

Science Paper

A Micromechanical Model for Mineral Replacement Reactions and Associated Deformation: From Pore Clogging to Solid Volume Increase

Viktoriya M. Yarushina¹, Yury Y. Podladchikov², Anatoly V. Vershinin³

¹ Institute for Energy Technology, ² University of Lausanne, ³ Lomonosov Moscow State University

Keywords: Deformation, fluid flow, chemical reactions, elasticity, viscosity, plasticity, force of crystallization, effective stress law, large deformation

<https://doi.org/10.2475/001c.140951>

American Journal of Science

Vol. 325, 2025

Deformation, chemical reactions, and fluid flow in geological formations are coupled processes. Recent experimental and observational studies suggest that mineral replacement is typically driven by coupled dissolution–precipitation processes, often leading to variable changes in porosity and solid volume depending on the specific reaction conditions. This article builds upon our previous micromechanical model for mineral replacement reactions and the associated deformation processes. Our new model accommodates externally applied stresses and stresses generated as a result of chemical reactions through elastic, viscous, and plastic deformation mechanisms. Our model predicts changes in both porosity and solid volume as a result of the chemical reaction, with these changes governed by the relative rates of deformation of the solid and pore volumes. Porosity reduction often limits the extent of the reaction, while solid volume increase, accompanied by a lesser reduction in porosity, facilitates achieving complete reactions. An interesting finding of our model is the emergence of two solid bulk moduli, typically associated with the presence of a non-connected pore space. However, in our case, they are associated with chemical alterations. We also introduce an effective stress law for reactive porous rocks. We use a two-phase continuum medium approach and local equilibrium thermodynamic models to investigate the coupling between reaction, deformation, and fluid flow on a larger scale. This framework offers valuable insights into the complex interplay between geological processes and the mechanical behavior of rocks undergoing mineral replacement reactions, with implications for understanding subsurface fluid flow and the evolution of geological formations.

1. INTRODUCTION

Coupled chemical reactions and deformation play a crucial role in understanding the dynamic processes that shape the Earth's surface and subsurface. In geology, these processes are fundamental for explaining the formation of rocks, minerals, and the overall evolution of our planet. For instance, the process of mountain building, known as orogeny, involves the deformation of rocks due to tectonic forces. During this process, chemical reactions occur within the rocks, leading to their metamorphism or transformation into new minerals (e.g., Schenker et al., 2015). Melt transport and chemical differentiation, essential for oceanic crust formation and intraplate volcanism, are aided by mechanical compaction and decompaction (e.g., Bessat et al., 2022). Deformation at tectonic plate boundaries involves coupling between rock deformation, fluid flow, and metamorphic reactions, where a propagating reaction front causes an effective, reaction-induced weakening of the het-

erogeneous rock (Schmalholz et al., 2020). Understanding coupled chemical reactions and deformation is crucial for predicting and mitigating geological hazards. Chemical reactions within fault zones can affect the strength and behavior of rocks, influencing their ability to slip or fracture during seismic events (e.g., Rohmer et al., 2016). In civil and petroleum engineering, chemical reactions lead to the degradation of the building materials and cement when in contact with carbon dioxide or strong acids (Fabbri et al., 2009; Lesti et al., 2013; Vrålstad et al., 2019). In environmental engineering, CO₂ storage in mafic and ultramafic rocks has gained attention as a potential solution for mitigating greenhouse gas emissions. These rocks can react with CO₂ through mineral carbonation, which converts CO₂ into solid mineral forms, providing long-term CO₂ storage options. However, a debate surrounds the possibility of achieving a complete reaction within these rocks and the role of fracturing in enhancing this process (Kelemen & Hirth, 2012; Snæbjörnsdóttir et al., 2020; Van Noort et al., 2017; Yarushina & Bercovici, 2013).

a Corresponding author: Viktoriya.Yarushina@ife.no

The models of coupled processes incorporate equations for fluid flow, chemical transport, and mechanical deformation. These equations are governed by the principles of conservation laws in thermodynamics, ensuring mass, momentum, and energy conservation throughout the system (Malvoisin et al., 2015; Vrijmoed & Podladchikov, 2022; Yarushina & Podladchikov, 2015). However, to fully describe the system's behavior, a complete set of governing equations is required. This is achieved through the development of closure equations, which establish the necessary additional relationships between key variables, such as stress and strain, porosity and permeability, porosity and reaction, porosity and effective pressure, and reaction rate and temperature. Differences in the formulation of closure equations can lead to significant variations in model predictions (Malvoisin et al., 2021). These closure equations are either obtained by extrapolating the experimental data or derived from micromechanical models, which consider the processes occurring at the scale of individual grains or particles.

Mineral replacement reactions have traditionally been explained by solid-state mechanisms, where one phase transforms into another via volume diffusion through the crystal lattice. However, such processes are typically too slow under geological conditions unless very high temperatures are present, as diffusion rates increase rapidly with temperature. When fluid is involved, mineral replacement is more effectively described by a coupled dissolution and reprecipitation process (A. Putnis, 2009). Two major types of fluid-mediated replacement models have been proposed. The first type, often referred to as interface-coupled dissolution-precipitation, emphasizes chemical control at the reaction front. In this model, the parent mineral dissolves at the interface, creating a localized supersaturation that promotes nucleation and growth of the product phase (Anderson et al., 1998; A. Putnis, 2002, 2009). This mechanism relies on the chemistry of the boundary layer fluid and diffusion across short distances, explaining pseudomorphic textures through close spatial coupling of dissolution and precipitation. The second class of models includes those that incorporate mechanical or stress-driven processes. Some models propose that a growing product phase exerts stress on the adjacent parent mineral, the so-called “force” of crystallization, inducing pressure-driven dissolution (Fletcher & Merino, 2001; Merino & Dewers, 1998; Schmid et al., 2009). These models account for rheological feedback between crystal growth and the mechanical response of a surrounding rock matrix, particularly under confined or non-hydrostatic conditions. In contrast, classic pressure solution models (Rutter, 1976; Weyl, 1959) describe mineral dissolution at stressed grain contacts with subsequent diffusion and reprecipitation at distant, unstressed surfaces. Here, dissolution and precipitation are often spatially and temporally decoupled, and the rate-limiting step is typically solute diffusion through thin fluid films. While interface-coupled models effectively explain the role of fluid composition, supersaturation, and boundary layer transport, they may neglect the mechanical constraints present in confined systems. Pressure solution models predict a

very limited extent of reaction due to loss of porosity and reactive surface area (Malvoisin et al., 2017). Yet, field observations report that natural rocks can undergo 100% hydration/carbonation (Kelemen & Matter, 2008). The stress-based models of Fletcher and Merino (2001); Merino and Dewers (1998), and Schmid et al. (2009) consider alterations and deformation due to mineral growth but do not consider their feedback on porosity evolution. Recent experimental and observational studies suggest that mineral replacement is associated with both the change in the solid volume and porosity (Malvoisin et al., 2020; A. Putnis, 2002; C. V. Putnis et al., 2021).

Thus, the plausible solution is to combine both approaches by considering a microscale model where porosity changes and mineral replacement will be combined and driven by changes in the fluid chemistry. Microscale models are often based on simplified analytical solutions obtained for idealized conditions that may not capture the full complexity of real-world situations. For example, it is often assumed that deformations that develop in the rock are small and obey the linear elastic law. At the same time, thermodynamic databases such as that of Holland and Powell (1998) present a nonlinear Murnaghan equation of state (EOS) for the deformation of common minerals. Observations show that reaction-induced volume change can be as large as 30–70% (Lyu et al., 2015; Malvoisin et al., 2020). One way to tackle this discrepancy is to derive nonlinear finite strain analytical solutions. However, it may not always be possible, and the results obtained will be too cumbersome to be practical. Another approach is to keep simplified solutions but compare them with nonlinear finite strain numerical simulations to assess their validity (Moulas et al., 2023). If the analytical solution matches the results of the numerical simulation, it provides confidence in the accuracy of the mathematical model.

In this work, we present a new analytical model and supporting numerical results that extend the micromechanical approach introduced in Yarushina et al. (2023), with key enhancements. Building on that framework, we derive macroscopic compaction relations for reacting porous materials by accounting for elastic, viscous, and plastic deformation of the solid matrix. Our approach accounts for the influence of chemical reactions on microscale deformation, and crucially, incorporates plastic failure or fracturing ahead of the reaction front. This feature improves fluid access to reactive surfaces and naturally limits unrealistic stress buildup within the evolving microstructure. A central contribution of this study is the development of an effective rheology in which porosity evolves as a function of the relative deformation rates of the solid and pore volumes. This provides a more general and physically grounded framework for exploring the coupled evolution of deformation and reaction in porous media. Our model targets mineral replacement reactions occurring under deforming conditions, as illustrated in [figure 1](#). In this setting, a reactive fluid within the pore space interacts with the solid matrix to form a product phase with different mechanical and transport properties. The analytical formulation is developed within a 2D plane strain approximation, appropriate for systems with

cylindrical symmetry, and can be extended to fully 3D cases in an analogous manner. The inclusion of fracturing mechanisms allows the model to realistically capture porosity generation, enhanced transport, and stress relaxation near the reaction front. To complement the analytical model, we present nonlinear finite-strain numerical simulations that validate and extend the analytical results. These numerical investigations are an important addition to the work of Yarushina et al. (2023), broadening the model's applicability beyond linear regimes. Finally, we formulate a closed, macroscopic system of equations that governs the coupled evolution of fluid flow, reaction, and deformation. This framework is broadly applicable to both natural systems and engineered processes involving reactive porous materials.

2. EFFECTIVE RHEOLOGY OF REACTING POROUS MEDIA

In this section, we follow the micromechanical procedure developed in Yarushina et al. (2023) to define an effective medium representation of a reactive porous material undergoing deformation. Our goal is to derive macroscopic rheological laws that capture the essential coupling between chemical reactions and deformation within a fluid-saturated porous medium. The model is constructed to explore the range of behaviors between two end-member regimes: porosity-preserving and porosity-clogging mineral replacement reactions. Rather than representing discrete modes, these two regimes emerge naturally from the relative rates of deformation and reaction and thus define a continuous spectrum of behaviors.

We consider a representative elementary volume (REV) of a porous matrix, fully saturated with a single, reactive fluid. Chemical alteration is assumed to be driven by a fluid phase that is out of equilibrium with the surrounding solid, initiating a reaction at the fluid-solid interface and progressing into the solid matrix (fig. 1A). The model assumes isothermal conditions and does not account for thermal stress. We acknowledge that the reactive surface area and mineral distribution are critical in natural settings; however, our model simplifies these complexities by assuming a uniform reactive interface. This simplification allows us to focus on the coupled evolution of porosity, reaction, and mechanical deformation, and should be viewed as a first-order approximation of more complex, heterogeneous systems.

We idealize the geometry of the REV as a 2D array of cylindrical pores surrounded by concentric shells of deformable solid (fig. 1B). This 2D formulation serves as a computationally tractable abstraction of the 3D problem. While the dimensionality reduction simplifies mathematics, it implies that the pores behave as infinitely long cylinders in the out-of-plane direction. This assumption limits the model's ability to capture certain 3D features such as complex non-isotropic stress states or complex pore shapes. Nonetheless, comparisons with experimental data and prior modeling efforts suggest that this cylindrical approximation captures the essential mechanics of porosity

evolution and solid deformation (Carroll & Holt, 1972; Yarushina et al., 2020; Zimmerman, 1991). Zimmerman (1991, p. 91) and Mavko et al. (1998, p. 42) suggest that while different pore shapes affect the numerical coefficients, the functional dependence of rock compressibility on stress and porosity remains the same across a wide range of pore geometries. The model allows for fluid mobility across the porous network, assuming interconnected pores that facilitate mass transport between neighboring regions. We do not explicitly model fluid flow but assume that the fluid is always present in the pore space and that reaction rates are not limited by large-scale fluid supply but by local interface kinetics and deformation.

Geomaterials such as basaltic rocks and cementitious materials exhibit both instantaneous elastic deformation and time-dependent viscous creep, as documented in experimental studies (Heap et al., 2011; Nermoen et al., 2015; Neville et al., 1983; Sabitova et al., 2021; Wolterbeek et al., 2016; Yarushina et al., 2021). We incorporate these two deformation mechanisms as limiting cases of the solid matrix response. To define the mechanical loading in the model, we apply boundary conditions at the inner and outer surfaces of the cylindrical volume. In the viscous formulation, the fluid pressure p_f is applied at the pore wall, while the total confining pressure p_t is applied at the outer boundary (fig. 1B). In the elastic model, the corresponding pressure rates, $\dot{p}_f$ and $\dot{p}_t$, are prescribed at the internal and external boundaries, respectively. This difference arises because viscous constitutive relations are formulated in terms of stresses and velocities, so boundary pressures directly influence stress and flow. In contrast, the elastic constitutive equations are rate-based, where velocities are related to stress rates rather than stresses themselves, requiring the specification of pressure rates at the boundaries. These boundary conditions govern the stress evolution within the solid shell and control its mechanical response to ongoing reaction and deformation.

We consider reactions where the mass of immobile species is conserved. For instance, during the hydration of periclase, magnesium and oxygen remain in the solid phase despite compositional changes. Although these elements remain immobile, ensuring their conservation within the solid matrix, the overall mass of the solid increases as water is incorporated to form brucite. Similarly, during the hydration of olivine, silicon, magnesium, and iron remain immobile as they are retained within the newly formed hydrated mineral, serpentine. In the carbonation of portlandite, calcium and oxygen are immobile species, remaining in the solid phase as portlandite transforms into calcite. In addition to these mineral alteration reactions, various other types of reactions also conserve the mass of immobile species, provided they remain in the solid phase without undergoing dissolution or volatilization. Additional examples can be found in Appendix A.

