



DUBBLE – EXPERIMENT REPORT

We kindly request you to answer the questions (max 2 pages) and return the form to NWO **within 2 months of the completion of the experiment** to dubble@nwo.nl

Beam time number: 26-01-909		File number: 195.068.567
Beamline: BM 26A	Date(s) of experiment: 6/4/2011-11/4/2011	Date of report: 22/4/2011
Shifts: 15	Local contact(s): Miguel Silveira, Segey Nikitenko	

1. Who took part in the experiments? (Please indicate names and affiliations)

At ESRF: Dr. Miguel Silveira (KU Leuven, DUBBLE), Dr. Thilo Behrends (Earth Sciences, Utrecht University)

Collaborators: Dr. Caroline Slomp, Dr. Tom Jilbert (Earth Sciences, Utrecht University), Dr. Laszlo Vincze (XMI-group of Ghent University)

2. Were you able to execute the planned experiments?

YES, but instead of Se we focussed on the distribution and coordination chemistry of Mn in the samples

3. Did you encounter experimental problems?

YES, the data acquisition was frequently interrupted for several reasons (acquisition software crashed or acquisition was not started), problems with the monochromator led occasionally to energy shifts in the data.

4. Was the local support adequate?

YES, perfect

5. Are the obtained results at this stage in line with the expected results as mentioned on the project proposal?

YES

6. Are you planning follow-up experiments at DUBBLE for this project?

YE

7. Are you planning experiments at other synchrotrons in the near future?

NO

8. Do you expect any scientific output from this experimental session (publication, patent, ...)

YES, until end 2011

9. Additional remarks

Technical aspects

The collection of XRF and XAS spectra with a focused beam using a polycapillary was technically demanding. The installation of the hardware and aligning the optics was, in comparison to standard XAS experiments, very time consuming. In total, about 5 shifts were required for installing and optimizing the system, although the DUBBLE staff was very supportive and worked very efficiently. The allocated beamtime of 15 shifts was sufficient for collecting a considerable amount of data, but 15 shifts are also at the lower limit for these type of experiments.

We encountered several problems during data acquisition. Often the program reported an error message and stopped or the acquisition did not start which required permanent supervision of the system and frequent restarts of the XAFS acquisition software. Furthermore, a couple of times the monochromator apparently failed in finding the correct starting position which led to energy shifts in the spectra (up to about 10 eV). These problems hampered the experiments but did not jeopardize its success. For analyzing samples with high spatial heterogeneity, it would be a great improvement to have the feedback system operational, which is able to keep the beam position stable

Based on additional preliminary analyses of the samples we decided not to collect XAS spectra at the Se K-edge but to focus on manganese (Mn) in this experiment because the Mn profiles turned out to be very interesting and the collection of XAS spectra of high quality for Mn seemed more promising than for Se in these samples. The environmental behavior of manganese is, similar to that of selenium, strongly redox dependent and Mn profiles in sediments are used to reconstruct redox conditions in the sediment and the overlying water during the genesis of these sediments.

Results

In the experiment two blocs of solidified sediments were analyzed. These blocs were collected from long sediment cores, because they contain sections from periods, in which the sedimentary regime has apparently drastically changed. On each of the two blocs, a segment with a vertical extension of 15mm was analyzed during the experiment.

In a first approach, XANES spectra were collected along vertical scans without using the polycapillary optics. The vertical distance between locations at which we collected XANES spectra was 0.4 mm, which was about the vertical size of the beam. The width of the beam was about 6mm. XANES spectra were collected in fluorescence mode using the 9-element Ge-detector. The edge step of the XANES spectra is shown as a function of vertical position exemplarily for one sediment core in Fig.1.

After installing the polycapillary, the core was stepwise scanned with a resolution of 0.05 mm at an energy above the Mn K-edge by still using the 9-element Ge-detector (Fig. 1, FD counts). Then, some short sequences from the cores were selected and, again, XANES spectra were collected along these sequences with a vertical resolution of 0.05 mm. Afterwards, the Ge-detector was replaced by a Vortex silicon drift detector for XRF analysis. When using this detector, consecutive vertical scans of about 15mm length were collected with a resolution of 0.05 mm. Scans were performed at energies above and below the Fe K-edge. This was done in order to avoid interference of the strong Fe fluorescence with the fluorescence signal of other elements. During the scans the fluorescence of the elements Ca, K, Ti, Fe, Mn, and S was recorded (panels in the figures showing vortex counts). Finally, the polycapillary was removed and EXAFS scans from three significant spots were collected using the regular beam.

