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Leïla Serène, Christelle Batiot-Guilhe, Naomi Mazzilli, Philippe Leonide, Christophe Emblanch, et al.. Use of trace elements to distinguish flows from different types of carbonated rocks. IAHS-AISH Scientific Assembly 2022, May 2022, Montpellier, France. pp.1-22, 10.5194/iahs2022-329 . hal-03817369

HAL Id: hal-03817369

<https://hal.science/hal-03817369>

Submitted on 17 Oct 2022

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UNIVERSITÉ
DE MONTPELLIER



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

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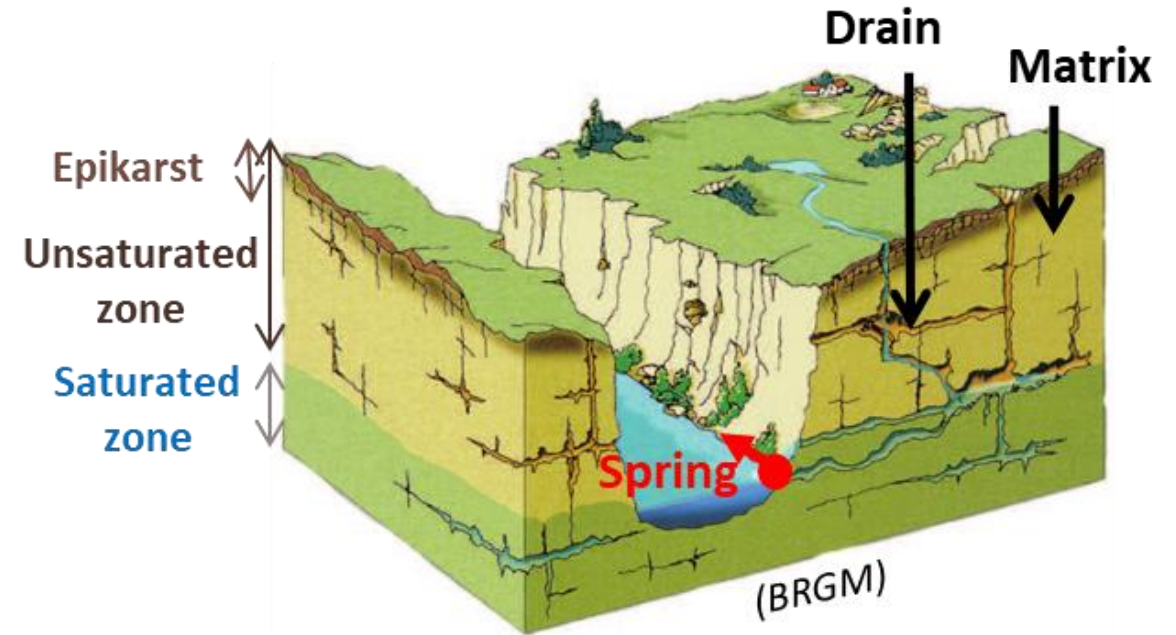
Karst : a valuable but complex water resource

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



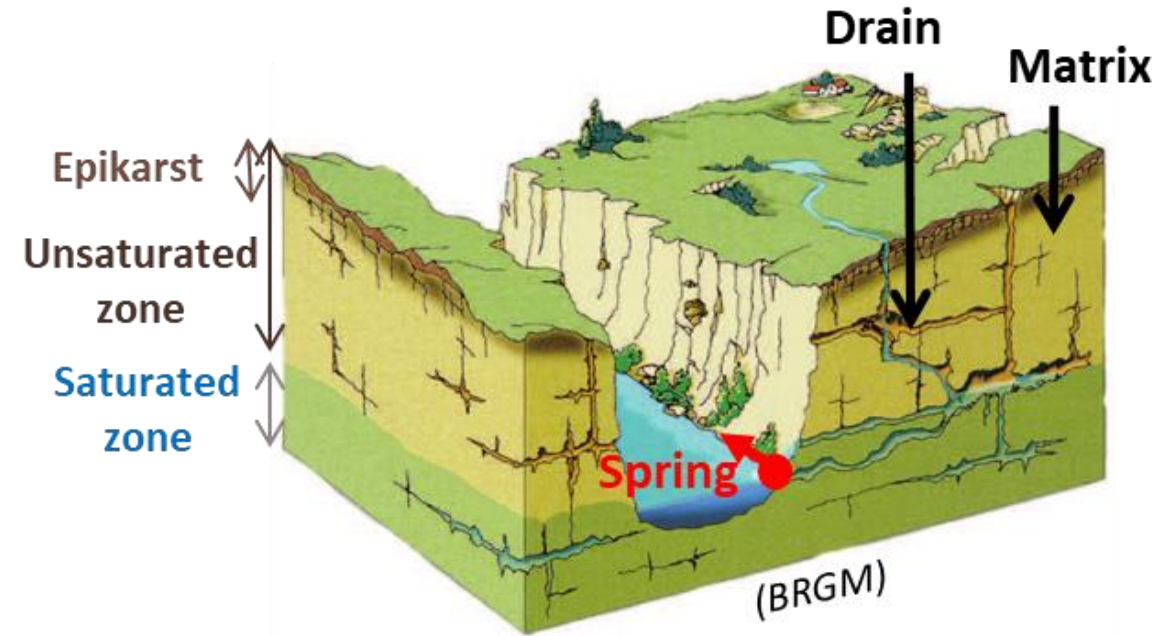
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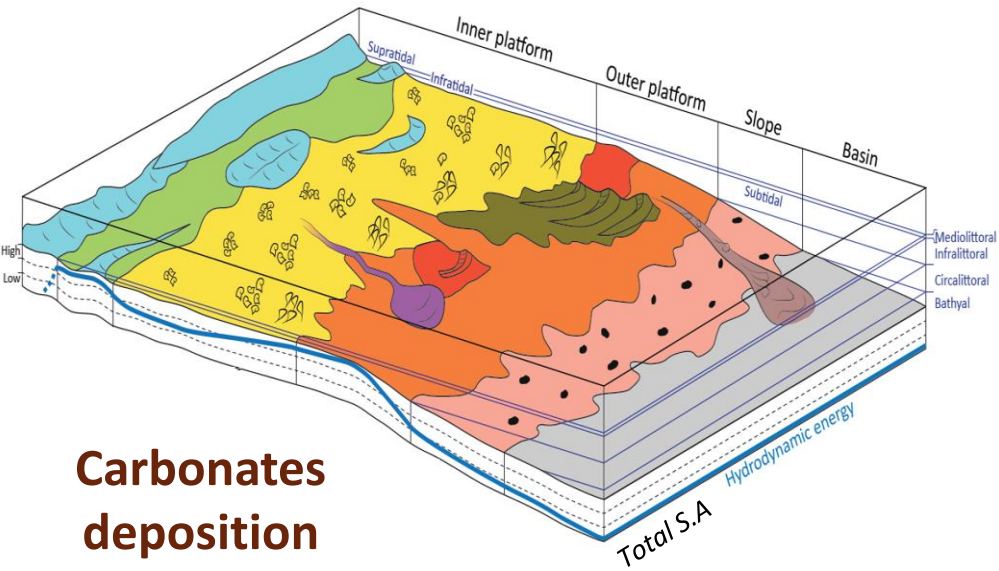
Karst specificities

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Why is karst such a complex media?

