Modern activity and ancient signatures preserved by metals in microbial mats of lake environments

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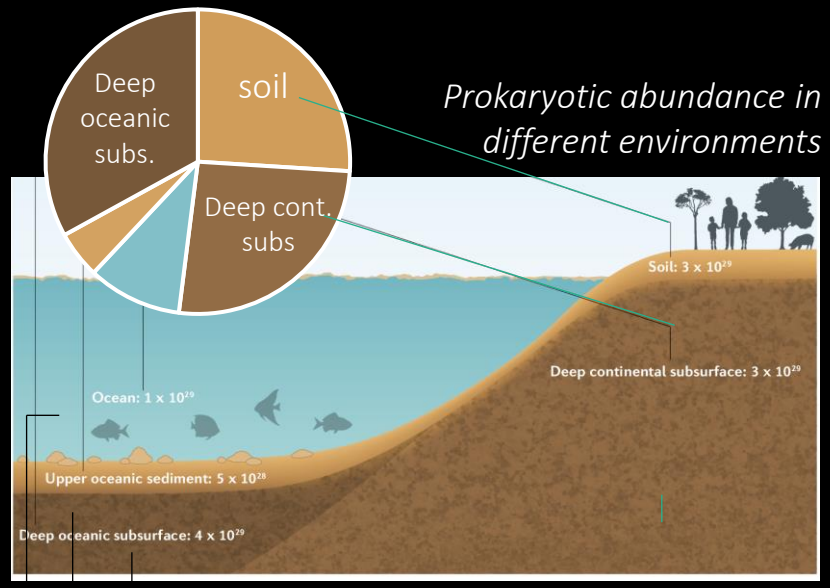
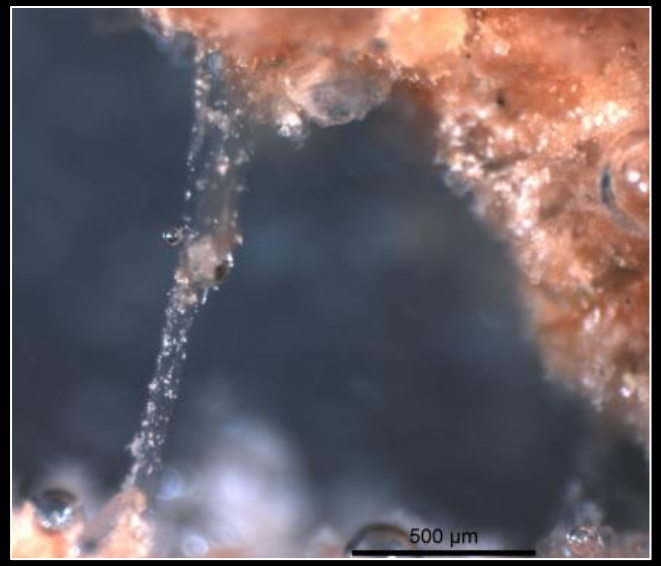
Fonds national suisse

Current microbial life and its environment

80 % in the geosphere, et 80% in biofilms and EPS :
biofilms are among the first macrotraces of life on Earth



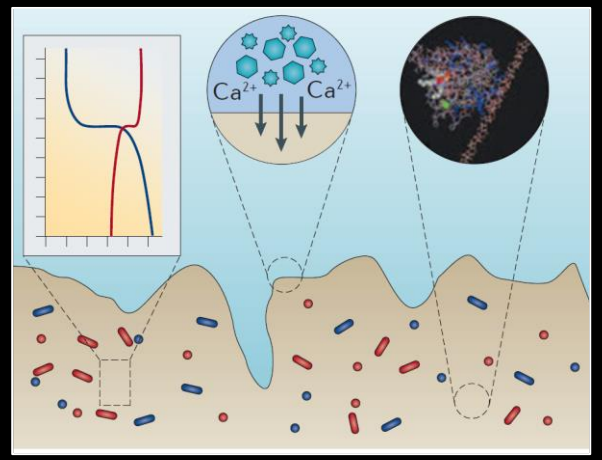
Flemming & Wuerzt, 2019 *Nature Microbiology Reviews*



Exopolymeric substanes : Thomas et al., 2015

Microbial mat of the Dead Sea

Lepot 2020 Earth Science Reviews



Flemming et al., 2016 *Nature Microbiology Reviews*

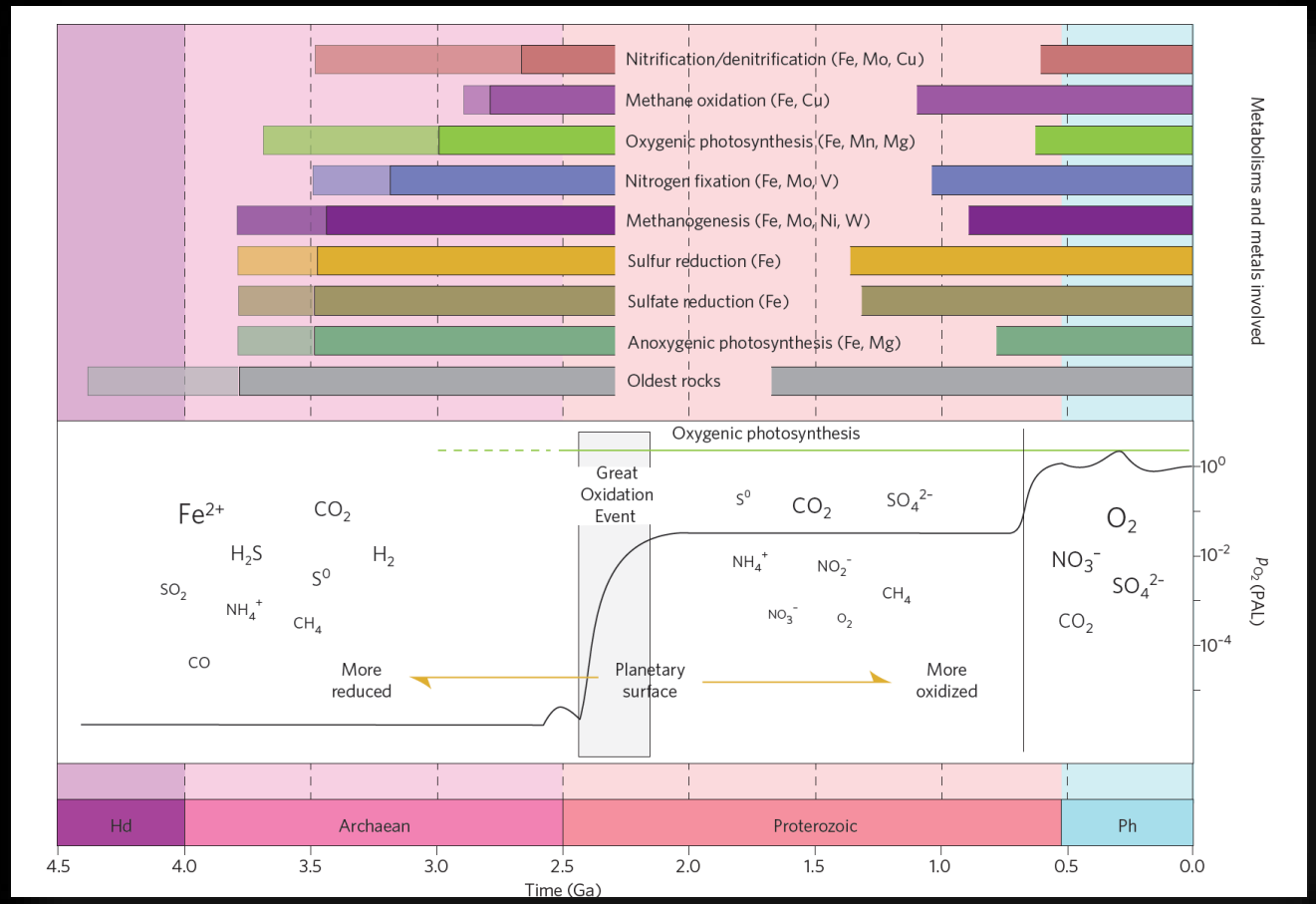
EPS

EPS passively retain elements and harbour intense microbial processes actively cycling metals

Can this metal enrichment be preserved with time ?

Metals as biosignatures : Microbial cycling and enzymatic specificity (including oxydoreductase)

Concept of metallomes for recognizing ancient metabolic activity



Moore et al., 2018 *Nature Geosciences*

Is this recorded in the Archean geological record : OM clots, microbial mats and stromatolites ?

Possibly but not always the case, and many factors may influence metal content in OM carbonates or organomineralizations.

(e.g. Sforna et al., 2014 ; Hickman-Lewis et al., 2020 ; Baumgartner et al., 2020 ; Sforna et al., 2016)

Case of the Dead Sea sinkhole system and its microbial mats (modern system to compare with archean one: Tumbiana lake)

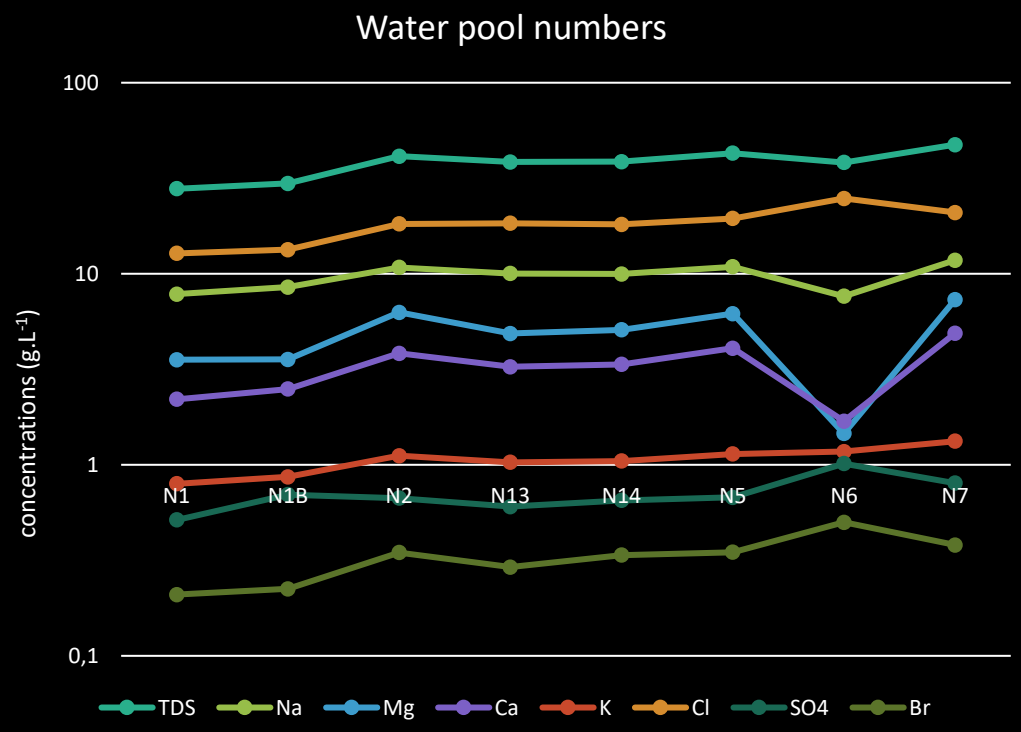
Landsat image

Sinkholes on the Dead Sea Eastern shore

Hypersaline system with microbial mats

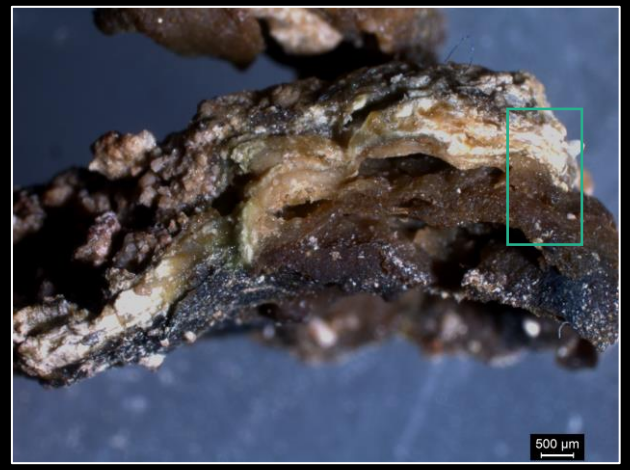
Approach
Dead Sea pools

- Bulk and in situ mapping of major and trace elements
- In situ autofluorescence of microbial mat
- DNA fingerprinting of each system
- Metagenomics to tackle specific metabolisms



