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Reactive transport under stress: Permeability evolution in deformable porous media

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Abstract

We study reactive transport in a stressed porous media, where dissolution of the solid matrix causes two simultaneous, competing effects: pore enlargement due to chemical deformation, and pore compaction due to mechanical weakening. We use a novel, mechanistic pore-scale model to simulate flooding of a sample under fixed confining stress. Our simulations show that increasing the stress inhibits the permeability enhancement, increasing the injected volume required to reach a certain permeability, in agreement with recent experiments. We explain this behavior by stress concentration downstream, in the less dissolved (hence stiffer) outlet region. As this region is also less conductive, even its small compaction has a strong bottleneck effect that curbs the permeability.

Our results also elucidate that the impact of stress depends on the dissolution regime. Under wormholing conditions (slow injection, i.e. high Damkohler number, Da), the development of a sharp dissolution front and high porosity contrast accentuates the bottleneck effect. This reduces transport heterogeneity, promoting wormhole competition. Once the outlet starts eroding, the extreme focusing of transport and hence dissolution— characteristic of wormholing—becomes dominant, diminishing the bottleneck effect and hence the impact of stress at breakthrough. In contrast, at high flow rates (low Da), incomplete reaction upstream allows some of the reactant to traverse the sample, causing a more uniform dissolution. The continuous dissolution and its partial counteraction by compaction at the outlet provides a steady, gradual increase in the effect of stress. Consequently, the impact of stress is more pronounced at high Da during early stages (low permeability), and at low Da close breakthrough. Our work promotes understanding of the interplay between dissolution and compaction and its effect on the hydromechanical property evolution, with important implications for processes ranging from diagenesis and weathering of rocks, to well stimulation and carbon sequestration.

Keywords: Hydro-chemo-mechanical coupling, Mineral dissolution, Pore-scale simulations, Wormholing, Mechanical compaction, Permeability evolution

1. Introduction

The transport of reactive fluids in porous media is a fundamental process in many earth systems, including weathering and diagenesis of rocks, contaminant transport, subsurface remediation, hydrocarbon recovery, and CO_2 sequestration. Reactive transport is a complex, nonlinear process: the transport and reactive properties and hence the rate and spatial distribution of fluid flow and reaction strongly depend on the microstructure, which in turn keeps evolving in time with the reaction [13, 43, 34].

Much interest has been given to the dissolution of the solid matrix and the consequent evolution of the porosity and permeability. A rich range of behaviors (regimes) has been shown to emerge, depending on the interplay between advection, diffusion, and reaction. This interplay can be characterized by a pair of

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dimensionless numbers: (i) the Damkohler number, Da, describing the relative rate of reaction vs. advection; and (ii) Peclet, Pe, the ratio of advection vs. diffusion, or, equivalently, their product PeDa (reaction vs. diffusion, termed Peclet-Damkohler or kinetic number) [4, 18, 43]. It has been shown that for slow reactions (relative to the flow rate, small Da), ample reactant is provided throughout the sample, leading to relatively spatially-uniform dissolution, and steady enhancement of permeability [4, 18, 44]. In contrast, at higher *Da* (the so-called transport-limited regime), most of the reactant is consumed by preferential dissolution of the most conductive flow paths ("wormholes"). This further enhances their conductivity relative to other, less conductive regions, leading eventually to runaway permeability increase [12, 4, 21].

In many cases, the medium is under stress, such that dissolution ("chemical deformation") also induces mechanical deformation. Chemomechanical deformation and the coupled changes in the transport and mechanical properties is key in many appli-

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cations, such as enhanced hydrocarbon recovery and carbon geosequestration [11, 38, 7]. Considerable attention has been given to the study of rough fractures, due to the importance of fracture flow and their relatively simple quasi two-dimensional (2-D) geometry [e.g. 27, 14, 15, 22, 3]. Fewer works addressed porous media such as soils [8] and rocks [49, 11, 16, 6, 33, 38, 28], mostly focusing on the evolution of the mechanical properties.

The evolution of transport properties has been recently studied experimentally, in rock cores subjected to external stress and flushed by a reactive fluid (see Vanorio [45], Clark and Vanorio [9] and the references therein). These experiments show considerable reduction in mechanical stiffness, and inhibition of permeability enhancement by compaction, in spite of net removal of solid mass. A model providing fundamental understanding of the interplay between dissolution and mechanical compaction and its effect on the permeability evolution, is lacking, providing the motivation for this paper. Existing models of stressed rock dissolution either address much larger scales (reservoir) [33], much smaller scales (describing changes to the local microstructure but not to permeability, a macroscopic property) [16], or consider other mechanisms for porosity reduction such as pressure solution and re-precipitation [49].

A major challenge towards understanding chemomechanical deformation is its dependency on porescale mechanisms and heterogeneity, inherent in geologic media. While the importance of pore-scale processes has long been recognized, rigorous studies are only recently made possible owing to advancements in experimental and computational capabilities, as highlighted in a recent special volume of review papers [42]. The natural complexity of pore-scale processes associated with heterogeneity makes characterization [34, 42, and the references therein] as well as modeling and interpretation [32, 48, 47, 40, 42] extremely challenging, in particular when mechanical deformation is involved [16, 8, 28]. Despite of the advancements in experimental techniques, numerical simulations remain highly attractive [32, 48, 47, 28, 40].

In this paper, we present a novel pore-scale model, which, to the best of our knowledge, is the first to describe the permeability evolution caused by coupling between dissolution and compaction in a porous medium. Our simulations show that increasing stress inhibits the permeability evolution, requiring longer times or larger volumes injected to reach a certain permeability, in agreement with experiments. We also expose the interplay with the flow rate (Da), that is the different effect of stress in wormholing vs. a more uniform dissolution regime. We find that at high Da, stress acts to reduce transport heterogeneity, promoting wormhole competition.