From carbonated platform to karst aquifer

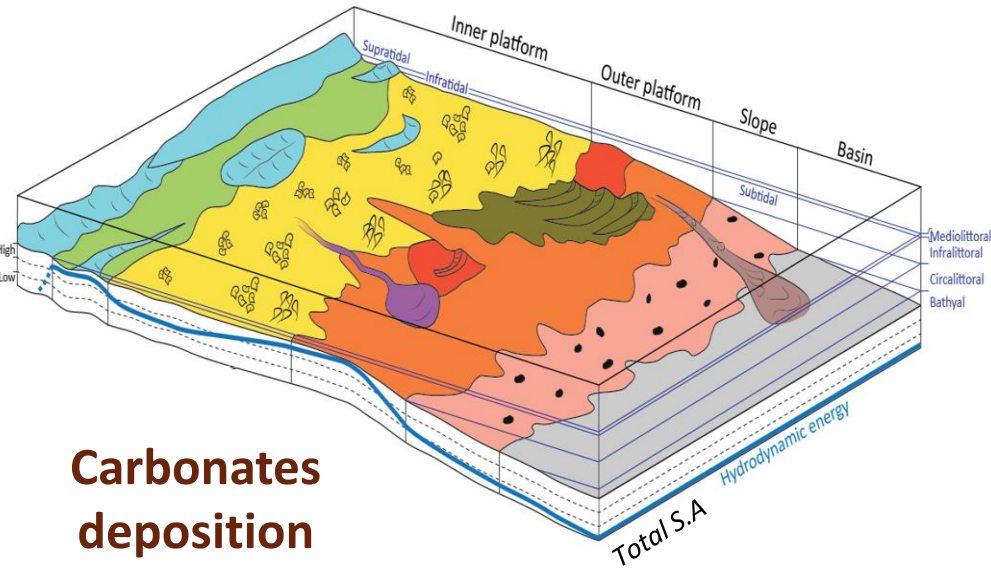


**Carbonates
deposition**

Variability of carbonate
sediments

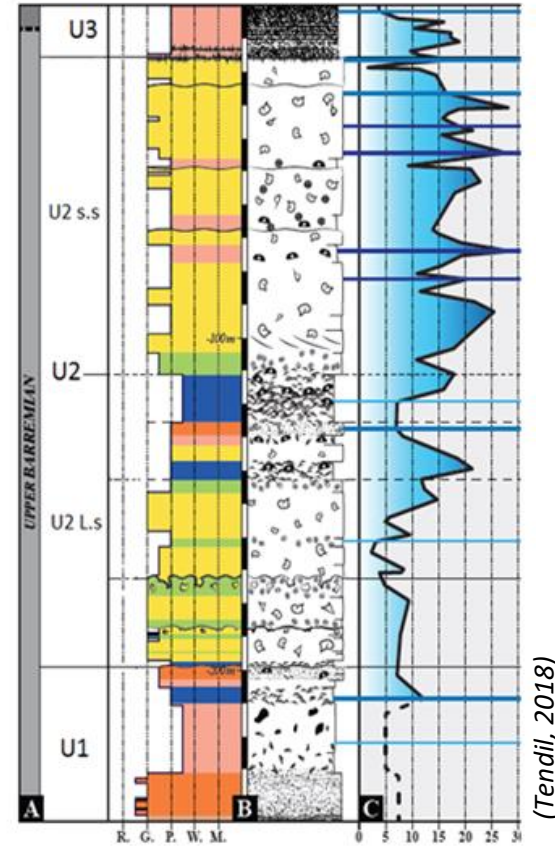
From carbonated platform to karst aquifer

Diagenesis



Carbonates deposition

Texture Lithology Porosity (%)



Variability of carbonate sediments

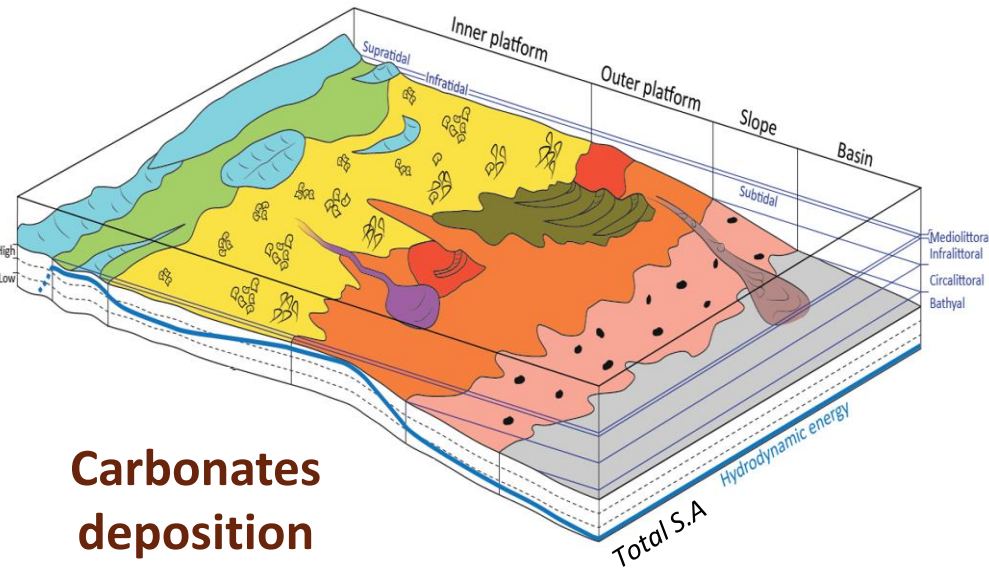
Diagenetic variability

From carbonated platform to karst aquifer

Karstification

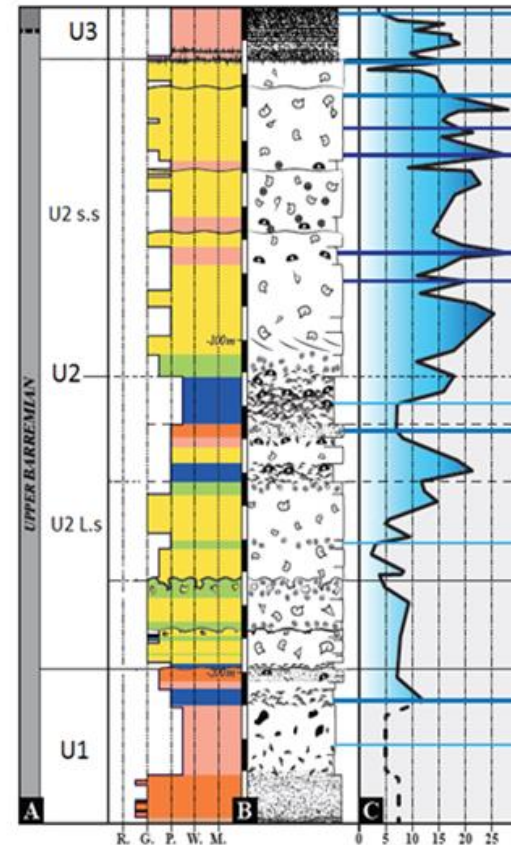
Diagenesis

Karstification

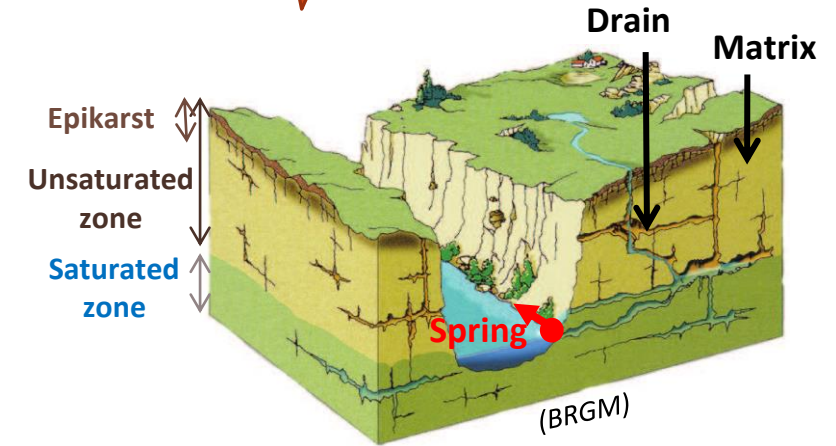


Carbonates deposition

Texture Lithology Porosity (%)



(Tendil, 2018)

