Dissolution and precipitation during flow in porous media

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Outline

• Introduction

• Theoretical study + simulation:
  • Equations at and above the Darcy scale → smoothly varying porosity and permeability (Aharonov et al., 1997a)
  • Microscopic simulation of dissolution:
    • Lattice-Boltzmann technique (Szymczak et al., 2004)
  • Mantle
Introduction

• Fluid flow coupled with chemical reactions ⇒ long range interactions, disequilibrium and change in solid geometry

• Influence flow patterns and chemistry within the mantle

• Diffusive porous flow unstable along adiabatic PT gradient ⇒ formation of channels

• Formation of dikes

• Dissolution channels observed as dunes (cm – 100m scale)

• Dunites are formed by constant replacement of peridotite as a result of dissolution of pyroxene + crystallization of olivine in a liquid migration by porous flow through mantle

(Kelemen et al., 1995)
Theoretical study

Based on:

• Conservation of mass
• Darcy’s law

Assumptions:

• Single component system
• Densities $\Box_s$, $\Box_f$ constant
• Linear gradient of solubility
• Dispersion/diffusion coefficient equal in all directions
Constant boundary pressure force \( \Rightarrow \) the flux \( Q \) freely adjust to changing \( k \)

\[
\phi = \frac{\phi_i}{1 + B \phi_i^{n-1} (n-1)t}^{n-1}
\]

\[
B = \frac{\rho_f}{\rho_s}
\]

\[
\phi_i = \phi(t = 0)
\]

- : Dissolution

+ : Precipitation

\( \rightarrow \) Rate of change of porosity changes with time

\( \rightarrow \) Dissolution: Unstable increase in \( \phi \) with \( t \)

\( \rightarrow \) Precipitation: \( \frac{\partial \phi}{\partial t} \rightarrow 0 \) as \( t \rightarrow \infty \)
Constant flux boundary condition

\[ \phi = \phi_i \pm BQt \]

+ : Dissolution
- : Precipitation

→ Rate of change of \( \mathbf{x} \) constant when \( Q \) constant

→ Dissolution: No unstable growth of \( \mathbf{x} \), since \( Q \) is constant even though the free space increase

→ Precipitation: Reduces \( \mathbf{x} \) faster

Since \( k \) changes, but \( Q \) constant → pressure must adjust with \( z \):

\[ p_e(l, t) \approx l \left( \left[ \frac{\phi_i}{\phi_i \pm BQt} \right]^n - 1 \right) \]

From Darcy’s law
Depth \( z=1-l \)

→ Dissolution: \( p_e(z) \downarrow \) since the same \( Q \) occupies an increasing void space

→ Precipitation: \( p_e \uparrow \) (since \( k \Downarrow 0 \rightarrow p > p_c \Rightarrow \) hydraulic fracturing)
Controlling parameters

**Damköhler number:**

\[ Da = \frac{L}{L_{eq}} \]

Ration between the size of the system \( L \) and the chemical equilibrium length \( L_{eq} \):

**Peclet number:**

\[ Pe = \frac{\omega_0 L}{D} \]

\( \omega_0 \): characteristic fluid velocity

\( D \): diffusion/dispersion coefficient

Ratio between rate of transport by combined diffusion and dispersion to rate of transport by advection.
Statistical properties and morphology due to flow and reaction as a function of time

Autocorrelation function $C(r)$:

Correlation between scalar property $\Phi$ at position $r'$ and $r'+r$:

$$C(r) = \frac{1}{V} \int_V \Phi(r'+r)\Phi(r')dr'$$

$C(r) \uparrow$: High porosity regions preferentially found up or downstream to other high porosity regions $\rightarrow C(r)$ measure of channeling

$C(r) \downarrow$: Destruction of correlated paths

Evolution of histograms of flux and porosity:

