MASTS Postdoctoral and Early Career Researcher Exchange (PECRE) Fellowship Final Report

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Host institution: European Synchrotron Radiation Facility, Grenoble, France.

Mineralogy of nanoparticulate and colloidal iron filtered from river and seawater.

Background

Iron plays a key role in global biogeochemical cycles. In aquatic systems, interactions often involve Fe-bearing nanoparticles and colloids (10 to 100 nm), which are generally amorphous. Mechanistic understanding of transport and bioavailability of these colloids and nanoparticles is hampered by the lack of knowledge of iron mineralogy and speciation in this physical size fraction. This paucity of knowledge is, in part, due to their increasingly dilute nature as salinity increases in aquatic environments such as estuarine fjoridic systems, creeks and on to the sea shelf. This dilute nature results in microscopic sample volumes, insufficient for conventional Mössbauer spectroscopy. The ^{57}Fe Synchrotron Mössbauer Source (SMS) at ID18, ESRF can be used to determine iron speciation and mineralogy in microscopic sample volumes. However, SMS has not yet been used to investigate aquatic colloids and nanoparticles. We have developed a filtration cascade to successfully isolate and concentrate these particles. My PECRE visit to ID18 at the ESRF has been paramount in the further development of these techniques, essential to the sample preparation, and has facilitated the prediction of successful data collection. This has resulted in a recent proposal submission to the ESRF, applying for allocated beamtime in 2018. We await the outcome.

ESRF Visit June/July 2017

My visit to ID18 at the ESRF was treated as an internship. I underwent all staff/user training to ensure safe working at the synchrotron and on the beamline (ID18). This included laser safety training so that I could assist with all the user groups at the beamline whilst I was there.

For the full time I was at ID18, SMS techniques were used; mostly high heat/high pressure experiments. I was trained in the use of the software to operate the SMS and performed the beamline operations routine (SMS): alignment of the optics; data collection and trouble shooting. I worked closely with Dr Aleksandr Chumakov (Scientist in charge at ID18), Dr Valerio Cerantola (Post Doc at ID18) and Dr Catherine McCammon (Bayerisches Geoinstitut, University of Bayreuth) to develop my knowledge of SMS techniques and operation. These scientists were also instrumental in the development of my sample preparation, which included compiling an excel tool to calculate *ideal sample thickness* and sample holder materials suitability.

Dr Chumakov and I tested three river/coastal colloidal/nanoparticle samples using SMS. With the help of Dr McCammon, the data from these tests was used, alongside elemental concentration data (ICP-MS) and known SMS data from a selection of materials, to test the effectiveness of the *ideal sample thickness tool* in predicting data collection success. This exchange allowed me to experience the working beamline, which was essential for the development of my sample preparation. It also

provided the unique opportunity to run test samples. This has been an invaluable experience to facilitate method development, by providing an insight into SMS techniques and beamline operation. I have benefited from the knowledge and input of leading scientists, collection of sample material data, development of sample thickness calculation methods and insight into the optimal SMS working conditions that are needed to measure future samples. My time spent on ID18 highlighted the necessity to run a series of low temperature measurements. As a result, we are manufacturing a cryostat mount that will accommodate my sample holders. Spending time at ID18 also provided contact and collaboration with leading scientists using SMS, who kindly provided knowledge and feedback on my application for allocated beamtime at ID18.

Outputs:

1. The visit to the ESRF gave me experience of using synchrotron-based Mössbauer related instruments and techniques. This enhanced my understanding of the equipment and its capabilities.
2. I tested my prepared samples (nanoparticles from river and coastal waters) using the SMS. This allowed me to examine the capabilities of the instrument for my sample type and the success of my sample preparation.
3. As a result of the training and experience at the ESRF, I have optimised my sample preparation to enhance the capabilities of SMS data collection.
4. Exposure to the host and visiting scientists at the ESRF, and interaction with them, has not only helped me develop as a scientist, but has opened up new possibilities and links with research globally.
5. **As a result of the training and testing of my samples at the ESRF, I have submitted a proposal for allocated beamtime in 2018. I await the outcome of this.**
6. **A poster presentation of the method development at the ESRF at Goldschmidt 2017, Paris. Talks were presented at AMBIO VIII, Oban, 2017 and MASTS ASM 2017.**

Future plans enabled by PECRE:

It is hoped that the recent beamtime application will be successful, however, the Lead Scientist at ID18, Dr A. Chumakov, has agreed to run a small number of my samples in his own time. This has only been as a result of the time I spent there this year, and the discussions between myself and Dr Chumakov.

Benefits to the MASTS community:

The MASTS Marine Biogeochemistry Forum calls for a better understanding of responses to biogeochemical rate processes and their sensitivities. Developing the tools to provide a more mechanistic understanding of the transport and bioavailability of aquatic Fe-bearing colloids and nanoparticles will help to inform biogeochemical models. Application of the method will provide insight into iron biogeochemical processes from rivers, through coastal zones, to full salinity sea water, spanning many of the MASTS themes. It is expected that demonstrating the usefulness of this technique at the ESRF will provide a route for the MASTS community to apply SMS techniques.