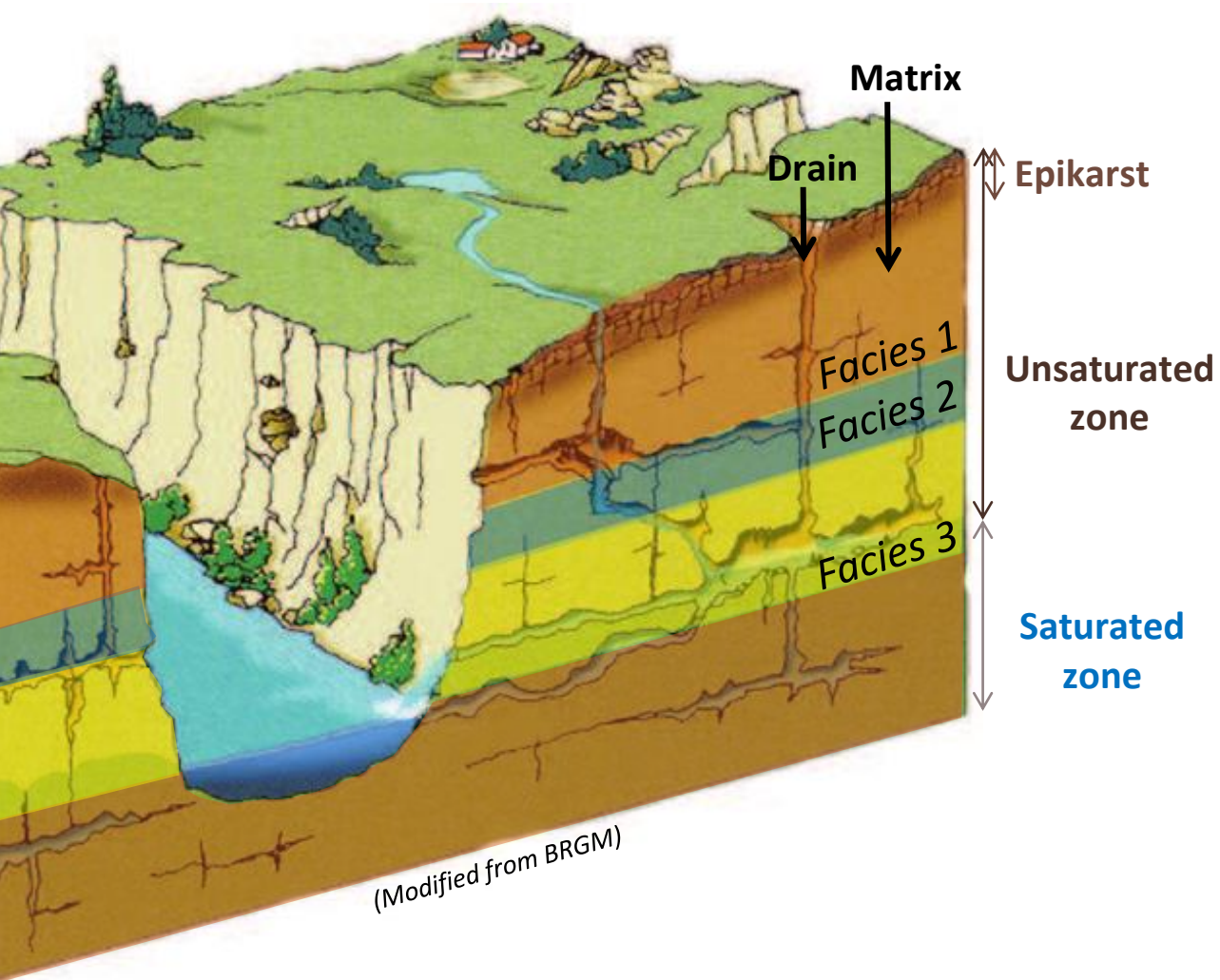


Hydrodynamic and hydrochemical variability of flows in unsaturated zone

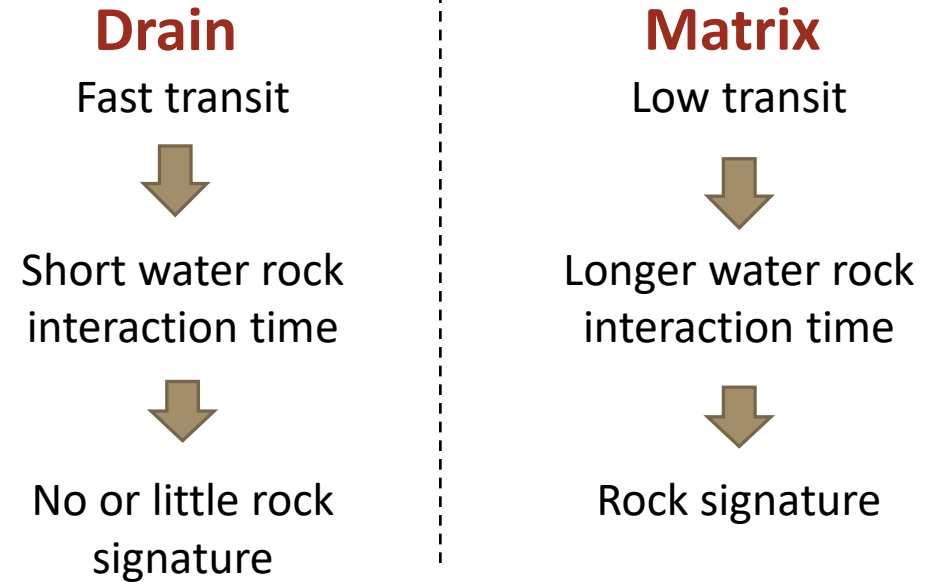
Variability of carbonate sediments

Diagenetic variability

Aim of the study

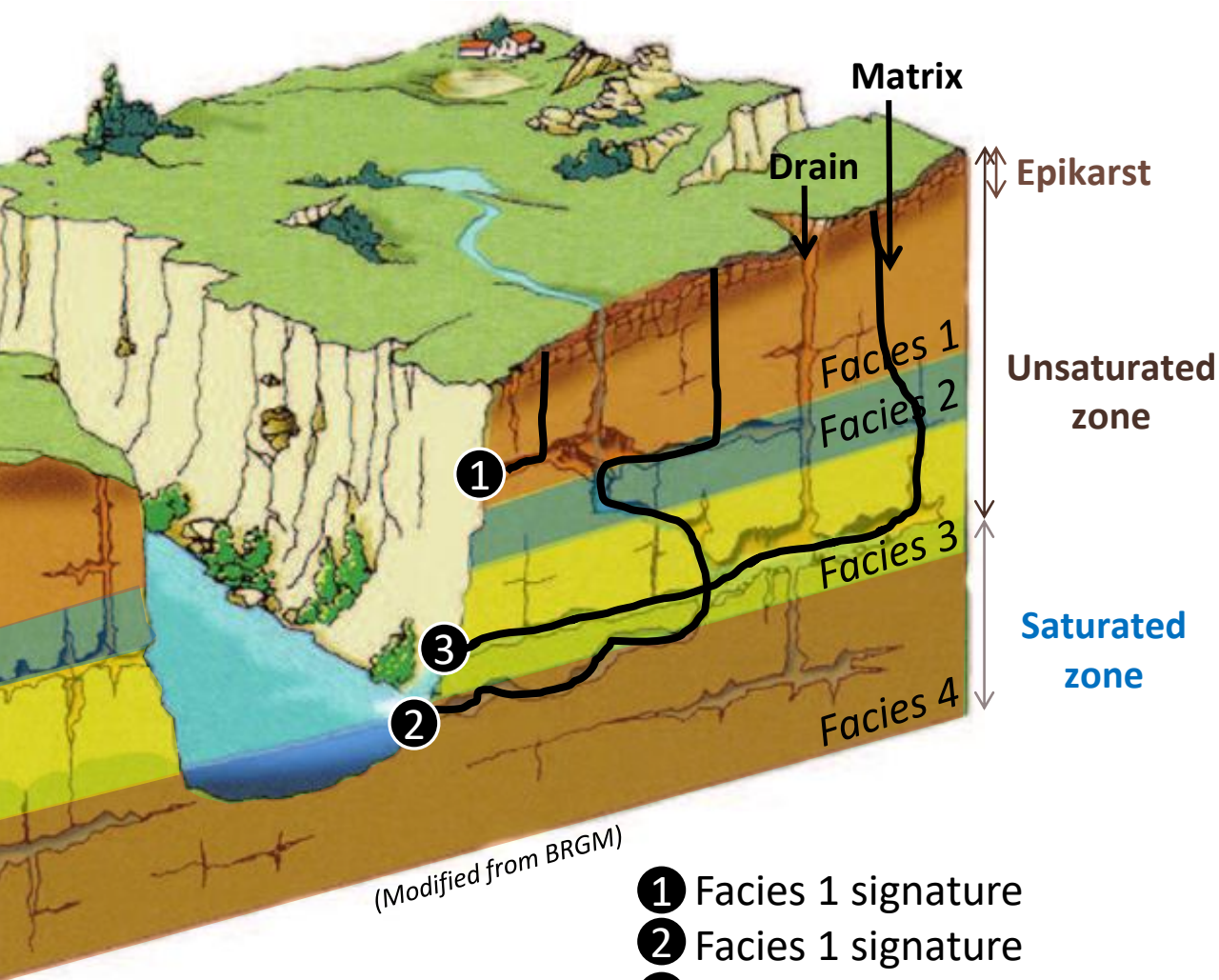


Path taken by water



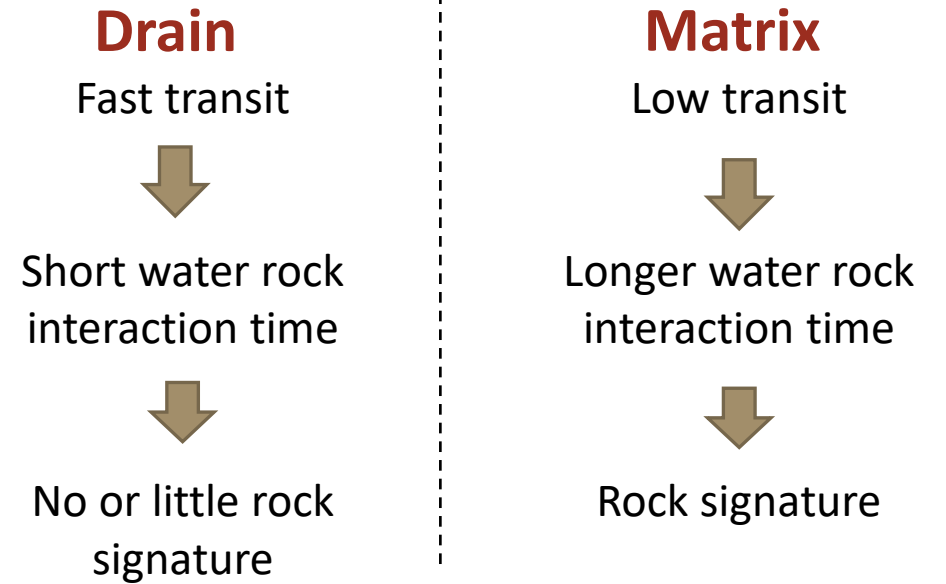
(Modified from BRGM)