Width $\rightarrow$ Variability
Temporal evolution of the permeability

Dissolution:
- Unstable growth
- High $Da \Rightarrow$ more rapid growth

Precipitation:
- Independent of $Da$

$Da=100$
$Da=10$

Linear prediction
3D isosurface of Q for dissolution

- Elongated permeability structures parallel to flow direction

- $k_0 > \langle k_0 \rangle \Rightarrow$ flux $\uparrow$
  $\Rightarrow$ dissolution $\uparrow$
  $\Rightarrow$ positive feedback
Most precipitation occurs close to entrance to preferred paths for flow:

⇒ entrance clog up
⇒ flow diverted to other paths
⇒ diffuse and uniform flow
⇒ narrowing flux and porosity histogram
Histograms of flux and porosity

- Initial random configuration for dissolution
  - Dissolution
  - Precipitation
  Initial= 12/25

- Dissolution: Variability in $Q$ ↑
- Precipitation: smoothing effect

- Change in variability in $\theta$ smaller, but same characteristics as for $Q$
Histogram of correlation function of porosity

- Initial random configuration for dissolution
  - Initial random configuration for dissolution
  - Precipitation

- Dissolution: $C(r) \parallel$ to flow direction $\ast$, consistent with elongated channel formation

- Precipitation: $C(r) \parallel$ to flow direction $\ast$, overlapping the random initial correlations
Porosity correlation function along flow direction at a given lag of 1/6 for dissolution

- $Da=100 \Rightarrow$ unstable growth of $C$
- $Da \downarrow \Rightarrow$ channels growth ★
- $Da=5; Pe=200: C \uparrow$, but not unstable growth
  - $Pe=10$: No increase $\rightarrow$ uniform
Porosity correlation function along flow direction at a given lag of 1/6 for precipitation

- ~ independent on $Da$ and $Pe$
- Precipitation $\uparrow$
  $\Rightarrow$ flow diverted
  $\Rightarrow$ low $k$ regions form adjacent to high $k$ regions
  $\Rightarrow$ negative change in $C$

![Graph](image-url)

$C(lag=1/6)$

time (in nondimensional units)

Legend:
- $Da=10, Pe=200$
- $Da=100, Pe=200$
- $Da=100, Pe=10$
- $Da=10, Pe=10$
Porosity profile over transition zone

\[ \bar{\chi} \] average over \( x \) and \( y \)

\( t = 0.5 \)

- Difference between dissolving and precipitation regions \( \uparrow \) with time
Excess pressure profile for transition zone

\[ t=0.5 \]

- Overpressure ↑ close to transition
- Difference between dissolving and precipitation regions ↑ with time
Dissolution

- Elongated channels in flow direction
- Depends strongly on $Da$ and $Pe$
- Channels form for $Da \gg 1$
- Channel growth $\star$ for $Da \star$
- Unstable growth of permeability
- Minor increase in correlation perpendicular to flow
  $\Rightarrow$ matrix anisotropic
- $Pe \downarrow \Rightarrow$ width of channels $\uparrow$, spacing between channels $\uparrow$, channel growth rate $\downarrow$
Precipitation

- Permeability ↓ with time
- Rate of decrease ↓ with time
- Increasing uniform flow with time
- No significant difference for different $Da$ and $Pe$
Transition zone

• Monotonically increasing overpressure

• Permeability ↓ in precipitation region ⇒ overpressure ↑

• Overpressure ↑ until > strength of porous matrix → fractures

System

• $Da$ and $Pe$ are the controlling parameters in a coupled flow and reaction system

• $Da$ and $Pe$ depend on system size

• The evolution of the system is highly dependent on boundary conditions (constant flux/pressure)
Limitations and improvements

• Dissolution and precipitation differ only by sign and are reversible in the model.

• Only looked at single mineral component and fluid component.

• Need a better description of porosity-permeability relation and microscopic distribution of precipitation.