2. Pore-scale model

2.1. Conceptual model and computational approach

We simulate the injection of a reactive fluid into a porous medium held under a fixed confining stress. Our model accounts for the gradual, continuous dissolution of the solid matrix, and its coupling with mechanical weakening and compaction, excluding deformation by mechanisms such as fracturing [39, 9], detachment of mineral grains [30, 9], and pressure solution and welding of microporous zones [22, 16, 9]. Seeking fundamental understanding rather than quantitative prediction for a specific type of medium, we use here a simplified analog model medium: a 2-D network of cylindrical channels between soluble solid blocks. The coupling between dissolution and compaction at the pore-scale is captured by combining two discrete, overlapping representations: (i) pore network modeling of reactive transport and (ii) a network of interacting linear elastic porous solid blocks. Each discrete model unit (termed "cell" hereafter) includes one solid block, bounded by four "halfchannels"-the respective void space associated with that cell (Fig. 1). Considering such model medium greatly simplifies the computation of fluid transport, reaction and chemomechanical deformation. This allows us to use sufficiently large domains required to capture the pattern evolution, repeated over multiple realizations (different samples with similar statistical properties) essential for systematic, mechanistic understanding in light of the sensitivity to the microstructural details. While it is possible to accurately represent the microstructure of natural geologic media with models such as direct numerical simulations or Lattice-Boltzmann [48, 32, 37], their computational cost prohibits a similar systematic investigation in large domains including mechanical effects, motivating our approach.

Numerically, coupling of the different processes is provided through staggering, evaluating sequentially at each time step the following: (1) liquid pressures and fluxes, from mass conservation of liquid; (2) liquid composition, reaction rate and amount of dissolved mass, from conservation of solute mass; (3) stress distribution and pore deformation from force balance; and (4) update transport and mechanical properties due to the combined effects of dissolution and compaction, to be used in the subsequent time step. Our use of staggering, with a quasi-static description of reactive transport and compaction is justified by the disparate time scales of the different processes: the time required to reach equilibrium of ion concentration is much longer than that for fluid pressures to equilibrate, which in turn is much slower than mechanical deformation and stress equilibration. Therefore, the process hindering the rate of changes in the matrix hydromechanical properties is the dissolution, allowing us to treat all other processes as occurring instantaneously at every time step [3]. That is,



Figure 1: Schematics of our pore-scale model of reactive transport in a stressed, deformable porous medium. We capture the coupling between chemical and mechanical deformation through a discrete representation, combining: (i) pore network modeling of reactive transport, with (ii) interacting network of linear elastic blocks. (a) We simulate the injection of a reactive fluid into a sample held under fixed isotropic stress, σ . The sample is square, with two open faces (inlet and outlet, in the *y* direction) and two impermeable ones (in *x*). (b) The pore space is discretized into a 2-D regular network of cylindrical pores connected by volumeless nodes (or junctions), squeezed in between solid blocks. Heterogeneity is provided by variations in pore sizes. (c) The basic model unit ("cell") includes a solid block, with four engraved "half-channels". The network properties are updated at each time step considering both the chemical and mechanical effects of dissolution.

we approximate the continuous evolution of the sample properties by a discrete sequence of geochemical and mechanical equilibrium configurations.

Details of the different model components describing these processes are outlined below. Our description of reactive transport and dissolution closely follows the pore network model in Budek and Szymczak [5], which in turn is based on the model by Hoefner and Fogler [21]. Therefore, we only briefly describe it here, elaborating further on the coupling with mechanical compaction.

2.2. Reactive transport

2.2.1. Fluid flow

We consider a dilute liquid solution (e.g. CO_2 rich water), neglecting the effect of its pressure and concentration on its density. For a given configuration (network geometry), we solve for the fluid fluxes by enforcing steady-state fluid mass conservation (the continuity equation) at each pore junction (node) *i*,

$$\sum_{j} q_{ij} = 0, \tag{1}$$

where q_{ij} is the volumetric flow rate through pore ij $(q_{ij} > 0$ indicates flow from node *i* to *j*), and the summation is over all neighboring nodes, *j* (Fig. 1b). Assuming Stokes flow, the interpore fluxes are

$$q_{ij} = C_{ij} \Delta p_{ij},\tag{2}$$

where $C_{ij} = a_{ij}R_{ij}^2/(8\mu l_{ij})$ is the pore conductivity, R_{ij} and $a_{ij} = \pi R_{ij}^2$ are the pore radius and crosssectional area, and μ is the fluid viscosity. The term $\Delta p_{ij} = (p_i - p_j)$ is the pressure drop between the two nodes, which are l_{ij} apart. The linear system in Eq. 1 provides the fluid pressure at the nodes. Note that this formulation assumes that flow is driven by pressure alone, i.e. horizontal flow; to generalize the formulation to include gravity effects, node pressures p_i should be replaced by the total energy, e.g. in terms of hydraulic head.

2.2.2. Reactant transport and dissolution reaction

Following Hoefner and Fogler [21], Budek and Szymczak [5], we consider quasi-static solute transport, namely that the concentration field attains equilibrium instantaneously following a perturbation to the transport properties by dissolution and compaction. This assumption is justified when changes to transport properties occur on a much longer timescale than that of the transport itself [26], which applies for the conditions considered here (see Appendix A). We adopt a simple representation of the chemistry, formulated for a single reactant with a linear kinetic law, $J_r = \lambda c_w$, where λ is the surface reaction rate coefficient and c_w is the reactant concentration at the pore surface. While most dissolution reactions are complex, such a simple description provides a reasonable approximation for many systems [5, 36]. Another simplifying assumption is that for each pore, solute transport is dominated by advection in the longitudinal (axial) direction, and by diffusion in the radial (transverse) direction. This is valid as long as the local (pore-scale) values of Peclet remain sufficiently large, $Pe \gg 1$, which applies here (see Appendix A). With this, the diffusive flux is evaluated from the difference between the concentration at the surface c_w and the cross-sectional averaged ("mixing cup concentration") value c, by $J_{\text{diff}} = DSh(c - c_w)/2R$. Here D is the molecular diffusion coefficient, and Sh is the Sherwood number [20]. Noting that the local reaction rate is set by radial diffusion to the pore surface, we can equate the two fluxes, $J_{diff} = J_r$, which provides a relation between the surface and pore-averaged concentrations

$$c_w = \frac{c}{1 + 2\lambda R/DSh},\tag{3}$$

and an expression for the reaction rate in terms of the averaged concentration, $J_r = \lambda^{\text{eff}} c$, where the effective reaction rate coefficient is

$$\lambda^{\rm eff} = \frac{\lambda}{1 + 2\lambda R/DS h}.$$
(4)

The dimensionless group $g = 2\lambda R/DSh$ describes the relative rate of kinetics vs. transverse diffusion: For $g \ll 1$, reaction is limited by kinetics and $\lambda^{\text{eff}} \approx \lambda$, whereas for $g \gg 1$, it is limited by diffusion and $\lambda^{\text{eff}} \approx \alpha$, $\alpha = DSh/(2R)$ being the mass transfer coefficient [20, 5].

