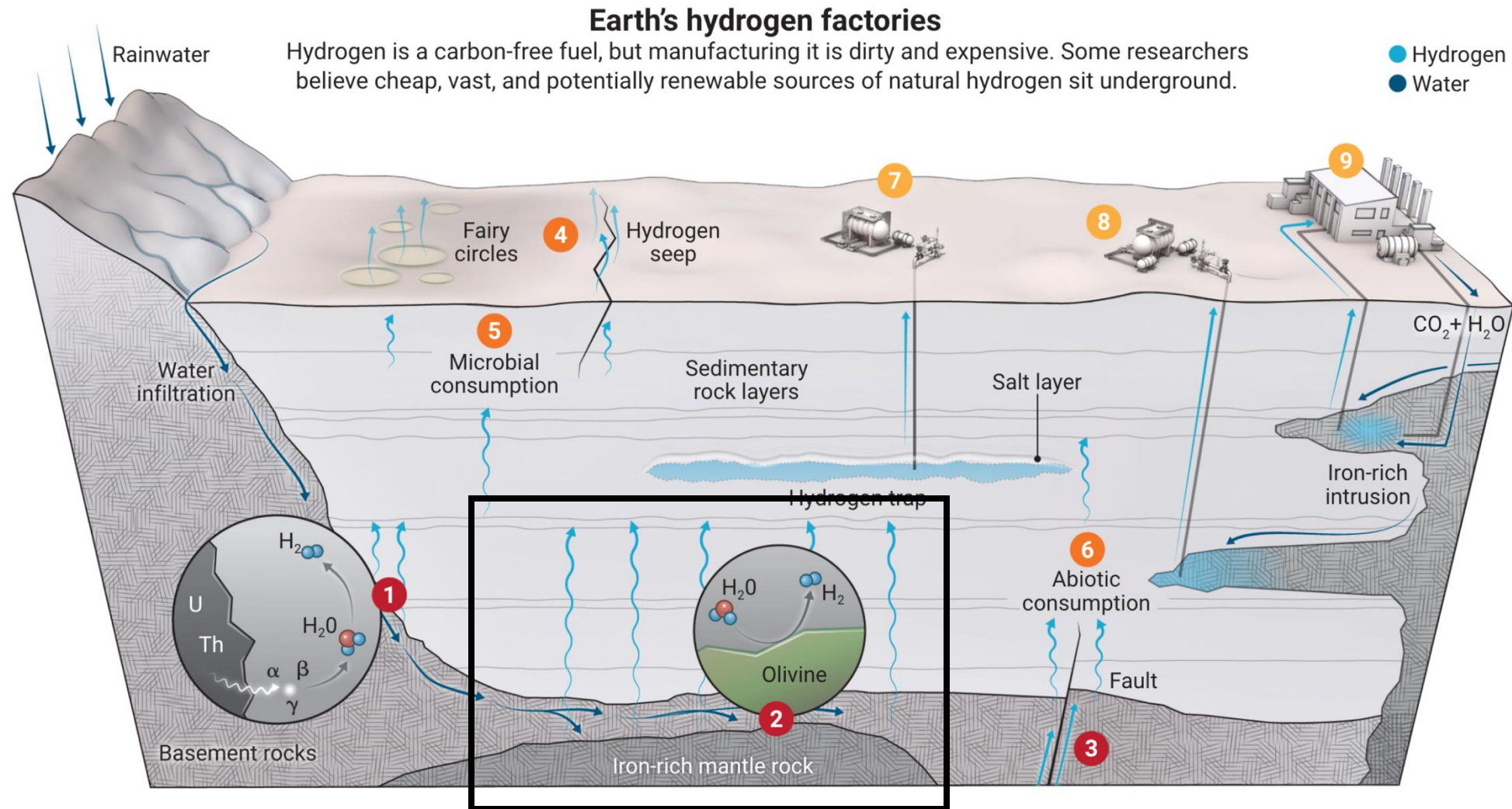


La variable oubliée, l'impact de la salinité sur la production naturelle de H₂ lors de la serpentinisation

Guillaume Siron

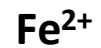
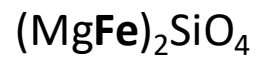
H₂ cycle



Serpentinization



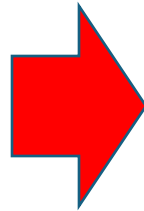
Olivine



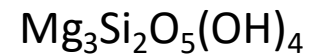
+



Water



Serpentine



+



Magnetite



+



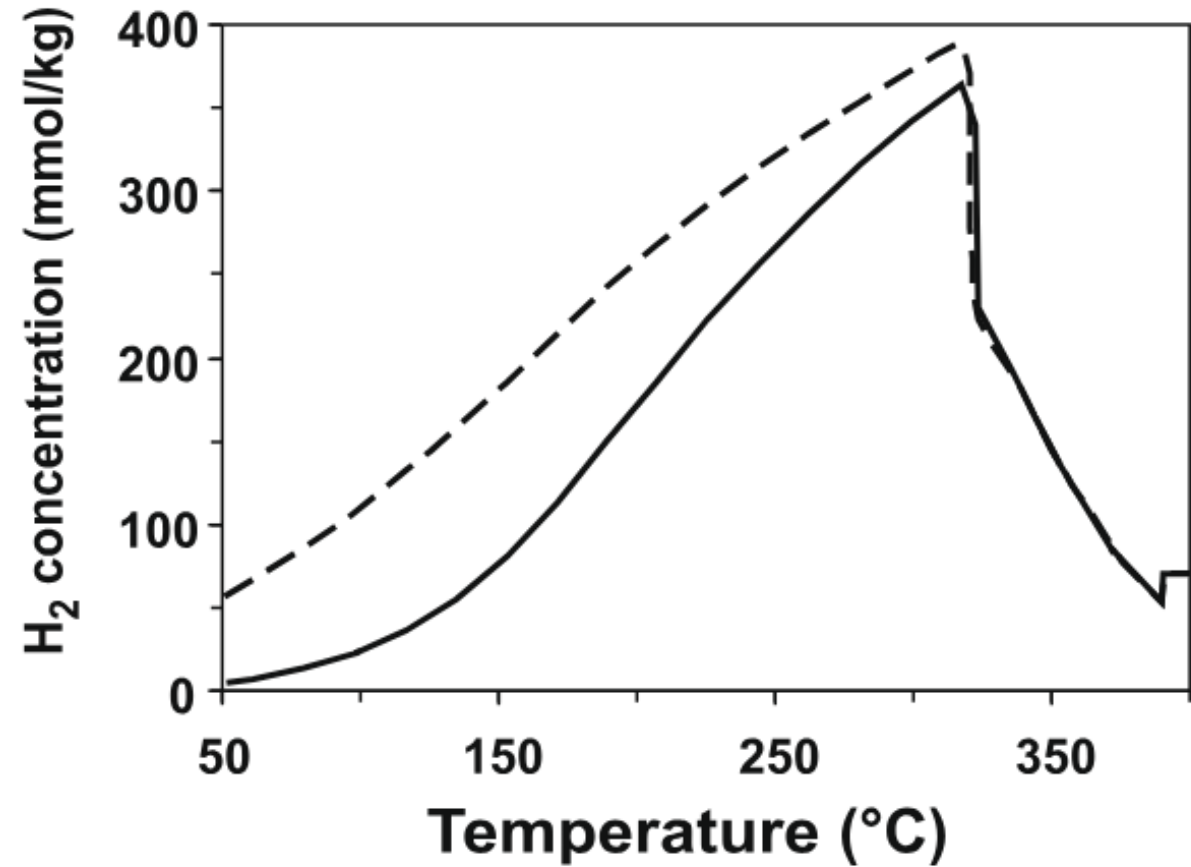
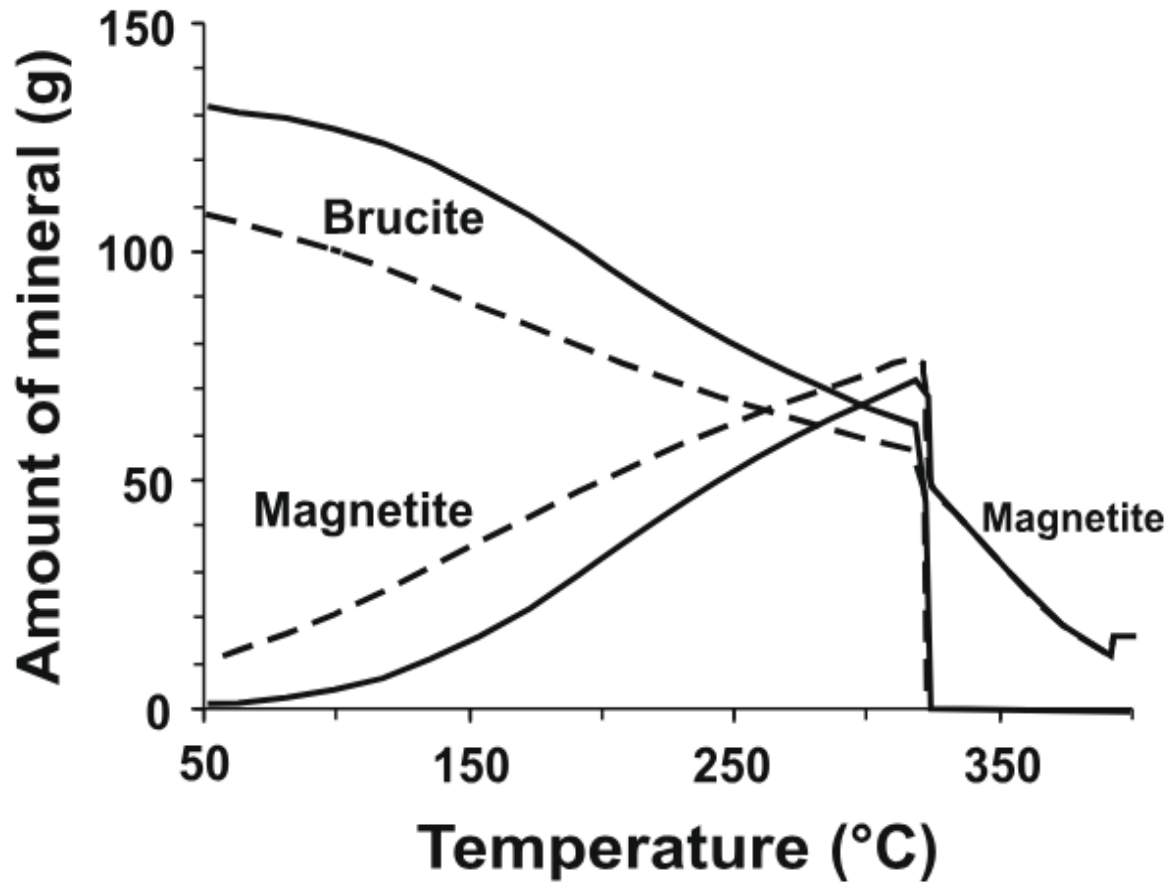
Hydrogen



Serpentinization \Rightarrow important source of hydrogen

Oxidation of Fe in minerals

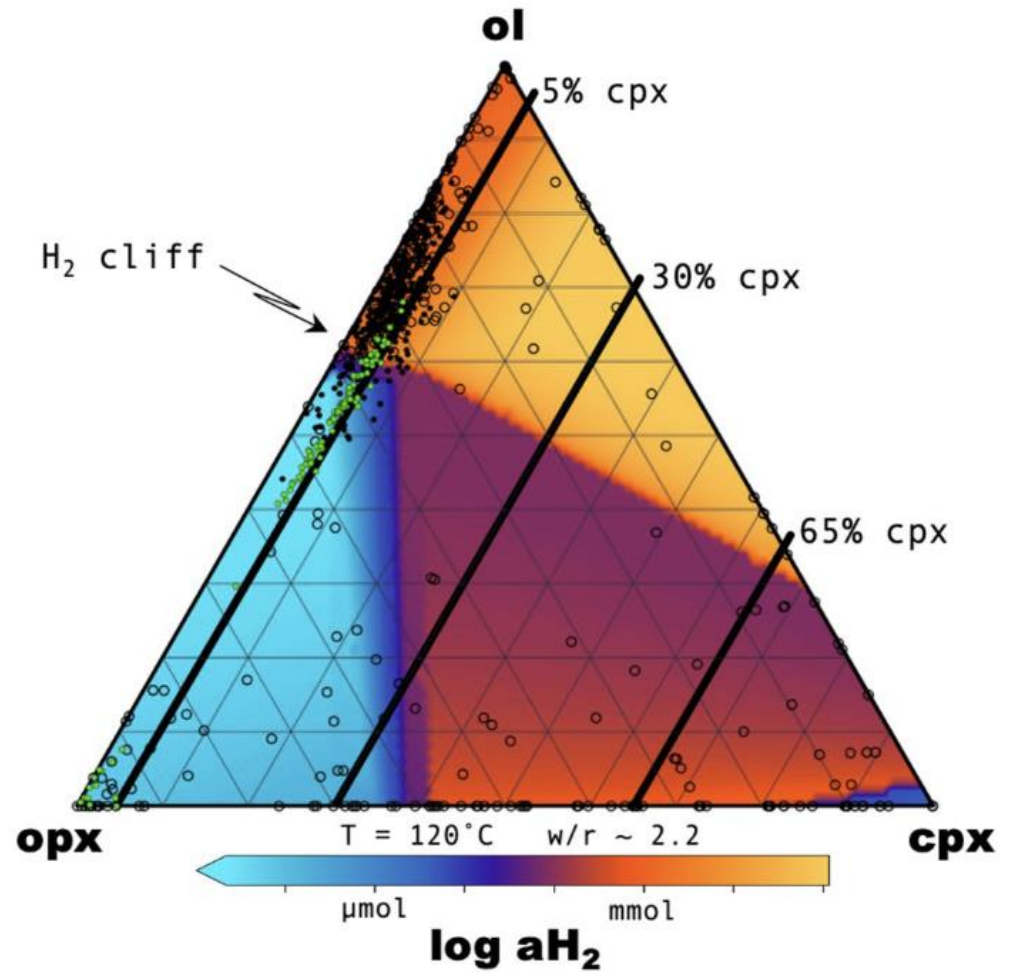
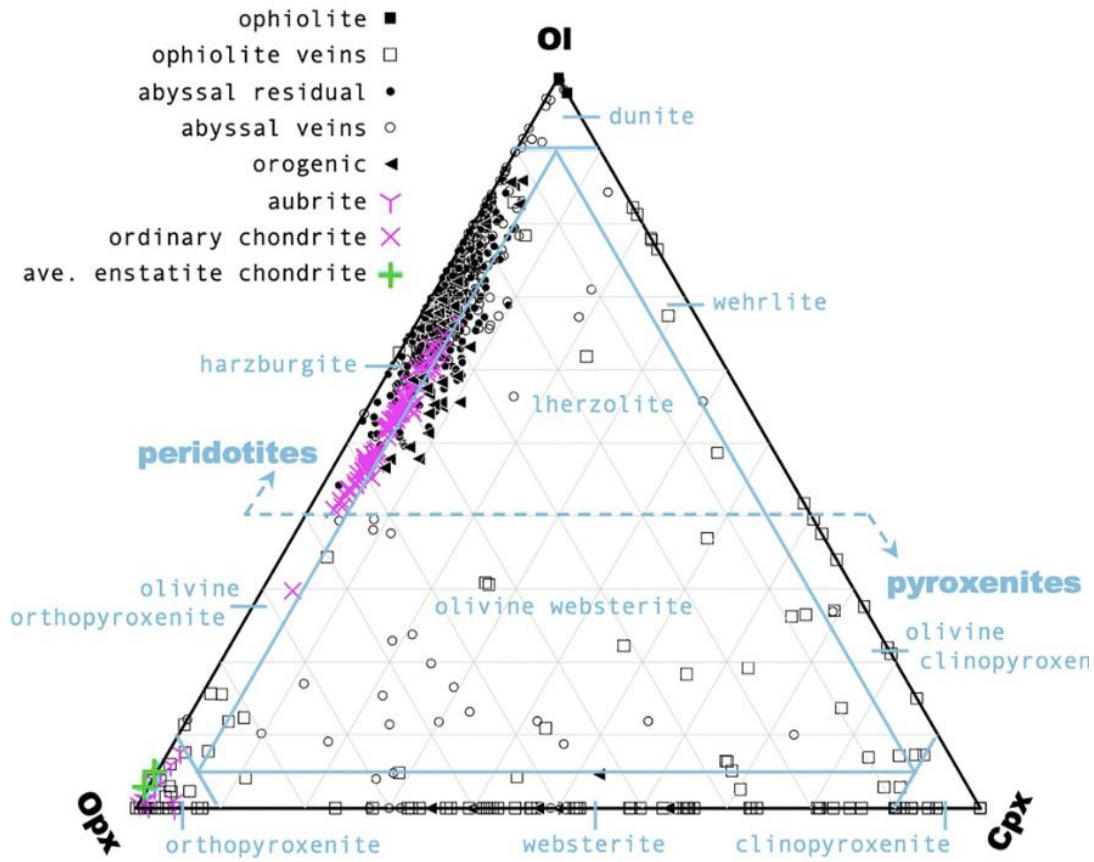
Serpentinization



