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Use of trace elements to distinguish flows from different types of carbonated rocks

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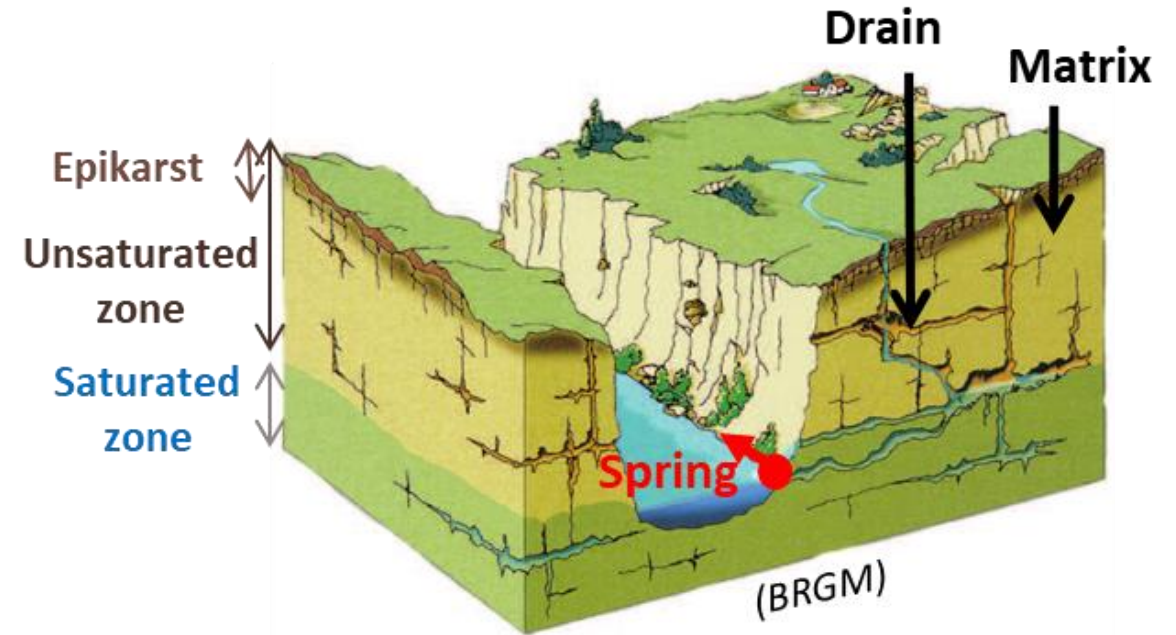
Karst : a valuable but complex water resource

Karst water resource *(Stevanović, 2019)*

- 9.2% of the world's drinking water
- 13% of the total global withdrawal of groundwater

Karst specificities

- Heterogeneous and compartmentalized systems
- Dual flows (fast/slow)
- Vulnerability associated to fast flow



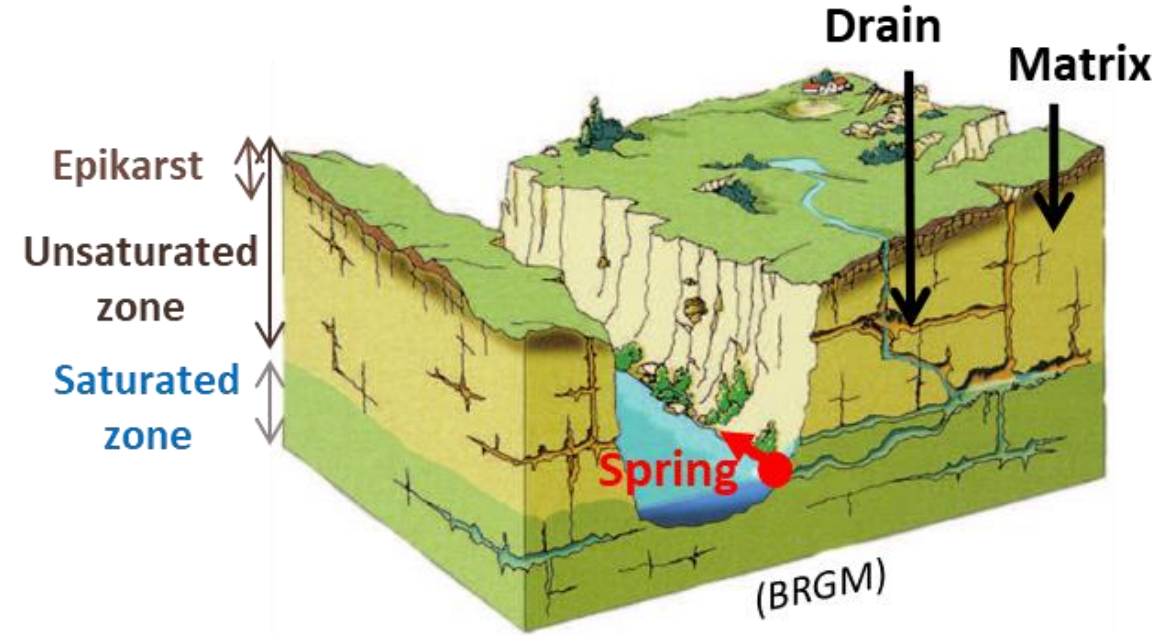
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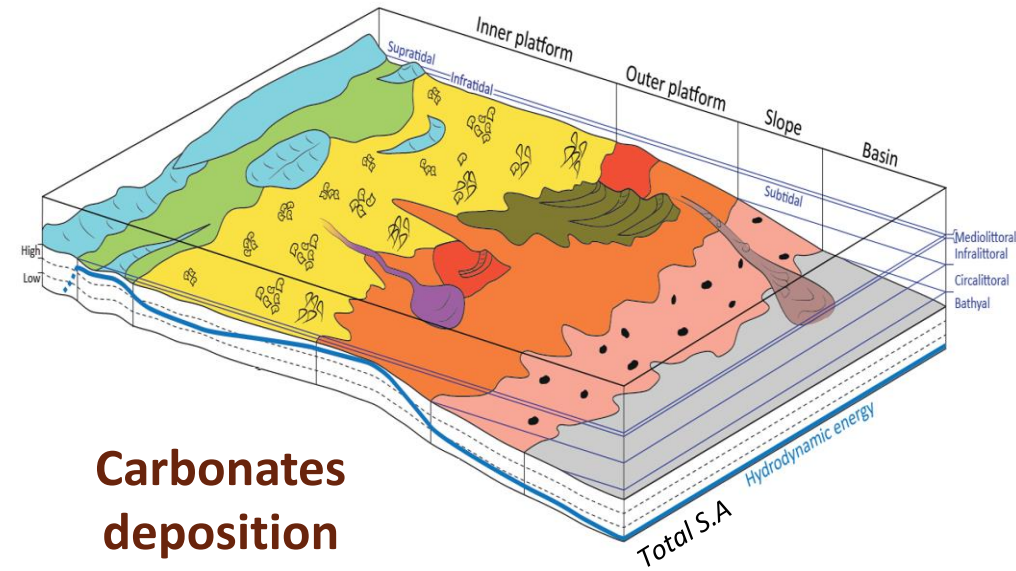
Karst specificities

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- Dual flows (fast/slow)
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Why is karst such a complex media?

