#### Programma Nazionale di Ricerche in Antartide (PNRA)

### Final project report

*Project ID* 2002/6.09

Title Physics and Chemistry of Tropospheric Aerosol in Antarctica

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Duration Two years (2002/2003)

Assigned funding 25.819,00 Euro

#### **Activities and results**

**Premise:** the results should be considered in the framework of a multiannual programme, in continuous development. The first part of the description concerns definitively acquired results – even if considerable improvements took actually place in the years following 2003. The second part concerns results which were partial, but essential in view of the next developments (which actually occurred later on): sampling campaigns in Antarctica (2002/2003, 2003/2004), measurements on the samples, methodological improvements.

#### First part:

# (A) Results of a "bulk" analysis of size segregated aerosol samples, collected with a 12-stage impactor, at Baia Terra Nova (Lat. 74°42′43″S, Long. 164°06′58″E) during the 1999/2000 austral summer.

Sixteen such samples were kindly supplied to us by the IIA-CNR, Rome group and measured by us at LNL-INFN. Size range limits were 16. and 0.0465  $\mu$ m. PIXE analysis allowed to obtain size distributions of mass concentration (ng m<sup>-3</sup>) of up to 12 elements (including Na and Fe), as well as convenient representations with lognormal or power law distributions.

Moreover, several distinct types of (partially unconventional and including size-dependence) Principal Component Analyses (PCA) were performed. Results include: the identification, elemental profiles and size distributions of sea-salt aerosol, crustal aerosol and of the submicrometric sulphur accumulation mode; the existence and amount of an internal mixing of the crustal component with sea-salt aerosol; the evidence of the chemical interactions of the gaseous (or possibly, particle) sulphur compounds, with the supermicrometric sea-salt aerosol particles, as detected by means of sea-salt aerosol enrichments in S, with respect to sea-water composition (sea-salt-Sulphur, ssS) and thus, by means of the measurement of "non-sea-salt-Sulphur, "nssS"; the increasing importance of these phenomena for decreasing particle diameter; the interpretation of this fact as an evidence favouring the occurrence of the above mentioned interactions on the surface, rather than in the volume of the particles; indications of a role of crustal materials in the interactions of S compounds with the aerosol particles; the fact that the interactions with the supermicrometric sea-salt particles (as measured by nssS) may give rise to a non-negligible contribution – with respect to those responsible for the submicrometric S accumulation mode (as measured by the area under its lognormal function) – to the fluxes of S compounds coming out of the atmosphere.

The above results show that, despite some limitation of PIXE (in particular, N and its compounds are not detected), its typical properties (in particular, detection of a number of elements of prevailing crustal origin, in insoluble compounds, not detected in Ion Chromatography, "IC"), together with an extensive use of PCA, offer a considerable interest in this field. The importance of internal mixing in sea-air transport processes should also be mentioned. An integrated use of complementary analytical methods (typically IC) would obviously be desirable.

It should furthermore be noted that the above results were obtained by means of an averaging procedure over the full set of samples and, thus, over the total time required for the corresponding samplings. Due to the quality of the samples, we preferred not to perform the analysis at the level of individual samples. The

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highly improved quality of the samples collected in the 2002/2003, 2003/2004 and in the following campaigns, allows now to perform the analyses at an individual level. In this way, on one hand, time-dependent results are now obtained (as it was hoped in our original program); on the other hand, results concerning size distributions of elements, etc, are now much more detailed, due to the much better quality of the measurements and to the absence of the fluctuations connected with the averaging procedure.

## (B) Results of a single aerosol particle, "SAP", analysis of size segregated samples in the supermicrometric size range.

The samples belong to the previously mentioned (in A) set of samples and the measured subsamples correspond to the first three stages of the impactor.

The first phase of our attempt to apply microPIXE analysis to supermicrometric Antarctic coastal aerosol was successfully achieved. The resulting multielemental data (concerning 2000 particles) allowed to perform (by means of a dedicated program) a peculiar system of Principal Component Analyses, (PCA) applied to several distinct groups of particles (each group of particles being characterized by a set of well defined elements). Three main results were obtained: (1) the ability of the whole system of PCA's to satisfactorily explain the multielemental data; (2) the dominance, in general, of two Principal Components, "PC's": sea-salt and crustal, in variable amounts, in each particle; (3) the presence, in one sample, of a further PC, identified by bivariate analysis as composed by elements Phosphorus and Calcium and interpreted as an ornithogenic aerosol component (never observed previously).