Photosynthetic systems with formation of aragonite crusts and concretions

Pool 1 lamina and CaCO3 precipitations



$CaCO_3$ concretion Pool 1

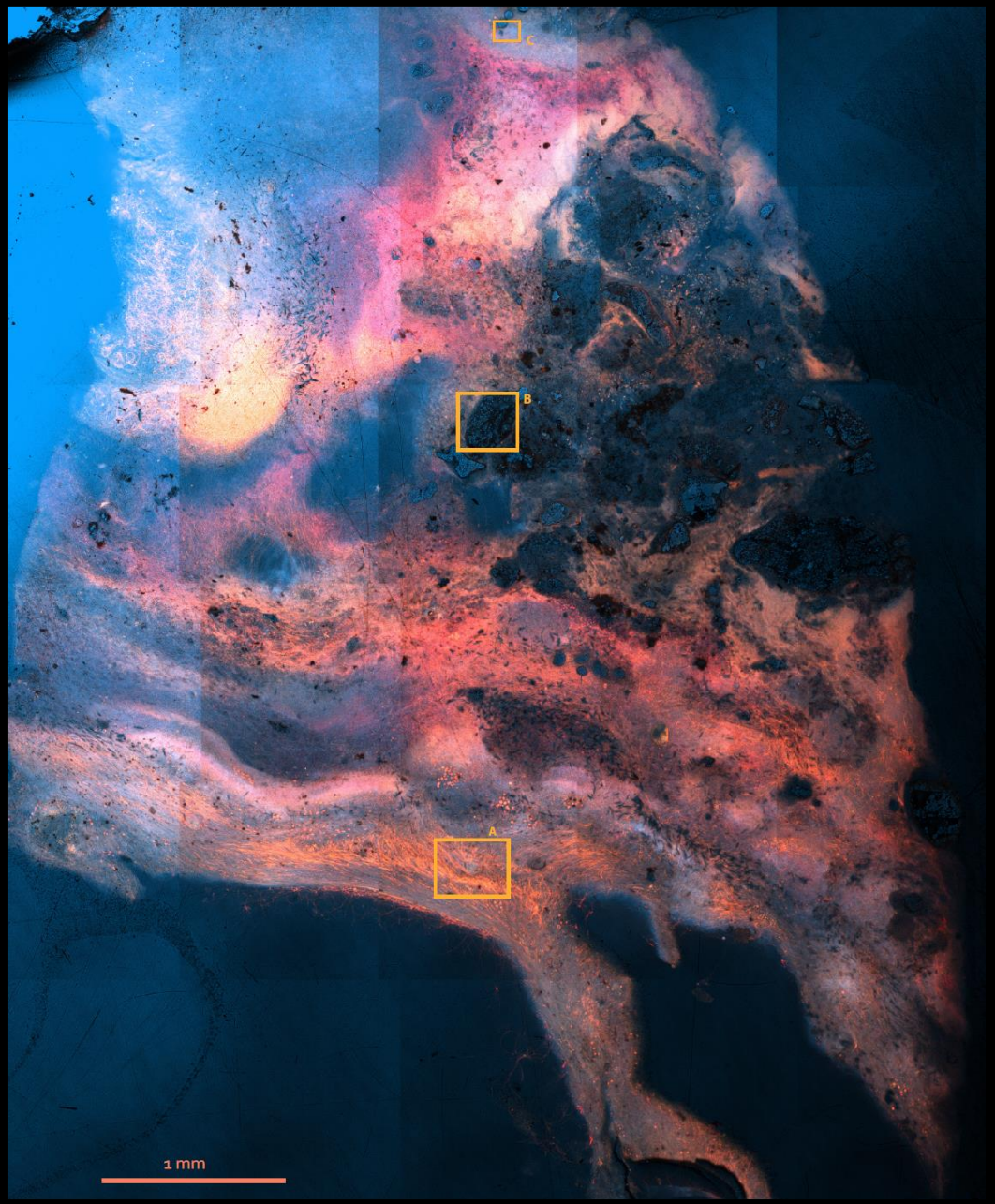
selected zone for in situ imaging

Pool 1 mineralized mat close-up

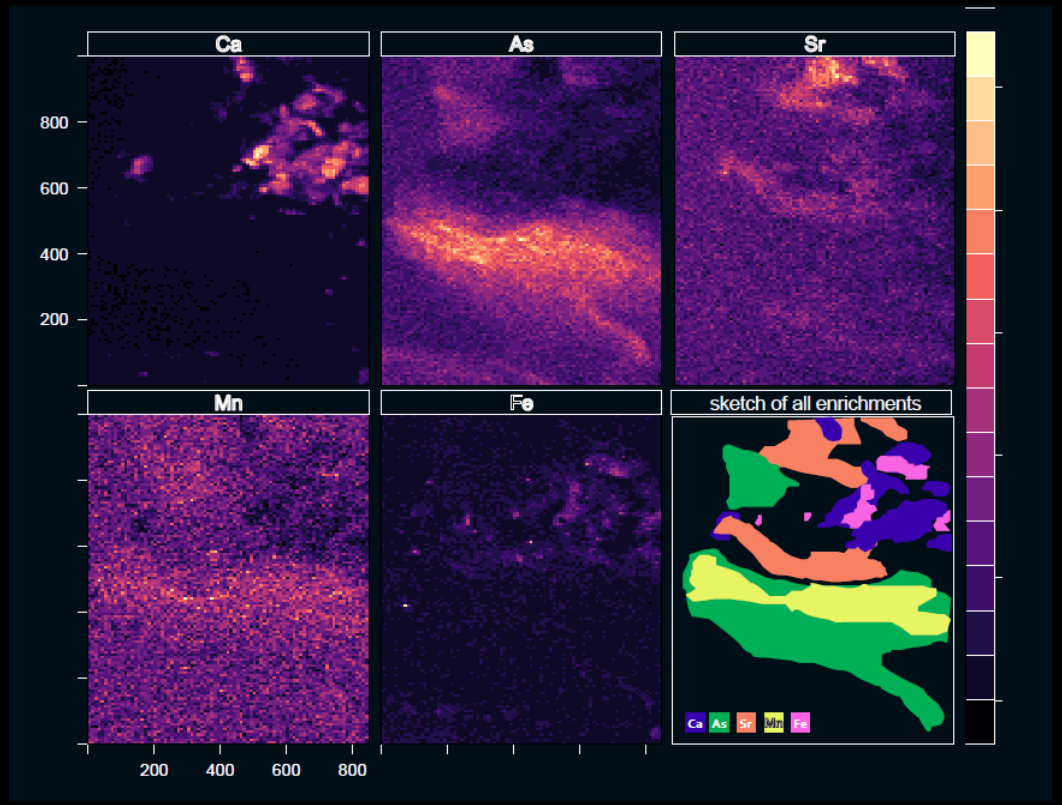
Pool 2 purple bacteria

Pool 6 mat crust

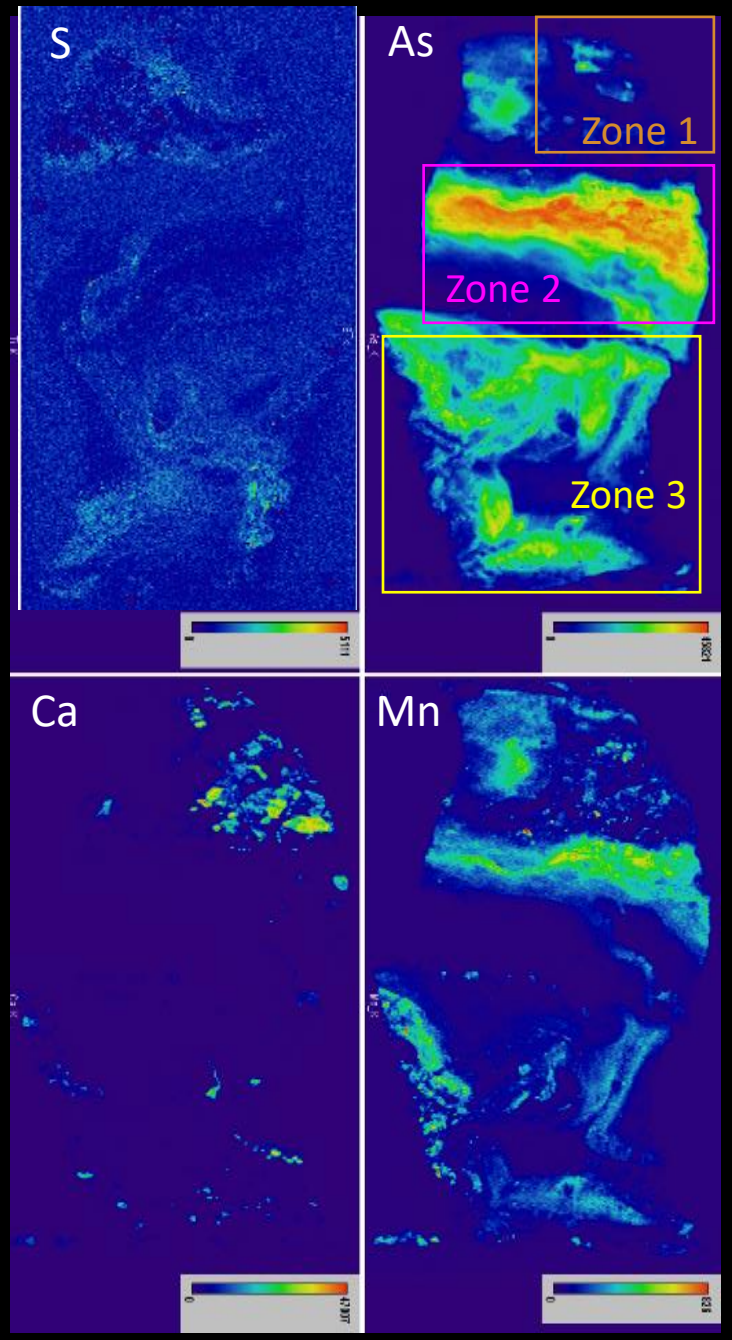
Epifluorescence microscopy and µXRF mapping of pool 1 mat



Auto-fluorescence microscopy image of the pool 1 microbial mat (DAPI + Rodamine filters, no staining)

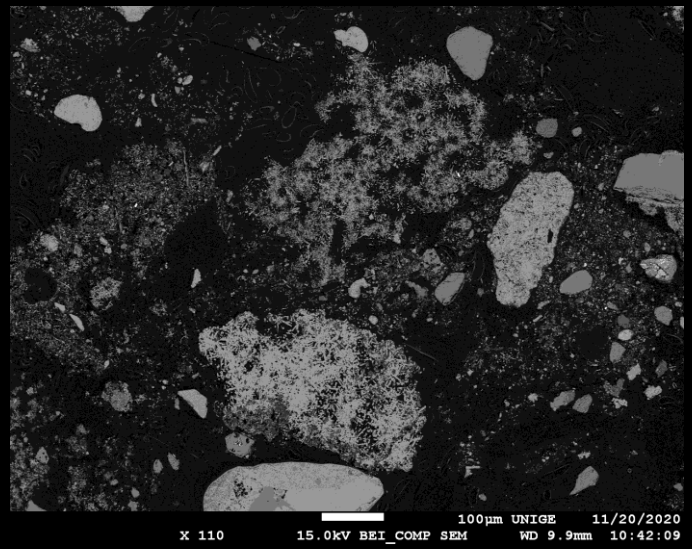


µXRF mapping showing $CaCO_3$ precipitation zone and As enrichment zone

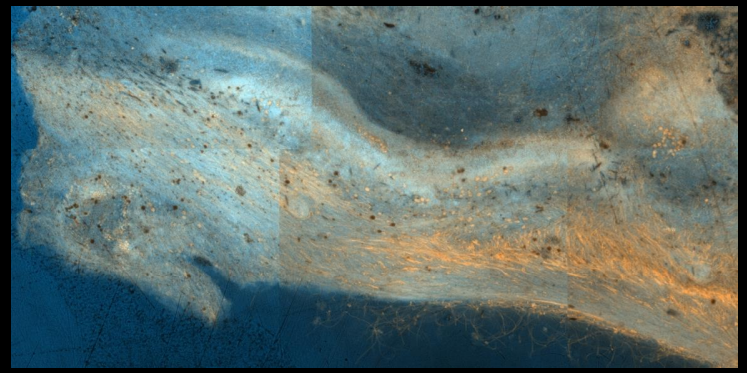


3 zones with different processes

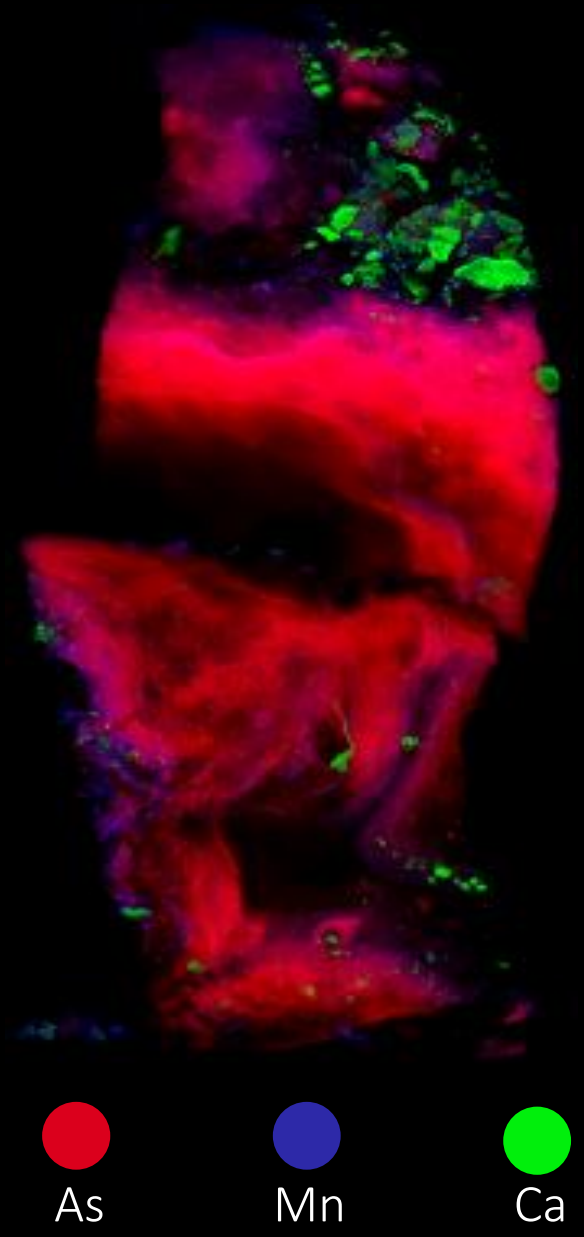
Zone 1 is authigenic carbonate-rich

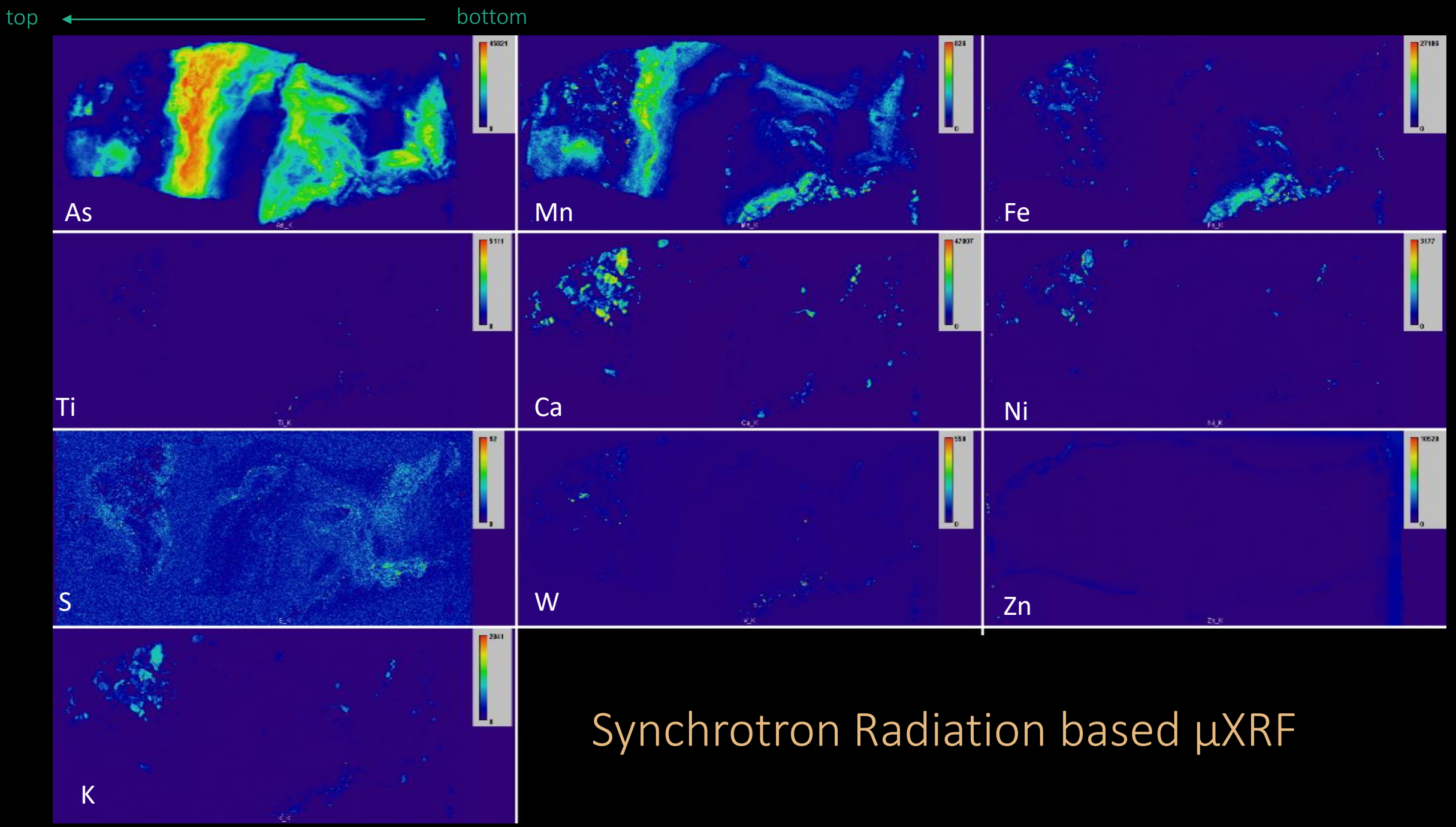


Zone 2 is As-rich and mineral poor. EPS mainly associated to Si and Mg (and As)



