BIOGEOCHEMICAL ORIGIN OF ARSENIC IN GROUNDWATER FROM THE LOIRE VALLEY MIOCENE FORMATION

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INTRODUCTION

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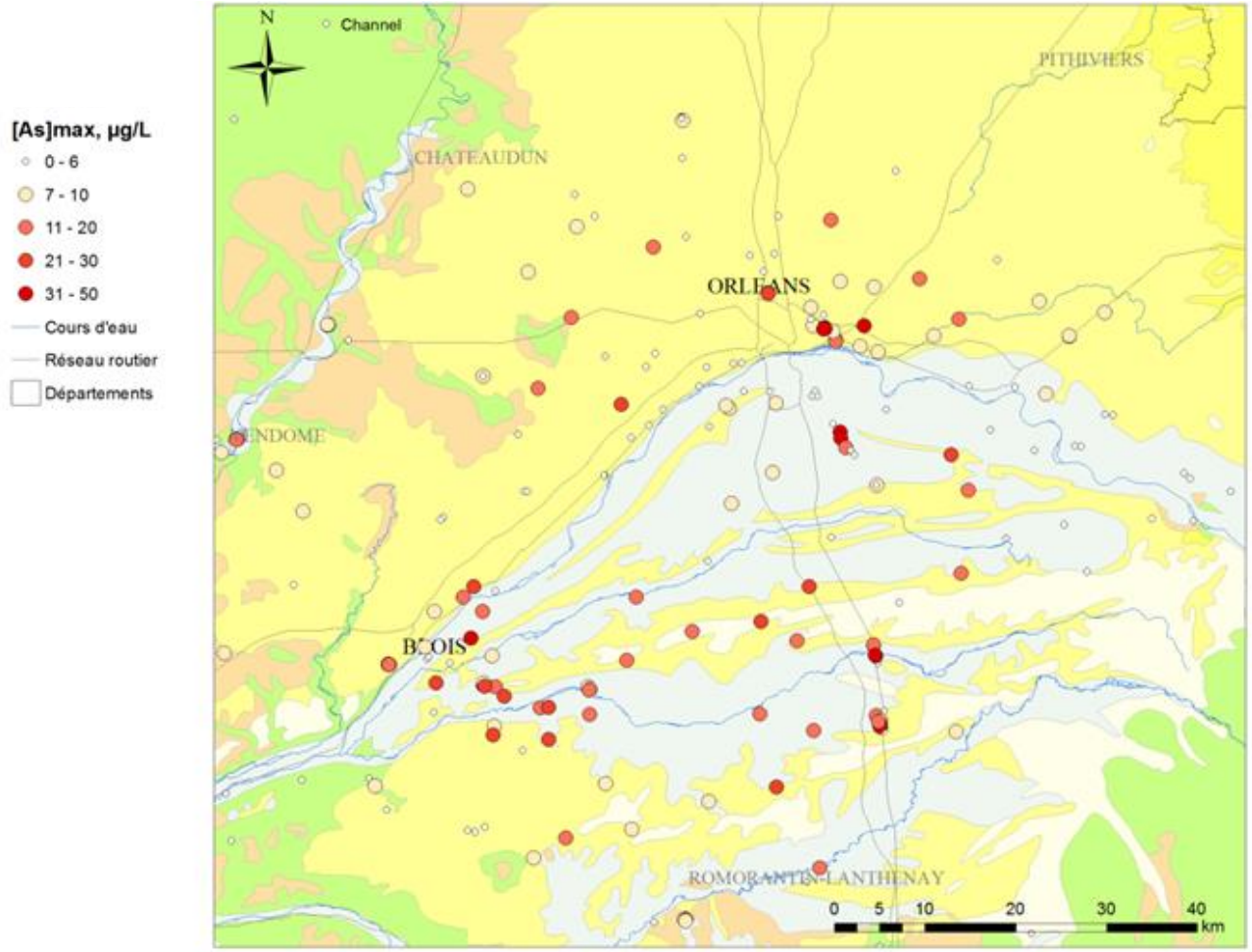
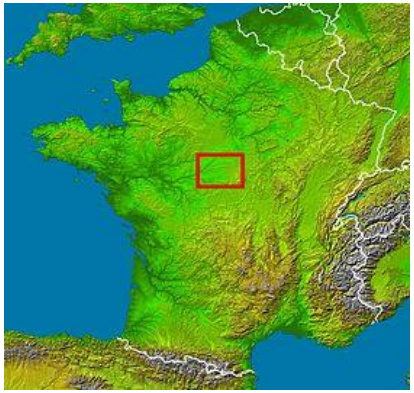
> Context





Sologne region (Centre Val de Loire, France)

- **As detected in groundwater**
- **Concentration exceeding the drinking water standard of 10 µg/L (WHO)**