The above results and methods opened the way in the years following 2003 and using new and better samples collected by us (2002/2003), to the following improvements: (a) extension of the measurements to a further impactor stage, thus covering the complete supermicrometric renge; (b) measurements of the absolute elemental masses (fg) in each particle; larger numbers of analyzed particles; improved software. In this way, the following scientific problems (which can hardly be faced with other methods) were dealt: (1) the internal mixing (in each individual particle) of sea-salt and crustal materials; (2) the properties of the enrichments in sulphur of the individual sea-salt particles and the role of crustal materials in the chemical interactions which give rise to such enrichments.

#### Second part:

#### Sampling campaigns and measurements on samples.

In the two campaigns, 2002/2003 and 2003/2004, concerning the period under consideration, a large number of high quality samples were collected, which made possible significant scientific results. On the other hand, we were faced, in the same period, with the deterioration and the breakdown of our x-

ray detector, a situation which gave rise to an enormous waste of energies and time. Only later on was it possible to overcome this obstacle with a new detector and to successfully measure all the 2002/2003 samples. No help was obtained in the above situation by the CSNA, to which we had unsuccessfully proposed to purchase a new detector.

#### **Products**

#### A - papers in scientific magazines

- 1. Paolo Mittner, Francesco Chiminello and Daniele Ceccato, Tropospheric aerosol at Terra Nova Bay (Antarctica): Geochemical components and their time distributions during four summer seasons. *Nucl. Instr. and Meth. in Physics Research Section B, Volume 189, Issues 1-4, (2002), pp. 266-271*
- 2. F. Chiminello, D. Ceccato and P. Mittner, Micro-PIXE study of tropospheric aerosols in an Antarctic coastal environment. *Nucl. Instr. and Meth. in Physics Research Section B:, Volumes 219-220, (2004), pp. 171-175*

#### **B** – book chapters

C - proceedings of international conferences

F. Chiminello, D. Ceccato, P. Mittner, Tropospheric aerosols at Terra Nova Bay (Antarctica): preliminary results
of single particle micro-PIXE analysis. Conference Proceedings Vol 80 - Italian Research on Antarctic
Atmosphere, M. Colacino (Ed.), SIF Bologna (2002), pp 263-276

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- 2. F. Chiminello, D. Ceccato, P. Mittner, Single Particle Micro-PIXE Analysis of Size Segregated Aerosol Samples Collected at Terra Nova Bay (Antarctica) Preliminary Results. Proceedings of IAC 2002 (Sixth International Aerosol Conference), September 9-13, 2002 Taipei Taiwan, Editor: Chiu-Sen Wang, ISBN 986-80544-1-9
- 3. F. Chiminello, D. Ceccato, P. Mittner, Single Particle Micro-PIXE Analysis of Size Segregated Aerosol Samples Collected at Baia Terra Nova (Antarctica). Proceedings of EAC 2003 (European Aerosol Conference 2003), August 31 September 5, 2005 Madrid Spain, Journal of Aerosol Science, Vol. 1, pp. s25-s26, ISSN: 0021-8502
- 4. F. Chiminello, P. Mittner, A. Trevisiol and D. Ceccato, Three Major Components of Natural Aerosol and Their Interactions at an Antarctic Coastal Site. Proceedings of 16<sup>th</sup> International Conference on Nucleation and Atmospheric Aerosols (ICNAA), Kyoto, Kyoto University press, editors: Mikio Kashara, Markku Kulmala ISBN 4-87698-635-5, (2004) pp. 649-652
- 5. F. Chiminello, P. Mittner, A. Trevisiol, D. Ceccato, Size Distribution, Geochemical Components and Interactions of Aerosol in an Antarctic Coastal Site. Proceedings of EAC 2004 Conference (European Aerosol Conference 2004), September 6-10, Budapest Hungary, Journal of Aerosol Science. p. s589-s590

#### D – proceedings of national meetings and conferences

- F. Chiminello, P. Mittner, A. Trevisiol, D. Ceccato, Elemental Size Distributions Of Natural Aerosol In An Antarctic Coastal Site. Proceedings of PM2004 (1º Convegno Nazionale sul Particolato Atmosferico) Milano 12 – 14 Maggio 2004
- 2. F. Chiminello, P. Mittner, A. Trevisiol, D. Ceccato, Size-Dependent Characterization Of Aerosols In An Antarctic Coastal Site. Proceedings of PM2004 (1º Convegno Nazionale sul Particolato Atmosferico) Milano 12 14 Maggio 2004

#### **E** – thematic maps

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F – patents, prototypes and data bases

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G - exhibits, organization of conferences, editing and similar

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#### H - formation (PhD thesis, research fellowships, etc.)

1. Arianna Trevisiol (Università di Padova, 2002/2003) Title: "Distribuzioni dimensionali, principali componenti geochimiche e interazioni degli aerosol in un sito costiero antartico"

#### **Research units**

Padova

Date: 09/02/2009

**Notes**