



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

Leïla Serène, Christelle Batiot-Guilhe, Naomi Mazzilli, Philippe Leonide, Christophe Emblanch, Eléonore Resongles, Rémi Freydier, Léa Causse, Milanka Babic, Julien Dupont, et al.

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UNIVERSITÉ  
DE MONTPELLIER



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

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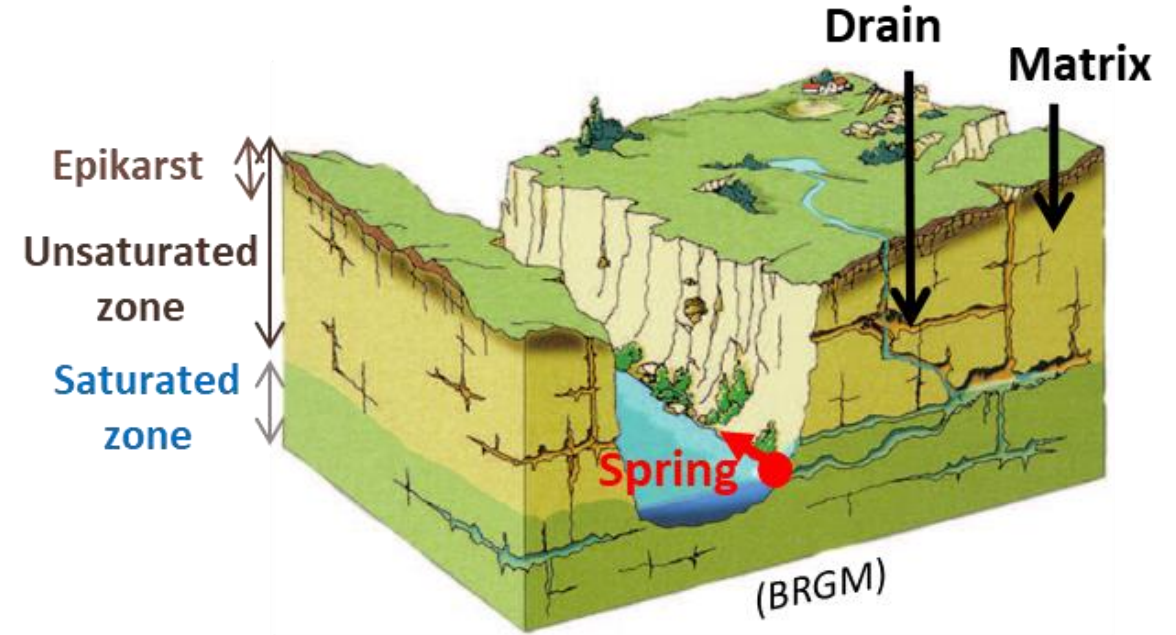
# Karst : a valuable but complex water resource

## 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



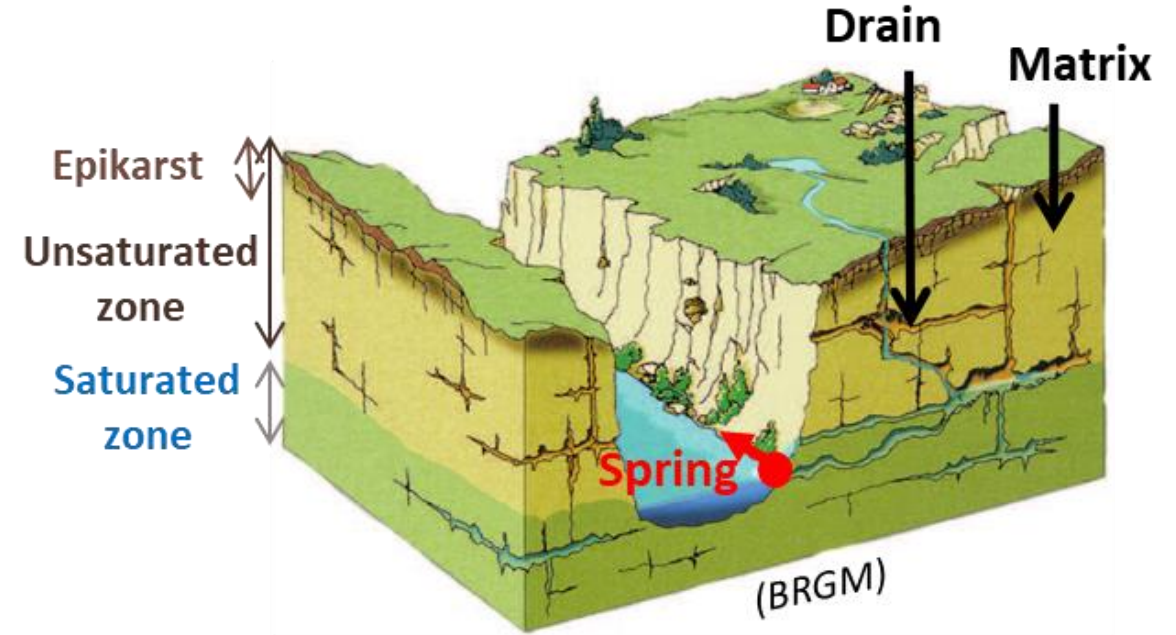
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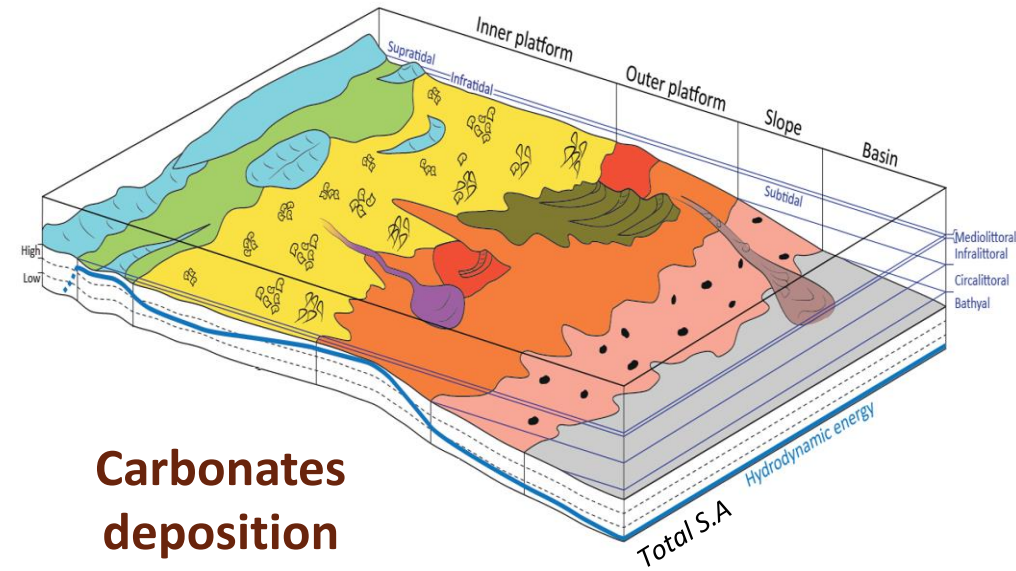
## Karst specificities

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- Dual flows (fast/slow)
- Vulnerability associated to fast flow



Why is karst such a complex media?