Zone 3 is the bottom of the mat, rich in arsenic, more S, less Mn. Secondary precipitation of $CaCO_3$

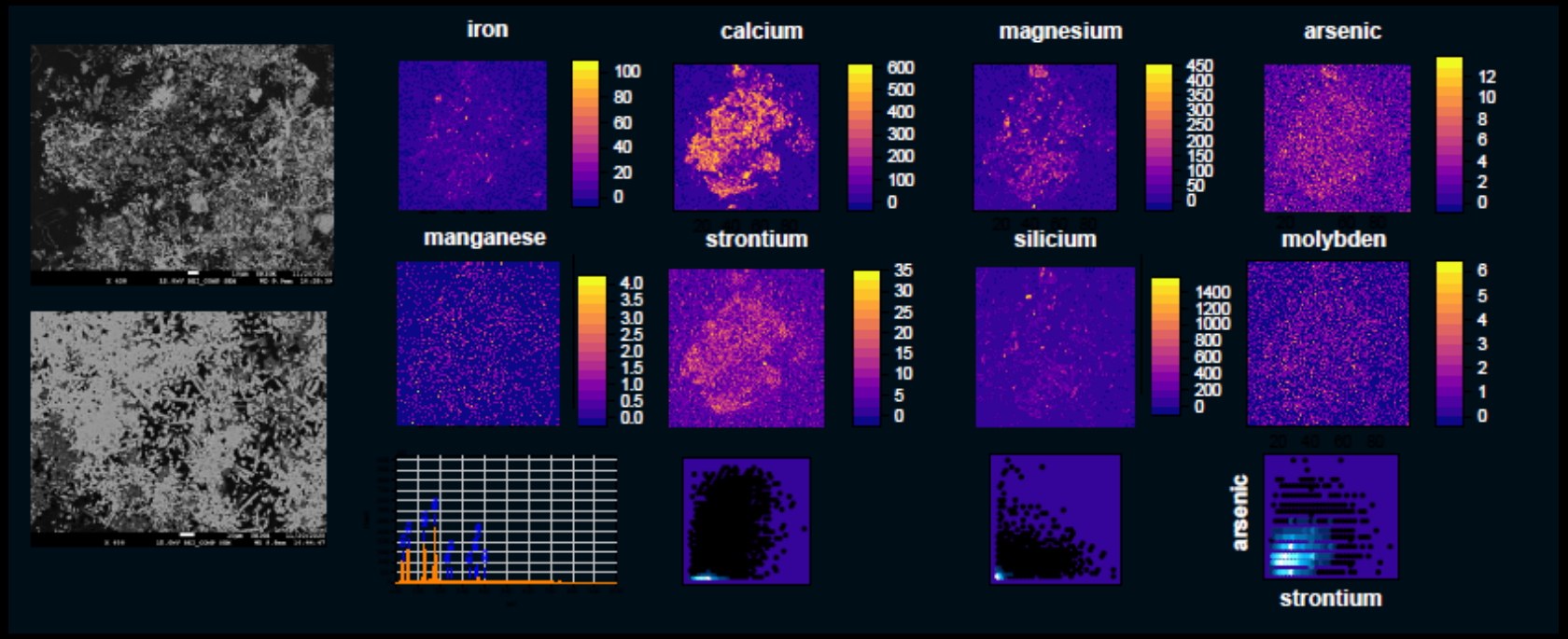


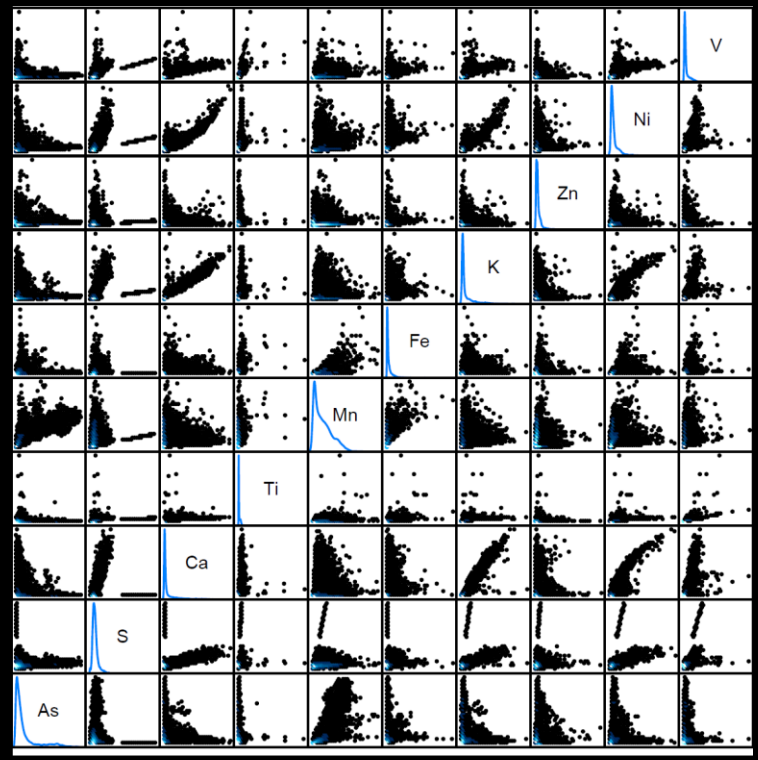


Synchrotron Radiation based µXRF

Zone 1 : authigenic carbonate-rich

Example 1

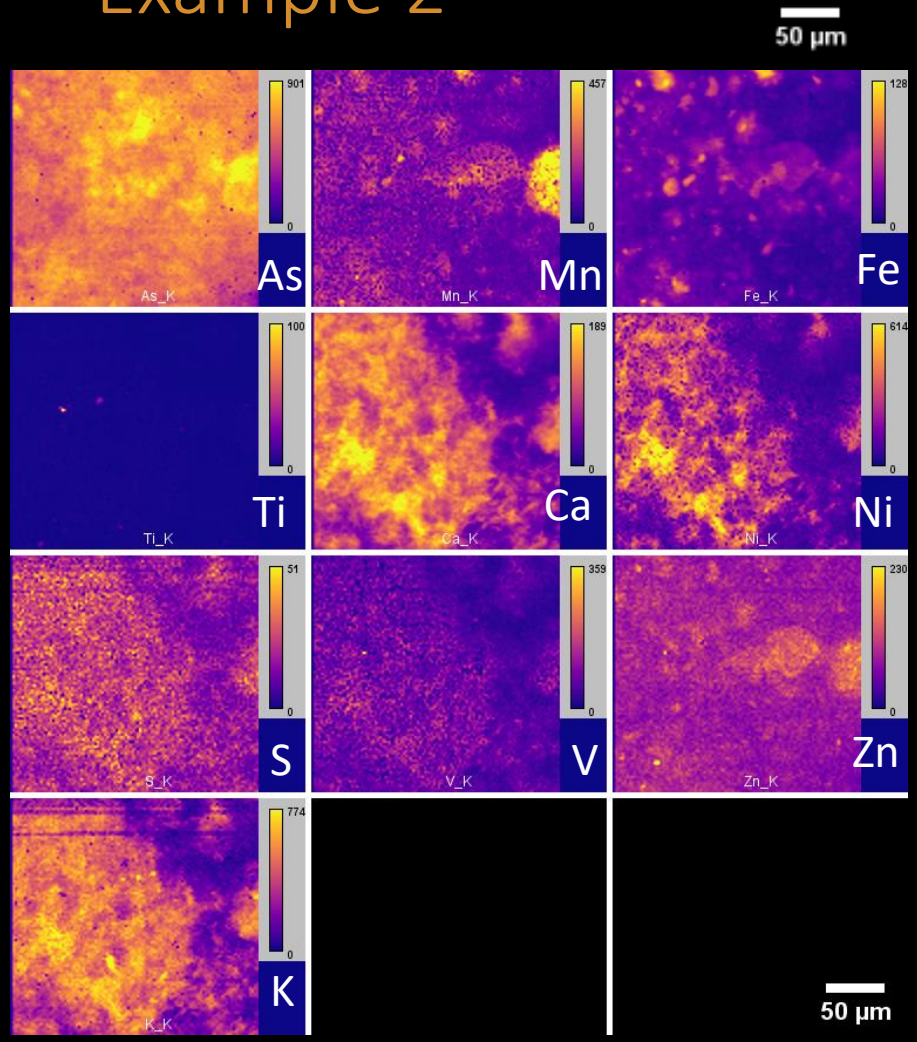


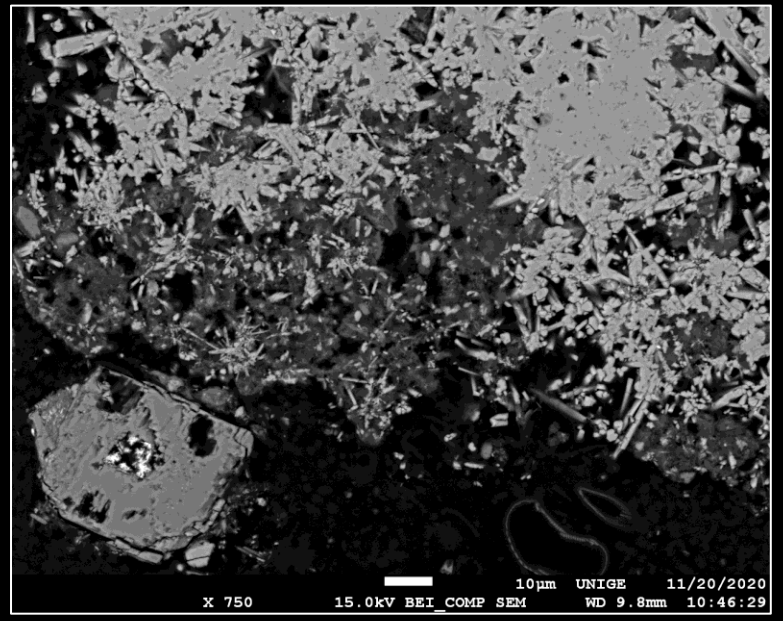


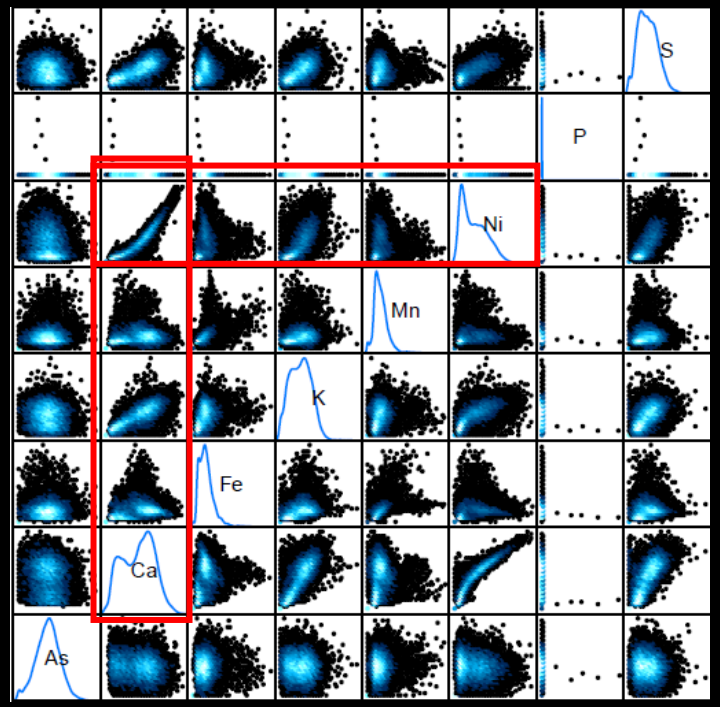
Aragonite needles (identified by Raman) precipitate in clusters from EPS matrix enriched in Mg and Si. As shows good correlation with Sr (marker of mineralized aragonite). Seems associated to mineral only (EPMA maps).

SR-µXRF supports relationship in this type of concretions between Ca and K and Ni. In some concretions, S or Zn might also associate to the concretions.

Example 2



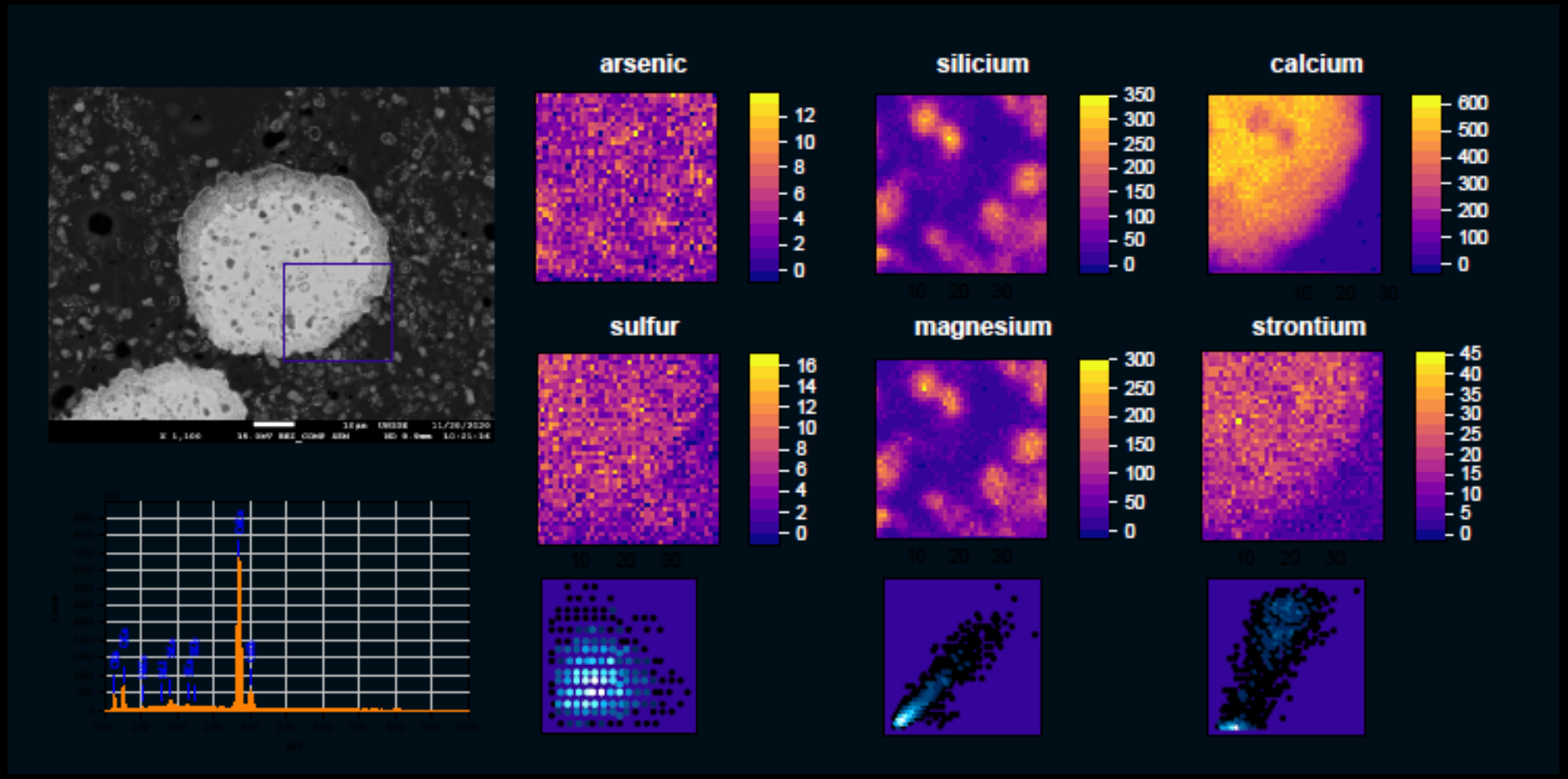




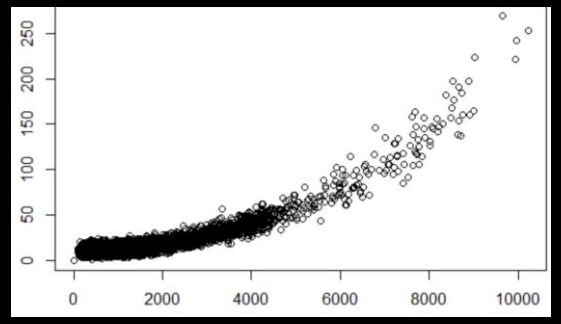
Carbonate show relationship with S, K and Ni, with progressive transformation of Mg-Si-rich EPS to well mineralized aragonite needles