The above allows us to formulate the 1-D steadystate solute conservation equation in the axial (flow) direction, ξ , in terms of the averaged quantity *c*,

$$q\frac{dc}{d\xi} = -2\pi R \lambda^{\text{eff}} c, \qquad (5)$$

providing an exponential concentration profile along each pore [24], $c(\xi) = c(\xi=0)e^{-2\pi R\lambda^{\text{eff}}\xi/q}$. Discretizing this equation and evaluating it at $\xi = l_{ij}$ provides an expression for the concentration of the incoming flux from pore ij into node i (computed for pores in which $q_{ij} < 0$)

$$c_{ij} = c_j^0 e^{-A_{ij}\lambda_{ij}^{\text{eff}}/q_{ji}},\tag{6}$$

where $A_{ij} = 2\pi R_{ij} l_{ij}$ is the reactive surface area, and c_j^0 is the concentration at node *j*, evaluated at the previous time step (denoted by the superscript 0) [21, 5]. Finally, the node concentration is resolved from the conservation of solute in each node,

$$c_{i} = -\frac{\sum_{j(q_{ij}<0)} q_{ij}c_{ij}}{\sum_{j(q_{ij}>0)} q_{ij}}.$$
(7)

2.3. Updating network properties due to chemomechanical deformation

We consider cylindrical pores which erode uniformly such that they retain their shape and length (here uniform, $l_{ij} = l$). This allows us to parametrize the network properties such as conductivity and reactive surface area by a single parameter: the pore radius, R_{ij} . With staggering, the properties are updated at each time step considering the combined effects of (i) dissolution, increasing the radius by $\Delta R_{ij}^{\text{chem}}$ and (ii) compaction, decreasing it by $\Delta R_{ij}^{\text{mech}}$, $R_{ij} = R_{ij}^0 + \Delta R_{ij}$, where $\Delta R_{ij} = \Delta R_{ij}^{\text{chem}} + \Delta R_{ij}^{\text{mech}}$ is the total change relative to the previous time step. The procedures for evaluating $\Delta R_{ij}^{\text{chem}}$ and $\Delta R_{ij}^{\text{mech}}$ are provided below.

2.3.1. Pore opening due to dissolution (chemical deformation)

The direct effect of dissolution on pore size is computed from the conservation of soluble solid. Equating the volume dissolved in a time step Δt to the change in volume of a cylinder provides

$$\Delta R_{ij}^{\text{chem}} = \frac{q_{ij} \Delta t c_i^0}{A_{ij} c_{\text{sol}} \nu} \left(1 - e^{-A_{ij} \lambda_{ij}^{\text{eff}}/q_{ij}} \right)$$
(8)

where c_{sol} is the concentration of soluble material in the solid, and ν (here equal to one) accounts for the stoichiometry of the reaction [5].

Our model includes two important aspects: merger of adjacent pores following extensive dissolution, and the finite amount of soluble solid in each cell, limiting the local dissolution. For a comparison of models with and without merging we refer the reader to Budek and Szymczak [5], noting that these models did not limit the dissolution. For simplicity, we use here the same threshold for merging and complete local dissolution. Thus, once all soluble solid associated with a cell has been consumed, (i) the dissolution reaction ceases and the transport and mechanical properties of that cell remain fixed throughout the simulation; and (ii) each pair of pores associated with that cell (one pair in each direction, x and y) is merged.

Computationally, pore merger is represented by an abrupt increase in the conductivity of the associated pores, while retaining the same spatial discretization of nodes and pores. That is, the pair of merged pores are each assigned a conductivity $C_{ij} = C_{ij}^*$, which depends on the spatial extent of dissolution. When a cell experiences complete dissolution, while its adjacent neighbors did not, the conductivity of the pores in between them is set to $C_{ij}^* = a_{ij}^* R_{ij}^{*2} / (8\mu l_{ij})$, where $R_{ij}^* = d_{ij}/2$, $d_{ij} = 4a_{ij}^*/P_{ij}$ is the pore's hydraulic diameter, and P_{ij} is its perimeter. In evaluating a_{ij}^* and P_{ij} we associate the following regions to each pore: (1) half of a cylinder with radius R_{ii} , plus (2) half of the (completely dissolved) unit cell, common to both pores of that pair. To allow consideration of merging due to focused dissolution in a single pore (only from one side of the cell), we set the cell height (out-of-plane size) to be twice the lateral (in-plane) size, such that the cell dimensions are $l \times l \times 2l$; with this, the radius of a single pore can approach l, and undergo merging (Fig. 1c). Once two adjacent cells completely dissolve, the pore separating them is assigned with the conductivity of two parallel plates, $C_{ii}^* = 2l^3/(3\mu).$

2.3.2. Pore compaction (mechanical deformation)

We model pore compaction caused by dissolution and weakening of the solid matrix, under fixed confining stress. Pore compaction is evaluated by enforcing mechanical equilibrium, which reduces here to the balance of forces. External confinement is applied through rigid planar walls which are in contact with the outermost (boundary) cells, adjusting the wall positions to maintain a desired stress. Resolving the mechanical deformation of a porous solid, even for the simplified case considered here of cylindrical voids aligned on a lattice, becomes extremely complex due to the spatial heterogeneity-the non-uniform distribution of stiffness and hence stress, induced here by the heterogeneous dissolution. Here, since we are interested in understanding how stress affects permeability evolution rather than accurately predicting the mechanical response, we make the following simplifications.