McCollum & Bach (2009)

Serpentinization and H₂ production are well known at seafloor
Maximum at about 300 °C, competition with Fe phases (Br, Ol)

Serpentinization



Ely et al. (2023)

Peridotite: variations in compositions
 ⇒ important and sharp variations in H₂ production

One (important) missing variable

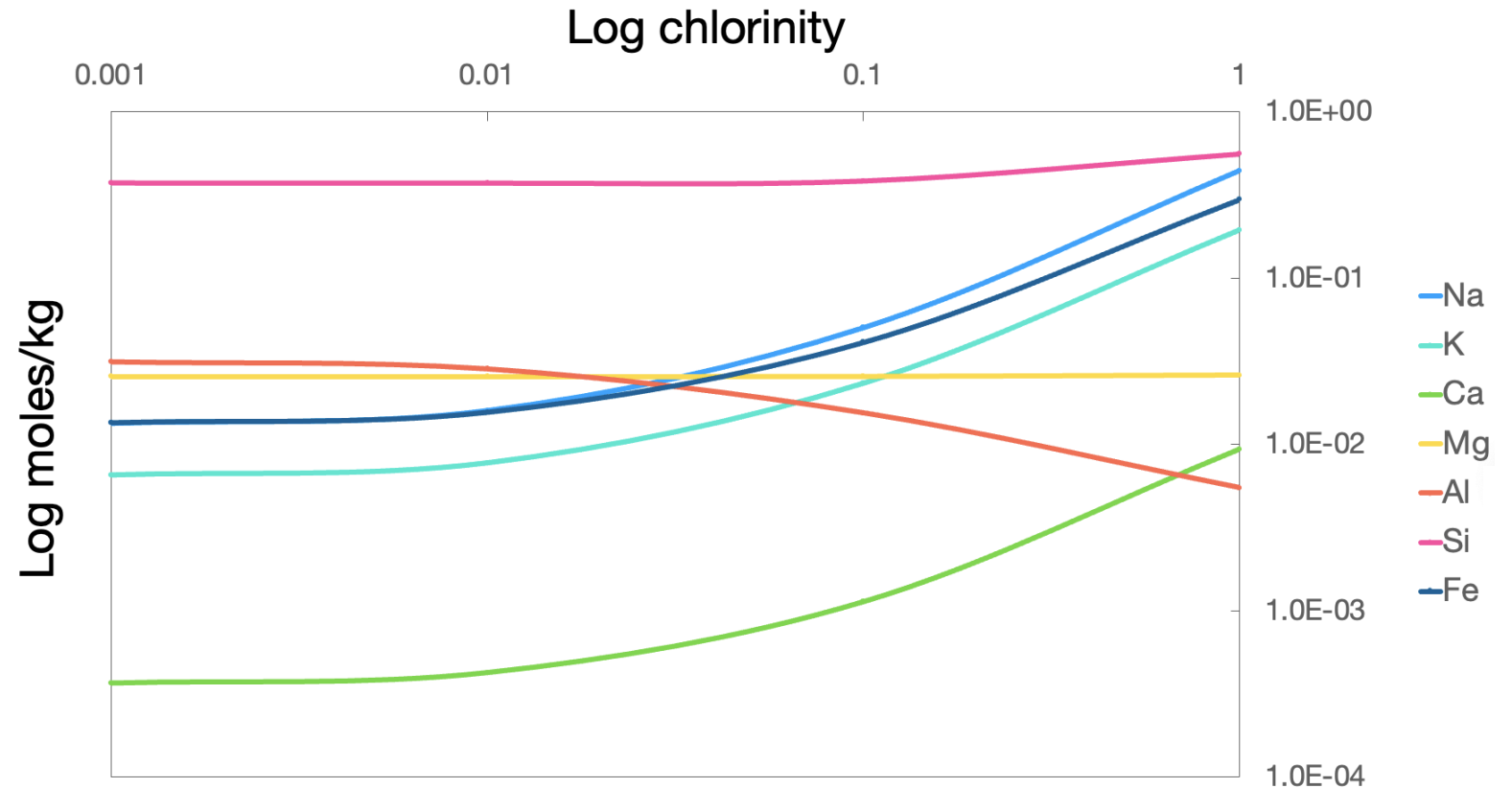
Cations complex with Cl:

HCl, NaCl, KCl, MgCl₂, FeCl₂, CaCl₂

→ Impact on solubilities

→ Impact on kinetics

Ms-Bt schist at 600 °C and 0.5 GPa



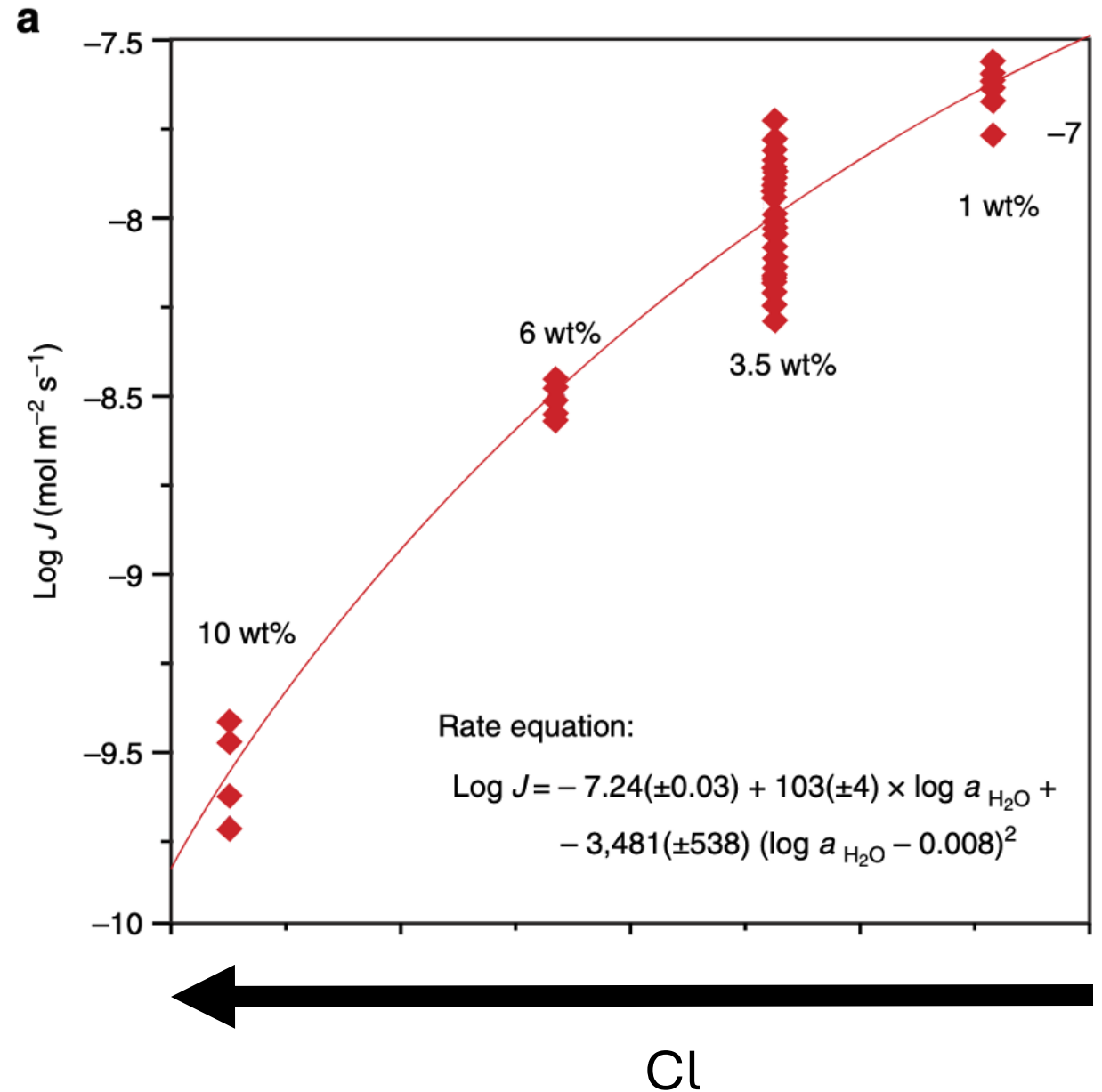
One (important) missing variable

Cations complex with Cl:

HCl, NaCl, KCl, MgCl₂, FeCl₂, CaCl₂

→ Impact on solubilities

→ Impact on kinetics



One (important) missing variable

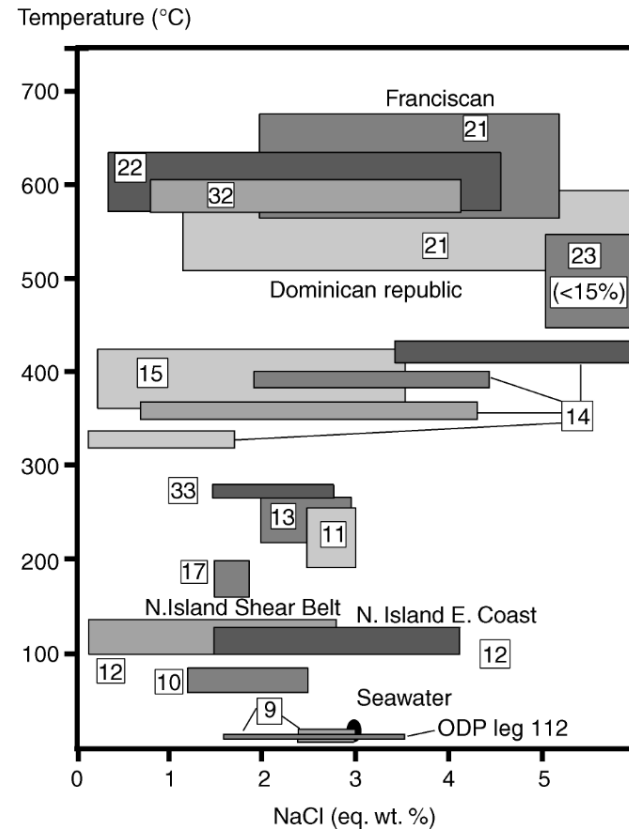
Cations complex with Cl:

HCl, NaCl, KCl, MgCl₂, FeCl₂, CaCl₂

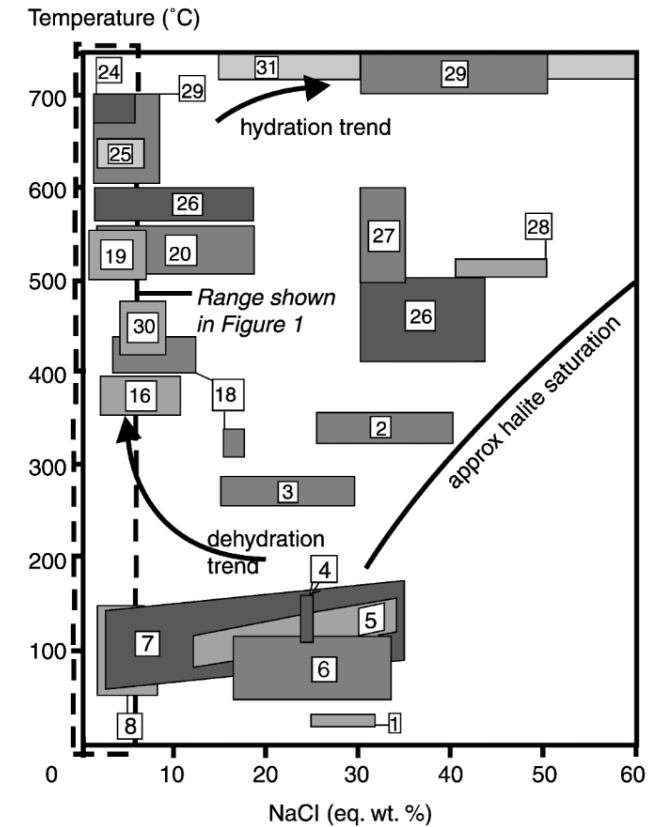
→ Impact on solubilities

→ Impact on kinetics

No evaporites



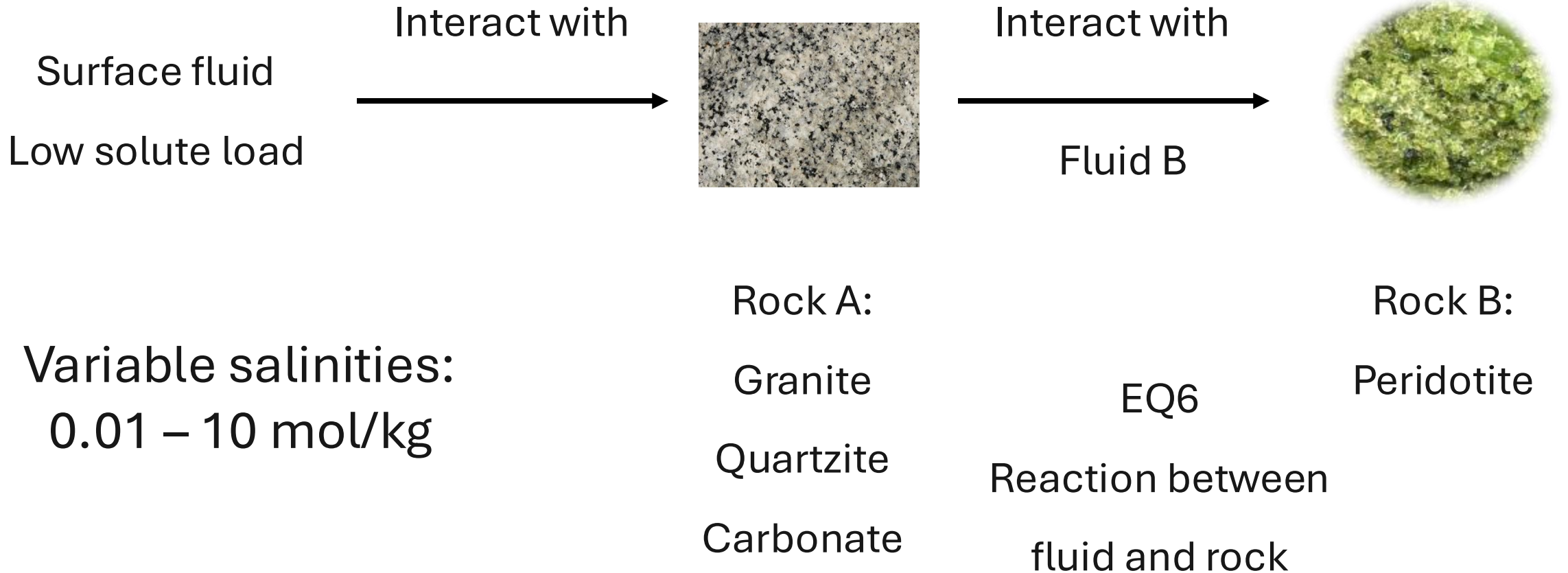
Evaporites



Yardley & Graham (2002)

