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Simulation of chemical reaction localization using a multi-porosity reactive transport approach

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ABSTRACT

Results of reactive transport laboratory experiments often suggest that pore scale heterogeneity induces localization of reactions (the generation of local micro environments favoring reactions that would not occur in a well-mixed Representative Elementary Volume, REV). Multi-Rate Mass Transfer (MRMT), which has been employed to reproduce hydrodynamic heterogeneity, may also be used to simulate geochemical localization. We extended the Water Mixing Approach (WMA) designed for single porosity media, to simulate chemical reactions caused by the mixing of mobile and immobile zones. The method is termed Multi-Rate Water Mixing (MRWM). The MRWM approach was employed to simulate laboratory experiments of CO₂-rich brine transport through carbonate rich samples (Luquot et al., 2016, in this issue). Chemical heterogeneity in space was reproduced by varying the mineral assemblages in immobile regions. This enabled us to reproduce the generally low pH environment while allowing for high pH local zones required for the localized precipitation of kaolinite, which has been observed in reality, but cannot be modeled with conventional reactive transport formulations. The resulting model is very rich, in that it can reproduce a broad range of pore scale processes in a Darcy scale model, and complex, in that the interaction between chemical kinetics and immobile zones physical parameters is non-trivial.

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1. Introduction

Reactive transport deals with geochemical processes that occur in porous media due to the physical transport of reacting chemical species. It plays a major role in many civil and/or environmental issues such as cleanup of contaminated aquifers, nuclear waste storage, mining and geological storage of CO₂. Reactive transport may be very complex and non-trivial. As a result, numerical models are an indispensable tool for understanding and predicting these processes. One problem encountered is the high level of heterogeneity, which can be both chemical and hydrodynamic. Reactive transport models typically assume local equilibrium with fast dissolution kinetic minerals. Even so, non-equilibrium is commonly observed and is attributed to this heterogeneity (Alcolea et al., 2008; Vogel et al., 2006). For instance, breakthrough curves

typically display tailing at late times (Valocchi, 1985; Carrera, 1993). This non-equilibrium may be due to diffusion into immobile regions, kinetic sorption or heterogeneity. This implies that reactive transport should be formulated as non-local in time which means that the concentration at a given point depends on its concentration history. A large number of formulations (Carrera et al., 1998; Dentz and Berkowitz, 2003; Haggerty and Gorelick, 1995; Silva et al., 2009; Sudicky, 1989), simulation approaches (Ray et al., 1997; Salamon et al., 2006; Suresh Kumar, 2008; Tsang, 1995; Willmann et al., 2008; Zhang et al., 2006, 2007) and analytical solutions (Toride et al., 1993) have been proposed to deal with non-local in time transport (see Dentz et al., 2011a, for a review).

In parallel with Darcy scale models, a number of researchers have overcome this non-locality by formulating transport at pore scale because chemical processes occur at pore scale (Steeff et al., 2005). One such formulation is the Lattice Boltzmann equation, which replaces the velocities of individual particles by a distribution function of velocities in which the population of particles moves (Benzi et al., 1992; Chen and Doolen, 1998; Kang et al., 2006; Acharya et al., 2007; Willingham et al., 2008). Another formulation is Smoothed Particle Hydrodynamics, which is based on the idea

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that a continuous field can be represented by a superposition of smooth bell-shaped functions centered on a set of points whereas the gradient of the field is given by the same superposition of the gradients of the smoothing function (Liu and Liu, 2010; Tartakovsky et al., 2007, 2009, 2015). A third option consists of simulating the pore network to explicitly simulate the pore volumes and connecting necks (Blunt, 2001; Blunt et al., 2002; Li et al., 2006; Meile and Tuncay, 2006; Raoof et al., 2010; Raoof and Hassanizadeh, 2012; Varloteaux, 2013). These formulations are very accurate in reproducing local physics, but are computationally demanding for large scale models or when many chemical species and reactions are involved. Moreover, the upscaling of the results to field scale has not yet been resolved.

Other researchers prefer continuous models at larger than pore scales to gain in computational cost and model simplicity. The classic approach consists on representing heterogeneity by a dispersion tensor, but it fails to quantify solute mixing accurately (Ginn et al., 1995; Kitanidis, 1988; MacQuarrie and Sudicky, 1990; Molz and Widdowson, 1988; Dreuzy et al., 2012), which is critical for reactive transport as reaction rates are driven by mixing (De Simoni et al., 2007). There are a number of approaches to quantify mixing rates more accurately. The most widely used are the Multi-Rate Mass Transfer (MRMT) and Continuous Time Random Walk (CTRW). MRMT is a non-local in time continuous formulation that simulates mass transfer between a mobile and multiple immobile regions by diffusive or first-order mass transfer terms (Benson and Meerschaert, 2009; Carrera et al., 1998; Donado et al., 2009; Fernandez-Garcia and Sanchez-Vila, 2015; Geiger et al., 2013; Gouze et al., 2008; Haggerty and Gorelick, 1995; Haggerty et al., 2000; Roth and Jury, 1993; Wang et al., 2005; Willmann et al., 2010; Zhang et al., 2007). Models similar to MRMT exist for diffusion from a fracture into the matrix of the rock (Cvetkovic et al., 1999; Gerke and van Genuchten, 1996; Grisak and Pickens, 1980; Małoszewski and Zuber, 1985; Moreno and Neretnieks, 1993; Shapiro, 2001). CTRW is a class of Random Walk methods in which not only particle displacements, but also time steps are modeled as a stochastic process (Montroll and Weiss, 1965; Berkowitz and Scher, 1998; Metzler and Klafter, 2000; Barkai and Cheng, 2003; Cortis, 2004; Dentz et al., 2004; Berkowitz et al., 2006). Its validity has been proven using pore network models (Bijeljic and Blunt, 2006). CTRW has been applied to reactive transport using particles explicitly, which is computationally demanding. But, in practice, CTRW and MRMT are equivalent (Dentz and Berkowitz, 2003; Neuman and Tartakovsky, 2009; Silva et al., 2009).

