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(Article begins on next page)

# PIXE and PIGE techniques for the analysis of Antarctic ice dust and continental sediments

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## Abstract

An analytical procedure has been implemented in this work for an accurate geochemical characterization and quantitative analysis of the fine dust (particles diameter < 5 μm) trapped in Antarctic ice cores and the fine fraction of potential source areas (PSA) sediments by size selection, filtering and PIXE–PIGE combined measurements. The underestimation of concentrations of the lighter elements, like Na, Mg, Al and Si, due to X-ray self-absorption inside each individual aerosol particle, was also evaluated and the analytical overall accuracy tested by means of measurements performed on size selected certified mineral standards.

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## 1. Introduction

Insoluble mineral aerosol (dust) deflated from continental surfaces is an important player in Earth's climate because of its influence on the Earth-atmosphere radiative budget [1]; moreover, records of past dust depositions on the Earth's surface obtained by analysis on insoluble particles trapped in polar ice sheets and temperate glaciers are an important proxy of past continental aridity and atmospheric transport activity [2]. In particular, the identification of the ice core dust source areas is an important tool for the understanding of present day and past pathways of atmospheric transport toward the poles and to infer information on the past environmental conditions of dust

source areas. To achieve this result it is very helpful to determine the geochemical and isotopic composition of atmospheric dust particles deposited over the ice sheets and archived in ice core samples and to compare it with the composition of the finer fraction of potential source areas (PSA) sediments [3].

The PIXE technique has proven to be a reliable tool for major and minor elements investigation of ice core dust [4]. This technique is unrivaled for the direct measurement on filters of the insoluble dust fraction, after ice melting and without any other sample pre-treatment (thus minimizing contaminations). However, the absolute quantity of the lighter elements, like Na, Mg, Al and Si, can be somewhat underestimated because of the X-ray self-absorption inside each individual aerosol particle (excluding particle stratification, as in our case). Since particles contained in a sample have different composition and size, this underestimation

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cannot be calculated considering the average composition of the aerosol sample. In order to evaluate this phenomenon and to improve the quantitative accuracy, PIGE analysis has been simultaneously carried out for the Al determination, as Al is the most abundant light element in mineral dust showing a high proton induced  $\gamma$ -ray emission cross-section [5]. Such approach was already successfully applied to the analysis of Na in urban aerosols [6].

Since dust, deflated from continental source areas, reaches the inner part of the ice sheets only after thousands kilometers of long-range transport, it undergoes a strong dimensional selection in the atmosphere. Consequently, ice core dust is only composed by fine particles: Antarctic dust, for example, is composed by particles with diameter  $<5\ \mu\text{m}$  and with a mode around  $2\ \mu\text{m}$  [7]. For this reason, a reliable comparison between the geochemical composition of ice core dust and source sediments can only be obtained by analyzing particles of a comparable size range for both sets of samples. Therefore, a selective sedimentation procedure has been carried on for the preparation of these samples. The same procedure was used to prepare samples of the size selected ( $<5\ \mu\text{m}$ ) fraction of pure Mineral Standard, while samples of the bulk fraction (size up to  $100\ \mu\text{m}$ ) of standards were obtained by simple filtration of solid without previous dimensional selection; standards samples have been used to check the overall accuracy of the PIXE–PIGE method.

Finally, due to the very small quantity of particulate matter archived in ice cores and the limited availability of sample volume, special attention was paid in filtering masses of standard similar to those deposited after filtration of real ice samples and in the individuation of the minimum required dust mass in order to obtain sufficient analysis statistics. Special care was also paid in correctly evaluating background contributions.