From carbonated platform to karst aquifer

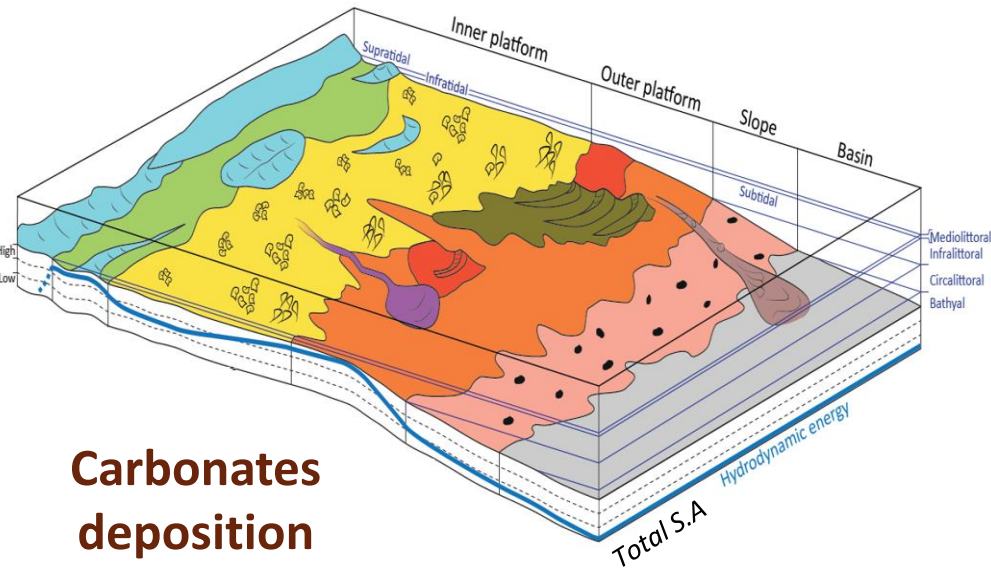


**Carbonates
deposition**

Variability of carbonate
sediments

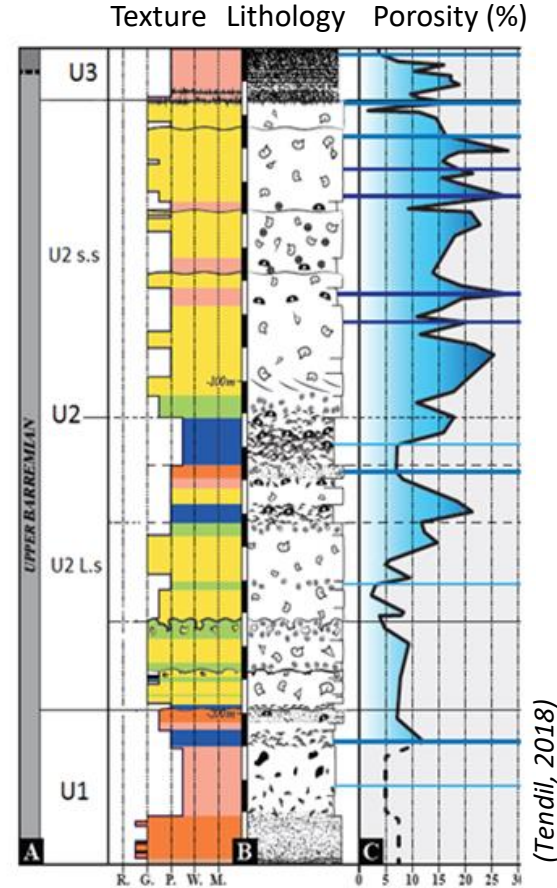
From carbonated platform to karst aquifer

Diagenesis



Carbonates deposition

Variability of carbonate sediments

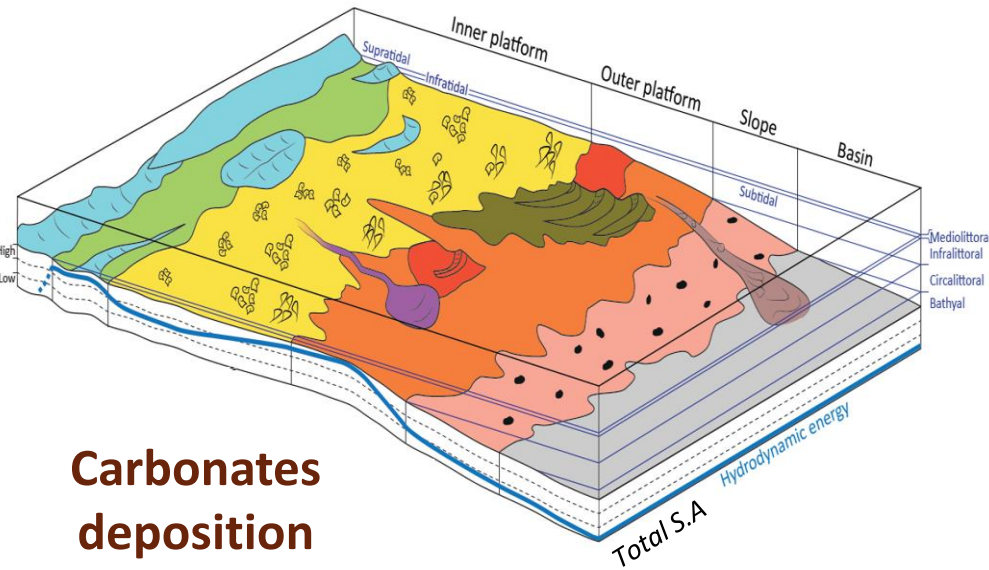


Diagenetic variability

From carbonated platform to karst aquifer

Karstification

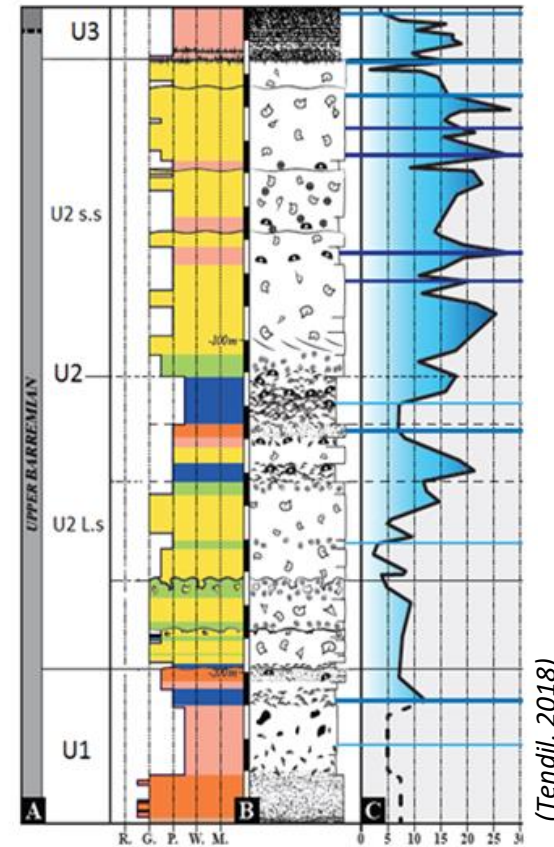
Diagenesis



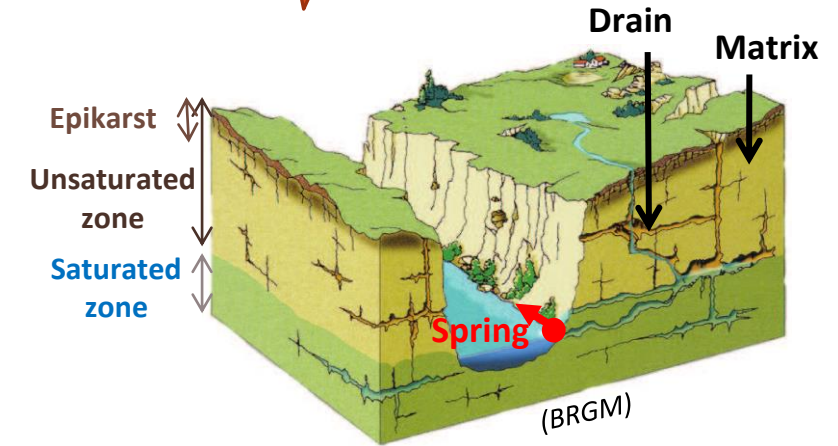
Carbonates deposition

Variability of carbonate sediments

Texture Lithology Porosity (%)

