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# UNDERSTANDING THE BROWNING PHENOMENON OF MEDIEVAL STAINED GLASS WINDOWS: IMPACT OF BACTERIA AND BACTERIAL EXUDATES ON THE DISSOLUTION OF A Mn-BEARING GLASS

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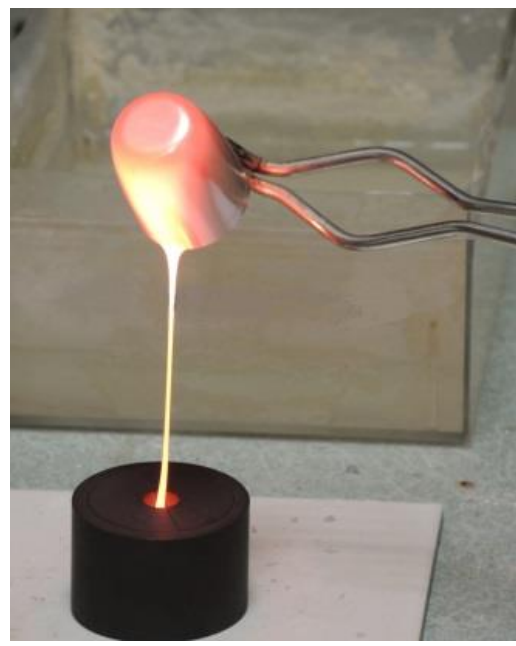


## Glass

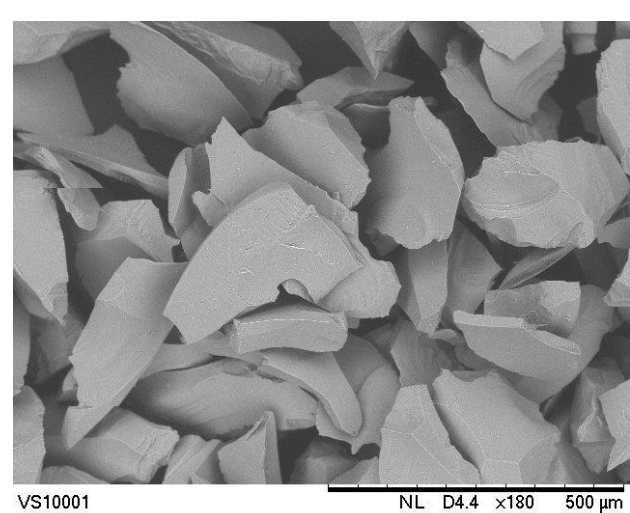
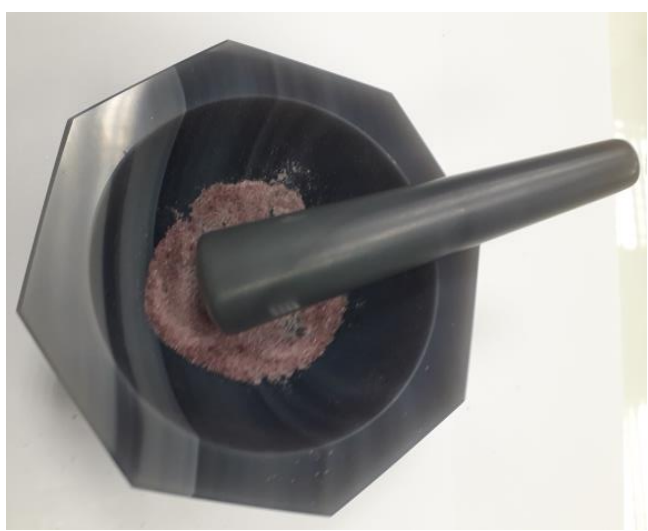
Medieval stained glass windows have a **potash-lime-silica** composition because of the use of plant ashes as flux.

	Wt %	mol %
SiO <sub>2</sub>	51.1	54.7
Al <sub>2</sub> O <sub>3</sub>	1.8	1.1
P <sub>2</sub> O <sub>5</sub>	3.6	1.6
Na <sub>2</sub> O	1,2	1.3
CaO	17.2	19.8
MgO	4.2	6.7
K <sub>2</sub> O	18.8	12.9
MnO	2.08	1.9

Production of glass representative of medieval stained glass windows in a high temperature furnace.