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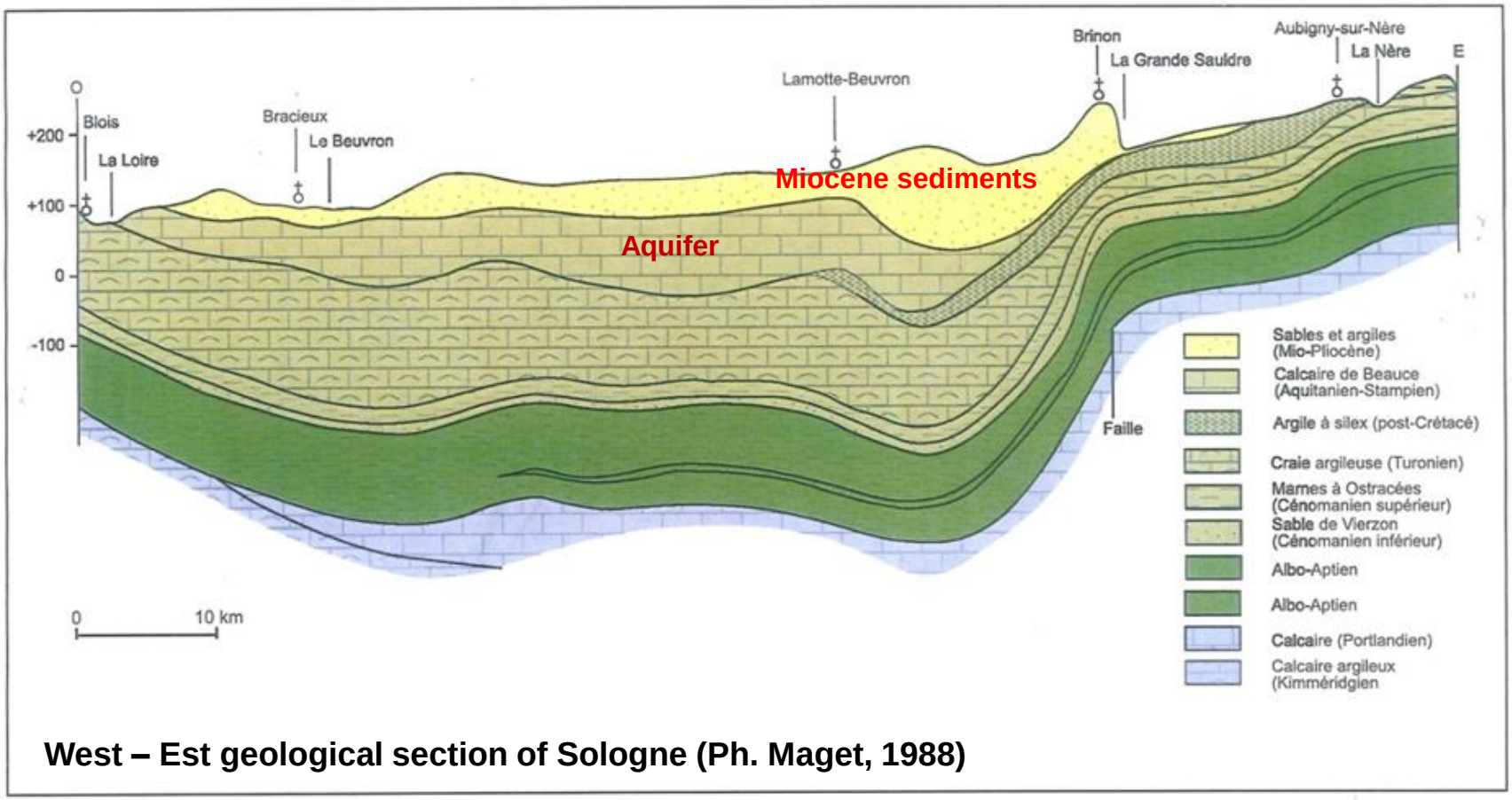
> Geological context



West – Est geological section of Sologne (Ph. Maget, 1988)

- Groudwater in the **Beauce limestone formation** (Aquitanien-Stampien)
- Miocene sand and clay deposit probably **confined** the Beauce groundwater

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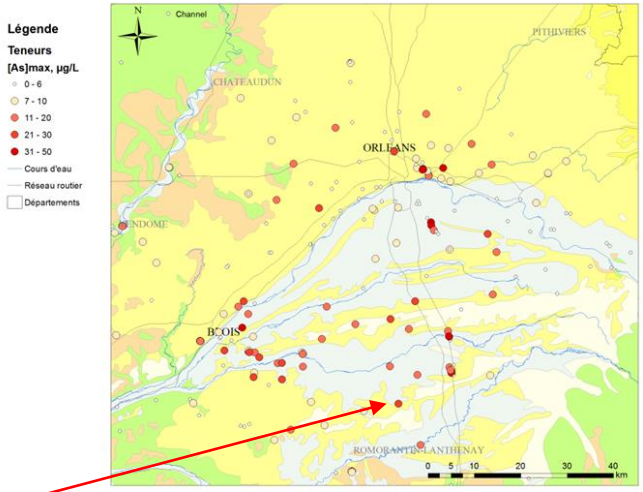
> Objectives

- Check if the variations in As concentration in the groundwater are related to fluctuations of the piezometric level
- Highlight geological formations rich in As
- Understand the biogeochemical processes associated with the As release

- **Selection of the drinking water well with highest As concentration**
  - Water well monitoring
  - Solid phases description
  - Batch experiment



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DRINKING WATER WELL MONITORING

> Drinking water well monitoring: Piezometric surface

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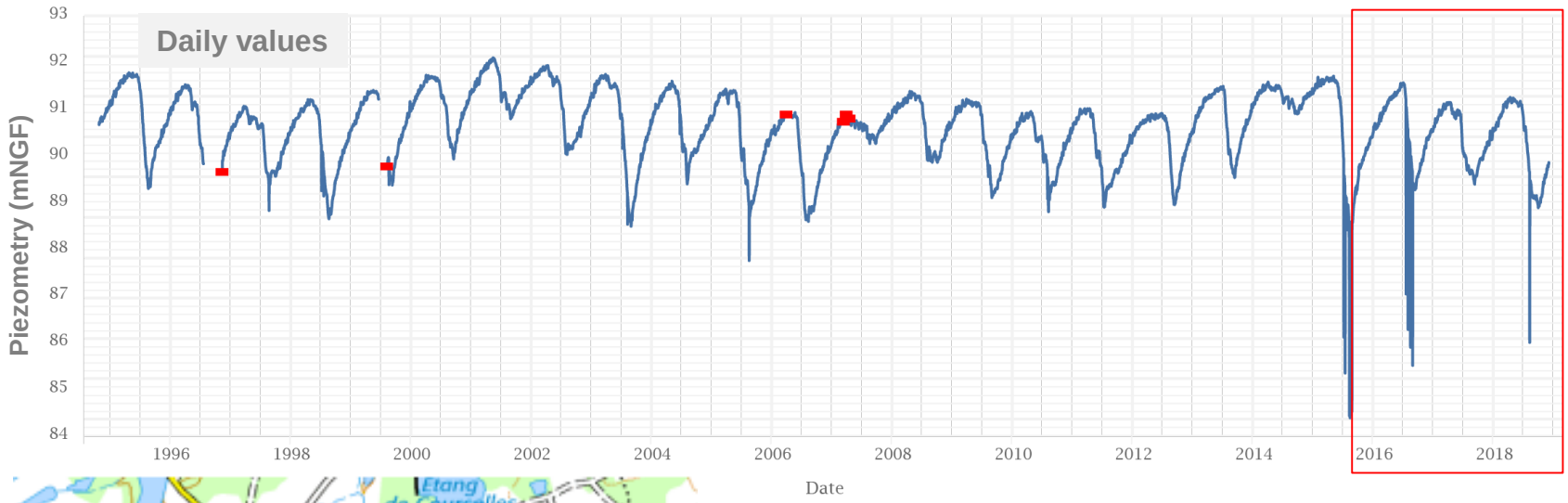