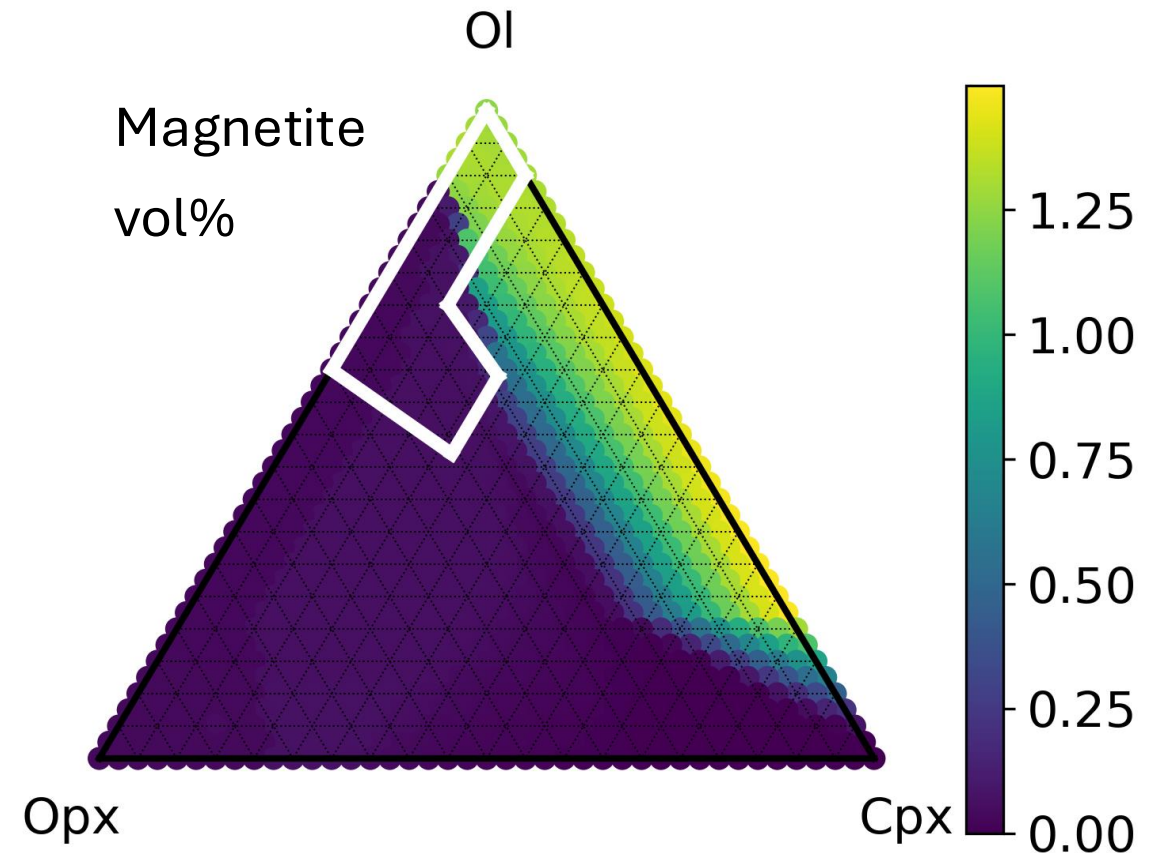
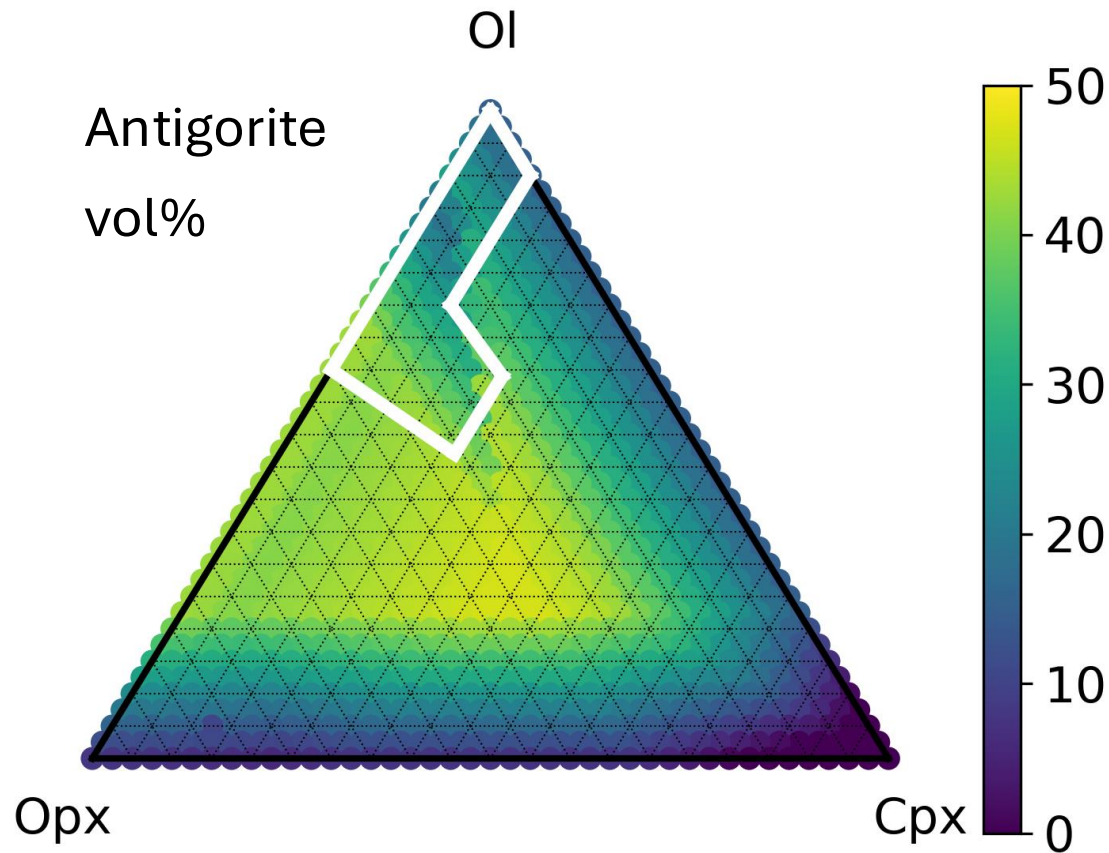
Thermodynamic modeling setup

0.5 GPa, 300 °C



Granitic upper crust

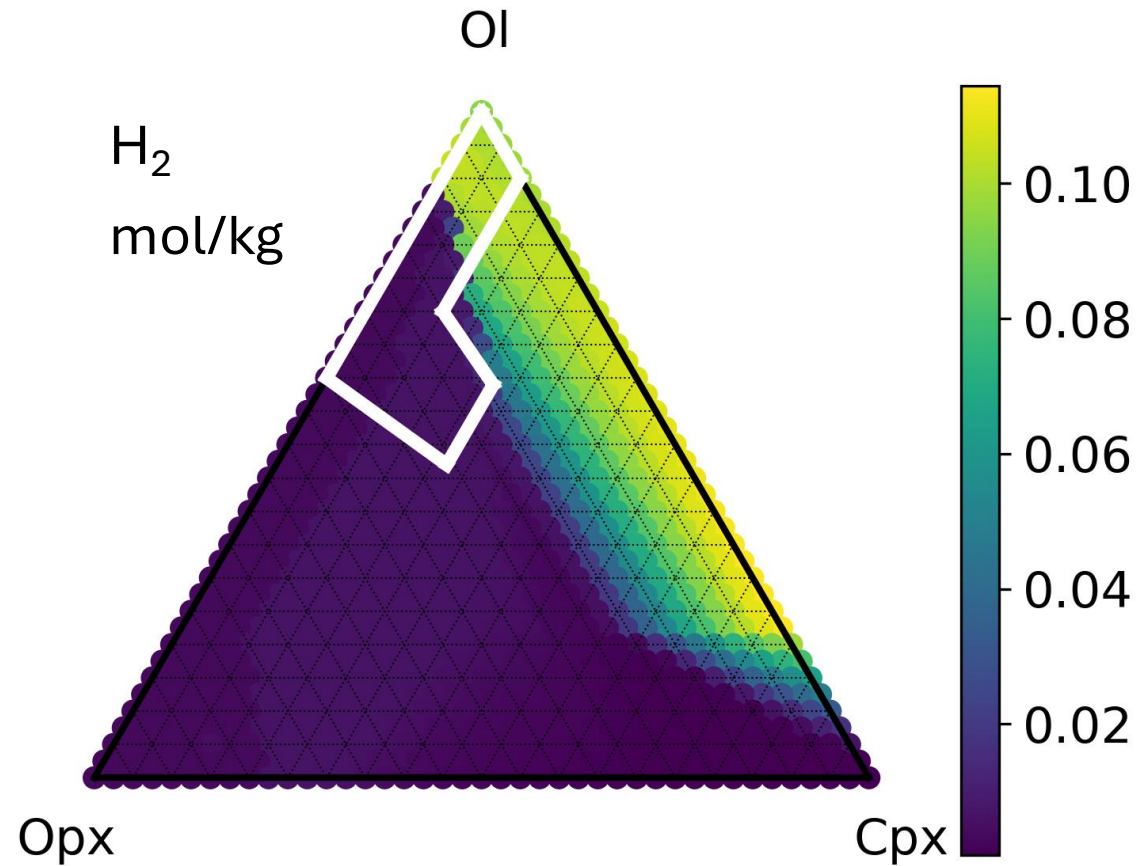
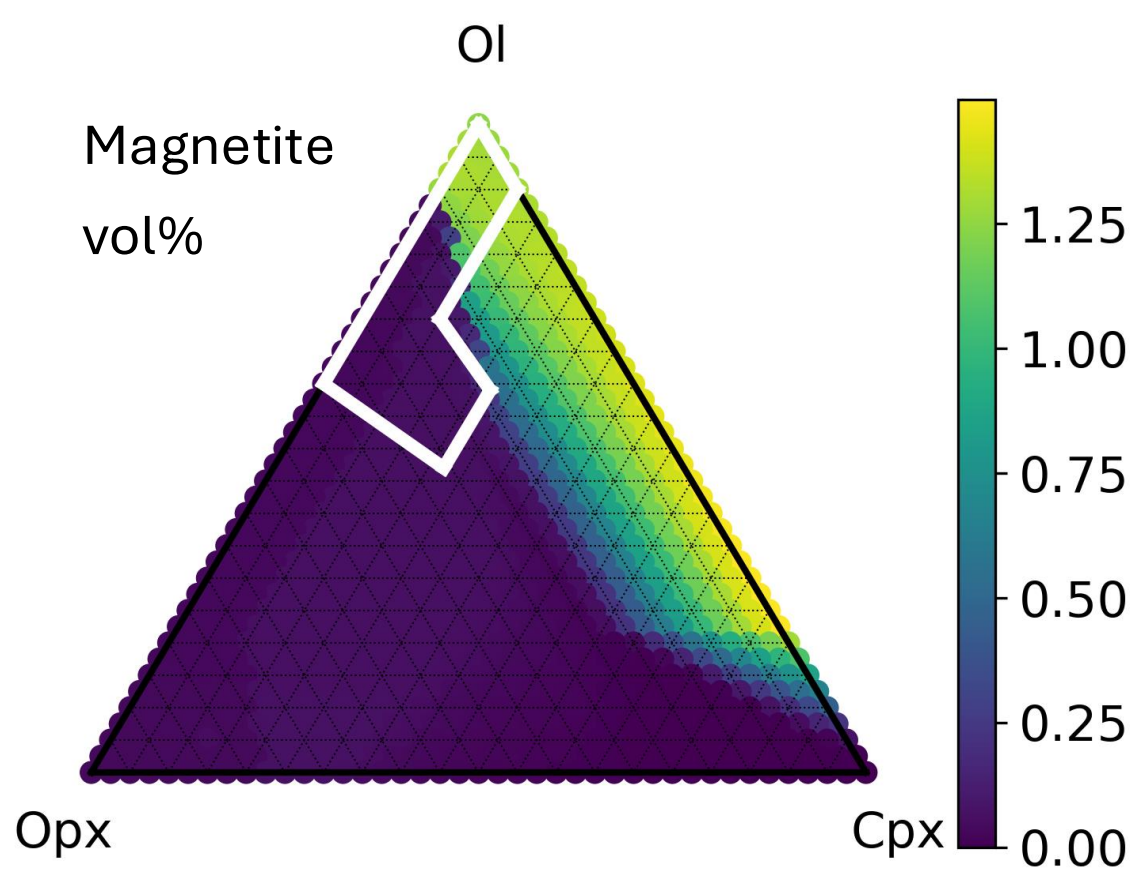
fluid after interaction with granite, $F/R=1$, $Cl=0.1$ mol/kg



Decoupling serpentinization \neq magnetite

Granitic upper crust

fluid after interaction with granite, $F/R=1$, $Cl=0.1$ mol/kg



Coupling Magnetite = H_2 content

Granitic upper crust

fluid after interaction with granite, $F/R=1$

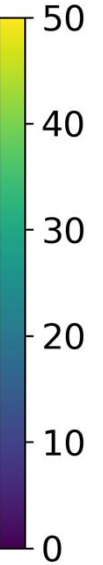
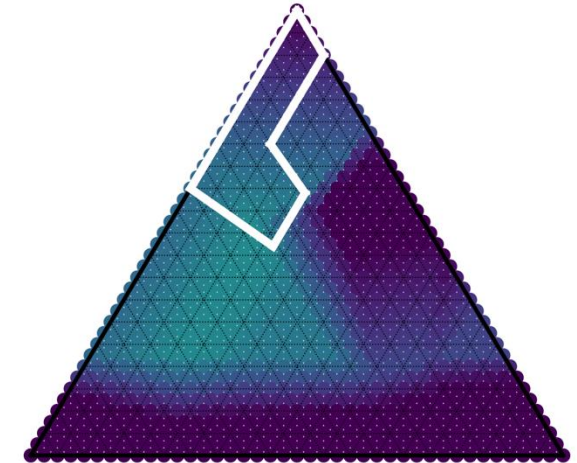
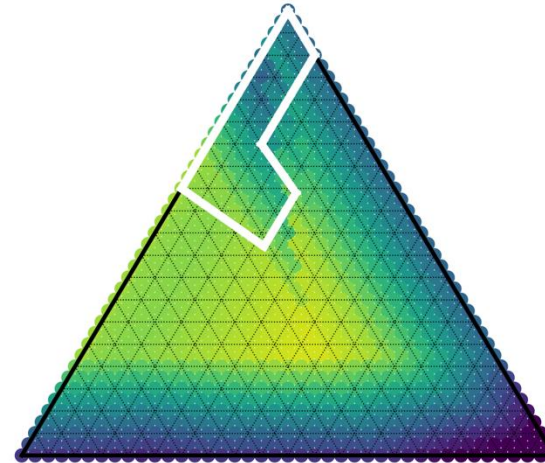
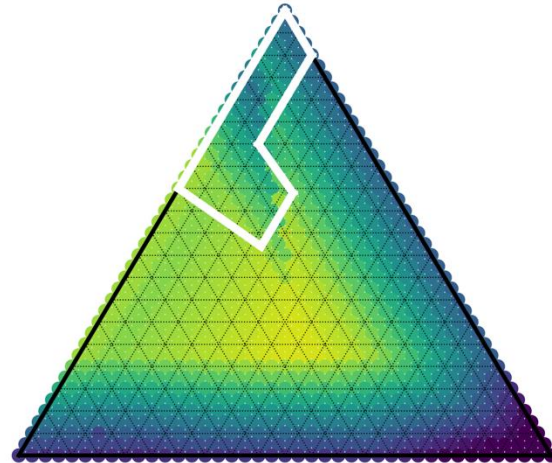
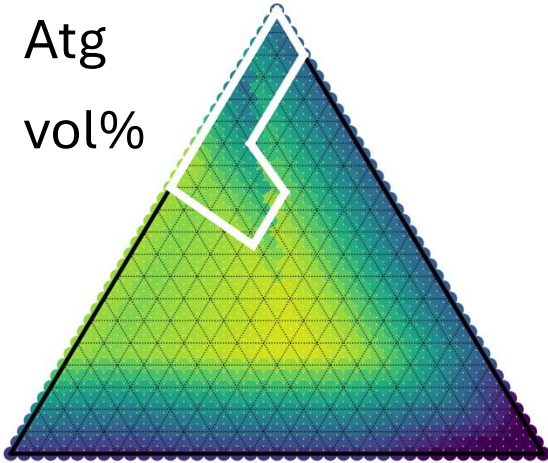
Cl = 0.01 M

