Condensation-induced self-patterning of a thin claye layer

Jérôme Martin, Frédéric Doumenc

Origin of vermiculations in caves ?

"Vermiculations are thin, irregular and discontinuous deposits of incoherent materials commonly found on the walls of caves and external surfaces and are a few centimetres in extents." *(Bini et al, Int. J. Speleol., 1978)*

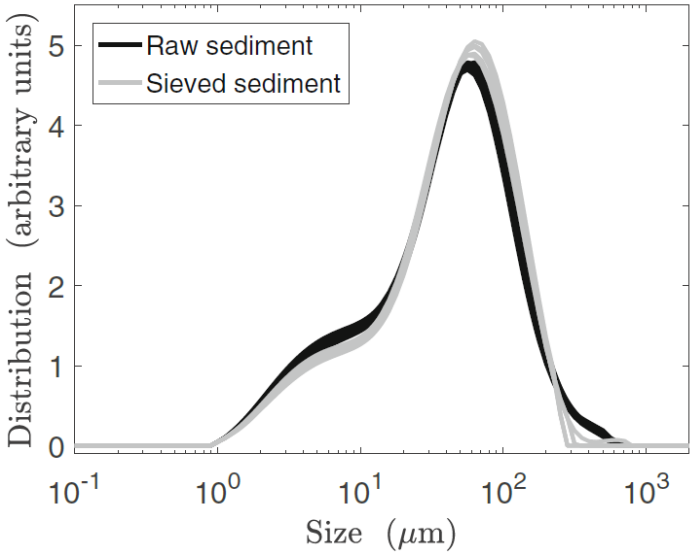
- Formation or evolution during « crisis ».
- Presence of water is a necessary condition.
- Effect of evaporation/condensation ?

Can we reproduce this natural phenomenon in lab experiments ?

Test material

Natural cave sediments collected in a cave in Dordogne (France)

Granulometry: **high polydispersity**



Mineralogical and chemical composition

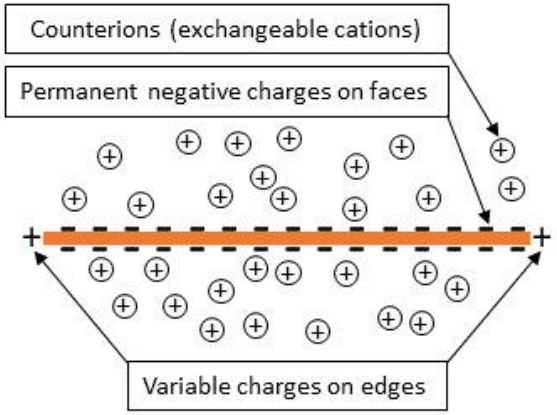
- Quartz (SiO_2)
- Calcium carbonate ($CaCO_3$)
- Metallic oxides
- Organic matter
- …
- Fine fraction: **smectite clay**

