Report for the short visit grant of FIMIN-network

1. *Purpose of the visit*

Main purpose of the short visit was to participate at the FIMIN-workshop Magnetic Methods in Biogeochemistry – from field to microscopy and Mössbauer spectroscopy. I went there to learn the basic background theories of the different methods, to learn for what investigations they can be used and to apply the methods. Additionally, if possible, I planned to measure my own samples during the workshop and the four extra days. Overall, the workshop and the measurements should provide new knowledge about possible measurement methods and first results which can be used in my Ph.D. –thesis.

2. *Description of the work carried out*

27.5.2010 field trip day:

Together with the LIFE-group and Bo Thamdrum we visited an iron rich field site at Gammel Lerje (close to Roskilde). We discussed different ways to sample, to transport and store samples. Then we tested sampling techniques for fresh water sediments and soils as well as porewater sampling.

28-30.5.2010 Mössbauer spectroscopy at LIFE-campus, Copenhagen (C. Bender Koch):

We learned the theory behind the measurements, the calibration of method and how to fit and to interpret spectrum. We trained calibration with reference material spectra, fitting and interpretation using spectra of samples from workshop participants.

31.5.-4.6.2010 Electron microscopy at DTU, Kongens Lyngby
(Group from R. Dunin-Borkowski; M. Posfei):

We learned the basic theory of the electron beam scattering microscopy (SEM) or transmission microscopy (TEM). In a practical, we modeled the effect of electron beam to understand what is the interaction volume and the difference between SEM and TEM. In brief lectures we were introduced to the analytical methods EDX/WDX and EELS. Electron diffraction was explained in more detail and analysis/interpretation of diffraction patterns was trained. A selection of SEM/TEM techniques were explained and demonstrated by specialists: FIB-SEM, TEM-holography and TEM-3D-topography. Sample preparation for solid and liquid or soft samples was explained in the sample preparation labs. We prepared soft powdered and liquid samples and investigated these samples with SEM, ESEM and TEM (figure 1).