The latter methods have been used to study the effect of hydrodynamic heterogeneity on reactive transport. Most of these studies used simple chemical systems of one or more chemical reactions (e.g., Donado et al., 2009; Willmann et al., 2010). Other studies have focused on more complex chemical systems (Ayora et al., 1998; Steefel and Lichtner, 1998). Research has been carried out on specific surface area heterogeneity (Cvetkovic and Gotovac, 2014) and on network fracture heterogeneities (Cheng et al., 2003; Frampton and Cvetkovic, 2007; Painter et al., 2008). The effect of chemical heterogeneity was addressed by Dentz et al. (2011b), but on an abstract system that did not allow acknowledging explicitly that porous media consist of multiple mineral phases, which create their own local conditions and precipitation/dissolution reactions. We use the term geochemical localization to describe the creation of local micro environments favoring reactions that would not occur in media that are fully mixed at the Representative Elementary Volume (REV) scale. We argue that geochemical localization is driven by mineral heterogeneity at the pore scale and may cause reaction heterogeneity at such scale. Geochemical localization has been observed by Luquot et al. (2016, in this issue), who performed percolation experiments under in situ temperature, pressure and salinity conditions to predict the different chemical reactions which

Fig. 1. Schematic spatial mineralogy distribution. The top image displays the 'real' distribution. The central image shows a classical MRMT distribution without considering mineralogical localization. The bottom image shows the distribution of the mineral phases in several immobile zones connected to a mobile node.

can occur during the migration of CO_2 -rich brine at the Heletz site (Niemi et al., 2012, 2016). These authors verified their experimental results using the CrunchFlow code (Steefel, 2009) that regards dispersion as the only mixing process. They obtained good matches between the experimental and numerical results for the main dissolved and precipitated minerals with fast reaction kinetics (carbonates and gypsum). Nevertheless, secondary mineral reactions were not predicted accurately (e.g., K-feldspar dissolution and clay precipitation). They concluded that these secondary reactions, which may play an important role in the change of hydrodynamic properties, occur at scales smaller than the REV and cannot be taken into account in conventional reactive transport models that are based on the Advection-Dispersion Equation (ADE).

We conjecture that geochemical localization can be reproduced using multi-porosity formulations, such as MRMT, provided that geochemical heterogeneity is included in the model. The objective of this work is to test such conjecture and to gain further insight into the effect of mineralogical and hydrodynamic heterogeneity. To this end, the MRMT based method was used, varying the mineral composition of mobile and immobile zones (see Fig. 1). A simplified chemical system based on Luquot et al. (2016, in this issue), was employed. The mathematical formulation of reactive transport used in the MRMT approach is described in Section 2. In Section 3, we discuss the numerical solution of these equations, which basically consists of extending the Water Mixing Approach (WMA) of Soler-Sagarra et al. (2016, for publication) to MRMT, obtaining the proposed Multi-Rate Water Mixing (MRWM). Models definitions and their results are presented in Section 4. Finally, Section 5 is dedicated to discussion and conclusions.

2. Governing equations

The standard formulation for reactive transport is based on applying the ADE to all chemical species with sink/source terms to represent reactions (i.e., sinks for reactants and sources for reaction products). This leads to a complex set of N_s ADE (N_s is the number of species), which uses the vector concentrations $\mathbf{c}$ [M/L^3] as state variable, and N_r constraints (mass action laws for equilibrium reactions and rate laws for kinetic reactions) for the chemical reactions. The system may be simplified by the use of components.

These are obtained by multiplying the concentration vector by a full-ranked kernel matrix $\mathbf{U}$, dimensions $(N_s - N_e) \times N_s$, where N_e is the number of equilibrium reactions so that equilibrium reaction rates are eliminated (Lichtner, 1985; Steefel and MacQuarrie, 1996). The advantage is twofold: equilibrium reaction rates are eliminated from the system and the dimension of the problem is reduced from $N_s + N_r$ to $N_s - N_e$. Therefore, the reactive ADE is usually formulated as mass balances of components. A variety of approaches are available to define the components (Fang et al., 2003; Friedly and Rubin, 1992; Krättele and Knabner, 2005, 2007; Molins et al., 2004; Saaltink et al., 1998; De Simoni et al., 2005; Yeh and Tripathi, 1989). Here, we use the method of Saaltink et al. (1998), which complements the aqueous reactions component matrix with a matrix $\mathbf{E}$ to eliminate rapid dissolution/precipitation reactions, further reducing the number of unknowns and equations.