Cl = 0.1 M

Cl = 1 M

Cl = 5 M

Atg
vol%



Higher salinity \Rightarrow lower serpentinization degree

Granitic upper crust

fluid after interaction with granite, $F/R=1$

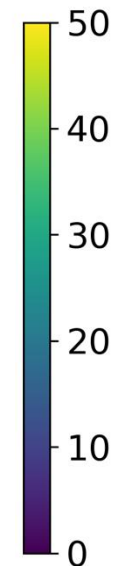
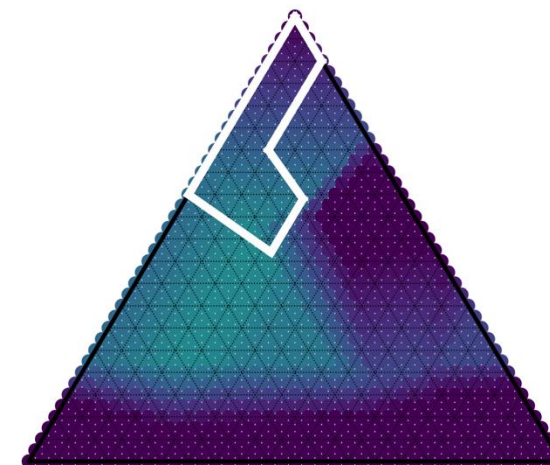
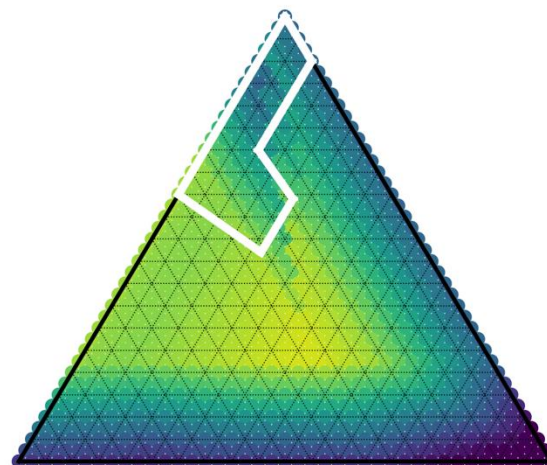
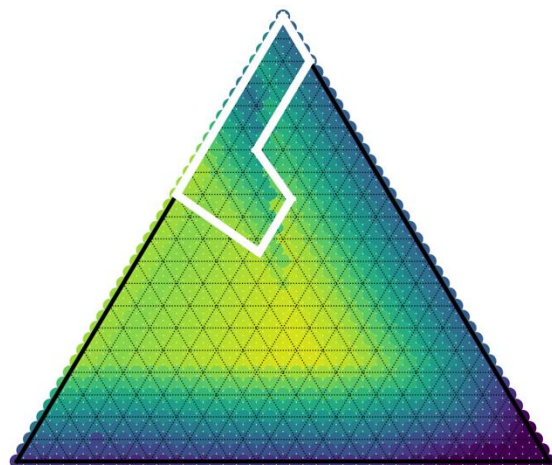
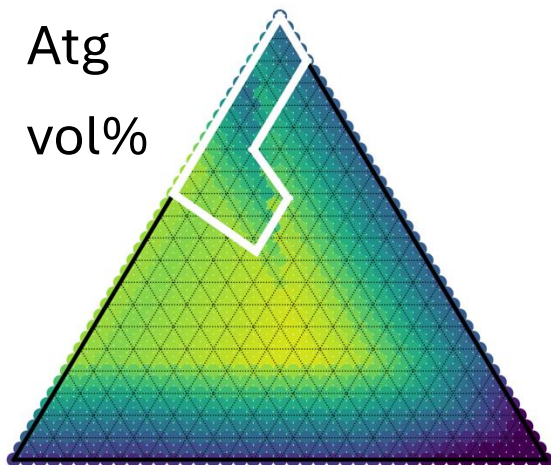
Cl = 0.01 M

Cl = 0.1 M

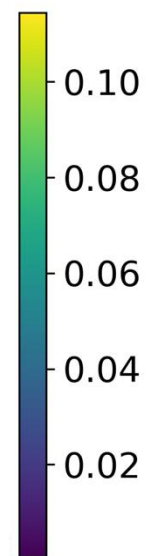
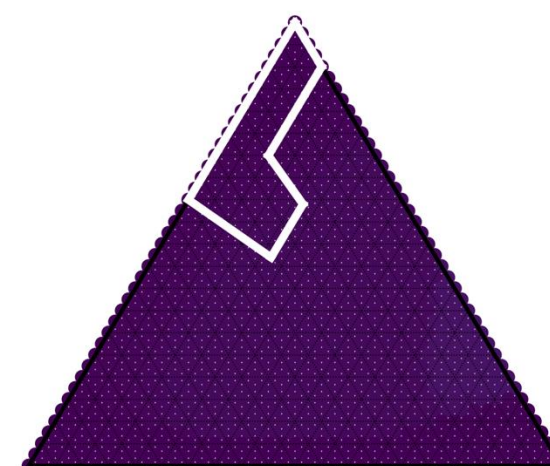
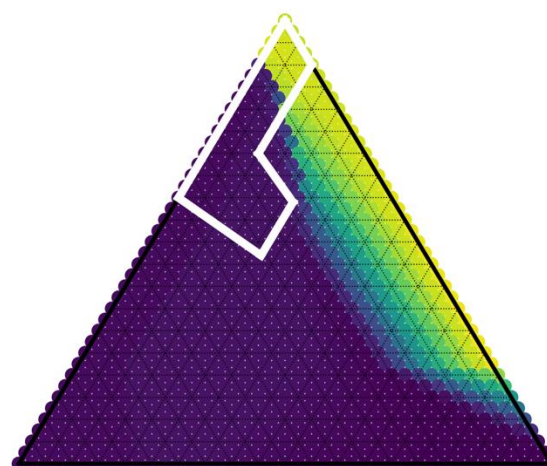
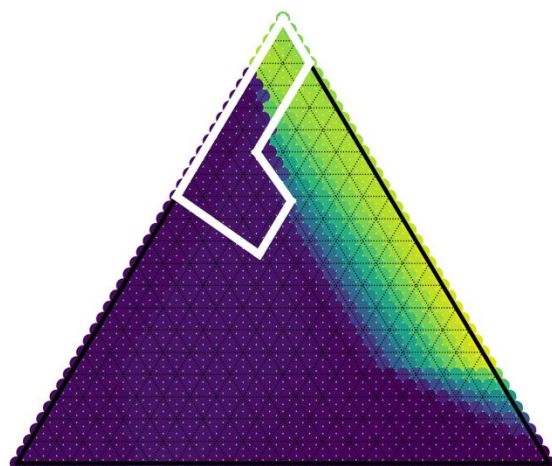
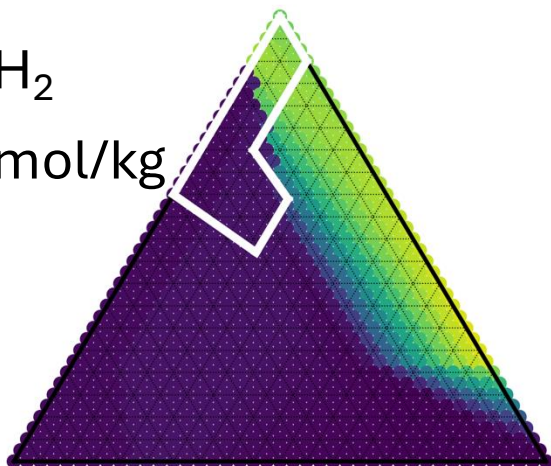
Cl = 1 M

Cl = 5 M

Atg
vol%



H₂
mol/kg



Higher salinity \Rightarrow lower H₂ production

Quartzite upper crust

fluid after interaction with quartzite, $F/R=1$

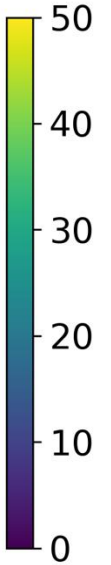
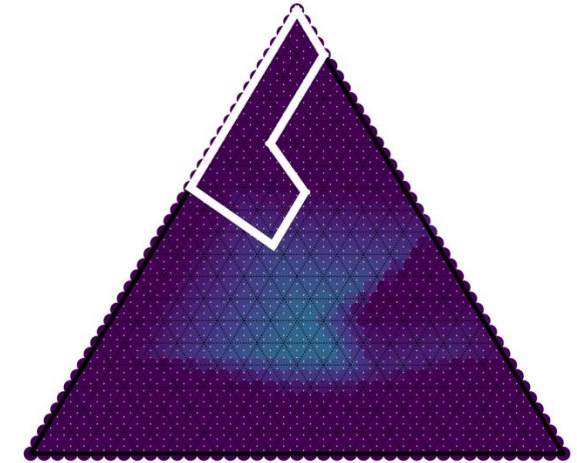
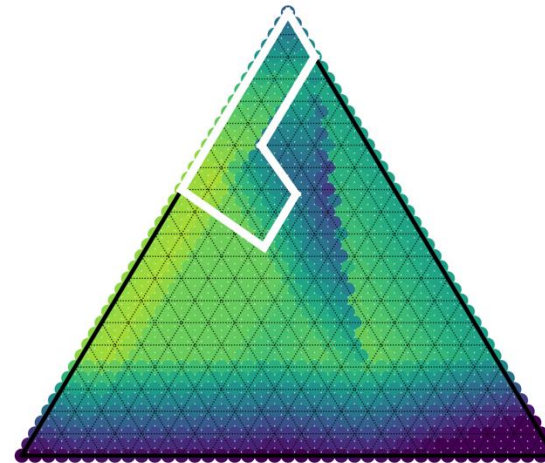
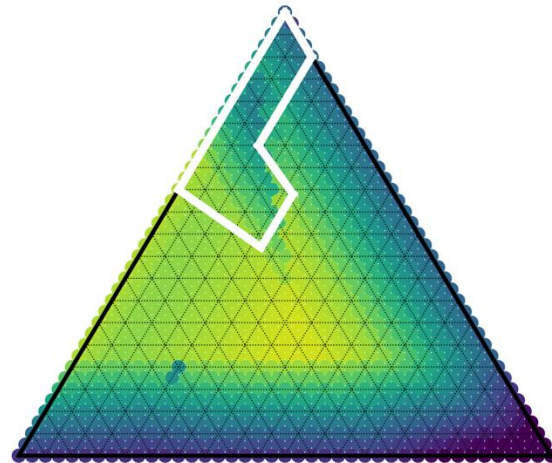
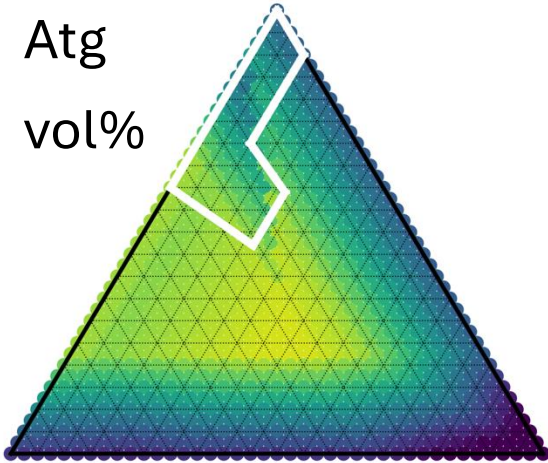
Cl = 0.01 M

Cl = 0.1 M

Cl = 1 M

Cl = 5 M

Atg
vol%



Similar to granite: higher salinity \Rightarrow lower serpentinization degree

Quartzite upper crust

fluid after interaction with quartzite, $F/R=1$

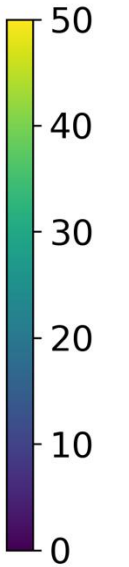
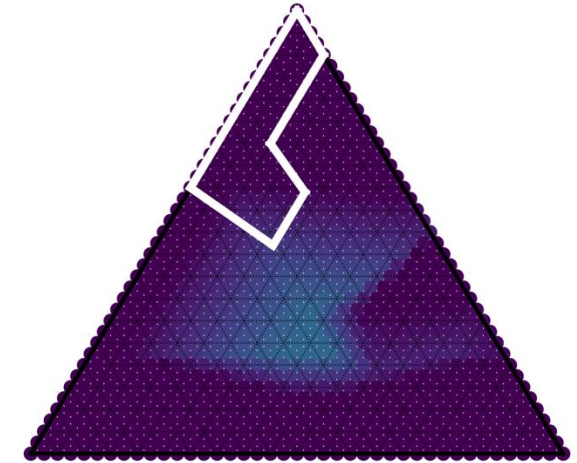
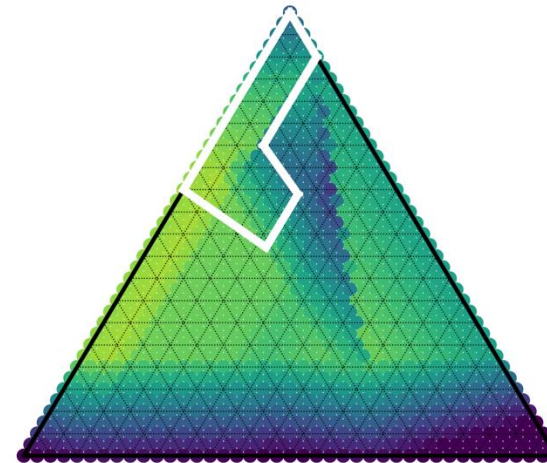
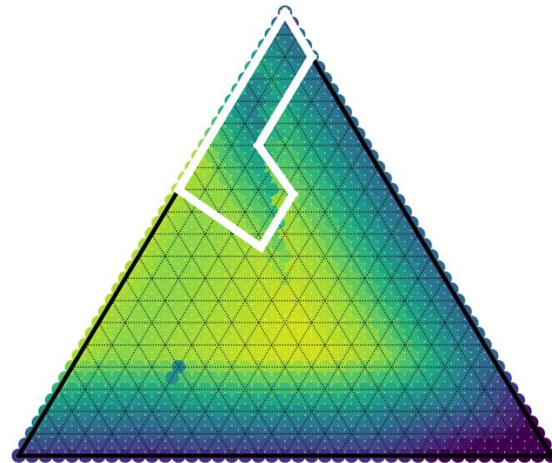
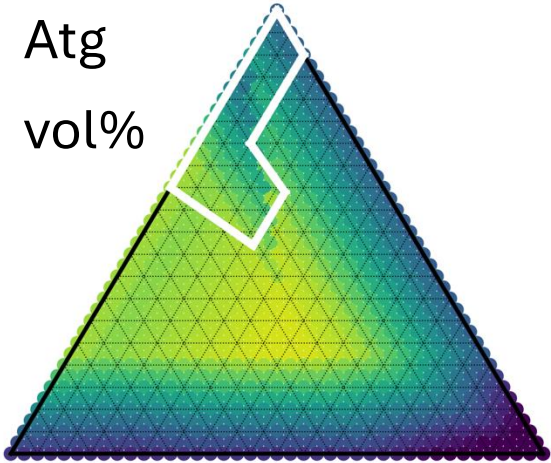
Cl = 0.01 M

Cl = 0.1 M

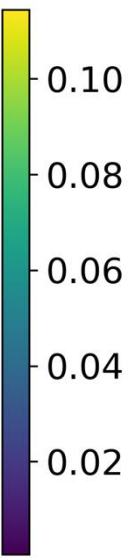
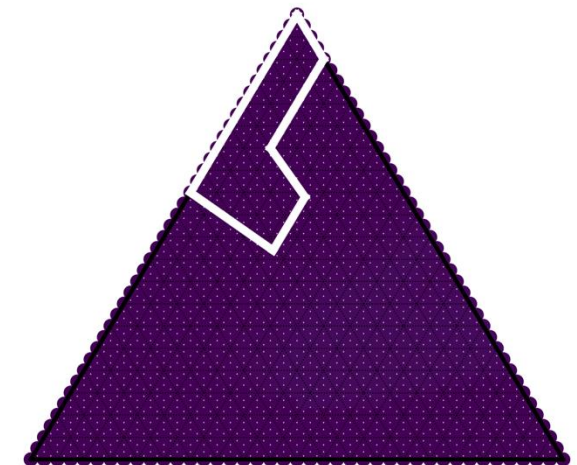
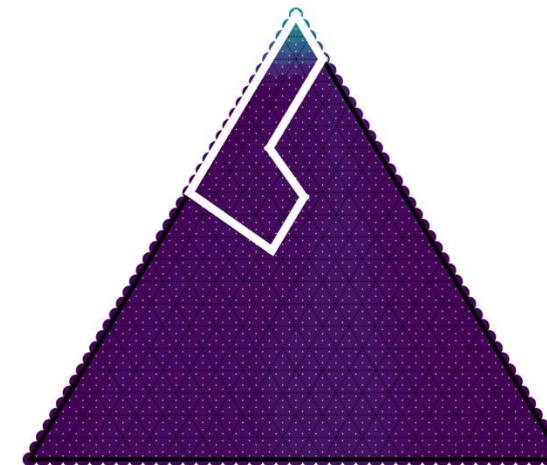
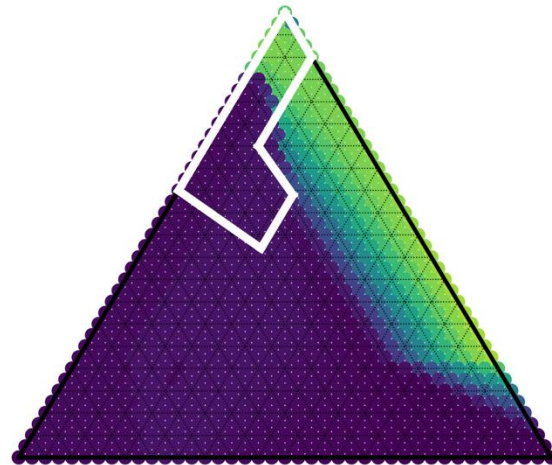
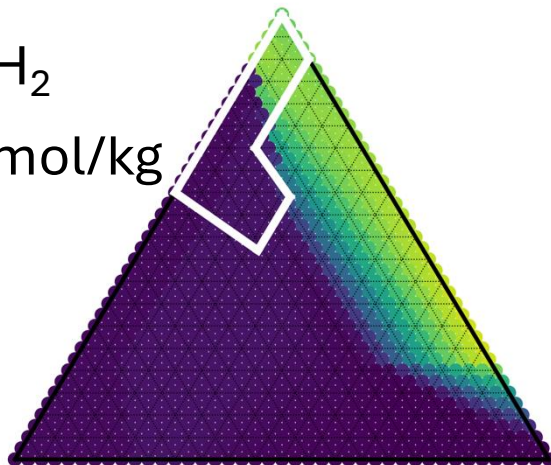
Cl = 1 M