- **Seasonal variation**
  - High piezometric surface: May/Jun
  - Low piezometric surface: Aug/Sep/Oct
- **6 samples** : Sep 2016, Jun 2017, Sep 2017, Dec 2017, Feb 2018, May 2018

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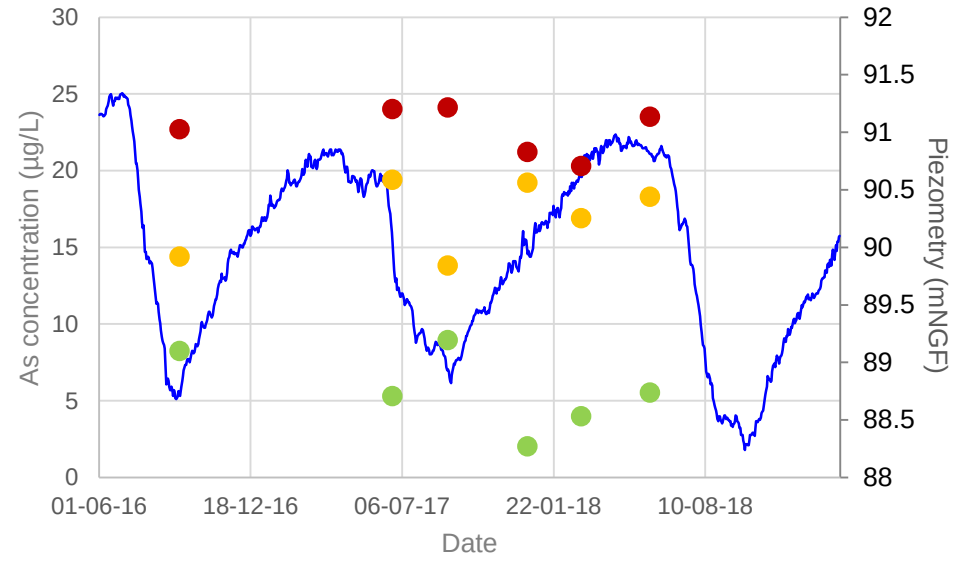
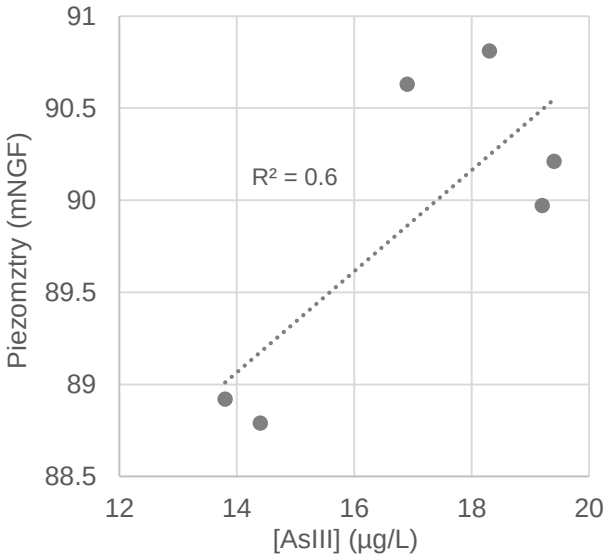
> Drinking water well monitoring: Arsenic concentration and speciation





- **As III is the main As species, with Fe and NH4, low O2 and redox**
- **As III increased with piezometric level**

=> As speciation controlled by seasonal variation of piezometry

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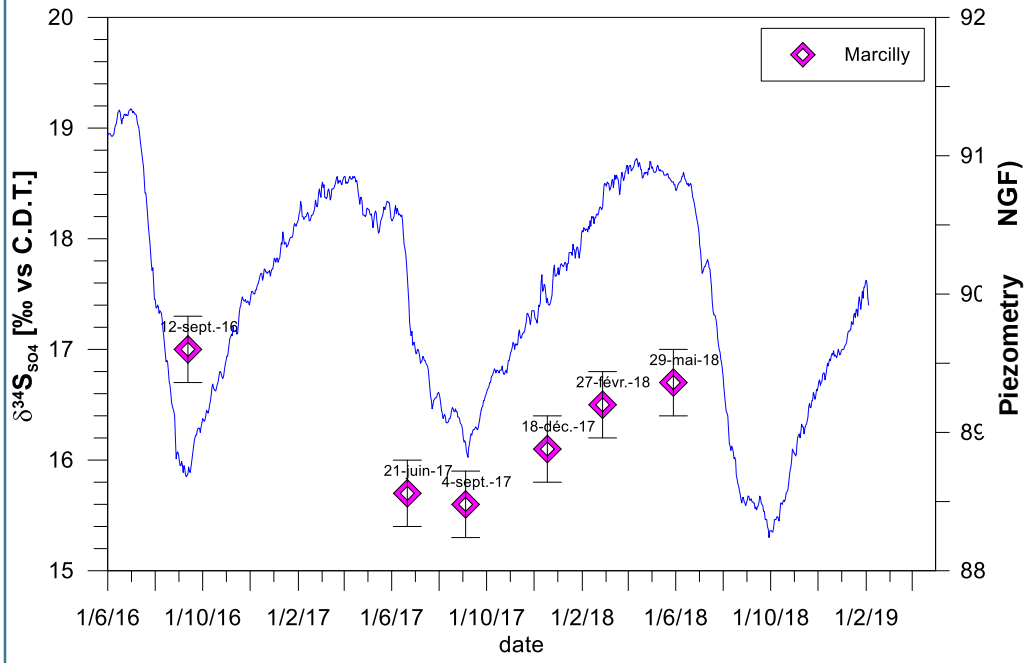
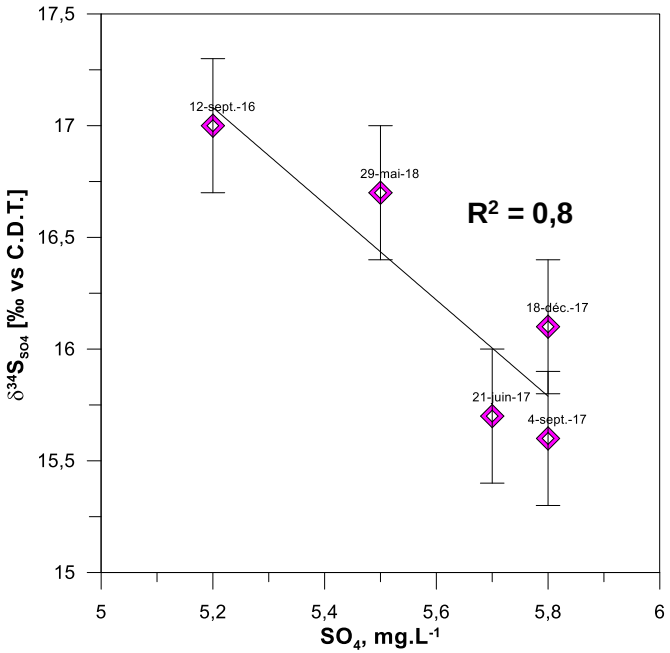
> Drinking water well monitoring : sulfur isotope fractionation