We used the above formulation in a MRMT framework (Donado et al., 2009; Willmann et al., 2010) but the framework was specially designed to allocate different chemical systems in each immobile zone. Therefore, the system of equations contains not only mass balances (transport equations) but also different chemical system in the mobile and immobile zones. The set of equations to be resolved may be written in compact form as:

$$\phi_m \frac{\partial \mathbf{u}_{am}}{\partial t} = \nabla \cdot (\mathbf{D} \nabla \mathbf{u}_{am}) - \mathbf{q} \cdot \nabla \mathbf{u}_{am} - \sum_{j=1}^{N_{im}} \alpha_j (\mathbf{u}_{am} - \mathbf{u}_{aim,j}) + \mathbf{f} + \mathbf{f}_{chem,m} \quad (1)$$

$$\phi_{im,j} \frac{\partial \mathbf{u}_{aim,j}}{\partial t} = \alpha_j (\mathbf{u}_{am} - \mathbf{u}_{aim,j}) + \mathbf{f}_{chem,im,j} \quad j = 1, \dots, N_{im} \quad (2)$$

$$\log \mathbf{c}_2 = \mathbf{S}_a (\log \mathbf{c}_1 + \log \gamma_1) - \log \gamma_2 - \log \mathbf{k}_a \quad (3)$$

$$\log \mathbf{c}_s = \mathbf{S}_s (\log \mathbf{c}_1 + \log \gamma_1) - \log \gamma_s - \log \mathbf{k}_s \quad (4)$$

$$0 = \mathbf{S}_{min} (\log \mathbf{c}_1 + \log \gamma_1) - \log \mathbf{k}_{min} \quad (5)$$

$$\mathbf{c}_a = \begin{pmatrix} \mathbf{c}_1 \\ \mathbf{c}_2 \end{pmatrix} \quad (6)$$

$$\mathbf{u}_a = \mathbf{E} \mathbf{U}_a \mathbf{c}_a \quad (7)$$

$$\mathbf{u}_s = \mathbf{E} \mathbf{U}_s \mathbf{c}_s \quad (8)$$

$$\mathbf{f}_{chem,l} = \mathbf{E} \mathbf{U}_s^t \mathbf{r}_k(\mathbf{u}_a, \mathbf{u}_s) - \phi_l \frac{\partial \mathbf{u}_s}{\partial t} \quad l = m, im \quad (9)$$

In these equations, subscript a , s and min stand for aqueous, sorbed and mineral concentrations and components, respectively, and m and im refer to mobile and immobile zones, respectively. Eq. (1) defines the transport equation in mobile domains but the third term in the right hand side represents a linear mass exchange between mobile and immobile zones. In this equation, vector $\mathbf{u}$ [M/L^3] contains component concentrations defined by Eqs. (7) and (8), ϕ [-] is porosity, t [T] time, $\mathbf{D}$ [L^2/T] the hydrodynamic dispersion tensor, $\mathbf{q}$ [$L^3/L^2/T$] Darcy flux, $\mathbf{f}$ [$M/L^3/T$] is a non-chemical sink/source term, $\mathbf{f}_{chem}$ [$M/L^3/T$] is a sink/source term for kinetic and sorption reactions and α_j [T^{-1}] is a first-order mass transfer rate coefficient. Eq. (2) defines the specific mass balance in the j th immobile region as a linear exchange with the mobile domain. N_{im} is the number of immobile zones connected to a mobile. Note that the sum of Eqs. (1) and (2) expresses the total mass balance in both mobile and immobile zones. Eqs. (3), (4) and (5) describe the mass action laws for equilibrium reactions in the aqueous, surface (sorption and cation exchange) and mineral phases, respectively. The vector of aqueous species concentrations ($\mathbf{c}_a$) is split into two vectors $\mathbf{c}_1$ and $\mathbf{c}_2$ of primary and secondary concentrations (Eq. (6)) such that $\mathbf{c}_2$ can be expressed as an explicit function of $\mathbf{c}_1$ by means

of Eq. (3). Vector $\mathbf{y}$ has the same subscripts as $\mathbf{c}$ and contains the activity coefficients. $\mathbf{S}_k$ and $\mathbf{r}_k$ in (9) are the stoichiometric matrix and the vector of reaction rates for kinetic reactions, respectively. Note that in the absence of kinetic reactions and adsorption, component $\mathbf{u}_{am}$ can be resolved as a conservative transport problem.

In these equations, the set of chemical reaction occurring at any point and defined by the stoichiometric matrices $\mathbf{S}$ are space dependent. That is, different chemical systems can be defined in different portions of the domain to represent large scale heterogeneity or in different immobile zones to represent sub-REV (pore scale) chemical heterogeneity. Therefore the definition of components will also be space dependent. A potential source of conflict may arise from adjacent cells with different chemical systems and thus different components. To circumvent them, we adopt the rule “dressing code defined by the host”, meaning that the mass balance of a cell, which can include contributions from adjacent cells, is defined for the components of the chemical system of that cell. This way, components are defined at every point with the local chemical system.