Cl = 5 M

Atg
vol%



H₂
mol/kg



Higher salinity \Rightarrow lower H₂ production

Carbonate upper crust

fluid after interaction with carbonate, $F/R=1$

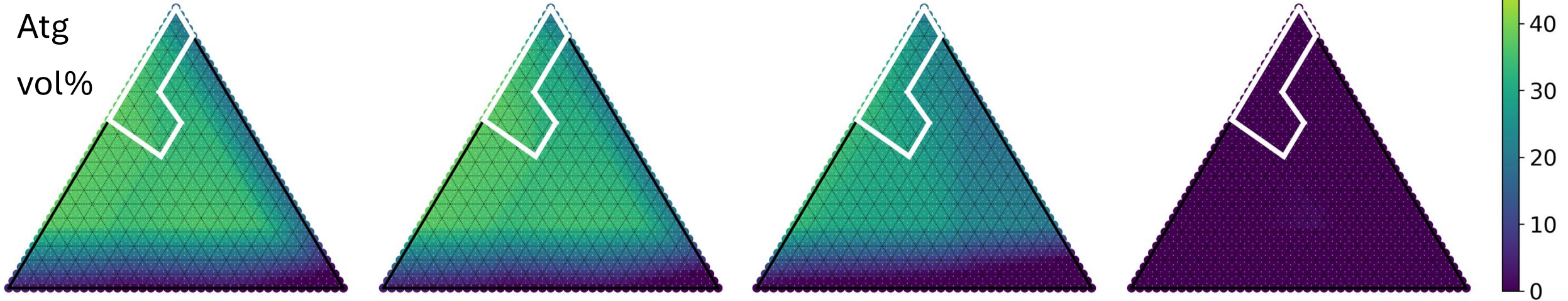
Cl = 0.01 M

Cl = 0.1 M

Cl = 1 M

Cl = 5 M

Atg
vol%



Lower serpentinization degree than granite/quartzite

Infiltrating fluid more oxidized

Lower serpentinization at high salinities

Carbonate upper crust

fluid after interaction with carbonate, F/R=1

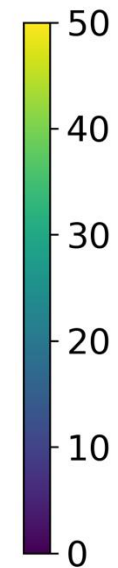
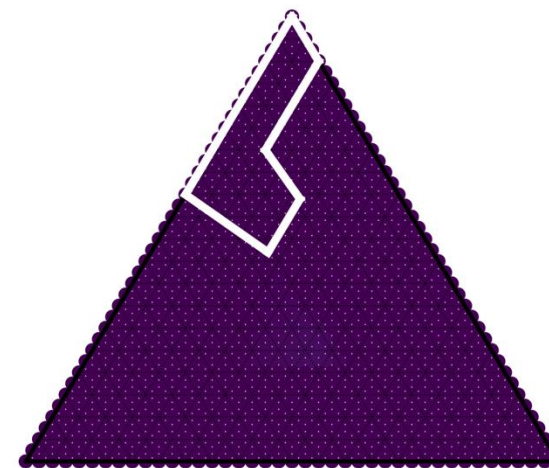
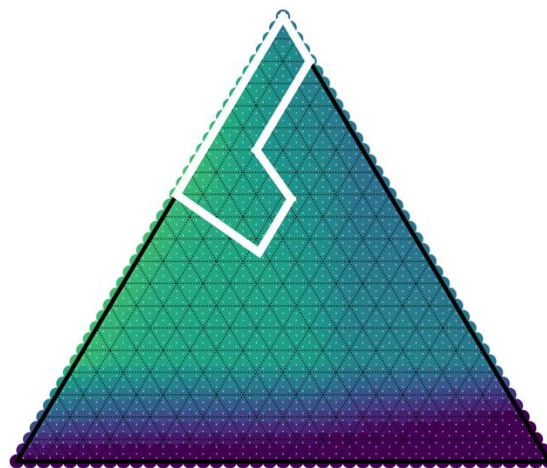
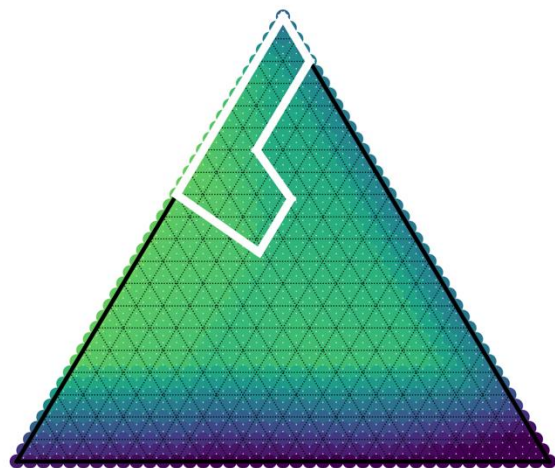
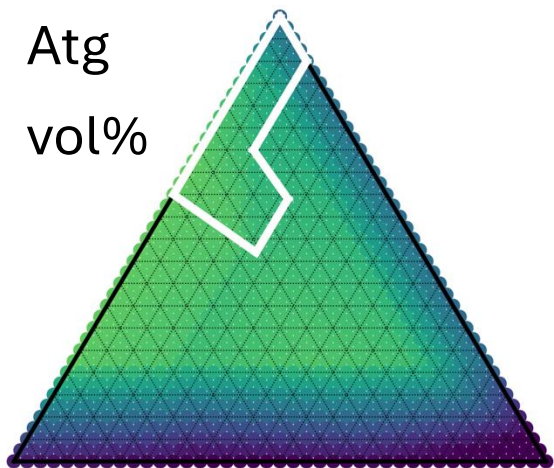
Cl = 0.01 M

Cl = 0.1 M

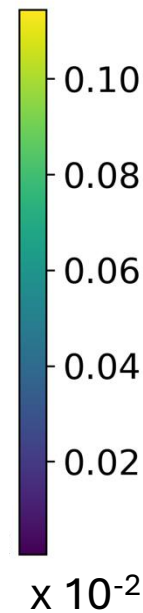
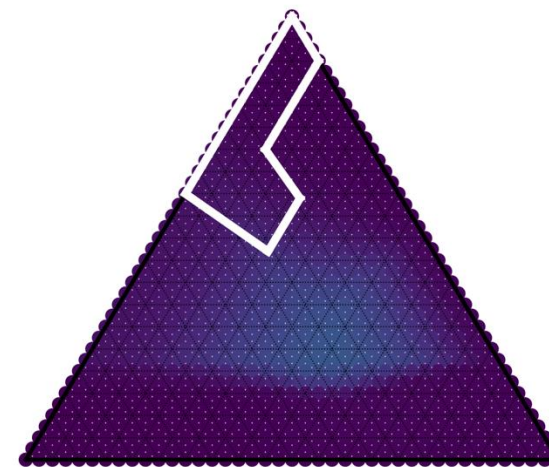
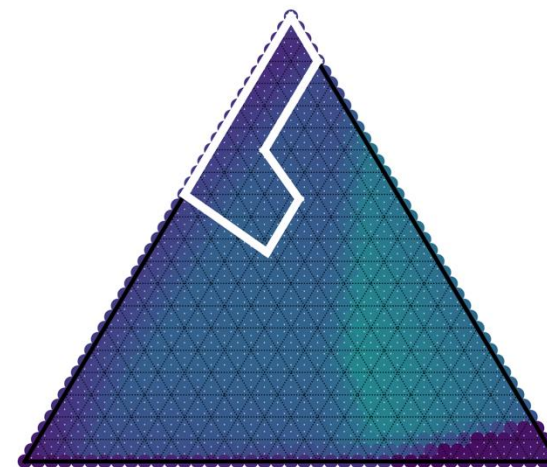
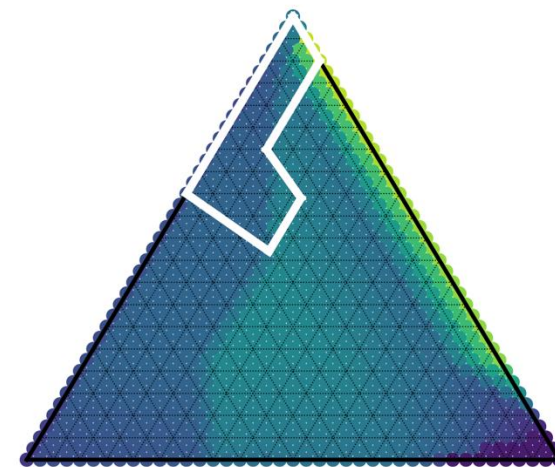
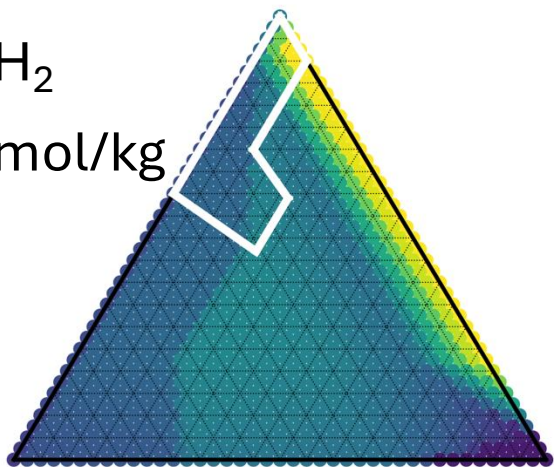
Cl = 1 M

Cl = 5 M

Atg
vol%



H₂
mol/kg



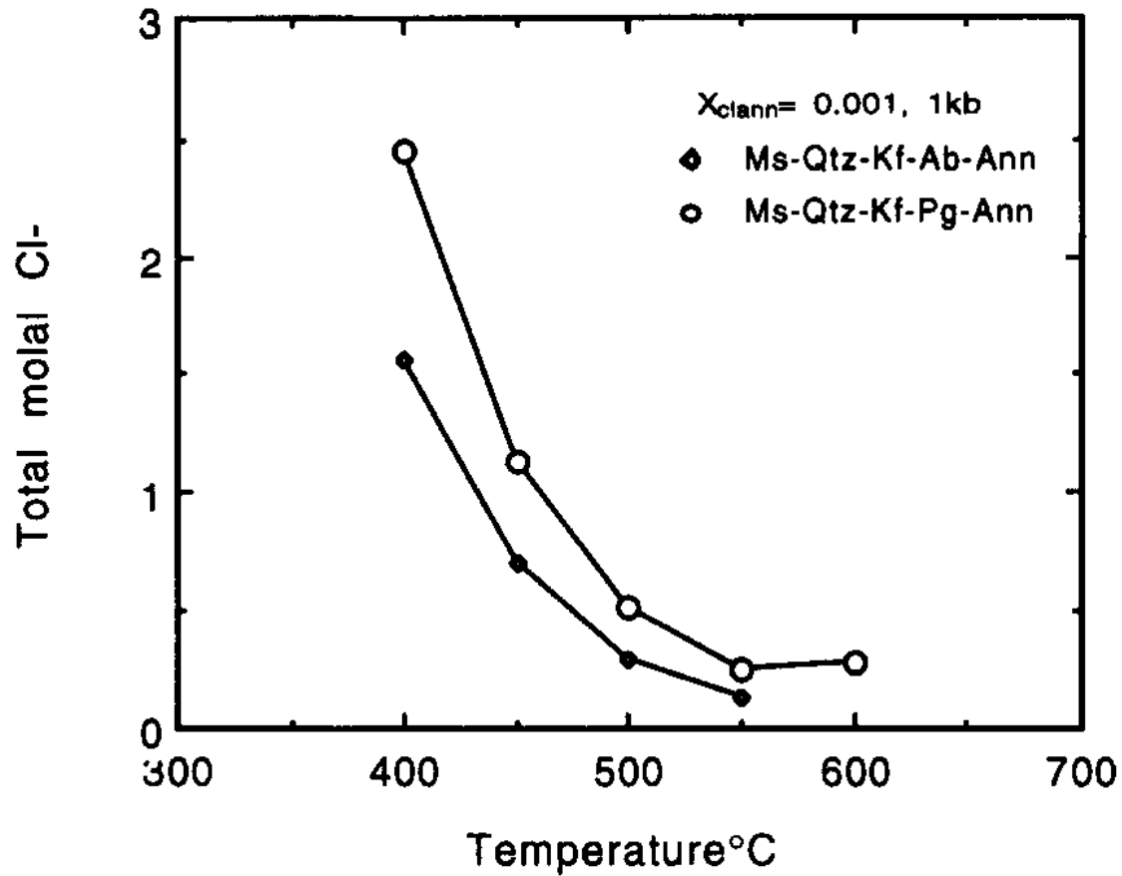
Lower H₂ production ⇒ 100 times less than granite/quartzite

Summary

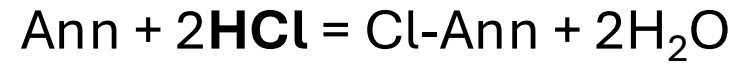
- Initial composition plays a major role in both serpentinization and H₂ production
- Serpentinization and H₂ production are (partly) decoupled
- Fluid: not just H₂O ⇒ importance of the upper crust on the amount of H₂ produced at depth
- High salinities will reduce the production of H₂
- Evaporites and carbonated upper crust might impact the H₂ production at depth

What is the behavior of Cl during serpentinization?