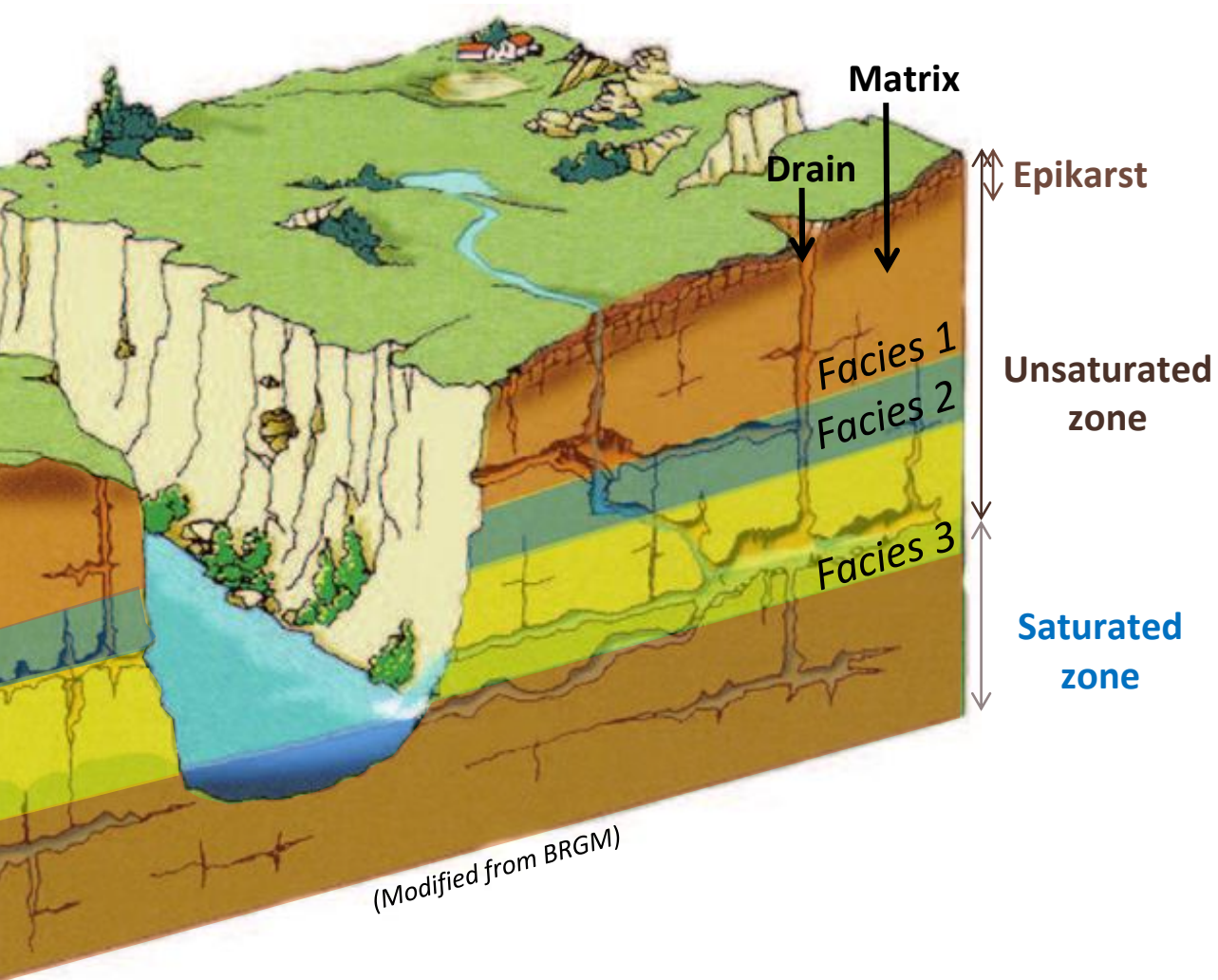


Diagenetic variability

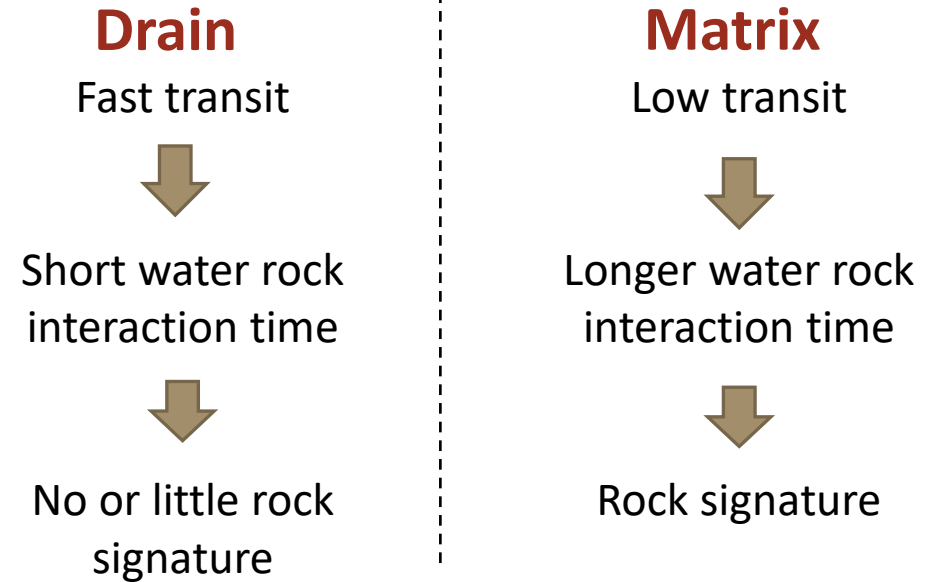


Hydrodynamic and hydrochemical variability of flows in unsaturated zone

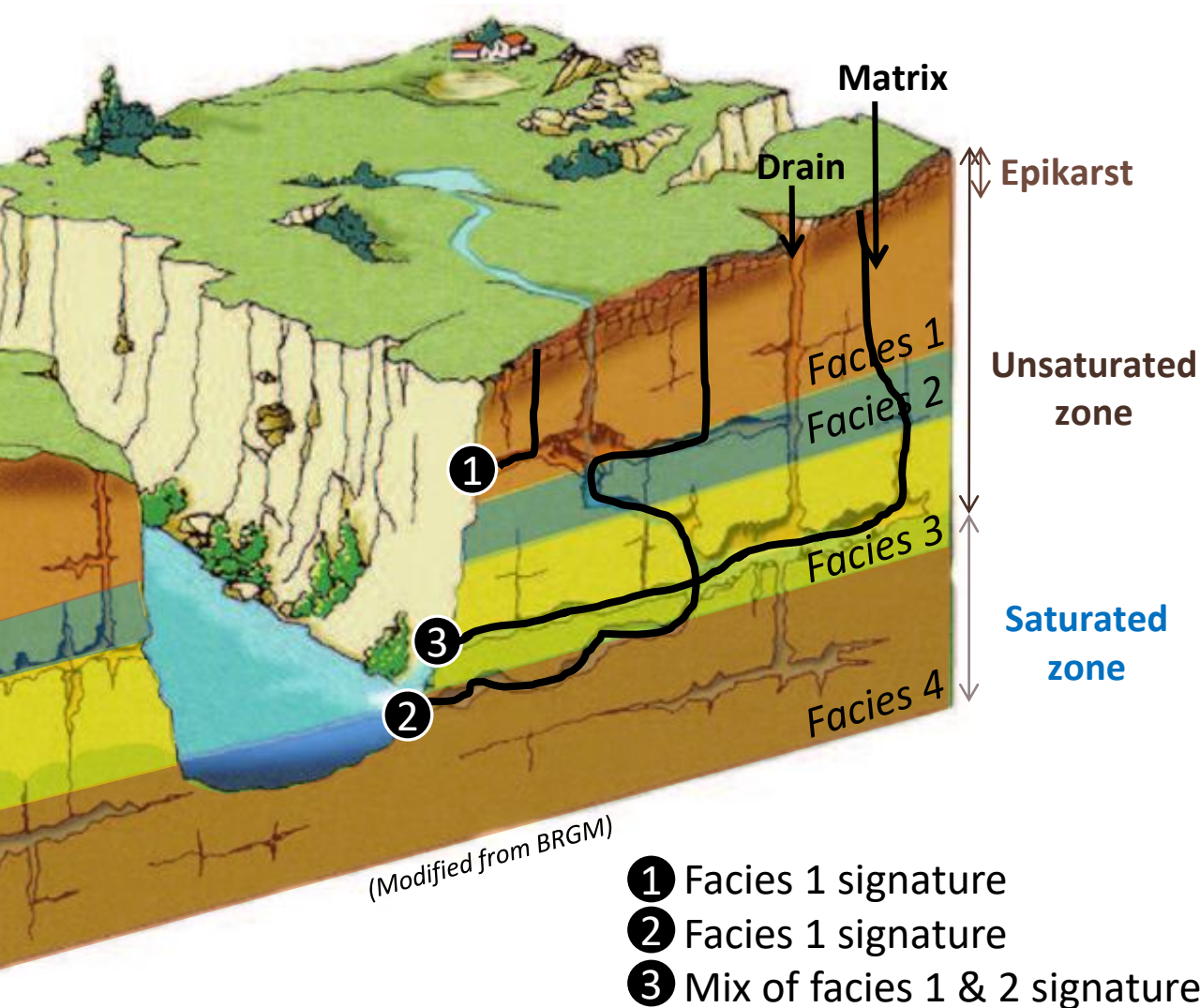
Aim of the study



Path taken by water



Aim of the study



Path taken by water

Drain

Fast transit



Short water rock
interaction time



No or little rock