Stage 1 : Mg + Si transitional phase
Stage 2 : As enriched in mineralizing phase, replacing Mg?
Stage 3 : K-Ni-rich aragonite needles

Example 3



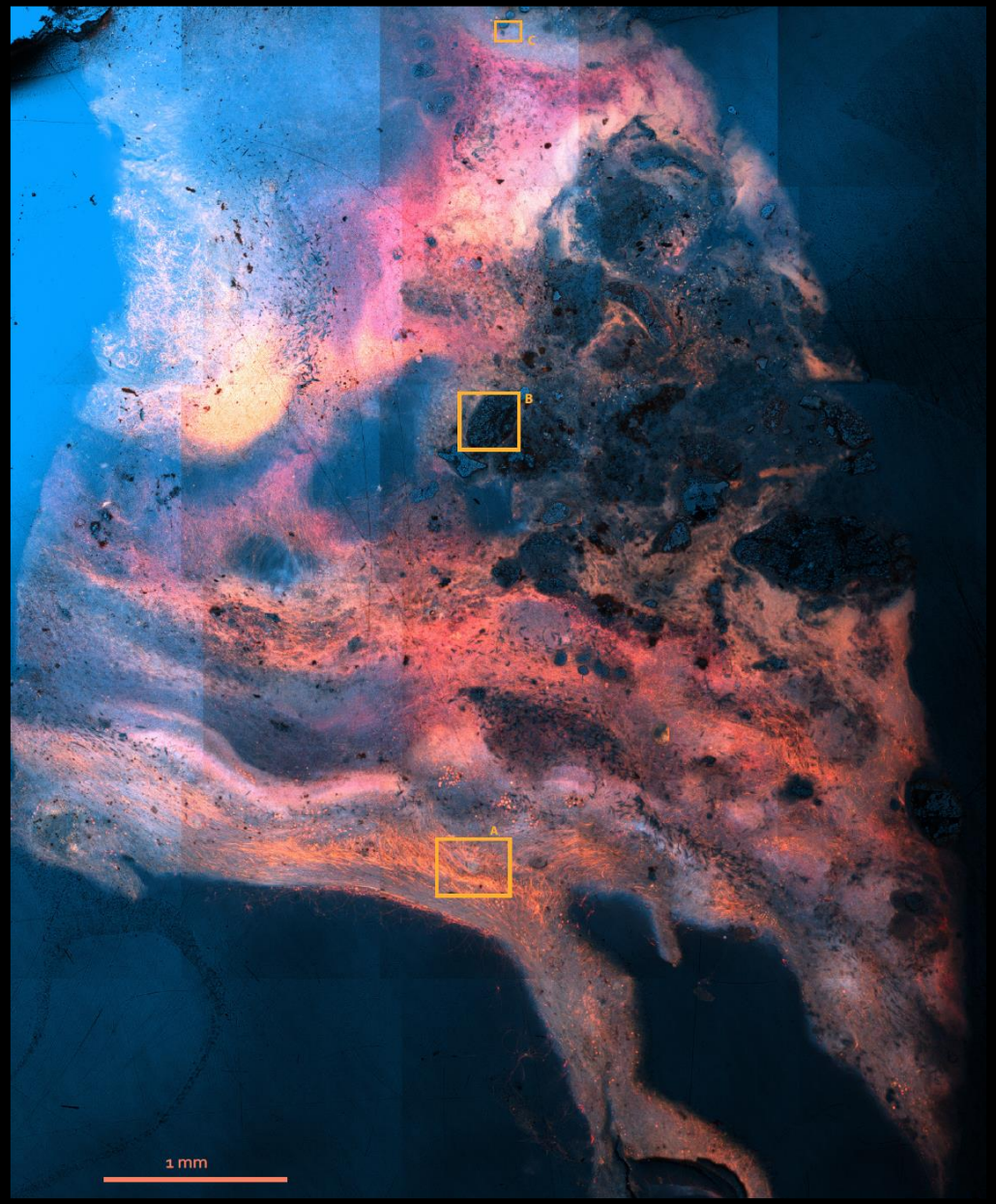
Ca vs Ni from µXAS mapping

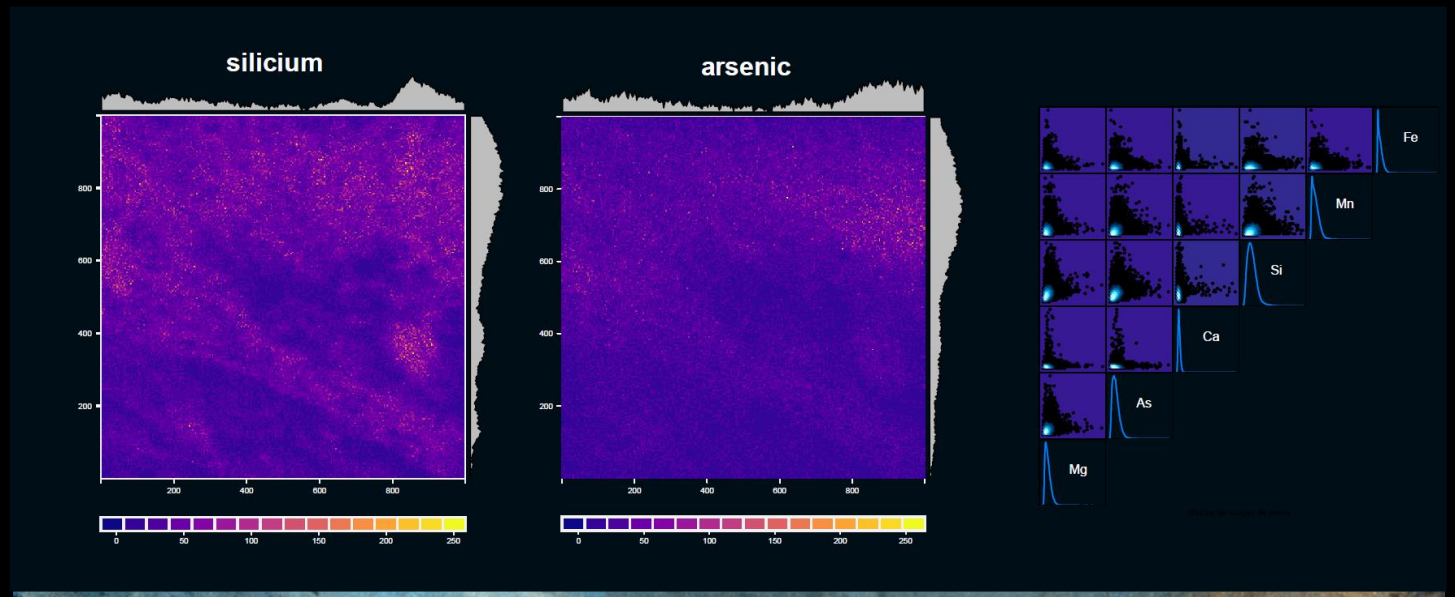


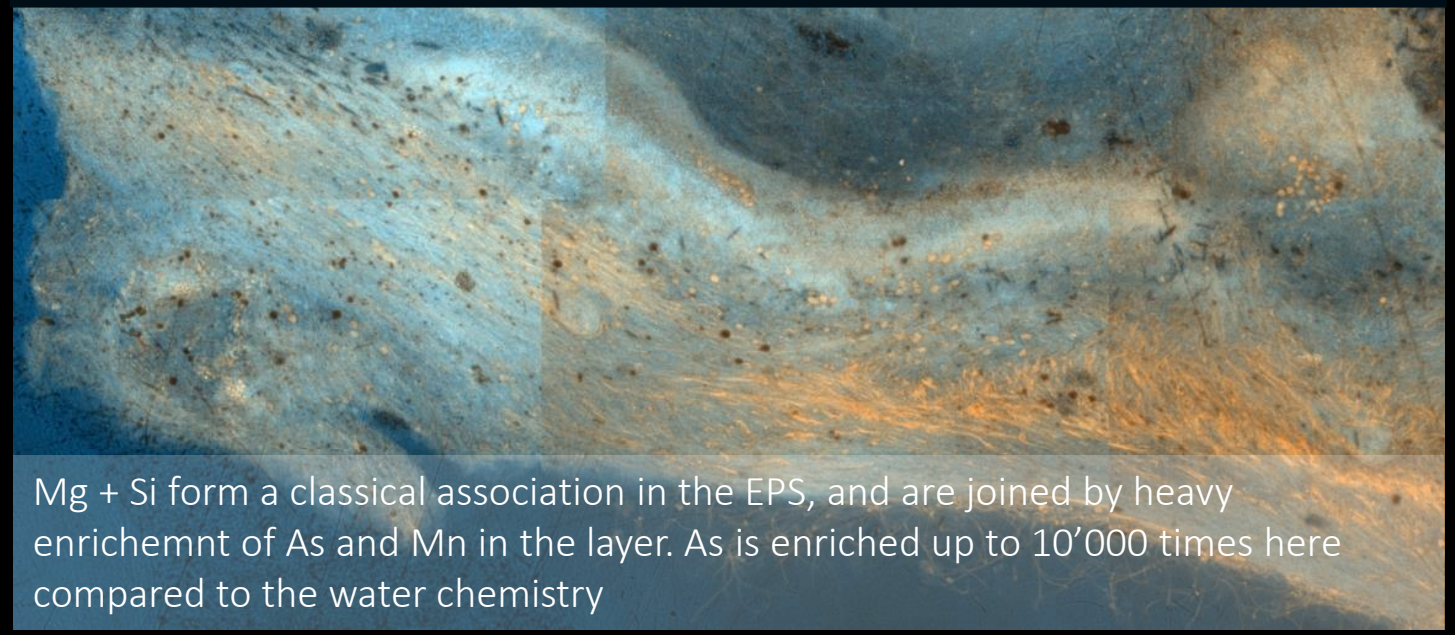
Exponential relationship ?

Mg-Si as transitional phase in EPS (observed from EPMA mapping).
Entrapped coccoid bacteria + Ni enrichment may support a rapid rise of alkalinity that could be provided by ureolytic activity.
Strong potential for Ni-enrichment of OM and carbonates by urease activity : Zhu et al., 2016

Zone 2 : arsenic-rich EPS, almost no $CaCO_3$



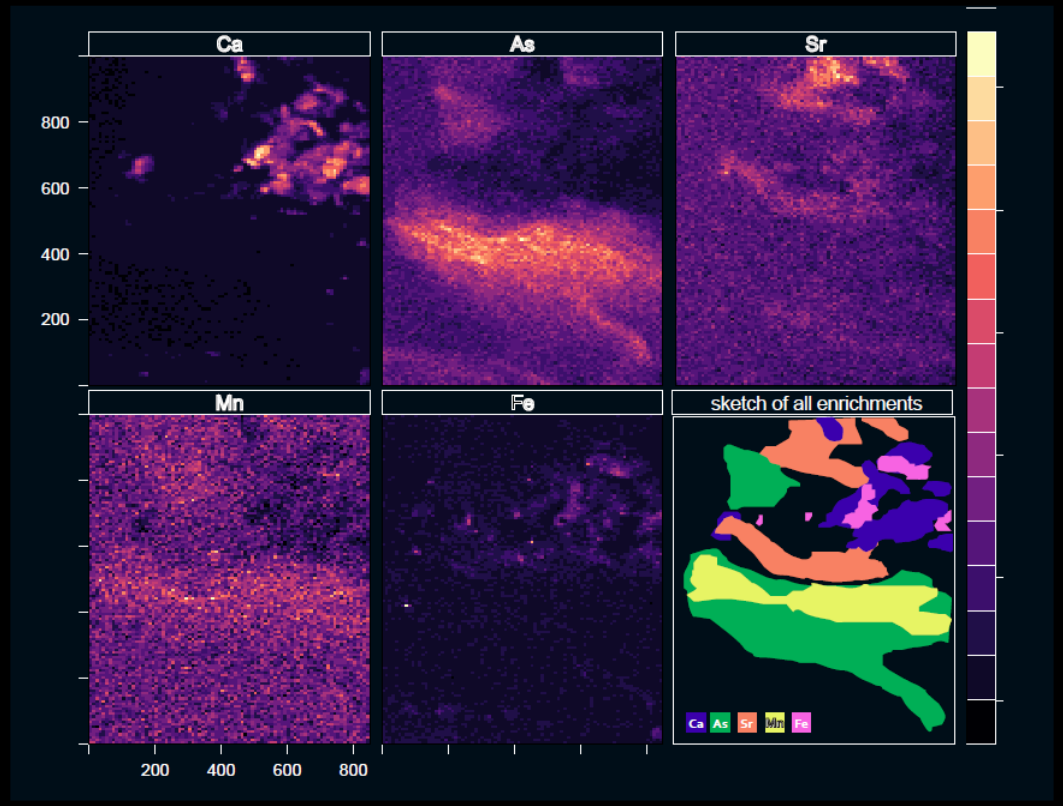


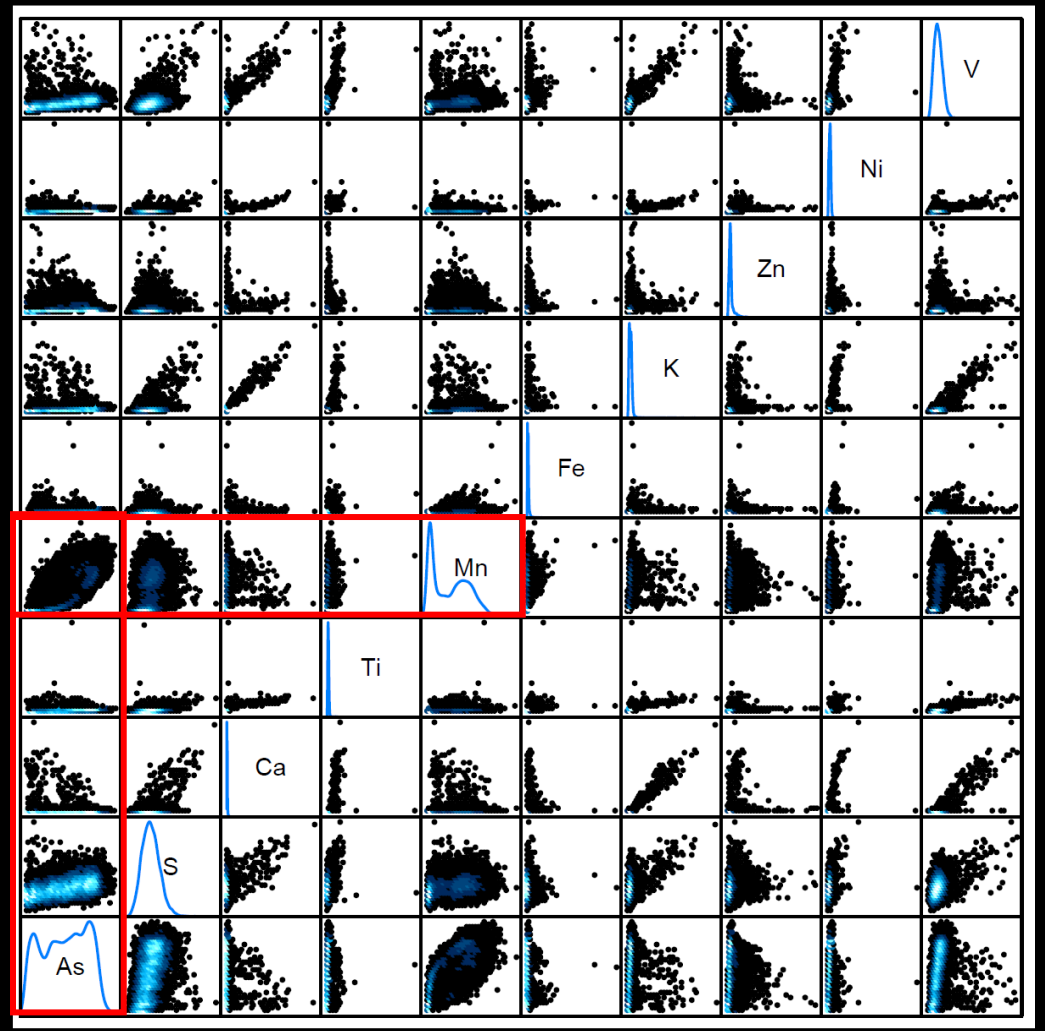


Mg + Si form a classical association in the EPS, and are joined by heavy enrichemnt of As and Mn in the layer. As is enriched up to 10’000 times here compared to the water chemistry

