^-]$. For this system, five mass balance equations, together with the nine mass action laws corresponding to the nine instantaneous reactions, are sufficient to describe the mass change in the aqueous phase.

The mass balance equation (expressed in molar units) for pore $i$ takes the following general form:

$$V_i \frac{d[\cdot]}{dt} = \sum_{Q_{ij} > 0} Q_{ij}[\cdot]_j + \sum_{Q_{ij} < 0} Q_{ij}[\cdot]_i + \sum_{j=1}^{nc} D_{ij} a_{ij} \frac{([\cdot]_j - [\cdot]_i)}{l} + S_i,$$

where $[\cdot]$ represents the molar concentration of one of the five key components; $V_i$ is the volume of pore $i$; $j$ is the index for a pore that is connected to pore $i$; $nc$

### Table 2
Reactions of interest, and their equilibrium constants adjusted to current simulation conditions (50 °C and 10$^7$ Pa)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$\log K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic reactions</td>
<td></td>
</tr>
<tr>
<td>CaAl$_2$Si$_2$O$_8$(s) + 8H$^+$ $\rightleftharpoons$ Ca$^{2+}$ + 2Al$^{3+}$ + 2H$_2$SiO$_4$</td>
<td>21.7</td>
</tr>
<tr>
<td>Al$_2$Si$_2$O$_5$(OH)$_4$(s) + 6H$^+$ $\rightleftharpoons$ 2Al$^{3+}$ + 2H$_2$SiO$_4$ + H$_2$O</td>
<td>3.80</td>
</tr>
<tr>
<td>Instantaneous reactions</td>
<td></td>
</tr>
<tr>
<td>H$_2$O $\rightleftharpoons$ H$^+$ + OH$^-$</td>
<td>-13.2</td>
</tr>
<tr>
<td>H$_2$CO$_3$ $\rightleftharpoons$ HCO$_3^-$ + H$^+$</td>
<td>-6.15</td>
</tr>
<tr>
<td>HCO$_3^-$ $\rightleftharpoons$ CO$_3^{2-}$ + H$^+$</td>
<td>-10.0</td>
</tr>
<tr>
<td>H$_2$SiO$_4$ $\rightleftharpoons$ H$_2$SiO$_4^-$ + H$^+$</td>
<td>-9.2</td>
</tr>
<tr>
<td>H$_2$SiO$_4$ $\rightleftharpoons$ H$_2$SiO$_4^-$ + H$^+$</td>
<td>-12.4</td>
</tr>
<tr>
<td>Al$^{3+}$ + OH$^-$ $\rightleftharpoons$ Al(OH)$_2$</td>
<td>8.76</td>
</tr>
<tr>
<td>Al(OH)$_3^-$ + OH$^-$ $\rightleftharpoons$ Al(OH)$_4^-$</td>
<td>18.9</td>
</tr>
<tr>
<td>Al(OH)$_2^+$ + OH$^-$ $\rightleftharpoons$ Al(OH)$_3^-$</td>
<td>27.3</td>
</tr>
<tr>
<td>Al(OH)$_4^-$ + OH$^-$ $\rightleftharpoons$ Al(OH)$_5^-$</td>
<td>33.2</td>
</tr>
</tbody>
</table>

* The method of adjustment is described in Section 5.
is the total number of neighbor pores; $Q_{ij}$ symbolizes the flow rate from pore $j$ to $i$; $D'_{ij}$ is the effective diffusion coefficient; $a_{ij}$ is the cross-sectional area between pores $i$ and $j$; $l$ is the distance between the centroids of adjacent pores and is a constant for the regular-latticed network; and $S_{ij}$ denotes the mass change rate due to kinetic reactions. On the right-hand side of the above equations, the first two terms take into account advective mass inflow and outflow rates, and the third term is the mass change rate due to diffusion between adjacent pores.

For each of the four components that is a collective representation of several species, its “effective” diffusion coefficient $D'_{ij}$ is derived by writing the reactive transport equations for each constitutive species. Summation of these transport equations leads to a derived effective diffusion coefficient that is essentially a weighted average of the diffusion coefficients of involved species weighted by their concentration differences between pore $i$ and pore $j$. Such a formulation is consistent with what is done in reactive transport modeling [64]. For example, for $C_T$,

$$D'_{ij,C_T} = \frac{D_{H_2CO_3}\left([H_2CO_3]_j - [H_2CO_3]_i\right) + D_{HCO_3}\left([HCO_3^-]_j - [HCO_3^-]_i\right) + D_{CO_2^-}\left([CO_2^-]_j - [CO_2^-]_i\right)}{([H_2CO_3]_j - [H_2CO_3]_i) + ([HCO_3^-]_j - [HCO_3^-]_i) + ([CO_2^-]_j - [CO_2^-]_i)}.$$  \hspace{1cm} (12)

The diffusion coefficients for individual species are taken from the literature [65,9]. Note that this formulation of mass balance equations takes into account fluctuations in local flow velocities. Hence, dispersion is not modeled explicitly and the diffusion process is restricted to pore-to-pore diffusion within the network.

The last term in Eq. (11), $S_{ij}$, represents the mass change rate due to kinetic reactions. It takes different forms for different components, depending on the reactions involved (expressed in molar units):

$$S_{i,CAc^+} = r_{A_c}n_{A_c,i},$$  \hspace{1cm} (13) $$S_{i,CT} = 0,$$  \hspace{1cm} (14) $$S_{i,SHt} = 2r_{A_c}n_{A_c,i} + 2r_{K_c}n_{K_c,i},$$  \hspace{1cm} (15) $$S_{i,ALt} = 2r_{A_c}n_{A_c,i} + 2r_{K_c}n_{K_c,i},$$  \hspace{1cm} (16) $$S_{i,HT} = -6r_{A_c}n_{A_c,i} - 4r_{K_c}n_{K_c,i},$$  \hspace{1cm} (17)

where $n_{A_c,i}$ and $n_{K_c,i}$ are, respectively, the surface areas of anorthite and kaolinite in pore $i$. The two reaction rates, $r_{A_c,i}$ and $r_{K_c,i}$, are calculated using the respective reaction rate laws (Eqs. (7) and (9)) and the local concentrations in pore $i$. The mass change rates due to kinetic reactions depend on the amount of the reactive mineral in each pore. In this pore network model, two types of pores are identified with regard to the mineralogy of the solid phases: reactive pores, with their solid phases containing both anorthite and kaolinite, and non-reactive pores, with their solid phases being quartz. For non-reactive pores, as the reactive minerals are not present, the surface areas of anorthite and kaolinite are zero and the mass change rates due to reaction are equal to zero.