• Need to consider compaction of solid phase.
Microscopic numerical simulation of dissolution
(Szymczak et al., 2004)

• Stokes flow
• Lattice-Boltzmann with continuous bounce back at solid-fluid boundaries
• Transport of dissolved species in pore spaces is modeled by an innovative random walk algorithm that incorporates chemical reactions at pore surface
Results for $Da=0.1$ $Pe=10$
Mantle
(Aharonov et al., 1995 + Kelemen et al., 1995)

• Potentially existing channeling instability in Earth’s upper mantle:
  Melt ↑
  ⇒ decompression
  ⇒ dissolution ↑
  ⇒ perturbation in porosity
  ⇒ flow ↑
  ⇒ dissolution ↑
  ⇒ porosity ↑
  \[\text{Positive feedback} \]

• Development of low porosity cap overlying high porosity conduits
  ⇒ hydrostatic overpressure ↑
  ⇒ fracture and magma transport to surface in dikes
References


• Kelemen, P., J. Whitehead, E. Aharonov, and K. Jordahl, 1995, Experiments on flow focusing in soluble porous media with applications to melt extraction from the mantle, J. Geophys. Res., 100, 475–496

Micro-scale
(*Aharonov et al.*, 1997b)

Fractal porosity $\chi_f$: associated with pits and protruding features
Euclidean porosity $\chi_e$: “Inflate balloon”

\[ \chi = \chi_f + \chi_e \]

- Diagenesis $\Rightarrow \frac{\phi_f}{\phi} \uparrow$
- Dimension $\uparrow$ with amount of diagenetic alteration
Fractal dimension as a function of ratio of probability of dissolution over precipitation

- $p_-/p_+$ $\uparrow \Rightarrow$ fractal dimension $\uparrow$
- $p_-/p_+ \rightarrow 1$ : loose in fractal behavior
- $p_-/p_+ \uparrow \Rightarrow$ rate of reaction limited growth $\downarrow$

$p_-$: Probability of particle dissolution
$p_+$: Probability of particle precipitation
Channel length – cm scale

Kelemen et al., 1995

- Inlet tube with dozens of small holes to diffuse flow
- Closed water reservoir
- Water reservoir, open at top
- Variable height outlet tube
- Mixture of salt & glass balls
- Foam
- Plexiglass with more than 50 small outlet holes

1200 s

1500 s

Laboratory experiments growth rate data:

- Channel length, L (cm)
- Time, t (sec)
- L = 4.60 e^{-0.0020t}
- R = .98
- L = 1.67 e^{-0.0019t}
- R = .99

Numerical experiments growth rate data:

- Channel length, L
- Time, t
- L = 1.14 e^{0.011t}
- R = .99
- L = 1.30 e^{0.007t}
- R = .97
Assumptions

- Single soluble component \((c_i^s=1)\) ⇒ Fluid phase:
  - Carrier fluid \((1-c_i)\) (no solid phase)
  - Dissolved component \((c_i)\)

- Densities \(\rho_s, \rho_f\) constant

- Dispersion/diffusion coefficient \(D\) equal in all directions

- Specific surface area \(A\) constant

- Linear gradient of solubility
Flow through porous media

\[ \phi \nabla = -\frac{k}{\mu} \nabla p \]

Darcy’s law

\[ \nabla p = \nabla p_e + (\rho_s - \rho_f)g \]

\[ k(\phi) = \frac{d^2 \phi^n}{b} \]

\( k \): Permeability
\( \mu \): Viscosity
\( d \): Typical grain size
\( n \): usually > 2
\( b \): constant

\( \phi \) << 1
\( \rho_s, \rho_f \) constant
Conservation of mass
Single soluble component system

\[
\frac{\partial \phi}{\partial t} = - \frac{\Gamma}{\rho_s}
\]

\[
\frac{\partial \phi}{\partial t} + \bar{\nabla} \cdot (\bar{v} \phi) = - \frac{\Gamma}{\rho_f}
\]

\[
\phi \frac{\partial c}{\partial t} + \phi \bar{v} \cdot \bar{\nabla} c = D \bar{\nabla} \cdot (\phi \bar{\nabla} c) - (1 - c) \frac{\Gamma}{\rho_f}
\]

\[
\Gamma = RA(c - c_{eq}) \quad \text{(Mass transfer term)}
\]