→ **Yield stress fluid**

Macroscopic particles bound by a smectite gel

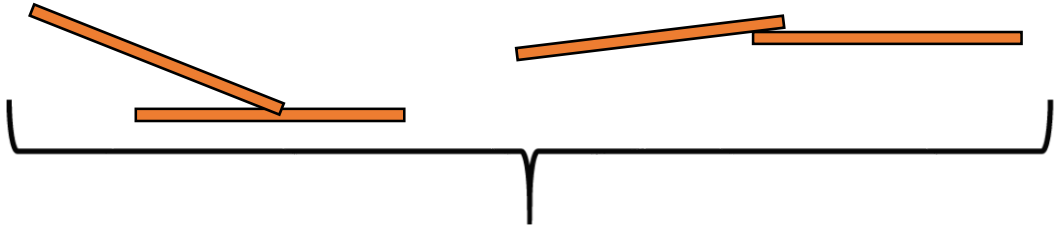
Smectite phase diagram

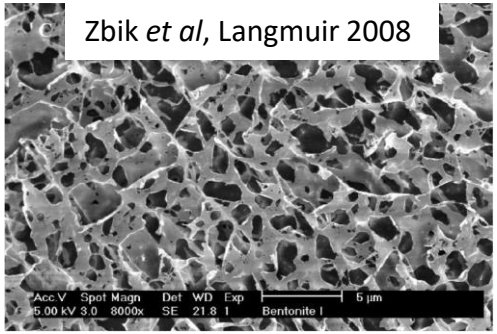
Smectite particle



Edge-face bounds

Edge-edge bounds





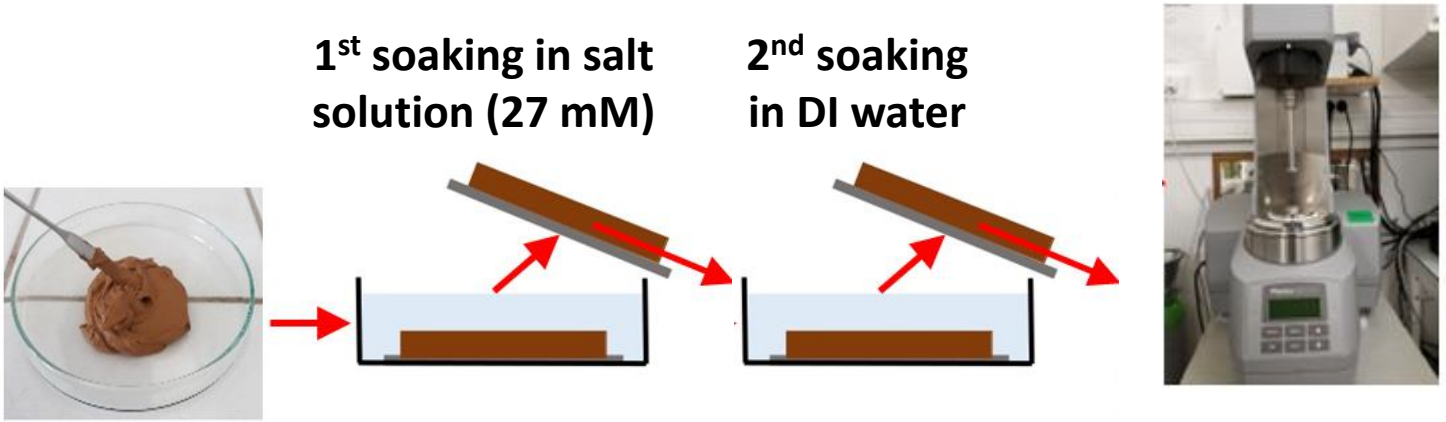
Gel phase

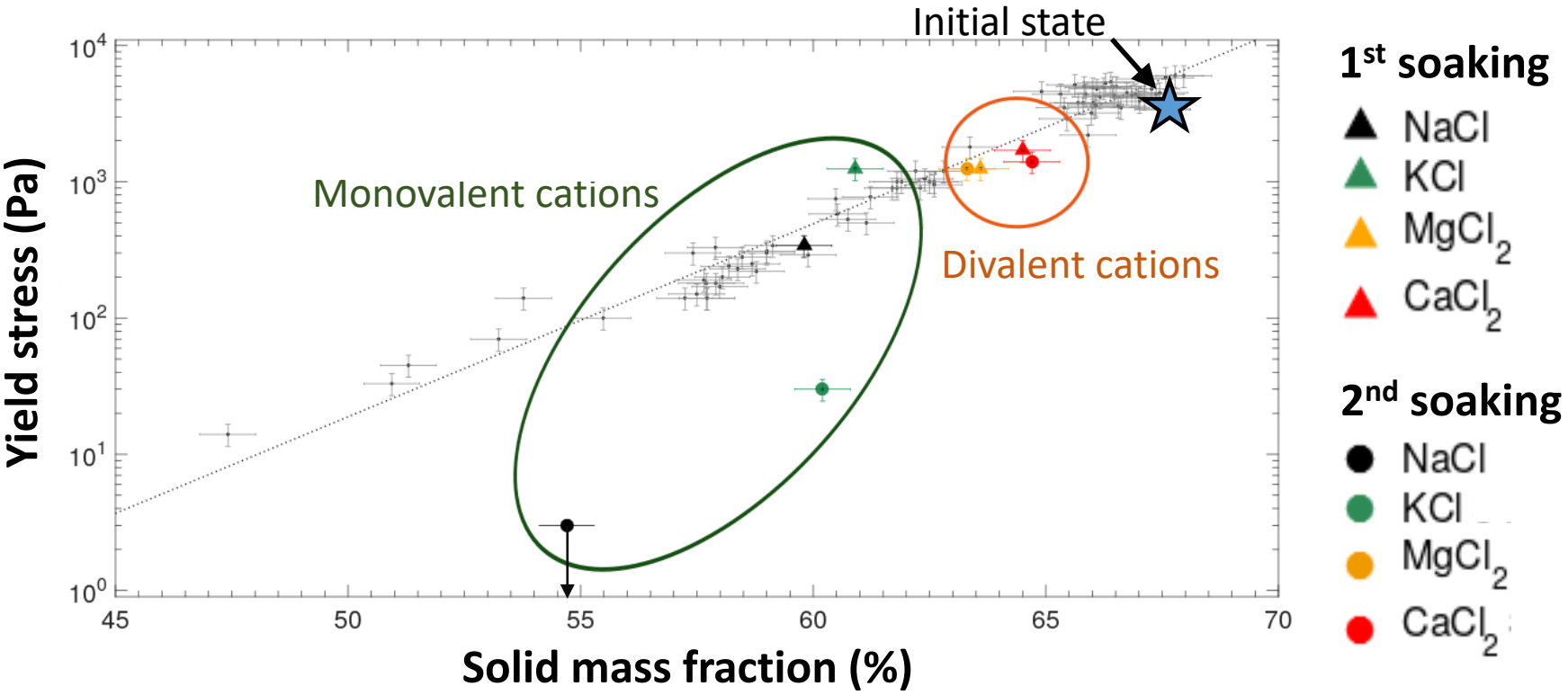
The phase diagram of smectites depends on the counterion valence