Aim of the study

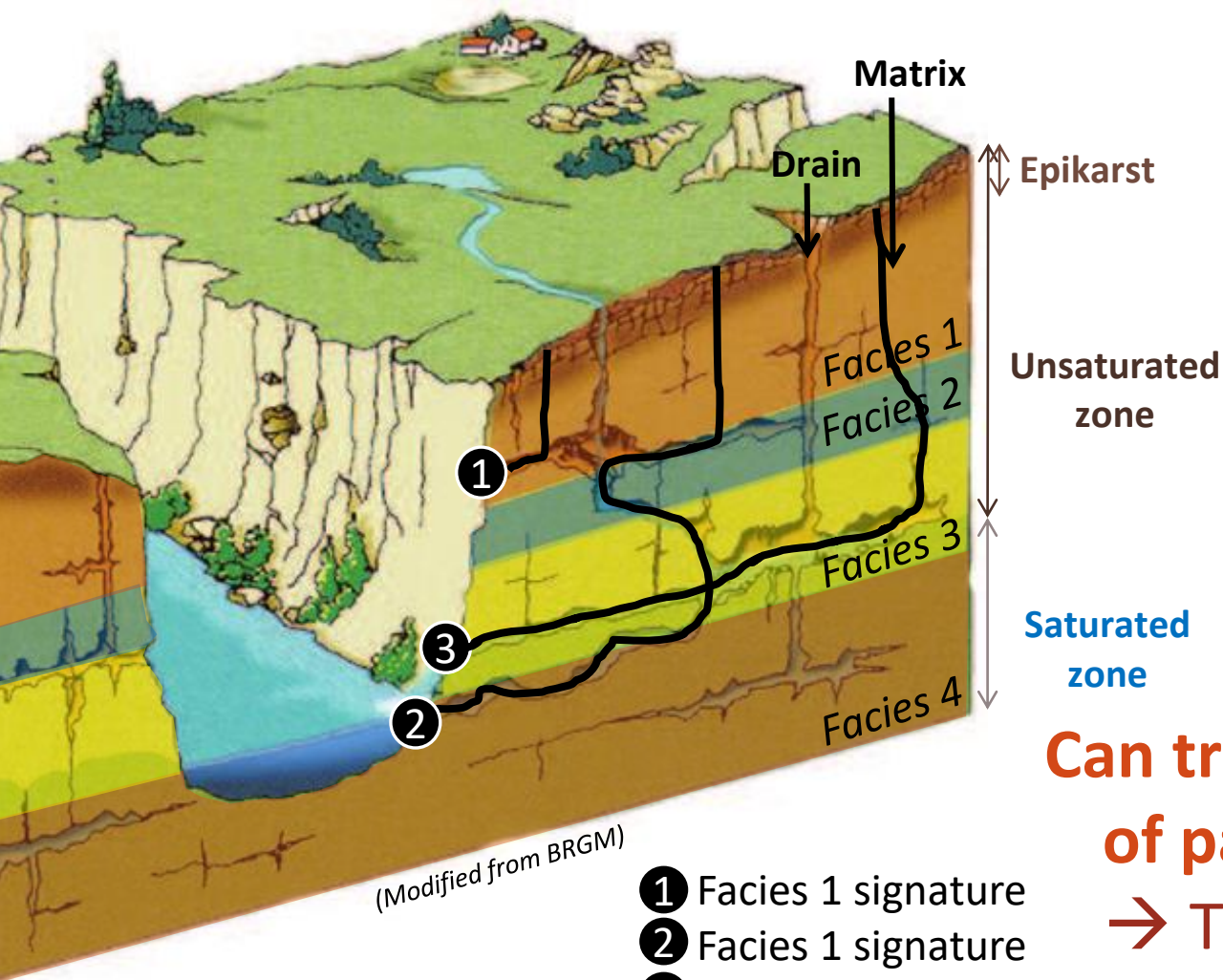


- 1 Facies 1 signature
- 2 Facies 1 signature
- 3 Mix of facies 1 & 2 signatures

Path taken by water



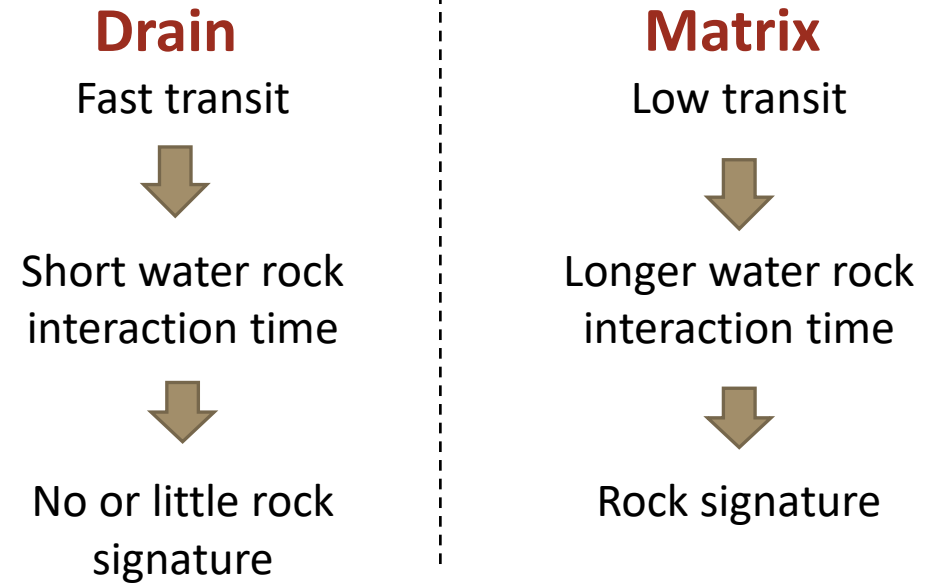
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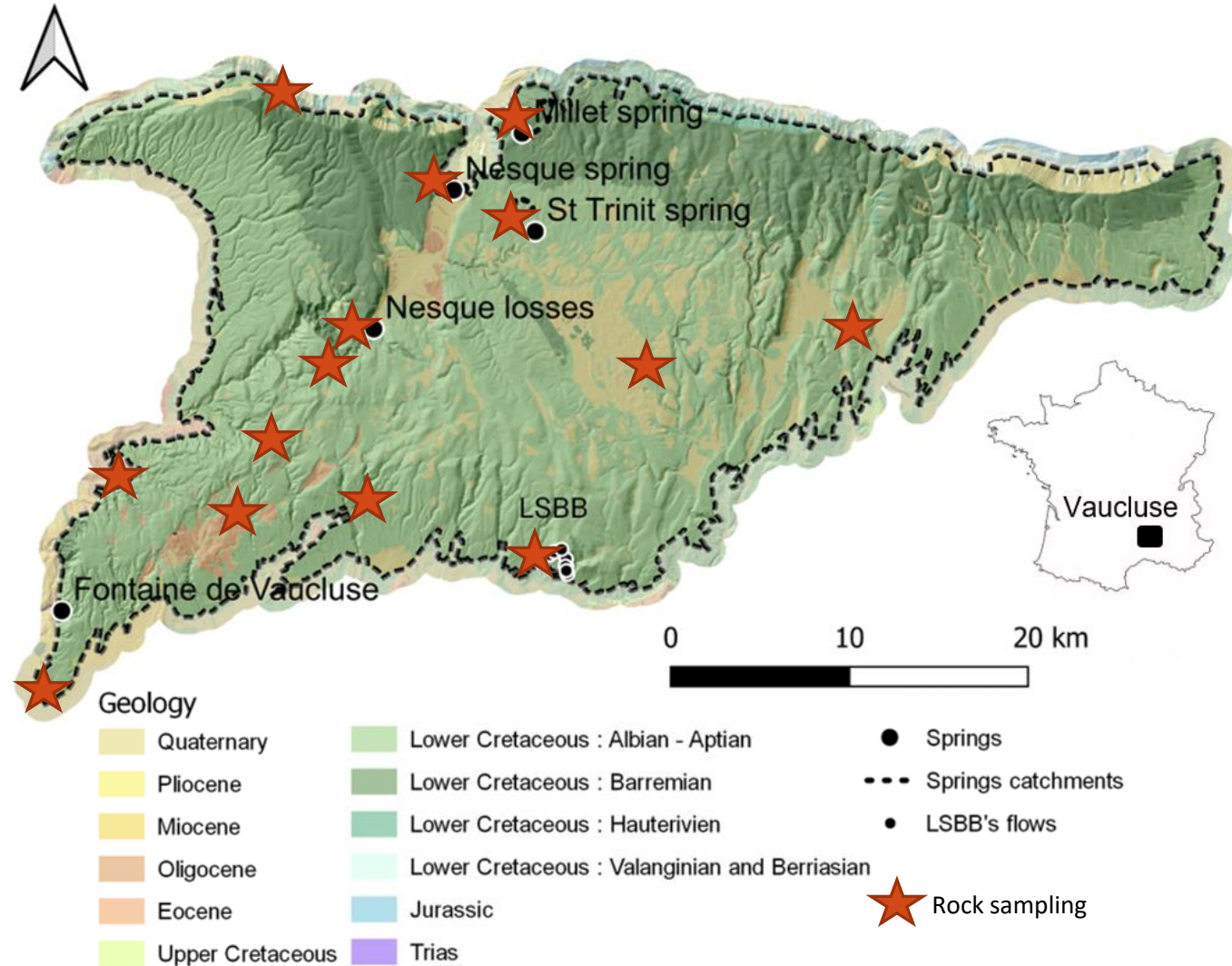
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Path taken by water



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

