

## ***In situ* electron microscopy monitoring of Mn oxides formation impacted by various functionalized organic surfaces**

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Manganese oxide minerals are among the most powerful oxidizers on the Earth's surface. They are therefore key minerals both for the origin of life and exobiology issues but also for those concerning current biogeochemical cycles. Most of these manganese oxides are formed by biomineralization processes carried out by microorganisms that must be deciphered to better understand the fate of metals and metalloids in subsurface environments. A recent study showed that liquid-cell scanning transmission electron microscopy (LC-STEM) enables to monitor *in situ* the growth of Mn-bearing minerals onto *Escherichia coli* cells. This study has also highlighted the critical role of the chemical functions carried by cell surfaces and exopolymers during biomineralization. However, the contribution of the different functional groups associated to these biopolymers during mineral nucleation and growth remains poorly defined. In order to better assess the role played by these different chemical functions during biomineralization, functionalized polystyrene beads were used here as analogs of biological surfaces. In addition to control beads without functionalization, nine representative types of functionalization were selected, ranging from simple carboxylic and amino groups, to strong chelating agents such as nitrilotriacetic acid (NTA), or more complex proteins such as streptavidin and collagen. Each bead type was exposed to Mn(II)-bearing solution, and mineralization dynamics was continuously monitored *in situ* by LC-STEM. Mn mineralization was observed for all ten bead types with the formation of pyrolusite (MnO<sub>2</sub>) at the bead surfaces, as the result of changes in Mn redox state in solution triggered by radiolysis resulting from water and electron beam interactions. For all bead types, mineralization can be described as a nucleation step followed by the formation of larger dendritic structures. However, nucleation site densities, precipitates morphologies, as well as the overall mineral growth kinetics were found to vary significantly between the different grafted chemical functions. The bead surface charge, estimated by electrophoretic mobility, only partly explains these differences in mineralization dynamics. Steric effects, hydrophobicity as well