## 2. Experimental

In the present work, we analysed three different sets of samples:

1. Antarctic ice core samples come from the EDC ice core, drilled at Dome C, in the East Antarctic Plateau, in the framework of the EPICA project (European Project for Ice Coring in Antarctica) [8,9]. The samples here analysed were sampled in sections corresponding to the main cold events of the last 220 kyr. A protocol of ice core samples preparation was followed in order to minimize contaminations [10]: it consists in melting ice samples and filtering the liquid through Nuclepore membranes (pore size:  $0.45\ \mu\text{m}$ ), taking particular care in rinsing the filtration apparatus after filtering to guarantee the highest recovery of dust particles.
2. Sediments from the southern hemisphere (SH) PSA were preferentially collected in deflation areas (arid or semi arid areas, fluvial plains, or areas characterised by seasonal hydrological regimes) characterised by the presence of massive amount of fine sediments, able to be deflated by wind activity and then long-range transported toward higher southern latitudes [11]. Satellites observations and model simulations of dust production and atmospheric transport were also used to drive the PSA selection. As stated above, granulometric selection is needed for a correct comparison between PSA sediments and the fine particles trapped in the Antarctic ice. The particle size selection was performed by selective sedimentation in ultra-pure water, following the Stokes law: after dimensional separation, only the superficial fraction, containing particles with diameter  $<5\ \mu\text{m}$  is filtered. The size selection was first tested by Coulter Counter (CC) measurements [3], then, after the PIXE–PIGE analysis, it was confirmed by SEM–EDS (Scanning electron microscopy–energy dispersive X-ray) analysis, as shown in Fig. 1.
3. Bulk and size selected ( $<5\ \mu\text{m}$ ) pure mineral standards have been analysed in order to test the accuracy of the PIXE–PIGE measurements by comparing our results with certified compositions. Standard materials have been chosen among those constituting the main mineral components of dust [12]. Since certified compositions are actually provided only for the bulk fraction of the standards, small differences between our data and the

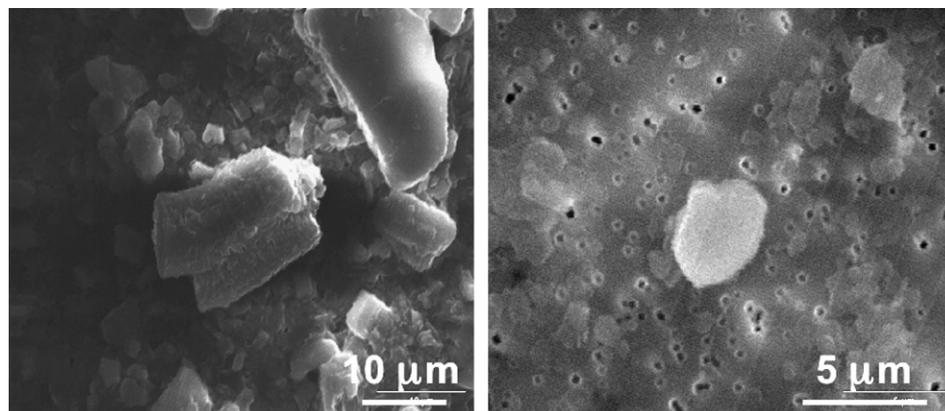


Fig. 1. SEM-EDAX images of Kaolinite mineral standard samples: bulk material (on the left) and size selected  $<5\ \mu\text{m}$  (on the right).

reference composition can be partially due to the dimensional selection; however, since only pure mineral standards were analysed in this work, only small compositional differences are expected among particles of different sizes.

The following samples have been analysed by PIXE and PIGE in the present work: 15 Antarctic ice dust samples, 25 size selected SH-PSA sediment samples, 12 size selected pure mineral standards (Kaolinite, K-feldspar, Illite and Quartz) at three different levels of areal concentrations and 4 depositions of the mineral standard bulk fraction;

Table 1  
Concentrations in  $\text{ng}/\text{cm}^2$  for elements of interest in a typical Antarctic ice dust sample and in a blank

	Ice dust sample	Blank
Na	100	<20 <sup>a</sup>
Mg	68	<12 <sup>a</sup>
Al	415	<9 <sup>a</sup>
Si	1470	36
K	125	<8 <sup>a</sup>
Ca	57	<7 <sup>a</sup>
Ti	30	<4 <sup>a</sup>
Mn	2.9	<1.0 <sup>a</sup>
Fe	310	5
Sr	1.1	<0.7 <sup>a</sup>

<sup>a</sup> Minimum detection limit at  $3\sigma$  confidence level.

in addition, several tests have been performed to evaluate the possible contribution of blank filters, sample containers and filtering apparatus to the obtained results. The mass deposited on filters is not constant for the different kind of samples: due to the low availability of ice core volume, Antarctic dust samples have a mass ranging from less than  $1\ \mu\text{g}$  to about  $15\ \mu\text{g}$ , while PSA sediments do not present such limitation and deposits range from few  $\mu\text{g}$  to a maximum of  $100\ \mu\text{g}$ . Depositions of standard material were controlled in order to fit the masses of real samples.