**R**: reaction rate constant of soluble component

**A(x,t)**: Specific surface area (fct. of \(x\), distribution of minerals at the pore-grain interface, whether \(m\) is dissolving or depositing)

**c_{eq}**: Equilibrium concentration
Nondimensionalization

\( \phi_0 \): Characteristic porosity  
\( k_0 \): Characteristic permability  
\( \phi_0 \): Fluid z-velocity  
\( L \): Characteristic length scale  
\( c_0 \): Characteristic concentration  
  (max equilibrium concentration)

Nondimensional variables ‘:

\[
\begin{align*}
L' &= \frac{d^2 \phi_0^n}{b} \\
\omega_0 &= \frac{k_0 \Delta \rho g}{\phi_0 \mu} \\
\bar{x} &= Lx' \\
\phi &= \phi_0 \phi' \\
p &= \Delta \rho g Lp' \\
v &= \omega_0 v' \\
t &= \frac{L}{\omega_0 c_0} \\
c &= c_0 c' \\
c_{eq} &= c_0 c_{eq}' (\bar{x}, t)
\end{align*}
\]
Basic set of equations

\[ \frac{\partial \phi'}{\partial t'} = -\frac{\rho_f}{\rho_s} \Gamma' \]

Temporal evolution of porosity due to reaction

\[ \nabla \cdot (k' \nabla p') = c_0 \frac{\rho_s - \rho_f}{\rho_s} \Gamma' \]

Poisson equation for pressure → total fluid conservation
Assuming constant \( k \) and \( c_0 \ll 1 \) ⇒ constant pressure gradient

\[ c_0 \phi' \frac{\partial c'}{dt} - k' \nabla p' \cdot \nabla c' = \frac{1}{Pe} \nabla \cdot (\phi' \nabla c') - (1 - c_0 c') \Gamma' \]

Change in mineral concentration due to reaction, diffusion and advection

\[ \Gamma' = Da(c' - c'_{eq}(x, t)) \]

Mass transfer rate

\[ k' = \phi'^n \]
Numerical experiment using modified relaxation Boltzmann Method
(Kelemen et al., 1995)

Saturation concentration of soluble material in fluid:
Top: 0
Bottom: 0.05

Initial undersaturated fluid
No solubility gradient

\[
\frac{dp}{dz} = \text{const}
\]
High porosity channels ⇒
Solid-liquid surface area ↓
and $L_{eq} \uparrow$

$\bullet_0(z) \Rightarrow L_{eq} \uparrow$

Grain boundary scale $\propto$

Larger $\propto_0$
and $\bullet_0 \rightarrow$
larger $\bullet$ ?

(Aharonov et al., 1995)
Conservation of mass
Multi component system

Total mass:
\[
\frac{\partial \rho_s (1 - \phi)}{\partial t} = \sum_i \Gamma_i
\]
\[
\frac{\partial \rho_f \phi}{\partial t} + \nabla \cdot (\rho_f \nabla \phi) = -\sum_i \Gamma_i
\]

Each mineral component:
\[
\frac{\partial \rho_s (1 - \phi) c_i^s}{\partial t} = \nabla \cdot [D_i^s \rho_s (1 - \phi) \nabla c_i^s] - \Gamma_i
\]
\[
\frac{\partial \rho_f \phi c_i}{\partial t} + \nabla \cdot (\rho_f \nabla \phi) = \nabla \cdot [D_i \rho_f \phi \nabla c_i] - \Gamma_i
\]

\[\Gamma_i = \sum_1^M \nu_{im} R_m\] (Mass transfer term)

\(M\): Mineral phases
\(\nu_{im}\): Stoichiometric proportion of component \(i\) in mineral \(m\).
\(R_m\): Dissolution or precipitation rate
\(c_i\): Mass fraction (\(\sum_i c_i = 1\))
Mantle
(Aharonov et al., 1997a)