# From carbonated platform to karst aquifer



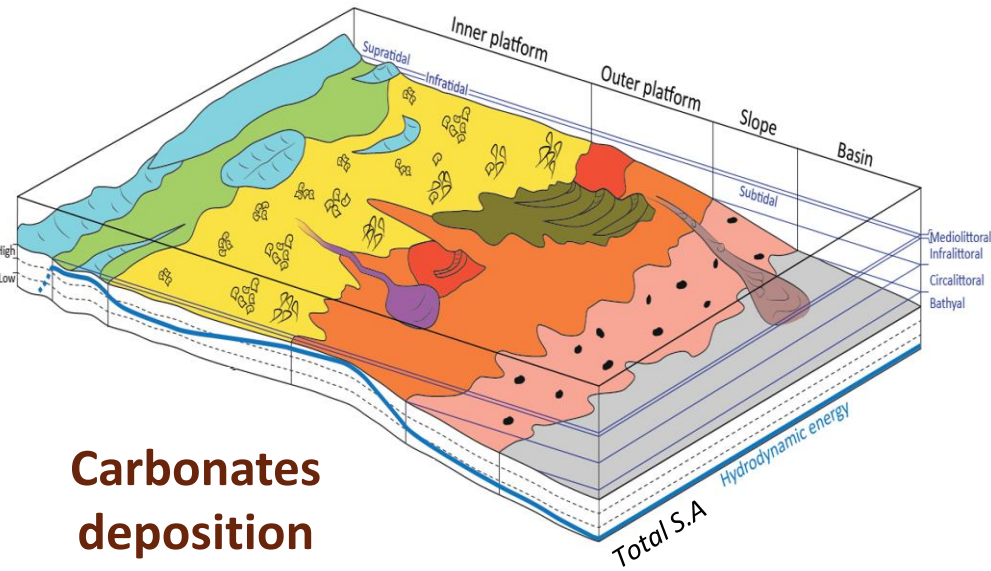
**Carbonates  
deposition**

Variability of carbonate  
sediments



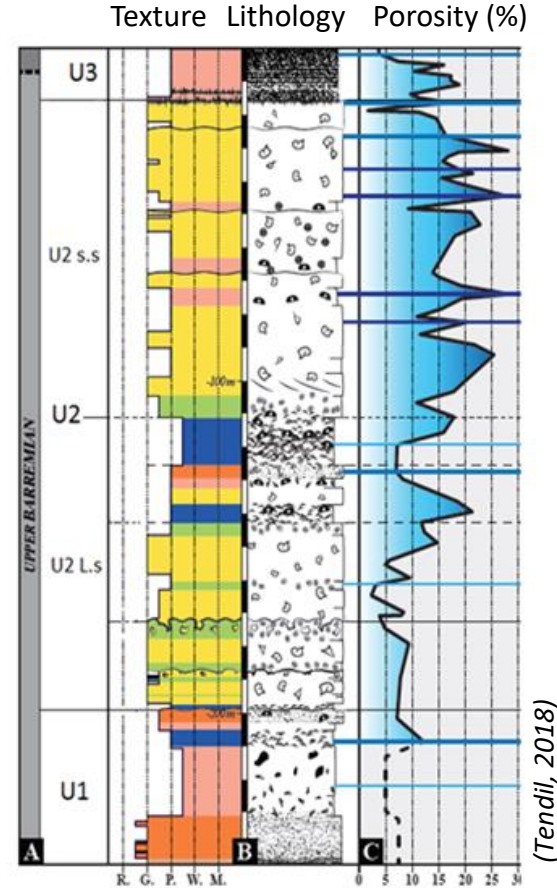
# From carbonated platform to karst aquifer

Diagenesis



Carbonates deposition

Variability of carbonate sediments

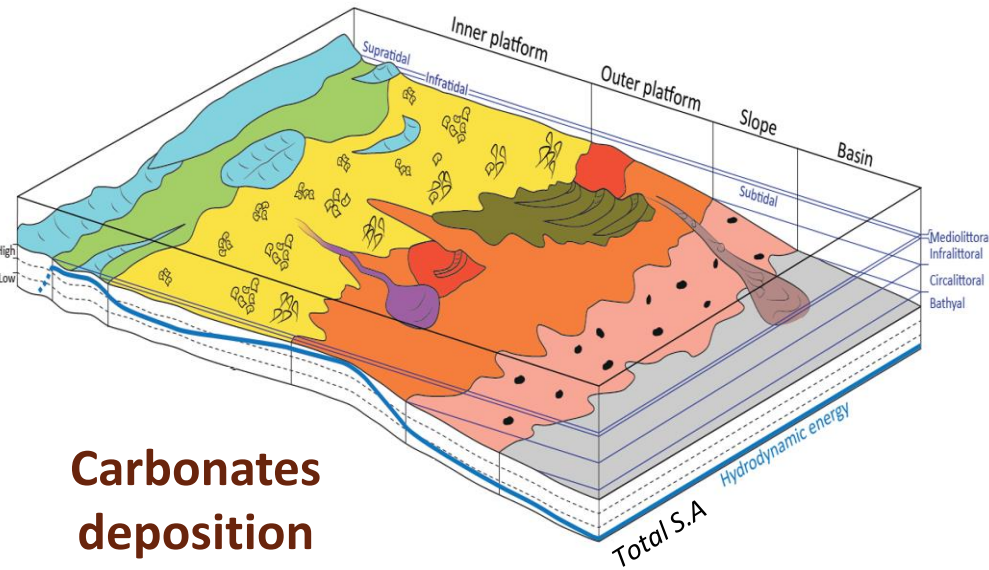


Diagenetic variability

# From carbonated platform to karst aquifer

**Karstification**

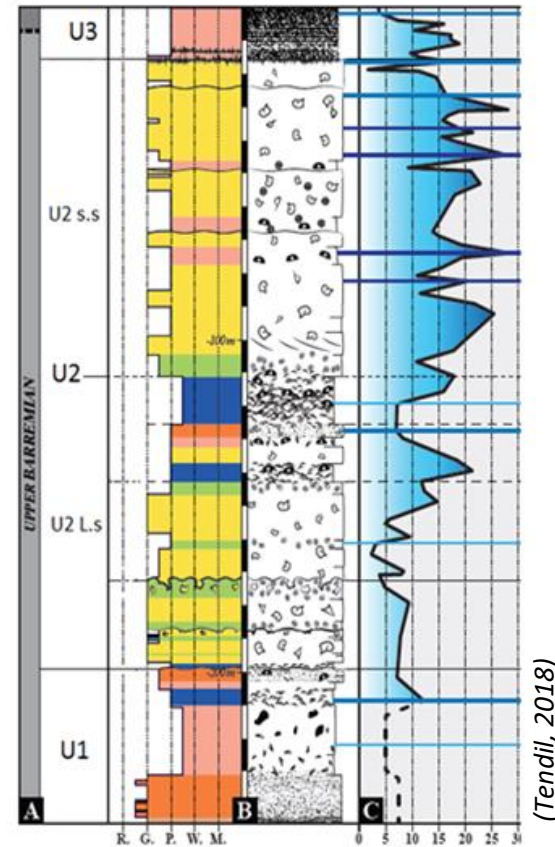
**Diagenesis**



**Carbonates deposition**

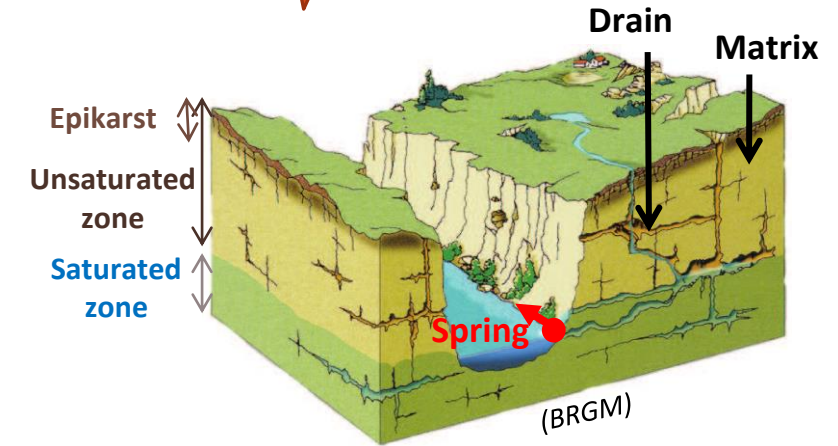
Variability of carbonate sediments

Texture Lithology Porosity (%)