Macroscopic porosity in the model is characterized by the ratio of the fluid volume, V_f , to the total volume, V (see table 1 for the list of notations). For cylindrical pores, it can be defined in terms of the pore radius, a , and the outer radius of a cylindrical shell, b , (fig. 1), so that

$$\varphi = \frac{V_f}{V} = \frac{a^2}{b^2} \quad (1)$$

The macroscopic extent of reaction, $\xi(t)$, can be defined as the volume fraction of the reacted portion of the solid:

$$\xi(t) = \frac{c(t)^2 - a(t)^2}{b(t)^2 - a(t)^2} \quad (2)$$

Changes in $\xi(t)$, and consequently in $c(t)$, are influenced by mass transfer or diffusion in cases where the reaction occurs under thermodynamic equilibrium or is extremely fast. In such cases, $\xi(t)$ should be determined by solving the full set of equations governing mass and momentum balance (see Sections 3 and 4). For reactions governed by chemical kinetics, the time derivative of the extent of reaction corresponds to the reaction rate, which can be expressed using various kinetic laws. The bulk volume strain is a function of changes in pore volume and changes in the volume of the solid matrix. These together lead to changes in the total volume. Thus, only two equations are needed to describe the expansion or compaction of porous materials. For the micromechanical approach, it is convenient to consider changes in porosity and the total volume. It is practical to rewrite the porosity equation in the following differential form used in further derivations:

$$\frac{d\varphi}{dt} = \frac{2\varphi}{a} \frac{da}{dt} - \frac{2\varphi}{b} \frac{db}{dt} = 2\varphi \left(\frac{v}{r} \Big|_{r=a} - \frac{v}{r} \Big|_{r=b} \right) \quad (3)$$

where v is the radial velocity of the solid. The applied far-field pressure, pore pressure, and ongoing chemical transformations induce non-uniform deformation on the microscale. Macroscopic, or averaged, volumetric deformation, is determined by changes in the total volume of the Representative Elementary Volume (REV):

$$\frac{d\varepsilon}{dt} = \frac{1}{V} \frac{dV}{dt} = 2 \frac{v}{r} \Big|_{r=b} \quad (4)$$

2.1. Elastic adjustment of the matrix

The constitutive equations for a linear elastic material relate the shear strain rate to the shear stress and the volumetric strain rate to the mean stress:

$$\frac{\partial v}{\partial r} - \frac{v}{r} = \frac{\dot{\sigma}_r - \dot{\sigma}_\theta}{2G} \quad (5)$$

$$\frac{\partial v}{\partial r} + \frac{v}{r} = \frac{\dot{\sigma}_r + \dot{\sigma}_\theta}{2K} \quad (6)$$

where G is the elastic shear modulus, K is the elastic bulk modulus, σ_r and σ_θ are the radial and tangential components of the stress tensor at the microscale. The dot represents the Lagrangian time derivative. Both reacted and non-reacted parts of the solid volume must be in mechanical equilibrium and satisfy the force balance equation

$$\frac{\partial \sigma_r}{\partial r} + \frac{\sigma_r - \sigma_\theta}{r} = 0 \quad (7)$$

These equations must be satisfied in the solid's reacted and nonreacted parts. Conservation of momentum requires normal stress to be continuous at the reaction front. Assuming that the mass of immobile species is conserved at the reaction front, as in hydration or carbonation reactions, the following jump condition must be satisfied:

$$(\rho_1 X_1 v_1 - \rho_2 X_2 v_2)|_{r=c} = \frac{dc}{dt} (\rho_1 X_1 - \rho_2 X_2) \quad (8)$$

where X is the concentration of the immobile component. Index 1 denotes quantities in the non-reacted phase, and index 2 marks the reacted phase. This jump condition is similar to the classical Stefan condition in thermal problems (Mainguy & Coussy, 2000; Rubinshtein, 1971), but it arises from mass balance rather than energy balance.

Equations – form a system of three equations with three unknowns: v , σ_r , and σ_θ . We solve these equations separately for the non-reacted and reacted parts of the volume, ensuring that σ_r is equal to the fluid pressure at the pore boundary and the total pressure at the external boundary, as illustrated in [figure 1](#). The remaining condition at the interface between two regions is provided by the equation . By substituting $c(t)$ with $\xi(t)$ using the equation, we obtain the following velocities:

$$v_1 = -\frac{1}{2r\hat{G}} \left(\frac{b^2}{b^2-a^2} A_{11} \frac{dp_e}{dt} + A_{12} \frac{dp_f}{dt} + A_{13} \frac{d\xi}{dt} \right) \quad (9)$$

$$v_2 = -\frac{1}{2r\hat{G}} \left(\frac{b^2}{b^2-a^2} A_{21} \frac{dp_e}{dt} + A_{22} \frac{dp_f}{dt} + A_{23} \frac{d\xi}{dt} \right) \quad (10)$$

and stresses around the pore

$$\dot{\sigma}_r^1 = -\frac{1}{\hat{G}r^2} \left(\frac{b^2}{b^2-a^2} B_{11} \frac{dp_e}{dt} + B_{12} \frac{dp_f}{dt} + (b^2 - r^2) \xi B_{13} \frac{d\xi}{dt} \right) \quad (11)$$

$$\dot{\sigma}_\theta^1 = -\frac{1}{\hat{G}r^2} \left(\frac{b^2}{b^2-a^2} C_{11} \frac{dp_e}{dt} + C_{12} \frac{dp_f}{dt} - (b^2 + r^2) \xi C_{13} \frac{d\xi}{dt} \right) \quad (12)$$

$$\dot{\sigma}_r^2 = -\frac{1}{\hat{G}r^2} \left(\frac{b^2}{b^2-a^2} B_{21} \frac{dp_e}{dt} + B_{22} \frac{dp_f}{dt} + (r^2 - a^2)(1 - \xi) B_{23} \frac{d\xi}{dt} \right) \quad (13)$$

$$\dot{\sigma}_\theta^2 = -\frac{1}{\hat{G}r^2} \left(\frac{b^2}{b^2-a^2} C_{21} \frac{dp_e}{dt} + C_{22} \frac{dp_f}{dt} + (1 - \xi)(r^2 + a^2) C_{23} \frac{d\xi}{dt} \right) \quad (14)$$

where $p_e = p_t - p_f$ is the effective pressure. All the coefficients in equations – are dimensional shorthand notations and do not represent meaningful physical quantities. A summary of these coefficients is provided in Appendix B.

2.1.1. Effects of nonlinearity and comparison with the numerical solution

The volumetric behavior of minerals is widely recognized to possess inherent nonlinearity, as acknowledged by Angel et al. (2018) and Moulas et al. (2023). Thermodynamic databases commonly employ nonlinear elastic equations of state (EOS) to describe the behavior of minerals (Holland & Powell, 1998, 2011). The extent of strain depends on the nature and magnitude of the reaction, as well as the mechanical properties of minerals. Various chemical reactions can generate finite strain, including hydration or carbonation reactions, that involve the addition of water or carbon dioxide molecules to compounds, leading to changes in molecular structure and volume. Notably, Malvoisin et al. (2020) observed a volume change of 59% to 74% during the serpentinization of dunite samples collected at depth during the Oman Drilling Project. Similarly, Lyu et al. (2015) reported data on significant shale swelling of up to 30% due to water adsorption.

We use numerical simulations to study the effect of finite strain and material nonlinearity of the minerals on the porosity and volume changes. Our numerical code is based

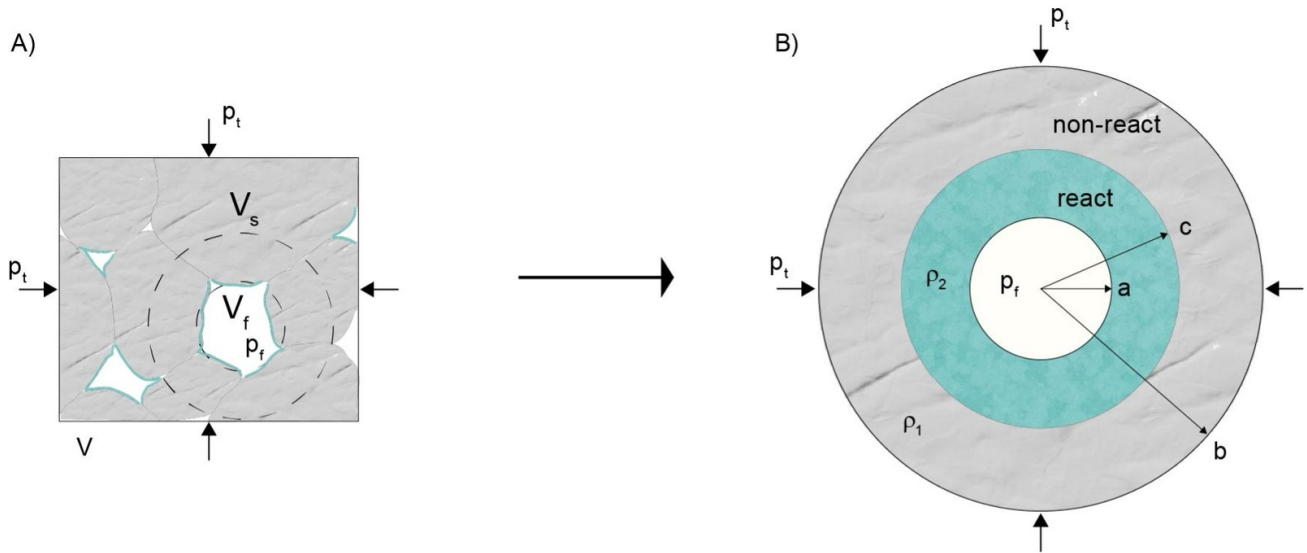


Figure 1. Schematic model for mineral replacement reaction. (a) The total volume, V , consists of solid, V_s , and pore fluid, V_f . The reaction starts at the fluid-solid contact and progresses into the solid volume (green). The fluid pressure, p_f , and the external total pressure, p_t , act on the volume in a viscous model. In the elastic model, the rates of fluid pressure, $\dot{p}_f$, and total pressure, $\dot{p}_t$, are prescribed at the internal and external boundaries of the volume, respectively. **(b)** Representative Elementary Volume (REV) for mineral replacement reaction in porous media. The reaction starts around the cylindrical pore and progresses into the initial solid phase. Reacted and non-reacted materials have different densities and mechanical properties. Pore radius, a , and radius of REV, b , are determined by porosity. A reaction rim of radius c grows into the shell starting from the pore radius, a .

on the Lagrangian hyperelastic formulation of Lurie (1990), Levin et al. (2013), and Levin et al. (2021). Numerical aspects of its implementation are described in Moulas et al. (2023). The nonlinear elastic behavior in our numerical model is described in terms of the strain energy function, W , as follows:

$$\sigma_j = \frac{\lambda_j}{i_3} \frac{\partial W}{\partial \lambda_j} \quad (15)$$

$$W = 2G(i_1 - 3) + \frac{K_0}{K'(K' - 1)} \left[i_3^{1-K'} + (K' - 1)i_3 \right] \quad (16)$$

Here, σ_i are the true (Cauchy) stress components, λ_i are the principal stretches, and i_1, i_3 are the invariant forms defined as

$$i_1 = (\lambda_1 + \lambda_2 + \lambda_3) - 3\sqrt[3]{i_3}, \quad i_3 = \lambda_1 \lambda_2 \lambda_3 \quad (17)$$

Equations reduce to the isothermal Murnaghan EOS for pure-hydrostatic compression. G , K_0 and K' are the nonlinear material parameters. In the linear limit, K_0 , and G reduce to the usual bulk and shear moduli.

In the numerical examples presented below, we set both the total confining pressure p_t and fluid pressure p_f to zero at the boundaries. This choice ensures that the resulting stresses are driven solely by the extent of the chemical reaction and associated deformation, rather than by externally imposed boundary loads. This approach provides conservative estimates that can be interpreted as perturbations from the geological stresses developed due to natural confinement. It is important to emphasize that the derived analytical solution is general and allows for arbitrary boundary pressures. Figure 2A and 2B illustrate increments of stress and displacements within the REV computed for

nonlinear hyperplastic materials under traction-free boundary conditions when $p_f = p_t = 0$ corresponding to a small increase in reaction progress from $\xi = 0.4$ by the amount given by $d\xi$. The incremental linear elastic analytical solution is also shown for comparison. The incremental nature of the analytical solution implies that the final values of the external loads and reaction progress are reached in several steps by applying small incremental changes to the external parameters and evaluating how the internal parameters, i.e., stress and displacement change in response to the small loads. This approach gives an improved estimate in case of large strains in comparison with small-strain elastic solutions. Figure 2A and 2B show a comparison of the numerical and analytical solutions for two different values of incremental steps in solution, given as increments in the reaction progress $d\xi$ at zero fluid and total pressures. They show that the analytical solution obtained with small incremental steps $d\xi = 0.01$ is indistinguishable from a fully nonlinear large-strain numerical solution. Larger increments in the analytical solution $d\xi = 0.1$ lead to minor deviations from the nonlinear numerical solution. Moreover, comparison of numerical solutions obtained for two different values of the nonlinear parameter K' , show that nonlinearity has an insignificant influence on the solution. The material's response to the applied load and reaction progress are mainly controlled by the linear elastic bulk and shear moduli.