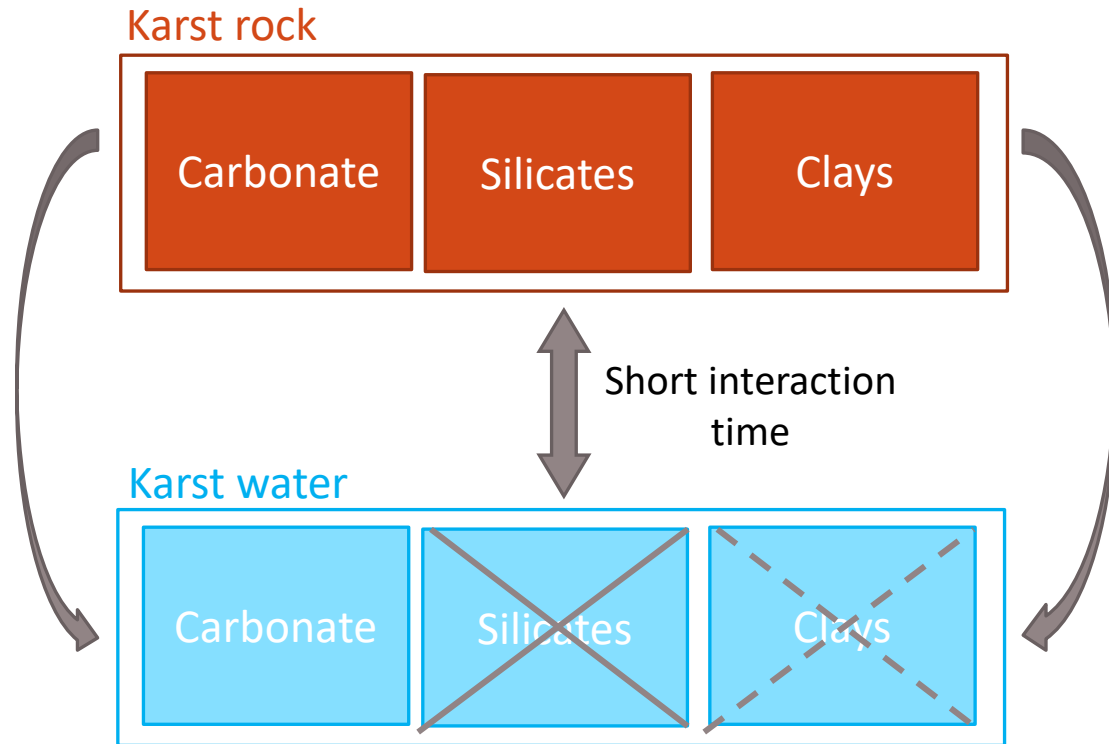
- Catchment of 1160 km² *Ollivier, 2020*
- Aquifer thickness up to 1500m
- Unsaturated zone average thickness 800m

Rock sampling

- 108 limestone samples
→ Representatives facies (several replicates)

Rock analysis

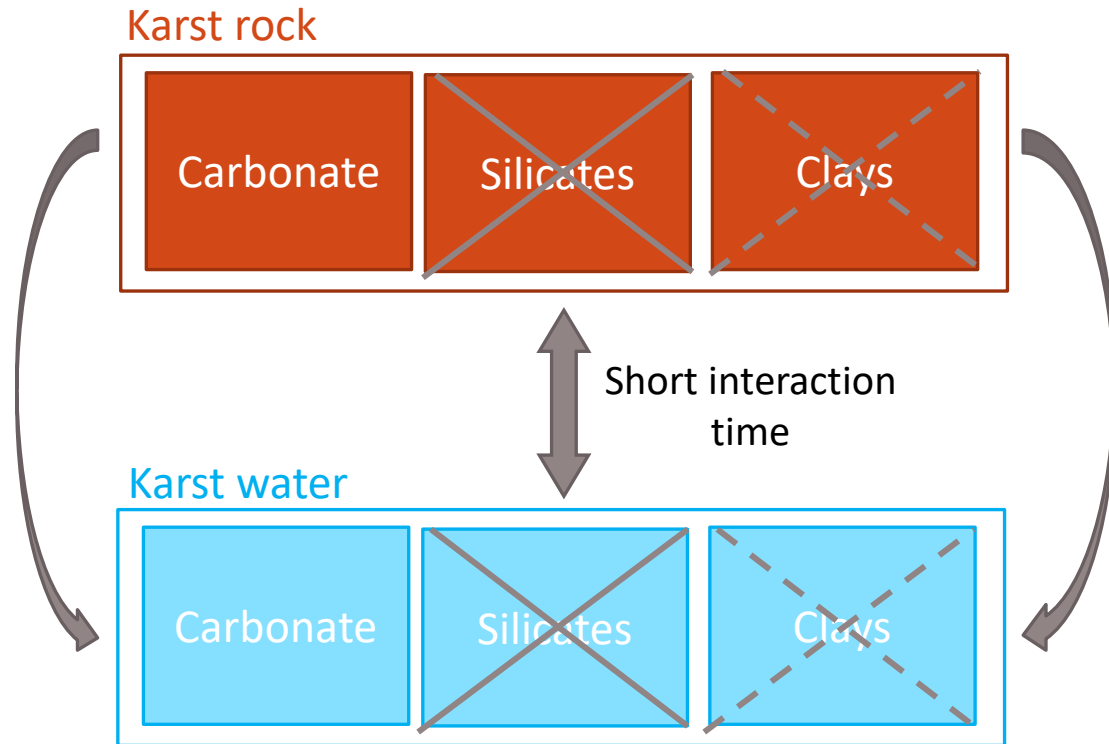
How to get a trace signal in the rocks that will be comparable to the signal in the water?