Such a representation of reactive pores is not a problem for modeling dissolution, but could pose a problem for modeling precipitation. Precipitation normally proceeds in two steps: nucleation and crystal growth [9,66]. For many minerals, nucleation is the rate-limiting step [43], because it has to overcome a surface free energy barrier and requires some degree of supersaturation. In the absence of a solid mineral phase, precipitation of that mineral requires both steps, while in the presence of a solid mineral phase, precipitation of that mineral can start as crystal growth. The large difference in these rates is the basis for our modeling assumption that precipitation can proceed only in so-called reactive pores.

### 3.2. Network construction

A 3D regular-lattice network model was constructed to represent a consolidated sandstone with reactive minerals occupying approximately 10% of the solid phase, which is within the typical range of the percentage of feldspars and clay minerals in sandstones. The porosity of the network is 0.14, and the permeability is $7.9 \times 10^{-10}$ cm$^2$, which falls in the typical range of consolidated sandstone properties [67,68]. The size of the network is $5.0 \times 1.7 \times 5.0$ mm$^3$, and the network contains 9000 pores ($30 \times 10 \times 30$ in $x$-, $y$-, $z$-directions, respectively). The bulk flow direction is in the $z$-direction. This network has several characteristics that distinguish it from network models that have been constructed for multiphase flow. First, pores do not have prescribed geometries; they are defined only in terms of surface area and volume. Second, pore throats are not represented explicitly except to assign an effective resistance to the flow and an effective cross-sectional area for diffusion. All void volume is contained in pore bodies.

Solution of the pore-scale mass balance equations requires the following values for each pore $i$: volume; conductances at pore junctions (for the calculation of flow rates); effective cross-sectional areas at connections of adjacent pores (for the calculation of diffusion terms); and surface areas. These parameters characterize each pore, while across the network they form statistical dis-
tributions. The parameters for each pore are randomly assigned from their respective statistical distributions, as discussed in this section.

3.2.1. Pore volume

Based on literature data for a Fontainebleau sandstone [69], pore volume is assumed to have a log-normal distribution. The mean for the log-transformed pore volume (mm^3) is $-3.42$, with the standard deviation of the log-transformed pore volume being 0.51. This corresponds to an arithmetic mean of pore volume being $6.6 \times 10^{-4}$ mm^3.

3.2.2. Pore hydraulic conductance

For the distribution of pore conductances, we have made two assumptions: (1) the distribution follows a log-normal distribution; and (2) the conductance between pores is correlated to the sum of the logarithm of their pore volumes. Regarding the first assumption, although data on distributions of pore-scale conductances generally do not exist, in the literature there is indirect evidence supporting the idea that the distribution of the conductances should be related to the distribution of grain or pore size, which is usually log-normally distributed [70]. The second assumption is based on observations for sandstones from experimental studies [71,72].

We define $C_{ij}$ (cm^4 g Pa^-1) as the conductance between two adjacent pores $i$ and $j$. The log-transformed conductance $X_{ij} = \ln C_{ij}$ has a normal distribution, with mean $\mu_X$, and variance $\sigma_X^2$. The summation of the log-transformed volumes of adjacent pores, $Y_{ij} = \ln V_i + \ln V_j$, also takes a normal distribution, with mean $\mu_Y = 2\mu_{Vr}$ and variance $\sigma_Y^2 = 2\sigma_{Vr}^2$. Assuming $X_{ij}$ and $Y_{ij}$ are jointly Gaussian distributed, the mean and variance of the log-transformed conductance for a pair of connected pores $i$ and $j$, $(\mu_X)_{ij}$ and $(\sigma_X^2)_{ij}$, are calculated as follows [73]:

$$
(\mu_X)_{ij} = \mu_X + \rho \frac{\sigma_X}{\sigma_Y} (Y_{ij} - \mu_Y),
$$

$$
(\sigma_X^2)_{ij} = \sigma_X^2 (1.0 - \rho^2),
$$

where $\rho$ is the correlation coefficient. For the connection between pores $i$ and $j$, the conductance is sampled from the log-normal distribution with mean $(\mu_X)_{ij}$ and variance $(\sigma_X^2)_{ij}$, which depend on the log-volume summation $Y_{ij}$. In this work, the value of $\mu_X$ and $\sigma_X^2$ were chosen to be $-6.1$ and 1.0 to be consistent with the permeability value ($7.9 \times 10^{-10}$ cm^2), as described in the next section. The value of $\rho$ is assumed to be 0.9 as we assume strong correlation between conductance and adjacent pore volumes.

3.2.3. Pore-to-pore cross-sectional area

The cross-sectional area between connected pores $i$ and $j$, $a_{ij}$, is required for the calculation of the mass transport due to diffusion. Considering an “effective” cylinder between pore $i$ and $j$, with conductance $C_{ij}$, and length $l$, the diameter of the cylinder $d_{ij}$ can be calculated by rearranging Poiseuille’s law:

$$
d_{ij} = \left( \frac{128\rho l \times C_{ij}}{\pi} \right)^{\frac{1}{2}},
$$

with $\nu$ being the viscosity of the flowing fluid. Correspondingly, the “effective” cross-sectional area $a_{ij} = \frac{1}{4} \pi d_{ij}^2$. The arithmetic average of the cross-sectional area for this network is about $1.02 \times 10^{-4}$ mm^2.

3.2.4. Surface area

Because there is no reliable literature data on the pore-scale distribution of surface area for consolidated sandstone, we use the following procedure. The surface area of pore $i$ is randomly sampled from an exponential distribution, with the restriction of not being less than the minimum surface area, which is calculated from the pore volume assuming a spherical pore. The values of surface areas of consolidated sandstones measured by Brunauer–Emmet–Teller (BET) method, often reported as the surface-to-volume ratio, cover three orders of magnitude, ranging from $10^3$ to $10^5$ cm^−1 [74–76]. In this work, the mean of the pore surface area was chosen to be $6.0$ mm^2, which results in a surface-to-volume ratio for the entire network of $1.3 \times 10^4$ cm^−1.