The separation of time scales of the various processes provides several simplifications. The fact that compaction is driven by slow changes in stiffness by the dissolution, allows us to approximate the deformation as a sequence of static equilibrium configurations, attained instantaneously following each perturbation. We also exclude the poroelastic effects of (i) changes in pore pressures-and thus to the flow fieldinduced by compaction, and (ii) the reverse effect of pore pressure on the stress field [23]. The former implies the so-called perfectly-drained conditions, justified here by the much faster equilibration of fluid pressure by flow relative to matrix dissolution driving the compaction (cf. Appendix A). Consideration of the latter by invoking the concept of effective stress becomes important for elevated fluid pressures [23].

A further simplification is provided by the aforementioned assumption that each pore retains its cylindrical shape and length. This reduces our description of pore deformation to 1-D, characterized via a single (radial) strain value for each pore. Our computation of the pore strain relies heuristically on linear elasticity and effective medium theory [31]. We consider a linear relationship between the stress and strain of each cell, $\sigma_I^{\beta} = \kappa_I \epsilon_I^{\beta}$, where σ_I^{β} and ϵ_I^{β} are the stress and strain in the β direction (*x* or *y*). The cell effective stiffness, κ_I , is evaluated using effective medium theory [31],

$$\kappa_I = \left[\frac{1}{\kappa_s} + \frac{\phi_I}{\kappa_\phi}\right]^{-1},\tag{9}$$

where ϕ_I is the cell's porosity—the ratio of pore to total volume, affected by both dissolution and compaction. The parameters κ_s and κ_{ϕ} are the solid bulk modulus and the pore stiffness, respectively, material properties which can be determined experimentally [31, 45]. We rely on the regular structure of our medium, and consider small relative deformations such that the offset from the cell's initial positions (on the lattice) remains small enough to decouple the deformations in the *x* and *y* directions.

The computational procedure used to establish mechanical equilibrium and associated compaction is as follows. At each time step we compute: (1) the stiffness of each cell, κ_I , cf. Eq. 9; (2) the effective sample stiffness in each direction, $\kappa_{tot}^{\beta} = (1/N_{\beta}) \sum_{s \in s^{\beta}} k_s$, where the summation is done over all "rows" of cells (total of N_{β}) aligned in the direction β , s^{β} (equivalent to the effective stiffness of springs in parallel), and $k_s = [(1/N_s) \sum_{I \in s} (1/\kappa_I)]^{-1}$ is the stiffness of row *s* (i.e. springs in series), consisting of N_s cells; (3) the boundary displacements (macroscopic strains), $\epsilon_{tot}^{\beta} = \sigma/\kappa_{tot}^{\beta}$, given the macroscopic external stress applied on the boundary walls, σ ; (4) the stress on cell *I*, σ_I^{β} , noting that with the decoupling in *x* and *y*, force balance in each direction β reduces to the equality of the stress on all cells in a given row s, $\sigma_I^{\beta}(I \in s) = \sigma_s^{\beta}$. The stress in row *s* is computed from $\sigma_s^{\beta} = \kappa_s \epsilon_s^{\beta}$, where the planarity of the boundaries implies uniform strain of all rows in a specific direction, $\epsilon_s^{\beta} = \epsilon_{\text{tot}}^{\beta}$; (5) the radial strain of each pore, $\epsilon_{ij} = \sigma_{ij}/\kappa_{\phi}$, assuming the radial stress on a pore is equal to the one acting on the cell, $\sigma_{ij} = \sigma_I^{\beta}$; and (6) the decrement in pore radius from geometrical arguments,

$$\Delta R_{ij}^{\text{mech}} = R_{ij}^{\prime} \sqrt{1 - \epsilon_{ij}} - R_{ij}^0.$$
(10)

Here, R'_{ij} is the radius considering the contribution of dissolution alone (excluding that of compaction) since the *beginning of the simulation*, and R^0_{ij} is the radius considering both dissolution and compaction; both R'_{ij} and R^0_{ij} are the known values from the *previ*ous time step. A pore can experience decompaction within a time step, $\Delta R^{\text{mech}}_{ij} > 0$, if stress redistributes such that it is released locally near that pore.

2.4. Simulation setup

2.4.1. Initial and boundary conditions

Simulations begin with a sample at geochemical and mechanical equilibrium, filled with a pure liquid, c(t=0) = 0. A liquid is injected from an inlet face at a fixed concentration $c = c_{in}$ and flow rate. The rate is held fixed throughout the dissolution, while permeability changes, by adjusting the pressure at the inlet nodes at every time step (keeping the outlet nodes at zero pressure). The main flow direction is from the inlet to the outlet face, with the two perpendicular faces being impermeable (see Fig. 1a). At the outlet pores, we enforce free-flow boundary conditions, computing their concentration from solute mass conservation (Eqs. 6-7). Mechanically, we implement a constant confining stress σ by adjusting the distance between the planar boundaries (the macroscopic strain), i.e. displacing uniformly the corresponding boundary cells.