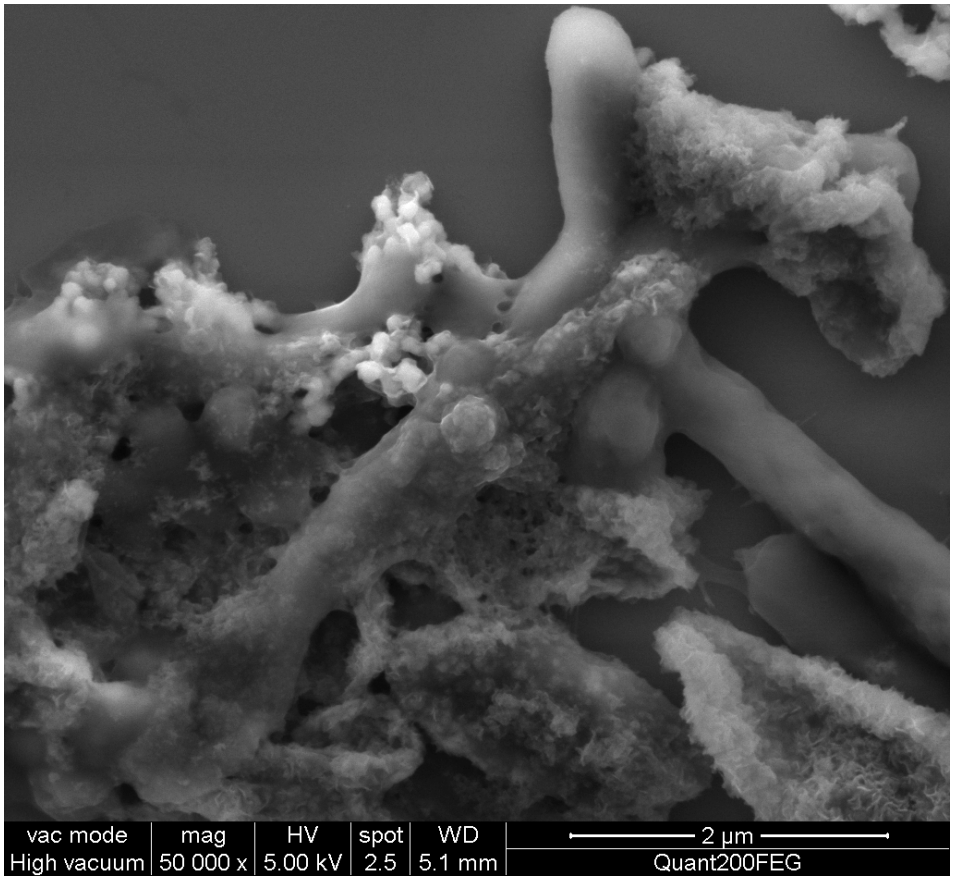

Figure 1 SEM image at high vacuum mode from 40°C *Leptothrix* Appels iron oxide sample. The two morphologies of L. Appels are visible the smaller rod shaped cells, forming cell chains and more oval cells. However, oval cell forms can also be collapsed cells. Cells are surrounded by iron oxides therefore single cells in the chains are barely visible. More cubic forms may be KCl crystals.

6.6-8.6.2010 LIFE Center, Copenhagen and Lund, Sweden (A.M. Hirt and group from I. Snowball):

We learned the theory behind magnetic methods and what measurements can be done. In Lund several magnetic methods were demonstrated for sediment cores and small samples/crystals.

Measurements of my samples during the workshop and four extra days:

I brought three abiotically formed iron oxides and three by *Leptothrix cholodnii* Appels (L. Appels) formed iron oxides. For abiotic and biotic oxides, Fe(II) was oxidized at pH 7 and 13µmol/l oxygen concentration at different temperatures. Different measurements were started during the workshop and will be continued (table 1).

Table 1 Methods applied to selected samples

method	**samples**
Mössbauer LIFE Denmark	10,20, 40 °C abiotic and *L.* Appels
FT-IR LIFE Denmark	10,20, 40 °C abiotic and *L.* Appels
XRD LIFE Denmark	10,20, 40 °C abiotic and *L.* Appels
E-SEM/SEM DTU Denmark	40°C *L.* Appels

3. Main results of my samples

XRD and Mössbauer spectra indicate Lepidocrocite as dominant iron oxide phase in abiotic and biotic samples. However, the spectra were deviating from synthetic Lepidocrocite, which points to a poor crystalline Fe-oxide. This can be seen in the XRD spectrum, where different peaks were dominant and others were not visible compared to synthetic Lepidocrocite, and in the Mössbauer spectrum with the broad and asymmetric lines of the Lepidocrocite doublet (Figure 2A). Moreover, we tried to investigate the biologically formed Lepidocrocite using SEM images. However, the crystals were too small to see at high magnification with SEM indicating that nano-sized Fe-oxides are formed (Figure 1).

XRD, Mössbauer and FT-IR results indicated differences between 40°C samples compared to 10;20°C samples of abiotic and biotic Fe-oxides. Additional XRD peaks appeared in the 40°C samples: a very broad organic matter peak in case of *L.* Appels sample and undefined very sharp peaks in abiotic sample. In the biotic samples, several peaks of the FTIR spectrum refer to organic substances and these peaks are intensified in the 40°C sample. In the spectra of abiotic samples, strong peaks for SO_4^{-2} were detected especially for the 40°C sample, so the unknown XRD peaks may belong to a sulfate-phase.

Additionally, the low temperature Mössbauer spectrum may indicate a difference between abiotic and biotic formed Fe-oxides. The *L*. Appels Mössbauer lines of the 40°C sample show a change of the background at 18K, indicating an earlier splitting into a sextet compared to abiotic 20°C sample (Figure 2B). This suggests that the biotic Lepidocrocite is better ordered compared to abiotic sample.