As described earlier, the solid surface for an individual pore is modeled as either containing reactive minerals or not. Within 9000 pores in total, 900 of them contain reactive minerals, which is consistent with the assumption that 10% of the solid phase is reactive mineral. We have chosen to randomly distribute the reactive minerals in clusters of size $2 \times 2 \times 15$ pores (in the $x$-, $y$-, $z$-directions, respectively), which is within the range of the spatial scale of feldspars distribution in sandstone [77]. In pores within the reactive clusters, 50% of the surface area is anorthite and 50% is kaolinite. The resulting distributions of values of $\mathcal{A}_{K,i}$ and $\mathcal{A}_{F,i}$ for the network include a large number of zeros for the non-reactive pores and a truncated exponential distribution for the surface areas in reactive pores.

3.3. Determination of the steady-state flow field

To determine the steady-state flow field of the network, fixed fluid pressures are imposed at the boundaries of the network in the z-direction, with no-flow boundary conditions applied in the other two directions, resulting in macroscopically one-dimensional flow. The flow rate between connected pores $i$ and $j$ is proportional to the pressure difference through the conductance:

$$
Q_{ij} = C_{ij}(P_i - P_j),
$$
where $P_i$ and $P_j$ are fluid pressures in pore $i$ and $j$, respectively. The inflows and outflows must balance for each pore $i$:

$$\sum_{j=1}^{nc} Q_{ij} = 0.$$  \hfill (22)

Combination of Eqs. (21) and (22) results in a linear algebraic system for the unknown pressure field. Given the boundary pressures, this system is solved for the pressure in each pore, from which the steady-state flow field is calculated.

At the continuum scale, the total flow rate follows Darcy’s law:

$$Q_T = \frac{k A \Delta P}{L},$$

where $Q_T$ (cm$^3$ s$^{-1}$) denotes the total flow rate through the network in the main flow direction, $z$; $k$ is the intrinsic permeability of the network (cm$^2$); $A$ represents the cross-sectional area of the network in the direction orthogonal to the main flow (cm$^2$); $\Delta P$ symbolizes the pressure difference between the two boundaries in z-direction; and $L$ is the length of the network in z-direction (cm). By rearrangement of the above equation, the permeability of the network can be calculated. The permeability is thus a function of the mean and variance of the conductance field, $\mu_X$ and $\sigma^2_X$, and the correlation with local volumes. As mentioned previously, these parameters were chosen so that the permeability corresponds to a typical value for sandstone. An iterative approach was used whereby the statistical parameters were varied until a flow field was generated that resulted in the desired permeability.

4. Continuum-scale reaction rates

4.1. The rates from the network model: $R_N$

For a porous medium, the “true” reaction rate at the continuum scale is the total mass change rate due to reactions at every reactive surface, normalized by the total amount of surface area of reactive minerals. The network model allows us to estimate such a “true” reaction rate at the continuum scale. The pore-scale mass balance equations are used to simulate changes in aqueous concentration over time in each pore. At each time step, the sum of the mass change rates due to mineral reactions for the entire network, divided by the total surface area of reactive minerals, gives the “true” reaction rate for the network. For example, for anorthite, the effective continuum-scale reaction rate for the network model is as follows:

$$R_{N,A} = \frac{\sum_{i=1}^{N,A} A_{rA,i} \phi_{A,i}}{\sum_{i=1}^{N} A_{r,i}},$$

where $n$ is the total number of pores. Expressed in mol cm$^{-2}$ s$^{-1}$, this rate is equivalent to the rate calculated by summing the mass change rate of Ca$^{2+}$ due to anorthite reaction across the network, and then dividing by the total anorthite surface area. An equation analogous to Eq. (24) is used to calculate the continuum-scale rate for kaolinite. The continuum-scale rates, $R_{N,A}$ and $R_{N,K}$, depend on local reaction rates ($r_{A,i}$ and $r_{K,i}$, respectively), as well as the coupling between the local rates and local surface area of reactive minerals. For non-reactive pores, as values of $\sigma_{A,i}$ are zero, the term $\sigma_{A,i} r_{A,i}$ is not counted in the calculation of $R_N$. As such, concentrations in non-reactive pores are irrelevant to the reaction rates, although they enter indirectly via the transport equations. The continuum-scale reaction rates are dependent only on the concentrations in reactive pores.

4.2. The rates from the continuum model: $R_C$

This section presents the methodology for calculating continuum-scale reaction rates using a continuum model, which is the fundamental building block of traditional forward modeling. Forward modeling generally employs a continuum approach \[63,64,78\], in which porous media are characterized by spatially-averaged properties at the scale of the grid block, thereby ignoring details at the sub-grid scale. It is common practice to apply reaction rate laws determined from well-mixed laboratory systems to calculate the reaction rates for the porous medium in an entire grid block. Furthermore, the mathematical forms and parameters of these rate laws are assumed to hold at the grid block scale despite possible nonlinearities in upscaling.

In a similar manner, the continuum model uses spatially-averaged values to represent system properties, assumes uniform concentrations in the aqueous phase, and applies lab-measured reaction rates directly at the continuum scale. In so doing, it ignores pore-scale heterogeneities a priori, and assumes no mass transport limitation from pore to pore. In the calculation that follows, the continuum model is constrained to have the same hydrodynamic properties, total surface area of reactive minerals, initial conditions and boundary conditions as the network model.

Because the reactions and the species involved are the same as in the network model, we follow the same systematic formulation to develop mass balance equations for the five components: Ca$^{2+}$, C$_T$, Si$_T$, Al$_T$, and H$_T$. For each key component, the mass balance equations take the following general form, applied over the entire volume of the pore network defined earlier:

$$V_T \frac{d[\cdot]}{dr} = Q_T[\cdot]_{in} - Q_T[\cdot]_{out} + S[\cdot],$$

where $Q_T[\cdot]_{in}$ and $Q_T[\cdot]_{out}$ are the inflows and outflows per unit volume at time $t$, and $S[\cdot]$ is the rate of change of concentration due to chemical reaction at the continuum scale.
where $V_T$ is the total pore volume across the network, $[\text{Ca}]_{in}$ corresponds to the concentration at the inflow boundary, and $[\text{Ca}]_c$ is the uniform concentration in the continuum model. On the right side of the equation, the first two terms account for the mass change rates due to advection, and the last term, $R_c$, represents the mass change rate due to reaction, which takes different forms for different components:

\[
S_{\text{Ca}^{2+}} = R_{\text{CA}} A_{\text{AT}},
\]