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

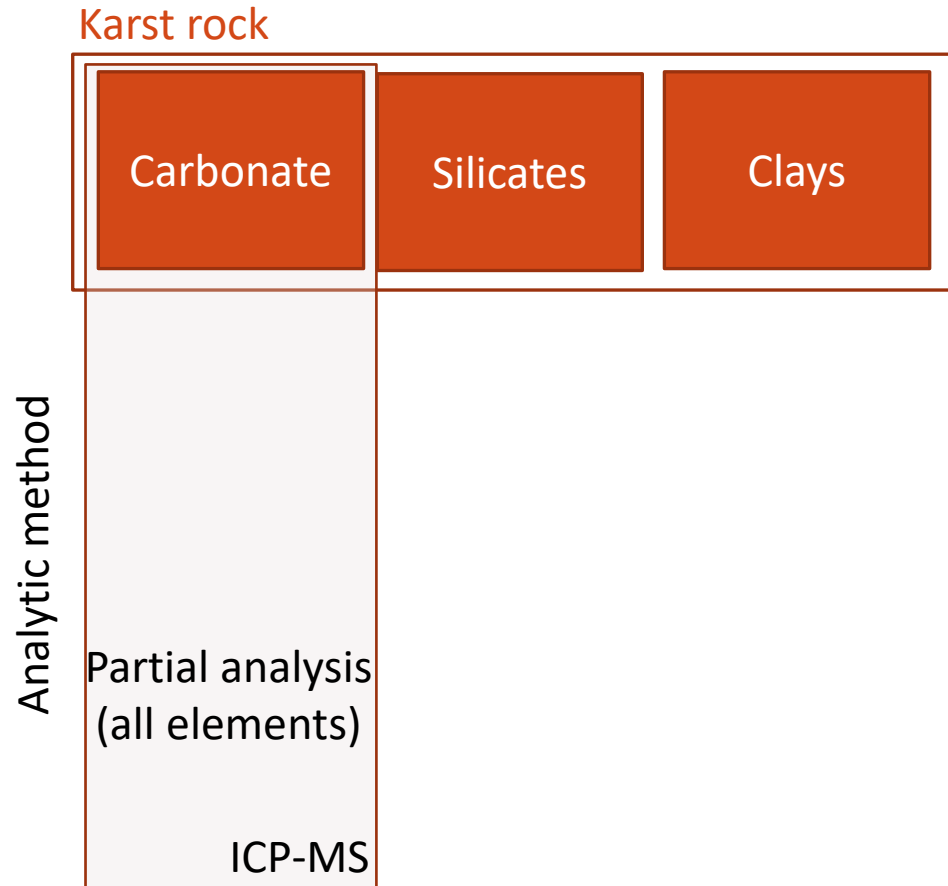
- Fast reacting system = short storage duration (few years max)
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Trace elements in rocks

- 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?

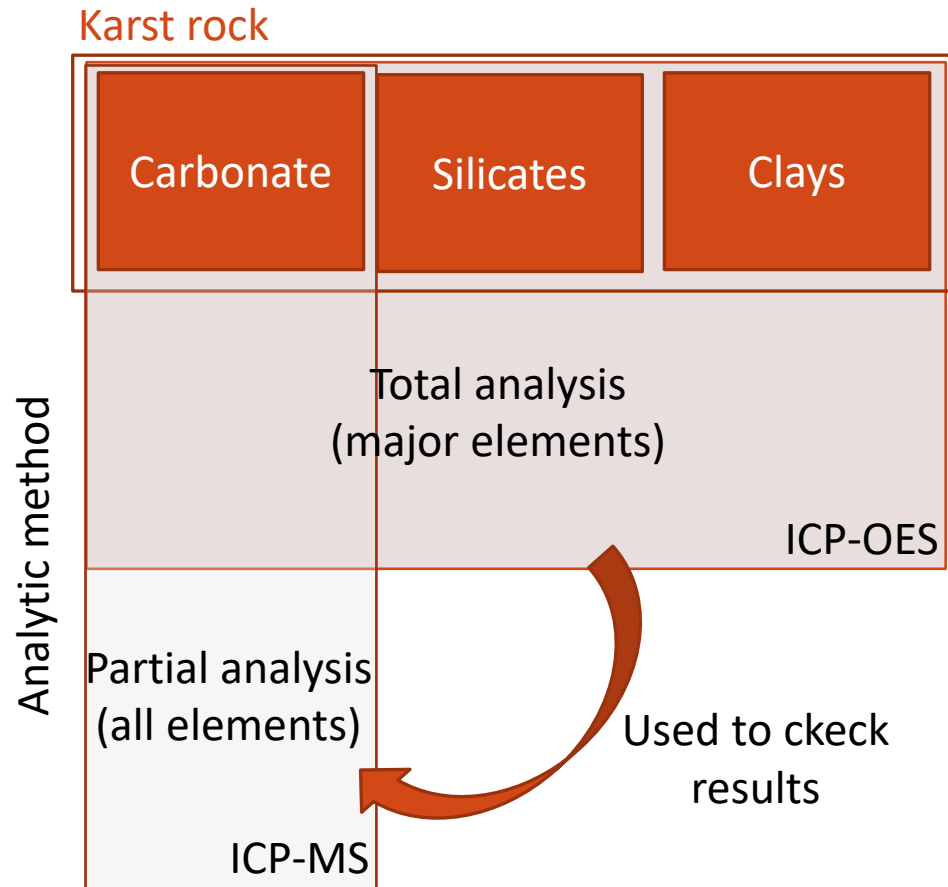


Analytic method development

- 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 Mendeleiev tab by ICP-MS

Rock analysis

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Analytic method development

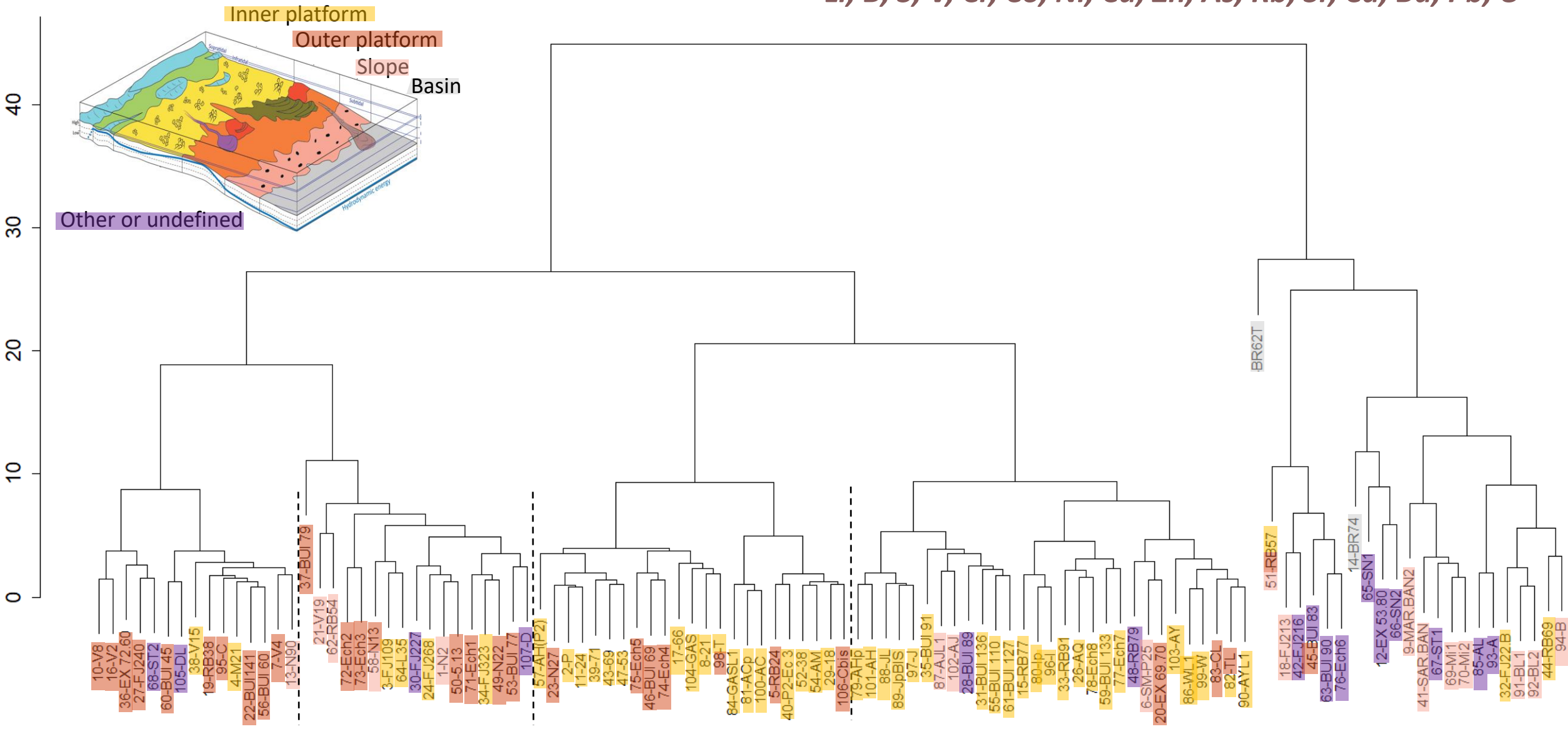
- Use of hydrochloric acid 0.15 M to avoid silicates dissolution (molarity < 0.18 M *Bastian et al., 2018*)
- Carbonated fraction of all samples analysed for all Mendeleiev tab by ICP-MS

