ESRF	**Experiment title:** Iron speciation in Arctic snow – understanding processes and sources in the Spitzbergen region (Svalbard)	**Experiment number**: 08-01-1045
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Names and affiliations of applicants (* indicates experimentalists):

PETROSELLI Chiara*, Università degli Studi di Perugia Dipartimento di Chimica, Biologia e Biotecnologie

BURGAY François* (PhD student)**,** Università Ca' Foscari Venezia, Environmental Sciences, Informatics and Statistics

BARBARO Elena, CNR Istituto per la Dinamica dei Processi Ambientali (IDPA)

SPOLAOR Andrea, CNR Istituto per la Dinamica dei Processi Ambientali (IDPA)

CAPPELLETTI David, Università degli Studi di Perugia Dipartimento di Chimica, Biologia e Biotecnologie

Report:

Scientific Background

Since the Martin's hypothesis has been published[1], a lot of efforts in understanding the possible role of iron in enhancing the Marine Primary Productivity (MPP), have been put. Iron exists in two different oxidation states: Fe(II) and Fe(III), with the first that is more soluble and bioavailable. Thus, studying its chemical speciation is a crucial step to assess its impact on MPP. For this purpose, several analytical methods have been used on different matrices[2-4], but few applications of the X-ray Absorption Near Edge Structure (XANES) and X-ray absorption fine structure (EXAFS) spetroscopies have been performed. Some pioneristic studies done on urban aerosols[5], suggested that this might be a promising approach to measure the oxidation state and local order of iron in other environmental matrices such as snow and rocks. In this study we present XANES and EXAFS studies on filtered snow and milled rock samples collected in the Spitzbergen Archipelago (Svalbard Islands) to investigate iron properties and aerosol transport mechanisms.

Experimental details, measurement strategy

XANES and EXAFS spectra at the Fe k-edge (7112 eV) have been collected at the CRG-LISA beamline (BM08). Fluorescence spectra have been recorded at room temperature in

moderate vacuum conditions for both filtered snow samples and soil pellets. The new experimental setup with a Si(111) crystal monochromator and a new ARDESIA SDD multi-element detector array[6] determined a drastic reduction of measurement times, allowing to perform the analyses over multiple samples. The beamline was run without mirrors and harmonic reduction was achieved by detuning the crystals at 70% of the maximum transmissivity. The wide beam (about 2*5 mm v*h) ensured representative bulk analyses and not single particle ones. Three scans per sample have been averaged, in order to improve the signal-to-noise ratio and beam damage could be excluded by comparing the first and the last spectrum of each series. The spectrum of a reference sample (metallic Fe foil) has been recorded at the same time of each sample scan in order to provide a reliable internal energy calibration.

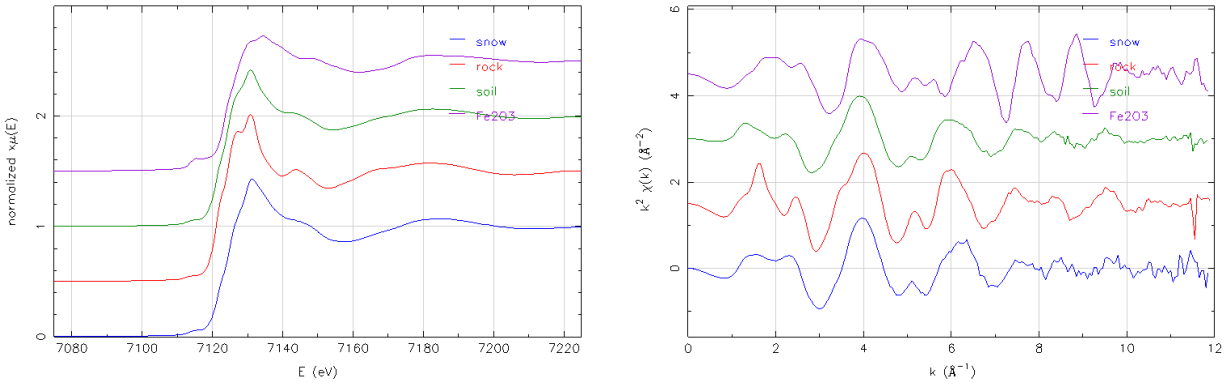
Samples details

The seven snow samples analysed have been collected in five glaciers and two shores in the Brogger Peninsula (Spitzbergen, Svalbard), melted and filtered on Teflon substrates. The chosen sampling sites are located at different heights above sea level, ranging between zero and 1120 m a.s.l., with the aim of investigating different sources and processes inside and above the planetary boundary layer. Regarding soil samples, six of them have been collected near the snow sampling sites, while four additional samples have been collected in summer when the snow coverage is minimum. The first ones consisted of rocks that have been milled, while the summer samples were already processed soils and have been sifted and the finest fraction (<0.4mm) has been chosen for analysis. All the soil samples have been pressed into pellets (d=13mm) using pure cellulose as a binder. The correct amount of sample and cellulose for fluorescence-suitable pellets has been calculated with the XafsMass software.

Results obtained

Despite several storage ring beam losses that reduced the available beam-time, during the experimental session we have been able to analyse seven snow samples, six milled rocks samples, four soil samples and four standard compounds available at the beamline. As regards snow samples, four pieces of the filter have been piled in order to improve the fluorescence response and the homogeneity of the sample. Fluorescence measurements on snow samples and blank Teflon filters show that the iron signal from the filter was always negligible with respect to the sample signal. Three scans per sample with 10s integration time per point were enough to obtain fully analysable spectra. The same measurement strategy has been applied to pellets, the negligibility of cellulose contamination has been verified and three scan per sample have been averaged. Standard compounds have been measured in transmission mode with 6s integration time, and three scans per sample have been averaged as usual. Figure 1 shows one spectrum for each sample typology as an example of the obtained spectral quality.

Figure 1 – XANES (left-hand panel) and EXAFS (right-hand panel) spectra for one snow sample, one milled rock sample, one sifted soil sample and one standard compound.



The spectra have all a good quality to ensure a detailed analysis; they present, as shown in Fig.1, several differences both in the EXAFS and XANES parts of the spectrum. Comparison with model compounds (iron oxides, sulphides, …) collected during previous experimental sessions will help the data analysis. Due to the high number of analysed samples, the data analysis, which is currently in progress, will take quite long time.

Essential bibliography

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