Zone 2 : arsenic-rich EPS, almost no $CaCO_3$ (after µXAS XRF mapping)

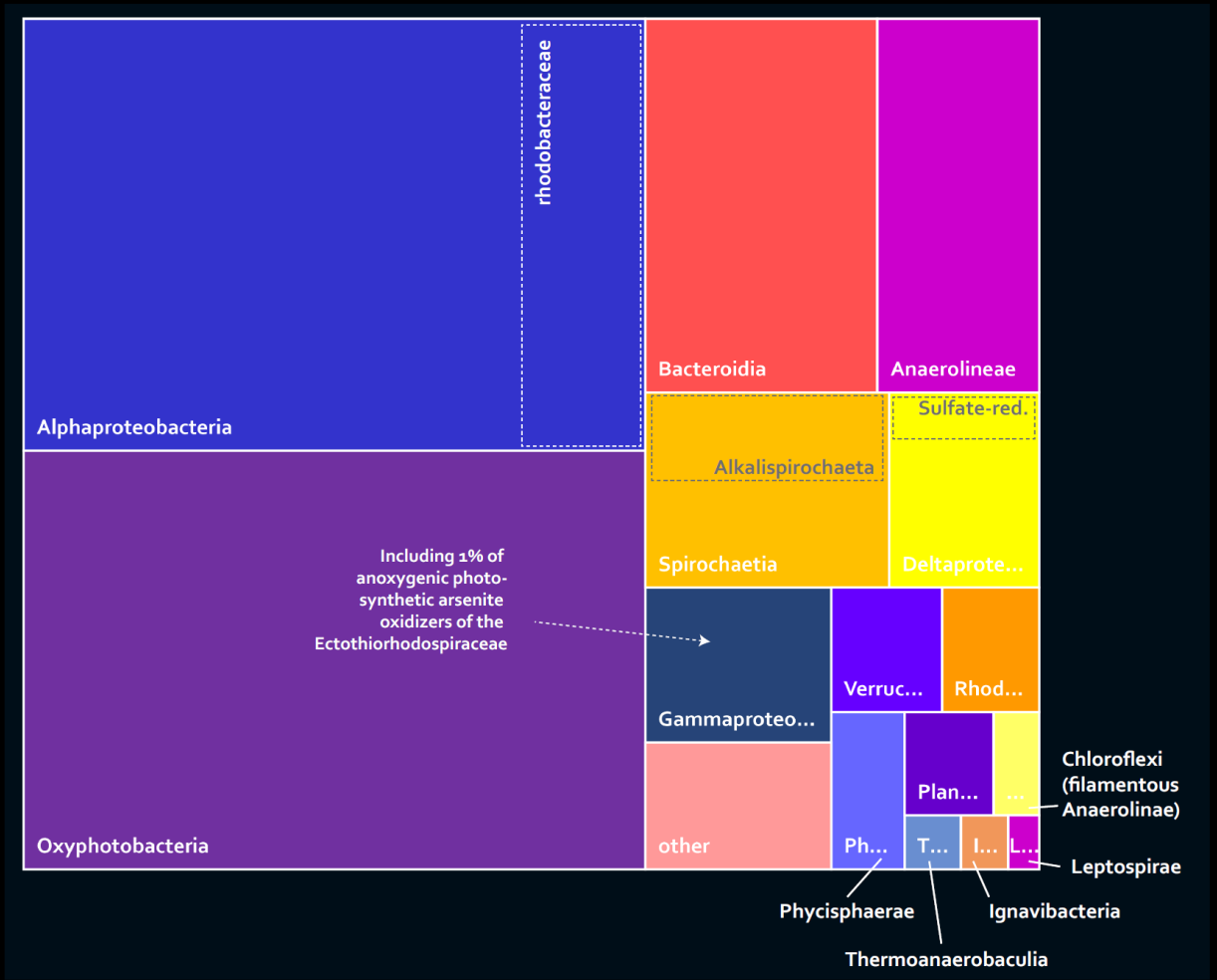
- As enrichment plateau with increasing Mn
- S and As are co-enriched
- Is there a lot of As-S related microbial cycling?
- Why such an enrichment in arsenic ?



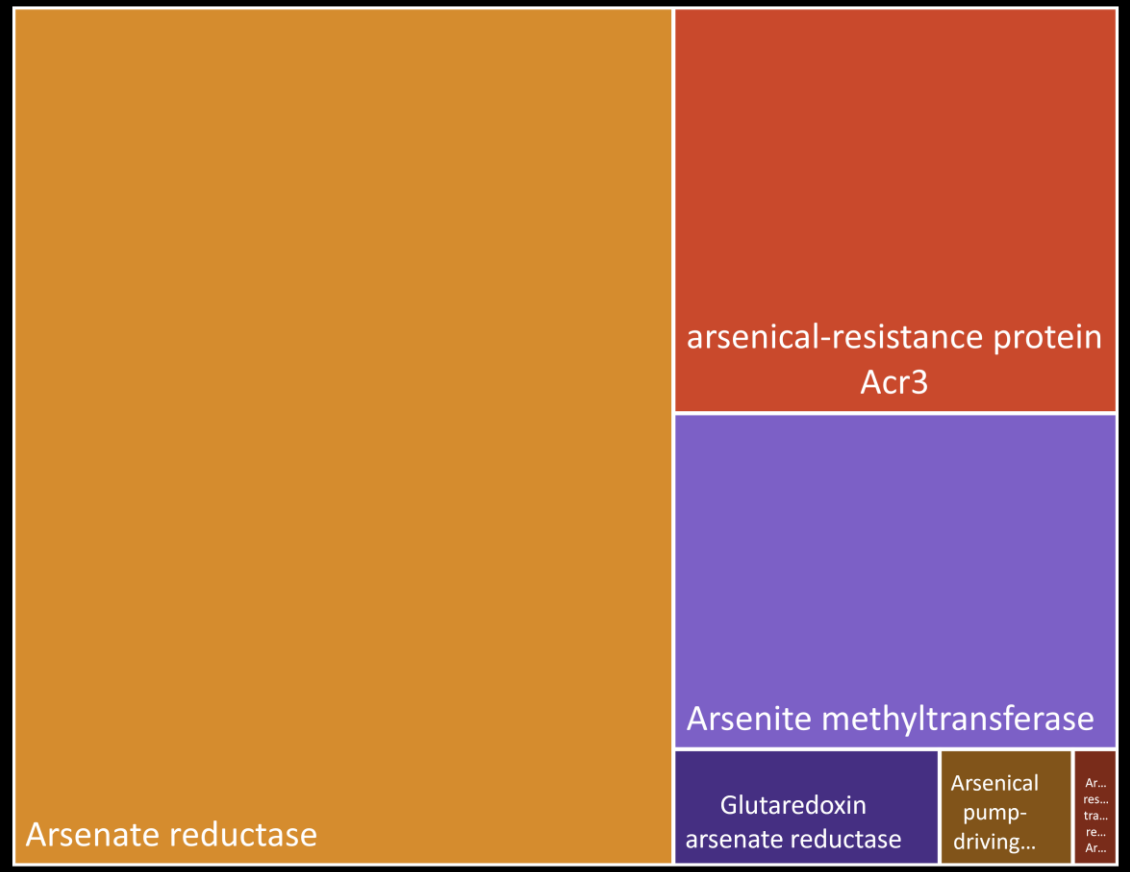


Genomic data for pool 1

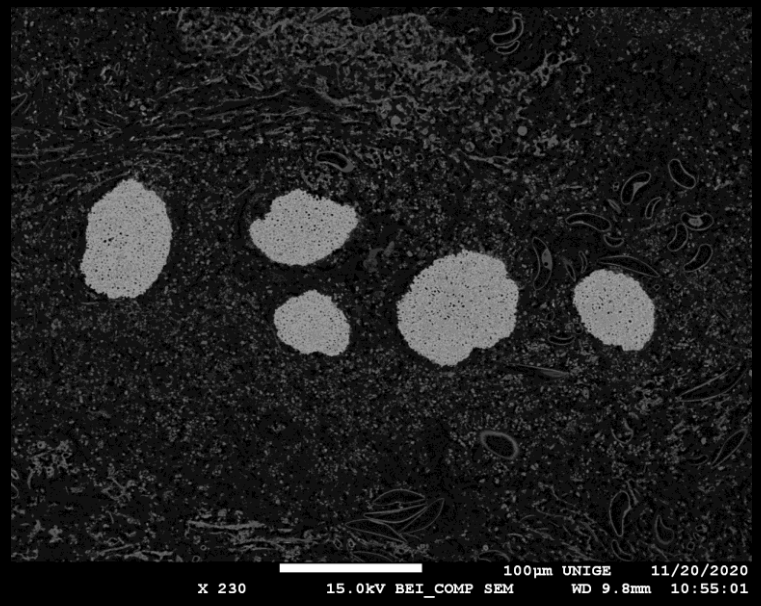
Community composition (16S rRNA genes)
cyano dominated, not many arsenotrophs, good amount of sulfate reducers

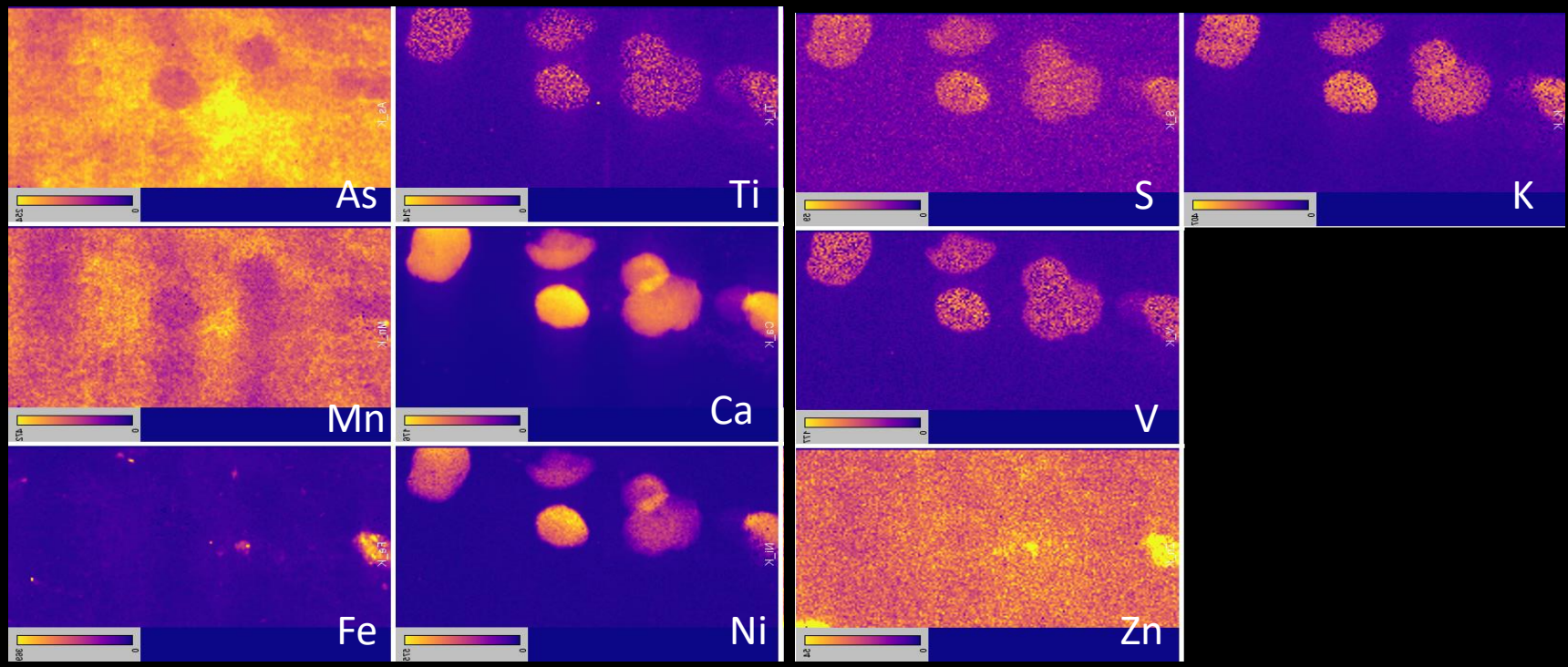


Arsenic associated genes (metagenomes)
No arsenite oxidation.
Arsenate reduction for arsenic detoxification
→ Confirmed by XANES peak showing mainly As(V) associated to OM