2.2. Elastoplastic adjustment of the matrix

As the reaction continues, stress discontinuity grows at the reaction front (fig. 2). Stresses might eventually reach the

Table 1. List of principal notations

Symbol	Meaning	Unit
a	Internal radius of RVE	m
b	The external radius of RVE	m
A_{ij}, B_{ij}, C_{ij}	Coefficients in the elastic solution summarized in Appendix B	
c	Position of the reaction front in RVE	m
C_s, C_f	Mass fraction of species in solid and fluid	
C_{tot}	Total mass concentration of species	kg/m ³
D_{C_f}	Effective diffusivity of species in fluid	s
g_i	Gravity	m/s ²
G	Elastic shear modulus	Pa
k	Permeability	m ²
K	Elastic bulk modulus of solid material within REV	Pa
K_s, K_d, K_ϕ	Macroscopic solid, drained and effective pore space bulk moduli	Pa
K_0, K'	Parameters in the nonlinear Murnaghan EOS	
p_t, p_f, p_e	Total, fluid, and effective pressures	Pa
q_D	Darcy's flux	m/s
r	Radial coordinate within RVE	m
t	time	s
v	Velocity within RVE	m/s
v_s, v_f	Solid and fluid velocity	m/s
V, V_s, V_f	Total, solid, and fluid volumes within RVE	m ²
X_s	Mass fraction of nonvolatile components in solid	
X_1, X_2	Mass fraction of immobile solid within RVE before and after reaction	
Y_1, Y_2	Yield limit of non-reacted and reacted part of REV	Pa
α	Biot-Willis parameter	
δ_{ij}	Kronecker delta, or identity matrix	
ε	Macroscopic volumetric strain	
η	Viscosity	Pa s
Θ	The density ratio of an immobile component before and after the reaction, equation	
κ_ϕ, κ_d	Reaction expansion coefficient of pore space and total volume	
κ_s	Reaction expansion coefficient of solid, equation (41)	
μ_f	Viscosity of fluid	Pa s
μ_1, μ_2	Solid shear viscosity within RVE	Pa s
μ_{C_f}	Specific chemical potential of species in fluid	J/kg
ξ	Reaction progress	
ρ_s, ρ_f, ρ_t	Densities of solid, fluid and total density of porous material	kg/m ³
ρ_1, ρ_2	Densities of non-reacted and reacted part of REV	kg/m ³
σ_i	Components of stress tensor within RVE	Pa
τ_{ij}	Macroscopic tensor of stress deviator	Pa
ϕ	Porosity	
χ	Sign of effective pressure in REV	

strength of the rock. This will lead to the development of the failure region either from the pore radius or ahead of the reaction front. Where the failure region will develop de-

pends mainly on the fluid pressure increase and reaction kinetics. Indeed, observations show that reaction-induced micro-cracks were developed in natural systems (Malvoisin

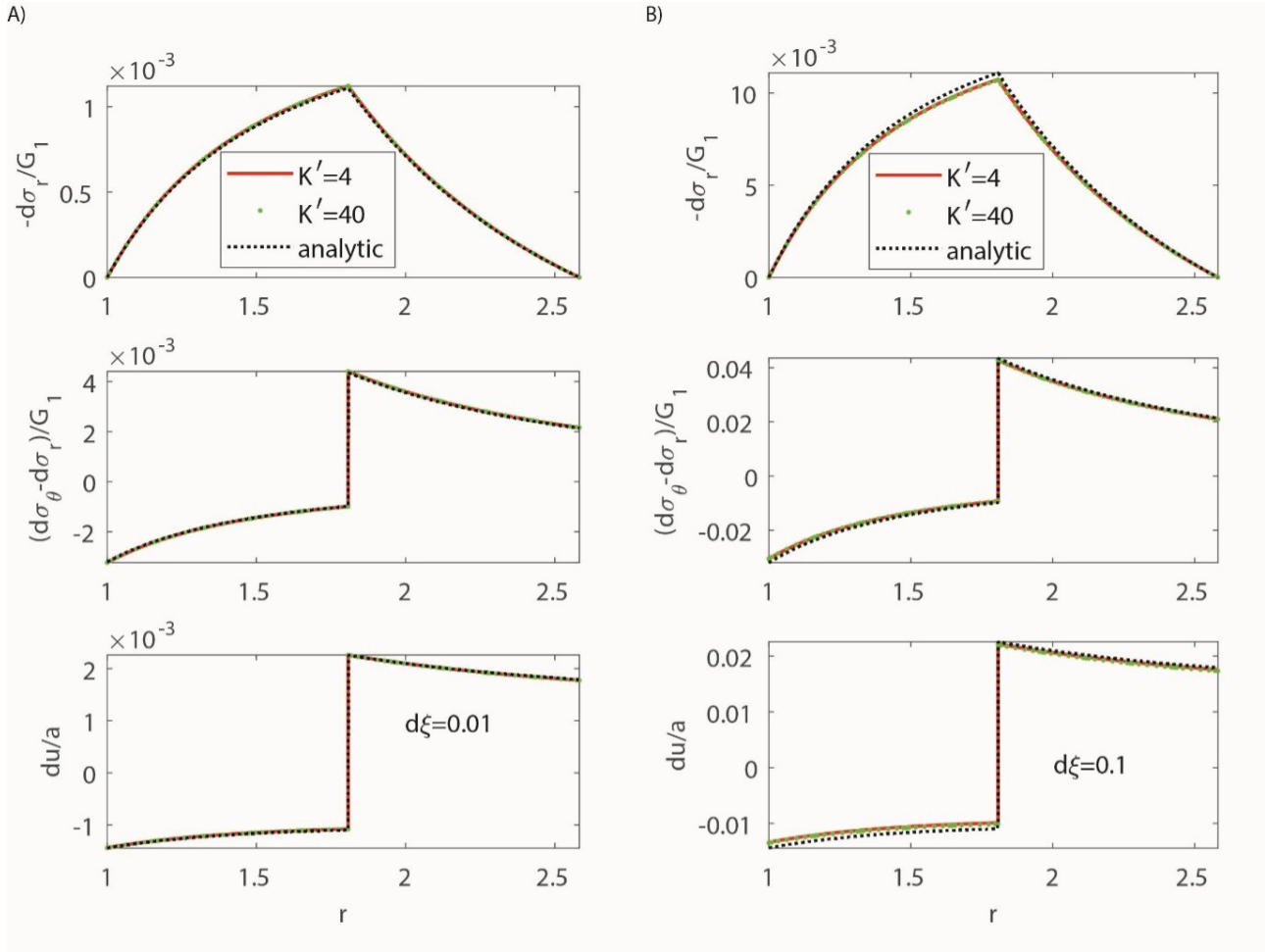


Figure 2. Comparison of elastic stress and displacement increments within REV: incremental analytical vs. fully nonlinear numerical solutions corresponding to a small increase in reaction progress from $\xi = 0.4$ by the amount of $d\xi$ as indicated on the figures. All simulations were performed at $\varphi = 0.15$, $\frac{\rho_2}{\rho_1} = 0.8$, $\frac{G_2}{G_1} = 0.7$, $\frac{K_1}{G_1} = 3.3$.

et al., 2020; Plümper et al., 2012) and laboratory experiments (Fabbri et al., 2009; C. V. Putnis et al., 2021). Failure around the pore radius might be expected when the reaction product is weaker than the original material, and the following condition is satisfied:

$$\begin{aligned} & \left| \sigma_r^2 - \sigma_\theta^2 \right|_{r=a} \\ &= 2G_2 \frac{\left| (\xi + (1-\xi)\varphi)p_e + G_1(1-\varphi)^2(1-\Theta)(1-\xi)\xi \right|}{(G_1\Theta(1-\xi)\varphi + G_2\xi)(1-\varphi)} \\ &= 2Y_2 \end{aligned} \quad (18)$$

where $\Theta = \frac{\rho_2 X_2}{\rho_1 X_1}$. Failure will start ahead of the reaction front if the reaction product is stronger than the original material and the following condition is fulfilled:

$$\begin{aligned} & \left| \sigma_r^1 - \sigma_\theta^1 \right|_{r=c} \\ &= 2G_1 \frac{\left| (\xi + (1-\xi)\varphi)\Theta\varphi p_e - G_2\xi(1-\varphi)^2(1-\Theta)\xi \right|}{(\xi + (1-\xi)\varphi) \left(\frac{G_1\Theta(1-\xi)\varphi}{+G_2\xi} \right) (1-\varphi)} \\ &= 2Y_1 \end{aligned} \quad (19)$$

Failure ahead of the reaction front will open pathways for fluid flow and will provide fluid access to new reactive surfaces. Below, we focus on the case when fractures develop

ahead of the reaction front. The analysis for the case when fractures are induced in the reacted region is similar.

We assume that the entire non-reacted region in [figure 1](#) is in a state of plastic failure and obeys the von Mises

$$\sigma_r - \sigma_\theta = 2Y_1\chi \quad (20)$$

where $\chi = \text{sign}(p_e)$. For simplicity, we assume that the solid is incompressible, i.e., that $\frac{1}{K} = 0$ in equations and . Together with the force balance equation and boundary conditions at the external radius, the failure criterion fully defines the stresses in the fractured, non-reacted zone:

$$\begin{aligned} \sigma_r^1 &= -p_t + 2Y_1\chi \ln \frac{b}{r}, \\ \sigma_\theta^1 &= -p_t + 2Y_1\chi \left(\ln \frac{b}{r} - 1 \right) \end{aligned} \quad (21)$$

The solution to the equation under the condition that $\frac{1}{K} = 0$ determines the following form of radial displacement

$$u^1 = u_c^1(t) \frac{c}{r} \quad (22)$$

Elastic equations – define the mechanical equilibrium in the reacted (non-fractured) zone, giving

$$\begin{aligned}\sigma_r^2 &= -p_f + 2G_2c \left(\frac{1}{a^2} - \frac{1}{r^2} \right) u_c^2(t), \\ \sigma_r^2 &= -p_f + 2G_2c \left(\frac{1}{a^2} + \frac{1}{r^2} \right) u_c^2(t)u^2 \quad (23) \\ &= u_c^2(t) \frac{c}{r}\end{aligned}$$

Unknown displacements at the reaction front $u_c^1(t)$ and $u_c^2(t)$ can be found by satisfying the equation, namely

$$u_c^1(t) = \frac{(1 - \Theta)c}{2} + \Theta u_c^2(t) \quad (24)$$

$$u_c^2(t) = - \left(p_e(t) + 2Y_1 \chi \ln \left(\frac{c}{b} \right) \right) \frac{ca^2}{2G_2(c^2 - a^2)} \quad (25)$$

Velocities can be found by differentiating displacements, giving

$$v_1 = v_2 \Theta + \frac{(b^2 - a^2)(1 - \Theta)}{2r} \frac{d\xi}{dt} \quad (26)$$

$$\begin{aligned}v_2 &= -a^2 \frac{a^2 + \xi(b^2 - a^2)}{2\xi G_2(b^2 - a^2)r} \frac{dp_e}{dt} + \\ &\frac{\chi Y a^2}{G_2 r} \frac{(b^2 - a^2)\xi + 2a^2}{4\xi^2(b^2 - a^2)} \left(\frac{\frac{|p_e|}{Y}}{+ \ln \left(\frac{(b^2 - a^2)\xi + a^2}{b^2} \right)} \right) \frac{d\xi}{dt} \quad (27)\end{aligned}$$

We replaced reaction radius, c , with reaction progress, ξ , using the equation. Figure 3 shows the obtained elastoplastic distribution of stresses and displacements in the REV under traction-free boundary conditions. The stresses in the REV are solely a result of the advancing reaction.

2.2.1. Effects of nonlinearity and comparison with the numerical solution

To evaluate the impact of nonlinearity, we compared the obtained analytical solution with the finite-strain numerical solution (fig. 3). Our numerical code incorporates an associative plastic flow rule with a von Mises yield criterion. Using a commonly adopted multiplicative approach, the strain gradient is decomposed into elastic and plastic components. For a more comprehensive understanding of the numerical implementation, further information can be found in the work by Moulas et al. (2023). Like in the previous elastic analysis, the influence of the nonlinear elastic parameter K' remains minor. The effect of plastic failure on the solution is more pronounced than nonlinear elastic effects. Our analytical solution was obtained assuming the entire nonreacted region experiences plastic flow. In the numerical solution, increasing load caused the gradual spreading of the plastic zone before reaching a fully plastic state. Comparison with the numerical solution shows that ignoring the gradual growth of the plastic zone in the analytical solution did not affect the result.