Glass casting at 1500 ° C



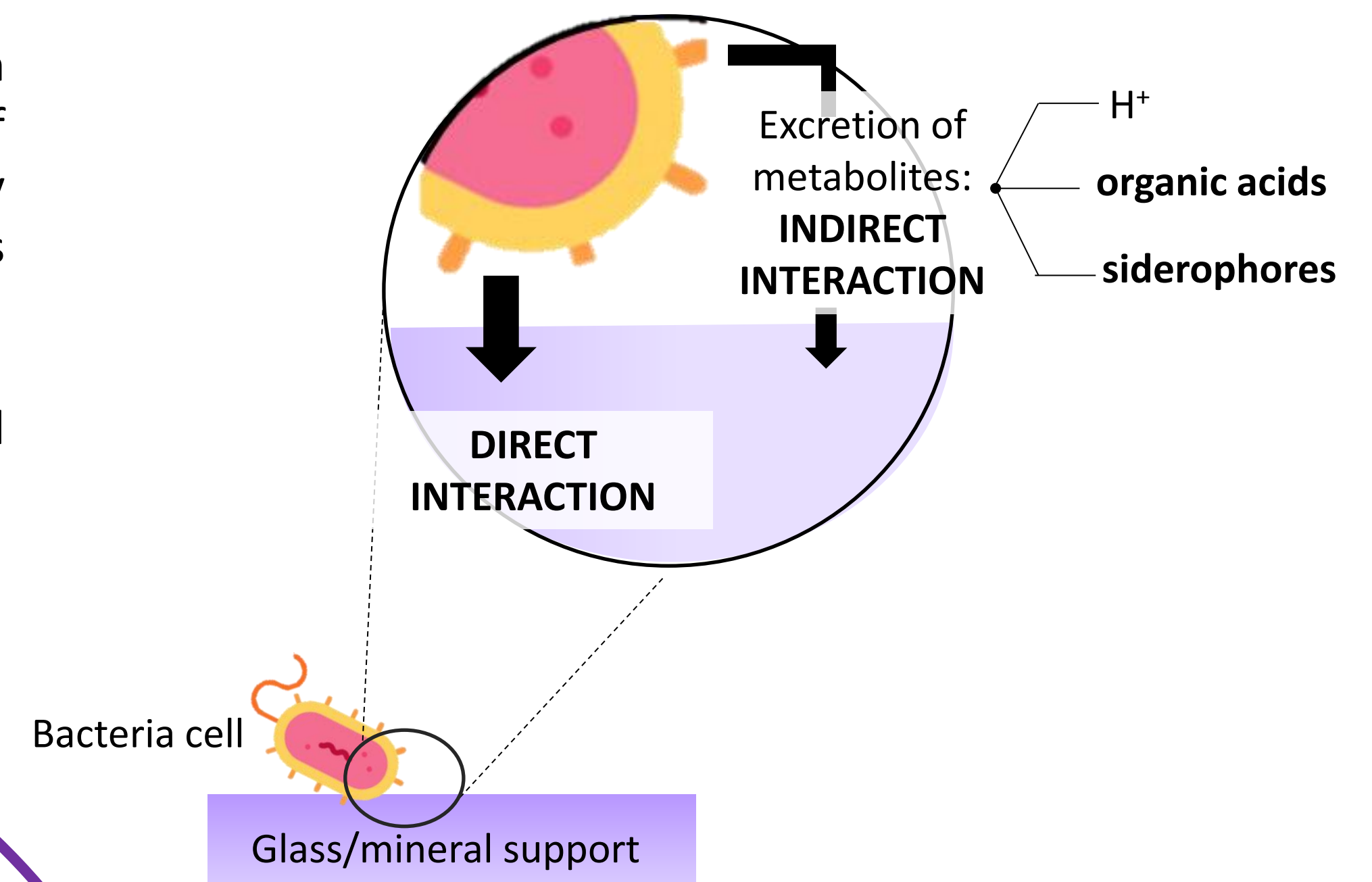
Grinding and sieving: 100-200 μm fraction

## The role of micro-organisms

Previous studies revealed enrichment in Mn in the browned areas and some of them have suggested that manganese migration to the surface, oxidation and/or precipitation might be linked to biological activity.