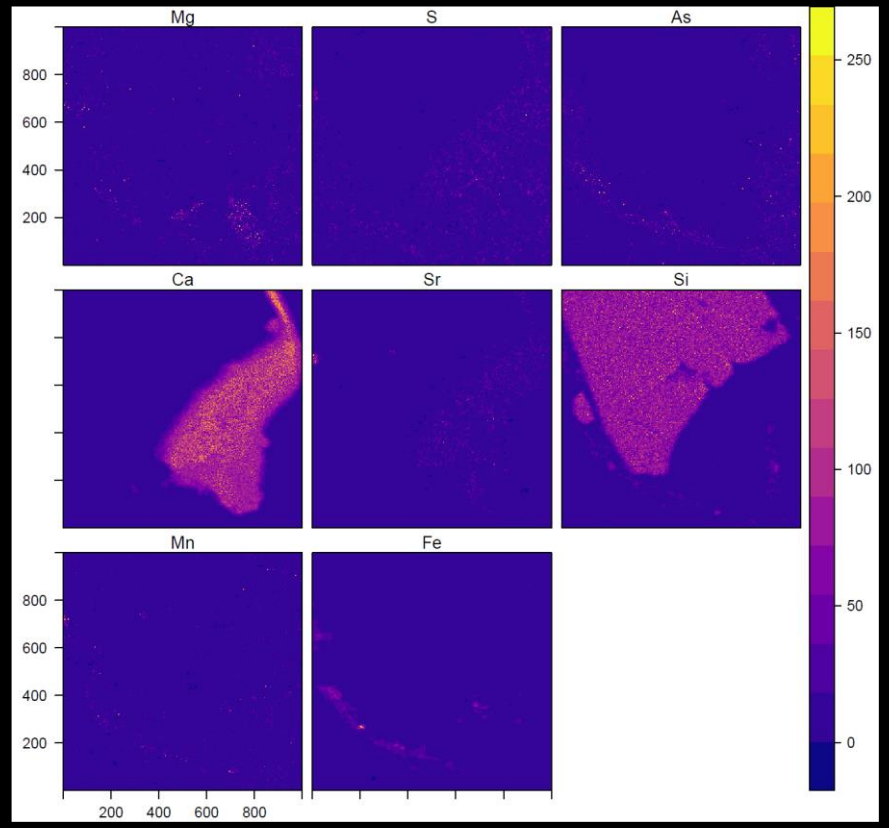
Zone 2 : rare mineralizations

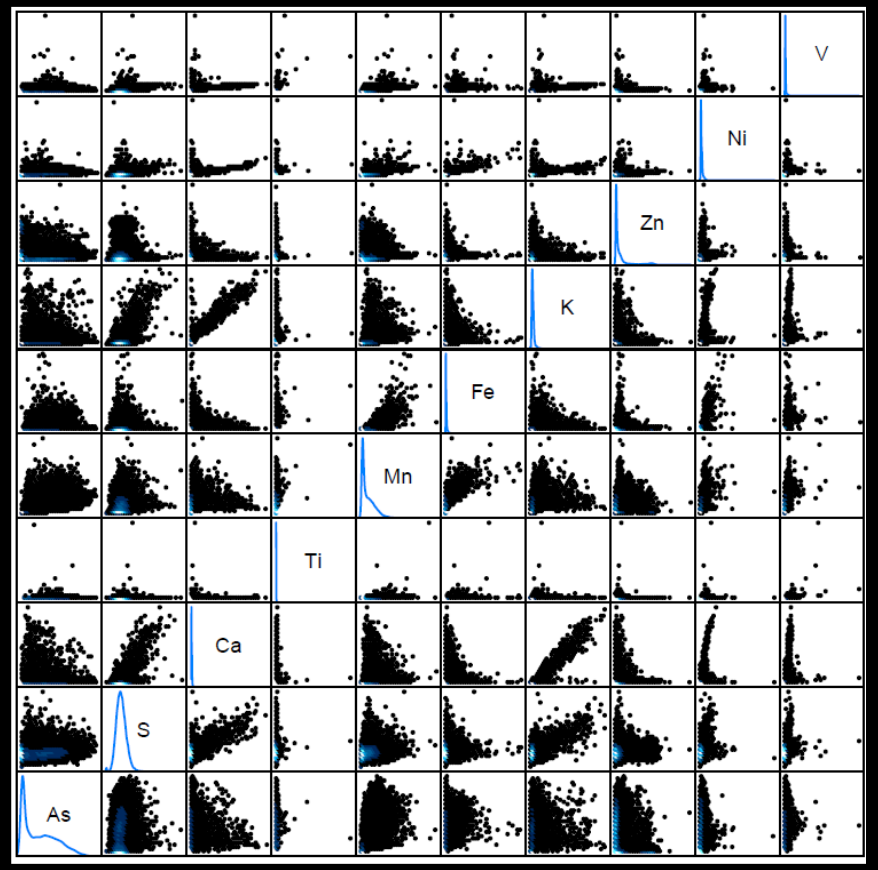




- A few CaCO3 occurrence ressembling those observed in zone 1
- Same Ni + K enrichment (more metals : V, Ti)
- Passive As enrichment in this layer? Timing of As influx into the pool ? No specific As-based energy gaining metabolism

Zone 3 mat bottom, rich in arsenic, more S, secondary precipitation of $CaCO_3$

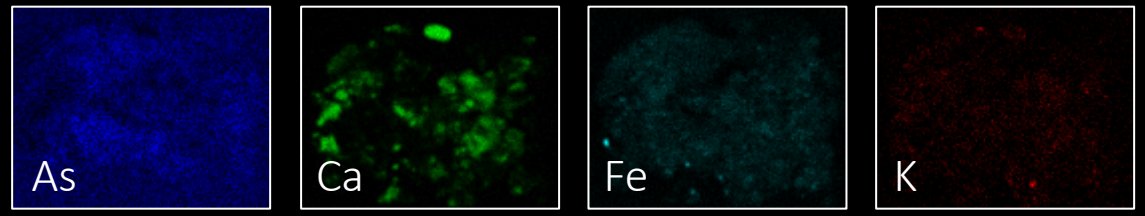




More detrital material. Ca precipitation still observed, and with similar signatures in this zone of the microbial mat. Less Ni enrichment, although some might still be present.

Pool 7 crust : evolution towards mineralized mats ?

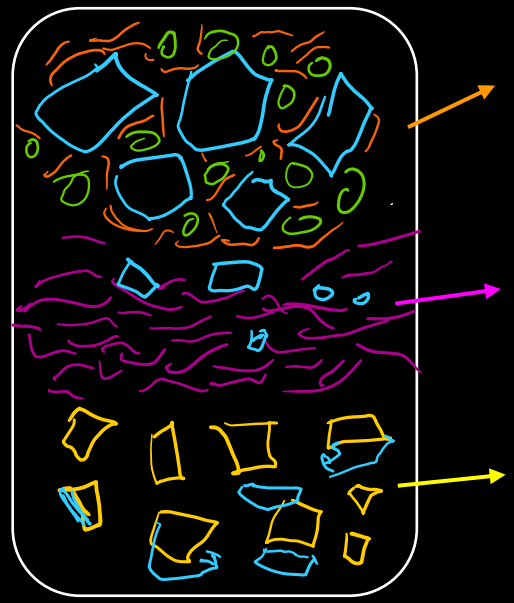
µXRF maps : no relationship of $CaCO_3$ with Ni nor K



Missing microbial communities

Missing trace elemental mapping and bulk chemistry

Model for metal enrichment in microbial mat of the Dead Sea



Photosynthetic (including diatoms) and ureolytic activity likely influence $CaCO_3$ precipitation
Ni-enriched aragonite concretions precipitated from Mg-Si rich EPS

10'000 enrichment in arsenic seems passive by EPS → driven by the environment
Binds S, Mn and V, and Mg and Si (classically associated to EPS)
Few $CaCO_3$ concretions are only K-rich.

Early diagenetic transformation of carbonates : EPS still bind As, associated to S. little Mn.
As phase change
Ca not associated to Ni but still to S and K→ sulfate reduction activity

Complex mix of environmental and microbially-related elemental enrichments in OM and CaCO3
→ additional data needed (bulk chemistry of sediments and water)

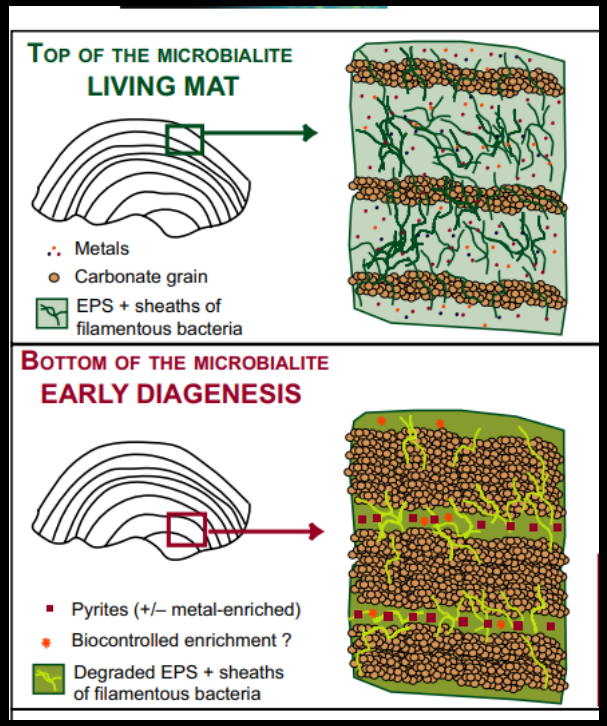
What does it mean for the geological record? Look at the Tumbiana stromatolites

Model of metal enrichment in Dead Sea microbial mat

Model for the Bahamas stromatolite (Sforna et al., 2016)

EPS passive concentration of metals in top layer

Pyritization and potential biocontrolled enrichments preserved in specific conditions after early diagenesis (sulfide/carbonates/



Photosynthetic (including diatoms) and ureolytic activity likely influence CaC03 precipitation from EPS, with partial As-enrichment and final Ni-enriched aragonite

10'000 enrichment in arsenic seems passive by EPS. Binds S, Mn and V
Few $CaCO_3$ are only K-rich.

Early diagenetic transformation of carbonates : EPS still bind As, associated to S. little Mn.
As phase change (to be observed by XANES)
Ca sometimes associated to Ni, still to S and K
What is the place of sulfate reduction activity ? Very few observed here… no pyritization → no removal of metals by sulfide phase

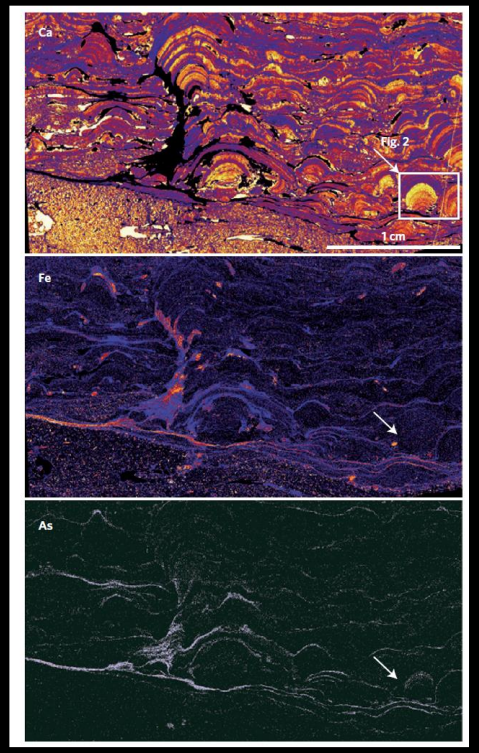
Model for the Dead Sea mat :

EPS passive concentration of metals

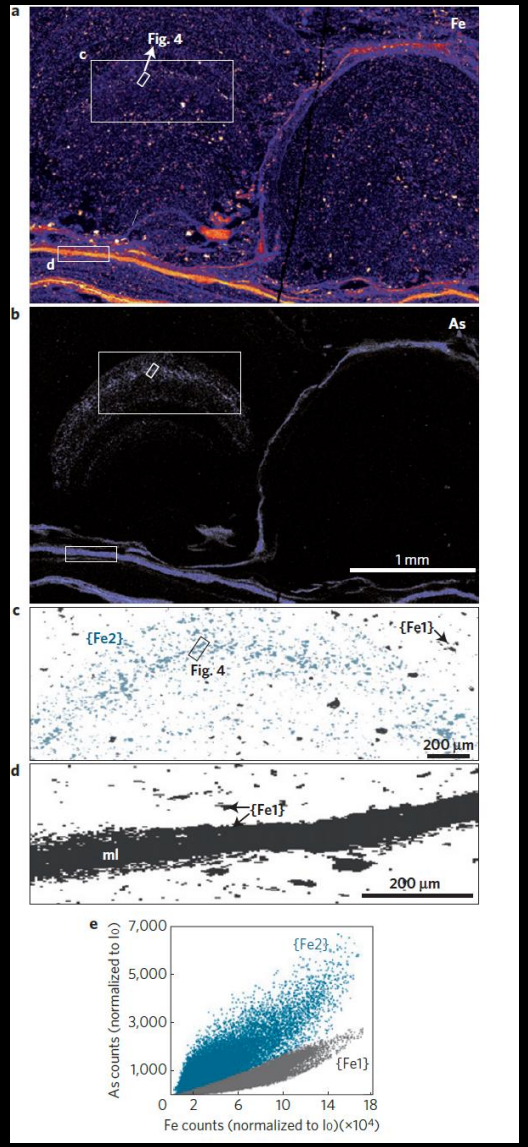
No pyrite, but Ni-rich CaCO3. Arsenic not associated to final mineral phases here, only OM→ could be kept in lamina if not degraded?

collab with A. Oehlert and C. Thaler to tackle final mineral phases concentrations and bio-controlled enrichments.

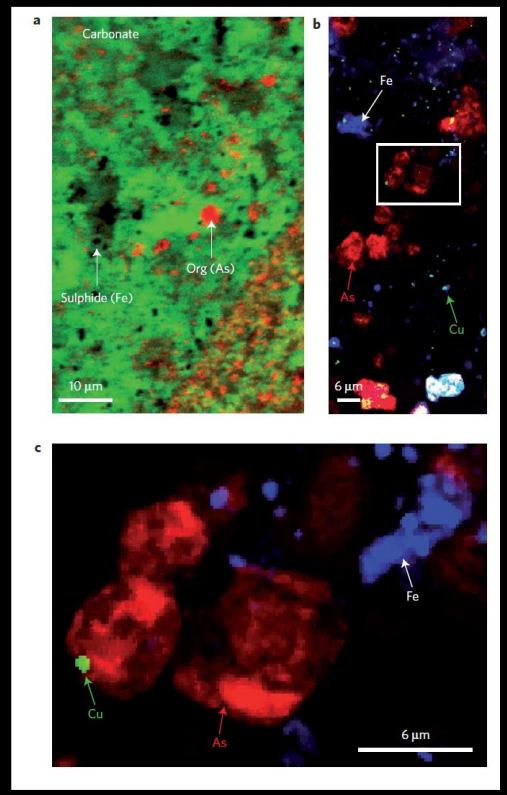
Comparison with mats and microbialites from the Archean : the As-rich Tumbiana stromatolites



Ca, Fe and As enrichment in the stromatolites. Sforna et al., 2014 Nature Geo.