Ion beam analysis (IBA) has been performed by a proton beam at the 3 MV Tandetron accelerator of the LABEC laboratory of INFN in Florence, with the external beam set-up [13]. Each sample has been irradiated for about 1000 s with a beam intensity ranging from 5 nA to 30 nA, depending on the sample load, over a spot of  $\sim 2\ \text{mm}^2$ ; during irradiation, the filter was moved in front of the beam so that most of the area of deposit was sampled. PIXE spectra were fitted using the GUPIX code [14] and elemental concentrations were obtained via a calibration curve from a set of thin standards of known areal density.

PIGE has been simultaneously applied for the Al determination, exploiting the 1013 keV  $\gamma$ -rays produced by the  $^{27}\text{Al}(p,p_2\gamma)^{27}\text{Al}$  reaction [5]. A beam energy of 3.06 MeV in vacuum has been selected in order to obtain a cross-section for the used reaction that remains constant despite the energy loss of the protons within the sample.

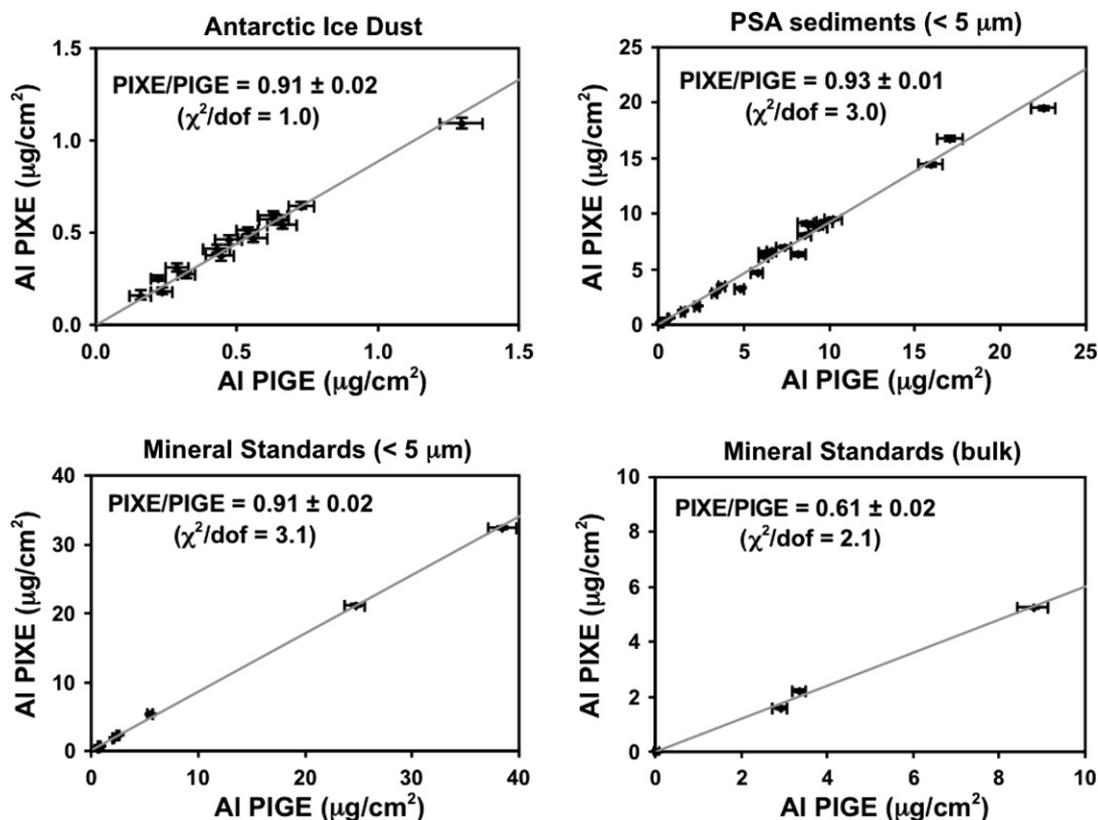


Fig. 2. Regression lines between Al concentration values measured by PIXE and PIGE in Antarctic ice dust, size selected sediments, size selected mineral standards and bulk mineral standards.