- **Monovalent counterions** => gel-sol transition at low ionic strength
- **Multivalent counterions** => gel phase even in DI water

Rheological behavior of cave sediment

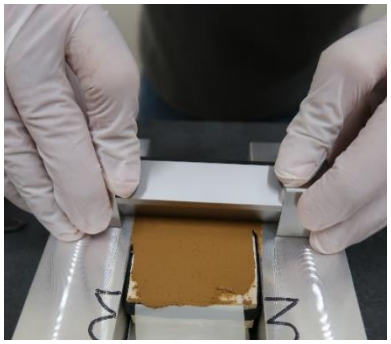
(Freydier et al, Rheologica Acta 2019)



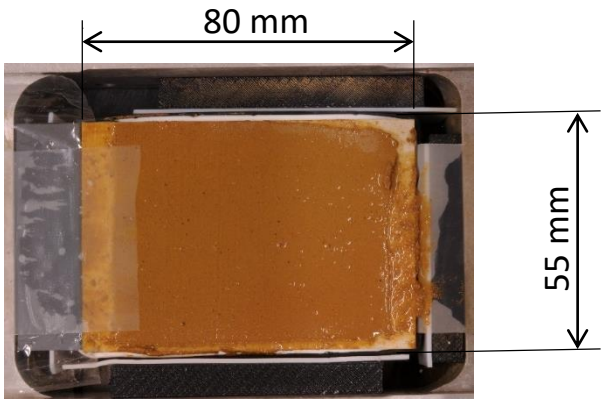


Experimental set-up

(J.Martin and F.Doumenc, EPL 2022)



150 µm-thick sediment layer coated on a limestone rock



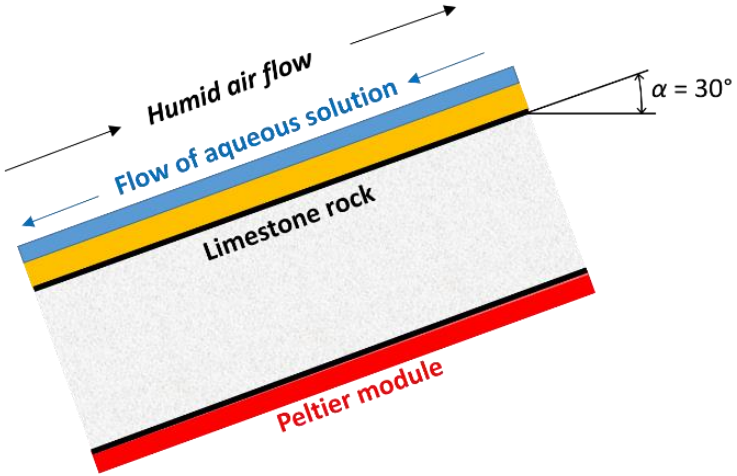
Two-step experiments

<u>Step 1:</u> flow of aqueous solution (3 hours)