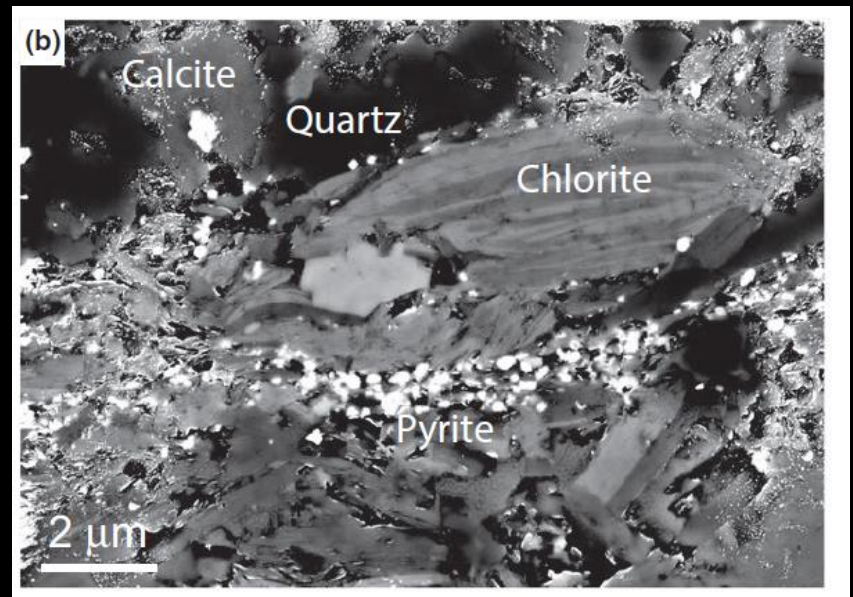


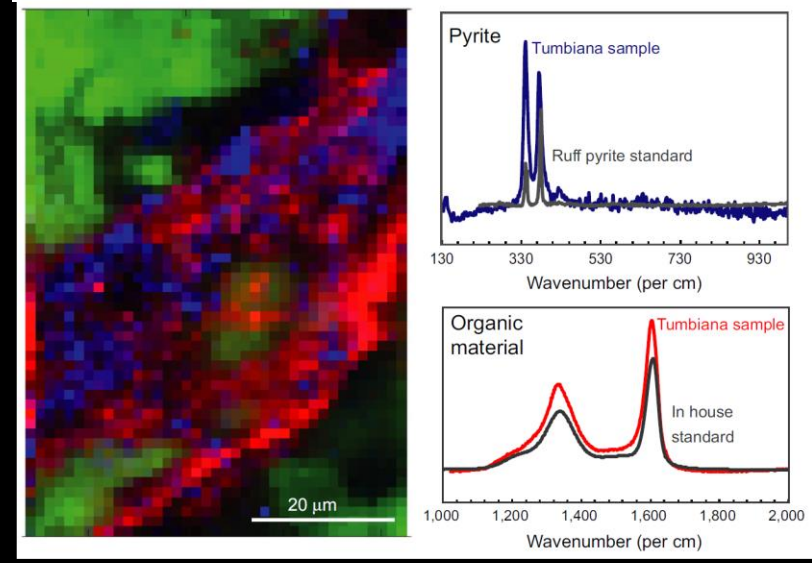
Fe and As relationship Sforna et al., 2014 Nature Geo.



As-rich globules interpreted as As-cycling cells in stromato layers Sforna et al., 2014, Nature Geo.

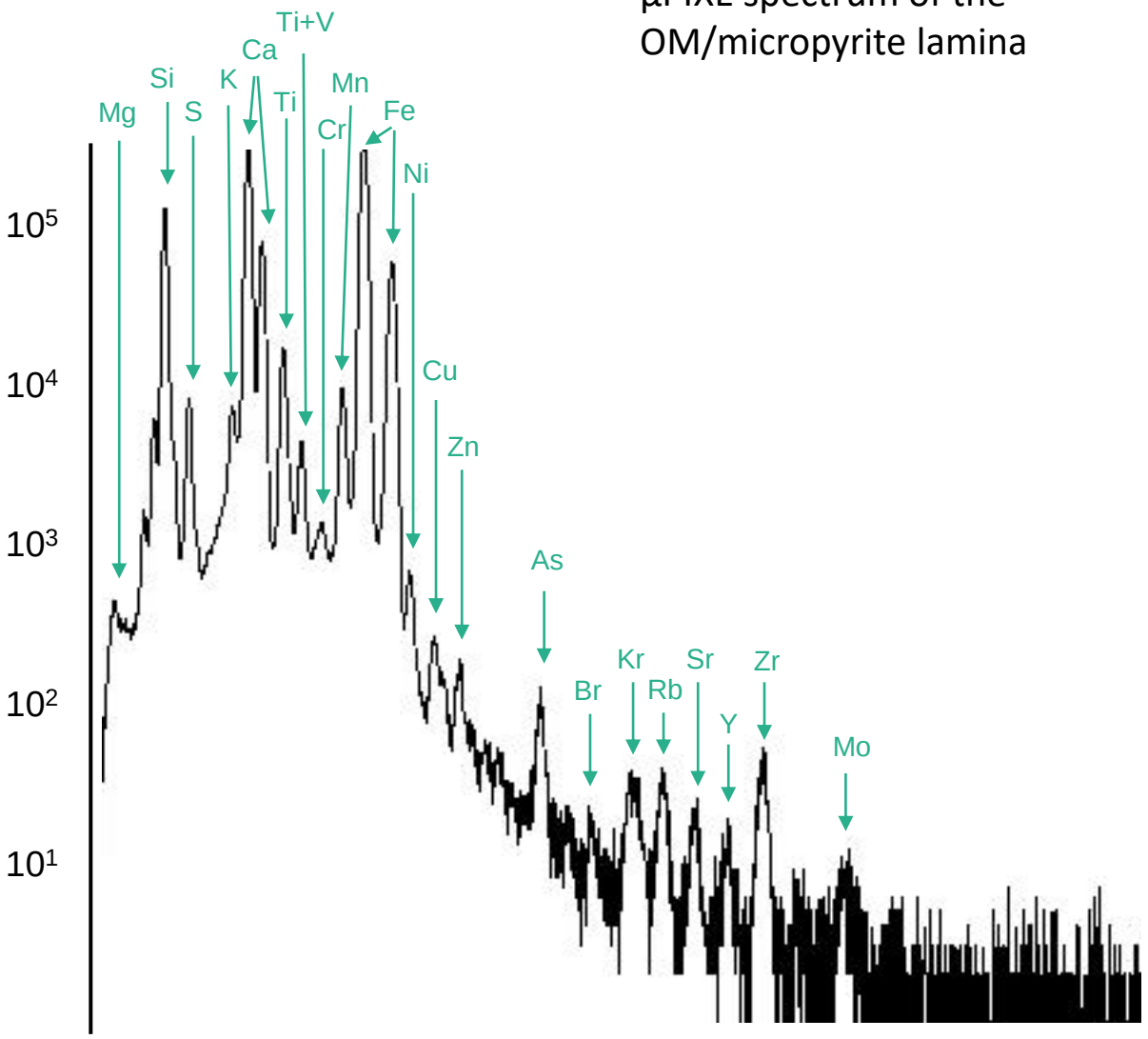
Micro-pyrite in OM-rich layers capping the stromatolites.
S isotopes consistent with MSR.
Marin-Carbonne et al., 2018 Geobiology.

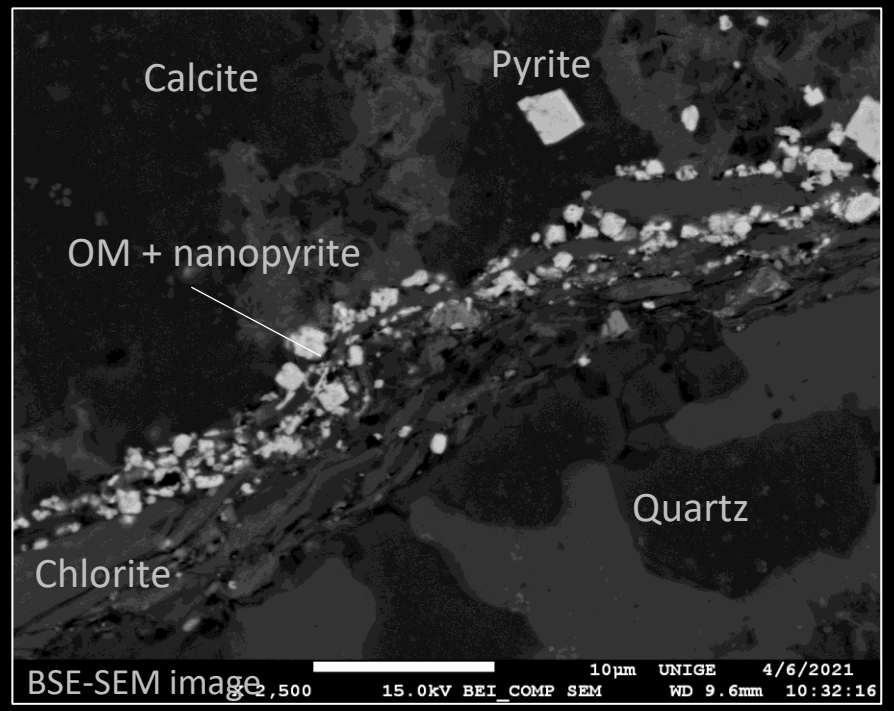




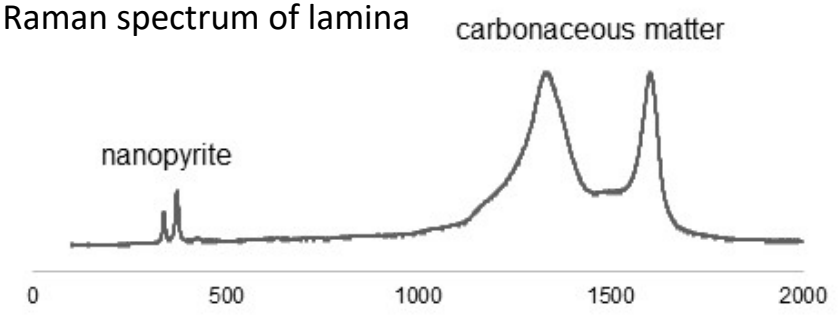
Elmental enrichments in carbonaceous matter layer capping the Tumbiana stromatolites

µPIXE spectrum of the OM/micropyrite lamina

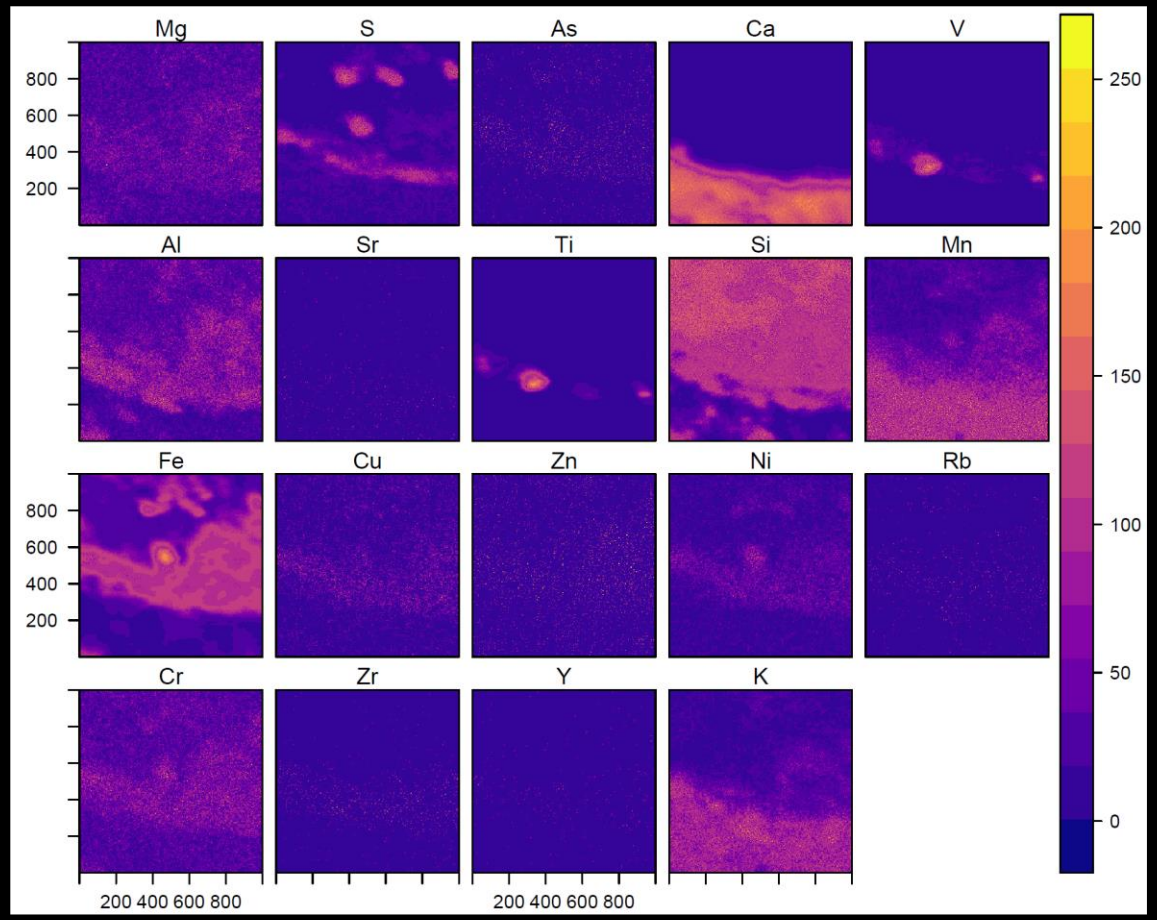




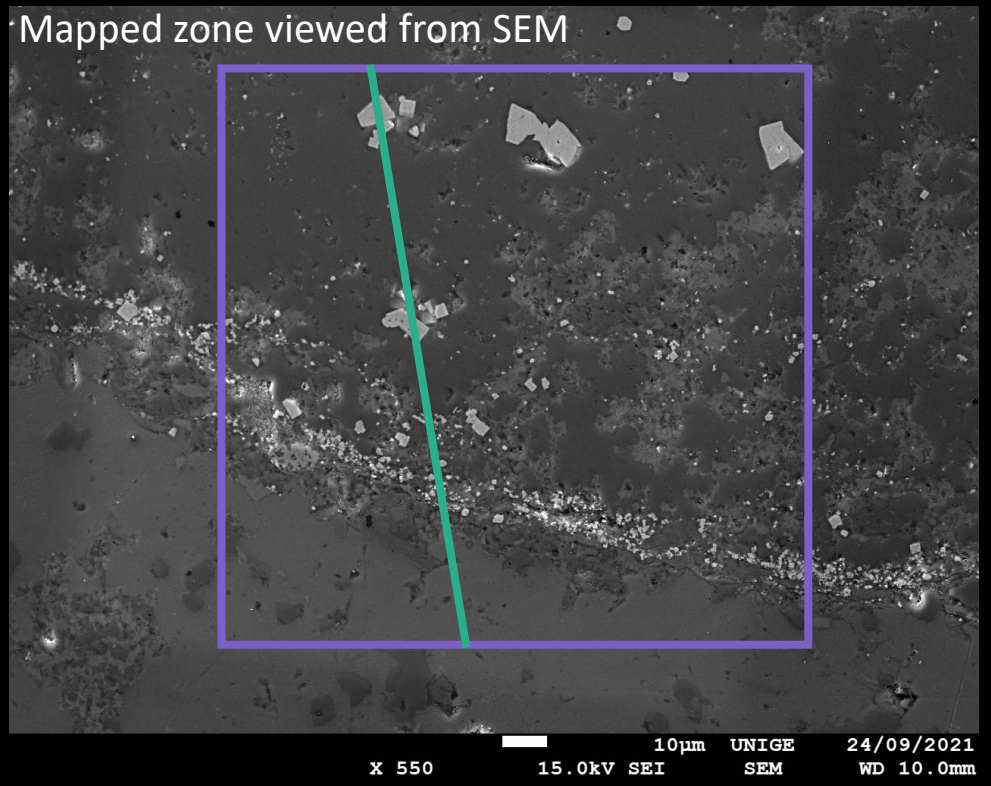
Raman spectrum of lamina



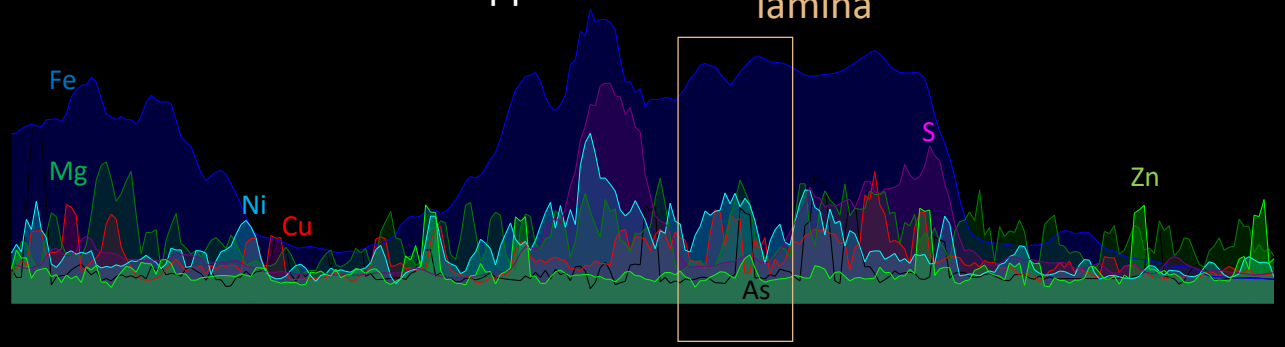
PIXE mapping of the Tumbiana stromatolite micropyrite/OM lamina