(26)

\[
S_{\text{Ca}^2} = 0,
\]

(27)

\[
S_{\text{CaSi}} = 2R_{\text{CA}} A_{\text{AT}} + 2R_{\text{CK}} A_{\text{KT}},
\]

(28)

\[
S_{\text{CaAl}} = 2R_{\text{CA}} A_{\text{AT}} + 2R_{\text{CK}} A_{\text{KT}},
\]

(29)

\[
S_{\text{CaH}} = -6R_{\text{CA}} A_{\text{AT}} - 4R_{\text{CK}} A_{\text{KT}},
\]

(30)

where $R_{\text{CA}}$ and $R_{\text{CK}}$ are the reaction rates of anorthite and kaolinite, respectively, and $A_{\text{AT}}$ and $A_{\text{KT}}$ are the total surface areas of anorthite and kaolinite. These mass balance equations look similar to those written for an individual pore in the network model, except that at the continuum scale there is no diffusion term, and the parameters characterizing pore $i$ are replaced by the parameters that describe the continuum-scale properties. The reaction rates from the continuum model, $R_{\text{CA}}$ and $R_{\text{CK}}$, are calculated using the uniform concentrations (converted to activities), and by applying the reaction rate laws directly. For anorthite,

\[
R_{\text{CA}} = (k_H [\text{H}^+]_{\text{C}}^{1.5} + k_{\text{H}_2\text{O}} + k_{\text{OH}^-} [\text{OH}^-]^3) (1 - \Omega_{\text{CA}}),
\]

(31)

where $\Omega_{\text{CA}}$ is calculated using uniform concentrations as well. For kaolinite, the rate expression is similar, following the reaction rate law shown in Eqs. (9) and (10). These rates represent the rates calculated in one grid block in forward modeling, where the grid block is taken to correspond to the entire network used in the network model.

4.3. The rates from volume-averaged concentrations: $R_N$

This section presents the methodology for calculating continuum-scale rates, $R_N$, using volume-averaged concentrations in reaction rate laws. The volume-averaged concentrations are analogous to those measured in field sampling, where groundwater is pumped from a well, and water from a large number of pores is mixed. Concentrations measured in the sample represent spatially-averaged values. A typical application in inverse modeling is to use these measured concentrations in conjunction with laboratory-measured reaction rate laws or equilibrium relationships to infer which minerals are dissolving, and which are precipitating [79].

The purpose of this calculation is to not develop a method of volume-averaging, but to use the network model to calculate the rates that resemble those estimated from field sampling. This allows us to examine the extent to which volume-averaged concentrations, $[\text{Ca}]$, provide accurate predictions of continuum-scale reaction rates. From the network model simulation results, we compute the volume-averaged concentrations, such as that of hydrogen ion:

\[
[H^+] = \frac{\sum_i V_i [\text{H}^+]}{\sum_i V_i}.
\]

(32)

Since activity coefficients are constant throughout the network (see Section 5), the value of the volume-averaged activity, $[\text{H}^+]$, is the product of the activity coefficient and the volume-averaged concentration. Then, for the anorthite reaction, we use the averaged activities to compute

\[
R'_{\text{CA}} = (k_H [\text{H}^+]_{\text{C}}^{1.5} + k_{\text{H}_2\text{O}} + k_{\text{OH}^-} [\text{OH}^-]^3) (1 - \Omega'_{\text{CA}}),
\]

(33)

where

\[
\Omega'_{\text{CA}} = \frac{\{\text{Ca}^{2+}\} \{\text{Al}^{3+}\}^2 \{\text{H}_2\text{SiO}_4\}^2}{[\text{H}^+]^2 K_{eq}}.
\]

(34)

A similar rate law applies for kaolinite. In so doing, the rate calculated from volume-averaged concentrations ignores pore-scale heterogeneities a posteriori. These reaction rates represent the rates that would be inferred from the measured concentrations via inverse modeling.

4.4. Comparison between continuum-scale reaction rates

We have defined three continuum-scale reaction rates: (1) $R_N$, derived from explicit mass balance calculation from the network model; (2) $R_c$, derived from uniform concentrations in the continuum model; and (3) $R'_N$, derived from averaged concentrations from the network model. Of these three upscaled reaction rates, we take $R_N$ to represent the “true” reaction rate, as it most closely takes into account the effects of pore-scale heterogeneities, and is consistent with the mass balance of the network system. Both $R_c$ and $R'_N$ are based on spatially-averaged properties (either a priori or a posteriori) and on reaction rate laws that were determined in the laboratory. Comparisons of $R_c$ and $R'_N$ to $R_N$ provide insights into how pore-scale heterogeneity influences continuum-scale reaction rates, and how well the use of average properties represents these heterogeneous systems.

For the comparison of $R_c$ to $R_N$, we define the ratio:

\[
\eta = \frac{R_c}{R_N}.
\]

(35)

If $\eta$ is close to unity, the differences between these two rates are not significant, which means that the effects
of pore-scale heterogeneities are not significant, and that the scaling effect is negligible. In such cases, the application of the lab-measured reaction kinetics at the continuum scale is appropriate in forward modeling. Otherwise, pore-scale heterogeneities are important and conventional forward modeling using continuum modeling may introduce significant errors.

For the comparison of $R_N$ and $R_N$, we define the ratio:

$$\beta \equiv \frac{R'_N}{R_N}$$  \hspace{1cm} (36)

If $\beta$ is close to unity, these two rates are similar, which means that volume-averaged concentrations are sufficient to describe the reaction rates and the scaling effect is negligible. Otherwise, it is not appropriate to calculate the reaction rates using volume-averaged concentrations, such as those determined from field sampling and used in inverse modeling.

The deviation of $\eta$ or $\beta$ values from unity provides a measure of the scaling effect of the reaction kinetics. If either $R_C$ or $R'_N$ has a different sign from $R_N$, then $R_C$ or $R'_N$ predicts a different reaction direction as compared to $R_N$; that is, one is predicting dissolution while the other is predicting precipitation, or other wise.