3. Numerical formulation

The solution to the mathematical equations in the previous section consists of extending the WMA of Soler-Sagarra et al. (2016, for publication) to MRMT by adding the mixing of mobile and immobile zones. In essence, WMA can be viewed as an explicit Eulerian-Lagrangian formulation. We use here an isochronal grid, where travel time between nodes equals the time step, which facilitates simulating advection by simply displacing concentrations from one cell to the next one downstream. Dispersion is simulated by mixing water of a cell with that of adjacent cells. The method is well suited to advection dominated problems. In this way we can express the aqueous concentration of a component at a mobile cell i as a function of concentrations of adjacent cells at a previous time step:

$$\mathbf{u}_{am,i}^{k+1} = \mathbf{u}_{am,i}^k + \sum_{n=1}^{Nm} \lambda_{in} (\mathbf{u}_{am,n}^k - \mathbf{u}_{am,i}^k) + \sum_{j=1}^{N_{im}} \lambda_{ij} (\mathbf{u}_{aim,j}^k - \mathbf{u}_{am,i}^k) + \mathbf{R}_i \quad (10)$$

where subscript i - indicates the position of i th cell at time step k , i.e. the upstream cell if an isochronal grid is used, λ_{in} is the mixing ratio, i.e. the proportion of n cell water that mixes with i cell water during the time step, N_m and N_{im} are the number of mobile and immobile cells connected to cell i , respectively, and $\mathbf{R}_i$ is the vector of contributions from kinetic and sorption reactions to aqueous components. For the sake of simplicity, the non-chemical sink/source term is represented by one of the mixing terms n . Therefore λ [-] can have different expressions depending on whether they represent the mixing fraction with adjacent mobile cells, the source term and exchange with the immobile zone, respectively.

$$\lambda_{in} = D_{in} \frac{A_{in} \cdot \Delta t}{L_{in} \cdot \phi_{m,i} \cdot V_i} \quad (11)$$

$$\lambda_{in} = \frac{Q_i}{\phi_{m,i} \cdot V_i} \Delta t \quad (12)$$

$$\lambda_{ij} = \frac{\alpha_{ij}}{\phi_{m,i}} \Delta t \quad (13)$$

where Δt is the time step, D_{in} [L^2/T] is the dispersion coefficient at the i - n interface, i.e. longitudinal dispersion in the flow direction or transverse dispersion, with area A_{in} [L^2], at a distance L_{in} [L], V_i is

the water volume of the cell, and Q_i is the flow rate of sources into cell i . R_i [$M/L^3/T$] in Eq. (10) is given by

$$R_i = u_{sm,i}^k - u_{sm,i}^{k+1} + \frac{EUS_k^t r_k(u_{am,i}^k)}{\phi_{m,i}} \Delta t \quad (14)$$

Advection is defined through $u_{am,i}^k$. Using an isochronal one dimensional mesh allows us to write

$$u_{am,i}^k = u_{am,i-1}^k \quad (15)$$

Substituting (15) into (10) yields:

$$u_{am,i}^{k+1} = \lambda_{ii} u_{am,i-1}^k + \sum_{n=1}^{Nm-1} \lambda_{in} u_{am,n-1}^k + \sum_{j=1}^{Nim} \lambda_{ij} u_{aim,j}^k + R_i \quad (16)$$

$n \neq i$

Note that the mixing ratio λ_{ii} [-] is simply the fraction of water that is not exchanged with adjacent cells:

$$\lambda_{ii} = 1 - \sum_{n=1}^{Nm-1} \lambda_{jn} - \sum_{j=1}^{Nim} \lambda_{ij} \quad (17)$$

$n \neq i$

A full numerical analysis of the solution method falls beyond the scope of this paper. Let us simply state here that the method is consistent, but stability is conditional and requires $\lambda_{ii} > 0$, which limits the maximum time step to be used. If this condition is met and an isochronal mesh is used, convergence is second-order for conservative transport. Speciation would have to be done once the components were calculated. In practice, however, speciation is done simultaneously with mixing calculations (Eq. (10)), because species concentrations are necessary for evaluating R_i , by means of Eq. (14). This calculation is also explicit and we assume that it will also be conditionally stable, but we have not been able to derive an easy to apply stability condition. Therefore, we have made sensitivity analysis to the time step size. In the results presented here, the solution was not sensitive to the time step. The algorithm is described by Soler-Sagarra et al. (2016, for publication) and is linked to chemical library CHEPROO, which is an Object Oriented code for geochemical calculations (Bea et al., 2009).

For the sake of simplicity, porosity changes caused by mineral precipitation/dissolution were neglected. Hence, flux may be regarded as steady state. Otherwise, the isochronal mesh would have to be recalculated at each time step and several parameters (such as permeability and mass transfer rate) should be recalculated for each new element causing numerical errors.

4. Application models

4.1. Model descriptions and parameters

The MRWM method was applied to a simplification of the G5 laboratory experiment performed by Luquot et al. (2016, in this issue). The G5 experiment involved injecting CO_2 rich brine into a sandstone sample from Heletz at a low flow rate. In order to study the localization of chemical reactions, we built four numerical models (Fig. 2) by varying the hydrodynamic and/or chemical heterogeneity. However, parameters such as inflow rate, porosity, domain bulk volume or total surface area of every mineral (except WMA-2) remained constant for all models.

We used a one-dimensional domain discretized by an isochronal mesh (i.e., transit time per cell equal to the time step). The first two models (WMA 1 and WMA 2) consisted of 150 mobile cells, each with a volume of $3.85 \times 10^{-9} m^3$. The other two models (MRWM 1 and MRWM 2) had the same total volume as the WMA models but

Fig. 2. Conceptual sketch of the different simulations. WMA and MRWM schemes are represented with 4 and 2 mobile nodes scheme, respectively. WMA numerical models use 150 mobile nodes whereas MRWM models use 75 mobile nodes.

Table 1

Physical hydrodynamic parameters used in the models. First column refers to those used in all models. First row of the second column refer to WMA models and third row to MRWM models, respectively.