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

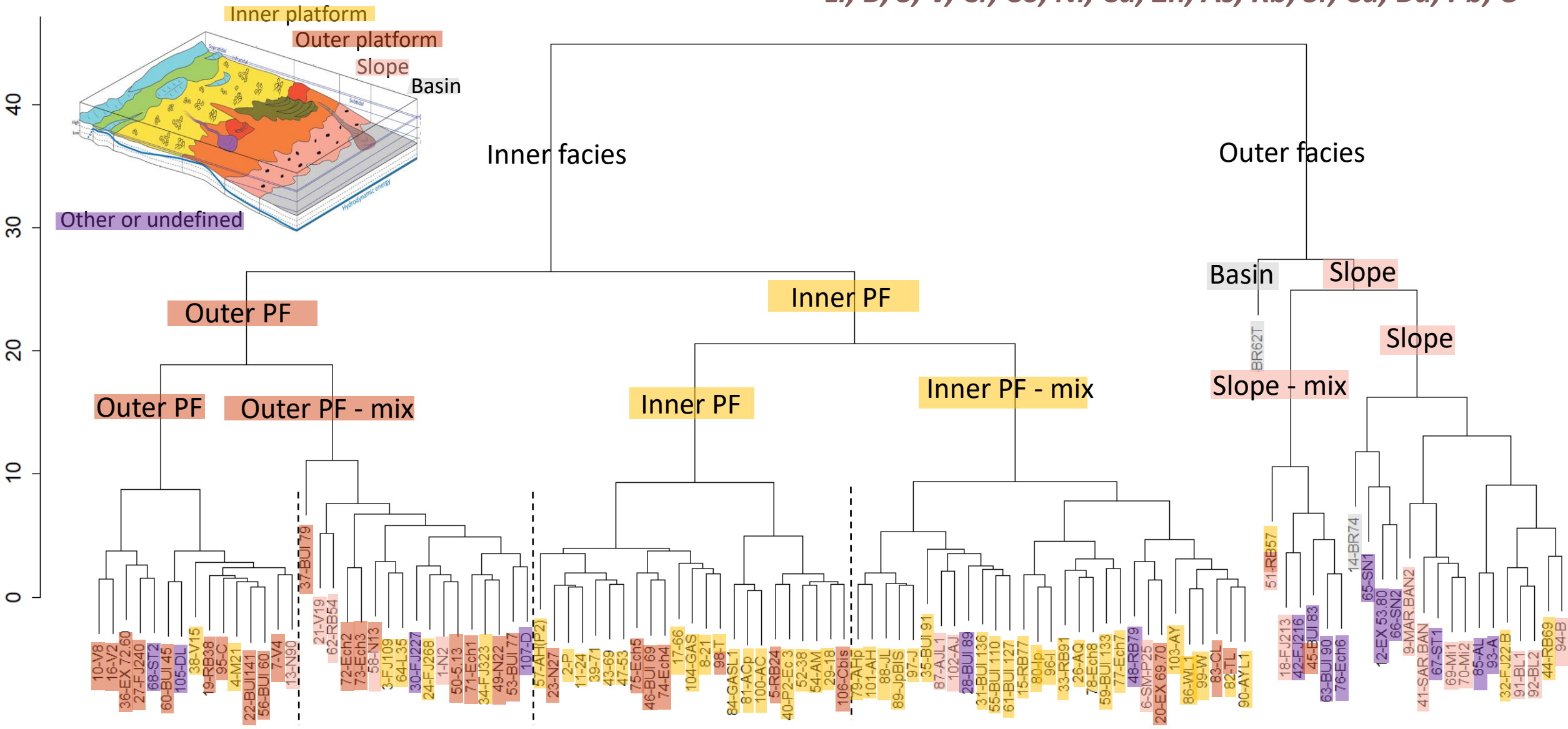
Clustering of rock samples

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



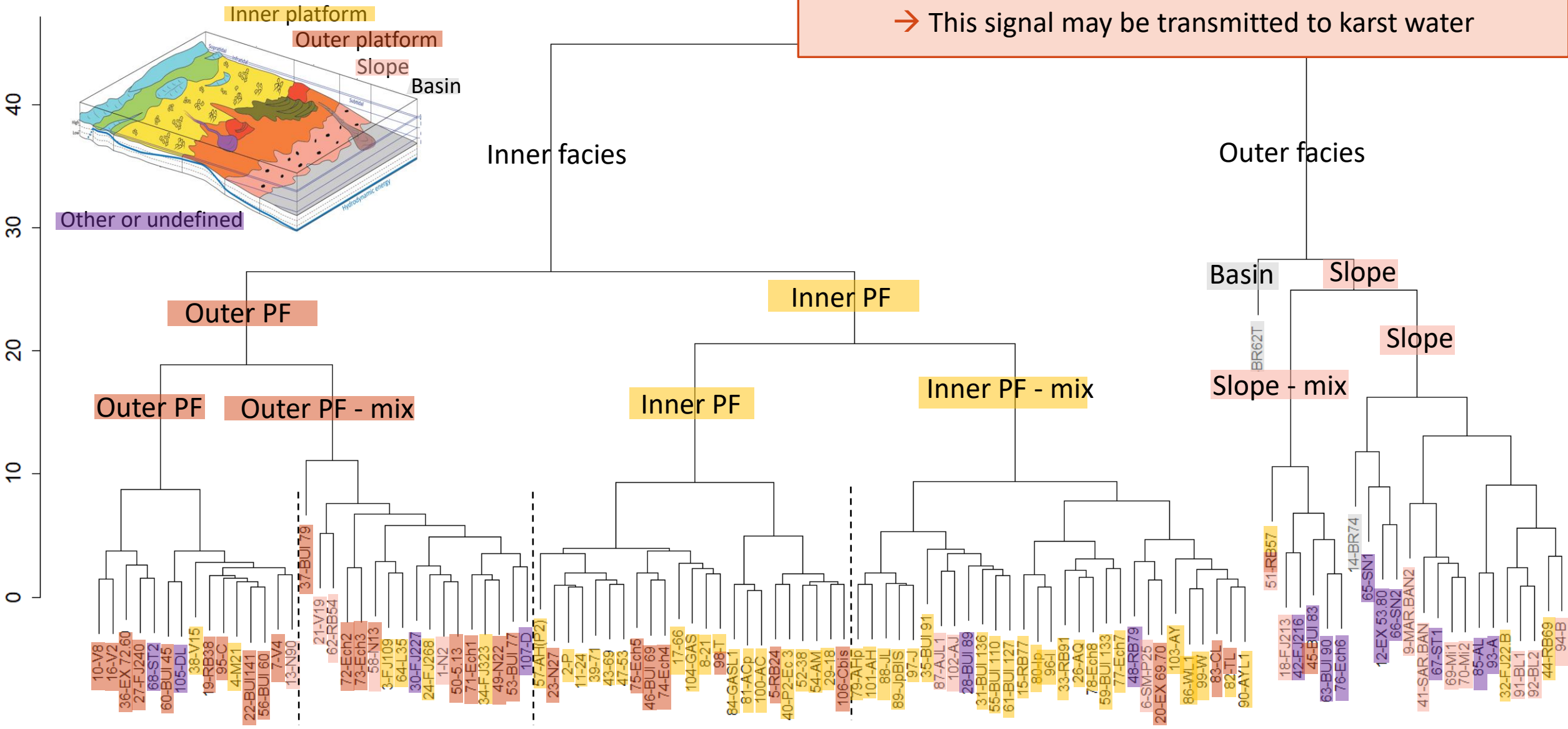
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Clustering of rock samples