2.4.2. Parameter values used in the simulations

We use parameter values representative of carbonate dissolution by CO₂-rich water, e.g. supercritical CO₂ injection into brine-saturated carbonate reservoirs. In all simulations, we use a domain of 100×100 nodes. We choose a sample with aspect ratio of one to minimize the interference of the lateral boundaries with wormhole development [10]. We set a pore length of $l=7\cdot10^{-5}$ m, and average initial radius of $\bar{R}=1.2\cdot10^{-5}$ m. We enforce an initial heterogeneity by assigning the pores with volumes drawn from a uniform distribution, $V_{ii} \in [1 - \omega, 1 + \omega]\bar{V}$, where \bar{V} is the average volume and ω is a measure of the heterogeneity, here $\omega = 0.8$. The initial sample porosity is $\phi = 0.1$, providing an initial permeability of $K=7.2 \cdot 10^{-13}$ m², within the typical range of values for carbonates [29]. Due to the initial heterogeneity in pore sizes, both solid volume and porosity vary among cells. We set $c_{in} = 0.001$ M, corresponding to pH=3 (typical conditions in carbon geosequestration), for which the system is sufficiently far from geochemical equilibrium to justify the approximation of first order reaction kinetics [36]. We use concentration of soluble solid of $c_{sol}=27$ M, diffusion coefficient of $D=3\cdot10^{-9}$ m²/s and reaction rate coefficient of $\lambda = 5 \cdot 10^{-4}$ m/s [36]. We use a fixed value of the fluid viscosity $\mu = 0.001$ Pa·s and Sh = 4 [5]. The amount of insoluble solid is a fixed, spatially-uniform fraction of the total cell volume, $\rho = 0.2$. To simulate wormholing and uniform dissolution we set averaged fluid velocity in the inlet pores of $\bar{v}=2.7\cdot10^{-3}$ and $2.7 \cdot 10^{-1}$ m/s. Mechanically, we apply a fixed stress, σ , ranging between 0 and 60 MPa, and set stiffness of $\kappa_s = 22$ GPa and $\kappa_{\phi} = 0.01\kappa_s$, characteristic of compliant rocks [45].

We note that the range of parameter values in carbonate reservoirs can be very large, varying with the type of rock, depth, and other factors. Porosity ranges between 0.01 and 0.35, permeability spreads by more than 3 orders of magnitude [29], the diffusion coefficient can reach 8.10⁻⁹ m²/s in deeper, warmer environments [36], and the insoluble fraction can vary between almost zero, and to up to 50% in clay-rich carbonates [19]. Finally, most of the conditions considered here fall within the range of those in the experiments in Vanorio [45], Clark and Vanorio [9]; these include the type of rock (limestone), fluid (CO2rich water, with pH 2.8-3.5), and injection rate (the one we used to simulate wormholing). Mechanically, however, we consider isotropic stress (of 0–60 MPa) and exclude poroelastic effects, whereas in the experiments stress is anisotropic and in some cases fluid pressures were relatively high (e.g. confining and differential stresses of 45 and 30 MPa, respectively, with fluid pressure of 15 MPa in Clark and Vanorio [9]).

We keep the numerical error associated with staggering and time discretization small by using a sufficiently small time step Δt , 20 and 0.5 s for $Da_{\text{eff}}=1$ and 0.01, respectively. This value was chosen by trial and error, running a set of simulations with decreasing time step until the pore volume to breakthrough (PV_{BT}) stabilized. Breakthrough is defined here as a ten-fold increase in the permeability, $K/K_0=10$, where *K* and K_0 are the current and initial permeability.

2.4.3. Characterizing the dissolution regime

The reactive transport conditions (dissolution regime) are described through a pair dimensionless numbers, typically Da and (ii) PeDa or Pe [4, 18]. For the current pore-network description, which also includes the effect of diffusion to the pore surface on the reaction rate, two dimensionless numbers arise naturally, and are thus more illustrative [5]: (i) Da_{eff} , an effective Damkohler number, a measure of the reaction rate vs. the mean fluid velocity in the pores; and (ii) *G*, the competition between reaction and diffusion, specifically the extent to which the dissolution

rate is hindered by diffusion (here, radial) to the pore surface,

$$Da_{\rm eff} = \frac{2\pi \bar{R} l\lambda/\bar{q}}{1 + \lambda 2\bar{R}/D{\rm Sh}}$$
(11)

and

$$G = \lambda 2\bar{R}/D\mathrm{Sh},\tag{12}$$

where $\bar{q} = \bar{a}\bar{v}$ is the volumetric flow rate at the inlet pores, \bar{a} being the averaged initial pore crosssectional area [5].

We focus here on two regimes: (a) heterogeneous dissolution or wormholing with $Da_{\text{eff}} = 1$, and (b) a more uniform dissolution, $Da_{\text{eff}} = 0.01$, fixing G = 1 in both (corresponding to *Pe* values of $6 \cdot 10^5$ and $6 \cdot 10^3$, respectively, cf. Appendix B). The value of Da_{eff} is controlled here through the inlet velocity. Compaction slightly changes the values of Da_{eff} and *G*, by up to ~5% and ~20%, respectively.

3. Results and Discussion

3.1. Permeability evolution

Our simulations demonstrate the intricate interplay between chemical and mechanical deformation, capturing the inhibition of permeability enhancement associated with stress-induced compaction, observed experimentally [45, 9]. Increasing the external stress results in longer time, or equivalently larger amounts of injected fluid, *PV*, required to reach a certain permeability (Fig. 2).

The effect of stress on the permeability strongly depends on the spatial extent of the dissolution, e.g. on the regime $(Da_{\rm eff})$, and changes with time. We quantify this through the difference in PV required to reach a certain K/K_0 under stress of σ =60 MPa relative to $\sigma=0$, $\Delta PV = [PV_{\sigma=60} - PV_{\sigma=0}]/PV_{\sigma=0}$. At early times (low K/K_0), the impact of stress is more noticeable for wormholing $(Da_{eff}=1)$; for instance, at $K/K_0=2$ the increment ΔPV is ~45% for $Da_{\text{eff}}=1$ vs. only ~10% for $Da_{\rm eff}$ =0.01. This trend however flips later on: at breakthrough, ΔPV is five times larger for $Da_{\text{eff}}=0.01$, with $\Delta PV \approx 50\%$ (Fig. 2). For both regimes, the reduction in dissolution efficiency (increase in PV) associated with stress causes the dissolution front to progress further downstream (e.g. compare insets in Fig. 2 at a given K/K_0). Regardless of stress magnitude, permeability enhancement remains much more efficient at high $Da_{\rm eff}$, consuming about a third of the reactant volume of that at $Da_{\rm eff}=0.01$ at breakthrough.