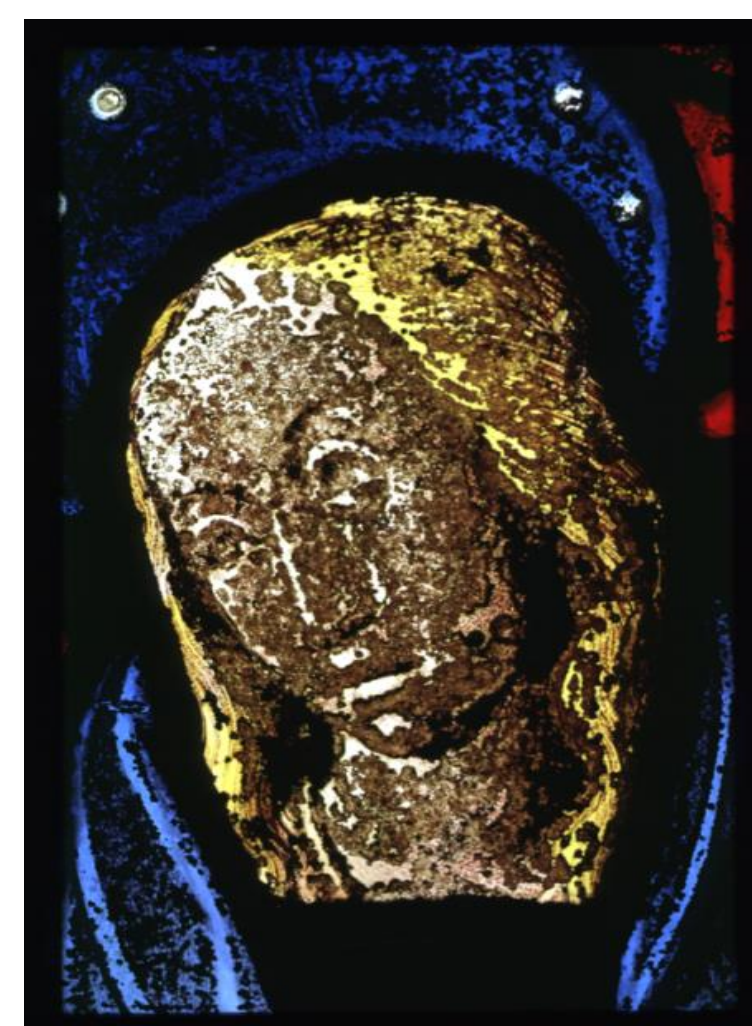
In natural environment, bacteria have an important role in biogeochemical cycles of elements such as C, S, P, Ca, K, Fe, Mn. They strongly influence the weathering of minerals and the bio-mineralization.

The glass support can be a source of micro and macro nutrients for micro-organisms.



## The browning phenomenon

The browning of medieval stained glass windows appears as **dark Mn-rich spots** inside the altered layer on the surface of the glass. It leads to a loss of transparency.

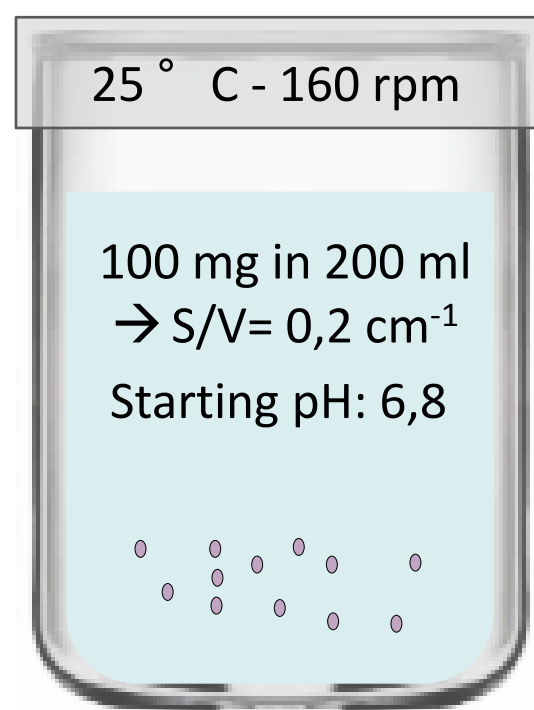


As Mn was introduced as a (de)colourant, the browning is often located on faces and purple shades

