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Si-rich surface layer formation during olivine dissolution: Implications for mineral carbonation

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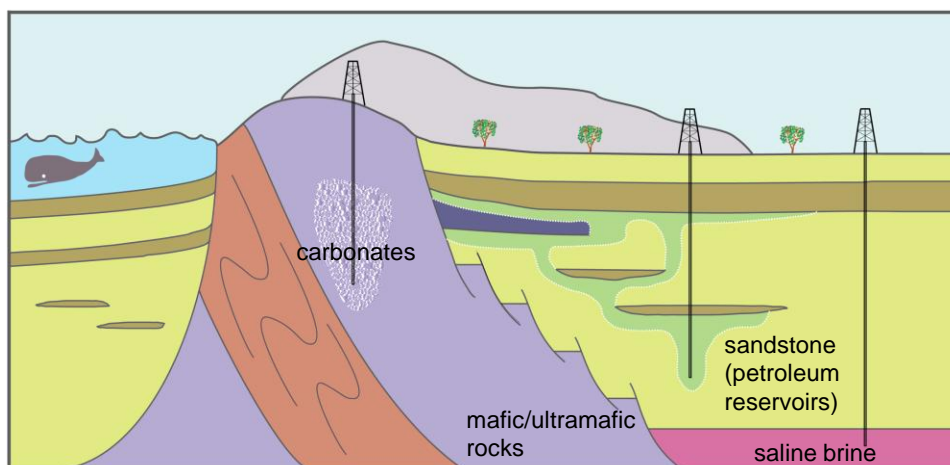
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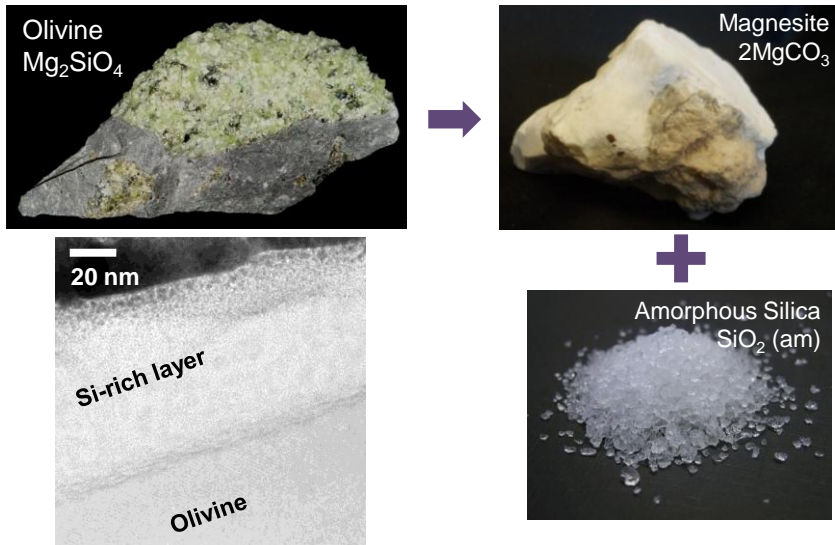



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Potential reservoirs for CO₂ storage



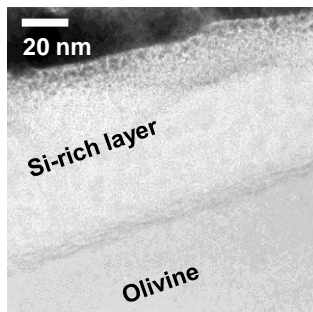
Mg-silicates react with CO_2 to form Mg-carbonates

Hypotheses for Si-rich surface layer formation

How does the Si-rich surface layer form?

Does it passivate the mineral surface?

Can we prevent its formation?