5. Simulation conditions and numerical computation

5.1. Simulation conditions and parameter estimation

The application of pore-scale network modeling to upscale geochemical reaction rates is illustrated with two simulation scenarios relevant to geological CO$_2$ sequestration. One scenario is that in which the network system is near the CO$_2$ injection site so that the boundary aqueous phase is in equilibrium with CO$_2$ of a typical injection pressure, 10$^7$ Pa, and is highly acidic (referred to hereafter as case A). The other scenario is that in which the network system is relatively far away from the injection site so that the boundary aqueous phase has a much lower CO$_2$ concentration. Here, we have chosen to represent this as an aqueous phase in equilibrium with CO$_2$ of a relatively low pressure, 10$^5$ Pa (referred to hereafter as case B). The difference in CO$_2$ concentrations generates different acidities in the aqueous phases that flow into the network system. Except for this difference, the simulation conditions are the same for the two cases.

In geological sequestration, CO$_2$ would typically be injected into subsurface formations at a depth of 1 km or greater. To be consistent with this depth, the simulations were run at a temperature of 323 K and a pressure of 10$^7$ Pa. The brine is represented by saline water with total dissolved salinity (TDS = 0.45 mol L$^{-1}$) that has taken into account the contribution of all important aqueous species in typical brine. Initially the brine is assumed to be in equilibrium with quartz and kaolinite, at pH 7.5. The electronic condition is satisfied with the addition of Ca$^{2+}$, which produces an initial concentration that is very small (7.9 × 10$^{-6}$ mol L$^{-1}$). There are no carbon-bearing species present in the brine. The brine at the inflowing boundary is assumed to have the same [Ca$^{2+}$] as in the initial aqueous phase within the network. The total carbon concentration and thus the pH in the boundary brine is determined using the semi-empirical relationship from Duan and Sun [80], based on equilibrium with separate phase carbon dioxide at a given temperature, pressure, and salinity. In case A, due to the large amount of CO$_2$ dissolved in the boundary brine, the boundary pH is 2.9. In case B, the boundary pH is 4.1. We chose to run the simulations for a nominal value using the flow velocity, $q = 5.8 \times 10^{-7}$ cm s$^{-1}$ [67].

The salinity is high enough that the activity coefficients of the reactive species deviate considerably from unity. These values were calculated using the Davies equation [81]. Because the brine TDS is high, it is assumed that the dissolution and precipitation of reactive species does not change the TDS significantly, and the activity coefficient of each species is considered constant both in time and space.

Equilibrium constants were taken from Morel and Hering [81] and adjusted to the system temperature and pressure using the software SUPCRT92 [82], as listed in Table 2. The reaction rate constants were adjusted to the given temperature using the Arrhenius equation [9], with the activation energies listed in Table 1. The diffusion coefficients were obtained and adjusted to the system temperature and salinity [9,65]. The effects of pressure on reaction rate constants and diffusion coefficients were considered insignificant, because the pressure effect on these parameters is relatively small compared to the effect of temperature [9].

Simulations were run within a limited time frame such that the total amount of minerals reacted produced only small porosity changes. Using empirical relationships between permeability and porosity [83–85], the predicted porosity changes result in changes of permeability less than 5%. Therefore, the porosity and permeability of the porous medium are considered constant during the simulation process. The system eventually reaches steady state, after which the concentrations of the aqueous species and the reaction rates do not vary as a function of time.

5.2. Numerical computations

For the network model, given initial and boundary conditions, as well as the predetermined flow field, we use the adaptive Runge–Kutta algorithm to simultaneously solve the mass balance equations for the con-
centrations of the five components in each pore at each time step [86]. The values of these five concentrations, coupled with the nine laws of mass action corresponding to the nine instantaneous reactions, are then used to calculate concentrations of all 14 species iteratively using a hybrid algorithm combining both the Newton–Raphson and bisection method. In this way we obtain the concentrations of all 14 aqueous species in each pore at each time step. The concentrations of the aqueous species in the continuum model are solved in the same way.

6. Results

In this section, we first present the results on the pore-scale heterogeneities of concentrations and reaction rates for case A, then briefly compare the pore-scale heterogeneities in case A and case B. After that, the evolution of the continuum-scale reaction rates are described, and the scaling effect is examined in the context of continuum modeling and volume-averaging. Finally, the resulting concentrations in the network model are examined with respect to network-scale equilibrium relationships.

6.1. Pore-scale heterogeneities: case A

The locations of reactive pores for two orthogonal planes in the network are shown in Fig. 2. For the simulation conditions of case A, the steady-state concentration fields of log[Ca $^{2+}$] and pH for the $y = 5$ plane are shown in Fig. 3. In general, the Ca $^{2+}$ concentrations and pH values are lower in pores near the left boundary due to the low calcium content and acidic condition of the inflowing water. As the inflowing water encounters reactive minerals, anorthite slowly dissolves and releases Ca$^{2+}$. Correspondingly, there is an increase in pH due to the increase in alkalinity. The concentrations of Ca$^{2+}$ and the pH in reactive pores are generally higher than those in nearby non-reactive pores, as indicated by the similar patterns of high-concentration clusters and low pH clusters (Fig. 3), to that of reactive pore clusters (Fig. 2). Non-reactive pores may also have elevated Ca$^{2+}$ concentrations and pH if they are close to reactive pores. For example, near the inflow boundary where $x$ is approximately 17 or 18, the high [Ca$^{2+}$] and pH are due to the proximity of these pores to the reactive clusters in the $y = 3$ and $y = 4$ layer.

The pore-scale concentrations vary considerably over the network: the values of [Ca$^{2+}$] cover 2.5 orders of magnitude, and hydrogen ion concentrations cover approximately half an order of magnitude. The frequency

---

Fig. 2. Locations of reactive pores for the $y = 5$ plane and for the $x = 18$ plane. Reactive pores are shown in red color.

Fig. 3. For one layer of pores in the middle of the network ($y = 5$): steady-state profiles of log[Ca$^{2+}$] (a) and pH (b). Boundary fluid flows in from the left (at $z = 0$).
distributions of log[Ca\(^{2+}\)] and pH for pores in the entire network are shown in Fig. 4 a and b. Both distributions are highly skewed. For Ca\(^{2+}\), approximately 9% of the pores have the minimum concentration values, which is equal to that of the inflowing boundary. Similarly, approximately 15% of the pores have the minimum value of pH. Calcium concentration has a bimodal distribution, in which a second peak arises at the large end of the concentration range.

For comparison, the distributions of log[Ca\(^{2+}\)] and pH in non-reactive pores are shown in Fig. 4 c and d. Because the non-reactive pores occupy 90% of the pores, their concentration distributions bear great similarity to the distributions for all pores, except at the right end of the concentration range, where concentrations in reactive pores play an important role. The distributions of concentrations in reactive pores have very different shapes from those for non-reactive pores, as shown in Fig. 4e and f (Note the different scale of frequency axis).