### 3. Results

As far as blank measurements are concerned, small quantities of Si and Br were always found as impurities in polycarbonate filters, while the sample preparation (filtering apparatus for ice core samples and, in addition, sonication procedures for PSA and standard samples) introduced small additional quantities of S, Cl, Cr and Fe. It is important to note here that blank values for elements of interest resulted always largely below the concentrations measured (see Table 1), and in the worst case (i.e. Si in particularly scarce ice core samples), around 5%. Moreover, the analysis of ice core samples showed that the quantity of filtered material in each sample (about 1–2  $\mu\text{g}/\text{cm}^2$  in the most scarce samples) was sufficient to obtain good statistics for both PIXE and PIGE.

Aluminium concentration has been measured simultaneously by PIXE and PIGE on all the analysed samples and the PIXE/PIGE ratio allowed us to evaluate how PIXE underestimate the concentration of this element on a sample by sample basis. Results are shown in Fig. 2 in terms of regression lines between values obtained by the two techniques. The average attenuation in Antarctic ice dust samples resulted  $\sim 10\%$  (average attenuation coefficient, calculated as PIXE/PIGE ratio, equal to 0.91): this quite low value confirmed that X-ray self-absorption effects in Antarctic dust are moderate, due to the small dimensions of aerosol particles reaching the East Antarctic Plateau. The same value, within experimental uncertainties, was found for size selected PSA sediments and Mineral Standards: this result confirmed that the selection of a size range comparable to Antarctic dust was successfully

achieved. As expected, a higher underestimation ( $\sim 40\%$ ) was found for bulk mineral standards.

In the hypothesis that Antarctic dust and sediments are mainly composed by a mix of pure mineral particles, we tried to use the measured Al attenuation coefficients to evaluate an effective dimension of these mineral particles and hence to estimate the attenuation coefficients for the other light elements for each sample. Due to the very similar attenuation of Al X-rays in the different minerals that contain this element (namely K-feldspar, Kaolinite and Illite), particle dimensions turned out quite similar in spite of the different mineral composition used for calculations. For example, applying a simple attenuation model for single spherical particles [15] and using a 0.91 attenuation coefficient (which is a realistic value, being the average Al PIXE/PIGE ratio for ice dust), an effective particle diameter of 0.90  $\mu\text{m}$ , 0.99  $\mu\text{m}$  and 1.00  $\mu\text{m}$ , for Illite, Kaolinite and K-feldspar, respectively, can be found. Using a 1  $\mu\text{m}$  diameter, the following attenuation coefficients can be estimated for the other elements: 0.79 for Na in K-feldspar; 0.87 for Mg in Illite; 0.90, 0.91, 0.92 and 0.94 for Si in Kaolinite, Illite, K-feldspar and Quartz, respectively; 0.97 for K in both Illite and K-feldspar. In the case of elements that are mainly present in only one mineral, like Na and Mg, the attenuation coefficients calculated for pure mineral particles may, in first approximation, directly be applied to real samples. The attenuation of potassium X-rays resulted the same and substantially negligible for both Illite and K-feldspar. Quite similar values turned out also for Si, thus allowing the use of an average over the different minerals.