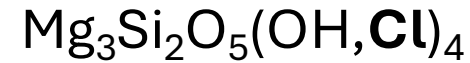
Cl in hydrous minerals



Equilibrium hydrous mineral-fluid:



In serpentine:



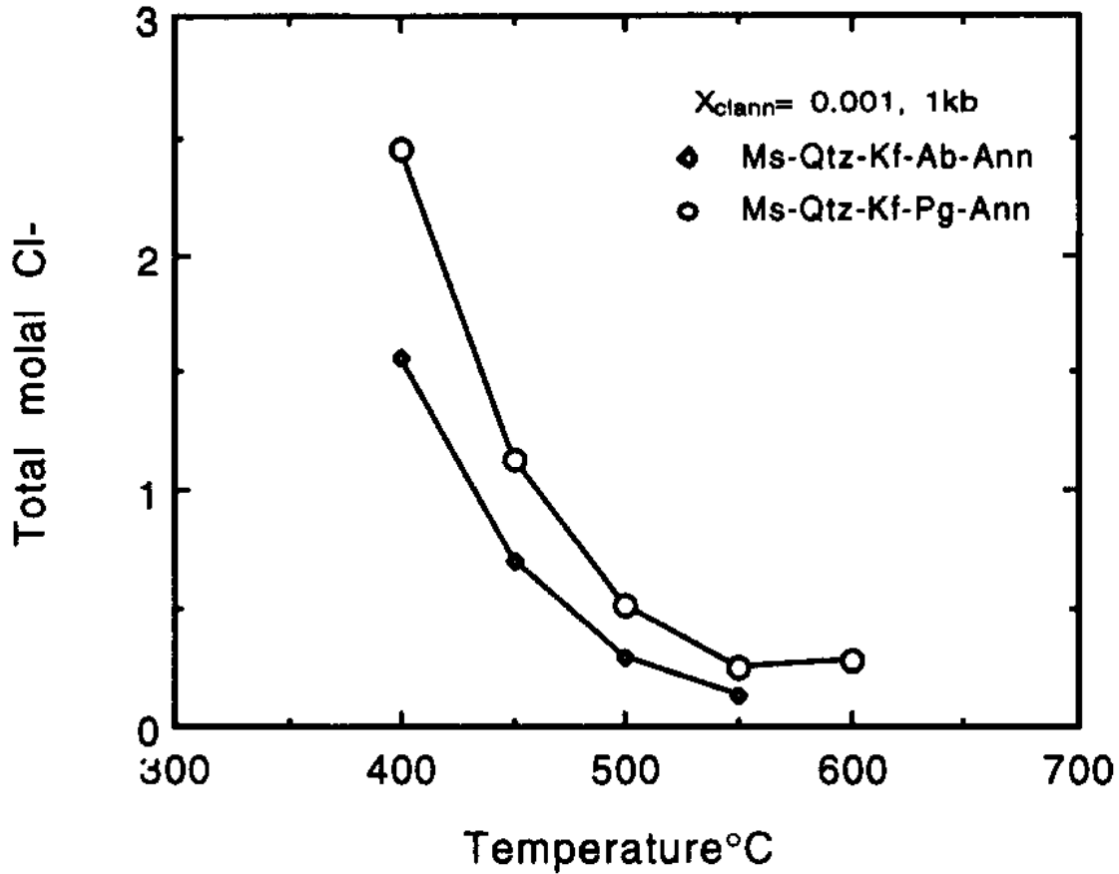
Zhu & Sverjensky (1991)

Strongly dependent on pH

Incompatible in most hydrous minerals

No data on serpentine

Cl in hydrous minerals

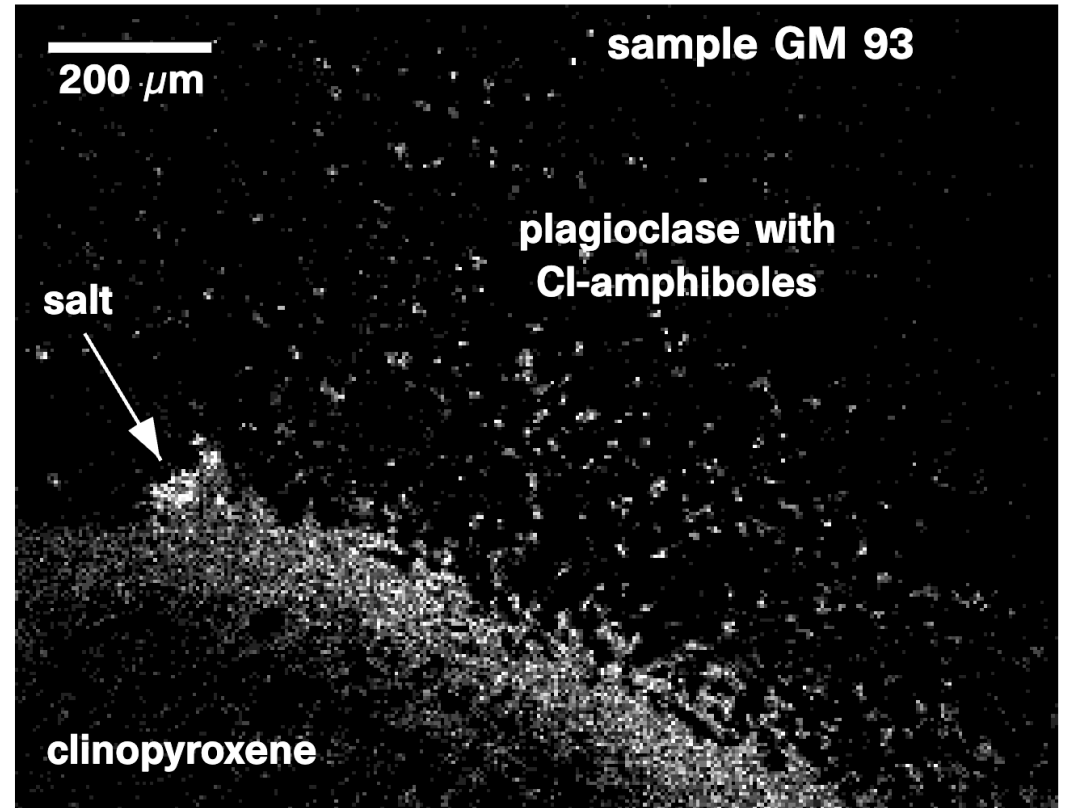


Zhu & Sverjensky (1991)

Strongly dependent on pH

Incompatible in most hydrous minerals

No data on serpentine

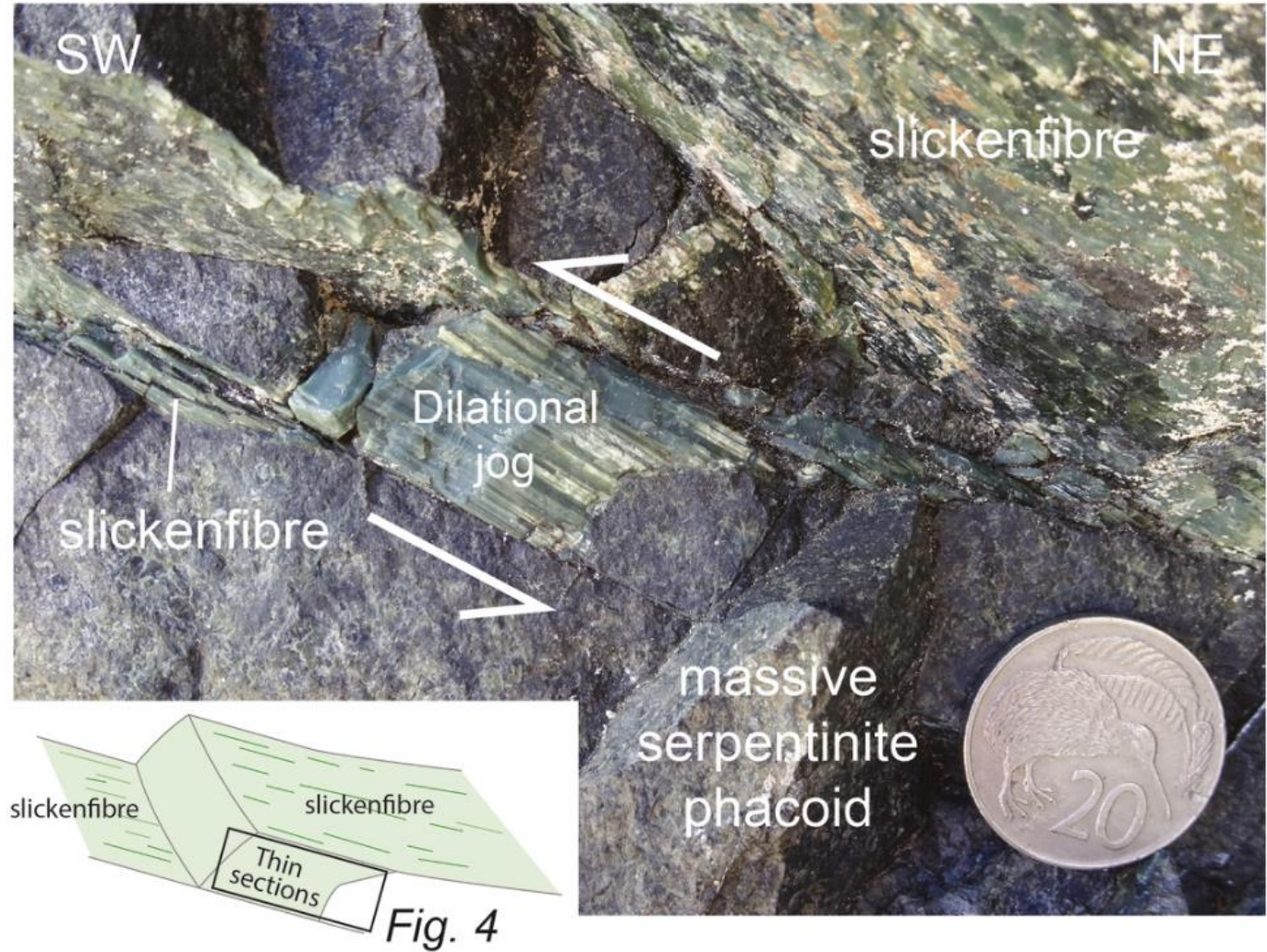
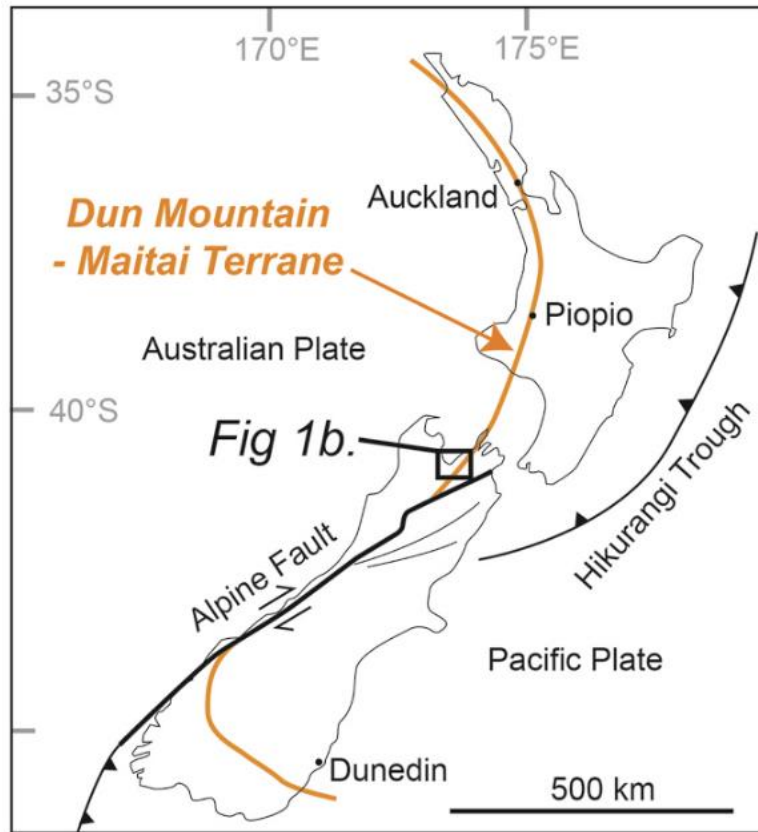


Cl-amphiboles with low Cl-content

Cl-amphiboles with high Cl-content

Markl & Bucher (1998)

Geological setting

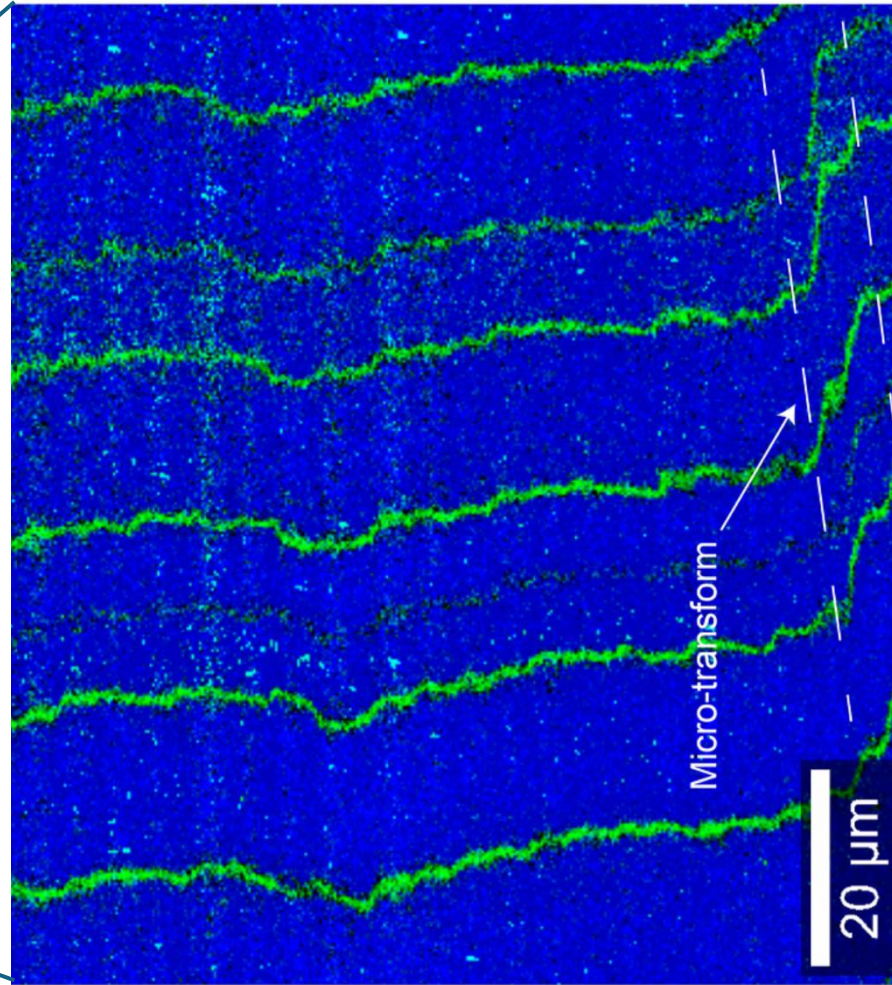


Smith et al. (2023)