They are less skewed, and have peaks that fall in the large ends of the concentration ranges, indicating the relatively high [Ca\(^{2+}\)] and pH in reactive pores.

Also shown in Fig. 4a and b are the logarithm of volume-averaged calcium concentration and the logarithm of volume-averaged hydrogen ion concentration (referred to hereafter as volume-averaged pH), as well as the logarithm of the uniform concentrations calculated from the continuum model. While both volume-averaged concentrations lie in the mid-range of the distributions for the entire network, they fall in the tail region at the low end of the concentration range in reactive pores. For pH, more than 90% of the reactive pores have values larger than the volume-averaged value. The uniform concentrations from the continuum model represent concentrations in reactive pores better, as they are closer to the modes of the concentrations in reactive pores.

Due to the dependence of reaction rates on aqueous concentrations, the pore-scale concentration heterogeneities lead to spatial variations in saturation states, and in reaction rates. Fig. 5 shows the steady-state distributions of saturation indexes (see Section 2.1) and reaction rates for anorthite. The saturation states cover approximately 10 orders of magnitude. However, they are all orders of magnitude smaller than unity, and therefore anorthite dissolution remains far from equilibrium in all pores. As such, anorthite dissolution rates are largely determined by inherent mineral reactivity and the activities of catalytic species. That is, the value of 1 – ΩA in Eq. (7) is approximately unity. In fact, at steady state, all the pores in the network have acidic pH conditions such that the anorthite dissolution rate in each pore is approximately:

\[
 r_{A,i} \approx k_H \left( \frac{H^+}{\Omega_A} \right)^{1.5}.
\]  

(37)

Thus, spatial variations in anorthite dissolution rates are entirely due to spatial variation in pH in reactive pores. As is consistent with the exponent in Eq. (37), the variance in the logarithm of \( r_{A,i} \) is roughly twice that of pH (as expected given that the square of 1.5 is 2.25). The hydrogen ion concentrations span roughly 0.65 orders of magni-
tude, and the anorthite dissolution rates cover approximately one order of magnitude, as shown in Fig. 5b.

As shown in Fig. 6, for kaolinite, the saturation indexes include both positive and negative values, indicating that dissolution is occurring in some pores and precipitation is occurring in others. As the values of saturation state are either in a similar order of magnitude as unity, or orders of magnitude larger, the spatial variation of local rates depends not only on pH heterogeneities, but also on concentration heterogeneities of Al$^{3+}$ and H$_4$SiO$_4$, with the dependence on $\{H^+\}$ raised to the power of approximately $5.0$ (refer to Eqs. (9) and (10)). Such high dependence of rates on concentrations results in large spatial variations in kaolinite reaction rates, as illustrated in Fig. 6b. In about 6% of reactive pores, dissolution occurs and the rates span almost two orders of magnitude; in more than 90% of reactive pores, precipitation occurs, and the rates span approximately 4.6 orders of magnitude. This is an interesting illustration of the effect of pore-scale heterogeneity.

### 6.2. Comparison of pore-scale heterogeneities for case A and B

Case B is different from case A in that its boundary fluid is much less acidic (with pH of 4.1, compared to 2.9 in case A). Due to the sensitivity of anorthite dissolution rate on hydrogen ion concentration, the reduced acidity results in smaller anorthite dissolution rates, and smaller differences in concentrations between reactive and non-reactive pores. As illustrated by Fig. 7a, the anorthite dissolution rates shift to smaller values, and cover a much narrower range, as compared to case A (Fig. 5b). For kaolinite reaction (Fig. 7b), not only do the rates cover a smaller range than in case A (Fig. 6b), but the reaction occurs only in the precipitation direction. Such differences in pore-scale heterogeneities between the two cases are quantified by the differences in the range of concentration and reaction rates in Table 3.

### 6.3. Comparison between continuum-scale reaction rates

To illustrate the differences between the rates from the continuum model and the continuum-scale rates from the network model, Fig. 8 shows $R_C$ and $R_N$ as a function of time for the two reactive minerals in case A. The anorthite dissolution rate increases with time, due to the gradual influx of highly acidic aqueous phase from the boundary. Eventually, the system reaches steady state, where the aqueous concentrations and reaction rates become constants. The release of Ca$^{2+}$,
Al$^{3+}$, and H$_4$SiO$_4$ from anorthite dissolution leads to the oversaturation of the aqueous phase with respect to kaolinite. As such, kaolinite precipitates, and the increase in its precipitation rate parallels the increase in anorthite dissolution rate.

For each reactive mineral, the two models predict very different evolutions of the reaction rates. The continuum model overestimates the anorthite dissolution rate for the duration of the simulation. At steady state, it overestimates the rate by 30%. For kaolinite, the continuum model initially predicts its dissolution (although, these slightly positive values of $R_C$ are difficult to see in Fig. 8b), which contradicts the prediction from the network model. Over time, the continuum model predicts kaolinite precipitation, but with a much smaller rate. At steady state, it underestimates the kaolinite precipitation rate by almost two orders of magnitude (with the ratio of $R_C$ over $R_N$ being 0.05). Overestimation of the anorthite dissolution rate and underestimation of kaolinite precipitation rate by the continuum model lead to an overestimation of the net dissolving rate of the solid phase by approximately a factor of 1.5 at steady state.

Fig. 9 shows a comparison of the time evolution of the rate calculated using volume-averaged concentration, $R_{0N}$, and the continuum-scale rate from the network model, $R_N$, for each mineral. The values of $R_{0N}$ underestimate those of $R_{NA}$ at the very start of the simula-

![Fig. 8. For case A: comparison of $R_C$ and $R_N$ evolution for anorthite (a) and kaolinite (b).](image1)

![Fig. 9. For case A: comparison of $R_{0N}$ and $R_N$ evolution for anorthite (a) and kaolinite (b).](image2)

Table 3

<table>
<thead>
<tr>
<th></th>
<th>$[Ca^{2+}]$</th>
<th>$[H^+]$</th>
<th>$r_{A_i}$</th>
<th>$r_{K_i}$</th>
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</thead>
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<td>0.65</td>
<td>1.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Case B</td>
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<td>0.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Values shown for each variable are the ranges in order of magnitude.