The quoted attenuation values are an example of realistic attenuation coefficients that can be found, however, in

Table 2  
Percentage composition of bulk and size selected ( $<5 \mu\text{m}$ ) pure mineral standards obtained by PIXE–PIGE measurements

	Na <sub>2</sub> O%	MgO%	Al <sub>2</sub> O <sub>3</sub> %	SiO <sub>2</sub> %	K <sub>2</sub> O%	CaO%	TiO <sub>2</sub> %	Fe <sub>2</sub> O <sub>3</sub> %
Kaolinite std – certified composition			46	52			1.6	0.3
Kaolinite bulk ( $\sim 35 \mu\text{g}$ )			45	53			1.6	0.2
Kaolinite – size selected $<5 \mu\text{m}$ ( $\sim 45 \mu\text{g}$ )			44	53			2.4	0.4
Kaolinite – size selected $<5 \mu\text{m}$ ( $\sim 10 \mu\text{g}$ )			44	53			2.3	0.3
Kaolinite – size selected $<5 \mu\text{m}$ ( $\sim 3 \mu\text{g}$ )			46	52			2.1	0.3
K-Feldspar std – certified composition	2.5		18	67	12	0.1		0.1
K-Feldspar bulk ( $\sim 25 \mu\text{g}$ )	3.2		19	64	13	0.15		0.1
K-Feldspar – size selected $<5 \mu\text{m}$ ( $\sim 220 \mu\text{g}$ )	2.5		19	64	14	0.2		0.2
K-Feldspar – size selected $<5 \mu\text{m}$ ( $\sim 20 \mu\text{g}$ )	2.8		19	64	13	0.2		0.2
K-Feldspar – size selected $<5 \mu\text{m}$ ( $\sim 5 \mu\text{g}$ )	2.2		20	65	13	-		0.1
Illite std – certified composition		1.2	31	57	10	0.4		0.4
Illite bulk ( $\sim 10 \mu\text{g}$ )		2.6	32	56	10	-		0.2
Illite – size selected $<5 \mu\text{m}$ ( $\sim 280 \mu\text{g}$ )		2.5	32	54	11	0.3		0.3
Illite – size selected $<5 \mu\text{m}$ ( $\sim 30 \mu\text{g}$ )		2.8	32	55	9	0.3		0.2
Illite – size selected $<5 \mu\text{m}$ ( $\sim 5 \mu\text{g}$ )		3.0	32	56	9	-		0.2
Quartz std – certified composition				100				
Quartz bulk ( $\sim 10 \mu\text{g}$ )			0.6	99				
Quartz – size selected $<5 \mu\text{m}$ ( $\sim 55 \mu\text{g}$ )			2.2	97				
Quartz – size selected $<5 \mu\text{m}$ ( $\sim 5 \mu\text{g}$ )			2.5	97				
Quartz – size selected $<5 \mu\text{m}$ ( $\sim 2 \mu\text{g}$ )			2.6	97				

Values for light elements have been corrected for self-absorption effects. The estimated experimental uncertainty is about  $\pm 10\%$ .

order to take into account changes in particle dimensions in the different collected samples, the calculations have been done using the Al PIXE/PIGE ratio measured in each sample.

The results obtained for the composition of the bulk and size selected single mineral standards are reported in Table 2, together with the reference certified values; concentrations of light elements have been corrected for self-absorption effects, as afore explained (using the experimental Al PIXE/PIGE ratio and the given mineral compositions and densities for each standard analysed). Percentage deviations with respect to certified values are always below 5% for main components (Si and Al), up to 10–15% for minor constituents and higher, but still sufficient for an accurate geochemical characterization of the dust samples, for elements present at trace level. These results confirmed the overall accuracy of the method, including sample preparation and IBA analysis. Since these samples are mono-mineral standards (all the particles have the same matrix composition), it has been possible to analyse them also by the GUPIX code considering samples of intermediate thickness containing one dependent invisible element (oxygen); obtained results (not shown) were consistent with those shown in Table 1.

#### 4. Conclusions

An analytical procedure has been implemented in this work for an accurate quantitative analysis of Antarctic dust and PSA sediments by size selection, filtering and PIXE–PIGE combined measurements. Results showed that no significant contamination is introduced by sample preparation and that the quantity of ice dust filtered in each sample was sufficient to obtain good statistics for both PIXE and PIGE.

PIGE measurement of Al concentration allowed us to quantify X-ray self-absorption effects for this element and to estimate these effects also for the other light elements. Relatively moderate attenuations were found accordingly with the small dimension of ice dust particles. The overall accuracy of the method was tested by the analysis of the bulk and size selected mineral standards.

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