signature

Matrix

Low transit

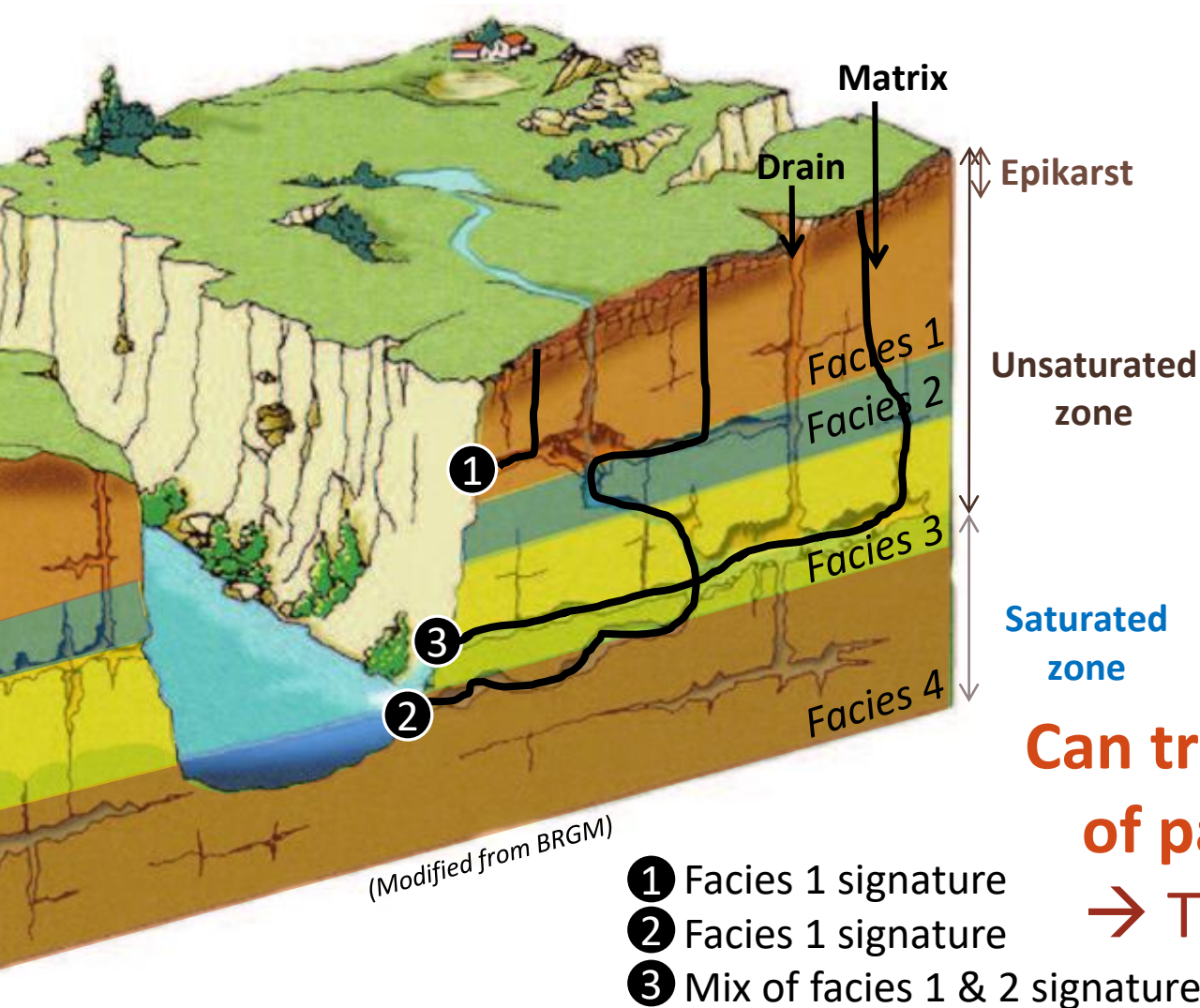


Longer water rock
interaction time

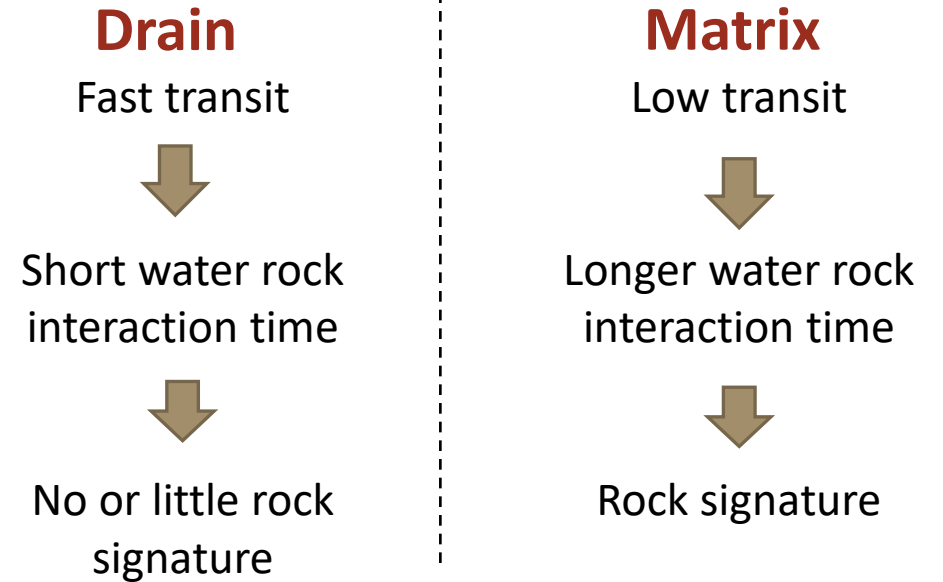


Rock signature

Aim of the study



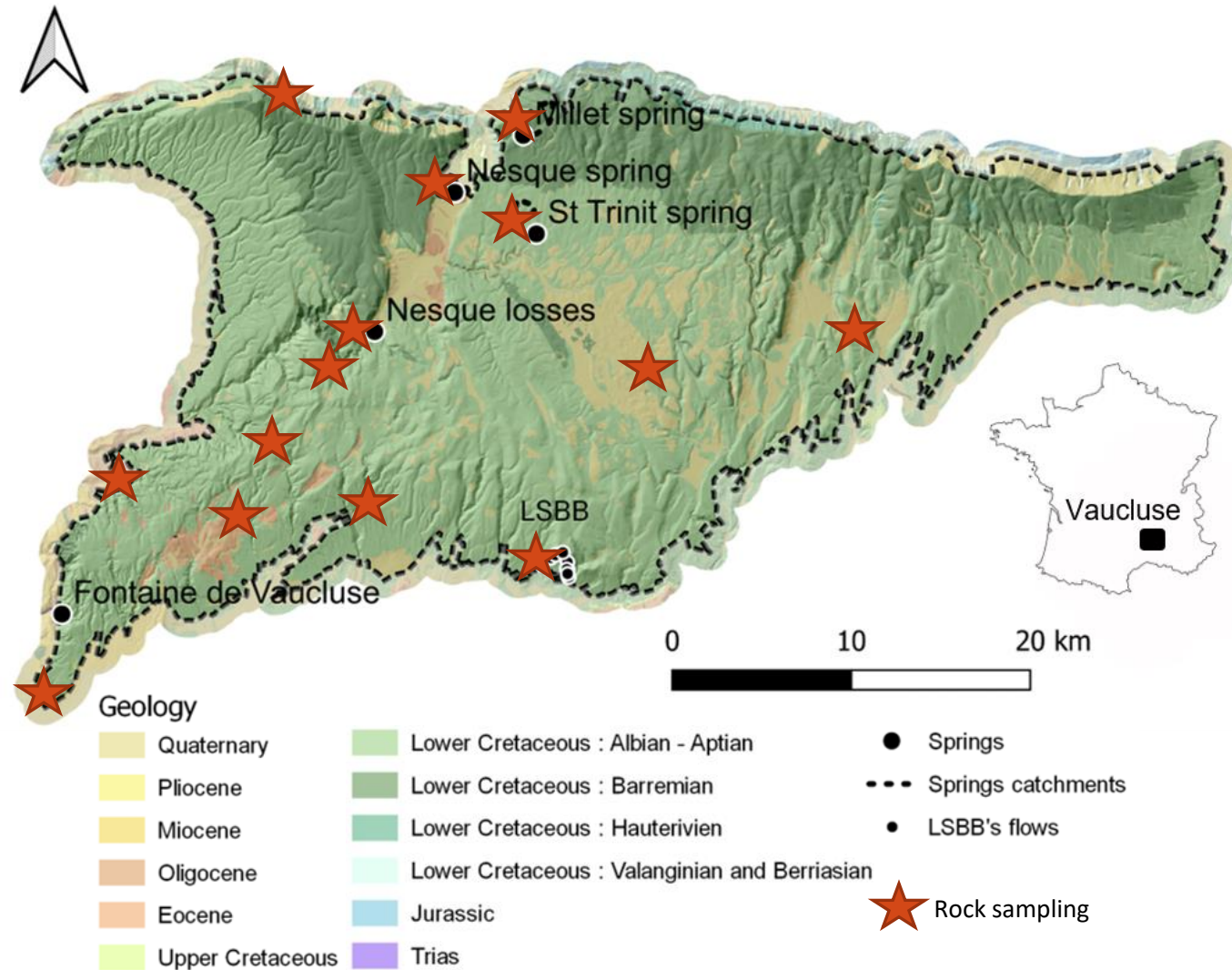
Path taken by water



Can trace elements be used as a natural tracer of path taken by water into karst systems?

→ Trace elements variations in karst rocks?