- saturated with $CaCO_3$

OR

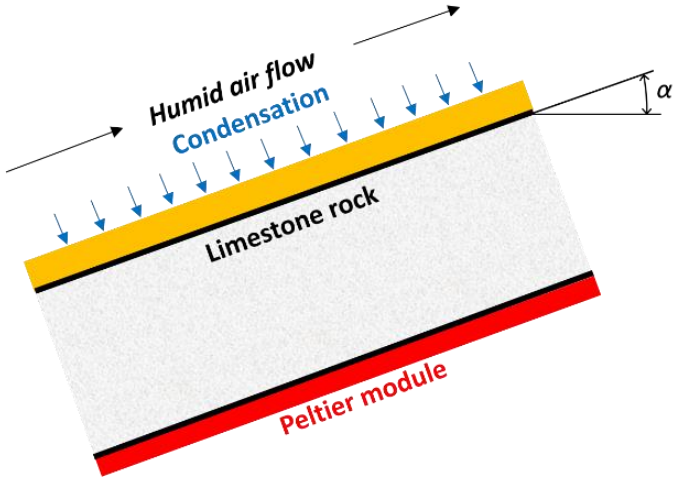
- saturated with $CaCO_3$ + 20 mmol/L NaCl



<u>Step 2:</u> condensation

Limestone rock cooled with Peltier modules

Condensation flux $\propto (T_{air} - T_{rock})$



Effect of solution composition during step 1

Solution saturated with $CaCO_3$ during step 1 **(no NaCl)**

Initial state

After step1
(3 hours)

After step 2
(24 hours)
$\Delta T \approx 10°C$

No NaCl during step 1 => No self-patterning

Step 1

- **solution saturated with $CaCO_3$ + 20 mmol/L NaCl**
- **duration: 3 hours**

Initial state

After 3 hours

Step 2

- **condensation:** $\Delta T = (T_{air} - T_{rock}) \approx 3°C$
- **tilt angle: 85°**
- **duration: 5 hours**

Initial state

Condensation

Effect of condensation rate and tilt angle

Solution saturated with $CaCO_3$ + **20 mmol/L NaCl** during step 1

Pattern at the end of the experiment

Tilt angle: 85°

$\Delta T \approx 3°C$

Tilt angle: 30°

$\Delta T \approx 0.3°C$

$\Delta T \approx 1°C$

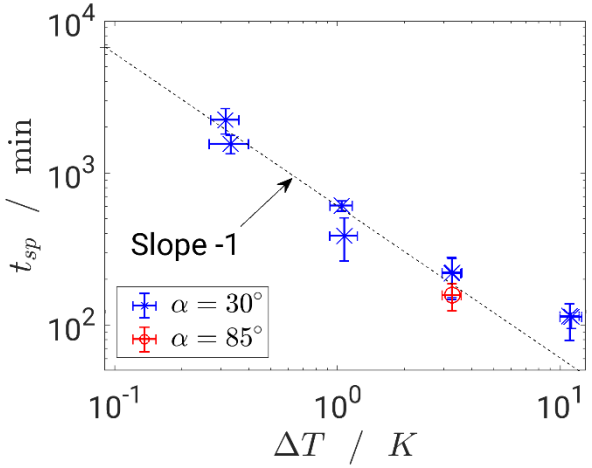
$\Delta T \approx 3°C$

$\Delta T \approx 10°C$

Time required to initiate self-patterning ?

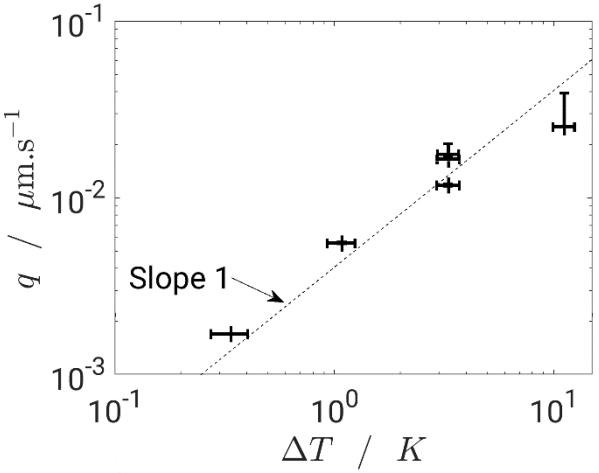
(Step 1: solution saturated with $CaCO_3$ + **20 mmol/L NaCl**)