All models	
Initial porosity (ϕ_m)	0.19
Input flow (Q)	$8.33 \times 10^{-10} m^3 s^{-1}$
Domain length	$1.5 \times 10^{-2} m$
Time increment (Δt)	0.904762 s
Mix. ratio mob. cells (λ_{in})	0.1
Mobile cell volume	$3.8 \times 10^{-9} m^3$
Specific models WMA 1, WMA 2	
Mobile nodes	150
Specific models MRWM 1, MRWM 2	
Mobile nodes	75
Immobile cell volume	$1.9 \times 10^{-9} m^3$
Initial immobile porosity (ϕ_{im})	0.19
Mixing ratio mobile-immobile cells (λ_{ij})	9.9×10^{-5}

only half of this volume was defined as mobile. The MRWM mobile cells (75) have the same volume as the WMA cells ($3.85 \times 10^{-9} m^3$). Therefore, the time step is the same for all the models because so are the flow rate, cell volume and mobile porosity. The fact that water flows only through half of the domain (the other half is immobile) causes velocity to be twice as high (hence, MRWM cells have lengths twice that of WMA cells and the number of mobile MRWM cells is half that of WMA cells).

Each mobile cell was connected to 2 immobile cells of $1.925 \times 10^{-9} m^3$ in the MRWM models. Hydrodynamic parameters are summarized in Table 1. The time step was set to 0.905 s with a total simulated time of 5 h. According to Eq. (11) this gives a mixing ratio of 0.1 between the mobile cells. With a transfer coefficient (α) of $2.07876 \times 10^{-5} s^{-1}$, the water mixing ratio between mobile and immobile cells becomes 9.9×10^{-5} , 1010 times lower value than for exchange between mobile cells.

Model mineralogical compositions are motivated by those of Luquot et al. (2016, in this issue), only simpler to facilitate interpretation (see Table 2). The only carbonate phase is dolomite. The model considers two minerals with fast reaction kinetics (dolomite and gypsum) as well as three slowly reacting minerals (quartz, K-feldspar and kaolinite). Total porosity (18.8%), rate laws for reacting minerals (Table 3) and effective reactive surface areas were taken equal to those of Luquot et al. (2016, in this issue) for experiment G5. The initial surface areas of secondary minerals (gypsum and kaolinite) were set to $1 m^2/m^3$ to initiate the precipitation. Gypsum was assumed initially present in small concentrations.

The brine composition is shown in Table 3. The composition of the injected solution is the same as that of the initial solution, after adding 0.11 mol of CO_2 per kg of water (equilibrium with CO_2 at 18 bar). This lowers pH and renders the solution unsaturated with respect to the main minerals.

Table 2

Brine composition of the Heletz field and those used here as well as the saturation index for the different minerals used in experiment G5 (Luquot et al., 2016, in this issue).

Brine compositions (mol/kg _w)			
Heletz brine eq. Gypsum		Brine composition used here	
Element	Concentration	Concentration pore water	Concentration injected solution
Ca	6.88×10^{-2}	6.88×10^{-2}	6.88×10^{-2}
Cr	1.29×10^{-6}	–	–
Cu	2.79×10^{-5}	–	–
Fe	2.17×10^{-5}	–	–
K	1.08×10^{-2}	1.08×10^{-2}	1.08×10^{-2}
Mg	2.13×10^{-2}	2.13×10^{-2}	2.13×10^{-2}
Mn	1.05×10^{-6}	–	–
Na	7.68×10^{-1}	7.88×10^{-1}	7.88×10^{-1}
Ni	3.03×10^{-7}	–	–
S	3.21×10^{-2}	2.48×10^{-2}	2.48×10^{-2}
Si	4.70×10^{-5}	4.70×10^{-5}	4.70×10^{-5}
Sr	1.13×10^{-4}	–	–
Cl	7.99×10^{-1}	8.99×10^{-1}	8.99×10^{-1}
Al	3.46×10^{-7}	3.46×10^{-7}	3.46×10^{-7}
C	3.28×10^{-4}	3.28×10^{-4}	1.10×10^{-1}
pH	7.30	7.30	2.33
Saturation index			
Mineral	log(IAP/K)	log(IAP/K)	
Quartz	–0.85	–0.81	
Dolomite	0.00	–11.94	
K-Feldspar	–1.33	–12.54	
Kaolinite	–0.05	–12.69	
Gypsum	0.00	0.00	

Table 3

Simplified mineral composition of the Heletz sandstone and parameters used in numerical models. Values of E_a are taken from Palandri and Kharaka (2004). Illite, ankerite and pyrite are not considered here.

Mineral compositions and reactive parameters								
Heletz mineral composition		Mineral composition used here and the corresponding reactive parameters						
Mineral	wt. %	wt. % ^{a, b}			Reactive surface area (m ² /m ³)	$k_{m,25}$ (mol m ^{–2} s ^{–1})	n H ⁺	E_a (kcal mol ^{–1})
		Zone_q,d,kf	Zone_q,d	Zone_q,kf				
Quartz	60.06 ± 2.13	67.28	75.19	59.39	4300	3.98×10^{-14}	–0.3	21.72
K-Feldspar	17.44 ± 2.05	20.25	0	40.49	4500	8.71×10^{-11}	0.5	12.36
Dolomite	8.87 ± 0.23	12.35	24.69	0	150	6.46×10^{-4}	0.5	8.63
Kaolinite	2.24 ± 1.31		0		1	4.90×10^{-12}	0.77	15.75
Gypsum	2.30 ± 0.84		0.12		1	1.62×10^{-3}	–	0
Illite	5.62 ± 0.93							
Ankerite	2.95 ± 0.11							
Pyrite	0.52 ± 0.11							

^a The zero values indicate the potential precipitated minerals taken into account in the model.

