Experimental investigation of reaction-driven stress development during mineral carbonation: Implications for approaches to in-situ peridotite carbonation

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Shell Gamechanger
In situ carbonation of peridotite for CO₂ storage

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The rate of natural carbonation of tectonically exposed mantle peridotite during weathering and low-temperature alteration can be enhanced to develop a significant sink for atmospheric CO₂. Natural carbonation of peridotite in the Samail ophiolite, an uplifted slice of oceanic crust and upper mantle in the Sultanate of Oman, is surprisingly rapid. Carbonate veins in mantle peridotite in Oman have an average ¹⁴C age of ~26,000 years, and are not 30–95 million years old as previously believed. These data and reconnaissance mapping show that ~10⁴ to 10⁵ tons per year of atmospheric CO₂ are converted to solid carbonate minerals via peridotite weathering in Oman. Peridotite carbonation can be accelerated via drilling, hydraulic fracture, input of purified CO₂ at elevated pressure, and, in particular, increased temperature at depth. After an initial heating step, CO₂ pumped at 25 or 30 °C can be heated by exothermic carbonation reactions that sustain high temperature and rapid reaction rates at depth with little expenditure of energy. In situ carbonation of peridotite could consume >1 billion tons of CO₂ per year in Oman alone, affecting all aspects of life and environment.

\[
\text{Mg}_2\text{SiO}_4 (s) + 2\text{CO}_2 (g) + 2\text{H}_2\text{O(l)} \rightarrow 2\text{MgCO}_3 (s) + \text{H}_4\text{SiO}_4 (aq)
\]

\[
\rightarrow \text{Large volume increase}
\]

\[
\rightarrow \text{Stress} \rightarrow \text{Fracture ?}
\]
Carbonation of Peridotite: General Concept
Kelemen & Matter (2008, PNAS)

- CO₂/water injection (hydrofracture)
- Reaction with peridotite → carbonates + silicates
- In-situ deposition/trapping
- Reaction increases T + rate
- Old fractures fill
- New fracs via reaction drive (+/- hydrofrac)
- Cycle continues
Some key questions

• Is this what happens in nature? How fast?

• Will reaction rates in fractures be fast enough?

• Can enough (fine) fractures be created?

• Will fractures remain permeable or clog / close?

• How much stress can precipitation in (micro)cracks generate?

• Can this cause on-going fracture?
Some key questions

- Is this what happens in nature? How fast?
- Will reaction rates in fractures be fast enough? ≥ pure olivine
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Fracture wall dissolution experiments (Van Noort et al., GCA, 2013)

Oman Peridotite
150° C, CO₂+H₂O
10 MPa

Mass loss (mg)

Universiteit Utrecht
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Theoretical stress at equil:

\[ \sigma_n^e = (\sigma_{rock} - P_f) \]

\[ \sigma_n^e \leq \frac{-(\Delta G^{PT} - \sum n_f \Delta G_f^{\sigma T})}{(\sum n_s \Omega_s^{\sigma T} - \sum n_r \Omega_r^{PT})} \] (GPa?)

e.g. Kelemen & Hirth (2012)
Wolterbeek et al (2017)

We set out to measure it!
Force/stress of crystallization: Experiments

\[ \sigma_{n}^{e} = (\sigma_{rock} - P_f) \]

1-D compaction
60-200°C,
Fixed piston !!
Van Noort et al.,
(Minerals, 2017)
Effective stress on sample measured with piston fixed:
- ~ 20 experiments
- Åheim Dunite powder or stacked discs
- Pre-loaded at 0-550 MPa
- 120-190°C, Initial stress 10-60 MPa
- 15-20 MPa water + CO₂
- 5-23 days

Sample (10-12 mm diameter, 1-5 mm thick)

Van Noort et al., (Minerals, 2017)
Samples showed:
- No stress development
- No swelling
- No compaction

ONE Exception (R0803)
- 2mm disc + 1mm powder
- 120 °C, $P_f \approx 15$ MPa
- Initial eff stress 40 MPa

(could not be reproduced)

Van Noort et al.,
(Minerals, 2017)
Stress versus no stress: Why?

Hypotheses for no stress:

• Insufficient reaction?

• No force due to
  -healing of impinging gb’s?
  -healing/clogging of pore throats?

• Failed experimental method?

So why a stress in R0803?

• Fluid pressure fluctuations?
• Microstructure?
Experimental method OK!

**MgO hydration**

165 °C, 17 MPa H₂O

Van Noort et al., (Minerals, 2017)

**CaO hydration**

Room T, Initial $\sigma_{eff} = 1-120$ MPa

Wolterbeek et al

(Acta Geotechnica, 2017)
Microstructure when no stress developed

- Extensive conversion of olivine to MgCO$_3$ + silica
- Little or no serpentinization / hydration
- Dense magnesite matrix
- Amorphous silica in interfaces
- Permeability drop of 2 -3 orders of magnitude

Zero stress development due to pore clogging and grain boundary healing ?? → Transport/diffusion limitation
Microstructure when stress did develop

- Very similar to other runs
- More amorphous silica spheres?
- Grain interfaces more open ??

Stress due to open interfaces?
Cause?? P-fluctuations in CO$_2$?
Not reproduced!
Summary / Discussion

• In our experiments: straight forward carbonation of olivine/peridotite seems to be dominated by clogging and healing

• Generally no stress produced – CO$_2$ diffusion too slow

• Significant stress produced in 1/20 experiments but not clear why and not reproduced (open interfaces?) – special conditions?

• IF clogging dominates in-situ then time to advance a crack by 1m due to internal precipitation will be diffusion controlled:

\[
t = \frac{2L^2}{D\Delta C \Omega_{ol}(x - 1)} = 300\text{–}6000 \text{ yr} = \text{too slow}
\]

= Major negative feedback on in-situ carbonation concept

• HOWEVER other workers infer that reaction-driven expansion (stressing) can produce fracturing
Experimental evidence for reaction-induced fracture

Zhu et al. (GRL, 2016): 1.5 molar NaHCO$_3$ sol, 200 °C, $P_f = 10$ MPa, Effective stress 3 MPa
Thoughts for the future

• What actually happens in nature? We need to know.
• Same as our experiments? No? Or yes = slow?
• What about hydration to form serpentine minerals?
• Does that cause reaction driven fracture?
• Are there ways to promote reaction driven fracture and/or the in-situ carbonation process?
  - Open system / flow-through?
  - Promote hydration?
  - Catalysis?
  - Pressure cycling?
  - “Moving” hydrofracture?

• Potential means more research needed! Expt + modelling!
The sorption-swelling problem in ECBM

Fundamental Question:

- Does the in-situ stress affect (reduce) sorption capacity?
Can swelling induced stresses get big enough to cause swelling-driven fracture?