2.3. Viscous and viscoplastic deformation of the rock

Viscous and viscoplastic solutions can be obtained quite similarly by replacing Hook's law with linear viscous Newton's law:

$$\frac{\partial v}{\partial r} - \frac{v}{r} = \frac{\sigma_r - \sigma_\theta}{2\mu}, \quad \frac{\partial v}{\partial r} + \frac{v}{r} = \frac{\sigma_r + \sigma_\theta}{2\eta} \quad (28)$$

Solution of equations together with the stress balance equation, condition at the reaction interface and boundary

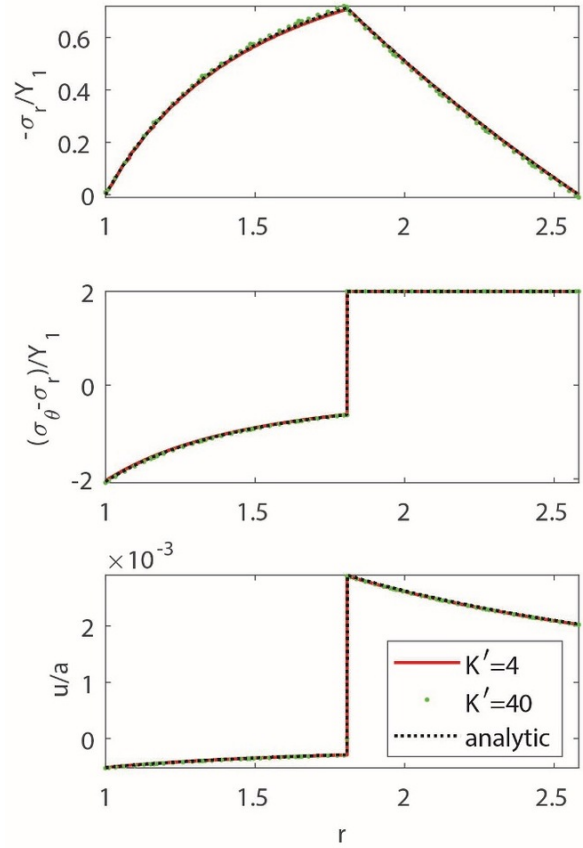


Figure 3. Comparison of elastoplastic stresses and displacements within REV: analytical vs. fully nonlinear numerical solutions corresponding to a reaction progress $\xi = 0.4$. Simulations were performed at $\varphi = 0.15$, $\frac{p_2}{p_1} = 0.8$, $\frac{G_2}{G_1} = 0.7$, $\frac{K_1}{G_1} = 100$, $\frac{G_1}{Y_1} = 1500$.

conditions give the following expressions for the velocities in the reacted and non-reacted zones for the purely viscous case:

$$v_1 = -\frac{1}{2r\hat{G}} \left(\frac{b^2}{b^2 - a^2} A_{11}p_e + A_{12}p_f + A_{13} \frac{d\xi}{dt} \right) \quad (29)$$

$$v_2 = -\frac{1}{2r\hat{G}} \left(\frac{b^2}{b^2 - a^2} A_{21}p_e + A_{22}p_f + A_{23} \frac{d\xi}{dt} \right) \quad (30)$$

The shorthand notations used in equations and are summarized in Appendix B. For the viscoplastic case, one has to add a yield criterion, obtaining the following velocities:

$$v_1 = \frac{(b^2 - a^2)(1 - \Theta)}{2r} \frac{d\xi}{dt} - \frac{a^2 \Theta (a^2 + (b^2 - a^2)\xi)}{2\xi(b^2 - a^2)r\mu_2} \quad (31)$$

$$v_2 = -\frac{a^2(a^2 + (b^2 - a^2)\xi)}{2\xi(b^2 - a^2)r\mu_2} \left(\chi Y_1 \ln \frac{a^2 + (b^2 - a^2)\xi}{b^2} + p_e \right) \quad (32)$$

2.4. Averaging

The previous relationships can be used to obtain expressions for the effective rheology of a porous, two-phase model. To derive macroscopic compaction equations for reacting materials, we substitute the obtained velocities given by equations and for the elastic case, and for the elastoplastic case, and for the viscous case, and for the viscoplastic case into the equations and . This results in the following elastic/elastoplastic compaction equations

$$\frac{d\varphi^e}{dt} = -\frac{1}{K_\varphi} \frac{dp_e}{dt} + \varphi \left(\frac{1}{K'_s} - \frac{1}{K''_s} \right) \frac{dp_f}{dt} - \kappa_\varphi \frac{d\xi}{dt} \quad (33)$$

$$\frac{d\varepsilon^e}{dt} = -\frac{1}{K_d} \left(\frac{dp_t}{dt} - \alpha \frac{dp_f}{dt} \right) + \kappa_d \frac{d\xi}{dt} \quad (34)$$

Viscous/viscoplastic compaction equations take the following form:

$$\frac{d\varphi^v}{dt} = -\frac{p_e}{\eta_\varphi} - \kappa_\varphi \frac{d\xi}{dt} \quad (35)$$

$$\frac{d\varepsilon^v}{dt} = -\frac{p_e}{\eta_d} + \kappa_d \frac{d\xi}{dt} \quad (36)$$

Cases with and without plasticity will have different coefficients in the compaction equations, as summarized in [tables 2–4](#). Combining both endmembers, we obtain the following macroscopic Maxwell-type viscoelastoplastic equations for reaction-induced volume change and porosity evolution:

$$\frac{d^s\varepsilon}{dt} = -\frac{1}{K_d} \left(\frac{d^s p_t}{dt} - \alpha \frac{d^s p_f}{dt} \right) - \frac{p_e}{\eta_d} + \kappa_d \frac{d^s \xi}{dt} \quad (37)$$

$$\frac{d^s \varphi}{dt} = -\frac{1}{K_\varphi} \left(\frac{d^s p_t}{dt} - \frac{d^s p_f}{dt} \right) + \varphi \left(\frac{1}{K'_s} - \frac{1}{K''_s} \right) \frac{d^s p_f}{dt} - \frac{p_e}{\eta_\varphi} - \kappa_\varphi \frac{d^s \xi}{dt} \quad (38)$$

In equations and , the reaction contributes to both porosity changes, as in classical dissolution-precipitation models, and solid volume change, as suggested by Malvoisin et al. (2021). In addition to explicit reactive terms in compaction equations, reactions also affect effective compressibility K_d , K_φ and viscosity η_d , η_φ . Interestingly, the progressing reaction, in combination with the compressibility of the solid phase, leads to the appearance of two solid bulk moduli K'_s and K''_s . These are usually attributed to the existence of a non-connected pore space (Detournay & Cheng, 1993). In our case, the difference between the two moduli results from the presence of a compressible solid phase with different mineralogical compositions and densities. Even when the bulk and shear moduli of mineralogical components are the same, these two moduli will still be different due to ongoing reaction and density differences. Effective bulk moduli and effective viscosities in equations and generally depend on porosity, reaction progress, density contrast, and material parameters of the constituents ([tables 2–4](#)). In the case of a reactive but incompressible solid, $K'_s = K''_s$. In the non-reacting limit with an incompressible solid, equations and reduce to compaction equations derived in (Yarushina & Podladchikov, 2015), which are shown to be consistent

with Biot's theory of poroelasticity (Biot, 1941) and Gassmann's relations (Gassmann, 1951).

3. PROPERTIES OF DERIVED RHEOLOGY

Solid compressibility, effective stress law, and independent set of equationsOur solution is obtained under the condition that immobile species are preserved in the system, i.e., that the following mass conservation equation holds:

$$\frac{\partial(\rho_s X_s (1 - \varphi))}{\partial t} + \frac{\partial}{\partial x_j} (\rho_s X_s (1 - \varphi) v_s^j) = 0 \quad (39)$$

where X_s is the mass fraction of nonvolatile components in the solid. X_s is closely related to the reaction progress, ξ , defined earlier:

$$\xi = \frac{X_s - X_{s,initial}}{X_{s,final} - X_{s,initial}} = \frac{X_s - X_{s,initial}}{X_{s,eq}} \quad (40)$$

Both X_s and ξ can be calculated for each given reaction based on the molar masses of the compounds (see examples for various reactions in Appendix A). Mass conservation for immobile species can be combined with derived compaction equations and , leading to the very general form of the equation of state for a solid:

$$\frac{1}{\rho_s} \frac{d^s \rho_s}{dt} = \frac{1}{K_s(1 - \varphi)} \left(\frac{d^s p_t}{dt} - \alpha' \frac{d^s p_f}{dt} \right) + \kappa_s \frac{d^s X_s}{dt} \quad (41)$$

Here, solid bulk modulus K_s can be a complicated function of porosity, stress state, and reaction. Yet, it is related to the drained and pore bulk moduli through the relation familiar from non-reactive poroelasticity (Yarushina & Podladchikov, 2015)

$$\frac{1}{K_s} = \frac{1 - \varphi}{K_d} - \frac{1}{K_\varphi} \quad (42)$$

Changes in density due to reaction only are defined by the additional reaction expansion coefficient (see [table 1](#) for notations)

$$\kappa_s = \frac{1}{1 - X_s} - \frac{\kappa_d}{X_{s,eq}} - \frac{\kappa_\varphi}{(1 - \varphi)X_{s,eq}} \quad (43)$$

The influence of fluid pressure on the density of the solid is given by the partitioning coefficient α' that depends on the nature of the reaction as well as on porosity:

$$\alpha' = \varphi \frac{G_2 \Theta \xi (1 - \varphi) + (\Theta - 1)(K_2 + G_2)}{G_2 \Theta \xi (1 - \varphi) + (\Theta - 1)(K_2 + G_2) \varphi} \quad (44)$$

When approaching the nonreactive limit, we recover the conventional relation $\alpha' = \varphi$ (e.g., Yarushina & Podladchikov, 2015).

By incorporating the equation along with the equations provided in [table 2](#), one can derive the following equation for the Biot-Willis parameter (Biot & Willis, 1957)

$$\alpha = 1 - \frac{1 - \alpha'}{1 - \varphi} \frac{K_d}{K_s} \quad (45)$$

that quantifies the partitioning of stress between the solid framework of the material and the pore fluid in the equation . The latter can be interpreted as an effective stress law for volumetric deformation. In the nonreactive limit $\alpha' = \varphi$, the equation reduces to the classical relation between elastic moduli and the equation to the classical elastic effective stress law. Note, however, that reaction

Table 2. Coefficients in the compaction equations with elastically compressible reaction product and incompressible pristine material, without plasticity

Elastic	Viscous
$\kappa_\varphi = \frac{\varphi(1-\varphi)(1-\Theta)((1-\xi)(K_2+G_2)G_1+K_2G_2\xi)}{K_2G_2\xi+\Theta G_1(1-\xi)((K_2+G_2)\varphi+\xi G_2(1-\varphi))}$	$\kappa_\varphi = \frac{\varphi(1-\varphi)(1-\Theta)(\mu_1(1-\xi)+\mu_2\xi)}{\Theta\mu_1(1-\xi)\varphi+\mu_2\xi}$
$\kappa_d = \frac{\kappa_\varphi\Theta(K_2+G_2)(\xi+(1-\xi)\varphi)}{(1-\varphi)^2(1-\Theta)((1-\xi)(K_2+G_2)G_1+K_2G_2\xi)}$	$\kappa_d = \kappa_\varphi \frac{\mu_2\xi}{\varphi(\mu_1(1-\xi)+\mu_2\xi)}$
$\frac{1}{K_\varphi} = \frac{\varphi((1-\xi)\varphi+\xi)}{(1-\varphi)} \times \frac{(K_2+G_2)(1-\Theta\varphi)-G_2\Theta(1-\varphi)\xi}{((G_2+K_2)\varphi+\xi G_2(1-\varphi))G_1\Theta(1-\xi)+K_2G_2\xi}$	$\frac{1}{\eta_\varphi} = \frac{\varphi(1-\Theta\varphi)(\xi+(1-\xi)\varphi)}{(1-\varphi)(\Theta\mu_1(1-\xi)\varphi+\mu_2\xi)}$
$K_d = K_\varphi \frac{\varphi(K_2(1-\Theta\varphi)+G_2(1-\Theta(\xi+(1-\xi)\varphi)))}{\Theta(\varphi K_2+G_2(\xi+(1-\xi)\varphi))}$	$\eta_d = \eta_\varphi \left(\frac{1}{\Theta} - \varphi \right)$
$\alpha = \frac{(K_2+G_2)\varphi}{\varphi K_2+G_2((1-\xi)\varphi+\xi)}$	
$\frac{1}{K'_s} = \frac{G_2\Theta\xi((1-\xi)\varphi+\xi)}{G_1\Theta(1-\xi)((G_2+K_2)\varphi+\xi G_2(1-\varphi))+K_2G_2\xi}$	
$K''_s = K'_s \frac{G_2\Theta((1-\xi)\varphi+\xi)}{G_2-G_1(1-\varphi)(1-\xi)\Theta}$	

Table 3. Coefficients in the compaction equations with failure ahead of the reaction front

Elastoplastic strong product	Viscoplastic strong product
$\frac{\kappa_\varphi - \varphi(1-\varphi)(1-\Theta)}{\kappa_d - (1-\varphi)(1-\Theta)} = \varphi - \frac{1}{\Theta}$	$\kappa_\varphi = \varphi(1-\varphi)(1-\Theta)$
$\kappa_d = (1-\Theta)(1-\varphi) - \frac{\chi Y_1}{G_2} \frac{\Theta\varphi}{\xi} + \frac{\Theta\varphi Y_1(\xi+\varphi(2-\xi))}{2G_2\xi^2(1-\varphi)} \left(\frac{ p_e }{Y_1} + \ln(\varphi+(1-\varphi)\xi) \right)$	$\kappa_d = \frac{\kappa_\varphi}{\varphi}$
$\frac{1}{K_\varphi} = \frac{\varphi(1-\Theta\varphi)(\varphi+(1-\varphi)\xi)}{G_2\xi(1-\varphi)}$	$\frac{1}{\eta_\varphi} = \frac{\varphi(1-\Theta\varphi)(\varphi+(1-\varphi)\xi)}{\mu_2\xi(1-\varphi)} \times \left(1 + \frac{Y_1}{ p_e } \ln(\varphi+(1-\varphi)\xi) \right)$
$K_d = K_\varphi \left(\frac{1}{\Theta} - \varphi \right)$	$\eta_d = \eta_\varphi \left(\frac{1}{\Theta} - \varphi \right)$

Table 4. Coefficients in the compaction equations with failure in the reacted region

Elastoplastic weak product	Viscoplastic weak product
$\kappa_\varphi = \frac{(1-\varphi)(1-\Theta)}{\Theta}$	$\kappa_\varphi = \frac{(1-\varphi)(1-\Theta)}{\Theta}$
$\kappa_d = 0$	$\kappa_d = 0$
$\frac{1}{K_\varphi} = \frac{\varphi+(1-\varphi)\xi}{G_1(1-\xi)(1-\varphi)}$	$\frac{1}{\eta_\varphi} = \frac{(1-\Theta\varphi)(\varphi+(1-\varphi)\xi)}{\mu_1(1-\xi)(1-\varphi)\Theta} \times \left(1 + \frac{Y_2}{ p_e } \ln \frac{\varphi}{\varphi+(1-\varphi)\xi} \right)$
$K_d = K_\varphi \left(\frac{1}{\Theta} - \varphi \right)$	$\eta_d = \eta_\varphi \left(\frac{1}{\Theta} - \varphi \right)$

progress generally depends on fluid pressure (Llana-Fúnez et al., 2012). Thus, the partitioning between the total stress and fluid pressure in the effective stress law for reactive systems can be modified even further.