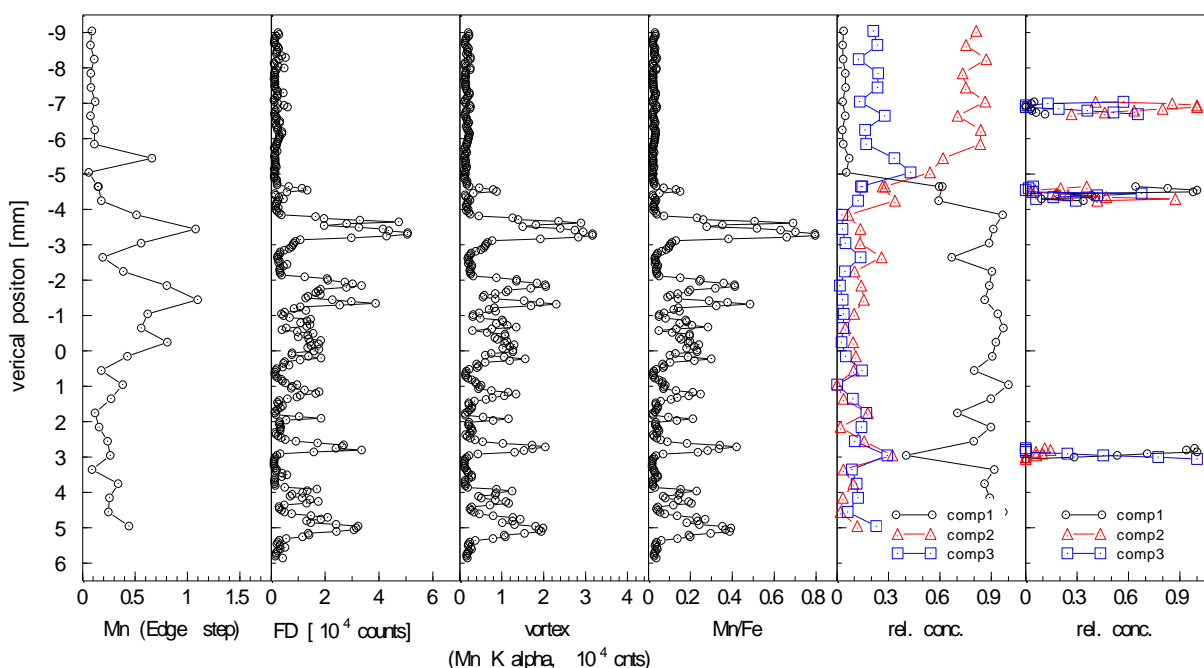


Fig.1 Example of results collected from one of the two cores. The right panel shows results from PCA for section which were analyzed with high vertical resolution. One of these sections is magnified in Fig. 2.

The vertical profiles of Mn fluorescence collected on the same trajectory but with different detectors (vortex detector and Ge 9-element detector) are, as expected, highly correlated. The intensity of the Mn fluorescence along the scans varies dramatically. The low resolution profiles, which were obtained when using the regular beam, follow very well the moving average (9 points) derived from the high resolution profiles (data not shown). This indicates, that the sample is highly anisotropic and that the vertical variability is much larger than that along the two other coordinates. These findings attest that the pronounced vertical stratification of the sediments, which can be visually recognized, is also reflected in the Mn profiles. Furthermore, the comparison of high and low resolution scans demonstrate that a focused beam is necessary to capture features in the Mn profiles with a vertical dimension of 0.2 mm and less.

In some parts of the sediments, usually with low Mn concentrations, the intensity of Mn fluorescence correlates with those of Fe and S. This suggests that in these parts of the sediment Mn is diagenetically enriched together with S and Fe. In sections characterized by high Mn content, Fe and Mn are inversely correlated and no correlation with S can be observed. Hence, in this part of the sediment Mn enrichment is decoupled from Fe diagenesis whereas the inverse correlation might be attributed to dilution effects due to the high concentration of deposited Mn.