The curves in Fig. 2 are obtained by ensemble averaging over multiple realizations, namely using different sample geometries with similar *statistical* properties. Wormholing instability is more sensitive to the initial conditions than uniform dissolution, showing greater variability between realizations. Therefore,



Figure 2: Our simulations demonstrate the inhibition of permeability enhancement by stress. Increasing stress, σ , lowers the dissolution efficiency, such that a larger volume of fluid, *PV*, is required to reach a given permeability, K/K_0 . Consequently, the dissolution front progresses further downstream at a given K/K_0 value (compare insets showing porosity). At early times (low K/K_0), stress effect is more noticeable at $Da_{\text{eff}}=1$ (panel a), delaying the sharp rise in permeability. For example, the difference in *PV* required to double the permeability ($K/K_0=2$) under $\sigma=60$ MPa vs. $\sigma=0$, is about five times larger for $Da_{\text{eff}}=1$ (~45%, panel a) than for $Da_{\text{eff}}=0.01$ (~10%, b). This trend is reversed later on: at breakthrough ($K/K_0=10$), the increase in PV_{BT} is about five times larger at $Da_{\text{eff}}=0.01$ than at $Da_{\text{eff}}=1$. The curves represent ensemble averages from multiple realizations (see text).

more realizations were required to obtain statisticallyrepresentative results: 200 for $Da_{\text{eff}}=1$, vs. only 15 for $Da_{\text{eff}}=0.01$, providing a standard error of PV_{BT} smaller than 1% (relative to the mean), and a standard deviation of ~10% and ~1% for $Da_{\text{eff}}=1$ and $Da_{\text{eff}}=0.01$, respectively.

3.2. Stress distribution

We explain the complex interplay between dissolution and compaction through the dynamic evolution of stiffness and stress distribution. While matrix dissolution in a region increases its compliance, the very same process has another, opposite effect: it decreases the load that region bears, since stiffer regions carry more of the load. The competition between these two mechanisms controls the compaction, affecting permeability. In particular, the permeability is governed by the least conductive region; here, this is the downstream region, which-being furthest away from the inlet-experiences the least dissolution. In both regimes, intensive dissolution upstream significantly increases the load downstream (Fig. 3a-b). Even minute compaction of the less conductive downstream region (see insets of Fig. 3) intensifies the bottleneck effect, limiting the permeability. Insets in Fig. 3 show longitudinal flow resistance, $1/C_{ii}^{y}$, normalized by the initial average resistance.

The effect of stress depends on its spatial distribution, which in turn depends on the evolving dissolution pattern. For $Da_{eff}=1$, dissolution is focused within the wormholes, creating a distinct dissolution front. Ahead of this front remains a *wide* undissolved and hence stiffer zone (extending from the most advanced wormhole tip to the outlet), upon which most of the load is distributed (Fig. 3a). The elevated stress on this region, which hardly experiences dissolution until breakthrough, significantly retards the permeability enhancement (insets of Fig. 3a). This decreases the transport heterogeneity, promoting wormhole competition (cf. Section 3.3). As wormholes propagate, stress is progressively relieved from the

newly dissolved region, and increases downstream. Once the outlet starts eroding, the focused dissolution characteristic of wormholing becomes dominant, diminishing the bottleneck effect and providing a sharp permeability increase (see Video 1 in supplementary materials for the dynamics).

The behavior differs at $Da_{\rm eff}=0.01$: the rapid injection and incomplete reaction allows some reactant to propagate further downstream, resulting in a more uniform dissolution and mechanical weakening throughout the sample. The continuous dissolution at the outlet region, experiencing both pore enlargement as well as its partial counteraction by compaction, leads to a steady, relatively-linear increase in the effect of stress on permeability (increasing the divergence among the curves in Fig. 2b). The effect of stress, which is initially larger at $Da_{\text{eff}}=1$, becomes more noticeable at $Da_{\rm eff}$ =0.01 as breakthrough is approached. In our 1-D flow settings, pores parallel to the flow direction (y) mostly control the permeability. Therefore, we plot in Fig. 3a-b the local stress in the transverse direction, σ_x^* . The highly heterogeneous distribution of stress in the longitudinal direction, σ_{v}^{*} , where the stress is concentrated at the stiffer regions between the wormholes [8] (Fig. 3c), has only a minor effect on permeability.

3.3. Wormhole competition

A further quantitative insight into the impact of stress on the complex dynamics at high Da_{eff} can be provided from analyzing the pattern evolution. Fig. 4a shows the relative increment in the number of wormholes at different confining stress (compared to $\sigma = 0$), η , measured in three regions of width 0.2L (centred at y=0.3, 0.5 and 0.7L), and averaged over 200 realizations. A wormhole is defined here as a contiguous region which has been completely dissolved. Stress increases the competition among wormholes, hence the number and length of secondary wormholes on the expense of the dominant wormhole (cf. insets in Fig. 2a). The increase



Figure 3: We explain the permeability evolution through the spatiotemporal distribution of stress. Intense dissolution upstream increases its compliance, hence the load carried by the stiffer downstream region. Since the latter is also less conductive (insets show flow resistance, see text), its compaction provides a bottleneck effect that constrains permeability. (a) For $Da_{eff}=1$, the sharp dissolution contrast between the upstream and downstream regions amplifies the bottleneck effect at early times (low K/K_0). Once the dissolution (i.e. main wormhole) reaches the outlet, the effect of this mechanism becomes less noticeable. (b) In contrast, for $Da_{eff}=0.01$, the incomplete reaction allows the dissolution to propagate throughout the sample, leading to a much smaller conductivity contrast (insets). Continuous dissolution at the outlet provides a steady increase in the effect of stress on permeability, which, near breakthrough, overtakes that $Da_{eff}=1$ (Fig. 2). Panels a–b show the local stress (normalized by the applied stress, $\sigma=60$ MPa) in the x direction, σ_x^* , responsible for compacting pores along the maximums at the stiffer regions between wormholes), has a much smaller effect on permeability. Each curve is an ensemble average at a given K/K_0 value; the corresponding volumes, $\overline{PV} = PV/PV_{BT}$, are also listed.

in transport heterogeneity, where the most advanced wormhole progressively draws more fluid from its less developed neighbors, is the mechanism responsible for the sharp increase in permeability (Fig. 2a). Application of stress reduces the transport heterogeneity, slowing down the propagation of the main wormhole, thus breakthrough. A demonstration of the interplay between the evolving transport heterogeneity and the dissolution is provided via a simple system consisting of two straight wormholes (Fig. 4b, inset), in which we measure the ratio of flow rates through the long and short wormholes, χ . Increasing stress is shown to divert less of the flow into the main wormhole (lowering χ), indicating a reduction in the degree of preferential fluid flow-and hence reactant transport (Fig. 4b).