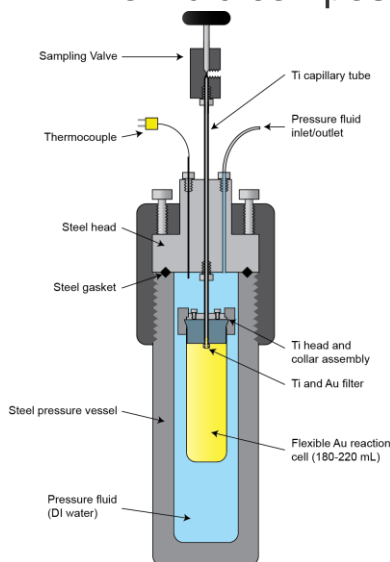


- Leached Si-rich layer
 - Preferential removal of Mg
 - Localized rearrangement of SiO_4
 - Little/no interaction with fluid
- Precipitated Si-rich layer
 - Mineral dissolves congruently, SiO_2 re-precipitates at the surface
 - Precipitated SiO_2 reflects isotopic composition of fluid

Is subsurface mineral carbonation feasible, or will the reaction be stopped by a passivating surface layer?

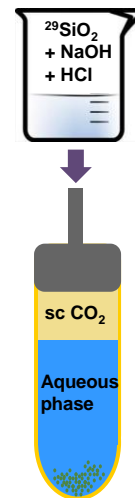
Which processes govern olivine (and silicate minerals in general) dissolution?

Dickson-style rocker bomb allows for measurement of fluid composition at reaction conditions

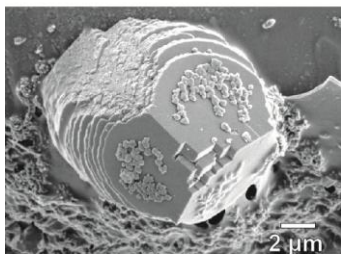
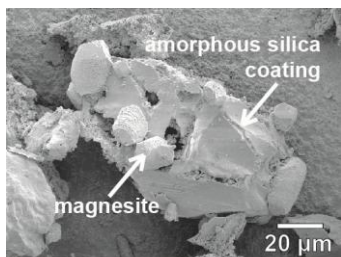
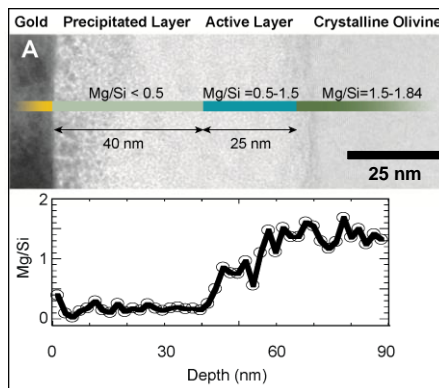


- 60°C
- 100 bar
- 0.5M NaCl
- 2 and 19 day experiments
- Rocking (mixed) and non-rocking

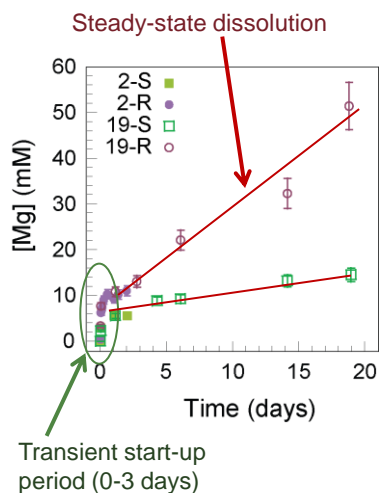
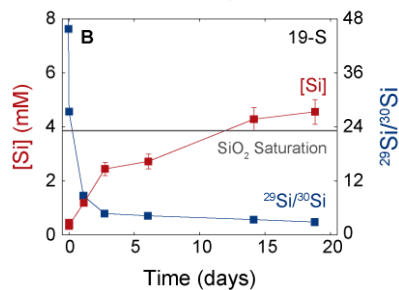
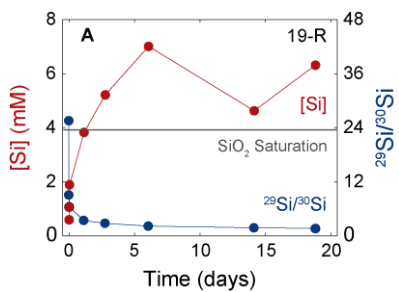
New set of capabilities for studying the geochemistry of 3-phase systems.



