1 Proposal Summary:

Incorporation of dopants in nanoparticles (NPs) is increasingly used to tune their properties such as their solubility, surface reactivity, magnetic or optical properties. From a risk assessment perspective, the role of dopants on the stability of nanoparticles in a natural system is poorly investigated. Our study aims at investigating the effect of Fe doping on the structural stability of Ge-imogolite nanotubes in contact with microorganisms. Interestingly, Ge-imogolite were shown to reduce bacterial growth while iron-doped nanoparticles (0.5% w/w) promoted growth improving the intra-cellular iron homeostasis. At the same time, Fe-doped Ge-imogolite were solubilized when exposed to bacteria while the non-doped Ge-imogolite were not dissolved. The goal of this beam time request is to assess the mechanisms by which the Fe, initially incorporated within the nanotubes, is metabolized by the bacteria by looking at Fe dynamic. We propose to follow Fe speciation by X-ray absorption Spectroscopy (XAS) to decipher the different transformations that the Fe undergoes from the Ge-imogolite structure to the bacteria cytoplasm including redox changes.

2 Obtained results

Fe-doped imogolite were exposed directly to *Pseudomonas fluoresns* directly, for 4 days (Feimogolite + bacteria). Alternatively, The Fe-imogolite were placed into a dialysis bag and the bacteria were grown outside the dialysis bag. After 2 days, the bacteria started releasing some siderophores (fluorescent) and after 4 days, 20% of the Fe-imogolite was degraded. We hypothesized that this degradation was due to the strong affinity of the siderophores to Fe.¹

The compounds remaining inside the dialysis bag after 4 days are called "Degraded Fe-imogolite) and the Fe released outside the dialysis bag are named "Fe released from Fe-imogolite".

The iron XANES at Fe k-edge (7.11 keV) was recorded.

The Fe within the structure of the imogolite was Fe(III), as previously reported²

The Fe stayed in a +3 oxidation state after the degradation by the siderophore, however some +2 species also formed, specially in the fraction of Fe released outside the dialysis bag. Furthermore the XANES and associated derivative change after the Fe-imogolite has been exposed to the bacteria, in adequation to the degradation we observed.

This can be attributed to the fact the Fe-imogolite were degraded by the siderophores, when Fe(III)-siderophore are formed, and then were assimilated by bacteria, where Fe(II) compounds are formed both via a reduction to recycle the siderophore³, and to be used in protein⁴.



Furthermore, we have run during this beamtime some preliminary data acquisition at Fe k-edge related to other projects

3 Further use of the results

These results were in accordance with our study, and will be used as a secondary proof or Fe cycle use in a later review about the impact of microorganisms on the biodegradation of nanomaterials.