- **Correlation between variation of piezometric level and $\delta^{34}S$ / SO_4 fractionation**
- **$\delta^{34}S$ is anti-correlated with SO_4 concentrations**

=> Indices of sulfate-reducing activity

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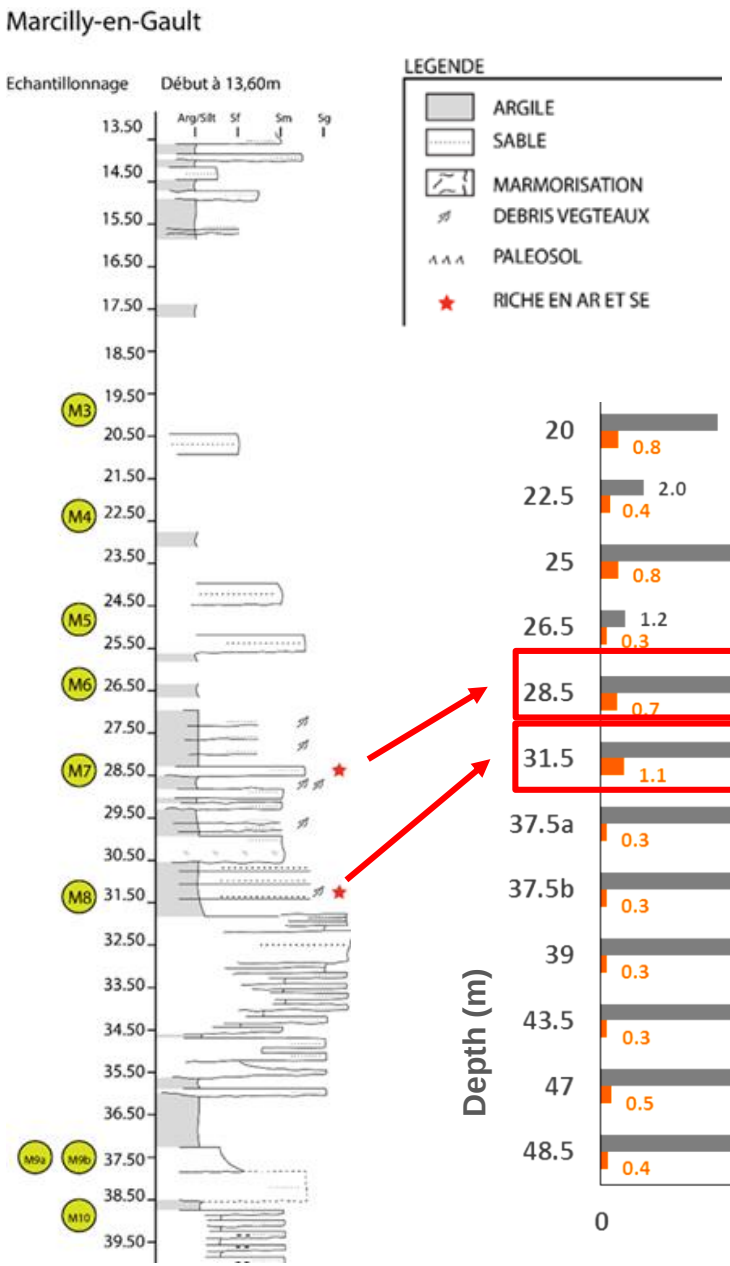
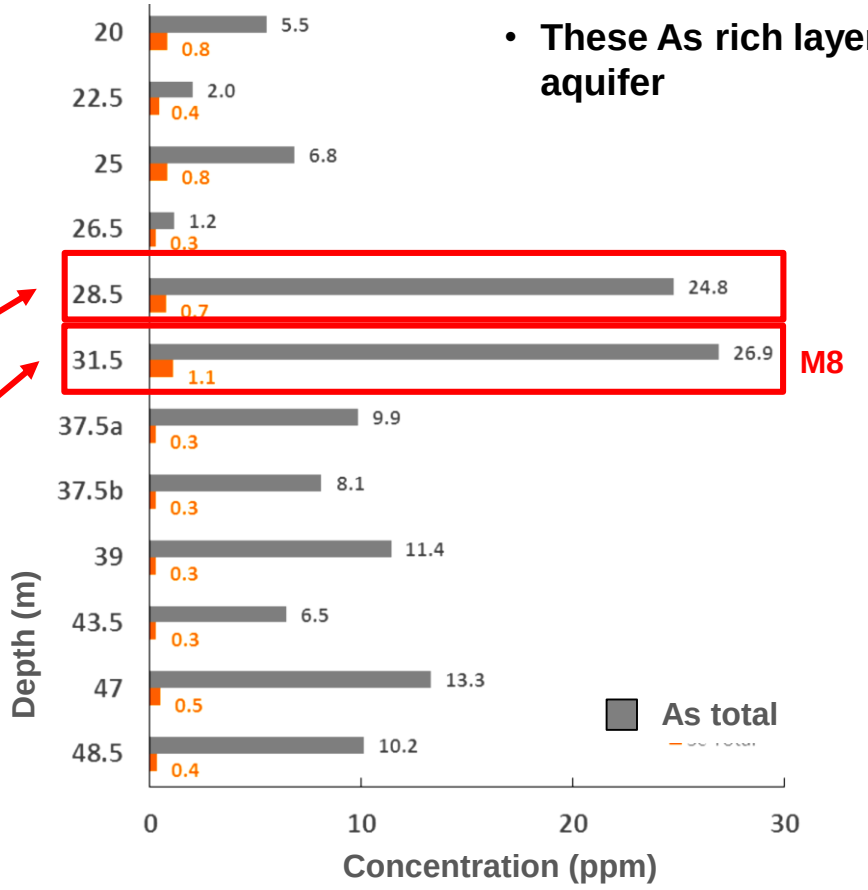
SOLID PHASES DESCRIPTION