Study site & sampling



Fontaine de Vaucluse karstic system

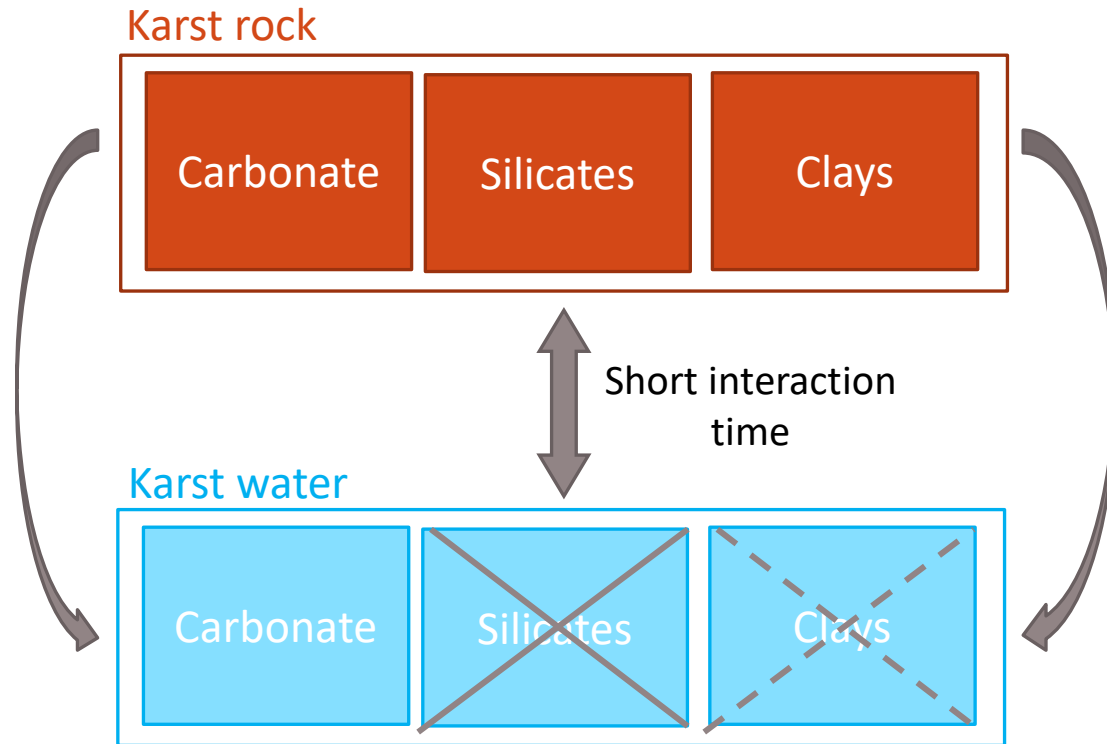
- Catchment of 1160 km² *Ollivier, 2020*
- Aquifer thickness up to 1500m
- Unsaturated zone average thickness 800m

Rock sampling

- 108 limestone samples
→ Representatives facies (several replicates)

Rock analysis

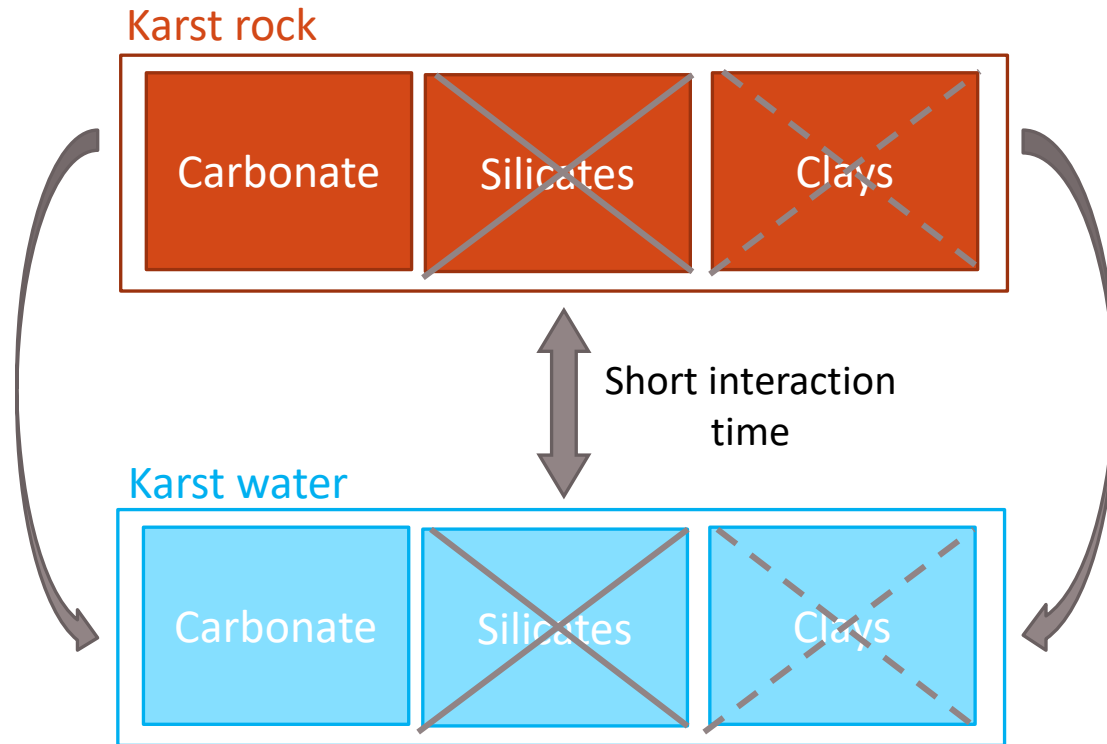
How to get a trace signal in the rocks that will be comparable to the signal in the water?



Water-rock interaction

- Fast reacting system = short storage duration (few years max)
- Not enough time to dissolve silicates (thousands years *Shand et al., 2007*)
- Clays have large water-rock interaction surface
- Major impact of carbonate dissolution

Rock analysis



How to get a trace signal in the rocks that will be comparable to the signal in the water?

Water-rock interaction

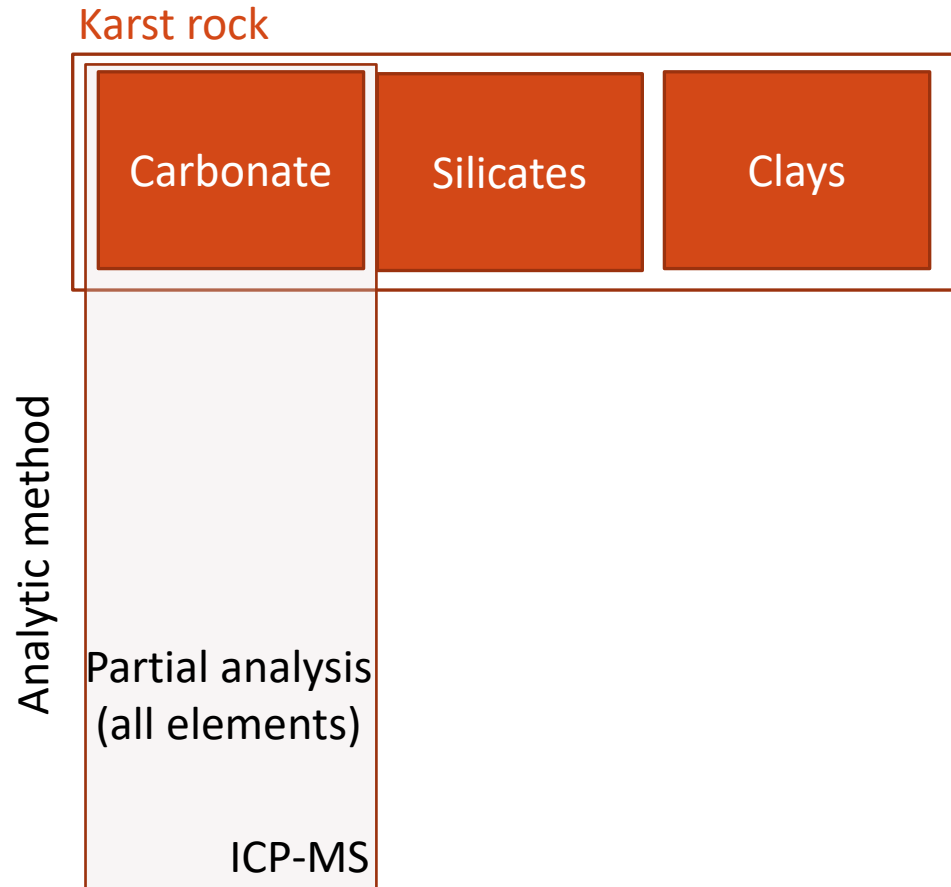
- Fast reacting system = short storage duration (few years max)
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- Major impact of carbonate dissolution

Trace elements in rocks

- Carbonate has low trace element content in comparison with silicates (*Shand et al., 2007*)
- carbonate signal may be hidden by the silicate one
- Necessary to analyse only the carbonated matrix of our samples

Rock analysis

How to get a trace signal in the rocks that will be comparable to the signal in the water?