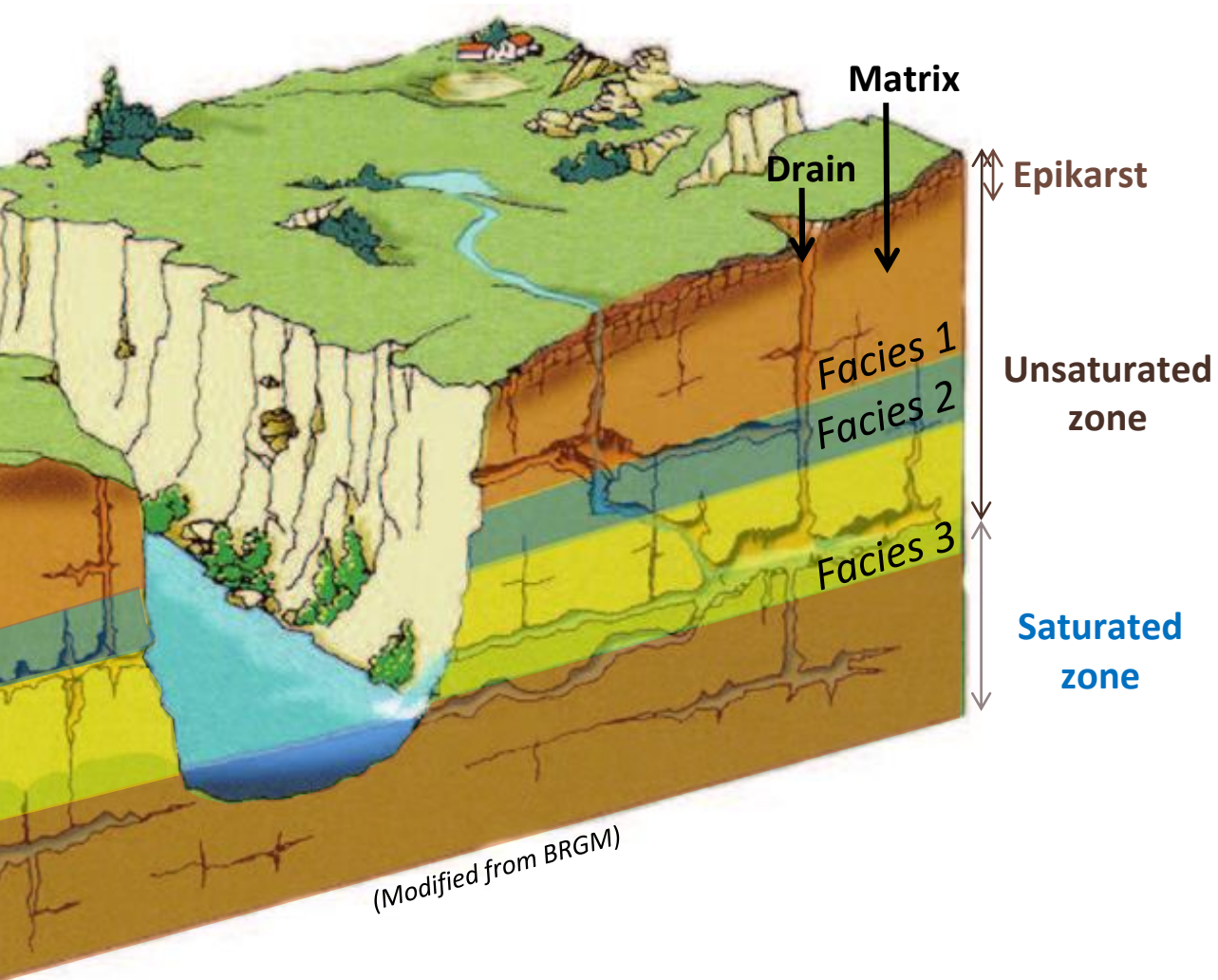
(Tendil, 2018)