We quantify the evolution of transport heterogeneity through the change in the probability distribution function (PDF) of the velocities with time. Fig. 4c shows the PDF of the natural logarithm of the normalized velocity, PDF[log(v_y/\tilde{v})], where v_y are the apparent velocities in the main flow direction y (the porewise flow rate, q_{ij} , divided by the cell's total area, l^2), and \tilde{v} is the average apparent *inlet* velocity. Initially (at *PV*=0), the transport is relatively uniform, with most of the velocities centered around the mean value. As dissolution progresses (*PV*=23400, corresponding to $0.6PV_{BT}$ for σ =60 MPa), wormholes start to form, providing another peak of higher velocities and a wider velocity distribution (a wider spread of values, reducing the height of the main peak around the mean), an indication of more heterogeneous transport [2]. At this stage, the effect of stress is still small. Closer to breakthrough (at PV=35100, $0.9PV_{BT}$ for $\sigma=60$ MPa), while the transport heterogeneity increases progressively in both cases, it does so less under stress: for $\sigma=60$ MPa there are slightly more velocities centered around the mean, and a smaller probability for low velocities.

Interestingly, stress was found to have an opposite effect-increasing transport heterogeneity-in a different system: *non-reactive* transport in a rough fracture [25]. The authors show that stress increases the number of solid-solid contacts, forcing the solute to pass through fewer, hence more preferential pathways. In our system, stress *reduces* the conductivity contrast among the wormholes, hence the dominance of the main wormhole, and the resulting transport heterogeneity and dissolution efficiency. Finally, we note that to date there are no experimental observations of the effect of stress on transport heterogeneity, possibly due to technical difficulties in obtaining pore-scale data in stressed porous media.

3.4. Implications for natural systems

The fundamental insights into the coupling of stress and reactive transport provided by our work must be complemented with investigation of more realistic conditions, using state-of-the-art computational and experimental capabilities [42]. Below, we discuss several possible extensions of our work in



Figure 4: Stress effects on wormhole competition (at Da=1). (a) The number of wormholes increases with stress, in particular downstream (at y=0.6-0.8L). This is quantified by the increment of the number of wormholes at breakthrough (vs. $\sigma=0$), η , measured in three bands of width of 0.2L. This behavior is associated with a decrease in transport heterogeneity, where reactant is being distributed more uniformly, inhibiting the propagation of the most developed wormhole. (b) The underlying mechanism is exemplified via a simple model system consisting of two straight wormholes (of length 0.6L and 0.5L, see inset). Increasing stress is shown to reduce the relative amount of flow through the more advanced one (normalized by that in the shorter one), χ . (c) Evolution of the PDF of the pore velocities (normalized values, see text) shows the increase in transport heterogeneity as wormholes evolve as a wider spread of velocity values, with smaller peak around the mean and increased number of high and low velocities. Transport heterogeneity is reduced with stress, evident from the slightly larger probability for velocities centered around the mean and smaller probability for low velocities.

that direction. First, it would be interesting to extend our model to consider more realistic pore geometry. 3-D pore geometry was shown to promote flow focusing and affect dissolution efficiency (e.g reducing PV_{BT}) [10, 17]. Under stress, this may increase the non-uniformity of the stress distribution, and accentuate the impact of stress on permeability. Natural media is also highly heterogeneous, in terms of microstructure and reactive properties. Heterogeneity can substantially affect the dissolution rate and patterns, and the permeability evolution [37, 1, 2]. A further consequence of heterogeneity is the spatial variability of the conditions, with implications on the ability to characterize the dissolution regime with the traditional sample-averaged quantities, e.g. Da and PeDa. That is, markedly different behaviors can emerge under conditions described by similar Da and PeDa values [41, 46, 37]. For instance, heterogeneity can significantly reduce the effective dissolution rate, leading to local heterogeneous dissolution at Da and *PeDa* values representative of uniform dissolution regime [37]. Our model allows a systematic investigation of the impact of the initial conditions and underlying microstructure. As an example, as supplementary materials we provide simulations of an experimental study of the impact of chemically and physically heterogeneous layered medium, capturing the intricate spatiotemporal effects of microstructural changes in one layer on the dissolution behaviour of the other [1].

We introduce mechanical effects into an already complicated model of reactive transport by making several simplifying assumptions in our mechanical module. Generalizing our model by relaxing these assumptions is another interesting venue for future research. Our conceptual model of a structured lattice (widely used in solid mechanics [35]), together with the assumption of small relative deformations such that forces in orthogonal directions can be decoupled, limits our model to consider isotropic loading. Relaxing this assumption will allow consideration of shear and bulging (Poisson effect), common in natural settings. Poroelasticity may strongly affect dissolution under certain settings; for example, high fluid pressures may reduce compaction and consequently the inhibiting effect of stress on permeability. Another potential direction of interest is consideration of pore stiffness degradation by microscopic changes in interparticle contacts [45]. Here, we consider only the primary effect of weakening by changes in the local porosity (fixing the value of κ_{ϕ}); degradation could be introduced in our model via a dissolution-dependent κ_{ϕ} .

4. Summary and conclusions

We study permeability evolution in a stressed, deformable porous media undergoing dissolution. We present a novel pore-scale model describing the coupling between (a) pore opening by chemical deformation and (b) mechanical weakening and pore compaction. Our simulations point to a complex, unintuitive effect of stress. As the upstream region dissolves, higher load is being carried by the stiffer downstream region. Since this region is also less conductive, even its small compaction has a significant bottleneck effect, such that larger injected volume (or equivalently, longer time) is required to reach a certain permeability.