^b q, d and kf are respectively used for quartz, dolomite and k-feldspar.

Forty-nine aqueous species were considered in the simulations. All the equilibrium constants (log K at 60 °C), including those for the mineral reactions, and stoichiometric coefficients were taken from the EQ3/6 database (Wolery et al., 1990). Activity coefficients were calculated using the extended Debye–Hückel formulation (b-dot model) with the parameters listed in the database.

4.2. WMA-1: model with homogeneous mineral zones

The WMA-1 model represents a homogeneous mineral distribution along the core sample with transport dominated by advection. It has the same configuration as the one used by Luquot et al. (2016, in this issue). The resulting dissolution and precipitation processes are in agreement with those of Luquot et al. (2016, in this issue) despite our simplified chemical system. The total volume of dissolved and precipitated minerals at the end of the simulation is presented in Table 4. We predict high dolomite dissolution near the sample inlet, which diminishes near the outlet (Fig. 3b). As a result, pH increases (Fig. 3a). The rate of dolomite dissolution falls at 3 mm

from the inlet due to the dependence of dolomite dissolution kinetics on pH (Table 3). Gypsum precipitates near the inlet, peaking also at some 3 mm from the inlet, due to the build-up of Ca driven by dolomite dissolution (Fig. 3d). The dissolution of K-feldspar is not displayed in Fig. 3 because it is similar to that of dolomite in shape, albeit with lower rates, because of a similar dependence on pH.

Kaolinite precipitates are transient. Some kaolinite precipitates during very early times ahead of the pH front, which is slightly delayed by dolomite dissolution, promoted by the arrival of K-feldspar dissolution products. However, this kaolinite dissolves subsequently (Fig. 4) upon the drop in pH. In fact, most of the time, the experiment runs under quasi-steady state conditions, with a slight increase in pH over time, as dolomite dissolution causes a small reduction in specific area and, thus, in reaction rate. As a result, only a small, but growing, amount of kaolinite remains at the last 3 mm of the sample (Fig. 3c), where pH stays above 4.6 throughout the simulation (Fig. 3a). Kaolinite precipitation is often driven by K-feldspar dissolution (Carroll et al., 2013; Fu et al., 2009; Luquot et al., 2012; Tutolo et al., 2015). However, it can also be affected

Table 4
Total volume of dissolved and precipitated minerals for the four simulations.

Total dissolved and precipitated mineral (m ³)					
Model	Quartz	Dolomite	K-Feldspar	Kaolinite	Gypsum
WMA-1	-3.05×10^{-14}	-3.65×10^{-9}	-5.10×10^{-14}	5.96×10^{-21}	1.49×10^{-9}
WMA-2	-2.30×10^{-14}	-2.89×10^{-9}	-4.13×10^{-14}	0	1.41×10^{-9}
MRWM-1	-4.35×10^{-14}	-2.93×10^{-9}	-4.41×10^{-14}	1.50×10^{-18}	9.50×10^{-10}
Mobile	-1.14×10^{-14}	-2.84×10^{-9}	-4.00×10^{-14}	0	9.23×10^{-10}
Immobile	-3.21×10^{-14}	-9.23×10^{-11}	-4.13×10^{-15}	1.50×10^{-18}	2.72×10^{-11}
MRWM-2	-3.49×10^{-14}	-2.91×10^{-9}	-7.48×10^{-14}	4.28×10^{-19}	9.48×10^{-10}
Mobile	-1.13×10^{-14}	-2.86×10^{-9}	-4.03×10^{-14}	0	9.23×10^{-10}
Immobile q,kf	-5.31×10^{-15}	0	-3.45×10^{-14}	1.76×10^{-21}	1.14×10^{-11}
Immobile q,d	-1.83×10^{-14}	-4.80×10^{-11}	0	4.26×10^{-19}	1.36×10^{-11}

Fig. 3. Variation along the sample length for different time steps (0.075 h, 2.5 h and 5 h) of (a) pH, (b) dolomite (c) kaolinite, and (d) gypsum concentration changes for simulation WMA-1. The dashed green line shows the minimum pH at which kaolinite precipitation occurs. For comparison, the final time step of WMA-2 variation concentration of pH, gypsum and kaolinite are shown. The Representative Elementary Volume (REV) bulk volume is $3.85 \times 10^{-9} \text{ m}^3$.

by the total alkalinity of the solution leading to an oversaturation with respect to kaolinite, as shown in Fig. 3. The dashed green line indicates the pH necessary to precipitate kaolinite. Despite the foregoing, the volume of precipitated Kaolinite is negligible.

4.3. WMA-2: model with heterogeneous mineral zones

The WMA-2 model uses the same average mineralogy and transport conditions as the model WMA-1. However, the initial mineralogy is different because heterogeneity is acknowledged. Odd cells are only composed of quartz and K-feldspar. All even cells contain quartz and dolomite. Simulations were performed both with the same total mineral surfaces as in WMA-1 (i.e., multiplying by two the specific surfaces of dolomite and K-feldspar in the corresponding cells) and with the same specific mineral surfaces. Results for the first case are not shown because they are virtually identical to those of WMA-1, which implies that mineral localization along the mobile flow path does not affect much the results, at least in this kinetics controlled case. There, in the following, we restrict the discussion to the case in which specific surfaces are identical to those of WMA-1, which can be viewed

as an analysis of the sensitivity of model results to mineral surfaces.