Electron microscopy images of reacted olivine

Johnson et al. *Chem. Geol.* 2014.Johnson et al. *In preparation.*

Solution Data



Rate Calculations: Isotope Ratio Method

Dissolution Rate, R_d

$$\frac{d^{29}\text{Si}}{dt} = \underbrace{v_{\text{Si},d} A_d R_d \left(\frac{^{29}\text{Si}}{\text{total Si}} \right)_d}_{\text{Appearance of Si in solution (from dissolving mineral)}} - \underbrace{v_{\text{Si},p} A_p R_p \left(\frac{^{29}\text{Si}}{\text{total Si}} \right)_t}_{\text{Disappearance of Si from solution (to secondary phase + exchange with mineral surface)}} \quad \text{Assume: precipitating phase has the same isotopic composition as the aqueous phase}$$

Precipitation Rate, R_p

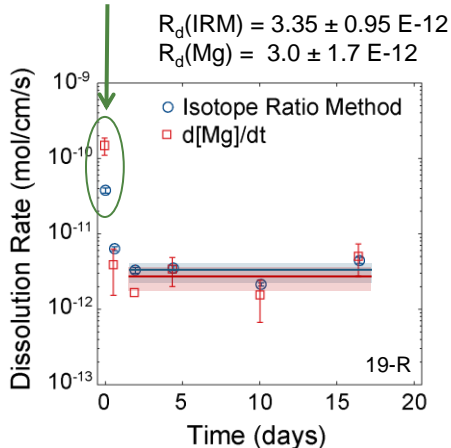
$$\frac{d\text{Si}}{dt} = v_{\text{Si},d} A_d R_d - v_{\text{Si},p} A_p R_p$$

$$\frac{1}{v_{\text{Mg}}} \frac{d\text{Mg}}{dt} = \frac{d\text{Si}}{dt} - v_{\text{Si},p} A_p R_p$$

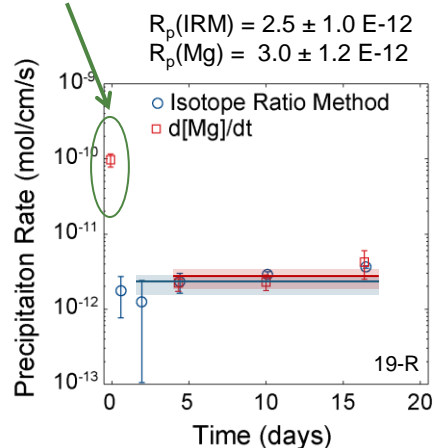
Assume: All Si missing from solution is the result of precipitation

Gruber et al. GCA 2013.

Higher Mg release than Si during first hour of reaction

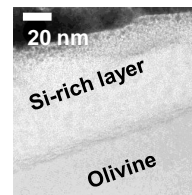
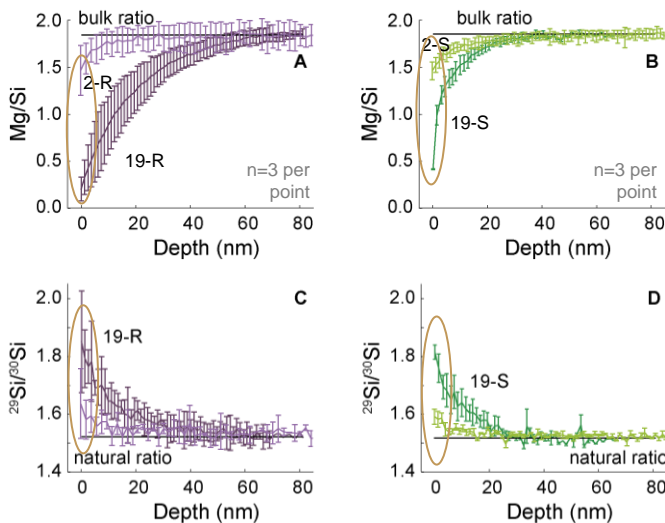


Precipitation rate = zero from isotope method



Preferential Mg release (incongruent dissolution) in the transient stage
During steady-state dissolution, $\text{SiO}_2(\text{am})$ precipitation and forsterite dissolution occur at the same rate.