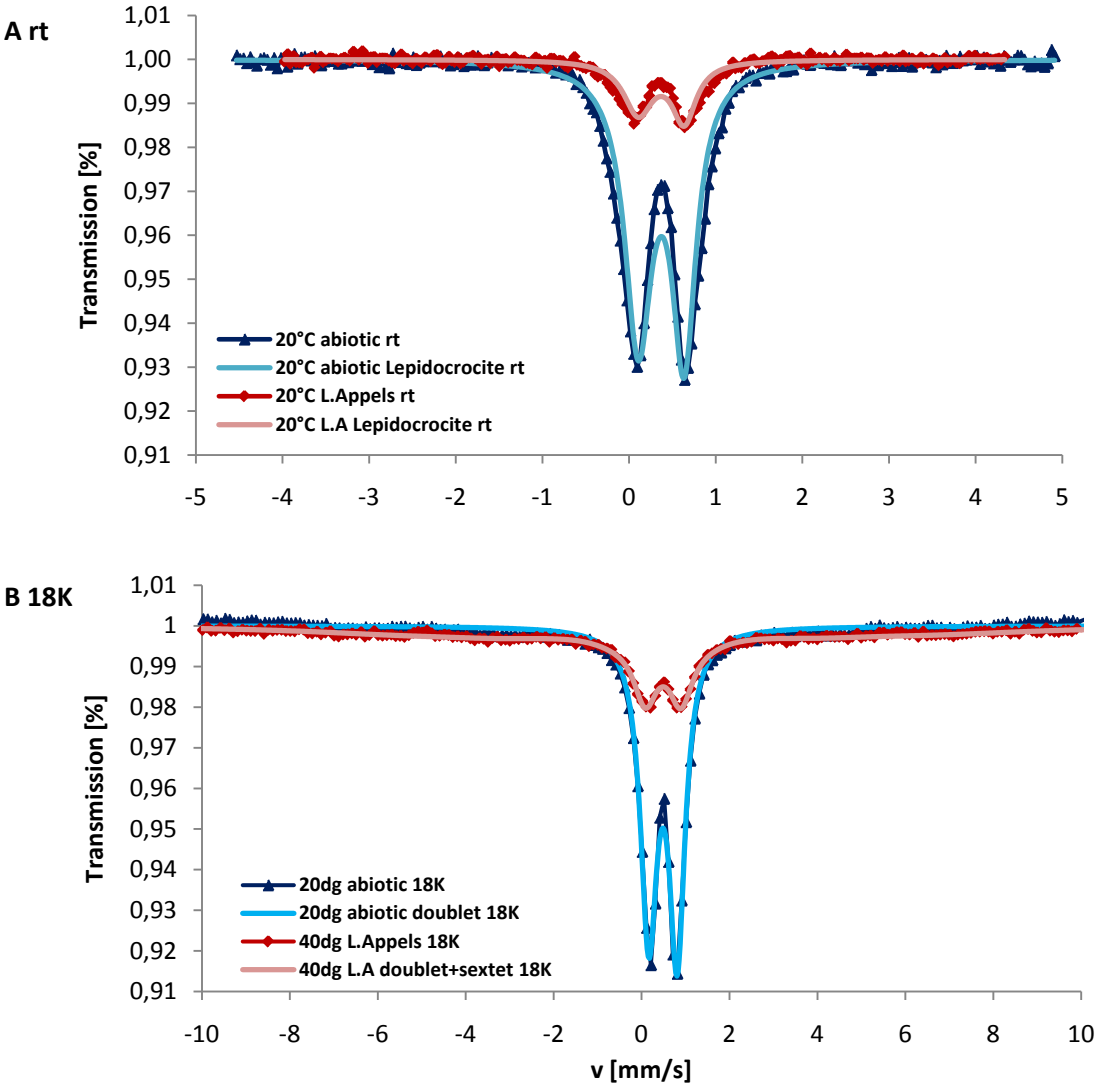

Figure 2 Mössbauer spectra (symbols) and fit (lines) of abiotic and *L.*Appels iron oxides measured at room temperature (A rt) and at 18K (B 18K). Absorption of abiotic iron oxides was larger than of biotic samples. At rt abiotic and *L.* Appels spectra lines were both asymmetric and they were broader than the fitted Lepidocrocite lines. At 18K *L.* Appels spectrum is more symmetric and the background absorption increases indicating upcoming sextet lines.

4. Future collaborations, comments and projected publications

The Mössbauer measurements of the samples will be completed at the LIFE-center. To me, Mössbauer spectroscopy together with XRD and FT-IR is a good option to characterize the iron oxides formed in my experiments. Helpful will also be to have a closer look at the Lepidocrocite crystals with TEM. The results of these first measurements will be part of my Ph.D.-thesis, therefore the grant as well as the people and institutes involved will be mentioned in the paper(s).

Overall, the workshop provided a lot of information about the different techniques and to discuss directly measurement ideas with specialists in the field. Besides, with the new knowledge it is also possible to use instruments at our institute directly (e.g. FT-IR). Finally, it was inspiring to get to know the hosts and participants with their projects and their views on iron.