- Modes of melt extraction from mantle may be controlled by whether melt partially dissolve the surroundings or crystallize during upwelling
- Flow through an increasing solubility gradient causes dissolution with negative mass transfer from rock to fluid
- Flow through decreasing solubility gradient causes precipitation
- Transition zone: occurs near base of the conductively cooled lithosphere
  - Where it occurs depends on advective heat transfer – not included in the model
  - Calculations show that advective heat transfer will not distort a regional steady state geotherm until channels \( \ll 0.1\% \) of solid
  - Speculations that melt will pond in sills within transition zone
  - Increasing overpressure may lead to hydrofracturing
  - Precipitation faster in fractures than matrix according to simulation, since fractures are highest permeability channels → healing → cycle (consistent with presence of dikes)
# Mantle
*(Aharonov et al., 1995)*

## Table 1. Characteristic Values Believed to Be Applicable to Earth’s Mantle

<table>
<thead>
<tr>
<th>Variable</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility gradient</td>
<td>$\beta$</td>
<td>$2 \times 10^{-6} \text{ m}^{-1}$</td>
</tr>
<tr>
<td>Linear dissolution rate</td>
<td></td>
<td>$10^{-12} - 10^{-6} \text{ m s}^{-1}$</td>
</tr>
<tr>
<td>Solid density</td>
<td>$\rho_s$</td>
<td>$3 \times 10^3 \text{ kg m}^{-3}$</td>
</tr>
<tr>
<td>Reaction rate constant</td>
<td>$R$</td>
<td>$10^{-9} - 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>Grain edge length</td>
<td>$d$</td>
<td>$10^{-4} - 10^{-3} \text{ m}$</td>
</tr>
<tr>
<td>Total surface area</td>
<td></td>
<td>$10^3 - 10^5 \text{ m}^2 / \text{m}^3$</td>
</tr>
<tr>
<td>Porosity</td>
<td>$\phi$</td>
<td>$10^{-3} - 10^{-2}$</td>
</tr>
<tr>
<td>Solid/liquid surface area</td>
<td>$S$</td>
<td>$(1 - 3) \times 10^{-1}$</td>
</tr>
<tr>
<td>Volume fraction of soluble phase</td>
<td></td>
<td>$10^{-2} - 10^{-1}$</td>
</tr>
<tr>
<td>Permeability exponent</td>
<td>$n$</td>
<td>$2 - 3$</td>
</tr>
<tr>
<td>Melt fraction</td>
<td>$F$</td>
<td>$0.05 - 0.2$</td>
</tr>
<tr>
<td>Solid upwelling rate</td>
<td>$V_0$</td>
<td>$10^{-10} - 10^{-9} \text{ m s}^{-1}$</td>
</tr>
<tr>
<td>Background fluid velocity</td>
<td>$w_0$</td>
<td>$10^{-9} - 10^{-6} \text{ m s}^{-1}$</td>
</tr>
<tr>
<td>Equilibration length</td>
<td>$L_{eq}$</td>
<td>$10^{-7} - 10 \text{ m}$</td>
</tr>
<tr>
<td>Damköhler number (L=100m)</td>
<td>$Da$</td>
<td>$10^9 - 1$</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>$D$</td>
<td>$10^{-12} - 10^{-10} \text{ m}^2 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>Peclet number (L=100m)</td>
<td>$Pe$</td>
<td>$10^8 - 10^3$</td>
</tr>
<tr>
<td>compaction length</td>
<td>$h$</td>
<td>$100 - 1000 \text{ m}$</td>
</tr>
</tbody>
</table>
Mantle

- Diffusive porous flow of melt may be unstable in regions in the upper mantle where liquid ascends along an adiabatic PT gradient (like MOR and hot spots)

- Dissolution channels are observed as replacive dunites (cm – 100m scale)

- Dunites are formed by constant replacement of peridotite as a result of dissolution of pyroxene + crystallization of olivine in a liquid migration by porous flow through mantle

(Kelemen et al., 1995)