Let us note at last that equations , and are linearly dependent. Thus, only two of them can be used simultaneously. Given that equations of state for various solids are well documented in thermodynamic databases such as Holland and Powell (1998) or Johnson et al. (1992), it is more

convenient to use the equation and determine their parameters from databases for each given pressure, temperature, and reaction.

3.2. The relative importance of reactive terms

The dominance of either volume expansion or porosity reduction is contingent upon the relative significance of the reactive terms in equations and . In the absence of failure during the reaction, the ratio of effective reaction expansion coefficients can be determined by equations

$$\frac{\kappa_d}{\kappa_{\varphi} \text{ (elastic)}} = \frac{G_2 \xi}{(G_1(1 - \xi) + G_2 \xi) \varphi}, \quad (46)$$

$$\frac{\kappa_d}{\kappa_{\varphi} \text{ (viscous)}} = \frac{\mu_2 \xi}{(\mu_1(1 - \xi) + \mu_2 \xi) \varphi}$$

During the initial stages of the reaction, when $\xi \ll 1$, the volume expansion induced by the reaction is minimal, primarily leading to porosity reduction akin to dissolution/precipitation models. However, as the reaction progresses, the importance of volume expansion becomes comparable to porosity reduction. In materials with low porosity or when porosity becomes clogged due to the reaction, volume expansion is more important than porosity reduction, facilitating further accommodation of the reaction.

If inelastic failure or micro-cracking ahead of the reaction front is involved, the volume expansion and pore size reduction due to the reaction become equally important in both elastoplastic and viscoplastic cases, as given by the following ratios of reactive expansion coefficients

$$\frac{\kappa_{\varphi} - \varphi(1 - \varphi)(1 - \Theta)}{\kappa_d - (1 - \varphi)(1 - \Theta)} \text{ (elastoplastic)} = \varphi - \frac{1}{\Theta}, \quad (47)$$

$$\frac{\kappa_d}{\kappa_{\varphi} \text{ (viscoplastic)}} = \frac{1}{\varphi}$$

In low-porosity rocks, volumetric expansion due to reaction will be more pronounced than porosity reduction in viscoplastic rocks and of the same order of magnitude in elastoplastic rocks, as follows from the equation . If failure occurs in the reacted zone, then the influence of the reaction on the total volume will be minimal and result only in the porosity changes due to the reaction.

3.3. Dependence of failure limit on reaction

Failure criteria and can be used to evaluate the influence of chemical reactions on the material's strength. The critical effective pressure required to start failure in the rate-independent elastoplastic case can be estimated as a minimum of p_c^1 and p_c^2 that are given below:

$$p_c^1 = \frac{G_2 \xi (1 - \varphi)^2 (1 - \Theta)}{\Theta \varphi (\xi + (1 - \xi) \varphi)} \xi + \chi Y_1 (1 - \varphi) \frac{G_2 \xi + G_1 \Theta \varphi (1 - \xi)}{G_1 \Theta \varphi} \quad (48)$$

$$p_c^2 = - \frac{G_1 \xi (1 - \varphi)^2 (1 - \Theta) (1 - \xi)}{\xi + (1 - \xi) \varphi} \xi + \chi Y_2 (1 - \varphi) \frac{G_2 \xi + G_1 \Theta \varphi (1 - \xi)}{G_2 (\xi + (1 - \xi) \varphi)} \quad (49)$$

Similarly, the failure limit in reacting viscoplastic rocks is given by a minimum of p_c^1 and p_c^2 that are given below:

$$p_c^1 = \frac{\xi \mu_2 (1 - \varphi)^2 (1 - \Theta)}{\Theta \varphi (\xi + (1 - \xi) \varphi)} \frac{d\xi}{dt} + \chi Y_1 (1 - \varphi) \frac{\mu_2 \xi + (1 - \xi) \varphi \Theta \mu_1}{\mu_1 \Theta \varphi} \quad (50)$$

$$p_c^2 = - \frac{\mu_1 (1 - \varphi)^2 (1 - \Theta) (1 - \xi)}{\xi + (1 - \xi) \varphi} \frac{d\xi}{dt} + \chi Y_2 (1 - \varphi) \frac{\mu_2 \xi + (1 - \xi) \varphi \Theta \mu_1}{\mu_2 (\xi + (1 - \xi) \varphi)} \quad (51)$$

In the limiting cases of no reaction $\xi = 0$ and fully reacted material ($\xi = 1$), the usual limits for critical effective pressure $|p_e|_{\xi=0} = Y_1(1 - \varphi)$ and $|p_e|_{\xi=1} = Y_2(1 - \varphi)$ are recovered (Yarushina & Podladchikov, 2010, 2015). [Figure 4](#) shows an example of the resulting critical pressure for viscous materials. Depending on whether the pristine material is weaker or stronger than the final reaction product, the material strength during the reaction will deteriorate or increase non-linearly. Experiments on exposure of Portland cement to CO₂-rich or H₂S-rich fluids indeed show an evolution of mechanical strength with reaction progress. Carbonated cement shows higher yield stress than unreacted cement (Lecampion et al., 2011), while cement exposed to H₂S loses its strength (Vrålstad et al., 2016). Cement weakening is associated with converting denser and harder iron to pyrite. In contrast, the conversion of portlandite into denser and harder calcite leads to the strengthening of cement.

3.4. Implications for the “force” of crystallization

Our model predictions contribute to reconciling the varying estimates of the “force” of crystallization. It has long been recognized that chemical reactions involving an increase in the solid volume, or crystal growth, can generate stresses (e.g., Korenaga, 2025; Steiger, 2005; Weyl, 1959 and references therein). These stresses are often evaluated in terms of the “force” of crystallization, defined as the difference between the pressure on a growing crystal's surface and the fluid pressure. Note that, as such, the “force” of crystallization has units of stress, not force. The thermodynamic models relate the “force” of crystallization to either the oversaturation of the solution phase (Correns & Steinborn, 1939) or the curvatures of the solid-liquid interface (Everett, 1961) and predict the “force” of crystallization that is on the order of several GPa (Wolterbeek et al., 2018). However, direct measurements of the “force” of crystallization generated during CaO hydration show stresses of up to 153 MPa, which constitute only 5% of the maximum value predicted by the thermodynamic theory for the “force” of crystallization (Van Noort et al., 2017; Wolterbeek et al., 2018). Similarly, experimental estimates for the “force” of crystallization during MgO hydration ranged from 20 to 200 MPa (Ostapenko, 1976). This mismatch can be attributed to the assumption of the ideal elastic behavior of a solid crystal in the previous models. As stresses reach the shear failure limit, which is on the order of several hundred MPa for many rocks, the inelastic processes will interfere with stress build-up. In our model, the “force” of crystallization can be estimated as the normal stress arising at the reaction front. It depends on the mechanical properties of the con-

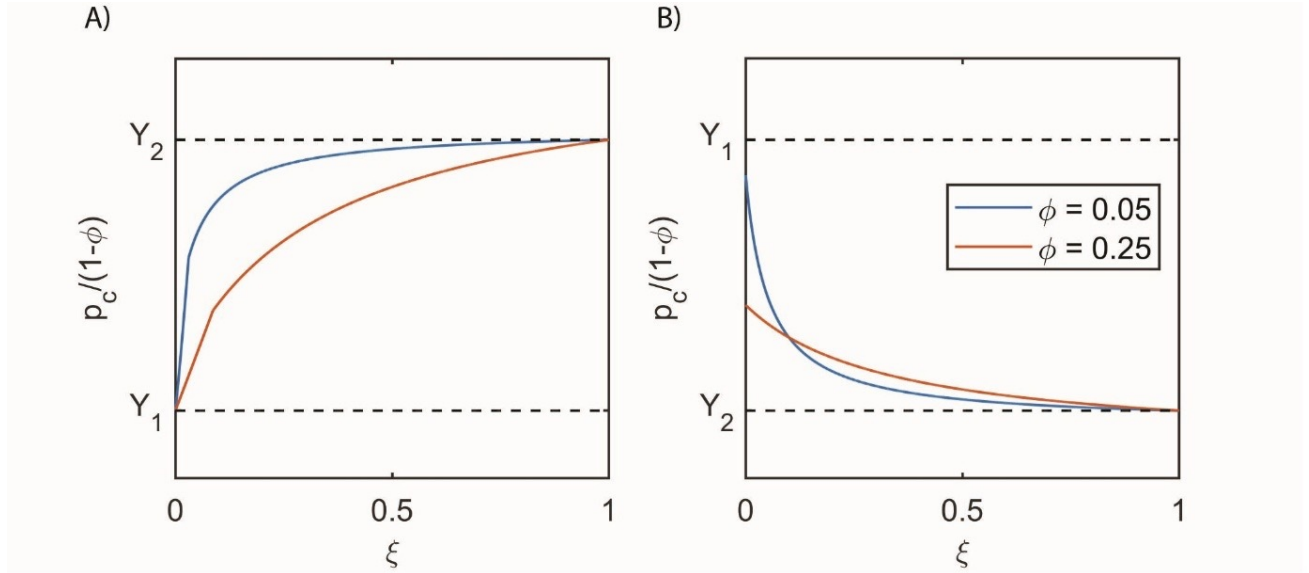


Figure 4. Model predictions for failure limits in reactive viscous porous materials. (a) The reaction product is stronger than the pristine material, $\frac{Y_2}{Y_1} = 3$, $\frac{\mu_2}{\mu_1} = 2$ (b) The reaction product is weaker than the pristine material, $\frac{Y_1}{Y_2} = 3$, $\frac{\mu_1}{\mu_2} = 2$. Simulations were performed at $\frac{d\xi}{dt} = 10^{-3}$, $\Theta = 0.8$ and two different values of porosity as indicated in the figure.

stituents, applied effective pressure, density change during the reaction, porosity, reaction kinetics, and the reaction progress:

$$F_c^{elastic} = \frac{dp_e}{\kappa_c^e} + \frac{G_1}{\kappa_c^e} \frac{(1-\xi)(\Theta-1)(1-\varphi)^2}{\xi + (1-\xi)\varphi} d\xi \quad (52)$$

$$F_c^{viscous} = \frac{p_e}{\kappa_c^v} + \frac{\mu_1}{\kappa_c^v} \frac{(1-\xi)(\Theta-1)(1-\varphi)^2}{\xi + (1-\xi)\varphi} \frac{d\xi}{dt} \quad (53)$$

Here,

$$\frac{1}{\kappa_c^e} = \frac{G_2\xi}{G_1\Theta\varphi(1-\xi) + G_2\xi}, \quad (54)$$

$$\frac{1}{\kappa_c^v} = \frac{\mu_2\xi}{\mu_1\Theta\varphi(1-\xi) + \mu_2\xi}$$

When plastic failure is not accounted for, the model may lead to high values of the “force” of crystallization for fast reactions (solid line in [fig. 5](#)). With the onset of shear failure, the “force” of crystallization is limited by the plastic flow. It depends on the applied external load, porosity, extent of reaction, and failure limit of the unreacted solid:

$$F_c^{plastic} = Y_1 \ln(\xi + \varphi(1-\xi)) + p_e \quad (55)$$

Its values are very close to the shear failure limit (dashed line in [fig. 5](#)). Given that the elastic, viscous, and plastic moduli and porosity depend on the curvatures of the solid-liquid interface and pore geometry and reaction progress, ξ , which is directly related to the supersaturation of the solution, our model is a generalization of both classical approaches by Correns and Steinborn (1939) and Everett (1961). Note, however, Mohr-Coulomb or Drucker-Prager failure criteria for rocks depend not only on the shear stress but also on the mean stress. Thus, under high lithostatic pressure, the failure criterion will be more difficult to reach, and thus, elastic or viscous estimates of the force of crystallization might be more relevant. This discussion is closely related to the broader debate surrounding tectonic overpressure—the phenomenon where pore pressures or local-

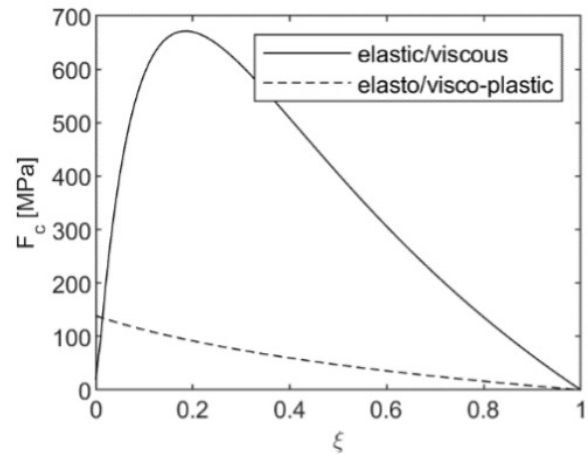


Figure 5. Model predictions for the “force” of crystallization in reacting elastic, viscous, elastoplastic, and viscoplastic porous media. For calculations, we assumed $\varphi = 0.25$, $\Theta = 1.2$, $G_1 = 543\text{MPa}$, $\frac{G_2}{G_1} = \frac{\mu_2}{\mu_1} = 1.5$, $Y = 100\text{MPa}$, $\frac{d\xi}{dt} = 0.02$.

ized stresses exceed lithostatic pressure in the Earth’s crust (Petrini & Podladchikov, 2000; Tajčmanová et al., 2014). Our model provides a framework for understanding how such overpressures might develop during mineral reactions that involve crystallization under confinement.

