The dependency of sepiolite precipitation and dissolution rates on the reaction activity

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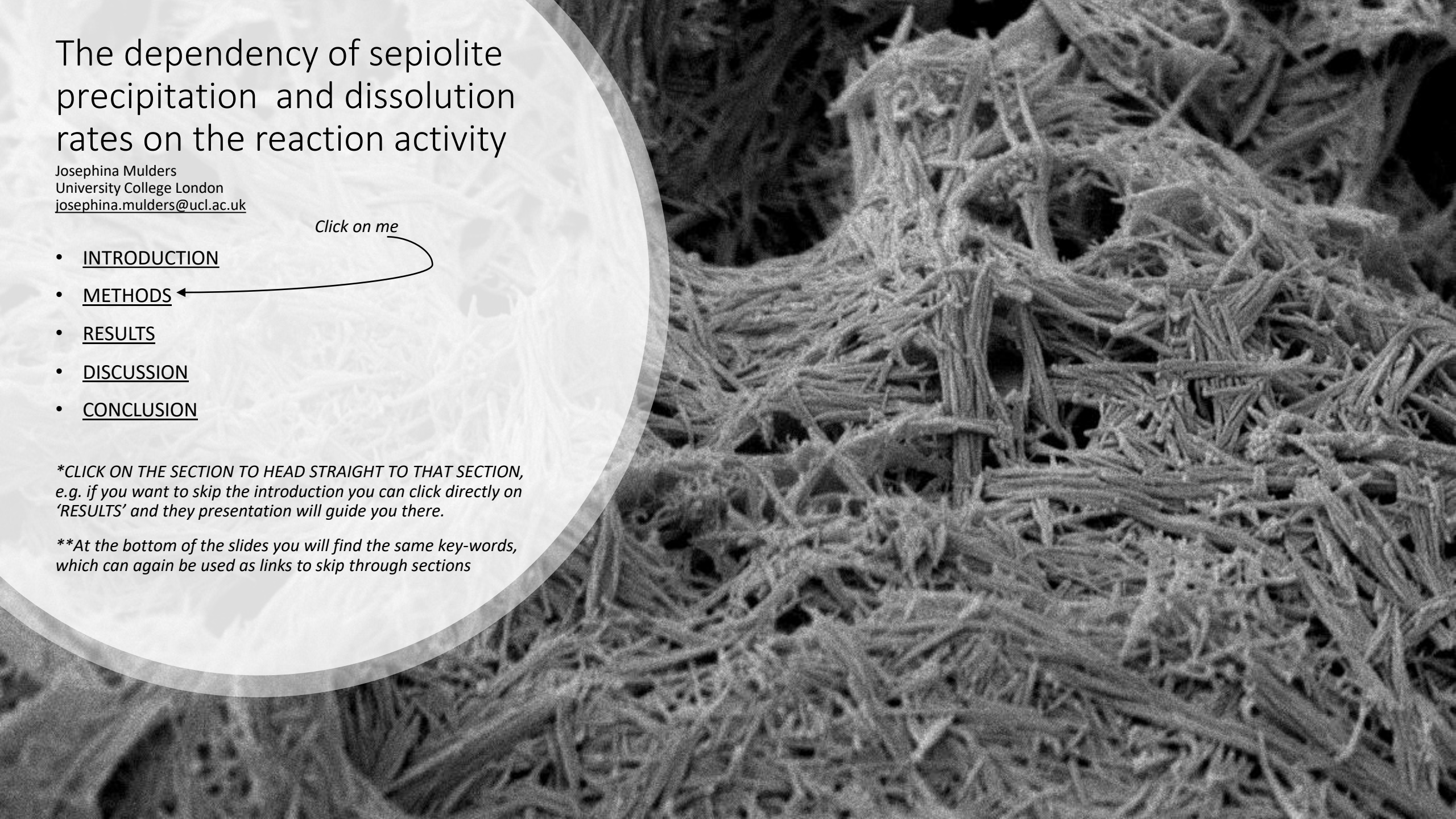
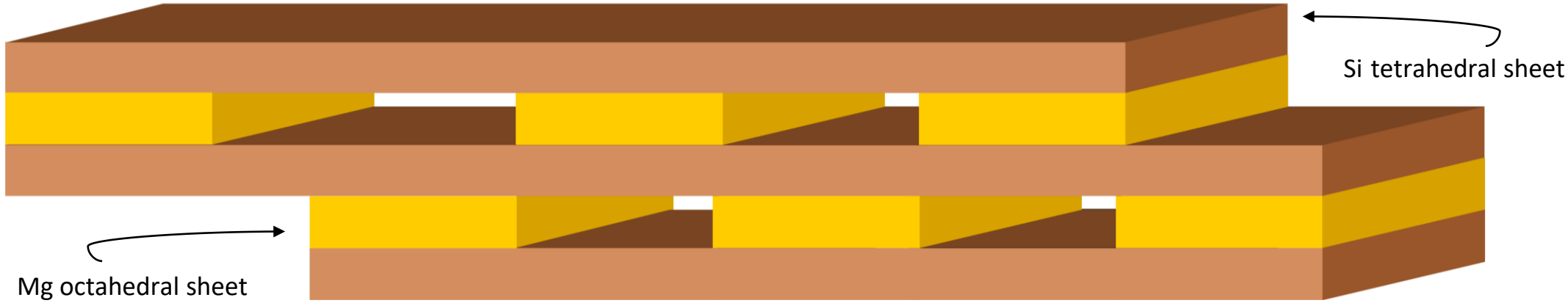