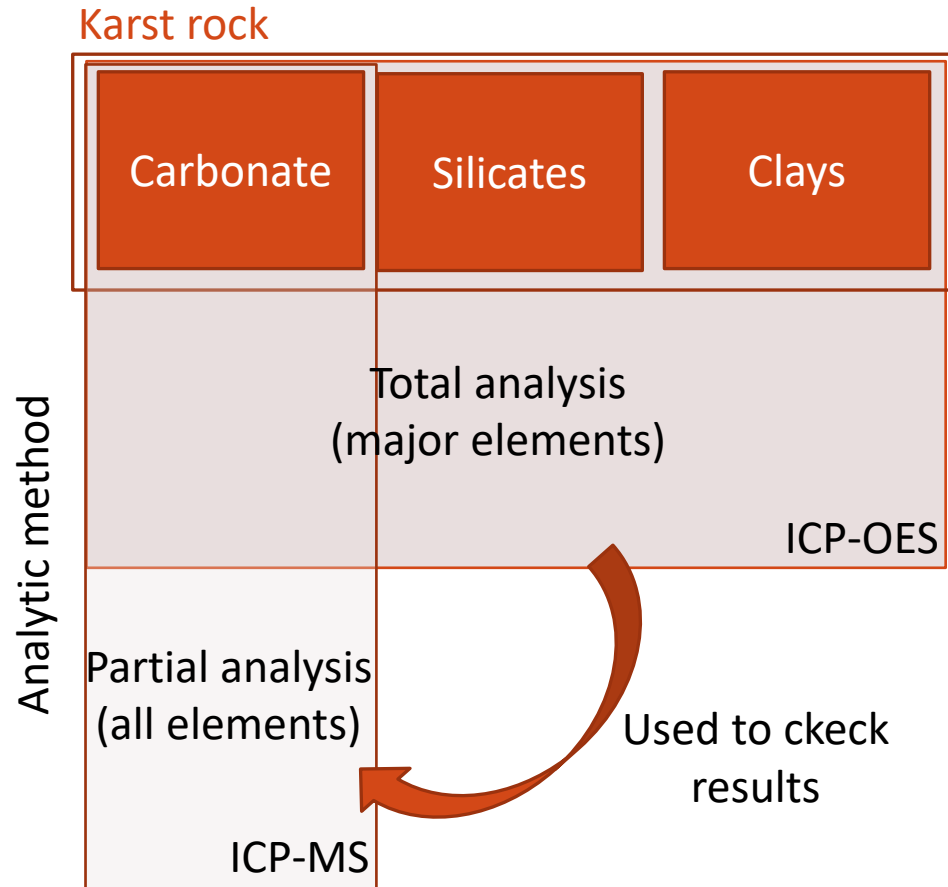


Analytic method development

- Use of hydrochloric acid 0.15 M to avoid silicates dissolution (molarity < 0.18 M *Bastian et al., 2018*)
- Carbonated fraction of all samples analysed for all Mendeleïev tab by ICP-MS

Rock analysis

How to get a trace signal in the rocks that will be comparable to the signal in the water?



Analytic method development

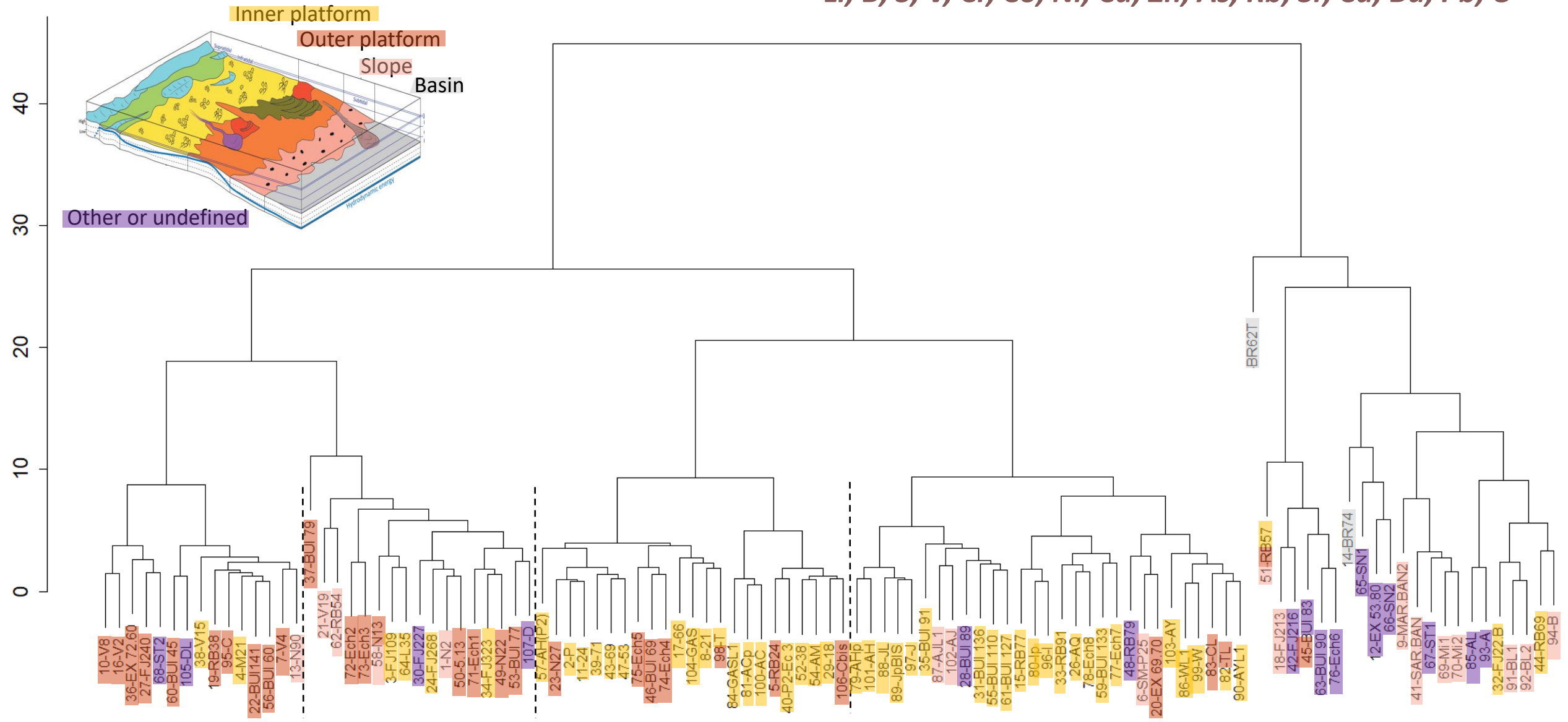
- Use of hydrochloric acid 0.15 M to avoid silicates dissolution (molarity < 0.18 M *Bastian et al., 2018*)
- Carbonated fraction of all samples analysed for all Mendeleïev tab by ICP-MS

Results validation and pre-treatment

- Total analysis of all samples performed by ICP-OES
- Check that all the carbonated fraction was considered by ICP-MS