4. CLOSED SYSTEM OF EQUATIONS FOR REACTIVE TRANSPORT IN DEFORMABLE MEDIA

The previous results can be used to derive a closed system of equations for reactive transport in deformable media. Consider a single chemical reaction in porous media saturated with a reactive fluid. Let us further assume that the solid phase consists of a nonvolatile component that remains in the solid and one or more volatile components that can easily be exchanged between the solid and fluid. We use its mass fraction to quantify the nonvolatile component in the solid phase $X_s = \frac{m_{\text{nonvolatile}}}{m_{\text{solid}}}$. The closed system of equations governing reactive transport in deformable porous rocks is summarized in [table 5](#). It consists of three total momentum conservation equations (1)–(3), three fluid momentum conservation equations in the form of Darcy's law, equations (4)–(6), the total mass conservation equation (7), and the mass conservation equation for the immobile species (8), as formulated by Malvoisin et al. (2017), Omlin et al. (2017), and Schmalholz et al. (2020).

When fluid consists of k components, concentration balance equations can be written for $k-1$ mobile species. A single balance equation must be formulated for a two-component fluid (such as a blend of H_2O and CO_2). It can be, e.g., the concentration of CO_2 with $C_f = \frac{m_{\text{CO}_2}}{m_{\text{fluid}}}$ and $C_s = \frac{m_{\text{CO}_2}}{m_{\text{solid}}}$, which changes due to chemical diffusion and advection (Beinlich et al., 2020; Vrijmoed & Podladchikov, 2022). Maxwell-type viscoelastic equations (10)–(15) given in [table 5](#) can relate deviatoric stress and shear deformation. Porosity equation (16) can describe compaction. We still need fluid and solid equations of state and closure equations for chemical reactions. If the system is in local equilibrium, closure relations for chemical potential μ_{C_f} , con-

centration of immobile solid X_s , and weight fraction of mobile components can be obtained from precalculated (lookup) tables. Given that fluid and solid can have quite complicated nonlinear equations of state depending on the temperature, pressure, and chemical composition, it is more convenient to use thermodynamic databases to recover those quantities as well (Beinlich et al., 2020; Vrijmoed & Podladchikov, 2022). Note that the commonly used mass exchange between fluid and solid (e.g., Rudge et al., 2011; Spiegelman et al., 2001) can be calculated from the mass balance equation for the solid instead of formulating explicit relations

$$\frac{1}{\rho_s} \frac{d^s \rho_s}{dt} - \frac{1}{1-\varphi} \frac{d^s \varphi}{dt} + \nabla \cdot \mathbf{v}_s = \Gamma \quad (56)$$

5. DISCUSSIONS AND CONCLUSIONS

A new micromechanical model for mineral replacement reactions and associated deformation is proposed. In contrast to previous models, where continuity of displacements is strictly enforced across the reaction front (Poluektov et al., 2018) or simply ignored at a risk of kinematic mismatch (Fletcher & Merino, 2001), we treat the reaction front as a sharp moving boundary with possible jumps in mechanical fields, analogous—mathematically—to second-order phase transitions, although not in the strict thermodynamic sense. We formulate the mass conservation law at the discontinuity. Stresses applied externally or generated during chemical reactions are accommodated by elastic, viscous, and plastic deformation. Obtained analytical solutions for deformation within the REV show good agreement with finite strain nonlinear numerical solutions.

An important outcome of the micromechanical model is the derivation of macroscopic (de)compaction equations that link changes in porosity and solid volume to stress,

Table 5. Closed system of equations for coupled flow, reaction, and deformation.

No	equation	variable	
1-3	$\rho_t \frac{d^s v_s^i}{dt} = \frac{\partial(\tau_{ij} - p_t \delta_{ij})}{\partial x_j} - g_i \rho_t$	$v_s^i - 3$	Conservation of total momentum
4-6	$q_D^i = -\frac{k(\varphi)}{\mu_f} \left(\frac{\partial p_f}{\partial x_i} + g_i \rho_f \right)$	$q_D^i - 3$	Darcy's law
7	$\frac{d^s \rho_t}{dt} + \frac{\partial}{\partial x_j} (\rho_f q_D^j + \rho_t v_s^j) = 0$	p_f	Conservation of total mass
8	$\rho_t = \rho_f \varphi + \rho_s (1 - \varphi)$	ρ_t	definition
9	$\frac{\partial(\rho_s X_s (1 - \varphi))}{\partial t} + \frac{\partial}{\partial x_j} (\rho_s X_s (1 - \varphi) v_s^j) = 0$	φ	Conservation of immobile species
10-15	$\frac{1}{2} \left(\frac{\partial v_s^i}{\partial x_j} + \frac{\partial v_s^j}{\partial x_i} \right) - \frac{1}{3} \frac{\partial v_s^k}{\partial x_k} \delta_{ij} = \frac{1}{2G_{eff}} \frac{d^s \tau_{ij}}{dt} + \frac{\tau_{ij}}{2\mu_{eff}}$	$\tau_{ij} - 6$	Viscoelastic shear rheology
16	$\frac{d^s \varphi}{dt} = -\frac{1}{K_\varphi} \left(\frac{d^s p_t}{dt} - \frac{d^s p_f}{dt} \right) - \frac{p_t - p_f}{\eta_\varphi} - \frac{\kappa_\varphi}{X_{seq}} \frac{d^s X_s}{dt}$	p_t	Compaction equation
17	$\frac{\partial C_{tot}}{\partial t} + \frac{\partial}{\partial x_j} \left(-\rho_f C_f \varphi D_{C_f} \frac{\partial \mu_{C_f}}{\partial x_j} + \rho_f C_f q_D^j + C_{tot} v_s^j \right) = 0$	C_{tot}	Balance equation for mobile species in the fluid, only for 2-component fluid
18	$C_{tot} = C_f \rho_f \varphi + C_s \rho_s (1 - \varphi)$	C_s	definition
19-23	$\rho_f = \rho_f(p_f, C_s)$ $\rho_s = \rho_s(p_t, C_s)$ $X_s = X_s(p_f, C_s)$ $C_f = C_f(p_f, C_s)$ $\mu_{C_f} = \mu_{C_f}(p_f, C_s)$	ρ_f ρ_s X_s C_f μ_{C_f}	From thermodynamics

fluid pressure, and chemical reaction. Our results demonstrate that the interplay between reaction-induced deformation and stress can lead to a spectrum of behaviors: at one extreme, solid volume increase outpaces pore volume expansion, reducing porosity and potentially limiting fluid access and reaction progress; at the other, solid and pore volumes evolve in a balanced way that maintains fluid connectivity and allows the reaction to proceed toward completion. This continuum highlights the importance of capturing the relative rates of deformation in the solid and pore space when modeling reactive porous media.

Inelastic failure at the pore scale limits the unrealistically high build-up of the “force” of crystallization and favors the solid volume increase. In our model, the “force” of crystallization is on the order of the yield strength of the rock, which agrees well with experimental data. We show that chemical reactions lead to the appearance of two solid bulk moduli, which are usually attributed to the existence of a non-connected pore space (Detournay & Cheng, 1993). We formulate the effective stress law for the reactive porous rocks, which resembles the classical elastic effective stress law. However, the partitioning between the total stress and fluid pressure in the reactive systems is slightly altered. Our model predicts the dependence of effective bulk moduli, effective viscosities, and critical failure limits on porosity, reaction progress, density contrast, and material parameters of the constituents. To fully account for the coupling between reaction, deformation, and fluid flow, we derive a self-consistent macroscopic closed system of equations ready for implementation in numerical codes.

Acknowledgments

V.Y. acknowledges support from the ACT PERBAS project (No. 340832), funded through the Accelerating CCS Technologies (ACT) initiative. A.V. acknowledges financial support by the Russian Science Foundation (project 25-77-32001). We gratefully acknowledge Evangelos Moulas, Mark Brandon, and Reinier van Noort for their valuable comments and suggestions, which helped improve the quality and clarity of the manuscript. We also thank the anonymous reviewers for their constructive feedback.

Author Contributions

V.Y. has written the manuscript, derived analytical solutions, and performed numerical analysis. Y.P. contributed to the development of ideas. A.V. developed the algorithm and software for the numerical solution under finite strains.

Data Availability

The numerical code used in this study is available for download from <https://zenodo.org/records/10021521>

Editor: Mark Brandon, Associate Editor: Evangelos Moulas

Submitted: October 19, 2023 EDT. Accepted: June 11, 2025 EDT. Published: July 29, 2025 EDT.



This is an open-access article distributed under the terms of the Creative Commons Attribution 4.0 International License (CCBY-NC-ND-4.0). View this license's legal deed at <https://creativecommons.org/licenses/by-nc-nd/4.0> and legal code at <https://creativecommons.org/licenses/by-nc-nd/4.0/legalcode> for more information.

REFERENCES

- Anderson, J. G., Doraiswamy, L. K., & Larson, M. A. (1998). Microphase-assisted “autocatalysis” in a solid-liquid reaction with a precipitating product—I. Theory. *Chemical Engineering Science*, 53(13), 2451–2458. [https://doi.org/10.1016/S0009-2509\(98\)00073-6](https://doi.org/10.1016/S0009-2509(98)00073-6)
- Angel, R. J., Alvaro, M., & Nestola, F. (2018). 40 years of mineral elasticity: a critical review and a new parameterisation of equations of state for mantle olivines and diamond inclusions. *Physics and Chemistry of Minerals*, 45(2), 95–113. <https://doi.org/10.1007/s00269-017-0900-7>
- Beinlich, A., John, T., Vrijmoed, J. C., Tominaga, M., Magna, T., & Podladchikov, Y. Y. (2020). Instantaneous rock transformations in the deep crust driven by reactive fluid flow. *Nature Geoscience*, 13(4), 307–311. <https://doi.org/10.1038/s41561-020-0554-9>
- Bessat, A., Pilet, S., Podladchikov, Y. Y., & Schmalholz, S. M. (2022). Melt Migration and Chemical Differentiation by Reactive Porosity Waves. *Geochemistry, Geophysics, Geosystems*, 23(2). <https://doi.org/10.1029/2021GC009963>
- Biot, M. A. (1941). General theory of three-dimensional consolidation. *Journal of Applied Physics*, 12(2), 155–164. <https://doi.org/10.1063/1.1712886>
- Biot, M. A., & Willis, D. G. (1957). The Elastic Coefficients of the Theory of Consolidation. *Journal of Applied Mechanics*, 24(4), 594–601. <https://doi.org/10.1115/1.4011606>
- Carroll, M. M., & Holt, A. C. (1972). Static and dynamic pore-collapse relations for ductile porous materials. *Journal of Applied Physics*, 43(4), 1626–1636. <https://doi.org/10.1063/1.1661372>
- Correns, C. W., & Steinborn, W. (1939). Experimente zur Messung und Erklärung der sogenannten Kristallisationskraft. *Zeitschrift für Kristallographie - Crystalline Materials*, 101(1–6), 117–133. <https://doi.org/10.1524/zkri.1939.101.1.117>
- Detournay, E., & Cheng, A. H. D. (1993). Fundamentals of poroelasticity. In *Analysis and Design Methods* (pp. 113–171). <https://doi.org/10.1016/b978-0-08-040615-2.50011-3>
- Evans, O., Spiegelman, M., & Kelemen, P. B. (2018). A Poroelastic Model of Serpentinization: Exploring the Interplay Between Rheology, Surface Energy, Reaction, and Fluid Flow. *Journal of Geophysical Research-Solid Earth*, 123(10), 8653–8675. <https://doi.org/10.1029/2017jb015214>
- Everett, D. H. (1961). The thermodynamics of frost damage to porous solids. *Transactions of the Faraday Society*, 57, 1541. <https://doi.org/10.1039/tf9615701541>
- Fabbri, A., Corvisier, J., Schubnel, A., Brunet, F., Goffé, B., Rimmelé, G., & Barlet-Gouédard, V. (2009). Effect of carbonation on the hydro-mechanical properties of Portland cements. *Cement and Concrete Research*, 39(12), 1156–1163. <https://doi.org/10.1016/j.cemconres.2009.07.028>
- Fletcher, R. C., & Merino, E. (2001). Mineral growth in rocks: Kinetic-rheological models of replacement, vein formation, and syntectonic crystallization. *Geochimica Et Cosmochimica Acta*, 65(21), 3733–3748. [https://doi.org/10.1016/S0016-7037\(01\)00726-8](https://doi.org/10.1016/S0016-7037(01)00726-8)
- Gassmann, F. (1951). Über die elastizität poröser medien. *Vierteljahrsschrift Naturforsch. Ges. Zürich*, 96, 1–23.
- Heap, M. J., Baud, P., Meredith, P. G., Vinciguerra, S., Bell, A. F., & Main, I. G. (2011). Brittle creep in basalt and its application to time-dependent volcano deformation. *Earth and Planetary Science Letters*, 307(1–2), 71–82. <https://doi.org/10.1016/j.epsl.2011.04.035>
- Holland, T. J. B., & Powell, R. (1998). An internally consistent thermodynamic data set for phases of petrological interest. *Journal of Metamorphic Geology*, 16(3), 309–343. <https://doi.org/10.1111/j.1525-1314.1998.00140.x>
- Holland, T. J. B., & Powell, R. (2011). An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids. *Journal of Metamorphic Geology*, 29(3), 333–383. <https://doi.org/10.1111/j.1525-1314.2010.00923.x>
- Johnson, J. W., Oelkers, E. H., & Helgeson, H. C. (1992). SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. *Computers & Geosciences*, 18(7), 899–947. [https://doi.org/10.1016/0098-3004\(92\)90029-q](https://doi.org/10.1016/0098-3004(92)90029-q)
- Kelemen, P. B., & Hirth, G. (2012). Reaction-driven cracking during retrograde metamorphism: Olivine hydration and carbonation. *Earth and Planetary Science Letters*, 345–348, 81–89. <https://doi.org/10.1016/j.epsl.2012.06.01>