t_{sp}: time at the onset of self-patterning



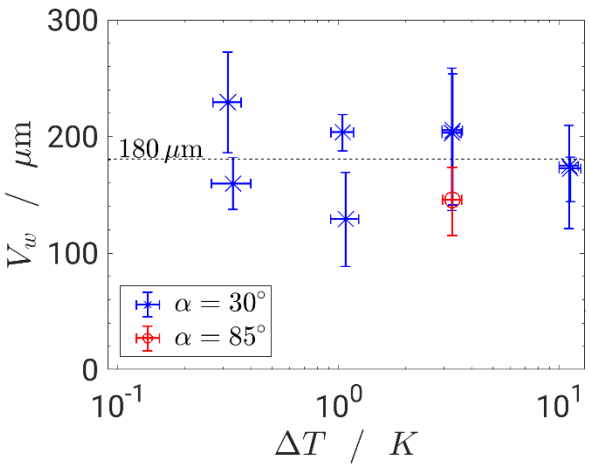
$t_{sp} \propto \Delta T^{-1}$

q: condensation rate



$q \propto \Delta T$

V_w: volume of condensed water per unit of surface



$V_w = q\ t_{sp} \approx 180$ µm

The sediment starts to flow for a constant volume of condensed water

***V_w*=water volume required to dilute NaCl in the pore liquid of the sediment and trigger the gel-sol transition of smectites**

Conclusion

Potential scenario for vermiculations crisis in painted caves of Dordogne:

Most of the time, smectite counterion is Ca^{2+} (limestone massif).
1- rise in concentration of monovalent cations (evaporation ? microbiological activity ?)
2- intake of low-mineralized water (condensation ?)

Other scenarii connected to smectite properties:
- Increase of pH.
- Rise in concentration of multivalent anions ?

Future works

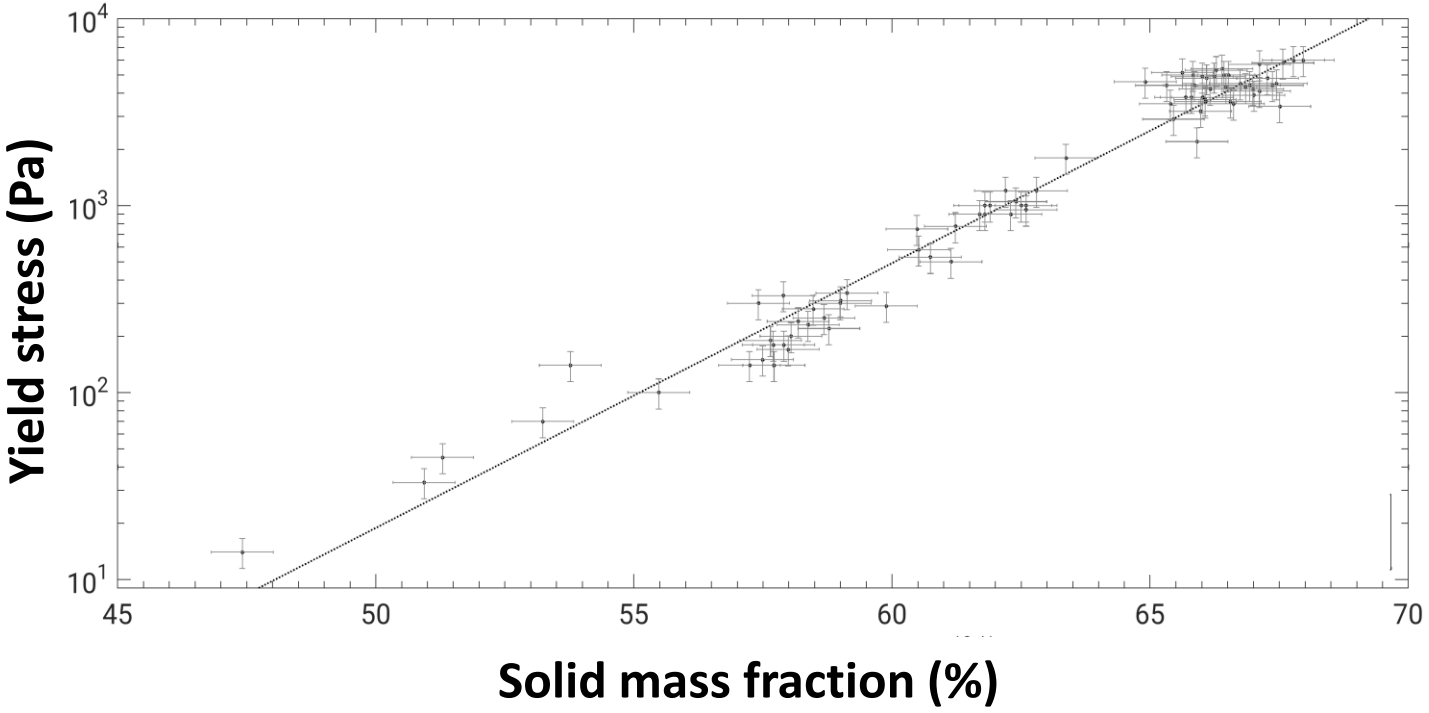
Field investigations of the chemical composition of thin water films on cave walls (poorly known)

Connection with the microbiological activity ?