Like the WMA-1 model, pH increases downstream as a result of dolomite dissolution (Fig. 3a). However, acid water penetrates deeper in the WMA-2 model and the change in the pH slope occurs at 6 mm instead of 3 mm. This is attributed to the slowdown in mineral distribution which implies that only half of the domain counteracts the input acidity. Dolomite and K-feldspar dissolution is slower than in the WMA-1 model (Table 4) despite the fact the model contains the same amount of mineral. Mineral distribution thus plays a role in the reaction. The reaction is transport-limited since the total amount of dolomite and K-feldspar remains identical.

No precipitation of kaolinite is predicted in the total mass balance in Table 4, because pH stays below 4.6 throughout the simulation (Fig. 3a). Nevertheless, as observed for WMA-1, kaolinite precipitates at early times ahead of the pH front (Fig. 4).

In the case of WMA-2 the fronts move faster with the result that no kaolinite remains after the simulated time of 5 h. Given that gypsum precipitation depends on dolomite dissolution, its peak is found further from the inlet than in the case of WMA-1 (Fig. 3d). In addition this peak is lower and more dispersed.

Fig. 4. Comparison of kaolinite concentration variation along the sample length for different early time steps for simulations WMA-1 and WMA-2. The Representative Elementary Volume (REV) bulk volume is $3.85 \times 10^{-9} \text{ m}^3$.

4.4. MRWM-1: model with homogeneous mineral immobile zones

Mobile and immobile zones, and their mineralogy are homogeneously distributed in the model MRWM-1, identical to those of WMA-1 (see Fig. 2).

As the volume of the mobile zone is smaller than in the previous models, the pore water velocity is higher. This leads to a deeper penetration of the acid water (Fig. 5), similar to that of model WMA-2. Dissolution of dolomite and K-feldspar in addition to gypsum precipitation occurs mainly in the mobile zone (Table 4). The pH remains relatively high in the immobile cells (around 5.3, Fig. 5) due to the limited exchange of acidity with the mobile zone. An autonomous equilibrium is established in immobile zones between the protons diffusing into the immobile zone and their consumption by dolomite dissolution. This moderate pH, together with the diffusion of Al and Si create favorable conditions for kaolinite precipitation in the immobile zone (see Fig. 5). In summary, limiting the diffusion of acidity is sufficient to promote chemical localization and favor the precipitation of kaolinite despite the fact that flowing water is too acid to sustain kaolinite precipitates.

4.5. MRWM-2: model with heterogeneous mineral distribution in immobile zones

Model MRWM-2 also contains mobile and immobile zones, but the mineralogy is heterogeneously distributed in the immobile zones using the same definition as in the model WMA-2. The results in the mobile zones are similar to those in MRWM-1 (Table 4 and Fig. 5). However, because of the mineralogical heterogeneity of the immobile zones, precipitation/dissolution is also different in each immobile zone. Obviously, dolomite dissolution occurs only in the immobile zone *q,d* (see Table 3 and Fig. 2). K-feldspar dissolves only in zone *q,kf*. The distribution of pH in the immobile zone *q,d* is similar to that of MRWM-1 (Fig. 5) because a similar autonomous equilibrium is reached between diffusion of protons and their consumption by dolomite dissolution. This causes kaolinite to precipitate, albeit in a smaller amount (Table 4) because K-feldspar is

Fig. 5. pH and kaolinite concentration variation along the sample length at final time steps for simulations WMA-1 (blue), MRWM-1 (green) and MRWM-2 (orange). Mobile zones are represented by continuum lines. Immobile zones are depicted by dashed or dotted lines. The Representative Elementary Volume (REV) bulk volume for WMA-1 is $3.85 \times 10^{-9} \text{ m}^3$. The REV bulk volume for MRWM models is $7.7 \times 10^{-9} \text{ m}^3$ and includes one mobile node and two connected immobile nodes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

not present in this zone, so that Al and Si need to diffuse from the mobile zone. Ironically, in the immobile zone *q,kf*, which contains K-feldspar, source of Al and Si for kaolinite, this mineral does not precipitate because pH is in slaved equilibrium with the mobile zone and remains low. These results are supported by the experiments of Luquot et al. (2016, in this issue), who observed that kaolinite tends to precipitate preferentially around dissolved carbonate crystals.

The above discussion supports the conjecture that motivated this work. Geochemical localization (i.e., the occurrence of reactions that would not occur in well mixed media) requires both mineralogical localization and transport limitation. In our case, it controls whether, where, and how much kaolinite precipitates (Table 4). Kaolinite precipitation occurs mainly in immobile zones where dolomite is dissolved and pH remains moderately high. We call the precipitation of Kaolinite slaved, because it results from the diffusion of reactants that were produced elsewhere and occurs solely because local conditions are favorable. As a result, it will come closer to equilibrium and, we conjecture, produce more crystalline precipitates than “autonomous” reactions.

The case of gypsum allows us to illustrate further the concept of autonomous and slaved reactions. Gypsum precipitates both in immobile zone *q,d* and zone *q,kf*. The difference between these two immobile zones is observed only on the inflow side of the domain (Fig. 6). Less gypsum is obtained in zone *q,kf* (Table 4) because it results from Ca and SO_4 diffusing from the mobile zone. Therefore, gypsum precipitation in zone *q,kf* can be regarded as a chemically “slaved” process, whereas gypsum precipitation zone *q,d* should be regarded as “autonomous” since the amount of precipitated mineral is controlled by the local dissolution of dolomite.

