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: **26-01-1094**		**File number:**
Beamline: **26A**	**Date(s) of experiment:** **27/11/2016 – 1/12/2016**	**Date of report:** **28 Jan 2017**
Shifts: **9**	**Local contact(s):** **Dr. Dipanjan Banerjee**	

1. **Who took part in the experiments?** (Please indicate names and affiliations)
   prof. dr. Caroline Slomp (UU)
   dr. Thilo Behrends (UU)
   drs. Nikki Dijkstra (UU)
   drs. Martijn Hermans (UU)

2. **Were you able to execute the planned experiments?**
   YES (If NO, please specify)
   Due to the fast progress we were able to include the analysis of some additional samples.

3. **Did you encounter experimental problems?**
   NO (If YES, please specify)
   We highly appreciate the recent improvements at the beamline. In particular, we are grateful for the revision of the fluorescence detector, that is no operating better than before, and the smart sample mounting system which allows fast positioning of the beam.

4. **Was the local support adequate?**
   YES
   The support was excellent. The set-up of the experiment has been performed in a very short period despite the fact that we needed to develop methods and adjust the parameters of the fluorescence detector for two elements. Due to the fast set-up and the fact the beamline is operating very robustly, we were able to analyse more samples than we hoped for.

5. **Are the obtained results at this stage in line with the expected results as mentioned on the project proposal?**
   Yes, see 9 for more details

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

   The results are part of three still continuing research projects and we expect to analyse new samples in the future.

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(If YES, please anticipate a date for submission of the envisaged publication/patent; If NO, please specify)

The results will contribute to PhD projects and are part of three sub-projects. We expect that the results of this experiment will hence be used in the corresponding manuscripts. The date for submission is difficult to anticipate in this moment as progress in additional experimental and analytical work is necessary for accomplishing the manuscripts.

9. Additional remarks

Short summary of most important results.

Fe XAFS spectra were collected from surface sediments retrieved from 8 stations in the Black Sea along a trajectory form the shelf to the deep part of the Black Sea. At some stations on the shelf, the sediments are deposited above the redoxcline; that is, the sediments are covered by oxic bottom waters. Sediments from the deeper part of the Black Sea are covered by sulfidic water. The difference in redox state of the overlying waters is reflect in the Fe XAFS spectra. Preliminary linear combination analysis indicates the presence of pyrite in sediments from below the redoxcline while the surface sediments above the redoxcline are dominated by the signal of residual (silicate-bound) Fe. These results are important to confirm findings from sequential extractions and their interpretation regarding the relationship between Fe diagenesis and bottom water chemistry.

Filters containing suspended material collected in the water column at the various stations have been analyzed. On some filters, Fe contents were considerably smaller than anticipated and demonstrate that observed plumes of suspended materials are predominately of biological origin and are only of limited relevance for the lateral Fe transport. In contrast, filters from greater depth contain considerable amounts of Fe. Preliminary linear combination analysis suggest that the suspended material also contains reactive Fe in the form of Fe oxides. Further analysis might provide more insight in the mechanism of Fe transport from the shelf to the deep sea in the Black Sea.

Material from incubation experiments were analyzed. The XAFS spectra indicate that Fe speciation in the starting material used in the experiments is not significantly different from the material collected in situ. This implies that homogenization and treatment of the material has not caused significant artifacts regarding Fe speciation. Indication were found that the growth of cable bacteria was accompanied with the accumulation of small amounts of Fe oxides at the sediment surface and confirms findings from sequential extractions.

Mn XAFS spectra were collected from Black Sea sediments showing elevated Mn contents based on elemental analyses. Results of linear combination fitting of XANES and EXAFS spectra give consistent results and show that birnessite, hausmannite and rhodochrosite are the main Mn phases in the sediment. These results are important as they provide evidence for the relevance of microbial Mn(II) oxidation for the Mn dynamics in these environments.

Additionally samples collected in the Baltic Sea shortly after an oxidation event of water in the deeper basins of the Baltic due to inflowing oxygen-rich water from the North Sea. The set of samples includes suspended material from different depths plus the corresponding surface sediments. These samples are unique as they provide a snapshot of processes involved in the intense deposition of Mn after oxidation events. The presence of Mn rich layers have been frequently reported but their formation have not been directly witnessed so far. XAFS analysis of the suspended material that dissolved Mn(II) is predominately microbially oxidized to birnessite. This birnessite becomes converted into rhodochrosite shortly after deposition and by this is accounts for the efficient burial of Mn after these oxidation events.