- Kelemen, P. B., & Matter, J. (2008). In situ carbonation of peridotite for CO₂ storage. *Proceedings of the National Academy of Sciences*, 105(45), 17295–17300. <https://doi.org/10.1073/pnas.0805794105>
- Korenaga, J. (2025). On the possibility of exhaustive carbonation in geological carbon storage. *Earth and Planetary Science Letters*, 652, 119200. <https://doi.org/10.1016/j.epsl.2024.119200>
- Lecampion, B., Vanzo, J., Ulm, F. J., Huet, B., Gernay, C., Khalfallah, I., & Dirrenberger, J. (2011). Evolution of portland cement mechanical properties exposed to CO₂-rich fluids: investigation at different scales. *Mechanics and Physics of Porous Solids (MPPS)-A Tribute to Pr. Olivier Coussy*, 129–152.
- Lesti, M., Tiemeyer, C., & Plank, J. (2013). CO₂ stability of Portland cement based well cementing systems for use on carbon capture & storage (CCS) wells. *Cement and Concrete Research*, 45, 45–54. <https://doi.org/10.1016/j.cemconres.2012.12.001>
- Levin, V. A., Podladchikov, Y. Y., & Zingerman, K. M. (2021). An exact solution to the Lamé problem for a hollow sphere for new types of nonlinear elastic materials in the case of large deformations. *European Journal of Mechanics A/Solids*, 90, 104345. <https://doi.org/10.1016/j.euromechsol.2021.104345>
- Levin, V. A., Zingerman, K. M., Vershinin, A. V., Freiman, E. I., & Yangirova, A. V. (2013). Numerical analysis of the stress concentration near holes originating in previously loaded viscoelastic bodies at finite strains. *International Journal of Solids and Structures*, 50(20–21), 3119–3135. <https://doi.org/10.1016/j.ijsolstr.2013.05.019>
- Llana-Fúnez, S., Wheeler, J., & Faulkner, D. R. (2012). Metamorphic reaction rate controlled by fluid pressure not confining pressure: implications of dehydration experiments with gypsum. *Contributions to Mineralogy and Petrology*, 164(1), 69–79. <https://doi.org/10.1007/s00410-012-0726-8>
- Lurie, A. I. (1990). *Nonlinear theory of elasticity*. Elsevier Science Publisher.
- Lyu, Q., Ranjith, P. G., Long, X., Kang, Y., & Huang, M. (2015). A review of shale swelling by water adsorption. *Journal of Natural Gas Science and Engineering*, 27, 1421–1431. <https://doi.org/10.1016/j.jngse.2015.10.004>
- Mainguy, M., & Coussy, O. (2000). Propagation fronts during calcium leaching and chloride penetration. *Journal of Engineering Mechanics*, 126(3), 250–257. [https://doi.org/10.1061/\(asce\)0733-9399\(2000\)126:3\(250\)](https://doi.org/10.1061/(asce)0733-9399(2000)126:3(250))
- Malvoisin, B., Brantut, N., & Kaczmarek, M.-A. (2017). Control of serpentinisation rate by reaction-induced cracking. *Earth and Planetary Science Letters*, 476, 143–152. <https://doi.org/10.1016/j.epsl.2017.07.042>
- Malvoisin, B., Podladchikov, Y. Y., & Myasnikov, A. V. (2021). Achieving complete reaction while the solid volume increases: A numerical model applied to serpentinisation. *Earth and Planetary Science Letters*, 563. <https://doi.org/10.1016/j.epsl.2021.116859>
- Malvoisin, B., Podladchikov, Y. Y., & Vrijmoed, J. C. (2015). Coupling changes in densities and porosity to fluid pressure variations in reactive porous fluid flow: Local thermodynamic equilibrium. *Geochemistry, Geophysics, Geosystems*, 16(12), 4362–4387. <https://doi.org/10.1002/2015gc006019>
- Malvoisin, B., Zhang, C., Müntener, O., Baumgartner, L. P., Kelemen, P. B., & Oman Drilling Project Science Party. (2020). Measurement of Volume Change and Mass Transfer During Serpentinization: Insights From the Oman Drilling Project. *Journal of Geophysical Research: Solid Earth*, 125(5). <https://doi.org/10.1029/2019jb018877>
- Mavko, G., Mukerji, T., & Dvorkin, J. (1998). *The rock physics handbook: tools for seismic analysis in porous media*. Cambridge University Press.
- Merino, E., & Dewers, T. (1998). Implications of replacement for reaction-transport modeling. *Journal of Hydrology*, 209(1–4), 137–146. [https://doi.org/10.1016/S0022-1694\(98\)00150-4](https://doi.org/10.1016/S0022-1694(98)00150-4)
- Moulas, E., Podladchikov, Y., Zingerman, K., Vershinin, A., & Levin, V. (2023). Large-strain elastic and elasto-plastic formulations for host-inclusion systems and their applications in thermobarometry and geodynamics. *American Journal of Science*, 323(2). <https://doi.org/10.2475/001c.68195>
- Nermoen, A., Korsnes, R. I., Hiorth, A., & Madland, M. V. (2015). Porosity and permeability development in compacting chalks during flooding of nonequilibrium brines: Insights from long-term experiment. *Journal of Geophysical Research: Solid Earth*, 120(5), 2935–2960. <https://doi.org/10.1002/2014JB011631>
- Neville, A. M., Dilger, W. H., & Brooks, J. J. (1983). *Creep of plain and structural concrete*. Construction Press.
- Omlin, S., Malvoisin, B., & Podladchikov, Y. Y. (2017). Pore Fluid Extraction by Reactive Solitary Waves in 3-D. *Geophysical Research Letters*, 44(18), 9267–9275. <https://doi.org/10.1002/2017gl074293>

- Ostapenko, G. T. (1976). Excess pressure upon solid-phases arising during reactions of hydration (according to experimental-data of periclase hydration). *GEOKHIMIYA*, 6, 824–844.
- Petrini, K., & Podladchikov, Y. (2000). Lithospheric pressure-depth relationship in compressive regions of thickened crust. *Journal of Metamorphic Geology*, 18(1), 67–77. <https://doi.org/10.1046/j.1525-1314.2000.00240.x>
- Plümper, O., Røyne, A., Magrasó, A., & Jamtveit, B. (2012). The interface-scale mechanism of reaction-induced fracturing during serpentinization. *Geology*, 40(12), 1103–1106. <https://doi.org/10.1130/g33390.1>
- Poluektov, M., Freidin, A. B., & Figiel, Ł. (2018). Modelling stress-affected chemical reactions in non-linear viscoelastic solids with application to lithiation reaction in spherical Si particles. *International Journal of Engineering Science*, 128, 44–62. <https://doi.org/10.1016/j.ijengsci.2018.03.007>
- Putnis, A. (2002). Mineral replacement reactions: from macroscopic observations to microscopic mechanisms. *Mineralogical Magazine*, 66(5), 689–708. <https://doi.org/10.1180/0026461026650056>
- Putnis, A. (2009). Mineral Replacement Reactions. *Reviews in Mineralogy and Geochemistry*, 70, 87–124. <https://doi.org/10.2138/rmg.2009.70.3>
- Putnis, C. V., Wang, L., Ruiz-Agudo, E., Ruiz-Agudo, C., & Renard, F. (2021). Crystallization via nonclassical pathways: nanoscale imaging of mineral surfaces. *ACS Symposium Series*, 1–35. <https://doi.org/10.1021/bk-2021-1383.ch001>
- Rohmer, J., Pluymakers, A., & Renard, F. (2016). Mechano-chemical interactions in sedimentary rocks in the context of CO₂ storage: Weak acid, weak effects? *Earth-Science Reviews*, 157, 86–110. <https://doi.org/10.1016/j.earscirev.2016.03.009>
- Rubinshtein, L. I. (1971). *The Stefan problem*. American Mathematical Society.
- Rudge, J. F., Bercovici, D., & Spiegelman, M. (2011). Disequilibrium melting of a two phase multicomponent mantle. *Geophysical Journal International*, 184(2), 699–718. <https://doi.org/10.1111/j.1365-246X.2010.04870.x>
- Rutter, E. H. (1976). A Discussion on natural strain and geological structure - Kinetics of rock deformation by pressure solution. *Philosophical Transactions of the Royal Society of London Series A-Mathematical Physical and Engineering Sciences*, 283(1312), 203–219. <https://doi.org/10.1098/rsta.1976.0079>
- Sabitova, A., Yarushina, V. M., Stanchits, S., Stukachev, V., Khakimova, L., & Myasnikov, A. (2021). Experimental Compaction and Dilation of Porous Rocks During Triaxial Creep and Stress Relaxation. *Rock Mechanics and Rock Engineering*, 54(11), 5781–5805. <https://doi.org/10.1007/s00603-021-02562-4>
- Schenker, F. L., Schmalholz, S. M., Moulas, E., Pleuger, J., Baumgartner, L. P., Podladchikov, Y., Vrijmoed, J., Buchs, N., & Müntener, O. (2015). Current challenges for explaining (ultra)high-pressure tectonism in the Pennine domain of the Central and Western Alps. *Journal of Metamorphic Geology*, 33(8), 869–886. <https://doi.org/10.1111/jmg.12143>
- Schmalholz, S. M., Moulas, E., Plümper, O., Myasnikov, A. V., & Podladchikov, Y. Y. (2020). 2D Hydro-Mechanical-Chemical Modeling of (De)hydration Reactions in Deforming Heterogeneous Rock: The Periclase-Brucite Model Reaction. *Geochemistry, Geophysics, Geosystems*, 21(11). <https://doi.org/10.1029/2020gc009351>
- Schmid, D. W., Abart, R., Podladchikov, Y. Y., & Milke, R. (2009). Matrix rheology effects on reaction rim growth II: coupled diffusion and creep model. *Journal of Metamorphic Geology*, 27(1), 83–91. <https://doi.org/10.1111/j.1525-1314.2008.00805.x>
- Snæbjörnsdóttir, S. Ó., Sigfússon, B., Marieni, C., Goldberg, D., Gislason, S. R., & Oelkers, E. H. (2020). Carbon dioxide storage through mineral carbonation. *Nature Reviews Earth & Environment*, 1(2), 90–102. <https://doi.org/10.1038/s43017-019-0011-8>
- Spiegelman, M., Kelemen, P. B., & Aharonov, E. (2001). Causes and consequences of flow organization during melt transport: The reaction infiltration instability in compactible media. *Journal of Geophysical Research: Solid Earth*, 106(B2), 2061–2077. <https://doi.org/10.1029/2000jb900240>
- Steiger, M. (2005). Crystal growth in porous materials—I: The crystallization pressure of large crystals. *Journal of Crystal Growth*, 282(3–4), 455–469. <https://doi.org/10.1016/j.jcrysgro.2005.05.007>
- Tajčmanová, L., Podladchikov, Y., Powell, R., Moulas, E., Vrijmoed, J. C., & Connolly, J. A. D. (2014). Grain-scale pressure variations and chemical equilibrium in high-grade metamorphic rocks. *Journal of Metamorphic Geology*, 32(2), 195–207. <https://doi.org/10.1111/jmg.12066>
- Van Noort, R., Wolterbeek, T. K. T., Drury, M. R., Kandianis, M. T., & Spiers, C. J. (2017). The Force of Crystallization and Fracture Propagation during In-Situ Carbonation of Peridotite. *Minerals*, 7(10). <https://doi.org/10.3390/min7100190>