Diagenetic variability

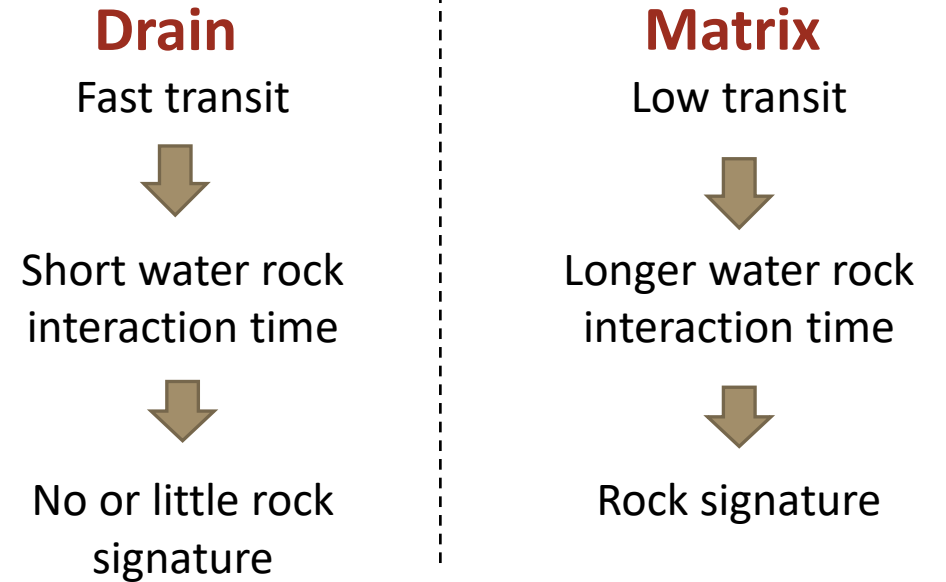


Hydrodynamic and hydrochemical variability of flows in unsaturated zone

# Aim of the study

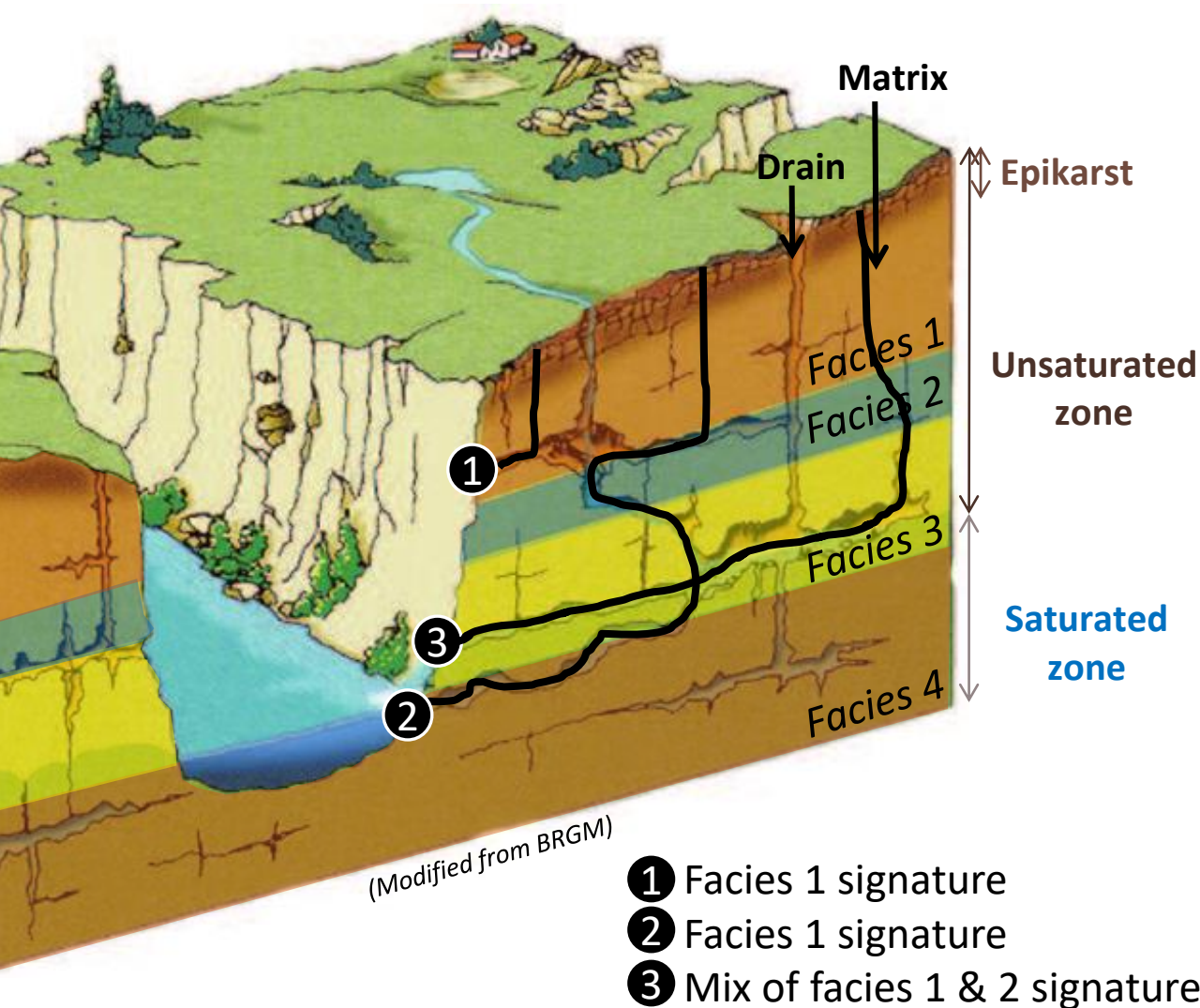


## Path taken by water





# Aim of the study



## Path taken by water

### Drain

Fast transit



Short water rock  
interaction time



No or little rock  
signature

### Matrix

Low transit