References:

tion, and then significantly overestimate $R_{N,A}$. At steady state, the ratio of $R_{N,A}^\prime$ over $R_{N,A}$ is 2.3. For kaolinite, $R_{N,K}^\prime$ predicts its dissolution over the entire time period (although $R_{N,K}^\prime$ is close to zero, it is actually positive), which is in contrast with the precipitation predicted by the network model. At steady state the ratio of $R_{N,K}^\prime$ over $R_{N,K}$ is $-1.8 \times 10^{-3}$. As such, values of $R_{N,K}^\prime$ not only predict the wrong reaction rate, but also the wrong reaction direction.

Compared to those in case A, the differences between continuum-scale rates are much smaller in case B. Table 4 presents the differences between the continuum-scale rates for the two simulation scenarios, in terms of the ratios between continuum-scale reaction rates. For case B, these ratios are much closer to unity than in case A, which means that the scaling effect is much smaller. For example, the value of $\beta_K$ is positive in case B, indicating the correct prediction of reaction direction by using volume-averaged concentrations. This smaller scaling effect is attributed to the less significant pore-scale variations in concentrations and reaction rates.

### 6.4. Equilibrium relationships at the continuum scale

As a result of pore-scale concentration heterogeneities, the equilibrium relationships for instantaneous reactions that are applicable at the pore scale may not hold at the continuum scale. For example, in aqueous solutions under the temperature, pressure, and salinity conditions of these simulations, the product of the activities of hydrogen ion and hydroxide ion equals the equilibrium constant $6.6 \times 10^{-14}$. However, the ionic activity product (IAP) values calculated from volume-averaged activities are not equal to their equilibrium constants. To illustrate this we show the temporal evolution of logIAP in case A for the water dissociation reaction $H_2O = H^+ + OH^-$, and $Al^{3+}$ speciation reaction $Al^{3+} + 4OH^- = Al(OH)_4^-$. In Fig. 10. For both reactions, the deviations of logIAP from log $K_{eq}$ are very large at an early time period, where the IAP values are orders of magnitude different from the values of the equilibrium constants. At steady state, the deviations reach constant values, IAP values 1.1 and 3.6 times their respective values of equilibrium constants for water and aluminum. In case B, the deviations of IAP values from equilibrium constants are much smaller. For example, at steady state, the IAP values are 1.0 and 1.2 times their respective values of equilibrium constants for water and aluminum.

### 7. Discussion

Simulation results have shown that under highly acidic conditions relevant to geological CO$_2$ sequestration, heterogeneities in physical and mineral properties can lead to pore-scale heterogeneities in concentrations and reaction rates, which results in scaling effects of reaction kinetics. With different boundary pH values, case A and case B differ significantly in the extent of the scaling effect. In both cases, the time scale of advection, calculated as the ratio of the network length to average flow velocity ($L/q$), is approximately 100 s. The diffusion time scale, calculated as the ratio of the square of the network length to the diffusion coefficient, is approximately 1000 s. The dashed lines indicate the value of log $K_{eq}$ for each reaction.

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**Table 4**

Comparison of the ratios of continuum-scale reaction rates for the two simulation scenarios

<table>
<thead>
<tr>
<th></th>
<th>$\eta_A$</th>
<th>$\eta_K$</th>
<th>$\beta_A$</th>
<th>$\beta_K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case A</td>
<td>1.3</td>
<td>0.046</td>
<td>2.3</td>
<td>-0.0018</td>
</tr>
<tr>
<td>Case B</td>
<td>1.1</td>
<td>0.56</td>
<td>1.2</td>
<td>0.089</td>
</tr>
</tbody>
</table>

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**Fig. 10.** Evolution of logIAP for case A: (a) water dissociation reaction $H_2O = H^+ + OH^-$; (b) $Al^{3+}$ speciation reaction $Al^{3+} + 4OH^- = Al(OH)_4^-$. The dashed lines indicate the value of log $K_{eq}$ for each reaction.
length to the diffusion coefficient \((L^2/D)\), is about \(10^3\)–\(10^6\) s. The time scale of reaction, however, differs in case A and B due to their different boundary pH values. For purpose of comparison, we estimate the time it would take for reaction alone to effect a change in concentration from the initial to the steady state condition. In case A, the steady-state anorthite dissolution rate is in the order of \(10^{-10.6}\) mol s\(^{-1}\) (almost three orders of magnitude larger than the average rate in individual pores due to the much larger surface area of reactive minerals at the network scale). Initially the anorthite dissolution rate is orders of magnitude smaller because of the high initial pH values. Therefore, on average, the anorthite dissolution rate is about \(10^{-10.9}\) mol s\(^{-1}\). In case A, the concentrations of calcium varied from the initial \(7.9 \times 10^{-6}\) to \(1.58 \times 10^{-4}\) mol L\(^{-1}\) at steady state, which corresponds to a mass change of \(8.9 \times 10^{-10}\) mol. As such, the corresponding reaction time scale is 70 s, slightly smaller than the advection time scale. This means that the rates of advection and reaction are comparable, with none of them dominating. The comparable rates of reaction and advection lead to large spatial variations in concentrations, which results in relatively large scaling effect. In case B, due to the much larger pH value, the average anorthite dissolution rate is in the order of \(10^{-12.7}\) mol s\(^{-1}\), corresponding to a reaction time scale on the order of \(10^3\) s that is much larger than the advection time scale. Compared to case A, the extent of spatial variations in concentrations is much smaller, and the scaling effect is smaller.

With the same extent of spatial variations in concentrations, spatial variations in reaction rates can vary for different reactions, due to the difference in rate dependence on concentrations. In general, for a given range of spatial variation in concentration, the larger the rate dependence on concentration, the larger the spatial variation in local reaction rates. For the anorthite reaction, the very large range of calcium concentrations observed in case A has little effect on the spatial variation in rates, because in a system in which anorthite dissolution is highly thermodynamically favorable and under acidic conditions, the anorthite dissolution rate is dependent only on hydrogen ion concentration. Although the variation of hydrogen ion concentration in case A spans less than one order of magnitude, due to the nonlinear dependence of the anorthite dissolution rate on the hydrogen ion activities, the values of \(T_{A}\) cover more than an order of magnitude. For case B, the nonlinear dependence of reaction rate on \([H^+]\) also produces greater variability in the reaction rate, but the effect is much less important than in case A. For kaolinite precipitation, due to the high dependence of rates on hydrogen ion activity (raised to the power of \(-5.0\)), the pH variations lead to significant spatial variation in rates, spanning approximately five orders of magnitude in case A and two orders of magnitude in case B. Nonlinear dependence on activities of chemical species, especially on \([H^+]\), is commonly observed for rate laws for mineral dissolution and precipitation reactions \([9,87]\). As such, we expect to see larger or smaller spatial variation in local reaction rates than those in local concentrations, depending on the mathematical form of the rate laws.