Schematic of sepiolite



Introduction

- **Clay mineral precipitation plays a crucial role in controlling chemistry of Earth's surface and shallow subsurface waters [1,2]**
  - Clays can provide nutrients [1]
  - The sluggish precipitation of clays could hinder weathering [3]
  - Adsorption of e.g. heavy metals on clay, could play a crucial role in the transport of these material through the environment [4]
- **Despite the importance of clay mineral dissolution and precipitation in natural environments, there are little constrains on the precipitation and dissolution rates of clays**
- **Clay mineral dissolution and precipitation rates are thought to depend on the reaction affinity, and thus on the saturation state of the system [5]**
  - Dissolution rate studies so far have only considered far from equilibrium conditions, while natural systems are often close to equilibrium [6]
- To gain a further understanding of clay mineral dissolution and precipitation mechanisms and rates and to gain a further understanding on the dependency of clay precipitation/dissolution rates on reaction affinity, **we studied sepiolite dissolution and precipitation rates as a function of solution saturation**
  - Sepiolite is a Mg-rich clay ($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$), which although it is are, is thought to one of the few authigenic clays to precipitate readily at room temperature

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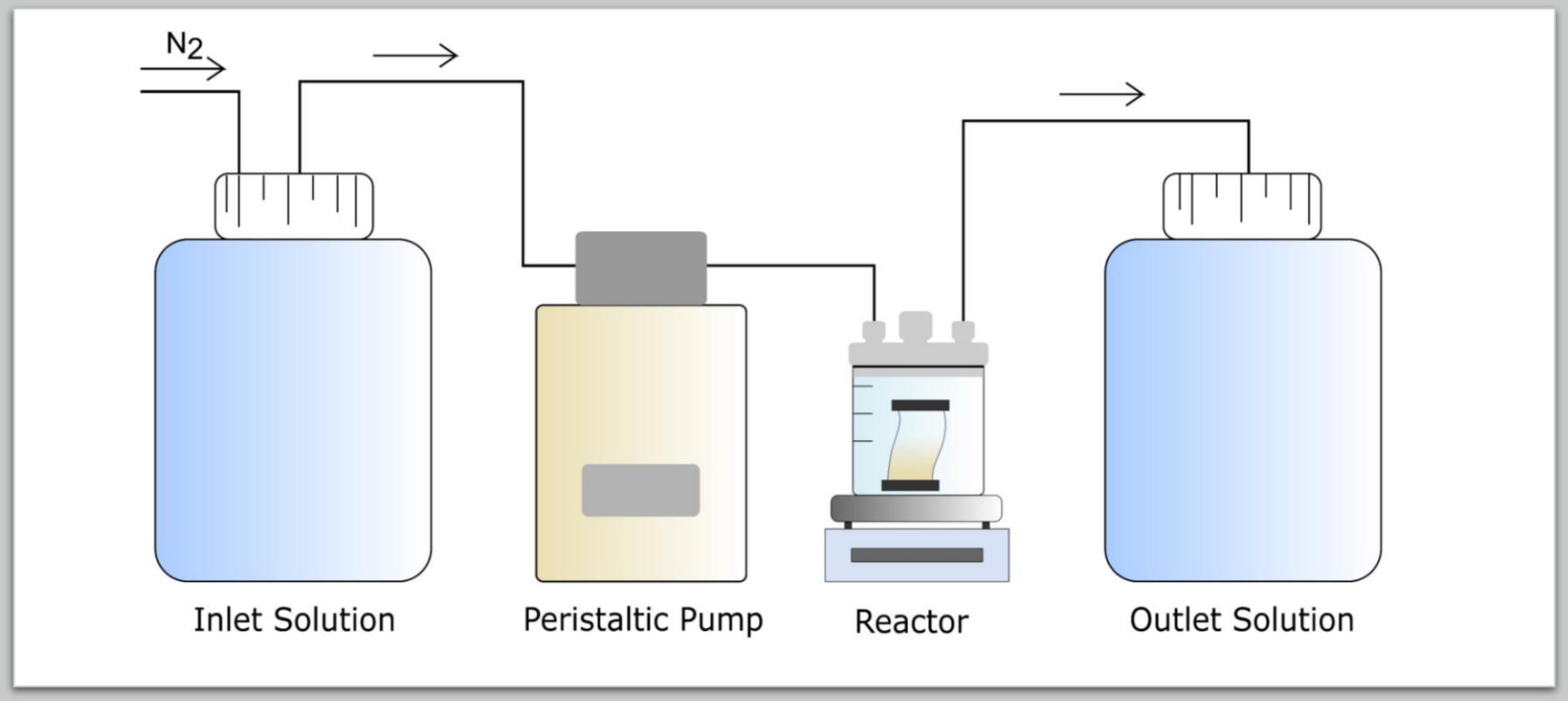
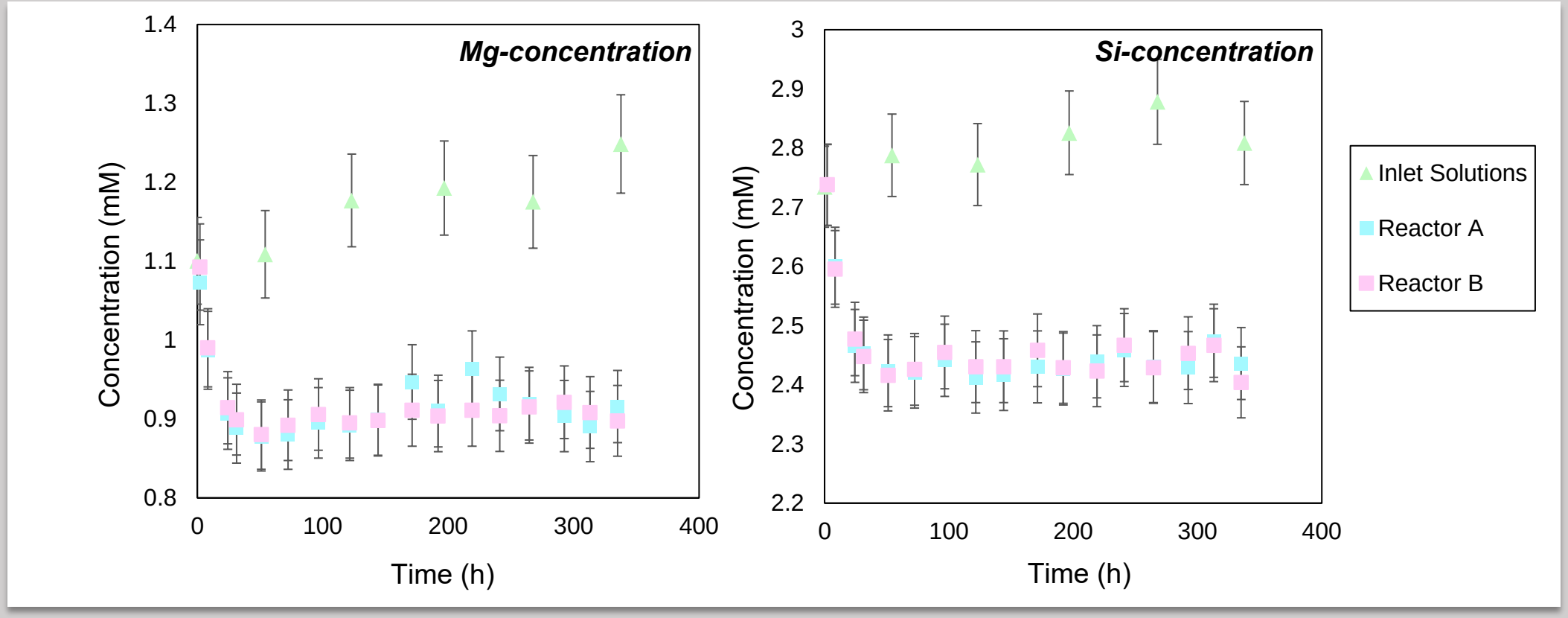