Coupled dissolution/precipitation hard to study

Easier to look at precipitation only first

Serpentine jog



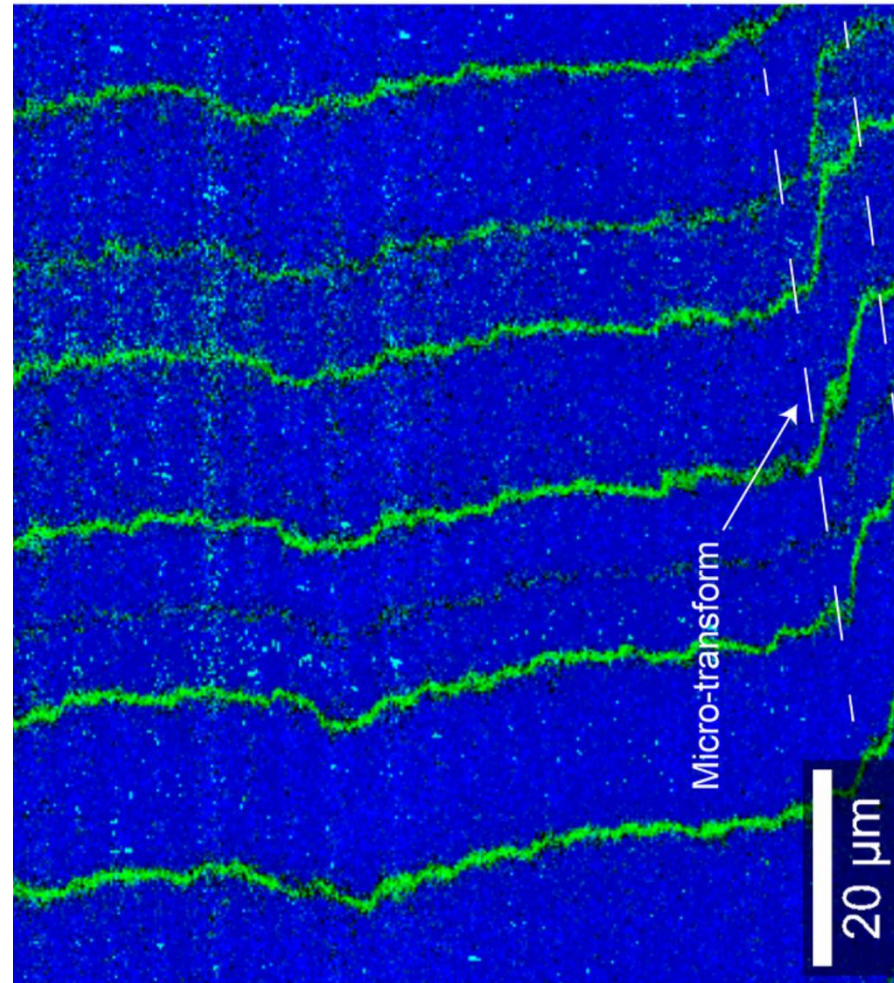
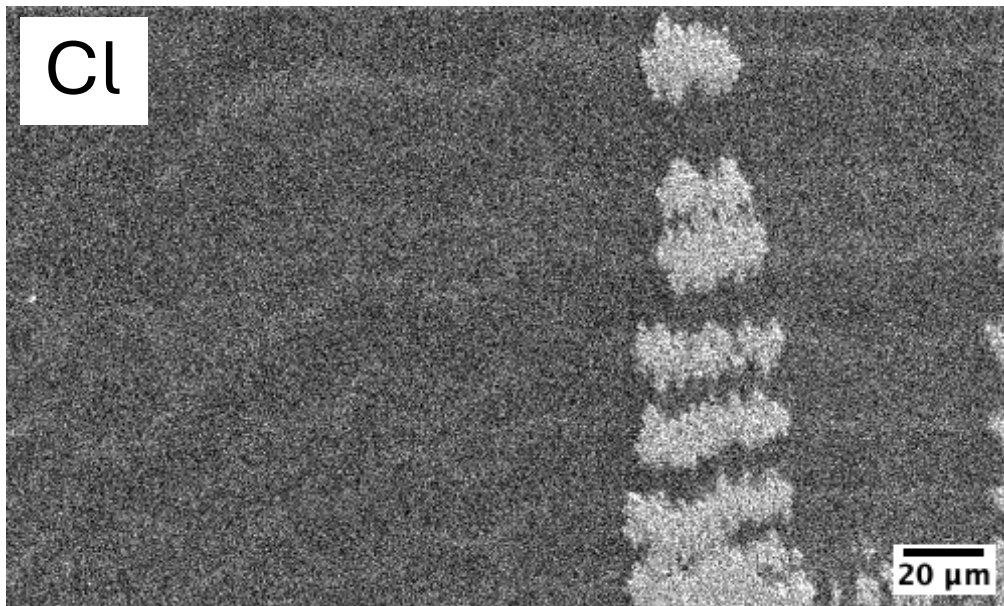
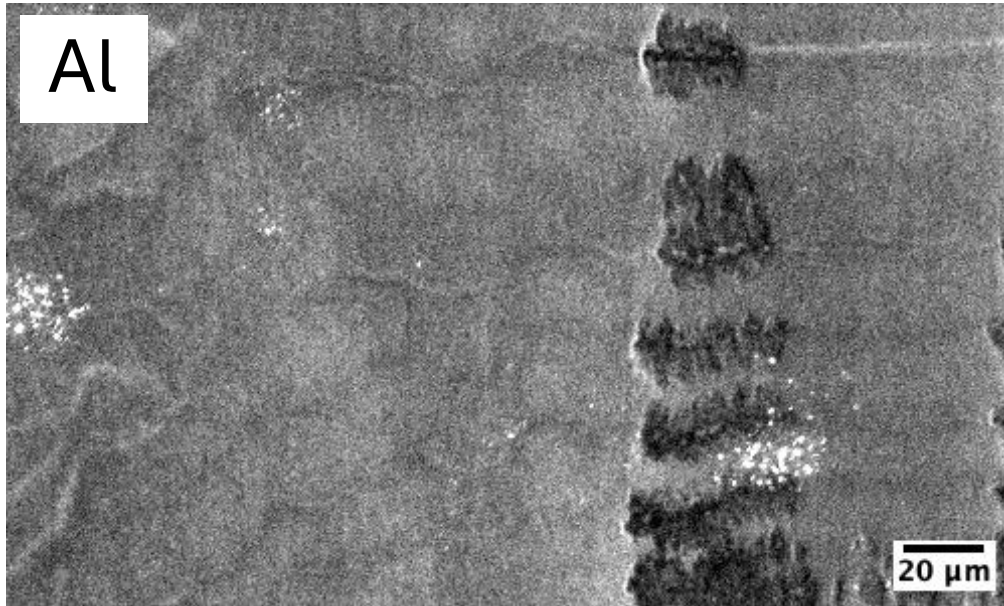
Smith et al. (2023)

Step 1: opening and fast cristalization of chrysotile (green)

Step 2: slow precipitation of lizardite (blue)

Repeat

Serpentine jog



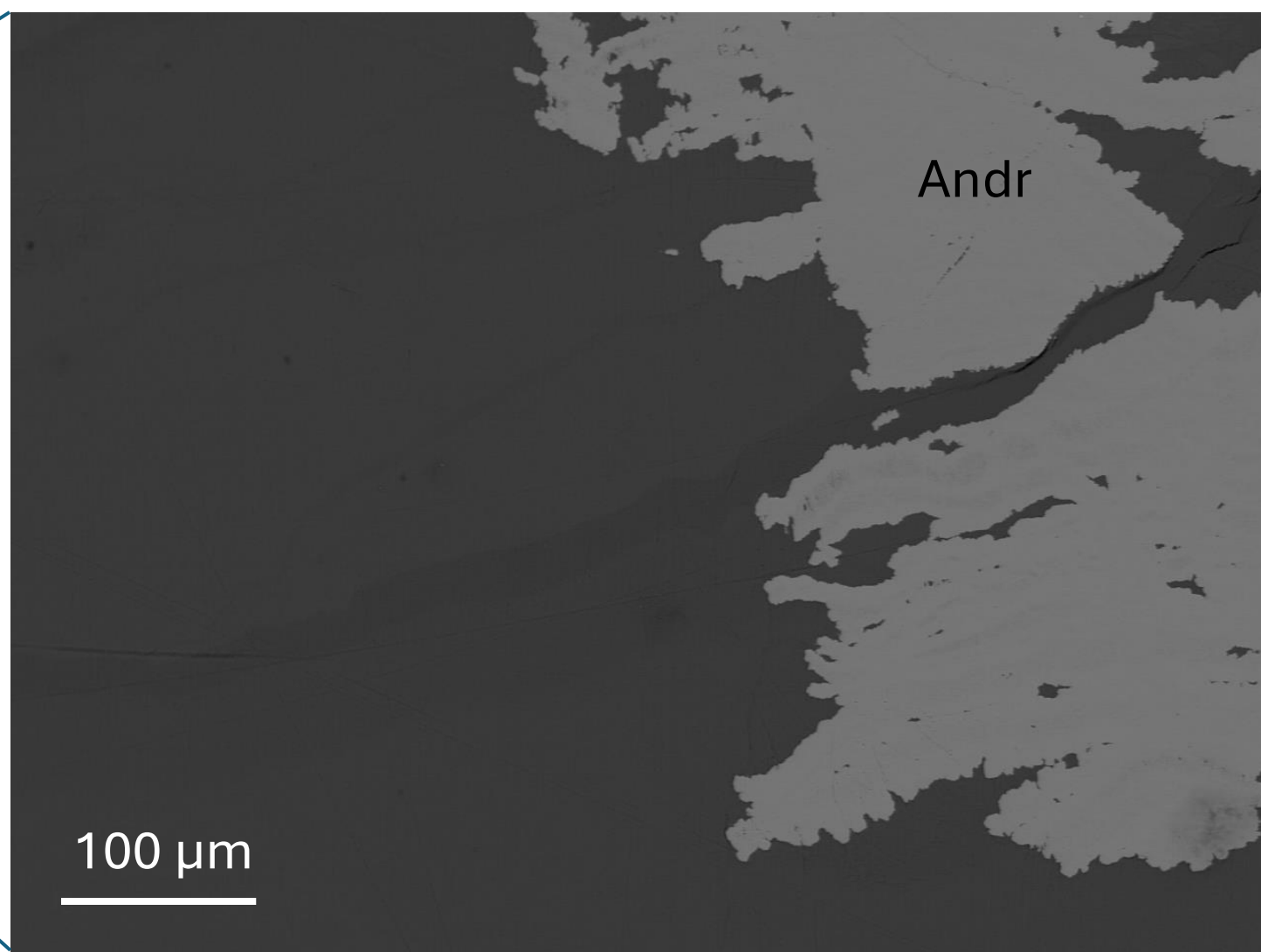
Smith et al. (2023)

Chrysotile: high Cl

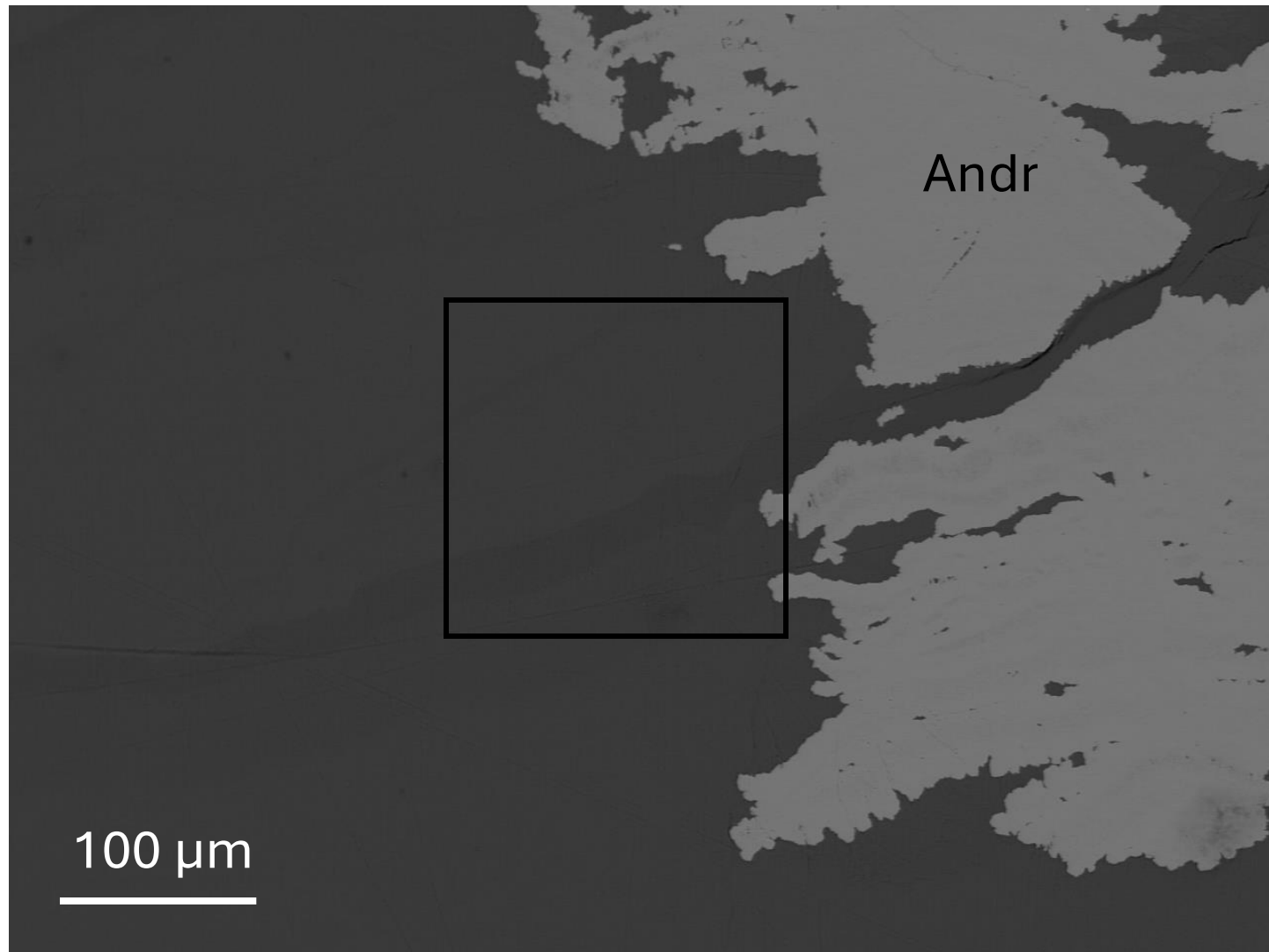
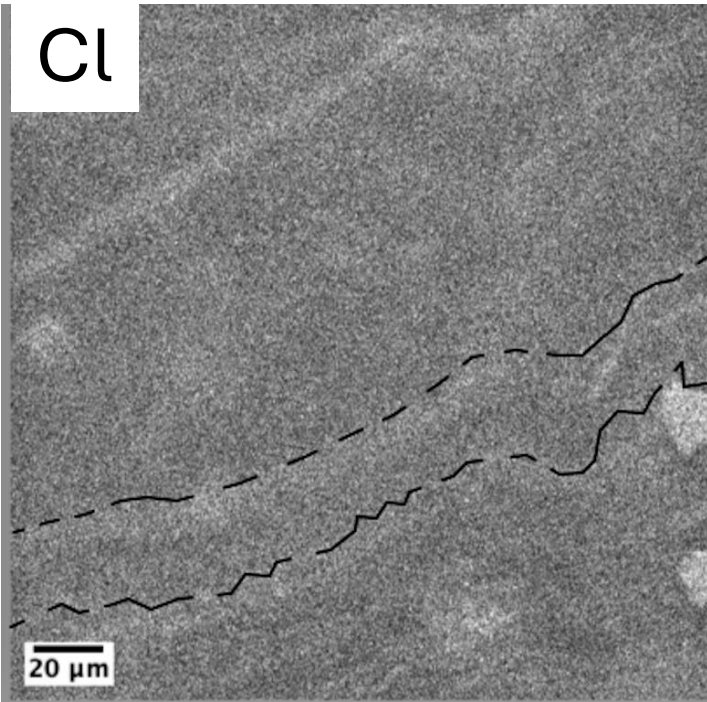
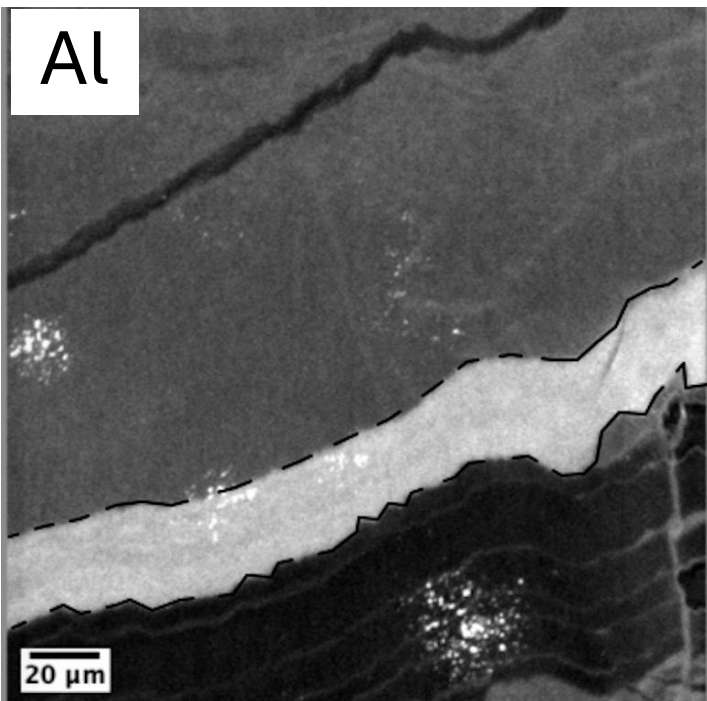
Lizardite: no enrichment in Cl