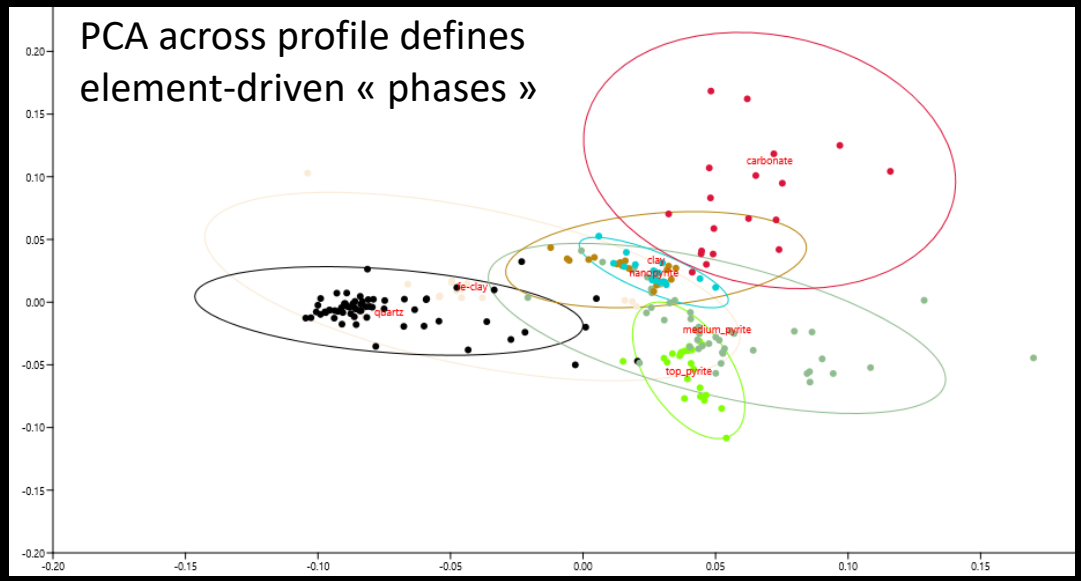
Mapped zone viewed from SEM



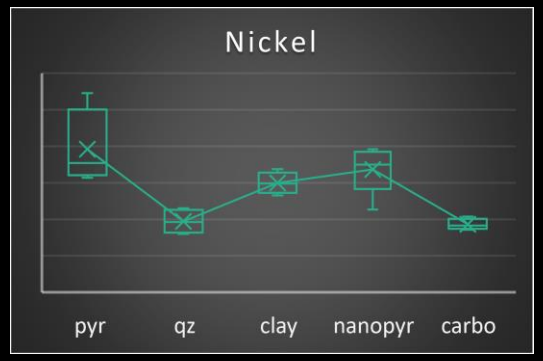
Profile accross the PIXE mapped zone

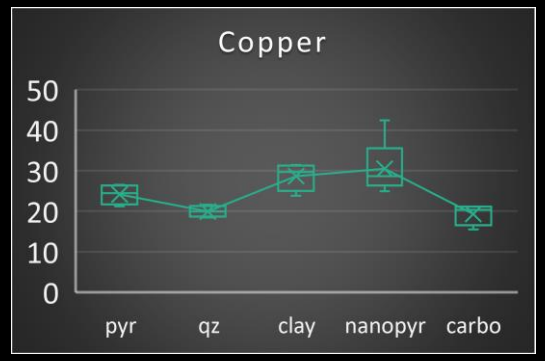


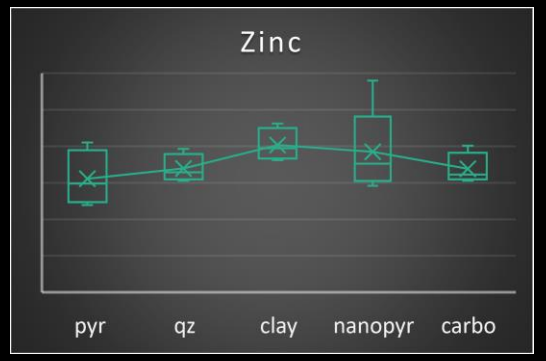
PCA across profile defines element-driven « phases »

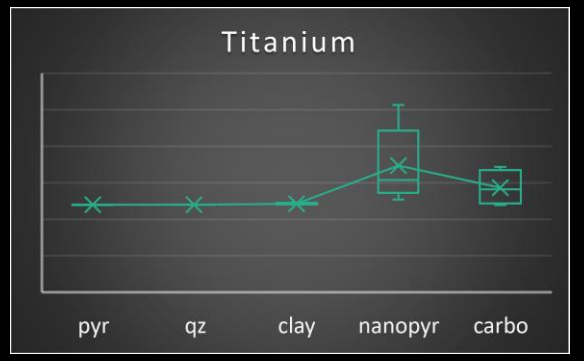


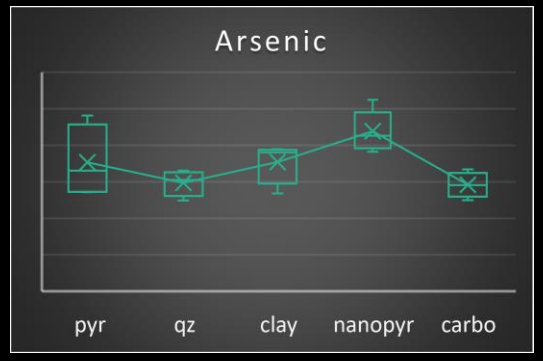
Changes in relative metal enrichments in the different « phases »

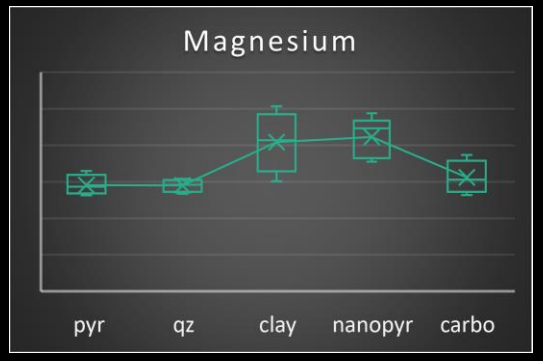


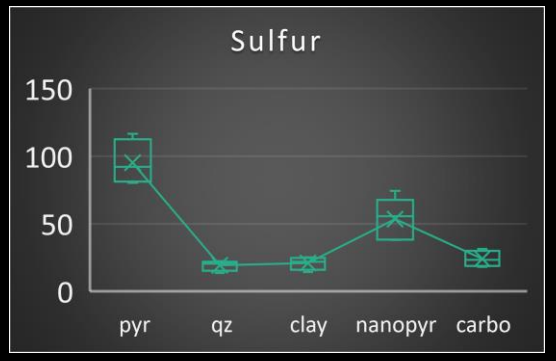


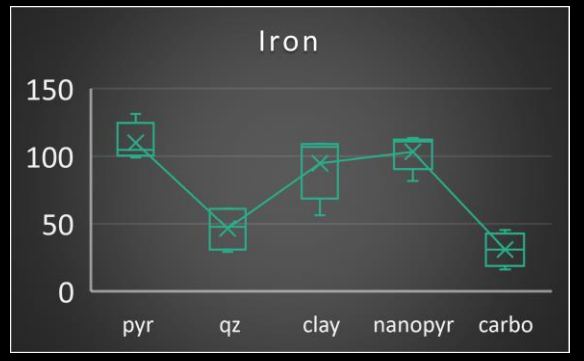






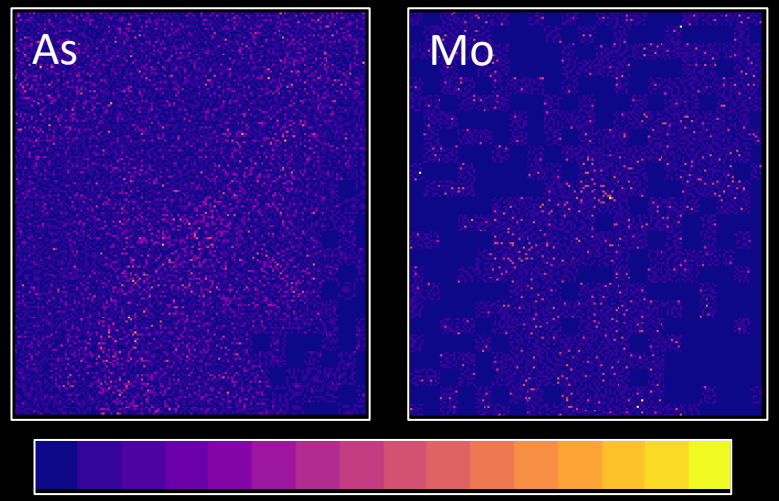


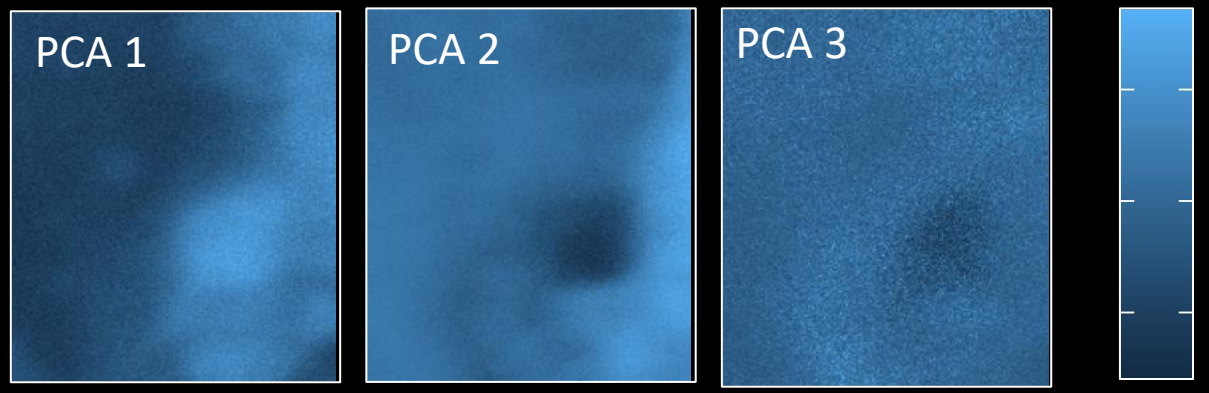


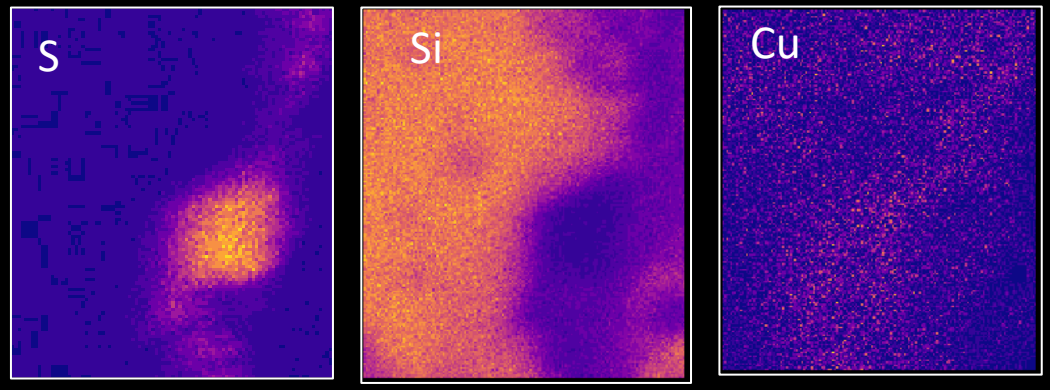


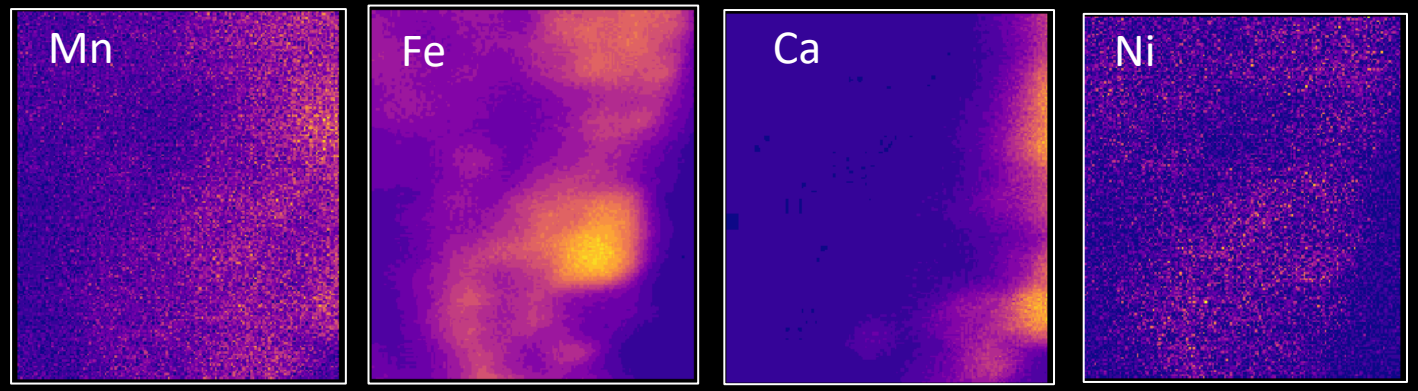
High variability in trace metal enrichment among phases.
All phases co-enriched in Zn
Nanopyrite/OM layer enriched in Molybden and As compared to clay, pyrite and carbonates
→ Two elements associated to microbial arsenic cycling : paleometallome signature ?

Correlation of As and Mo occurrence









As and Mo correlate and are have an important share of PCA 3, without being strongly enriched in pyrite (PC1) and carbonates (PC2)

Tumbiana stromatolite lamina

- Identification of a stromatolite OM lamina
- OM and nanopyrite intermingled with clay deposits
- The layers are enriched in As and Mo compared to other phases (clay, carbonates, pyrite)
- Other elements show no such enrichment
- Could this be a signature of arsenic microbial cycling by fossil Mo-bearing oxidoreductase ?

→ Enzymatic-driven metallic signal preserved in OM lamina of Archean rocks?

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