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A new method based on low background instrumental neutron activation analysis for major, trace and ultra-trace element determination in atmospheric mineral dust from polar ice cores

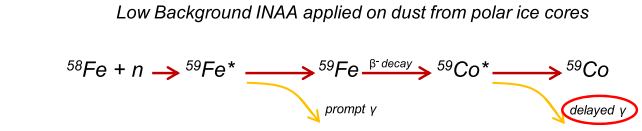
Giovanni Baccolo [a, b, c, *], Massimiliano Clemenza [c, d], Barbara Delmonte [b], Niccolò Maffezzoli [e], Massimiliano Nastasi [c, d], Ezio Previtali [c, d], Michele Prata [f], Andrea Salvini [f], Valter Maggi [b, c]

[a] Graduate School in Polar Sciences, University of Siena, Via Laterina 8, 53100, Siena, Italy
[b] Department of Environmental Sciences, University of Milano-Bicocca, P.zza della Scienza 1, 20126, Milano, Italy
[c] INFN, Section of Milano-Bicocca, P.zza della Scienza 3, 20126, Milano, Italy
[d] Department of Physics, University of Milano-Bicocca, P.zza della Scienza 3, 20126, Milano, Italy
[e] Centre for Ice and Climate, Niels Bohr Institute, Juliane Maries Vej, 30, 2100, Copenhagen, Denmark
[f] LENA, University of Pavia, Pavia, Italy

HIGHLIGHTS

- A new method based on neutron activation for the multi-elemental characterization of atmospheric dust entrapped in polar ice cores is proposed.
- 37 elements were quantified in μg size dust samples with detection limits ranging from 10^{-13} to 10^{-6} g.
- A low background approach and a clean analytical protocol improved INAA performances to unprecedented levels for multi-elemental analyses.

GRAPHICAL ABSTRACT



Limits of Detection (ng)

Na 0.7	Mg 30	Al 4	Si 3,000	K 25	Ca 200	Sc $6{\cdot}10^{-4}$	Ti 30	V 0.1	Cr 0.3
Mn 0.8	Fe 8	Ni 0.6	Co 0.006	Zn 0.1	As 0.03	Se 0.01	Rb 0.8	Sr 2	
Sb 0.01	Cs 0.005	Ba 10	La 0.08	Ce 0.09	Nd 0.2	Sm 0.005	Eu 0.005	Tb 0.003	
Ho 0.004	Tm 0.001	Yb 0.02	Lu 0.001	Hf 0.06	Ta 0.03	Hg 0.009	Th 0.04	U 0.09	

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ABSTRACT

Dust found in polar ice core samples present extremely low concentrations, in addition the availability of such samples is usually strictly limited. For these reasons the chemical and physical analysis of polar ice cores is an analytical challenge. In this work a new method based on low background instrumental neutron activation analysis (LB-INAA) for the multi-elemental characterization of the insoluble fraction of dust from polar ice cores is presented. Thanks to an accurate selection of the most proper materials and procedures it was possible to reach unprecedented analytical performances, suitable for ice core analyses. The method was applied to Antarctic ice core samples. Five samples of atmospheric dust (μg size) from ice sections of the Antarctic Talos Dome ice core were prepared and analyzed. A set of 37 elements was quantified, spanning from all the major elements (Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe) to trace ones, including 10 (La, Ce, Nd, Sm, Eu, Tb, Ho, Tm, Yb and Lu) of the 14 natural occurring

* Corresponding author. Graduate School in Polar Sciences, University of Siena, Via Laterina 8, 53100, Siena, Italy.
E-mail address: giovanni.baccolo@mib.infn.it (G. Baccolo).

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lanthanides. The detection limits are in the range of 10^{-13}–10^{-6} g, improving previous results of 1–3 orders of magnitude depending on the element; uncertainties lies between 4% and 60%.

1. Introduction

Ice cores from polar ice caps represent a unique climatic archive for the past [1,2]. Through the analysis of the chemical and physical properties of ice and its content it is possible to reconstruct several climatic and environmental parameters. Among the climatic proxies retrievable from ice cores an important role is played by the atmospheric mineral dust (onward "dust") entrapped in the ice and snow layers. The dust cycle is strictly connected to the climate: climate affects the production, transport and deposition of dust, but it is influenced by dust itself [3]. The determination of the chemical composition of dust retrieved from ice cores is a useful tool for paleoclimatic reconstructions. An immediate information linked to the composition of the dust deposited in remote areas as Antarctica is its provenance. The identification of geochemical correlations between dust samples extracted from ice cores and samples collected from potential source areas allows recognizing the main sources of dust in the different climatic periods. This is essential for the understanding of the past atmospheric circulation and for the validation of the atmospheric models [4,5]. Another important issue related to dust composition is its role within the biogeochemical cycles of some elements and the indirect influence on climate [6,7].