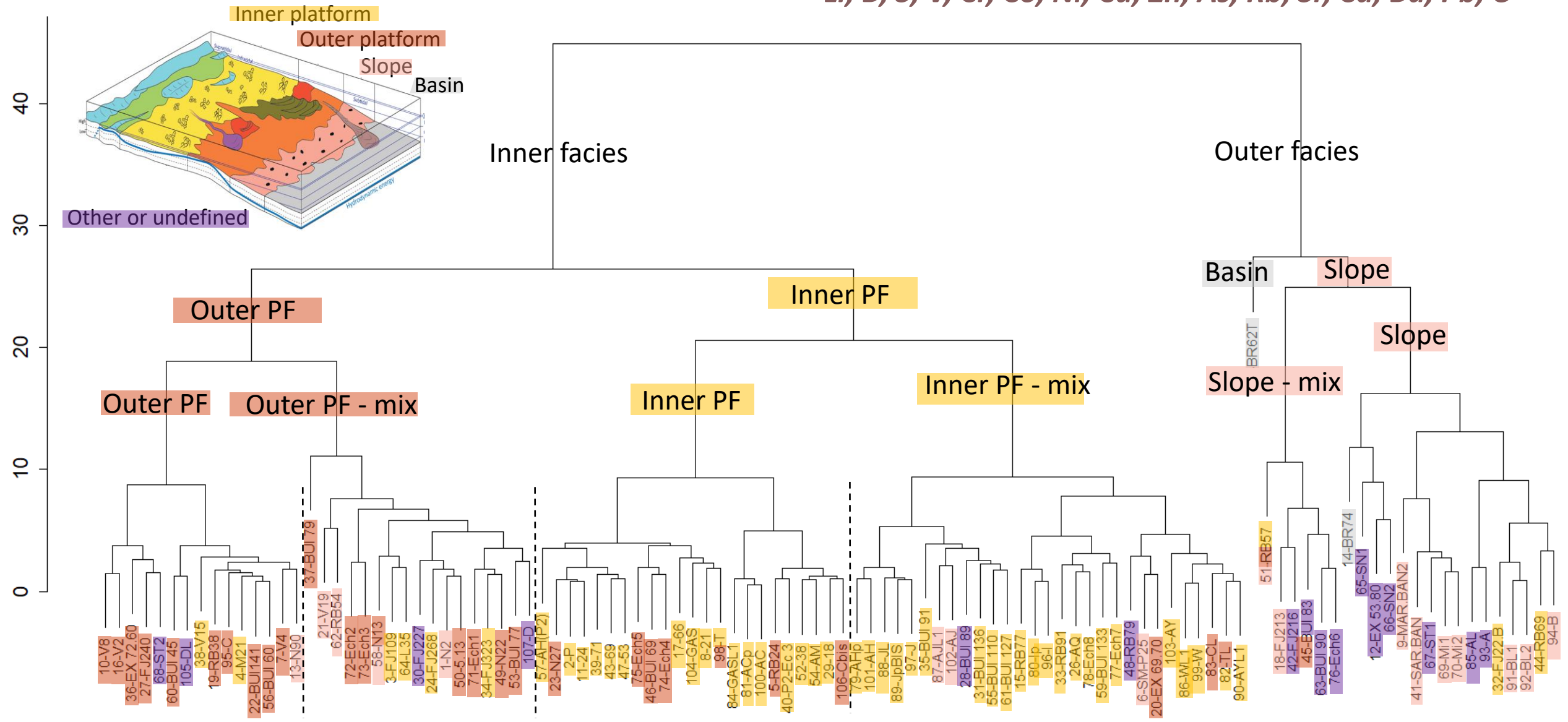
Clustering of rock samples

*Hierarchical clustering with 16 trace elements :
Li, B, S, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Cd, Ba, Pb, U*



Clustering of rock samples

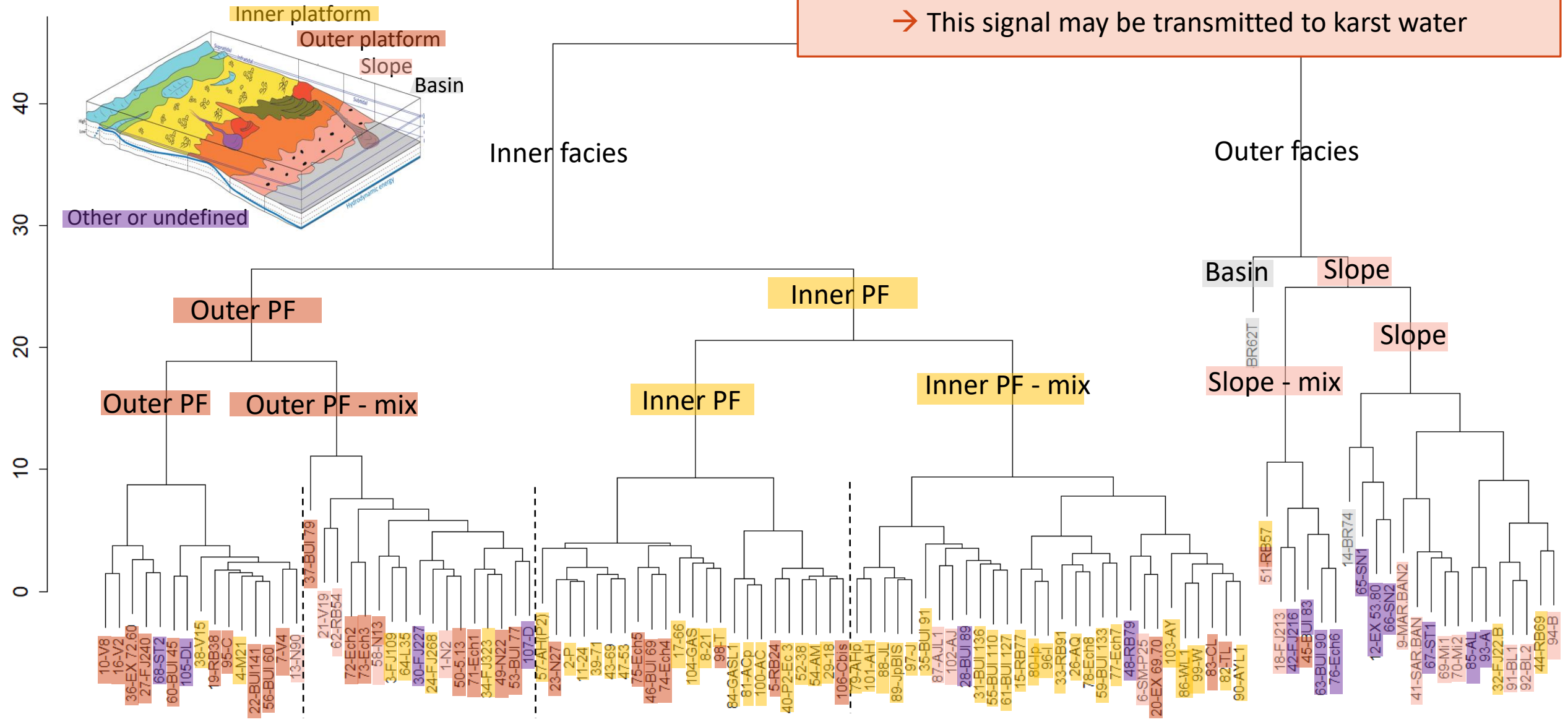
*Hierarchical clustering with 16 trace elements :
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Clustering of rock samples