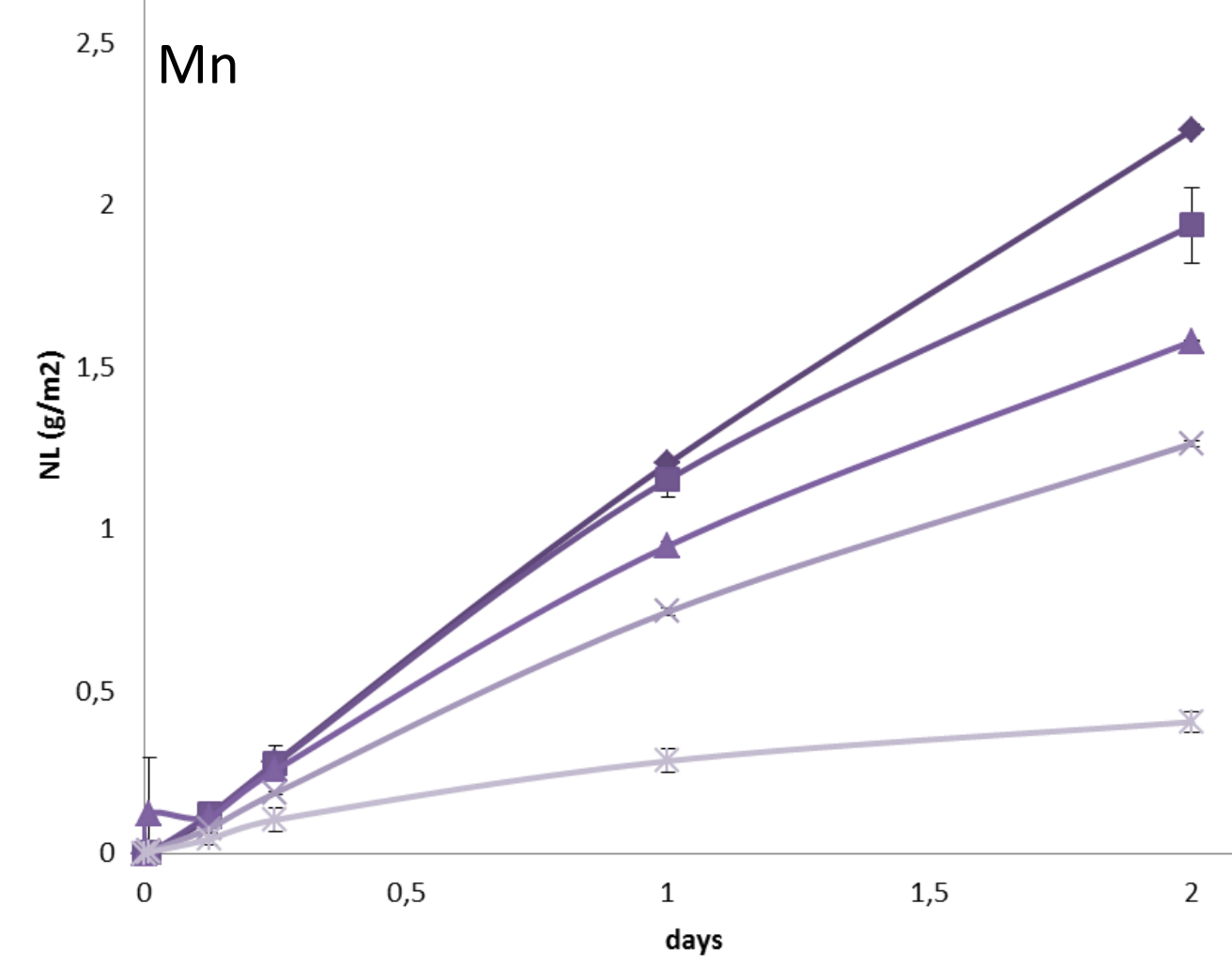
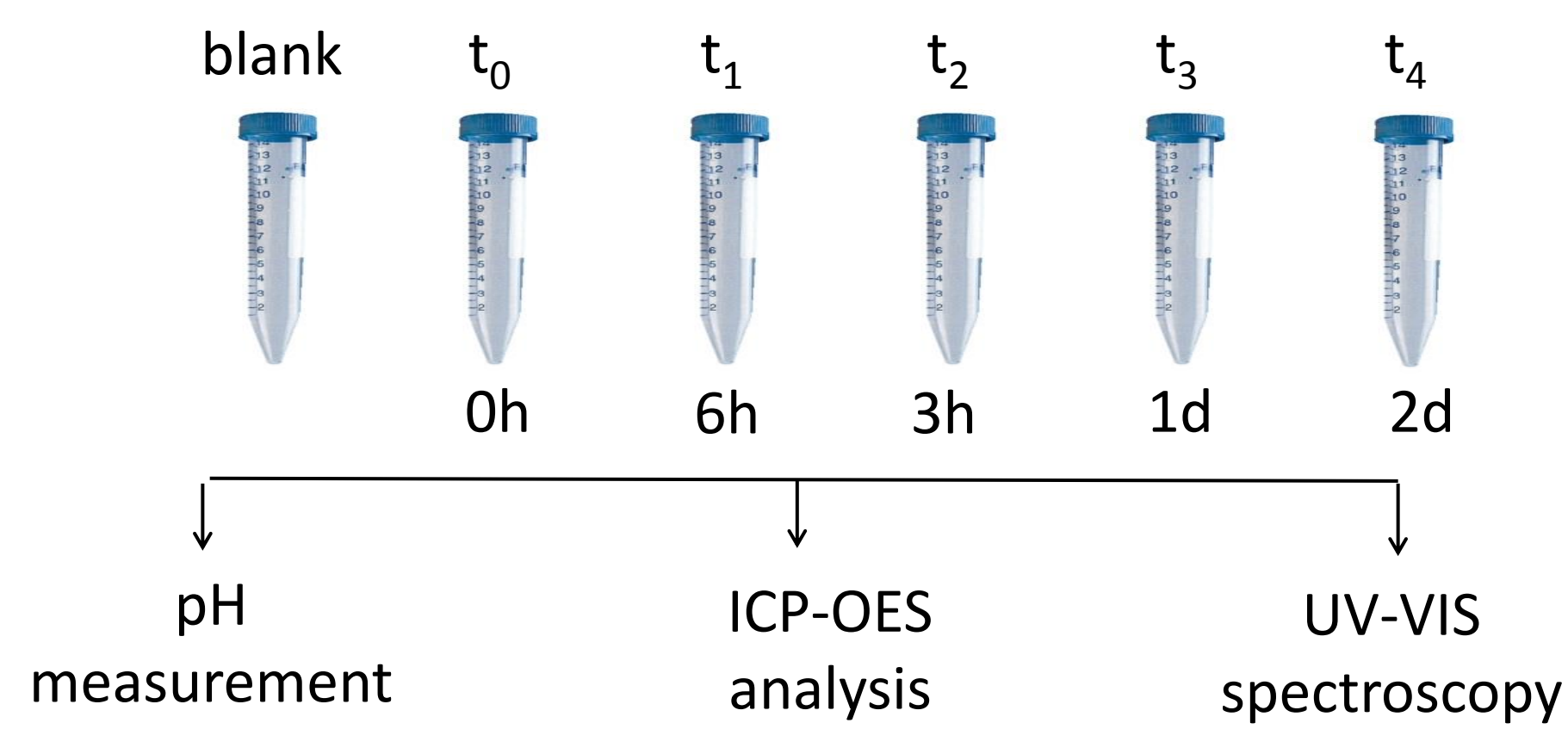
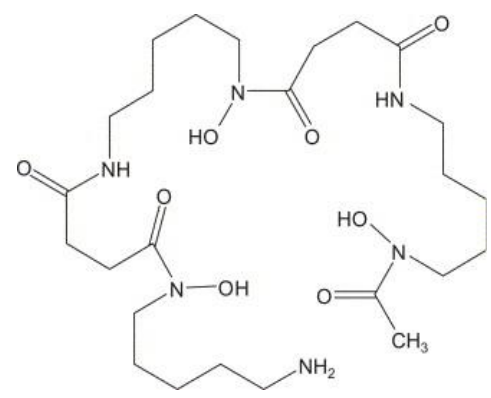
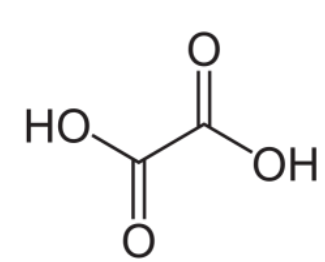
The mechanisms leading to its formation are not understood yet.

