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Iron oxidation state of aeolian mineral dust trapped in firn cores: XRF and XANES results

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Aeolian insoluble particles trapped in firn and ice cores are actively studied to understand the Earth climatic variations of the past. Mineral dust is mainly transported by wind and its mineralogical composition depends on dust provenance and geochemical structure of the principal source areas. We use to investigate dust mineralogical composition by using different techniques: (1) PIXE (Proton Induced X-ray Emission, Marino et al., *submitted*; Marino et al., this meeting), (2) XRPD (X-Ray Powder Diffraction, Dapiaggi et al., *submitted*), and (3) HR-TEM (High Resolution Transmission Electron Microscopy, Sala et al., this meeting).

In this work we present preliminary mineralogical data from X-ray absorption spectroscopy (XAS) at the Fe K-edge, collected on insoluble mineral from East Antarctic and Alpine ice cores.

A dedicated HV experimental chamber, devoted to the realization of XAS experiments on very low absorber concentration samples as been set up to perform both normalincidence X-ray Fluorescence (XRF) detection and Total X-ray Reflection Fluorescence and Absorption Spectroscopy measurements.

The new technique used in this work aims at studying and reconstructing the elemental composition of windblown dust. Because of the very low microparticle concentrations in the samples, specific procedures were adopted to prepare the samples.

Dust samples have been prepared in a cold room from melted ices of:

- Talos Dome firn core (159°04'E, 72°46'S, 2316 m a.s.l., mean accumulation rate 8 g cm⁻² yr⁻¹) drilled in the framework of the International Trans Antarctic Scientific Expedition (ITASE);
- Dome C ice core (DC, 123°24' E, 75°06' S, 3233 m a.s.l., mean accumulation rate 2.8 g cm⁻² yr⁻¹) drilled in the framework of the EPICA (European Project for Ice Coring in Antarctica) project;
- Colle del Lys firn core (CDL03, 45°92'N, 7°86'E, 4248m a.s.l., mean accumulation rate 134 g cm⁻² yr⁻¹) drilled in 2003 on a saddle on the Lys Glacier, in between the Italian Alps (Mt. Rosa).

Both firn and ice samples were decontaminated, then melted and deposited on polycarbonate filters in a 1000 class clean room c/o DISAT (University Milano-Bicocca, Milano, Italy).

The total dust content (for >1 micron particle size) was evaluated by using a particle counter Beckman Counter Multisizer III. Samples for Total Reflection XAS measurements were prepared by depositing the insoluble mineral dust on clean Si wafer substrates. The high quality of the XANES (X-ray Absorption Near Edge Structure) experiments allowed recognizing iron-inclusion mineral fractions in the very tiny Antarctic and Alpine samples.

Preliminary Results

XRF spectra obtained from Alpine firn samples show differences in elemental composition between Saharan and background insoluble particles, desert dust being enriched in calcium. On the other hand, XANES spectra at the Fe K-edge don't show relevant differences; their spectra are similar to the Illite standard mineral composition. Only two samples showed compositional differences and their spectra may be referred to a phlogopite mineral structure.

Analysis on Antarctic samples from TDC firn core allows to observe a spatial and temporal variability in aeolian dust composition over the last 250 years. Other analysis were performed on two ice samples from the EPICA - Dome C core; the samples are 138, 000 and 159,000 years old.

EPICA – Dome C and TDC 56A-1 samples show differences and little variations in the phyllosilicates structure respect to the TDC samples 56A-2/5.

These preliminary results support the hypothesis of a different modulation in atmospheric dust transport between Northern Victoria Land and the East Antarctic Plateau areas during glacial-interglacial variations.

Actually XANES results demonstrate that this non-destructive technique provides additional and unique information on dust mineralogy. Moreover, XAS experiments coupled to PIXE – XRPD and HR-TEM techniques allow obtaining more accurate mineralogical data on aeolian dusts.