The manner by which the permeability enhancement is curbed by stress depends on the dissolution regime (Da_{eff}). At high injection rates (low Da_{eff}), the relatively uniform dissolution leads to a steady increase in the effect of stress, caused by continuous dissolution at the outlet and its partial counteraction by compaction. In the wormholing regime (high $Da_{\rm eff}$), the undissolved region ahead of the dissolution front has an acute bottleneck effect. This acts to reduce transport heterogeneity by decreasing the conductivity contrast, promoting wormhole competition. At early times (low permeability), this mechanism strongly suppresses the permeability enhancement, much more than at low $Da_{\rm eff}$. Once the main wormhole approaches the outlet, this mechanism diminishes and focused transport and dissolution leads to a sharp permeability rise. Consequently, close to breakthrough the impact of stress becomes larger at low $Da_{\rm eff}$.

In conclusion, our work provides crucial insights into the coupling of chemical and mechanical deformation during reactive transport. These insights, complemented with those from studies of natural samples and conditions, improve our understanding of diagenesis and weathering of rocks, and our ability to design and control processes such as well stimulation and carbon sequestration.

Supplementary materials associated with this article can be found online at doi:10.1016/j.epsl.XXX.

Appendix A. Simplifying assumptions for porewise reactive transport

Following the pore network models in Hoefner and Fogler [21], Budek and Szymczak [5], we use a simple 1-D, quasi-static description of solute transport in each pore. In the below, we demonstrate the validity of this description by showing that the underlying assumptions hold for the parameter values considered here.

Quasi-static solute transport. We resolve the concentration field and the rate of dissolution considering a quasi-static (termed "quasi-stationary" in Lichtner [26]) description of solute transport in each pore, namely that a steady-state concentration profile is attained instantaneously following perturbations by matrix deformation. This assumption has been made in other discrete models, e.g. Bekri et al. [4], Hoefner and Fogler [21], Budek and Szymczak [5]. For a thorough discussion of the validity of this assumption see Lichtner [26]; below we briefly justify it for the conditions considered in our paper.

First, we demonstrate that the pressure field and fluid flow approach static equilibrium over much shorter timescale than that of changes to transport properties by matrix dissolution. This can be done by considering the volume of solid which is dissolved by a unit volume of reactive fluid, i.e. the so-called acid capacity number, $\gamma = c_{in}/(vc_{sol})$ [5]. For the conditions considered here (carbonate dissolution by CO₂ rich water) with $c_{in} = 0.001$ M, $c_{sol}=27$ M and $\nu = 1$, we obtain $\gamma=3.7 \cdot 10^{-5}$, justifying our approximation of steady-state flow. Next, to establish the

validity of the quasi-static transport, we use the conservation of soluble solid, $\partial R/\partial t = \lambda c/(\nu c_{sol})$, to compute the characteristic time of solid erosion by dissolution, $t_s = l/\lambda \gamma$, where we use $c = c_{in}$, and l as the characteristic length scale. This is compared with the timescales of advection $t_a = l/\bar{v}$, and of transverse diffusion $t_d = l/\alpha$, where $\alpha = DSh/(2R)$ is the mass transfer coefficient [20]. For our parameters range, $D = 3 \cdot 10^{-9} \text{ m}^2/\text{s}$, Sh=4, $\lambda=5 \cdot 10^{-4}$ m/s, $l=7.10^{-5}$ m and $\bar{\nu}=2.7.10^{-3}$ and $2.7.10^{-1}$ m/s, we obtain $t_s/t_d \approx 3.10^4$, and t_s/t_a values of $\sim 2.10^5$ and $\sim 2 \cdot 10^7$ for Da = 1 and Da = 0.01, respectively. Our above evaluation of the dissolution timescale t_s excludes transport limitations on reaction; including this effect will only increase t_s . We conclude that the use of a steady state solute concentration field is justified here.

Finally, as pointed out earlier, the fact that compaction is driven by dissolution implies that every process that can be considered instantaneous relative to *chemical* matrix deformation can be also considered such relative to *mechanical* deformation. This justifies our use of quasi-static solute transport considering chemo-mechanical deformation. We note that the very same argument also allows us to neglect poroelastic effects on fluid flow.

Pore-wise concentration profile. We consider 1-D transport in cylindrical pipes, where advection dominates transport and longitudinal diffusion is neglected. Diffusion is considered in computing the reaction rate, assuming the rate is set by transverse (radial) diffusion of the reactant to the solid pore walls. Advection in a pore dominates over diffusion as long as $Pe \gg 1$ (where the relevant value of Pe here is one evaluated at the pore-scale, $Pe = \bar{v}l/D$). For the conditions considered here, we obtain Pe values of 60 and 6000. The velocities we consider are typical of many settings, including karst systems, fractures networks, and in the vicinity of pumping wells [29]. We note that this assumption may be violated for much slower flows, for instance in deep stagnant aquifers or in fine-grained media.

Appendix B. Derivation of Pe from the dimensionless numbers Da_{eff} and G

For completeness, we provide here the link between the values of the dimensionless groups used here, Da_{eff} and G, and Pe. We first substitute the definition of G (Eq. 12) into Eq. 11, providing

$$Da_{\rm eff} = G \frac{DS h(\pi l)}{\bar{q}(1+G)}.$$
 (B1)

We then use the expressions $\bar{q} = \bar{v}\bar{a}$ and $\phi = \bar{a}l/l^3$, where \bar{a} is the averaged initial pore cross-sectional area, and multiply both sides by the sample length, *L*, to arrive at the following definition of *Pe* in terms of our dimensionless groups,

$$Pe = \frac{\overline{\nu}L}{D} = \frac{Sh(L/l)}{(1+G)(\phi/\pi)}\frac{G}{Da_{\text{eff}}}.$$
 (B2)

The conditions considered here, G = 1, $Da_{\text{eff}} = 0.01$ and 1, and Sh = 4, L/l = 100 and $\phi = 0.1$, provide *Pe* values of $6 \cdot 10^5$ and $6 \cdot 10^3$, respectively.

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