> Sediment logs and As concentrations





- **Levels rich in As are systematically found in flood plain clay levels, rich in organic matter by the presence of plant debris.**
- **These As rich layer are at the top of aquifer**

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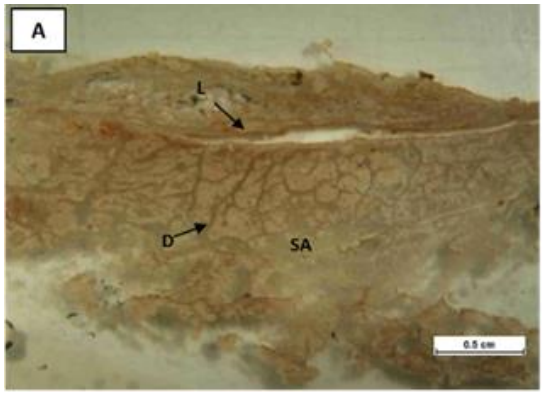
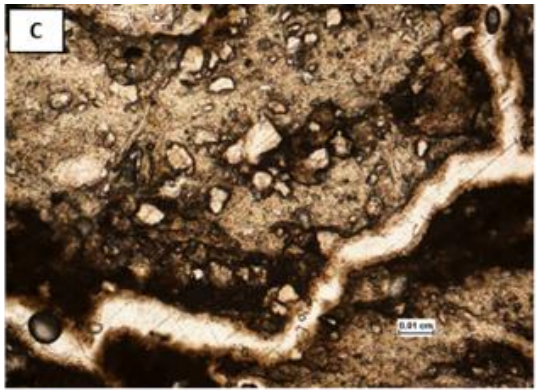
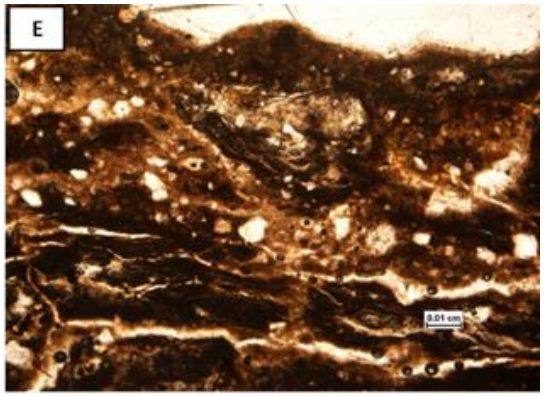
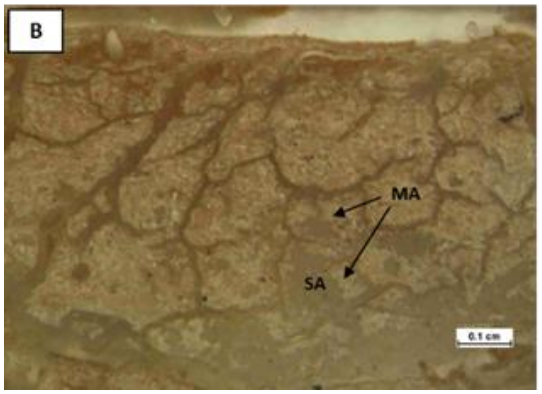
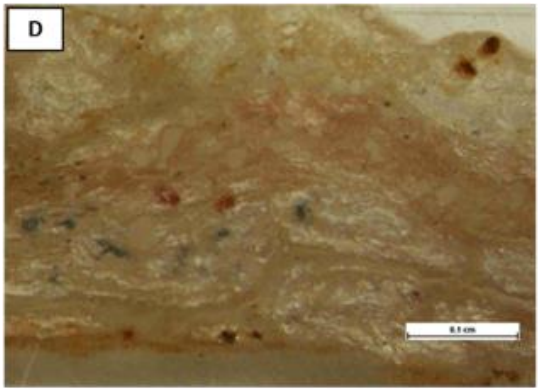
> Petrographic observations

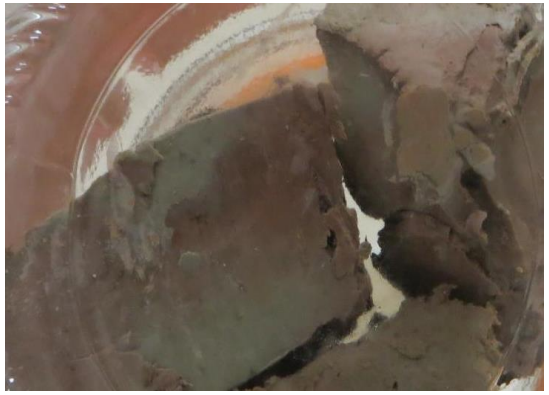












- **Clay/sand alternation**
- **Desiccation cracks**
- **Dark brown to red granules**

⇒ **Detritic layer deposit by Miocene fluvial system**
⇒ **As certainly originates from the erosion of the Massif Central**

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BATCH EXPERIMENT

> Batch experiment: protocol

Conditions :

- **Material M8** with water from the well (10% solid)
- Incubated at 20°C, in the dark, at 100 rpm
- **Changing Redox conditions**
- **No nutrient supply (except H2)**

Abiotic batch **Biotic batch (x3)**

T0 **T1** **(3 months)** **T2** **(6 months)**

Gas phase = N_2, H_2 → Gas phase = Air

- Physico-chemical parameters
- Majors ions
- As speciation of water
- As transforming bacteria enumeration