## Batch dissolution tests

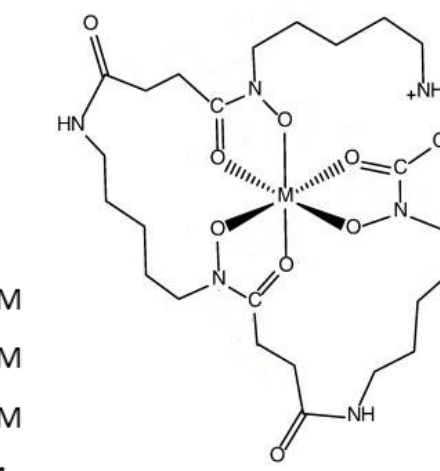
In order to improve our understanding of this phenomenon and investigate the direct and indirect implication of microorganisms, weathering experiments of a model glass were designed.



- Control: 1 mM NaHCO<sub>3</sub> buffer
- Oxalic Acid 1mM
- Siderophore DFOB 50 μM – 1mM
- OA 1 mM + DFOB 50 – 500 μM



- Formation of the complex Mn(III)HDFOB<sup>+</sup> observed by UV-VIS
- Few amounts of siderophore are sufficient to significantly enhance the dissolution rate
- The more concentrated DFOB the faster the dissolution