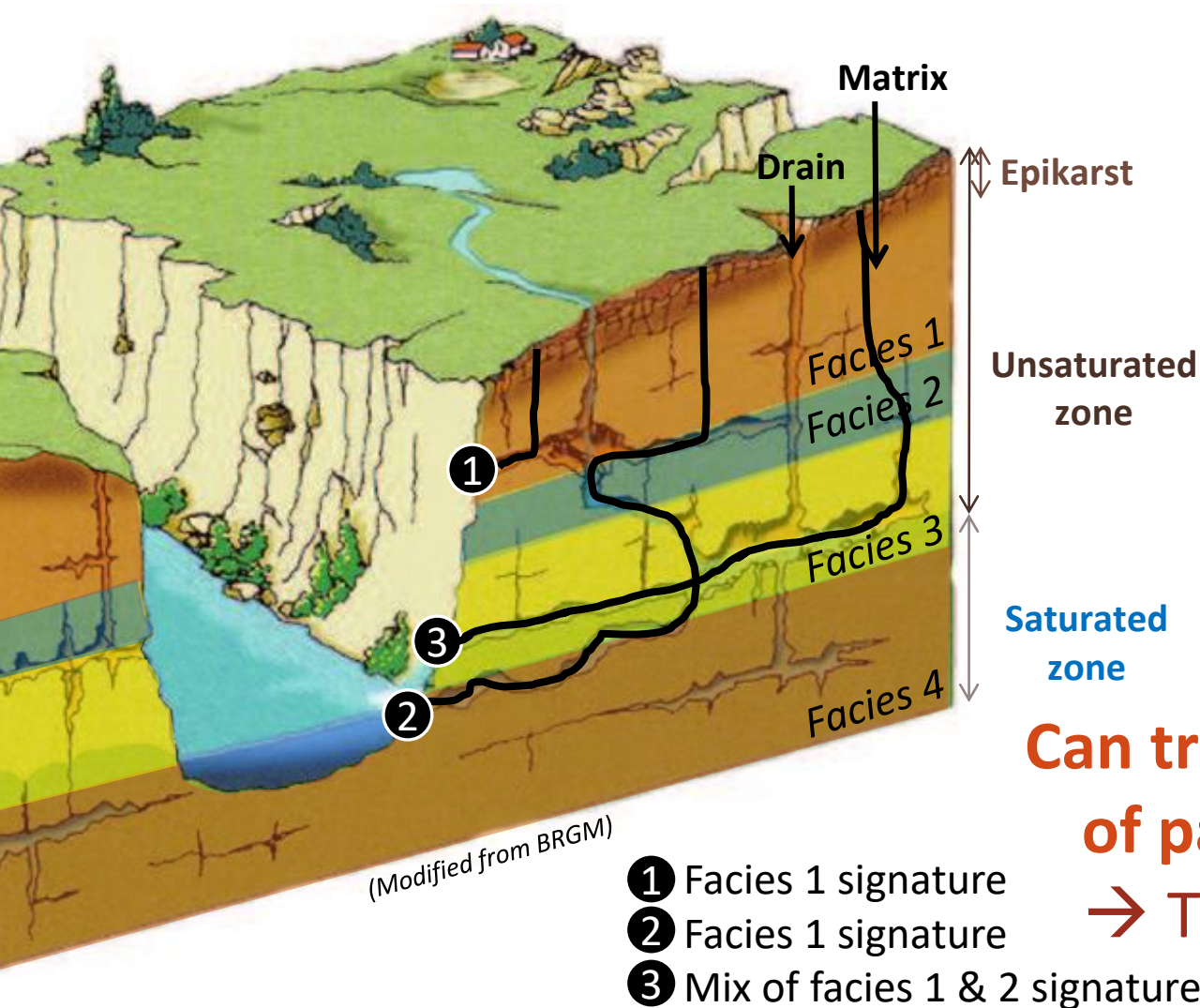


Longer water rock  
interaction time

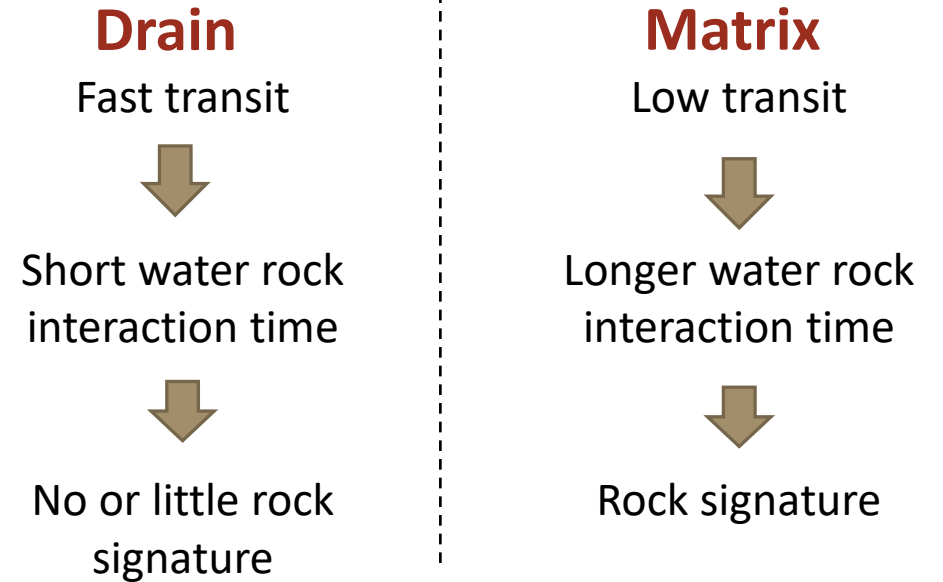


Rock signature

# Aim of the study



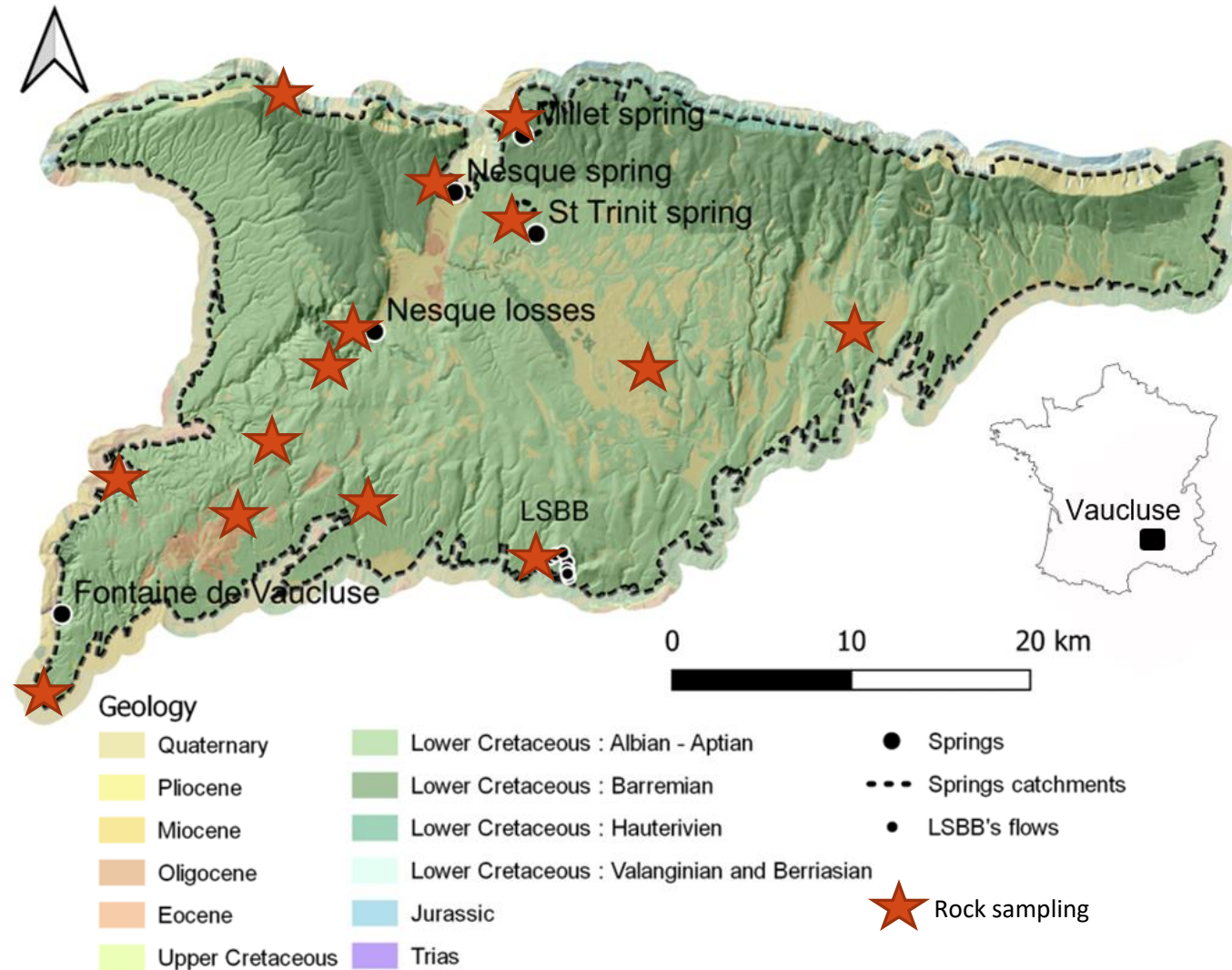
## Path taken by water



**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 km<sup>2</sup> *Ollivier, 2020*
- Aquifer thickness up to 1500m
- Unsaturated zone average thickness 800m