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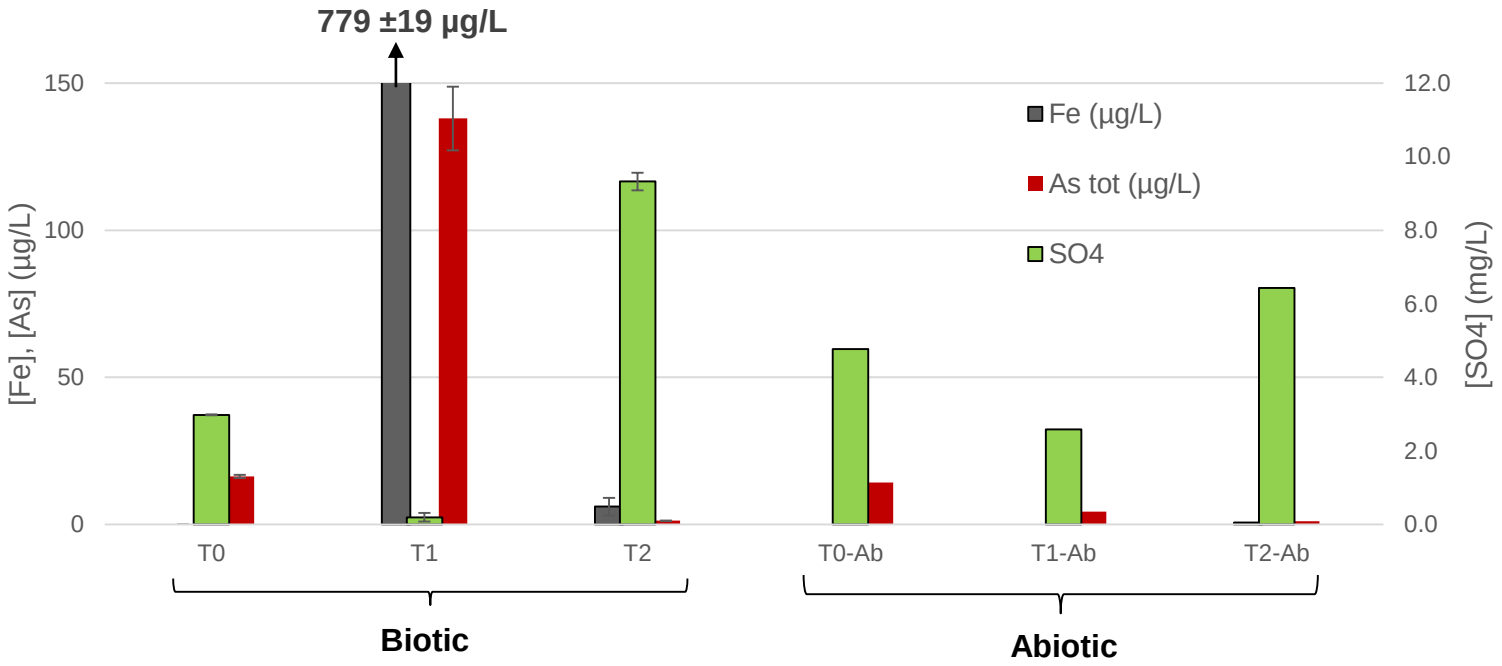
> Batch experiment : physicochemical parameters and SO4, Fe, As concentration



M8	pH	O2%	Eh (mV)
T0	8.1	65.3	92.7
T1	6.6	10.0	-121.9
T2	7.0	98.5	279.7
Ab-T0	7.7	62.0	91.0
Ab-T1	6.4	12.0	-120.3
Ab-T2	6.5	98.3	295.3

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> Batch experiment : As speciation

As species	T0	T1	T2	T0-Ab	T1-Ab	T2-Ab
As III	36 %	8 %	-	96 %	4 %	4 %
As V	58 %	1.5 %	50 %	4 %	96 %	96 %
DMA	-	-	50 %	-	-	-
Other species	-	≈ 90 %	-	-	-	-

- **Difference between biotic / abiotic**
- **Thio-As are probably main As species at the end of the anaerobic period**
- **Methylarsine formation induce by the return to aerobic condition**

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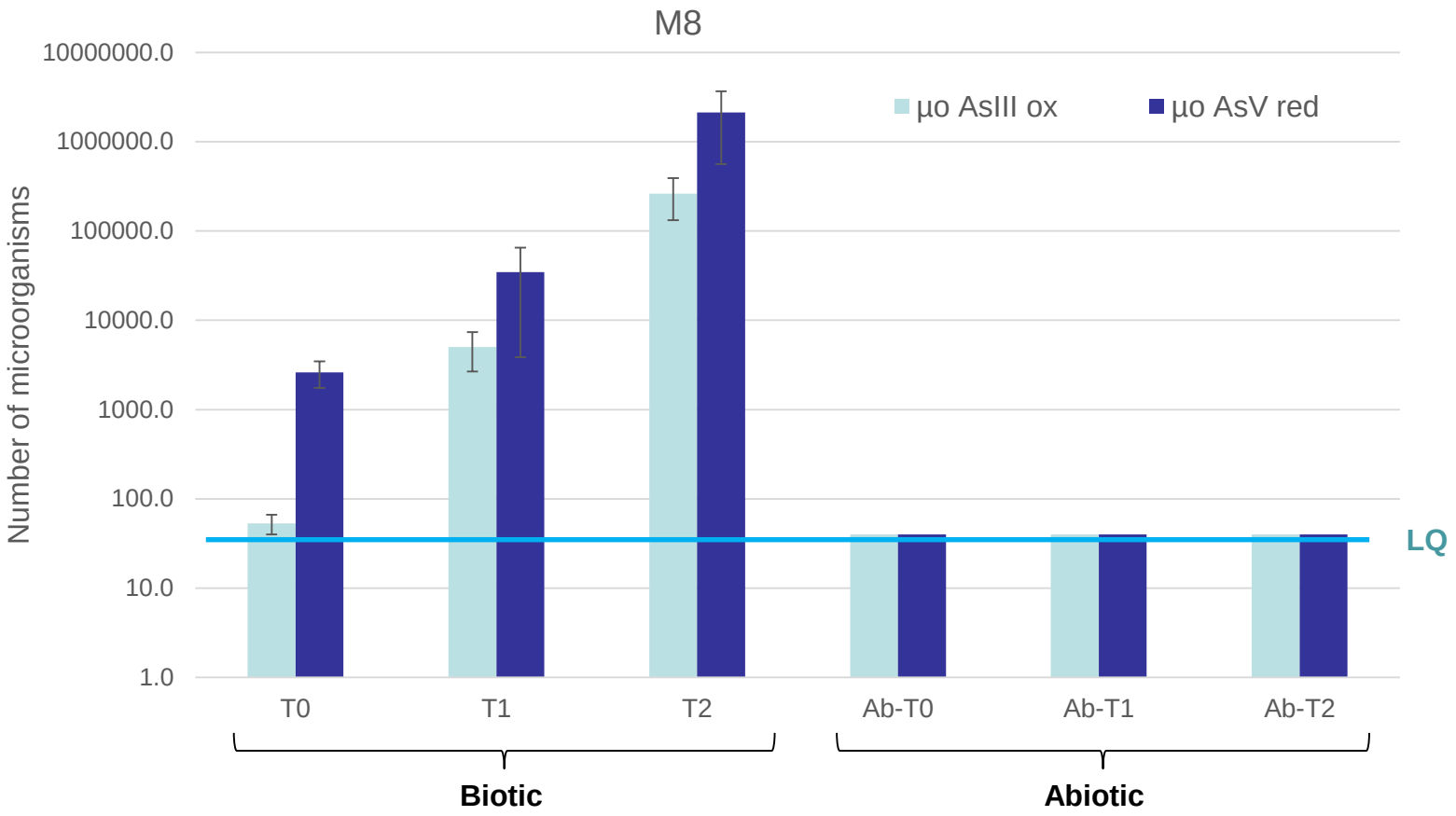
> Batch experiment : As transforming bacteria