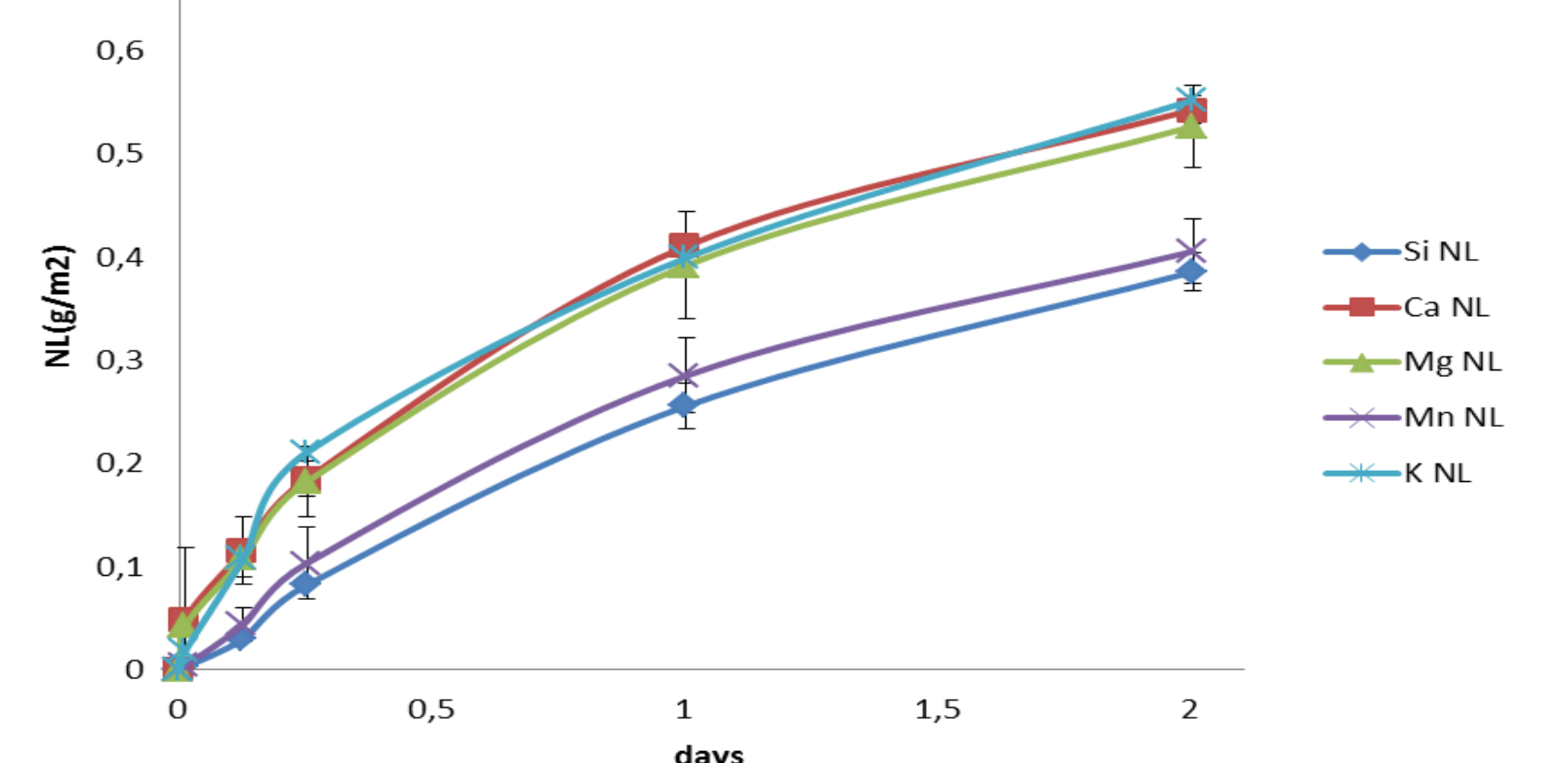
## Results

### NORMALIZED MASS LOSSES

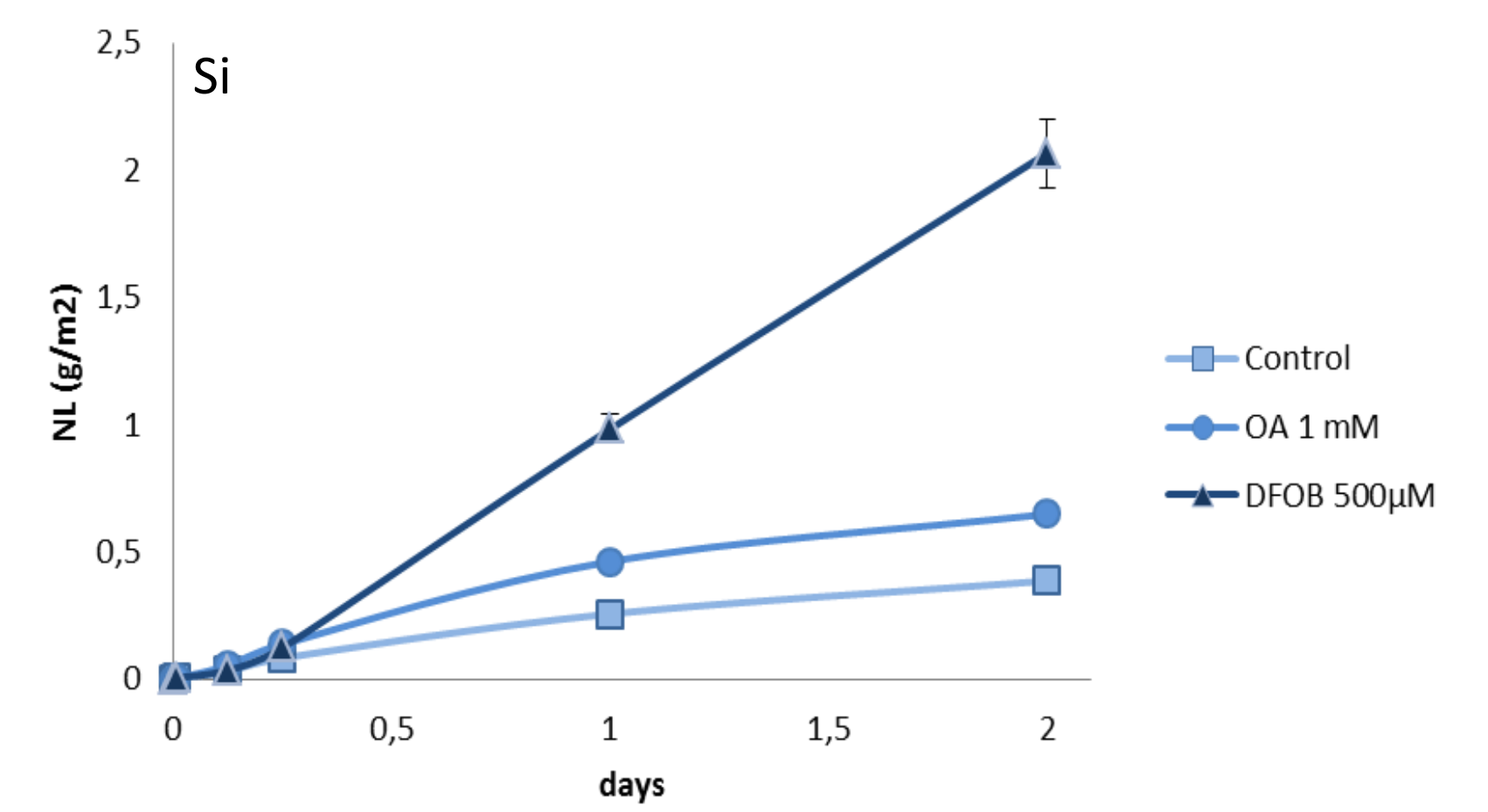
Concentration results are normalized to the reactive surface and to the glass composition:

$$NL_i = \frac{V \times [i]}{S \times x_i}$$

[i] : concentration in ppb  
S : glass surface  
V : volume of solution  
x<sub>i</sub> : mass fraction of the element i in the glass



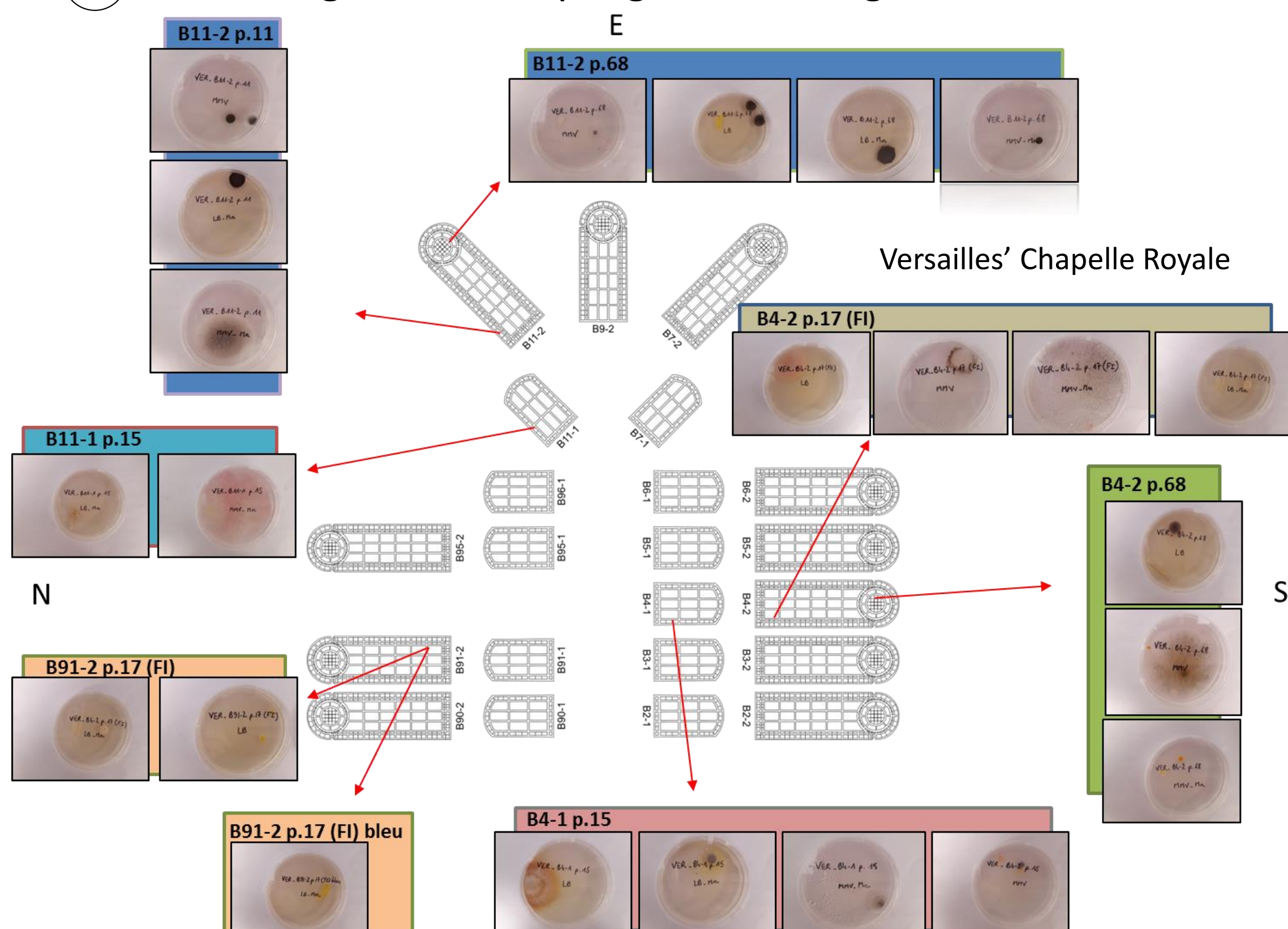
→ The glass follows a slightly **incongruent dissolution** in control conditions