Clear link between clustering and deposit environments

→ This signal may be transmitted to karst water



Conclusions & perspectives

Karst rock

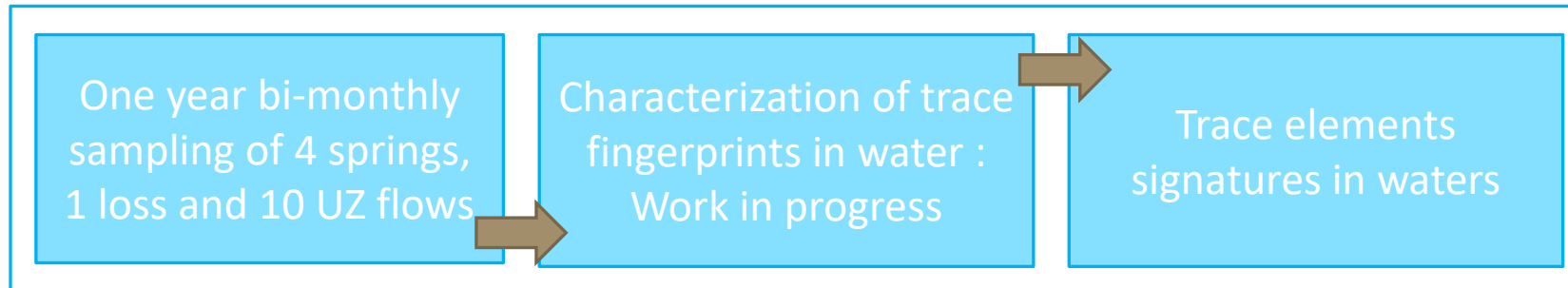


Conclusions & perspectives

Karst rock

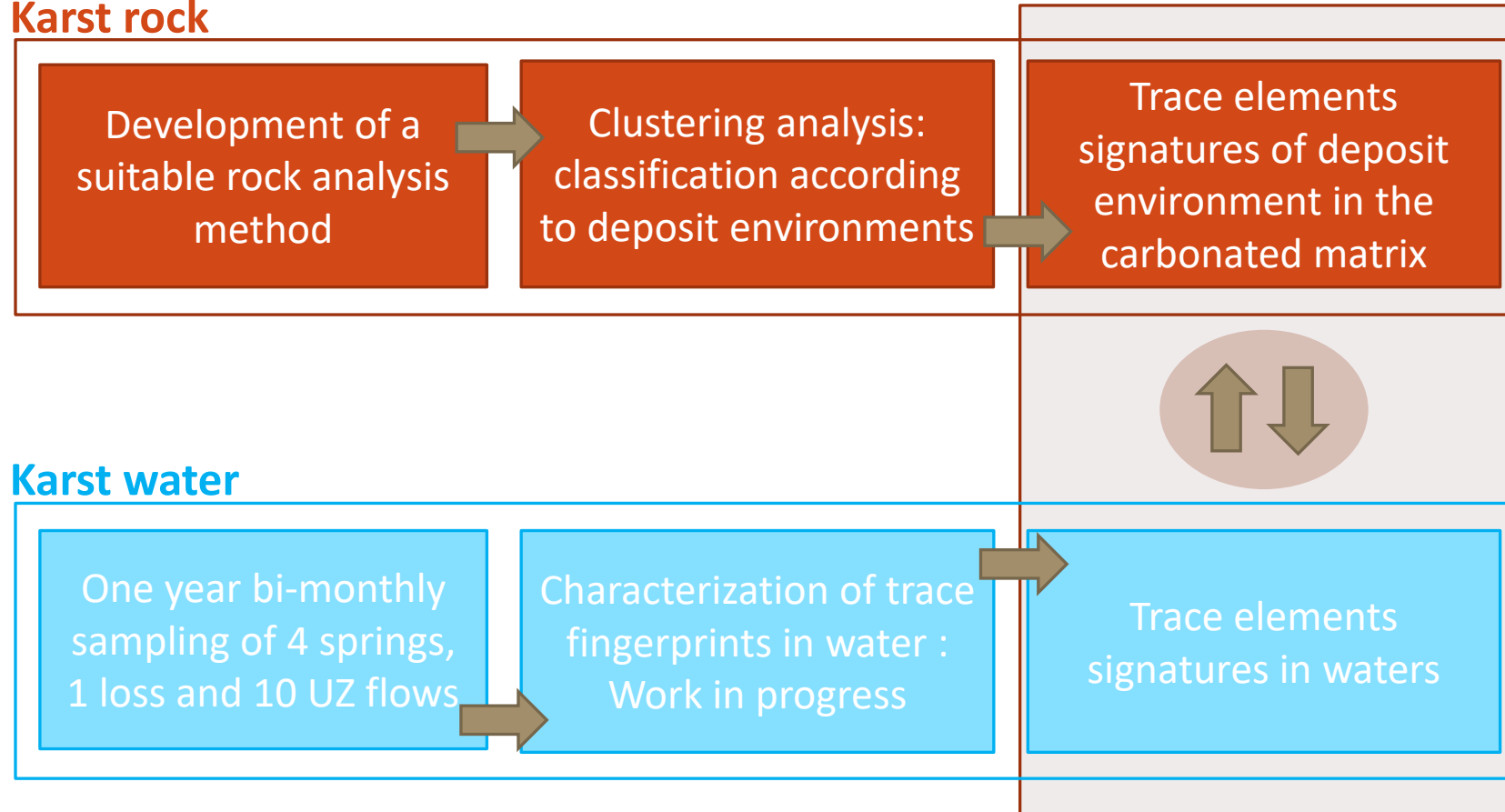


Karst water

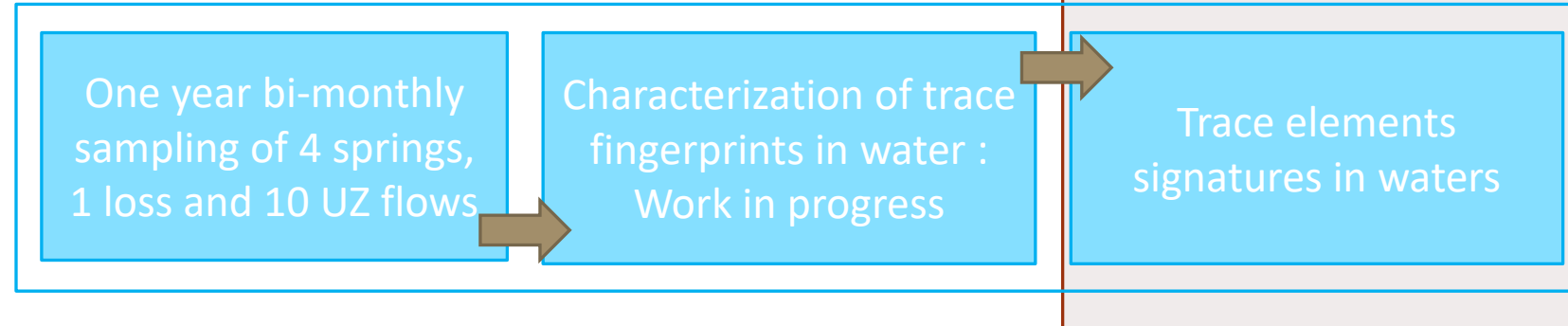


Conclusions & perspectives

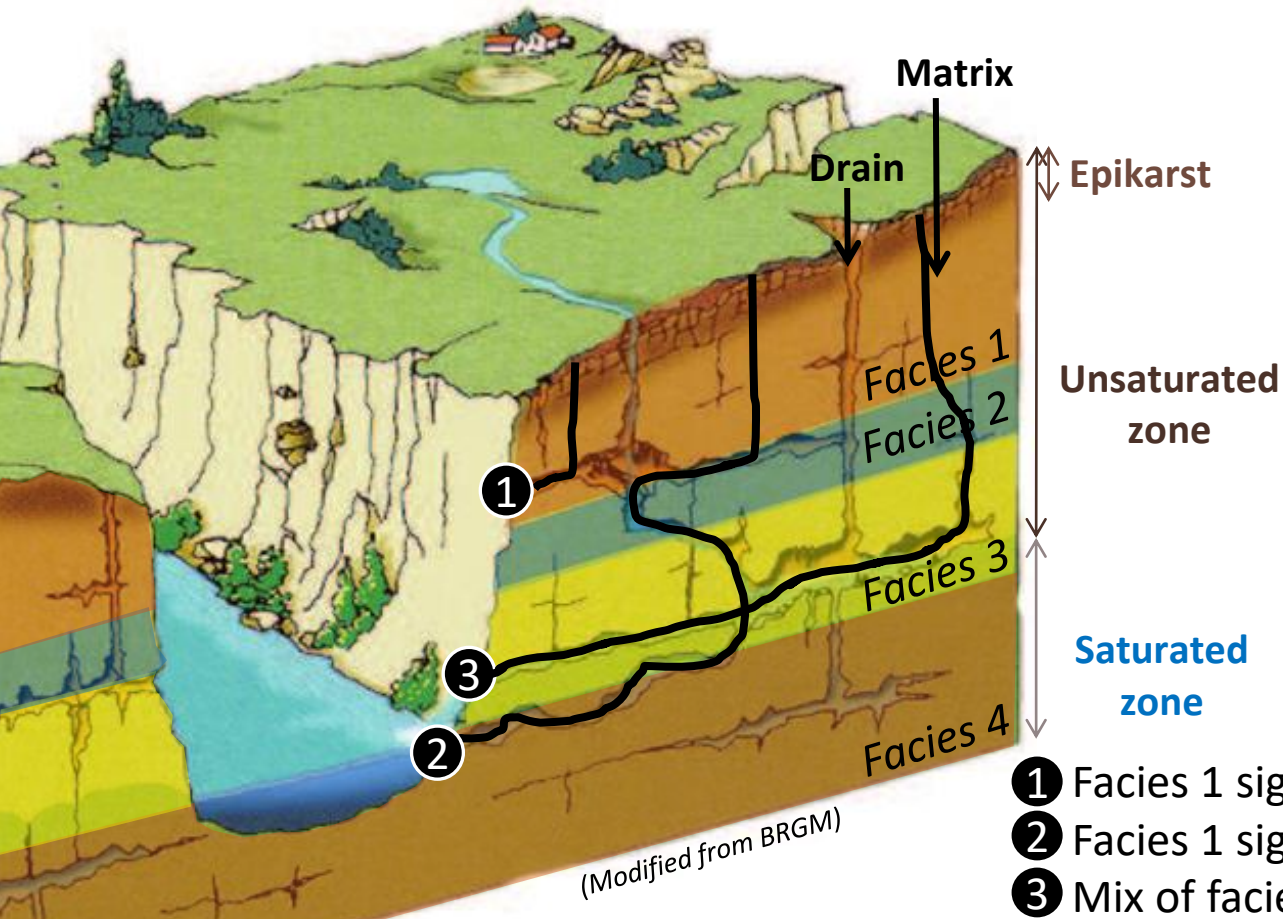
Karst rock



Karst water



Use of trace elements to distinguish flows from different types of carbonated rocks



Can trace elements be used as a natural tracer the path taken by water in karst systems?

- ① Facies 1 signature
- ② Facies 1 signature
- ③ Mix of facies 1 & 2 signatures

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Analytic method

Partial analysis protocole

- 1/ Weigh 50 mg of sample
- 2/ 10 mL of 0.15 M HCl
- 3/ Shake for 19 h at 300 rpm
- 4/ Filtration at 0.22 μm
- 5/ Evaporate at 70°C - lasts 2-3 days
- 6/ Add 15mL of HNO₃ 10%, weigh
- 7/ Ultrasound 15min
- 8/ Dilute 1mL in ICP-MS tubes, complete with water
- 9/ ICP-MS

Partial analysis

ICP-MS = Inductively coupled plasma **mass spectrometry**
→ *lower detection limits*

Total analysis

ICP-OES = Inductively coupled plasma
optical emission spectrometry