- **Growth of As transforming microorganisms**

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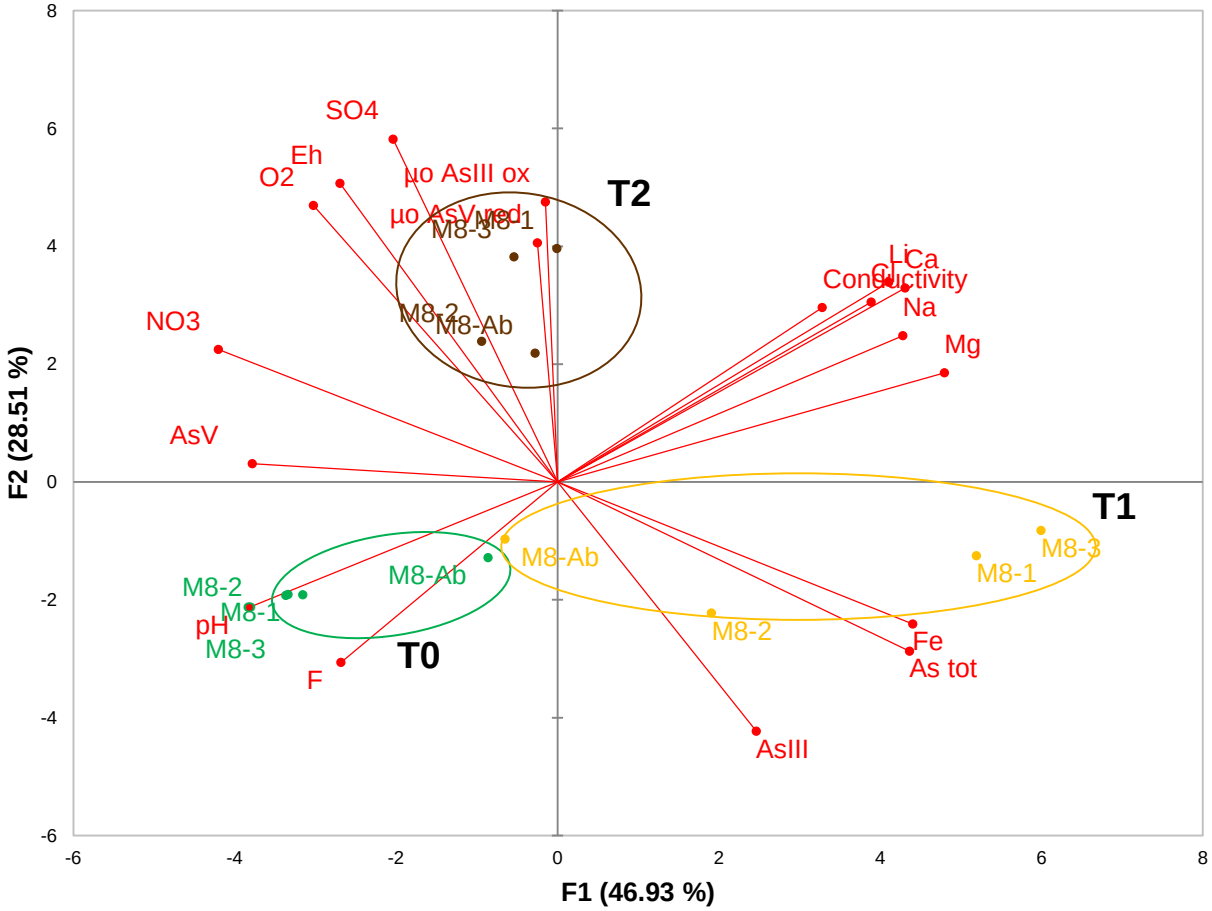
> Batch experiment : physico-chemical and microbiological parameters



- **As/Fe** correlation
- **As/SO4** anti-correlation
- Microflora influenced the As speciation

=> As in groundwater is related with anaerobic bioprocesses, Fe and sulphate reduction