Principal component analysis (ITFA software, Rossberg et al., 2006) of XANES spectra collected from 98 spots reveals that three components are sufficient to explain the majority of the variance in all spectra. With the iterative target test of the ITFA program, three end-member XANES spectra were extracted and their relative concentration in all samples was determined (Fig 1 and 2). The extraction of the isolated endmembers significantly improved when using the high resolution scans. Furthermore, the vertical sequence of different Mn phases can only be adequately followed when using the polycapillary optics. Comparison of the extracted endmember XANES spectra with those of standards together with preliminary EXAFS fitting indicate that the three components represent Mn in silicates, carbonates, and

sulfides, respectively. These phases correspond to very different depositional scenarios: absence of authigenic formation of Mn, pronounced Mn deposition without sulfidization, and Mn enrichment connected to sulfidization in the sediments. These scenarios, in turn, can be used to infer information about the characteristics of the overlying water column at the sampling collection. The high resolution scans can therefore be used to reconstruct the history of events at this location which had a pronounced influence on the stratification and composition of the water column.

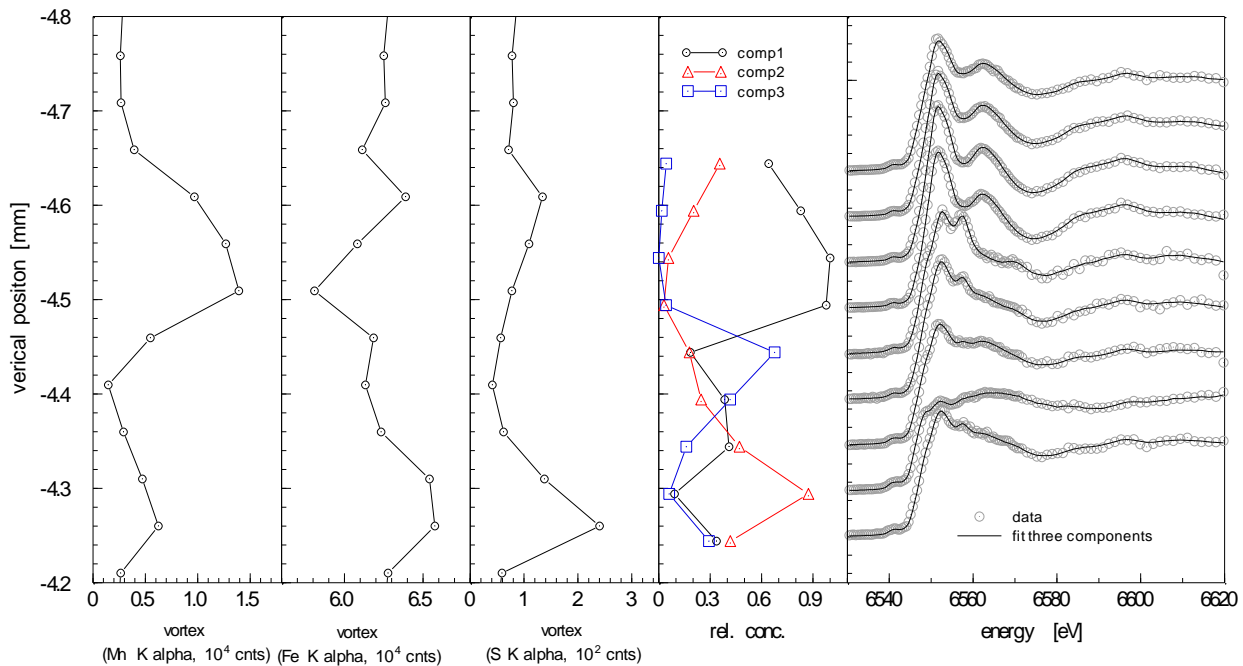


Fig 2. Example of a short sequence analyzed with high resolution. The lines in the right panel represent the reproduction of the spectra by using three components while the squares show the measured spectra. This figure provides an excellent example for the change in prevalence of different Mn phases on a small vertical scale.