Quantum Dots fate at the biofilm/mineral interface

M. DESMAU¹, A. GÉLABERT¹, C. LEVARD^{2,3}, G. ONA-NGUEMA⁴, Y. SIVRY¹, V. VIDAL^{2,3}, P. ENG⁵, J. STUBBS⁵, G. CHARRON⁶, G.E. BROWN JR.^{7,8}, M. F. BENEDETTI¹

- ¹ IPGP, Sorbonne Paris Cité, Univ. Paris Diderot, CNRS UMR 7154, Paris, France. desmau@ipgp.fr
- ² CEREGE, Aix-Marseille Univ., CNRS, IRD, France
- ³ iCEINT, Int Consortium Envir Implicat Nanotech, France
- ⁴ IMPMC, UPMC, 4 place Jussieu, Paris, France
- ⁵ GSECARS Lab., Chicago Univ., ANL, Argonne, IL, USA
- ⁶ MSC, Sorbonne Paris Cité, Univ. UMR CNRS 7057, France
- ⁷ Dept. of Geological Sciences, Stanford Univ., CA, USA
- ⁸ SSRL, SLAC, Menlo Park, CA 94025, USA

The increasing production and use of nanoparticles (NPs) can lead to their accidental release, and raises societal concerns regarding their impact to ecosystems. Among them, Quantum Dots (QDs) are composed of toxic element (Cd, Se) and are thus considered as potential environmental contaminants. Once released, NPs are likely to be accumulated in soils and sediments, where they will be exposed to mineral surfaces covered by bacterial biofilms. This interface is known to be highly reactive and could impose QDs transformations (aggregation, degradation, ...) that in turn will potentially impact the QDs environmental fate. Thus, this study focuses on the processes impacting QDs when exposed to the biofilm/mineral interface.

Shewanella oneidensis MR1 biofilms grown on oriented single crystals Al₂O₃ (1-102) were exposed to negatively charged CdSe/ZnS QDs surrounded by a thioglycolic acid coating. Long Period X-Ray Standing Waves Fluorescence Yield spectroscopy (XSW) were used to study the *in-situ* Se and Zn partitioning at the interface, while Grazing-Incidence EXAFS (Extended X-Ray Absorption Fine Structure) were performed to access the Se and Zn speciation.

Results indicate an important increase in Zn and Se concentrations at the biofilm/mineral interface with time, demonstrating the high accumulation potential of the interface over 10 hours. In addition, an extremely fast dissolution of a part of the ZnS shell was observed, highlighted by a loss of Se and Zn colocalization after only 1.5 hour of exposure. The released Zn(II) shows a preferential interaction with the phosphoryl group present within the biofilm matrix close to the mineral surface. In the meantime, the CdSe core seems to be preserved even after 24 hours. However, when exposed to a damaged biofilm exposed to UV light, no significant dissolution is observed. In turn, when exposed to QDs, the living cells number in biofilm decreased overtime, with a loss of 70% of living cells within 24 hours.