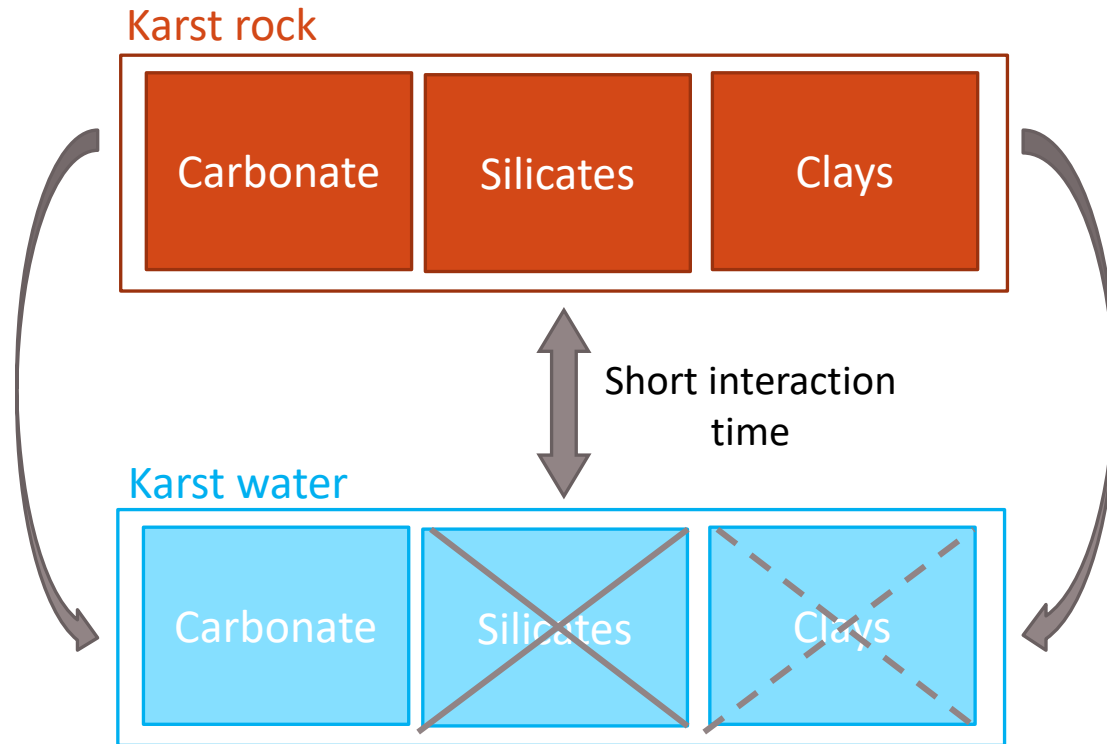
## Rock sampling

- 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?*

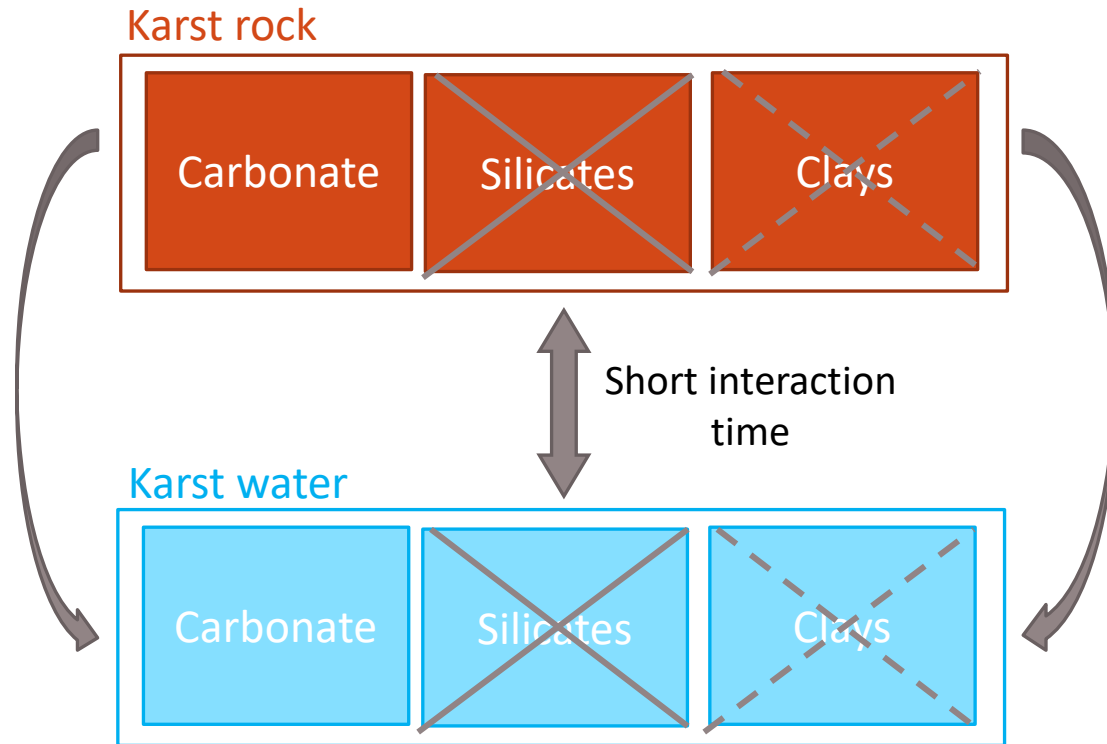


## Water-rock interaction

- 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

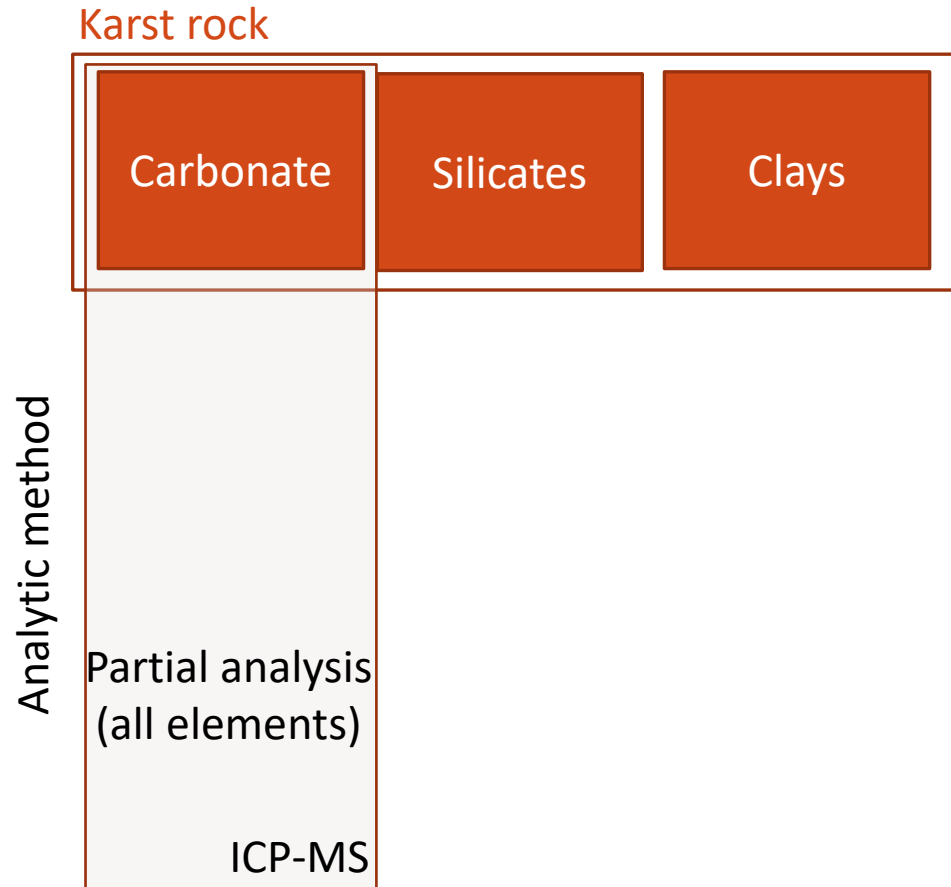
- Fast reacting system = short storage duration (few years max)
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- Clays have large water-rock interaction surface
- Major impact of carbonate dissolution

## 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?*

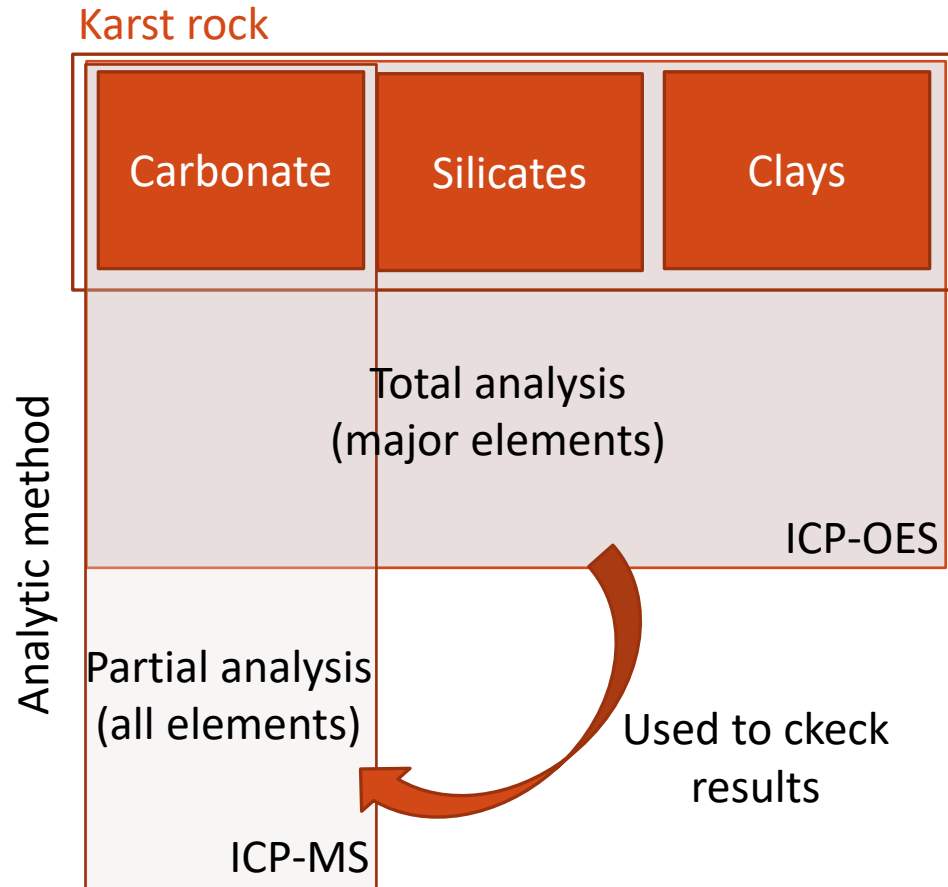


## Analytic method development

- 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

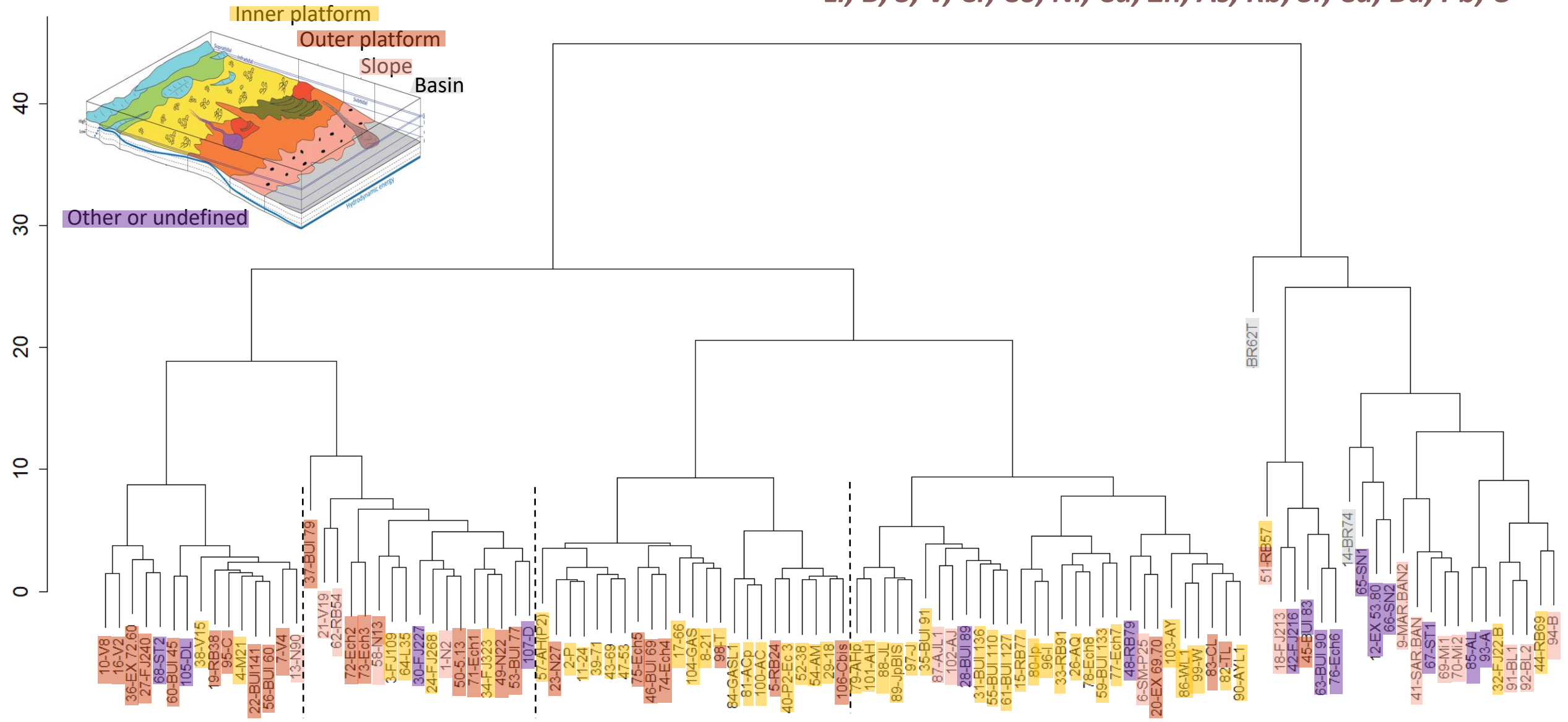
- Use of hydrochloric acid 0.15 M to avoid silicates dissolution (molarity < 0.18 M *Bastian et al., 2018*)
- Carbonated fraction of all samples analysed for all Mendeleïev tab by ICP-MS

