ESRF Experimental Report

08-01-1031: Chemical activities of environmental pollutants in aerosols stored in snow and ice-core from the Western China and Arctic Atmosphere

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1. Abstract

The current climate change and the increasing environmental pollution are among the most important global challenges. A deep understanding of these processes is needed at different spatial and temporal scales. In this context the aim of the proposal is to shed light on the role played by Fe and Hg on the Tibetan plateau and Polar regions and on their relationship with the atmospheric dust and aerosol cycle. We will focus our attention on the analysis of snow and ice samples retrieved from glaciers located in different areas of the planet. Snow and ice deposited on the glaciers represent an invaluable archive of climatic and environmental information, in particular with respect to the atmosphere. The Tibetan region and its glaciers are surrounded by the most populated and industrialized areas. On the other hand Antarctica, thanks to its remoteness with respect to human activities, can be considered as a global background, extremely useful to assess the global trends and mechanism, which are modifying the global biogeochemical cycles of many elements. The choice to focus the attention on Fe and Hg is driven by the role they play in the climatic and environmental systems. Classical chemical analyses have already shown that the concentration of many elements in snow and ice, also Fe and Hg, has increased dramatically in the last decades, but the knowledge of their chemical speciation is still lacking. One of the reasons for the lack of this information is clearly in the low concentrations. The small amounts of particulate matter deposited in the arctic snow and ice (in the order of a few $\mu g/cm^2$) imply that estimated concentration of Hg and Fe are 1- 3000 pg/m^3, 13-420 ng/m^3, respectively, which may largely vary with sites and time. Sample collection, concentration and preparation are therefore challenging and critical. This run has been devoted to a preliminary test of several samples (including standards of Fe and Hg compounds) based on the old optical configuration of the LISA beamline. Data will be used to optimize the next assignments according to the results achieved and the foreseen possibilities of the next optical configurations.

2. Experiment details and results

XANES measurements were collected in transmission mode for the standards and in XRF mode for the samples due to the low concentration of the particulate matter. For the XRF measurements we used the Ortec 12 elements Ge detector.

We collected XRF and XAS data on a batch of 30 samples, and a series of standards at the Fe K edge (hornblende, biotite, ferrihydrite, magnetite, goethite, haematite and coquimbite (CQ)) and Hg L_3-edge ($HgCl_2$, $HgSO_4$, HgS, HgO).

The aerosol and snow samples were mounted on polycarbonate filters, mounted in the vacuum chamber using a plastic support designed to minimise potential signal contamination for the XRF measurements and tailored to fit the LISA dove tail support.

A selection of Fe K-edge XANES results is presented in Fig.1. While analysis is in progress, it is already evident that the XANES display a significant variability in oxidation and coordination among the different dust sources. This first set of data will already give significant indications on the mineralogy of Fe in the aerosols. XANES will be analysed mainly through linear combination analysis of the standards acquired and the group's own reference materials database.

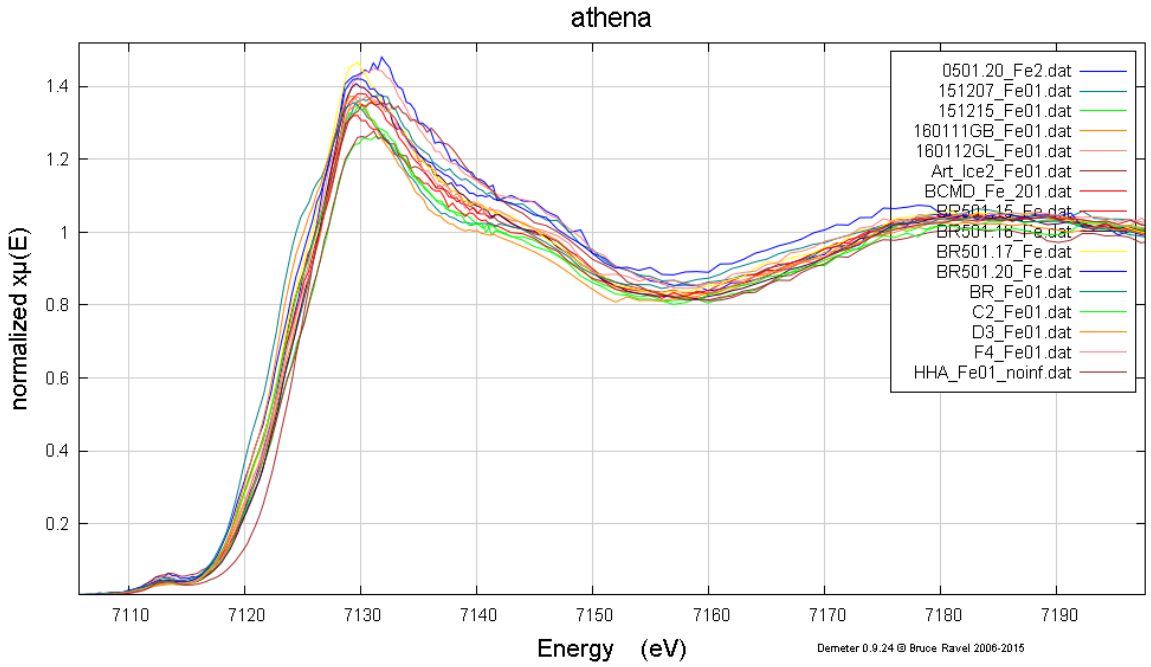

Fig. 1 Fe K-edge XANES from a selection of aerosol and arctic snow filter samples.