Appendix

Rheological behavior of cave sediment

(Freydier et al, Rheologica Acta 2019)



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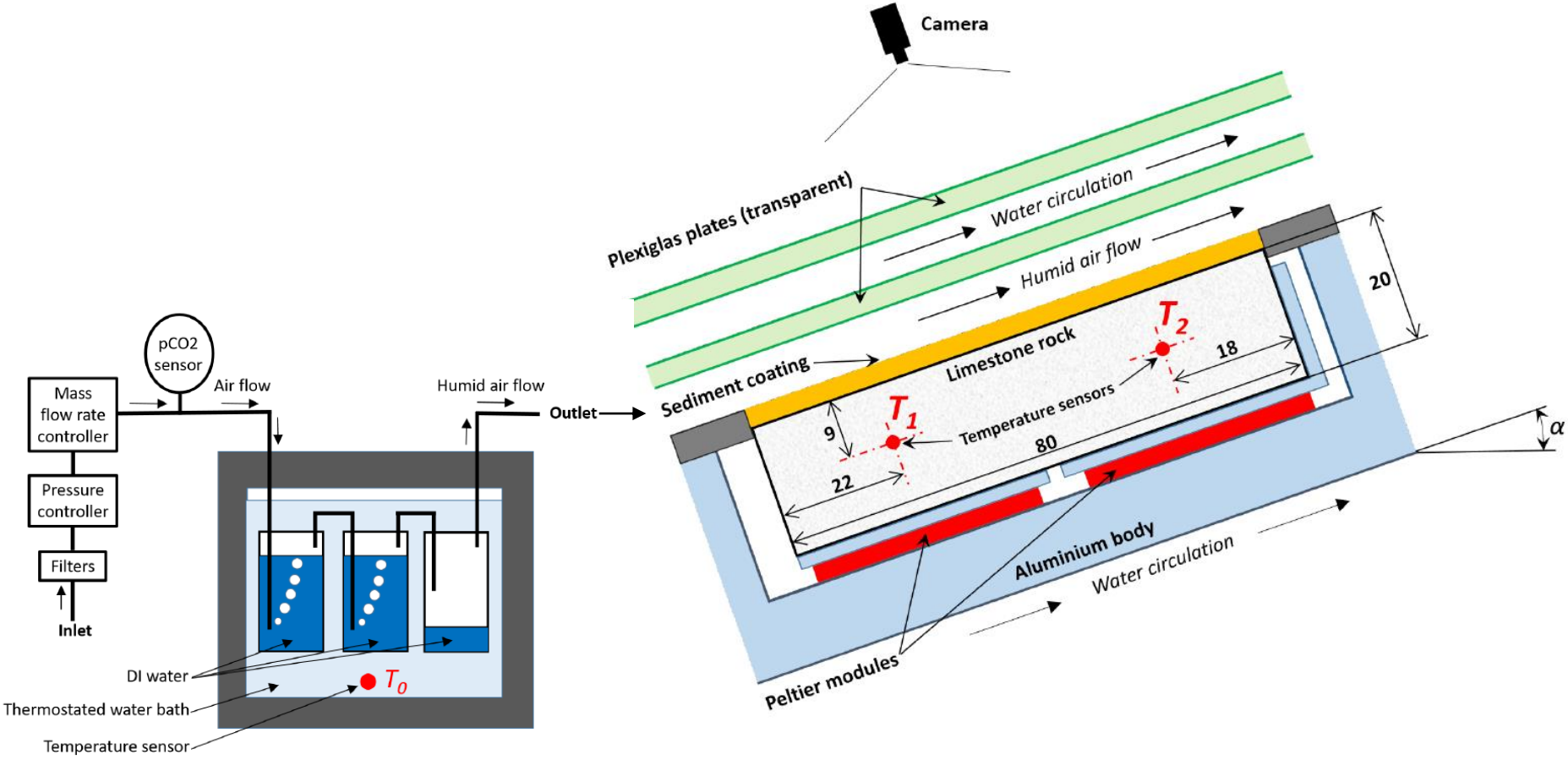

$$\Delta T = T_0 - \frac{T_1 + T_2}{2}$$