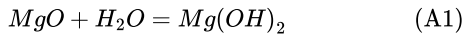
- Vrålstad, T., Saasen, A., Fjær, E., Øia, T., Ytrehus, J. D., & Khalifeh, M. (2019). Plug & abandonment of offshore wells: Ensuring long-term well integrity and cost-efficiency. *Journal of Petroleum Science and Engineering*, 173, 478–491. <https://doi.org/10.1016/j.petrol.2018.10.049>
- Vrålstad, T., Todorovic, J., Saasen, A., & Godøy, R. (2016). Long-term integrity of well cements at downhole conditions. *SPE Bergen One Day Seminar*. <https://doi.org/10.2118/180058-MS>
- Vrijmoed, J. C., & Podladchikov, Y. Y. (2022). Thermolab: A Thermodynamics Laboratory for Nonlinear Transport Processes in Open Systems. *Geochemistry, Geophysics, Geosystems*, 23(4). <https://doi.org/10.1029/2021GC010303>
- Weyl, P. K. (1959). Pressure solution and the force of crystallization: a phenomenological theory. *Journal of Geophysical Research*, 64(11), 2001–2025. <https://doi.org/10.1029/jz064i011p02001>
- Wolterbeek, T. K. T., Hangx, S. J. T., & Spiers, C. J. (2016). Effect of CO₂-induced reactions on the mechanical behaviour of fractured wellbore cement. *Geomechanics for Energy and the Environment*, 7, 26–46. <https://doi.org/10.1016/j.gete.2016.02.002>
- Wolterbeek, T. K. T., van Noort, R., & Spiers, C. J. (2018). Reaction-driven casing expansion: potential for wellbore leakage mitigation. *Acta Geotechnica*, 13(2), 341–366. <https://doi.org/10.1007/s11440-017-0533-5>
- Yarushina, V. M., & Bercovici, D. (2013). Mineral carbon sequestration and induced seismicity. *Geophysical Research Letters*, 40(5), 814–818. <https://doi.org/10.1002/Grl.50196>
- Yarushina, V. M., Makhnenko, R. Y., Podladchikov, Y. Y., Wang, L. H., & Räss, L. (2021). Viscous Behavior of Clay-Rich Rocks and Its Role in Focused Fluid Flow. *Geochemistry, Geophysics, Geosystems*, 22(10). <https://doi.org/10.1029/2021gc009949>
- Yarushina, V. M., & Podladchikov, Y. Y. (2010). Plastic yielding as a frequency and amplitude independent mechanism of seismic wave attenuation. *Geophysics*, 75(3), N51–N63. <https://doi.org/10.1190/1.3420734>
- Yarushina, V. M., & Podladchikov, Y. Y. (2015). (De)compaction of porous viscoelastoplastic media: Model formulation. *Journal of Geophysical Research: Solid Earth*, 120(6), 4146–4170. <https://doi.org/10.1002/2014jb011258>
- Yarushina, V. M., Podladchikov, Y. Y., & Wang, H. (2023). On the Constitutive Equations for Coupled Flow, Chemical Reaction, and Deformation of Porous Media. *Journal of Geophysical Research: Solid Earth*, 128(12). <https://doi.org/10.1029/2023JB027725>
- Yarushina, V. M., Podladchikov, Y. Y., & Wang, L. H. (2020). Model for (de)compaction and porosity waves in porous rocks under shear stresses. *Journal of Geophysical Research: Solid Earth*, 125(8), e2020JB019683. <https://doi.org/10.1029/2020JB019683>
- Zimmerman, R. W. (1991). *Compressibility of sandstones*. Elsevier Science.

APPENDICES

Appendix A. Examples of different reactions

Example 1. One-fluid reaction: hydration of periclase (periclase + water = brucite)

The transformation of periclase (MgO) into brucite (Mg(OH)₂) through the process of hydration is a subject of frequent investigation in the context of geodynamic processes occurring at tectonic plate boundaries (e.g., Schmalholz et al., 2020). This transformation can be described through the following simplified reaction:



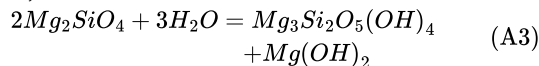
In this reaction, mobile components O and H can be present both in the fluid and solid phases. Thus, the mass fraction of the immobile compound in the solid, X_s , varies through the reaction. Magnesium (Mg) has a molar mass of $m_{s,Mg} = 24.31 \frac{g}{mol}$, hydrogen (H) of $m_{s,H} = 1.01 \frac{g}{mol}$, and oxygen (O) of $m_{s,O} = 16.00 \frac{g}{mol}$. Therefore, we set $X_{s,initial} = X_{s,MgO} = \frac{m_{s,Mg}}{(m_{s,Mg} + m_{s,O})} = 0.60$ for periclase and $X_{s,final} = X_{s,Mg(OH)_2} = \frac{m_{s,Mg}}{(m_{s,Mg} + 2m_{s,O} + 2m_{s,H})} = 0.42$ for brucite. With the help of an equation, the reaction progress is defined as

$$\xi = 5.56(0.60 - X_s) \quad (A2)$$

Since only one fluid is present, there is no need for a fluid component conservation equation.

Example 2. One-fluid reaction: hydration of olivine (olivine + aqueous fluid = serpentine + brucite)

The process of serpentinization, which includes the hydration of olivine, resulting in the formation of serpentine and brucite, i.e.,



is frequently regarded as pertinent to earthquake physics and is a natural analog to mineral carbon sequestration (e.g., Evans et al., 2018; Malvoisin et al., 2021). Both Mg and Si are preserved in this reaction. However, changes in their mass fraction are not independent from each other. Thus, it will represent the mass fraction of Mg in the solid. Given that $m_{Mg_2SiO_4} = 140.69 \frac{g}{mol}$, $m_{Mg_3Si_2O_5(OH)_4} = 277.11 \frac{g}{mol}$, and $m_{Mg(OH)_2} = 58.32 \frac{g}{mol}$, X_s will vary between

$$\begin{aligned} X_{s,initial} &= X_{s,Mg_2SiO_4} = \frac{m_{s,Mg}}{m_{Mg_2SiO_4}} = 0.17, \\ X_{s,final} &= X_{s,Mg_3Si_2O_5(OH)_4} + X_{s,Mg(OH)_2} = \frac{m_{s,Mg}}{m_{s,Mg_3Si_2O_5(OH)_4}} + \frac{m_{s,Mg}}{m_{s,Mg(OH)_2}} = 0.50 \end{aligned} \quad (A4)$$

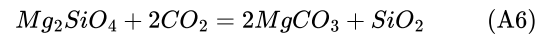
With these provided values, the equation will establish a correlation between the reaction progress and the mass fraction:

$$\xi = 3.03(X_s - 0.17) \quad (A5)$$

Since only one fluid is present, there is no need for a fluid component conservation equation.

Example 3. One-fluid reaction: carbonation of olivine (olivine + carbon dioxide = magnesite + quartz)

The carbonation of olivine is described with the simplified equation:



It primarily occurs in peridotite-rich rock formations, often deep within the Earth's mantle or in the Earth's crust. As this reaction converts mobile CO₂ into an immobile form, it has a great potential to permanently remove carbon dioxide from the atmosphere (e.g., Kelemen & Hirth, 2012). For this reaction, X_s will represent the mass fraction of Mg in the solid, with values between

$$\begin{aligned} X_{s,initial} &= X_{s,Mg_2SiO_4} = \frac{m_{s,Mg}}{m_{Mg_2SiO_4}} = 0.17, \\ X_{s,final} &= X_{s,MgCO_3} = \frac{m_{s,Mg}}{m_{s,MgCO_3}} = 0.29 \end{aligned} \quad (A7)$$

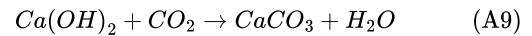
Then

$$\xi = 8.33(X_s - 0.17) \quad (A8)$$

Since only one fluid is present, there is no need for a fluid component conservation equation.

Example 4. Two-fluid reaction: carbonation of portlandite (portlandite + carbon dioxide = calcium carbonate + water)

Portlandite (Ca(OH)₂) is a main compound in borehole cements. Its reaction with CO₂



is an important process in borehole cement alteration during geological carbon storage (Lesti et al., 2013; Vrålstad et al., 2016; Wolterbeek et al., 2018). Carbonation of portlandite is also observed in the natural weathering of concrete and mortar structures over time, as well as in carbonation curing techniques used in construction and cement-based industries to enhance the strength and durability of concrete materials. Assuming that all Ca is precipitated and not washed out of the system, we can formulate the conservation equation for Ca, where the mass fraction of Ca in a solid with

$$\begin{aligned} X_{s,initial} &= X_{s,Ca(OH)_2} = \frac{m_{s,Ca}}{m_{Ca(OH)_2}} = 0.54, \\ X_{s,final} &= X_{s,CaCO_3} = \frac{m_{s,Mg}}{m_{s,CaCO_3}} = 0.40 \end{aligned} \quad (A10)$$

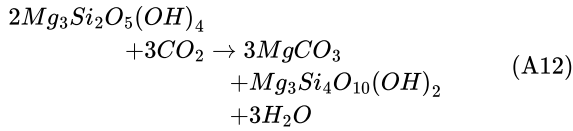
Then

$$\xi = 7.11(0.54 - X_s) \quad (A11)$$

Since this reaction involves two fluid phases, CO₂ and H₂O, the conservation of CO₂ can be formulated.

Example 5: Two-fluid reactions: soapstone formation from serpentinite (serpentinite + carbon dioxide = magnesite + talc + water)

Beinlich et al. (2020) studied soapstone formation from serpentinite as a natural analog for geological carbon storage. This process can take place via the reaction:



The mass fraction of immobile species (Mg) in the solid is defined as

$$\begin{aligned}
 X_{s,initial} &= \frac{X_{s,Mg_3Si_2O_5(OH)_4}}{m_{s,Mg}} = 0.09, \\
 X_{s,final} &= \frac{X_{s,MgCO_3} + X_{s,Mg_3Si_4O_{10}(OH)_2}}{m_{s,Mg}} + \frac{m_{s,Mg}}{m_{s,MgCO_3} + m_{s,Mg_3Si_4O_{10}(OH)_2}} \\
 &= 0.35
 \end{aligned} \quad (A13)$$

The reaction progress can be defined as

$$\xi = 3.85(X_s - 0.09) \quad (A14)$$

Appendix B. Coefficients in the elastic (viscous) solution with compressible constituents

Coefficients for the elastic solution with compressible constituents in the equations are given by the following expressions:

$$\hat{G} = c^2 (\Theta K_1 (1 - \xi) + K_2 \xi) G_2 G_1 + (\Theta G_1 (1 - \xi) a^2 + G_2 \xi b^2) K_1 K_2 \quad (A15)$$

$$A_{11} = (a^2 K_2 + c^2 G_2) (r^2 G_1 + c^2 K_1) \Theta + (b^2 - a^2) (r^2 - c^2) \xi K_2 G_2 \quad (A16)$$

$$A_{12} = r^2 (c^2 G_2 + a^2 (1 - \xi) K_2) \Theta G_1 + b^2 (c^2 \Theta K_1 + (r^2 - c^2) K_2) \xi G_2 \quad (A17)$$

$$A_{13} = (\Theta - 1)(b^2 - a^2) (r^2 G_1 + b^2 K_1) \xi K_2 G_2 \quad (A18)$$

$$A_{21} = c^2 (K_1 + G_1) (r^2 G_2 + a^2 K_2) \quad (A19)$$

$$A_{22} = (1 - \xi) a^2 (c^2 K_2 + \Theta (r^2 - c^2) K_1) G_1 + r^2 (c^2 G_1 + b^2 K_1 \xi) G_2 \quad (A20)$$

$$A_{23} = (1 - \Theta) (b^2 - a^2) (r^2 G_2 + a^2 K_2) (1 - \xi) G_1 K_1 \quad (A21)$$

$$B_{11} = \Theta (r^2 - c^2) (c^2 G_2 + a^2 K_2) K_1 G_1 + \xi (b^2 - a^2) (c^2 G_1 + r^2 K_1) K_2 G_2 \quad (A22)$$

$$B_{12} = c^2 (K_1 \Theta r^2 + \xi b^2 (K_2 - K_1 \Theta)) G_1 G_2 + r^2 (a^2 \Theta (1 - \xi) G_1 + \xi b^2 G_2) K_1 K_2 \quad (A23)$$

$$B_{13} = (b^2 - a^2) (1 - \Theta) K_1 K_2 G_1 G_2 \quad (A24)$$

$$B_{21} = c^2 (r^2 - a^2) (K_1 + G_1) K_2 G_2 \quad (A25)$$

$$B_{22} = c^2 (r^2 K_2 + a^2 (1 - \xi) (\Theta K_1 - K_2)) G_1 G_2 + r^2 (a^2 \Theta (1 - \xi) G_1 + b^2 \xi G_2) K_1 K_2 \quad (A26)$$

$$C_{11} = (c^2 + r^2) (c^2 G_2 + a^2 K_2) \Theta K_1 G_1 + (b^2 - a^2) (r^2 K_1 - c^2 G_1) \xi K_2 G_2 \quad (A27)$$

$$C_{12} = c^2 (K_1 \Theta r^2 + \xi b^2 (\Theta K_1 - K_2)) G_1 G_2 + r^2 (a^2 \Theta (1 - \xi) G_1 + \xi b^2 G_2) K_1 K_2 \quad (A28)$$

$$C_{21} = c^2 (r^2 + a^2) (K_1 + G_1) K_2 G_2 \quad (A29)$$

$$C_{22} = c^2 (a^2 (1 - \xi) (K_2 - \Theta K_1) + r^2 K_2) G_1 G_2 + r^2 (\Theta a^2 (1 - \xi) G_1 + G_2 \xi b^2) K_1 K_2 \quad (A30)$$

$$B_{23} = C_{13} = C_{23} = B_{13} \quad (A31)$$

For a viscous solution, K_1 , K_2 need to be replaced with η_1 , η_2 and G_1 , G_2 with μ_1 , μ_2 . Here, $\Theta = \frac{\rho_2 X_2}{\rho_1 X_1}$.