From the analytical point of view the physical and chemical analysis of polar ice core dust is a challenge. The two limiting factors are the extremely reduced concentration of dust within the ice [8] and the limited availability of ice core samples. Up to now several methods have been specifically developed for the characterization of ice core dust. Focusing the attention to compositional and provenance studies, isotopical analyses play a key role, with particular regard to Sr, Nd and Pb for which thermal ionization mass spectrometry is the reference technique [9–12], despite also inductively coupled plasma sector field MS (ICP-SFMS) and multi collector ICP-MS were successfully applied for the analysis of Sr, Nd, Pb and other radiogenic isotopes [13,14]. Other successful attempts to define a fingerprint or to recognize a temporal shift of the dust origin in polar ice core samples were made using selected elements like rare earth elements [15,16] (REE), platinum group elements [17] or other trace elements [18–22], mainly determined by ICP-SFMS. Major elements (Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe) composition of dust entrapped in polar ice was investigated through different techniques: proton induced x-ray emission and proton induced γ-ray emission [23], synchrotron x-ray fluorescence and x-ray absorption near edge structure [24], total X-ray reflection fluorescence [25] and laser ablation ICP-MS [26–28].

We propose a new method based on low background instrumental neutron activation analysis (LB-INAA) for the elemental characterization of the insoluble fraction of atmospheric dust entrapped in polar ice cores. Instrumental neutron activation analysis (INAA) is a well established technique for elemental analysis, especially dealing with complex samples, as geological and environmental ones, since it is poorly affected by recovery and interference issues [29–31]. This is not the first attempt to apply INAA to bare snow and ice [32–34] and neither to ice cores [35–38]. But the detection limits reported in these works are not suitable for an accurate geochemical characterization of the atmospheric dust found in polar ice cores. Only few elements were quantified (in most cases Na, Al and Cl) and high mass samples were requested. We tried to overcome these limitations applying a low background approach. When the radioactivity of the activated samples presents very low levels it is mandatory to apply passive and/or active methods to reduce the radioactive background. Some of the most common solutions are the selection of radio-pure shielding and detectors, the installation of the apparatus in an underground laboratory for a reduction of the cosmic radiation and the application of active shielding systems [39,40]. We developed a LB-INAA method specifically suited for the analysis of the atmospheric dust found in polar ice cores. For the first time appropriate levels of sensitivity, precision and accuracy were reached, leading to an accurate determination of 37 elements in μg-size dust samples.

2. Materials and methods

2.1. Apparatus

According to INAA samples are exposed to a neutron flux. The interaction between the atomic nuclei which constitute the samples and the neutrons induces nuclear reactions and the production of radioactive nuclei. When the latter decay it becomes possible to observe the emission of radiations and particles. INAA focuses the attention on the neutron capture reactions and on the emission of γ-rays, whose intensity and energy allow determining the elemental composition of the sample. The irradiation of the ice core dust samples was carried out at LENA (Applied Nuclear Energy Laboratory, Pavia, Italy), where a Triga Mark II nuclear reactor is installed. Within this facility we got access to 2 different lines, the "Rabbit" channel and the "Lazy Susan" one [41]. The "Rabbit" channel is designed for fast irradiations: it allows introducing the samples in the reactor for short times one by one; its application is the determination of short-lived radionuclides. The "Lazy Susan" channel was used for long irradiations and the observation of medium- and long-lived radionuclides, for further details see Table 2.

Two p-type high purity germanium detectors were used for the acquisition of the γ-spectra: a coaxial detector and a well-type one. Both are designed for low radioactive measurements, an essential requisite considering the reduced activity induced in the samples. To minimize the intrinsic radioactivity of the instruments only high radio-purity copper and aluminum and low cobalt content stainless steel were used for the internal parts of the detectors. In addition the preamplifier, the high-voltage filters, the cryogenic pump and the preamplifier were not placed near the detectors, where they could have been responsible of a radiation background increase. The detectors were also shielded from the environmental radiations using high purity lead (low ^{210}Pb content) and copper ingots. These solutions allowed to reach a radioactive background suitable for low-background measurements [42] and for the selection of materials used in rare event physics experiments [43,44]. The coaxial detector was used for the acquisition of the data concerning the short-lived radionuclides; it is installed at LENA, its relative efficiency is 30% and its energy resolution at the 1.332 MeV γ-line of ^{60}Co is 1.8 keV FWHM (full width half maximum). All the successive acquisitions concerning medium- and long-lived radionuclides,