⇒ no desiccation process

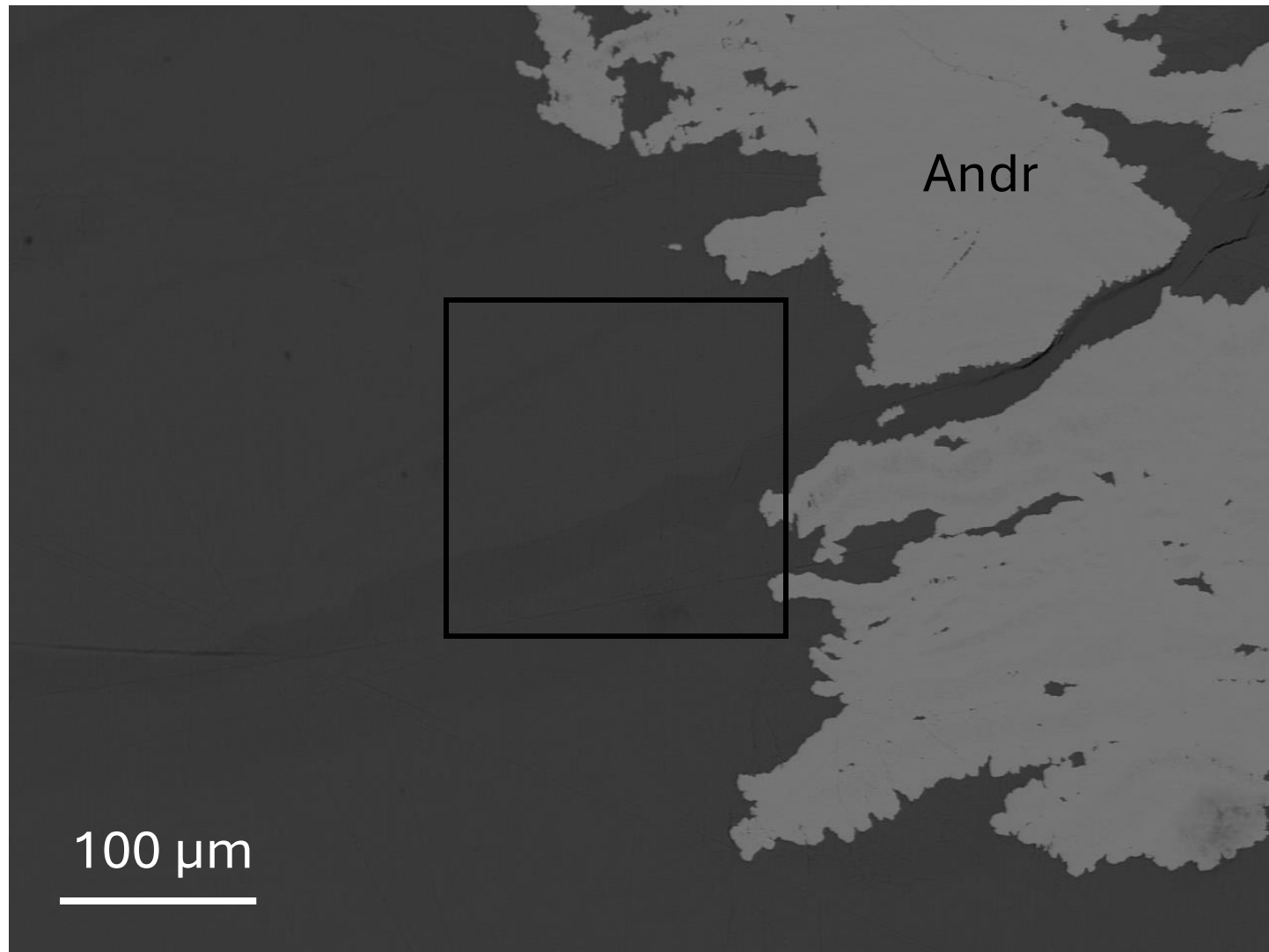
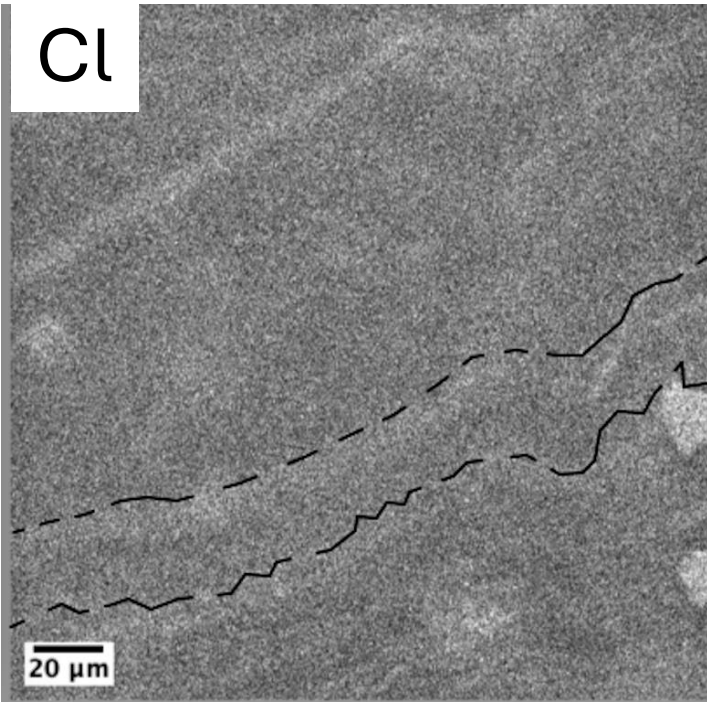
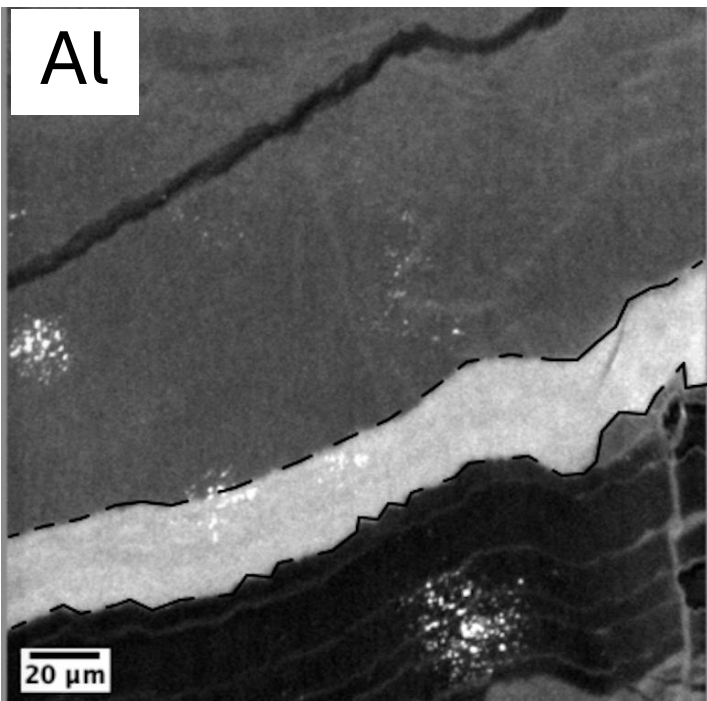
Last opening



How does the alternance begins?

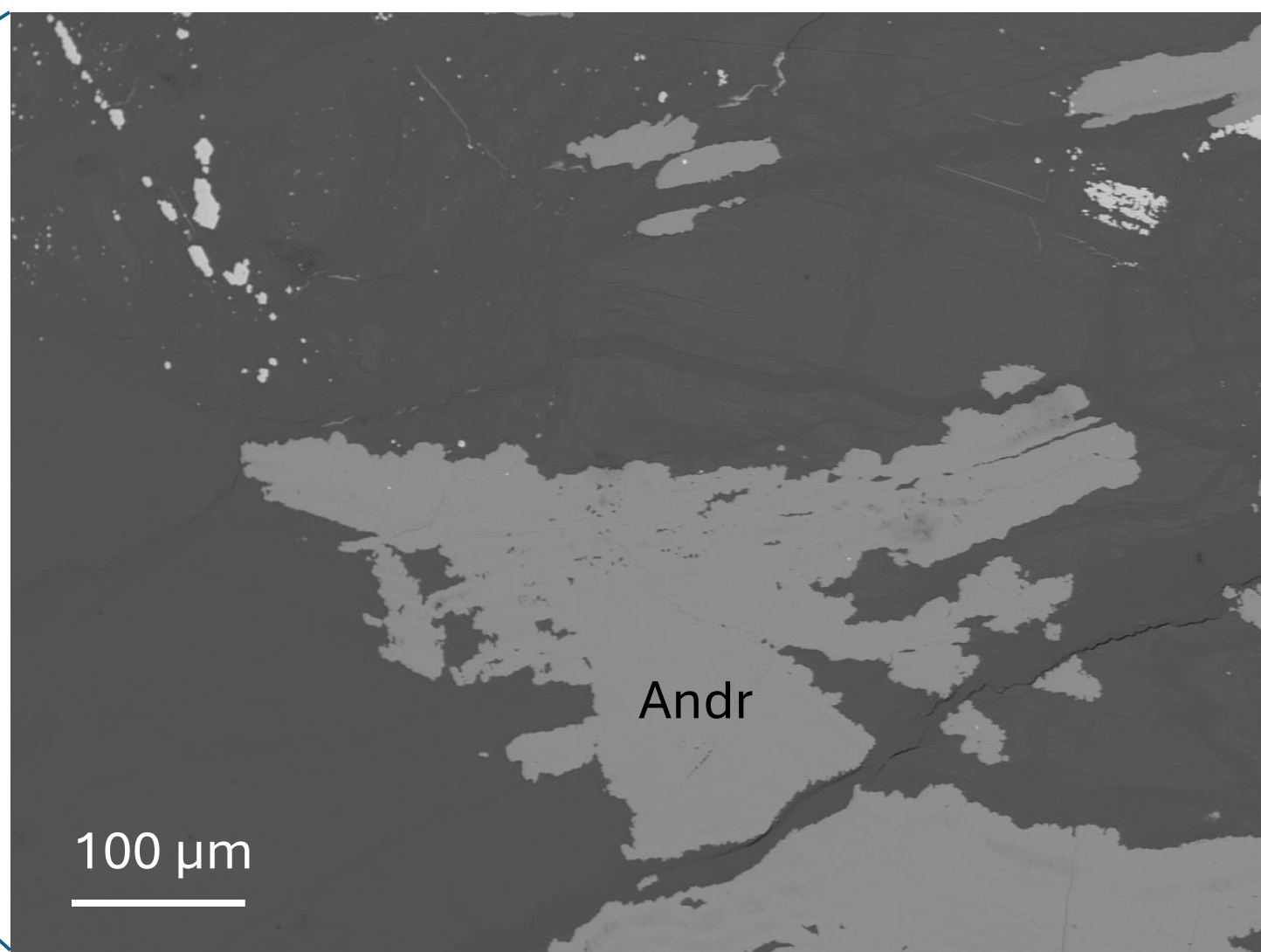


Large variations in trace elements between generations



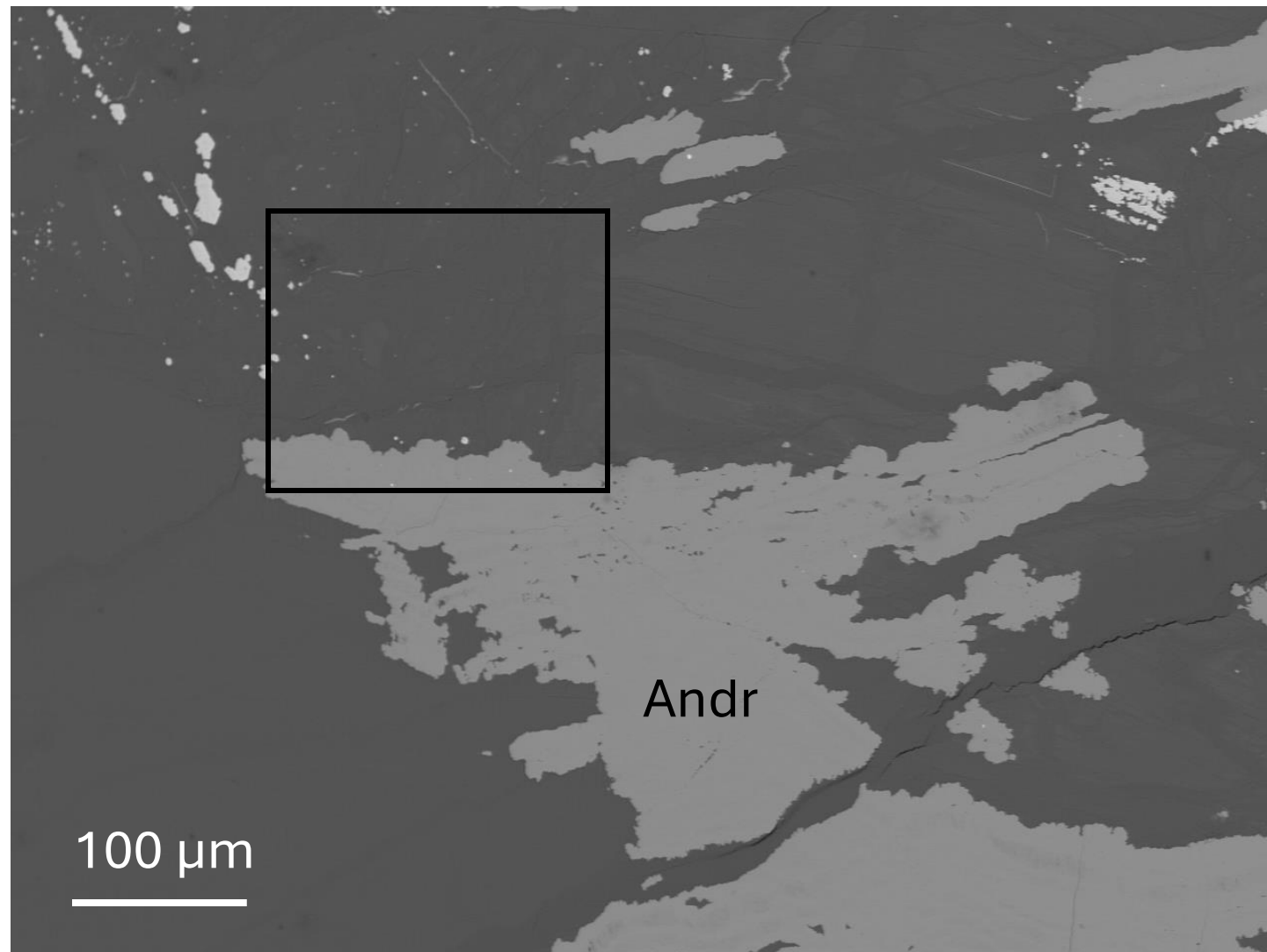
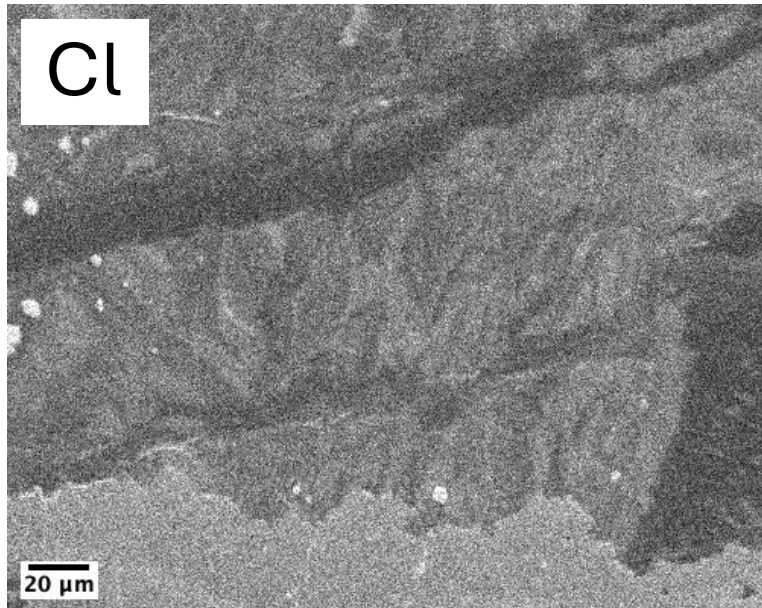
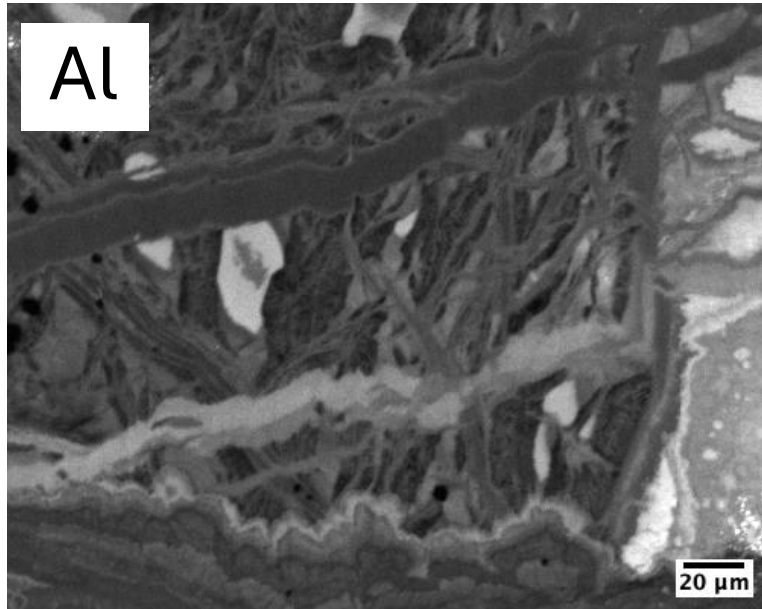
Large variations in trace elements between generations
Cl seems higher close to the bulk rock

Mesh serpentine



Can we see evolution in the mesh serpentine where several micro-fractures are filled?

Mesh serpentine



All micro-fractures filled with serpentine have different Cl contents

No clear trend, even for pseudomorphs

Take home message

- Initial peridotite composition is important
- The composition of the upper crust is likely going to affect the amount of H₂ produced at depth
- High Cl, carbonate rocks, such as evaporites, will significantly reduce the amount of H₂ produced
- The evolution of Cl incorporation in hydrous minerals, particularly serpentines, is largely unknown

Requires:

- **numerical models with accurate interactions of downgoing fluids with superficial rocks**
- **experiments to constrain the compatibility of Cl**

Thank you!