Methods

- Sepiolite seeded flow through experiments, crystalline sepiolite contained in dialysis tube
  - Inlet solution for precipitation experiment, sepiolite saturation index is 18 (pH = 9.21) at 60˚C
  - Dissolution experiments, at pH 8 and at 60˚C
  - Vary flow rates to change the saturation state in the reactor
  - Reactor placed in shaker bath to facilitate constant mixing and maintain a constant temperature
  - Bubble inlet solution with N_2 gas to prevent CO_2 dissolution
- Measure inlet and outlet Mg/Si concentrations, calculate rate from difference
- 1 experiment ran for three months, to confirm the precipitation of crystalline sepiolite

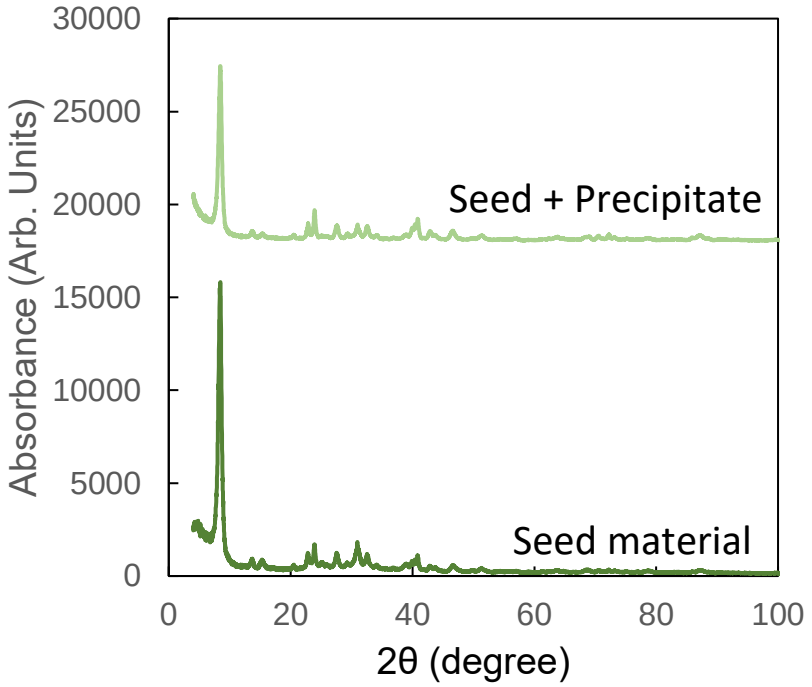


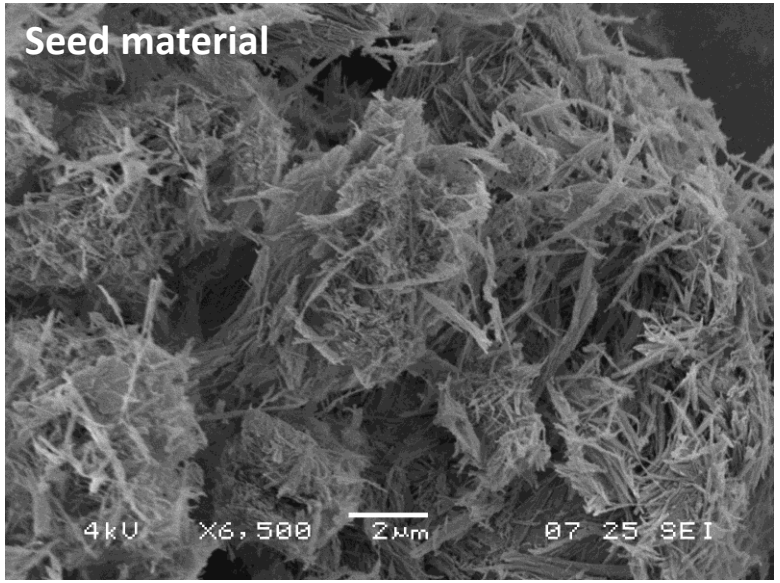
Results

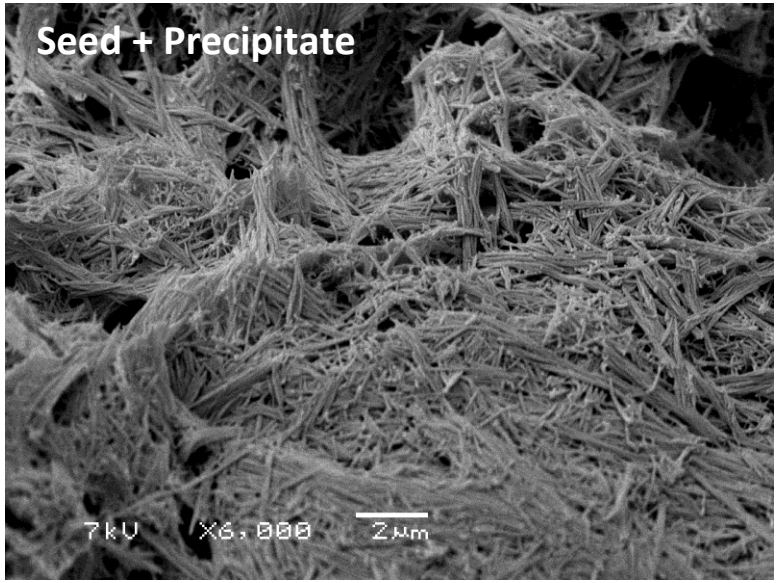
Temporal evolution of aqueous Mg/Si concentration of sepiolite precipitation experiments

- Temporal evolution of the sepiolite precipitation experiments indicate a significant decrease in the Mg and Si concentration over time.
- Results indicate a stoichiometric decrease of Mg/Si

Temporal evolution of the aqueous concentrations sepiolite dissolution experiment shows the reverse trend