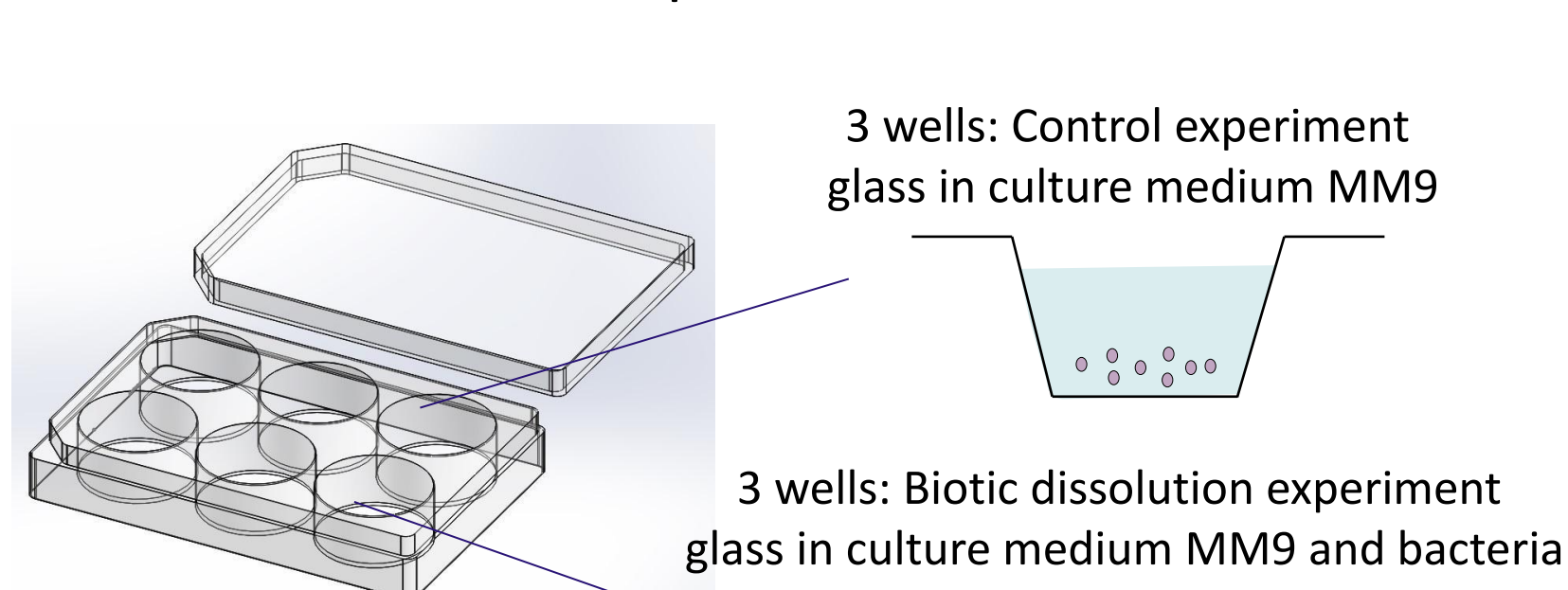
→ Enhancement of dissolution rate in presence of bacterial exudates

## Actually running tests and perspectives

### 1 Micro-organisms sampling on stained glass windows



### 2 Screening of glass-weathering potentials of sampled bacteria



### 3 Biotic dissolution tests in bioreactor



## Conclusion

The results show that the presence of bacteria and bacterial exudates modifies the dissolution mechanisms and kinetics, increasing dissolution rates and changing dissolution stoichiometry. This highlights that a biological activity could be involved in the solubilisation of Mn in a Mn-bearing glass, which is the first step of the appearance of the browning phenomenon.

## References

- [1] Ferrand et al. (2015) Analytical Chemistry 87 3662–3669
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- [3] Kruff et al. (2013) Journal of Inorganic Biochemistry 129 150–161
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