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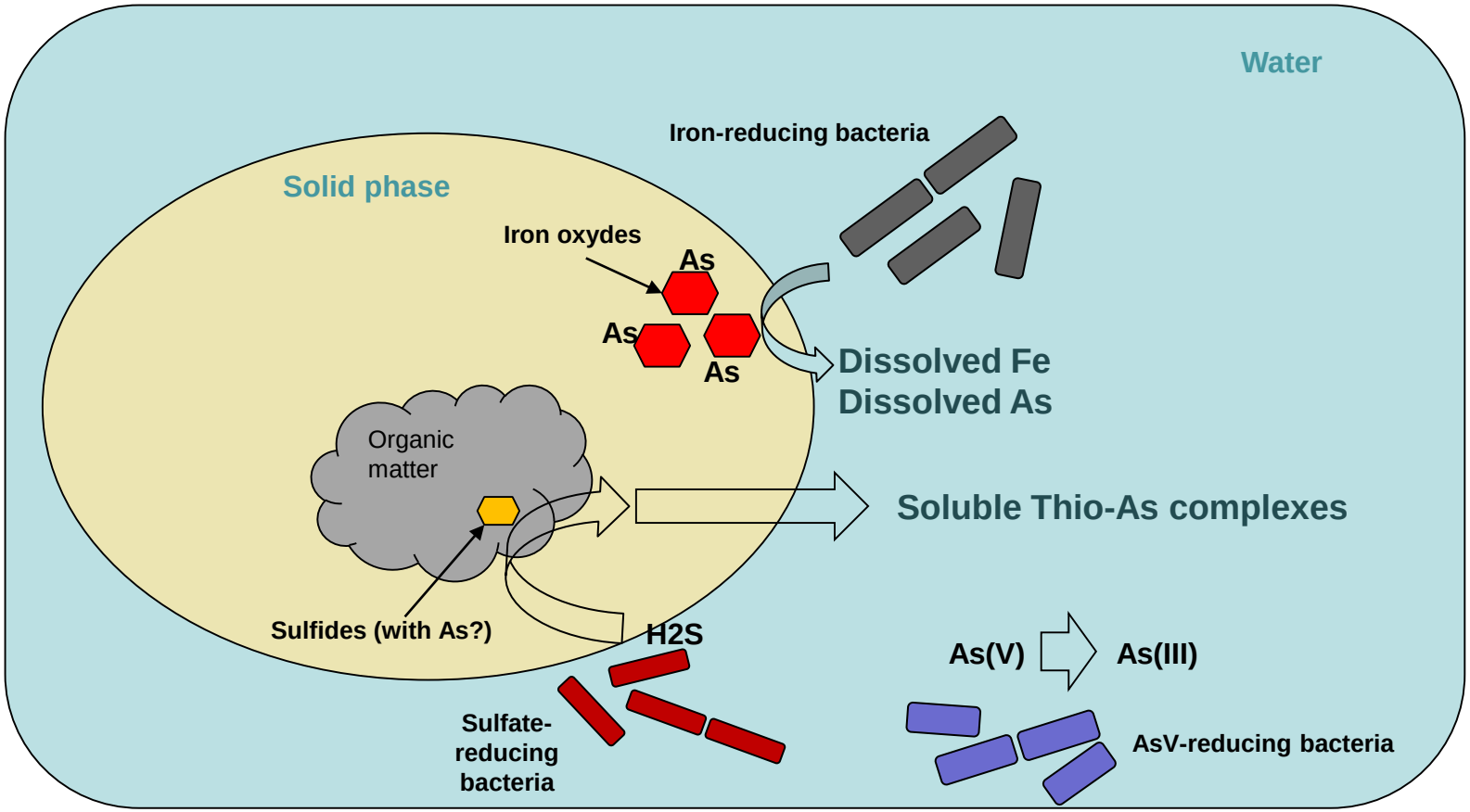
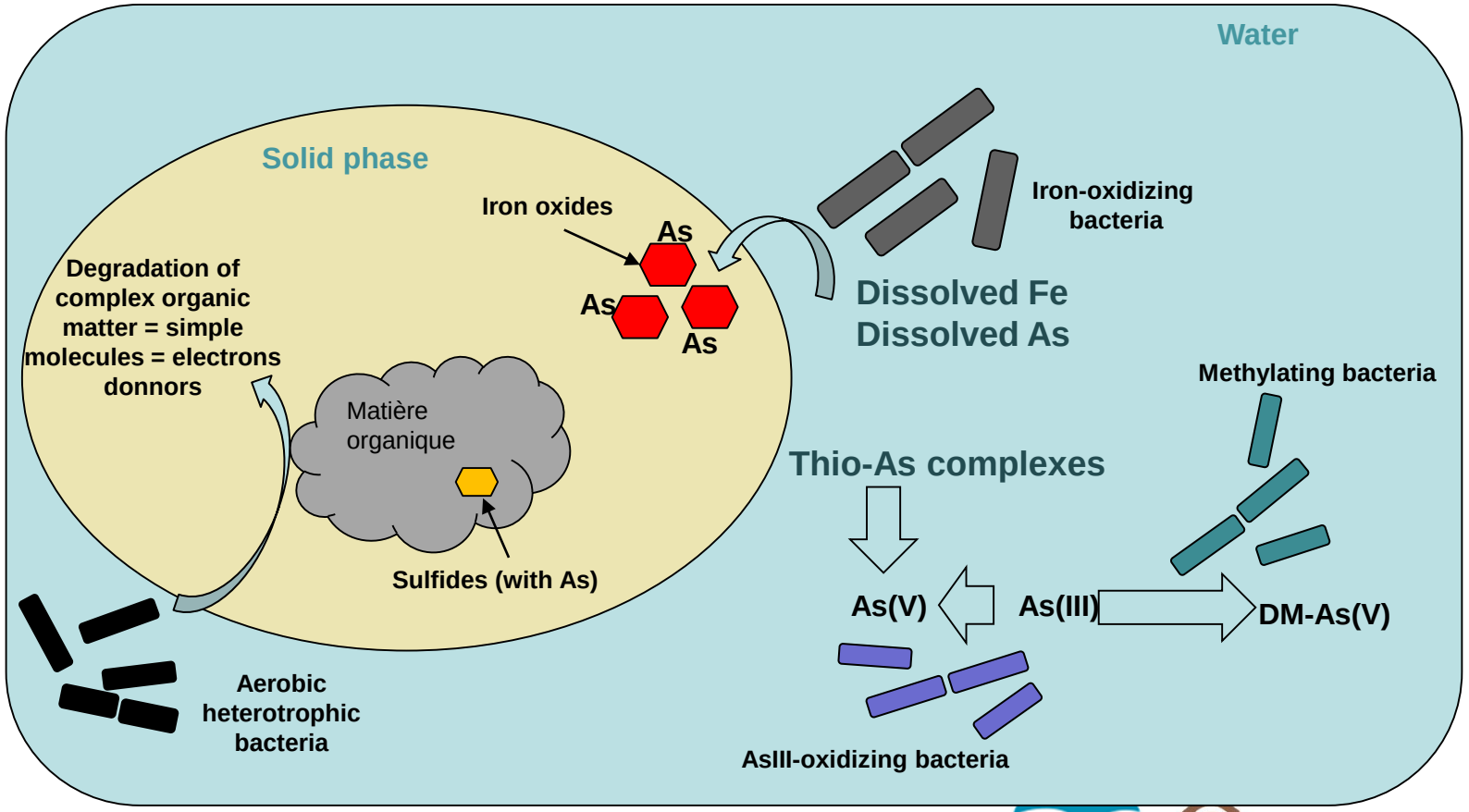
CONCLUSION

> Hypothesis: mechanisms of arsenic release in groundwater



Anaerobic period

> Hypothesis: mechanisms of arsenic release in groundwater



Aerobic period

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> Main conclusions :

- Arsenic origin is linked to a detritical geological formation at the top of the aquifer
- As is mainly released in low redox conditions consistent with the confined groundwater
- The evolution of piezometric surface influences the As speciation in-situ
- Microbes play a major role in As mobility, Fe and S sulfur involved
- Microbes generate the formation of As species (methylated, thio-complex) absent in abiotic conditions
- Global Climate change may accentuate variations of piezometric surface thus amplify the biogeochemical processes of As release.

Thank you for your attention

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