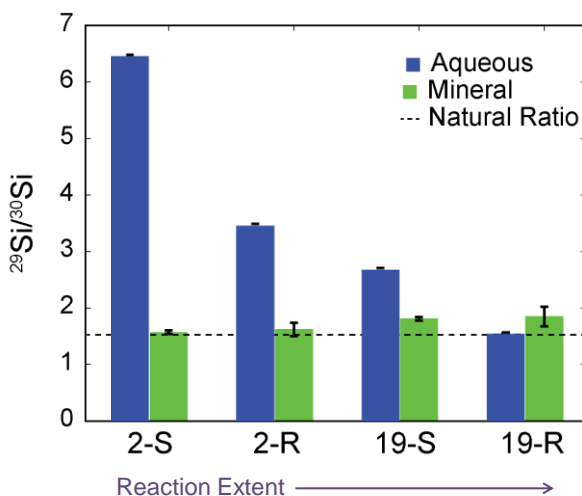
SIMS depth profiling of reacted olivine



Significantly more ^{29}Si on mineral surfaces reacted for 19 days relative to 2 days.

Total thickness of Si-rich layer > Depth of ^{29}Si penetration

Comparison of mineral and aqueous phases



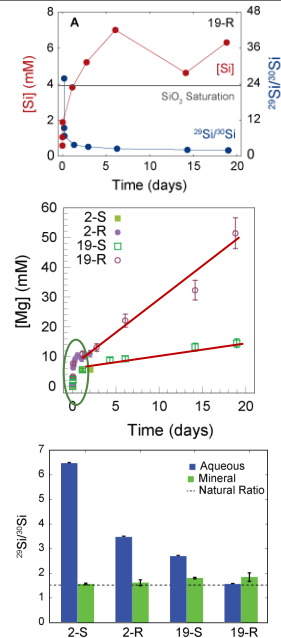
19-day experiments show 15% more ^{29}Si enrichment than 2 day experiments

Depth averaging difficult to quantify

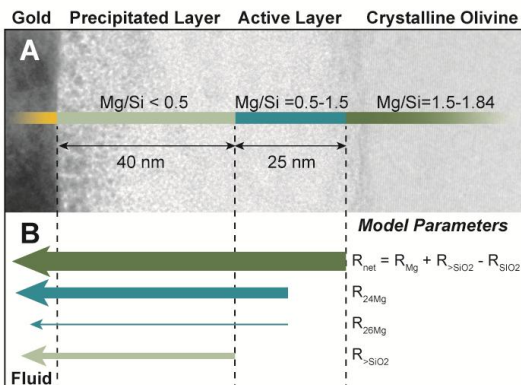
Exchange between Si(aq) and Si(min) slow relative to net dissolution

Recap

- Dilution of ^{29}Si spike with time
- Transient start-up \rightarrow incongruent dissolution
- Steady-state dissolution/precipitation (rocking)
 - $R_d = 3.0\text{E-}12$
 - $R_p = 2.7\text{E-}12$
- ^{29}Si incorporation in minerals reacted for 19 but not 2 days \rightarrow SiO_2 precipitation only after $\text{SiO}_2(\text{am})^{\text{sat}}$



Leached + precipitated layers, but no passivation



Maher et al. *In preparation*.

- Leached/Active layer
 - Not enriched in ^{29}Si
 - Composition is function of depth
- Precipitated layer
 - Enriched in ^{29}Si
 - Contains little Mg
 - Porous, does not passivate the surface

**Provides a link between mineral surface dynamics and bulk dissolution rate; no passivation by surface layers.
May be generally applicable to multi-oxide silicate minerals.**

Using new kinetic knowledge to assess feasibility of *in situ* mineralization

- 1-3 years to mineralize 1 ton CO₂ in 33 tons of basalt (~10 m³)
- How does changing reaction parameters affect the bottom line for *in situ* storage?
 - Degree of mixing
 - Si-rich layer formation/secondary phase formation
 - Flow rates
- Life Cycle Assessment is ongoing

Acknowledgements



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