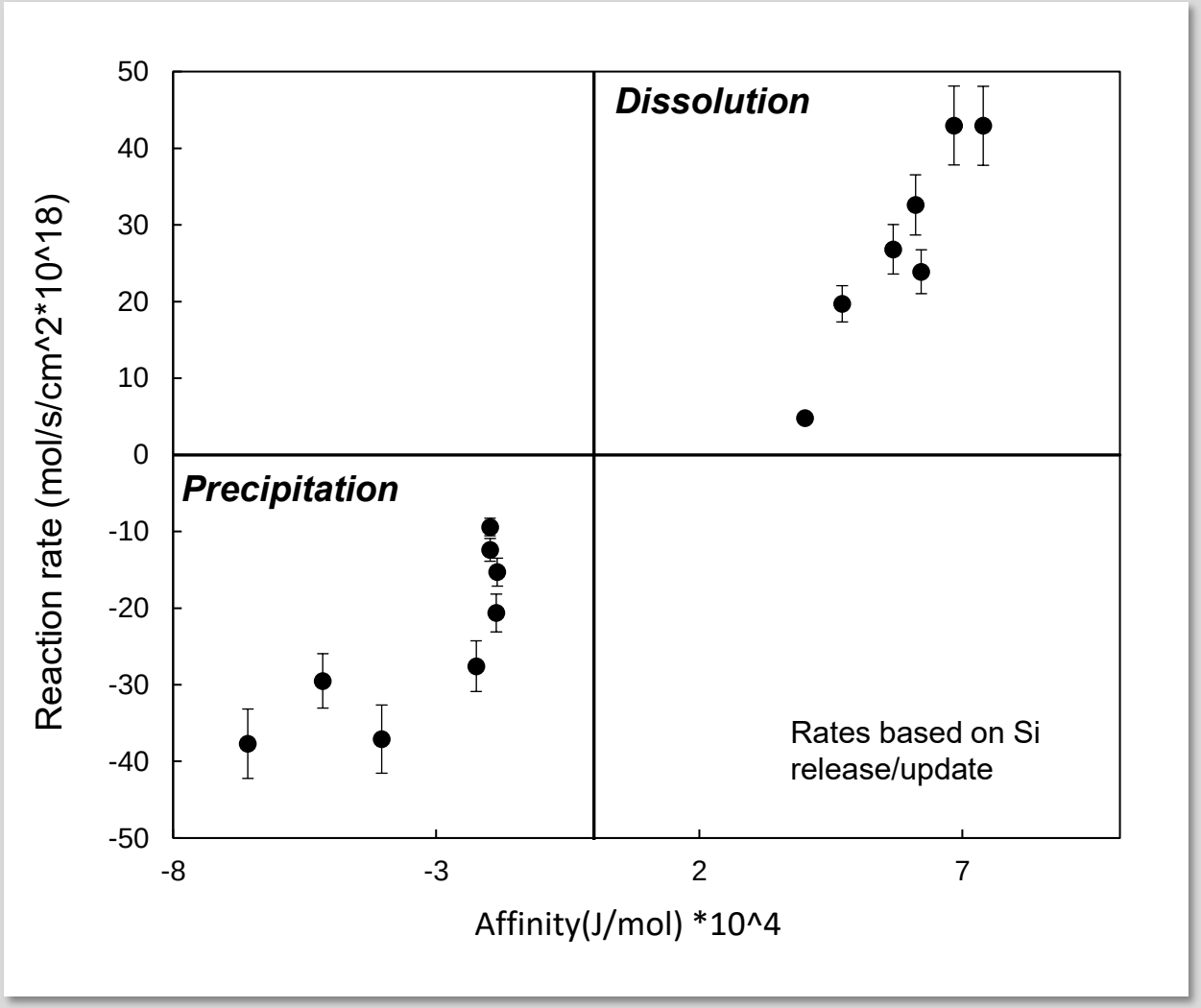
Results

Results from the long-term precipitation experiments show no notable difference between the seed material and the precipitated material, indicating the growth of crystalline sepiolite directly from solution

- Of the collected material approximately 30wt.% is newly precipitated material. Hence, if the precipitated material would be structurally different from the seed material, this would be visible in X-ray Diffraction (XRD) analysis and scanning electron microscopy (SEM) imaging
- XRD spectra indicate that the precipitated material is pure sepiolite
- SEM images indicate no morphological difference between the seed material and the precipitate

Discussion

- Reaction rates decrease as the reaction affinity decreases
- At far from equilibrium conditions, the dependency between affinity and reaction rate is linear and thus follows transition state theory
- At near-equilibrium conditions, this dependency becomes non-linear
    - Non-linearity has previously been associated with a decrease in the availability of active surface sites [7]
    - Non-linearity might be related to the relative difficulty of the system to overcome the nucleation barrier, as the solution approaches equilibrium



Conclusion

- Sepiolite dissolution follows transition state theory at far from equilibrium conditions
- However, at near equilibrium condition the dependency between reaction rates and reaction affinity becomes non-linear, suggesting a limitation in the number of active surface sites
- The effect of changes in the saturation state on the precipitation/dissolution rates are significant and could (partially) account for differences between measured mineral dissolution/precipitation rates and rates measured in the field

References

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