## 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

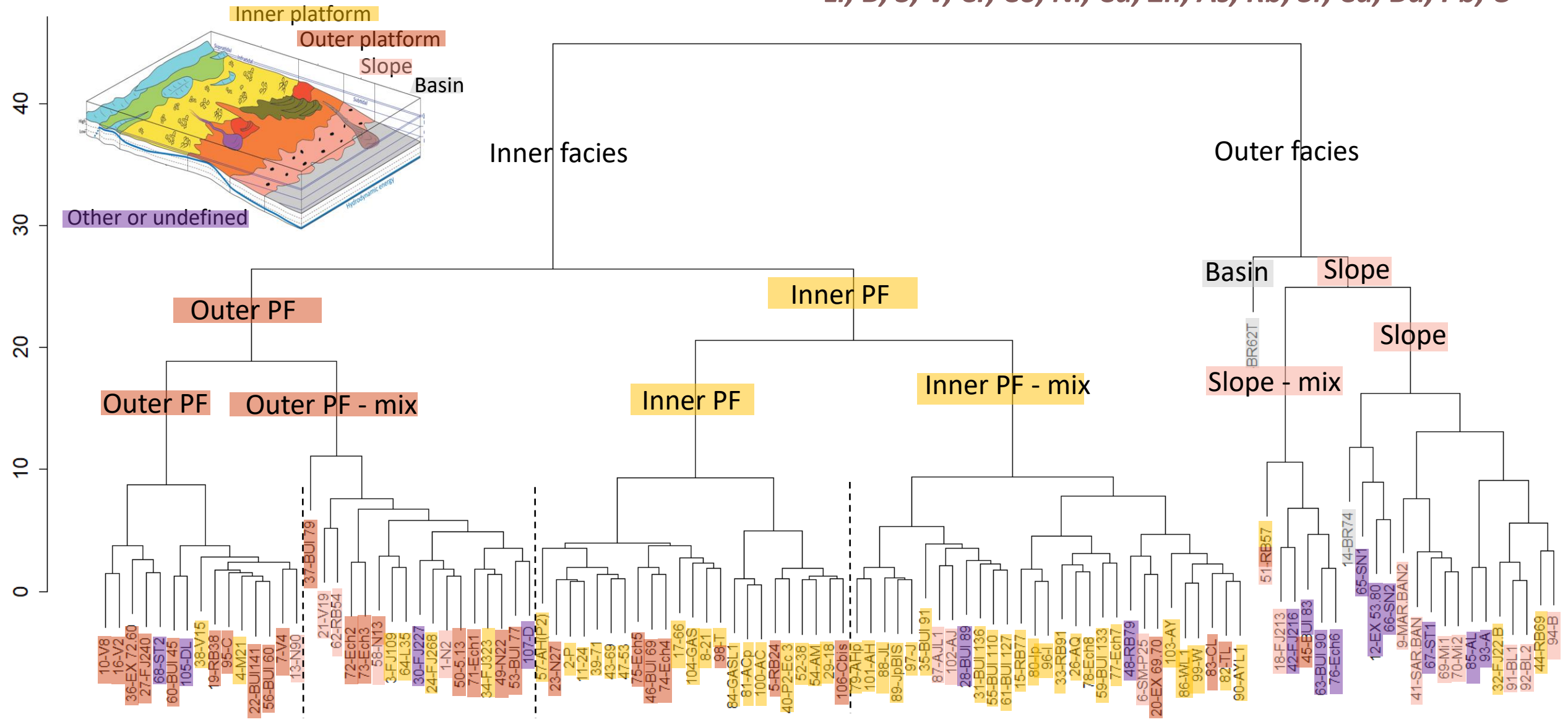
*Hierarchical clustering with 16 trace elements :  
Li, B, S, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Cd, Ba, Pb, U*





# Clustering of rock samples

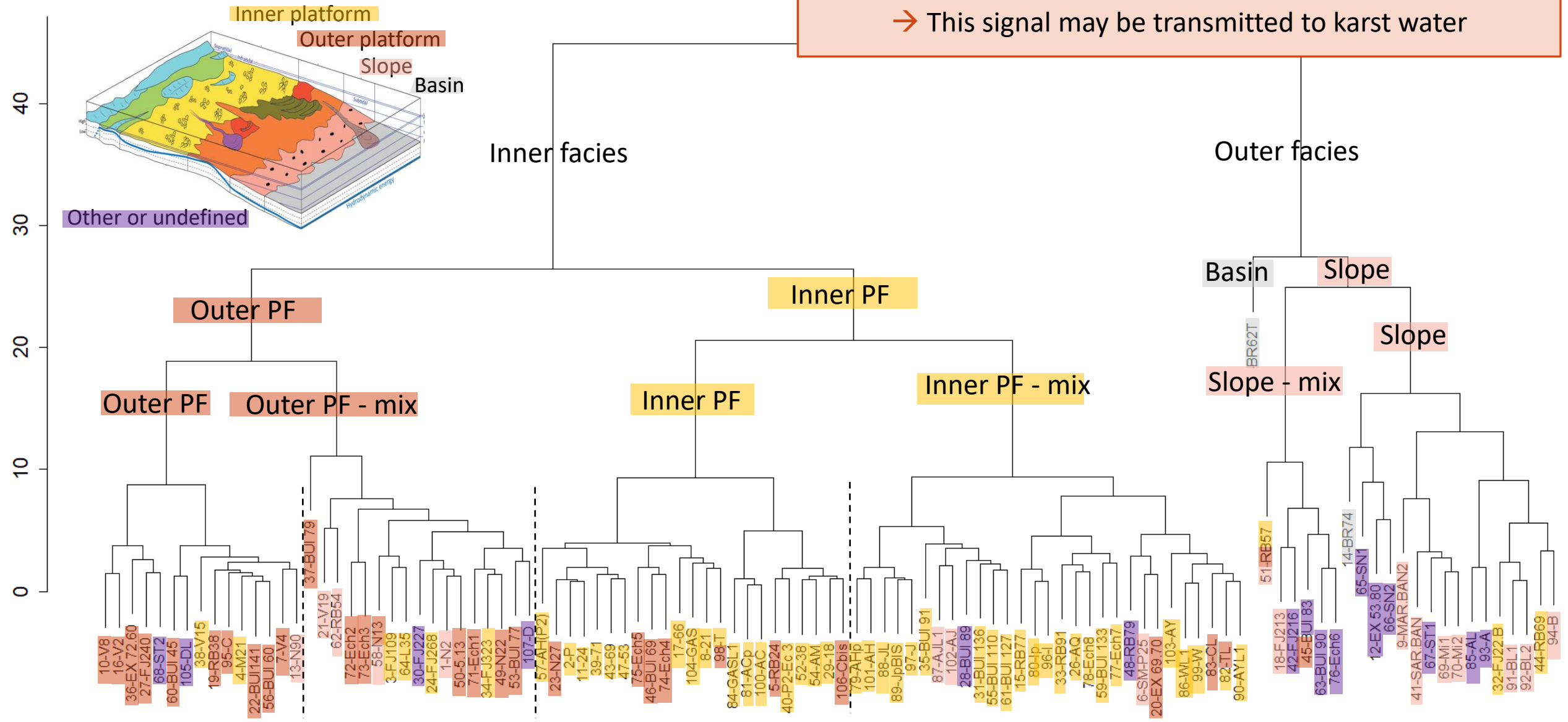
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# Clustering of rock samples