The very large spatial variation in local concentrations has significant implications for the error produced by reaction rates estimated using volume-averaged concentrations, as is analogous to what is done when interpreting field measurements using inverse modeling. The consumption of hydrogen ions from anorthite dissolution raises the pH such that the pH in reactive pores is higher than the pH in the non-reactive pores. However, volume averaging is a non-discriminating calculation that includes concentrations in both reactive and non-reactive pores. Because the reactive pores occupy only 10% of the network, the volume-averaged pH is more representative of pH in non-reactive pores, which underestimates the pH in reactive pores. Because chemical reaction rates depend only on concentrations in reactive pores, the concentrations in non-reactive pores play no role in driving or inhibiting the reaction rates in the porous medium (except indirectly via mass transport mechanisms). Therefore, although volume averaging produces concentrations that are true representations of the total mass of a species per total fluid volume, these values do not always serve as good indicators of the concentrations that drive the chemical reactions. Our work has shown that when volume-averaged concentrations are used in the prediction of continuum-scale reaction rates, significant errors can result and the scaling effect is large, especially in case A where there exist significant differences between concentrations in reactive and non-reactive pores. These errors led to the overestimation of the anorthite dissolution rate and the incorrect prediction of kaolinite reaction direction. In case B, with smaller discrepancies between concentrations in reactive and non-reactive pores, the scaling effect is much smaller.

A discrepancy between the reaction rate from the continuum model and that from the network model was also observed, especially in case A. This difference was less significant than the error produced from volume-averaging. The difference between \(\text{Re}_C\) and \(\text{Re}_N\) may appear to be small, however, this “small” difference in rates can lead to significant differences in predictions of the dynamics of reactive transport processes for a longer time scale. Overestimation of mineral dissolution rates by a factor of 2 will nominally lead to underestimation of reaction time scales by a factor of half. Furthermore, in models that predict long-term reaction progress, the overestimation of reaction rates will eventually overestimate the rates of porosity change. The strong dependence of permeability on porosity, often raised to the power of 3, can magnify the effects of the
initial “small” difference in reaction rates to produce a considerable error in the predicted flow field. The overestimated flow rates will further produce even larger reaction rates. Therefore, the error in rates can amplify to a significant amount, and the continuum model may ultimately predict highly erroneous reactive transport phenomena in subsurface systems (see [11], and references therein), and calls for efforts incorporating effects of porous medium heterogeneities in these relationships. This remains an open research question.

8. Summary and conclusions

This work establishes a novel methodology to use pore-scale network modeling to examine scaling effects in geochemical reaction rates. Pore-scale network models are constructed to represent the detailed physical and mineral properties of porous media. Reactive transport processes are simulated at the pore scale, and the continuum-scale reaction rate \( R_N \) is calculated for the entire network and is taken to be a measure of the “true” reaction rate. To explore the scaling effects, we also calculate two additional continuum-scale rates that ignore pore-scale heterogeneities and use the lab-measured reaction rates directly: \( R_C \), the rate obtained through continuum modeling, and \( R'_N \), the rate obtained using volume-averaged concentrations. Values of \( R_C \) are compared to \( R_N \) to examine the extent to which the continuum approach used in forward modeling would lead to erroneous prediction of reaction rates in porous media. Values of \( R'_N \) are compared with \( R_N \) to examine the extent to which field-measured concentrations, such as those used in inverse modeling, accurately predict the continuum-scale reaction rates.

The application of this method was illustrated with a pore-scale network model that represents a consolidated sandstone, with reactive minerals being anorthite and kaolinite occupying 10% of the pore space and gathering in pore clusters of size 2 \( \times \) 2 \( \times \) 15. The network contains 9000 pores, corresponding to the spatial scale of several millimeters in \( x \)-, \( y \)-, \( z \)-direction. Simulations were run under conditions relevant to CO\(_2\) sequestration: one with the boundary fluid in equilibrium with a high pressure of CO\(_2\) (case A), and the other with a less amount of CO\(_2\) (case B).

Simulation results have shown that in case A, the relatively large anorthite reaction rates arising from the highly acidic boundary fluid leads to order-of-magnitude spatial variations in concentrations and reaction rates, which can be poorly represented by uniform or averaged concentrations from models that ignore pore-scale heterogeneities. As such, the rates calculated from these single-valued concentrations in lab-measured reaction rate laws would introduce large errors and the scaling effects are significant. Under such conditions, the equilibrium relationships that apply at the pore scale may not hold at the continuum scale, which suggests that common practice of reactive transport simulations may impose...
CO2 concentrations can produce conditions under which the scaling effects in the two cases suggest that elevated ally leads to smaller scaling effects. The differences in the scaling effects in the two cases suggest that elevated CO2 concentrations can produce conditions under which scaling effects are significant.

These findings have potentially significant implications for reactive transport modeling. In general, the significance of pore-scale heterogeneity will depend on a variety of factors, including, for example, hydrodynamic conditions, and the total amount and spatial distributions of reactive minerals. Although the observed significance of the pore-scale heterogeneities and scaling effect are specific to our current network model and simulation conditions, the results imply that elevated CO2 concentrations in deep aquifer systems can generate conditions under which scaling becomes important for reactive transport modeling. Under conditions where spatial heterogeneities exist and scaling becomes important, geochemical modeling must be approached carefully, and that general scaling laws incorporating the heterogeneity effect need to be developed.

Overall, pore-scale network modeling has proven to be an effective research tool to upscale reactive transport processes from the pore scale to the continuum scale. It allows for the investigation of details at the pore scale which cannot be done with traditional experimental studies, and thereby allows for identification of important pore-scale details that are essential to describe the reactive transport processes at the continuum scale. This novel application of pore-scale network modeling may be useful to study scaling issues associated with other geochemical reactions in heterogeneous porous media, and therefore is likely to provide new perspectives for resolving the long-standing lab-field rate discrepancy.

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Appendix A. Supplementary data

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References


