Impacts of functionalized organic surfaces in Mn oxides formation *in situ* monitored by electron microscopy

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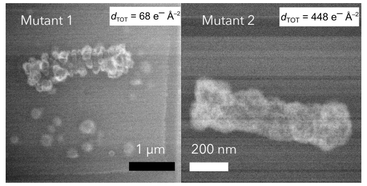
Introduction

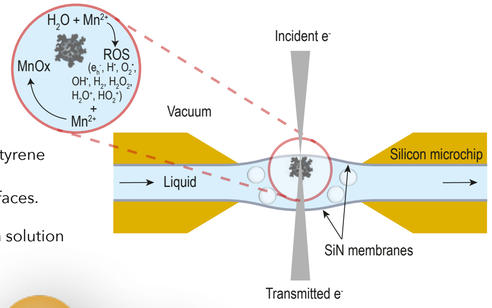
- Biomineralization partly controls metal(loid)s cycling in subsurface environments
- Mn oxides are among the strongest oxidisers at the Earth's surface
- Mn oxidation is a process mainly driven microorganisms (bacteria, fungi…)
- Mn-bearing minerals growth onto *Escherichia coli*: critical role of the chemical functions carried by cell surfaces and exopolymers (Couasnon et al., 2020).



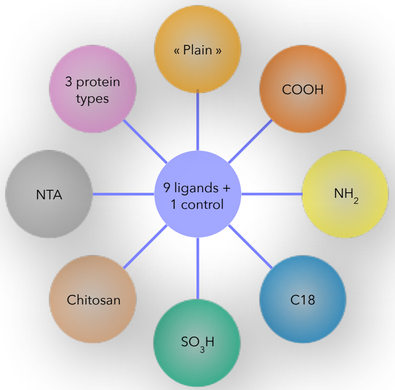
Contribution of organic functional groups to nucleation and mineral growth?

Methods

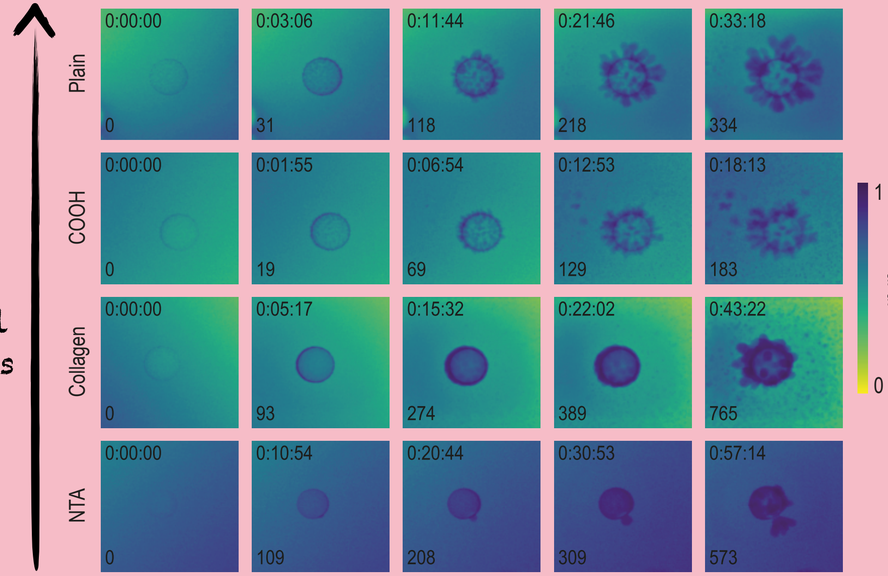
- Liquid-Cell Scanning Transmission Electron Microscopy enables to induce and monitor manganese mineralization on surfaces



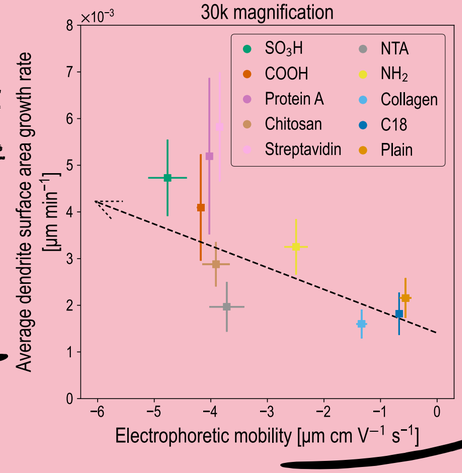
- Functionalized polystyrene beads : analogs of microorganisms' surfaces.
- Bead exposed to Mn solution



- RAMAN analysis to identify the nature of precipitates
- Electrophoretic mobility for bead surface charge



Functionalization of organic surfaces influences the formation of **manganese oxides**!



Growth rate of the area of one dendrite

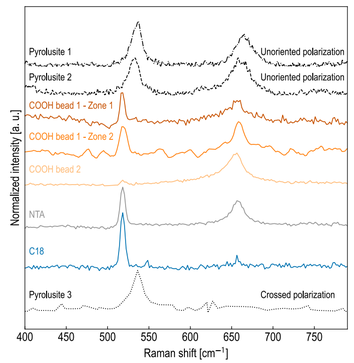
Estimation of the surface charge of the beads

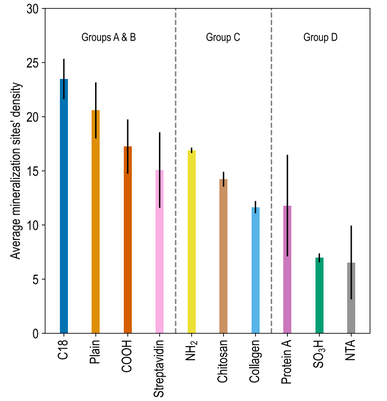
Results

- Mineralization progresses with time – formation of Mn structures

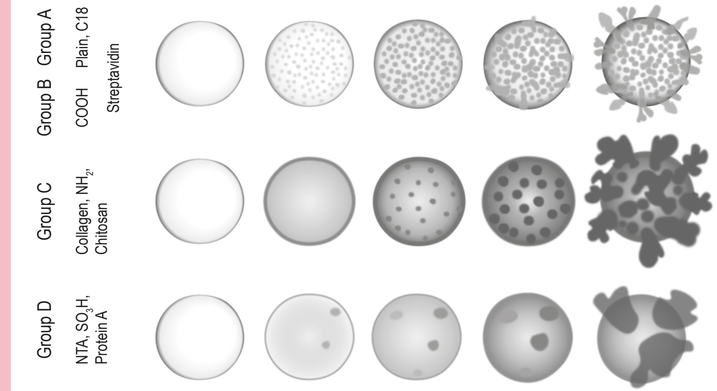
Electron beam + water —Radiolysis→ ROS generation —+ Mn^{2+}→ Manganese oxides

- Crystallised manganese oxides: pyrolusite (MnO_2) identified by Raman spectroscopy
- Average density of mineralization sites growing as dendrites





- **4 groups** with comparable morphological features and Mn mineralization dynamics



- **2 steps**: homogeneous mineralization followed by dendritic growth
- Functional group density = impact on initial mineralization
- The more negative the electrophoretic mobility, the higher the dendrite surface area growth rate

Discussion/Perspectives

- **Surface charge** only partly explains differences in mineralization dynamics
- What are the other **parameters** controlling mineralization? Steric effects? pH? Affinity to metals?
- **Molecules** located at the **microorganisms**' surfaces play a role for **biomineralization** processes