Fig. 6. Comparison of gypsum concentration variations along the sample length at final time steps in immobile zones q,kf (pointed) and zones q,d (dashed) for simulations MRWM-2. The Representative Elementary Volume (REV) bulk is $7.7 \times 10^{-9} \text{ m}^3$ and includes 1 mobile node and two connected immobile nodes.

Fig. 7. Comparison of total volume variation of gypsum and kaolinite in immobile zones at final time steps for simulation MRWM-1 applied to different water mass ratio exchanged between mobile and immobile zones.

4.6. Sensitivity to immobile zone parameters

The immobile volume and exchange mass coefficients of models MRWM-1 and MRWM-2 have been chosen somewhat arbitrarily. The discussion of results of these two models makes it clear that the impact of multi-rate model parameters on the reactions is non-trivial, as it is controlled by several simultaneous processes. On the one hand, kinetically limited reactions are controlled by residence time ($\phi_{im,j}/\alpha_j$), but also by the flux of reactants, which is proportional to α_j , and whether their concentrations are the result of an autonomous or a slaved process.

The rate of slaved reactions can be easily derived from Eq. (2) by assuming that the slaved reaction is governed by first order kinetics (i.e., $f_{chem,j} = \mu \cdot u_{aim,j}$, where $u_{aim,j}$ is the concentration of the species or component controlling the reaction rate). This yields $r = \mu \alpha_j / (\alpha_j + \mu) \cdot u_{am}$, assuming that the reaction of the controlling species or component in the mobile domain, u_{am} , is (quasi) stationary. This implies that [1] the reaction rate is independent of the fraction of immobile region ($\phi_{im,j}$) or residence time, but [2] it will depend equally on both the local reaction rate constant and the exchange rate. The reaction grows with both α_j and μ and is controlled by the smallest of them. That is, the reaction rate is small when either of them is small and large when both are large.

The situation is more complex in the case of autonomous reactions. Fig. 7 illustrates the effect of reducing the mixing fraction between mobile and immobile zones (λ_{ij}), which is equivalent to reducing α_j . On the one hand, kaolinite precipitation increases because of the resulting high pH, even though a smaller amount of K-feldspar is dissolved. This reflects that the supply of Si and Al due to K-feldspar dissolution is sufficient to feed kaolinite precipitation, which was limited by pH. On the other hand, gypsum precipitation is reduced, which reflects a reduced supply of Ca and/or SO_4 , both limited by the reduced exchange rate.

5. Discussion and conclusions

We developed a multi-continuum formulation model (MRWM), which was applied to simulate geochemical localization. This model aims at reproducing the effect of pore scale heterogeneity by creating localized micro environments favoring reactions that would not occur in the traditional ADE reactive transport models where local homogenization and full mixing are assumed. To this end, we used the MRMT approach with diverse mineral compositions for different cells. Transport was calculated by the WMA of Soler-Sagarra et al. (2016, for publication), which was extended to account for immobile zones and chemical localization.

We applied this method to four models inspired by dissolved CO_2 flow-through experiments performed on sandstone samples from Heletz (Luquot et al., 2016, in this issue). Model results confirm the original conjecture that coupling chemical and hydrodynamic heterogeneities exerts a significant influence on reactive transport processes. Specifically, including immobile zones containing dolomite allows us to simulate kaolinite precipitation, which would not occur if concentrations were homogenized. This results indicates that kaolinite precipitation is pH controlled and precipitated only close to carbonate dissolution or at least a pH buffer as observed by Luquot et al. (2016, in this issue). In summary, localization and how it is represented in the model controls whether, where, and how much kaolinite precipitates.

The MRWM model requires three additional parameters for each immobile domain: porosity, exchange rate and mineralogy. We found that the spatial distribution of dissolution and precipitation processes is sensitive to all of them. As a result, the behavior of the model is complex and hard to anticipate. In an attempt to facilitate the explanation of model results and parametrization, we distinguish between “slaved” and “autonomous” reactions. Autonomous reactions occur between reactants produced locally. For example gypsum precipitation in a dolomite zone is an autonomous reaction because it is driven by dolomite dissolution in this zone. Actual rates are the result of interactions between the two kinetic laws (e.g., dolomite dissolution and gypsum precipitation) with the mobile-immobile exchange rate and the immobile porosity. As a result, these reaction rates are hard to predict. Slaved reactions occur between reactants produced elsewhere that diffuse into (away from) the precipitation (dissolution) site, where conditions are favorable. An example of these is the precipitation of kaolinite in a dolomite immobile domain controlled by the local high pH even though SiO_2 and Al result from dissolution of K-feldspar in other zones. The behavior of these reactions appears to be more predictable than that of autonomous reactions because the reaction rate is controlled monotonically by both the exchange and the local kinetics rates. However, things may be more complex than they look, because local conditions for slaved reactants may be controlled by autonomous reactions. For example, kaolinite precipitation is controlled by pH, which is the result of an autonomous reaction (dolomite dissolution).

It may therefore be concluded that, although the MRWM model is very powerful in reproducing the effect of pore scale chemical processes in Darcy scale models, reliable parameterization is difficult and further research is warranted before application.

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