Clear link between clustering and deposit environments
 → This signal may be transmitted to karst water



Conclusions & perspectives

Karst rock

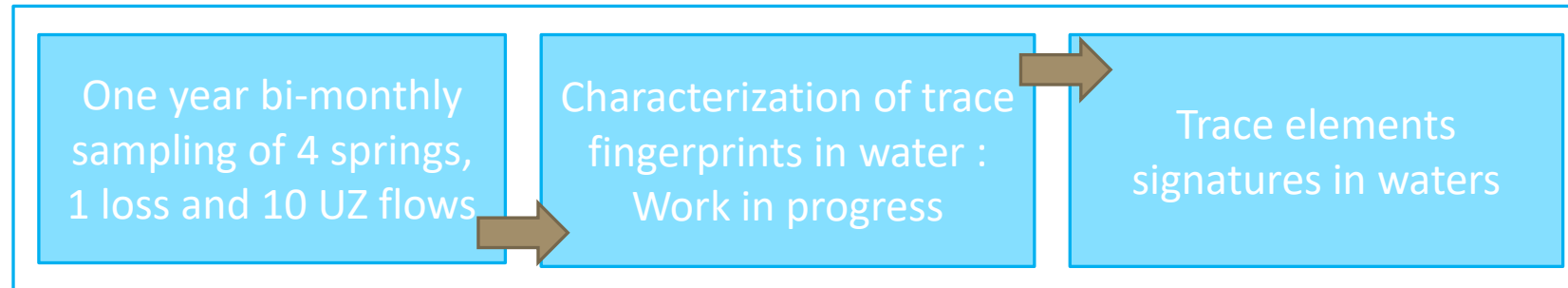


Conclusions & perspectives

Karst rock



Karst water

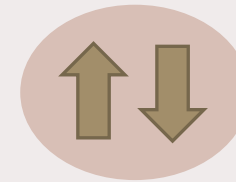
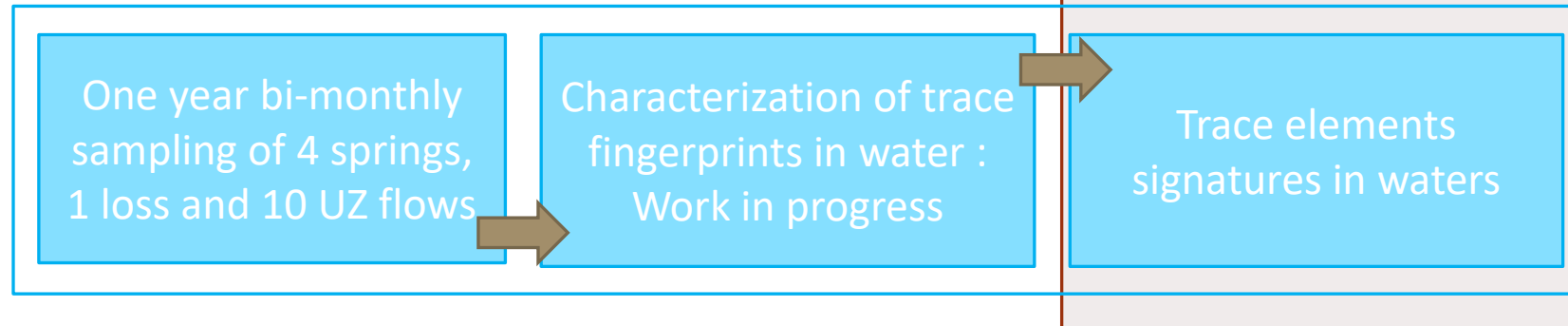


Conclusions & perspectives

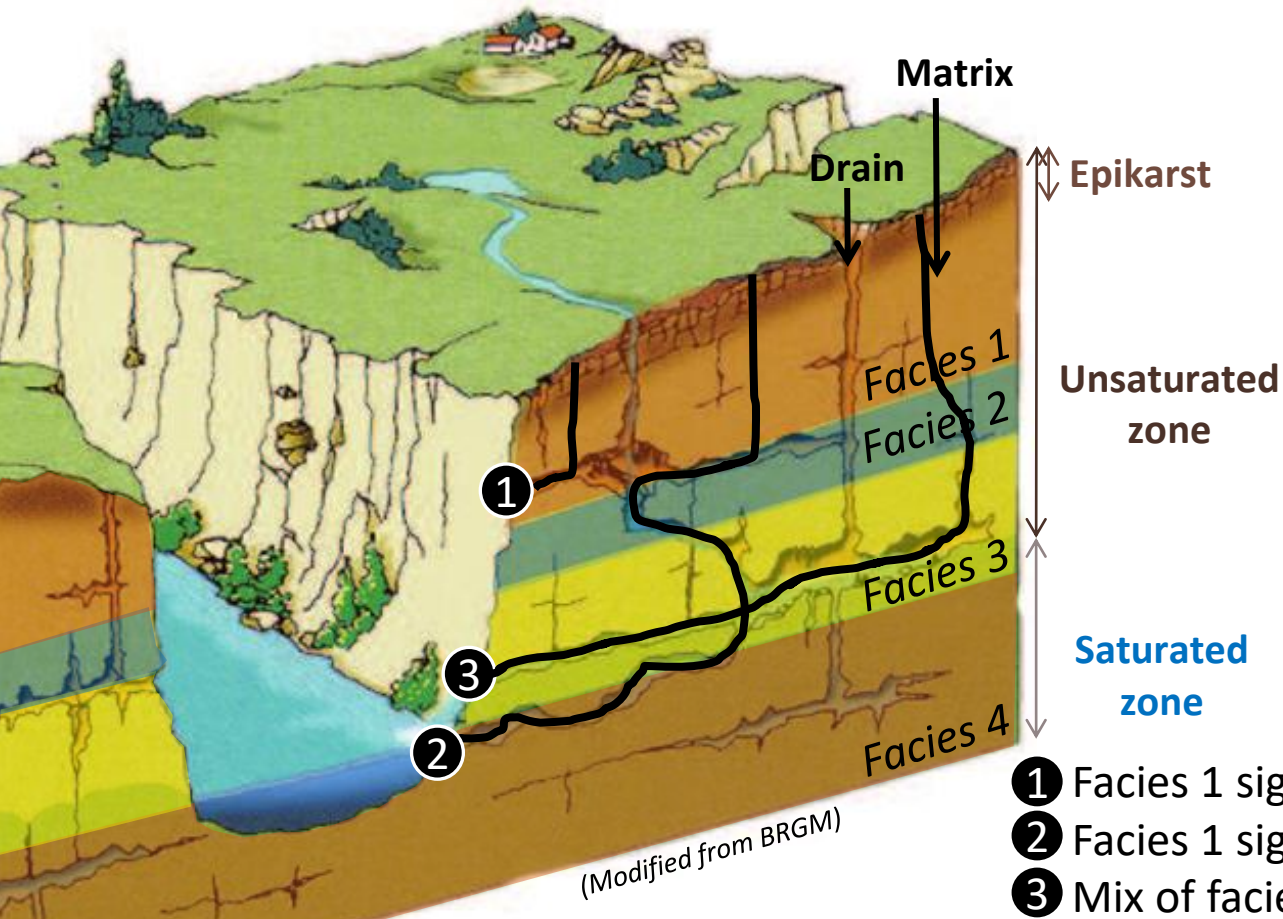
Karst rock



Karst water



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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**