Clear link between clustering and deposit environments

→ This signal may be transmitted to karst water



# Conclusions & perspectives

## Karst rock

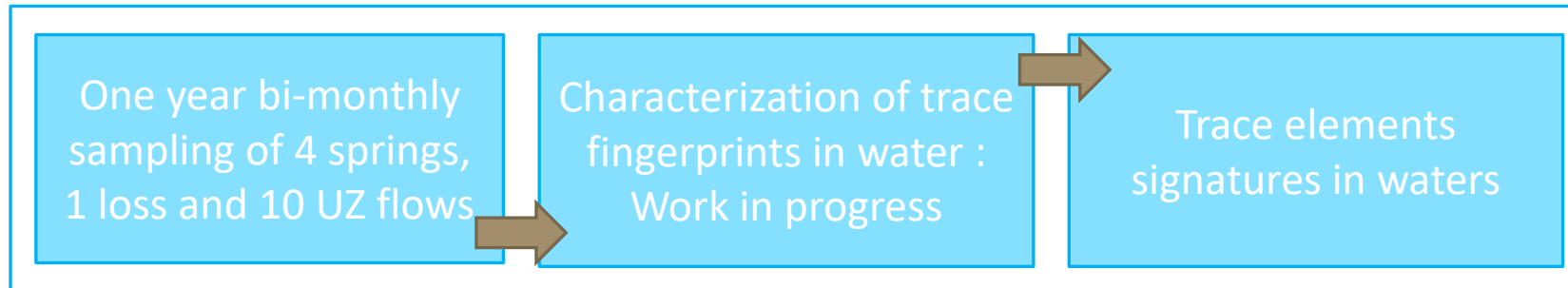


# Conclusions & perspectives

## Karst rock



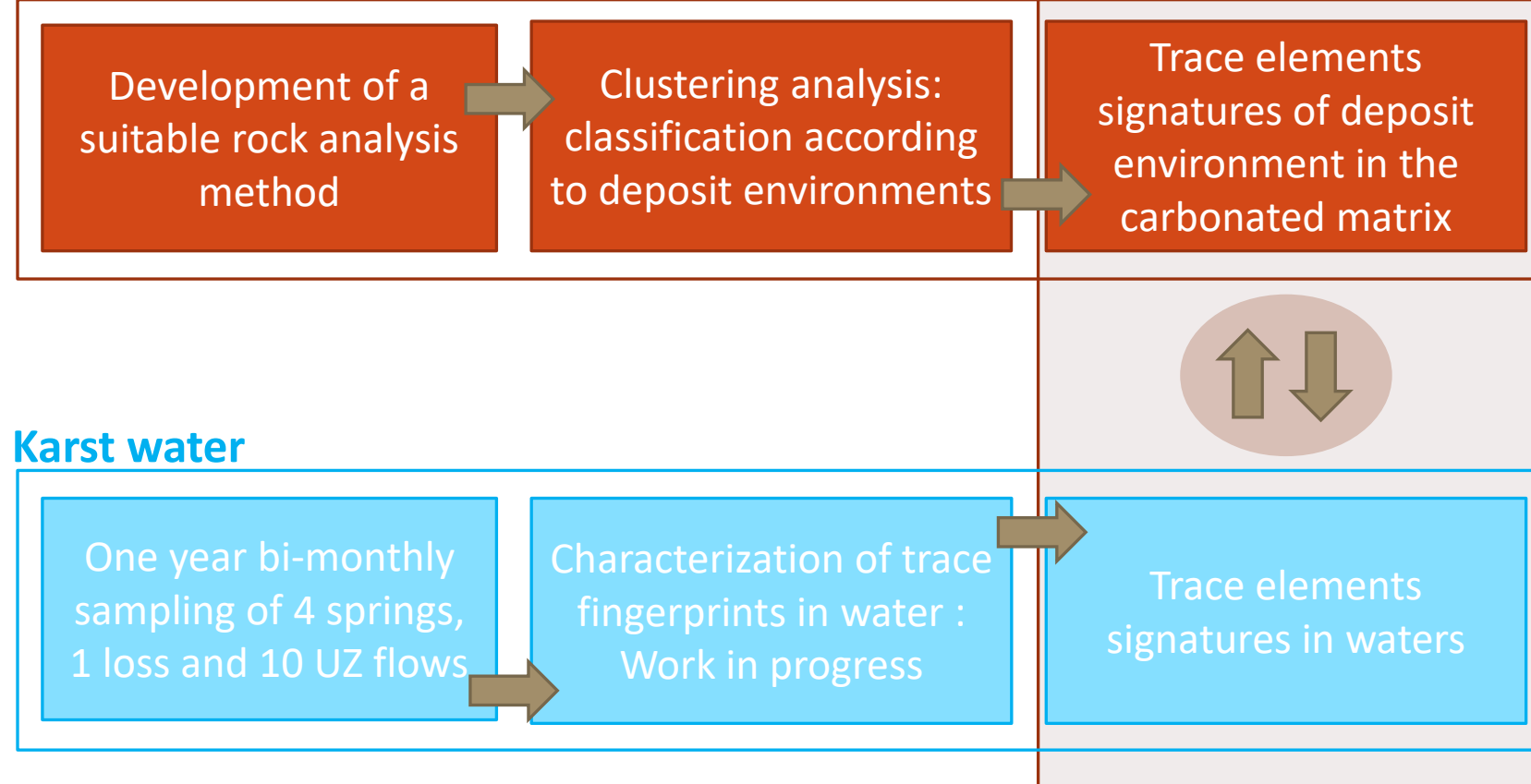
## Karst water



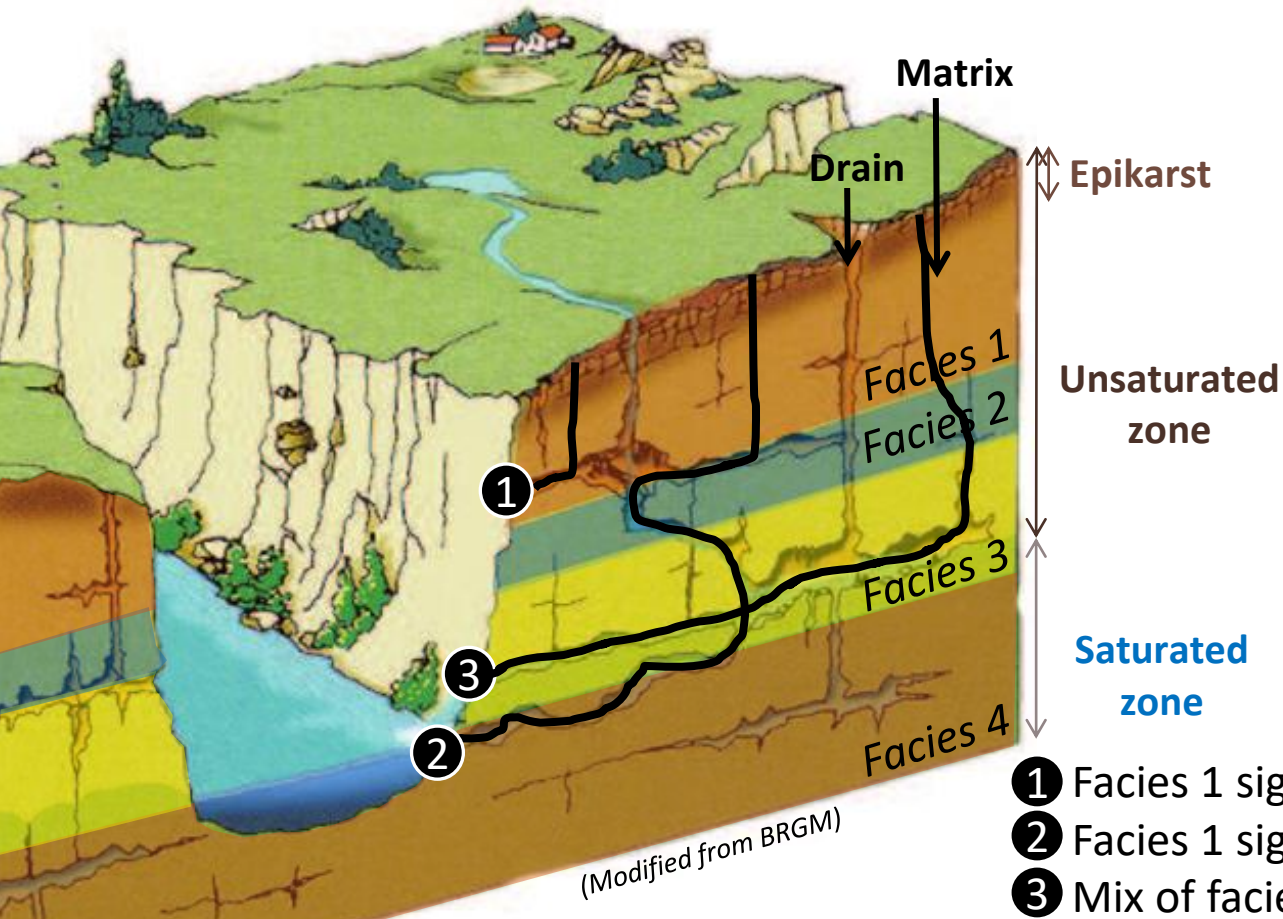


# Conclusions & perspectives

## Karst rock



# 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  $\mu\text{m}$
- 5/ Evaporate at 70°C - lasts 2-3 days
- 6/ Add 15mL of HNO<sub>3</sub> 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**