Regarding Hg, these first tests showed measurements of Hg were not possible with this configuration. Figure 2 shows the result of 600 seconds XRF acquisition on the BR and HHA samples. The 12-elements detector peak/background and in particular a high background base did not allow the detection of the Hg L emission lines so making it impossible the acquisition of XAS data. The Si(311) configuration was in addition clearly not optimal for low level signal measurements – the loss of flux due to the high order reflection setup on the sagittal focusing scheme is substantial (we estimated ~3 x 10^9 ph/s on sample during this run). The new monochromator allowing for a quick crystal exchange, combined with the adoption of the toroidal mirror focusing should give substantial advantages in this direction. The new mechanics will allow in addition moving quickly between energies so acquisition of XRF at high energy, Hg and Fe K edge XAS will be possible on the same sample, minimising potential contaminations due to repeated sample manipulations. We strongly encourage the development of a continuous acquisition mode for the monochromator, as a noticeable increase of the overall efficiency was successfully demonstrated at BM23, DUBBLE and at Diamond.
For the following experiments, we will propose to utilise a Silicon Drift detector (available from the INRM Antarctica program), optimised for high energy resolution and characterised by a very high peak/background figure. This detector has demonstrated in the past excellent low level detection capabilities, and the acquisition electronics interface will allow immediate integration to the beamline acquisition system for XAS measurements. Preliminary discussions with the local contact have indicated that the detector can be mounted in the present vacuum chamber, through one of the service ports, with the use of a simple interface vacuum flange. For XRF, this detector will overcome the limitations in acquisition of low energy lines from light elements coming from the thick 300 μm Be window mounted on the Ortec unit. The possibility to collect fluorescence at energies up to ~1-2 keV is going indeed to be essential for the elemental analysis measurements requested in our proposal.

We have to mention a long dead time we experienced due a network communication failure between the VME acquisition rack and the control system based on LabView, a complex issue solved by the local contact after several hours of efforts. As a side consideration, we fully support the foreseen introduction of a fully SPEC-based acquisition and control system, which will improve the overall reliability through a high level of support and will present to the users a robust and consistent acquisition software platform.

3. Conclusions and future work

Fe K edge and preliminary XRF data have given good indications about the variability of mineralogy on snow, ice and aerosol dust samples with different provenances. Substantial improvements in the detection

limits, reliability and detection efficiency are clearly foreseen for the next runs thanks to the introduction of the new monochromator, control system and optical layout, combined with the use of a dedicated detector for low level signal acquisition and low energy capabilities. Those improvements will certainly allow collection of full XRF and should allow for the acquisition of Hg L-edge XAS data. All the Hg standard systems have been measured also at the L-edge, however experiments have been performed in transmission and nothing can be inferred on the real possibility to measure Hg in fluorescence on our samples.

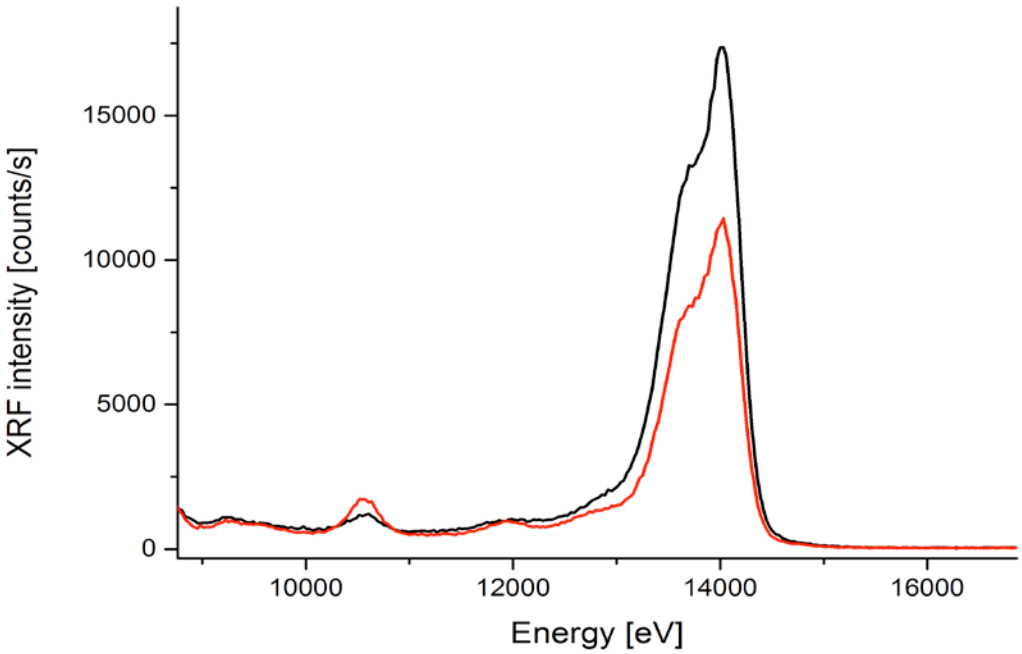

Fig. 2 600s MCA data from two aerosol samples measured with the 12-elements ORTEC Ge detector. The comparison of XRF spectra in these soil samples shows that the Hg $L_{\beta 2}$ edge emission peak (11907 eV) is barely detectable above the background.

5. References

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6. Publications resulting from this work

None at present.