ESRF	**Experiment title:** XANES study on monodisperse MxFe3-xO4 nanoparticles obtained by synthetic and biological routes	**Experiment number**: HC-2420
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Report:

We have performed XANES measurements at BM25A on $M_xFe_{3-x}O_4$ (M = Co, Mn, Ni) ferrite nanoparticles (NPs) synthetized by two different methods, biomineralization by magnetotactic bacteria and a soft chemical procedure. In our proposal (number 39229) we stated our intention to grow the *Magnetospirillum gryphiswaldense* bacteria in culture media supplemented with Co or Mn citrate, in addition to Fe citrate, to promote the incorporation of Co or Mn to the structure of biomineralized Fe_3O_4 NPs, called magnetosomes. It is worth mentioning that previous studies by M. Tanaka et al. have demonstrated successful Co, Mn and Cu doping into magnetosomes [1]. However, no XANES experiments have been performed on magnetosomes doped with transition metal ions before. A high-temperature solution phase reaction of Fe, Mn or Ni precursors in the presence of oleic acid and oleylamine was also proposed and used to prepare monodisperse doped ferrite NPs.

Firstly, the XANES spectra of magnetosomes, i.e. magnetite nanoparticles biominerallized by magnetotactic bacteria, doped with Co or Mn have been measured. Particularly, 2 samples of Co-doped magnetosomes with 2 different Co concentrations were measured at both Co and Fe K-Edges, and 1 sample of Mn-doped magnetosomes was measured at Mn and Fe K-Edges. All measurements were performed on fluorescence mode at room temperature. Besides, different references were

measured on transmission mode to elucidate wether the dopant (Co or Mn) is actually incorporated on the magnetosome, with a $Co_xFe_{3-x}O_4$ or $Mn_xFe_{3-x}O_4$ ferrite structure, or accumulated by the bacteria forming a different metal complex. The standards used were: stoichiometric commercial ferrites, $CoFe_2O_4$ and $MnFe_2O_4$, the precursors Co and Mn citrate, and, in the case of Mn, model compounds similar to those binding Mn within biological samples, Mn-EDTA, Mn-ATP and Mn-phosphate. We are currently analyzing the obtanied data.

Secondly, the XANES spectra of the following samples synthetically prepared have also been measured in transmission mode at room temperature. 4 Mn-doped ferrites with different nominal Mn concentrations: $Mn_{0.13}Fe_{2.87}O_4$, $Mn_{0.18}Fe_{2.82}O_4$, $Mn_{0.27}Fe_{2.73}O_4$ and $Mn_{0.36}Fe_{2.64}O_4$, and 4 Ni-doped ferrites with different nominal Ni concentrations: $Ni_{0.31}Fe_{2.69}O_4$, $Ni_{0.43}Fe_{2.57}O_4$, $Ni_{0.70}Fe_{2.30}O_4$ and $Ni_{0.86}Fe_{2.14}O_4$. XANES results will allow us to unravel the actual transition metal ions concentration and distribution among the octahedral and tetrahedral sites in the ferrite structure.

[1] M. Tanaka et al., *J. Mater. Chem.*, **22**, 11919-11921 (2012).
[2] D. Carta et al., *J. Phys. Chem. C*, **113**, 8606-8615 (2009).