Ser. Cient. INACH 42:37-45, 1992

Study of Antarctic Aerosol using X-Ray Fluorescence and Single Particle Analysis

CARLOS M. ROJAS[1], RENÉ E. VAN GRIEKEN[1] and M. EUGENIA CANTILLANO[2]

ABSTRACT

During the XXIV Scientific Antarctic Expedition, supported by the Instituto Antártico Chileno, a set of 8 aerosol samples was collected at the Chilean Antarctic Base "Bernardo O'Higgins". The samples were analyzed by electron-probe X-ray microanalysis (EPXMA) and energy-dispersive X-ray fluorescence (EDXRF). Concentrations of the detected elements (Si, P, S, K, Ca, Fe, Ni, Cu, Zn and Pb) are much higher than those reported in the literature. The aerosol had a predominant marine origin and high Zn concentrations suggest the presence of an anthropogenic source such as incineration waste. Individual particle analysis showed that the fine fraction had an average diameter of 0.67 μm, whereas that of the coarse fraction was 5.6 μm. Both fine and coarse mode aerosols presented a lognormal size distribution.

Key words: Single particle analysis, EPXMA, aerosols, Antarctic, EDXRF, air sampling, microanalysis.

Estudios del aerosol antártico usando fluorescencia de rayos X y análisis de partículas aisladas

CARLOS M. ROJAS[1] RENÉ E. VAN GRIEKEN[1] y M. EUGENIA CANTILLANO[2]

RESUMEN

Durante la XXIV Expedición Científica Antártica, realizada por el Instituto Antártico Chileno, se recolectó un conjunto de 8 muestras de aerosoles en la Base Antártica "Bernardo O'Higgins" las que fueron analizadas mediante fluorescencia de rayos X. La concentración de los elementos encontrados (Si, P, S, K, Ca, Fe, Ni, Cu, Zn y Pb) es mucho más alta que aquella informada en la literatura. Los aerosoles tuvieron un origen predominantemente marino y las altas concentraciones de Zn sugieren la presencia de una fuente antropogénica, tales como desechos de incineraciones. El análisis individual de partículas mostró que la fracción fina tuvo un diámetro promedio de 0,67 μm, mientras que el de la fracción gruesa fue de 5,6 μm. Ambas formas, fina y gruesa, presentaron un tamaño de distribución log normal.

Palabras claves: Análisis de partículas aisladas, EPXMA, aerosoles, Antártica, EDXRF, muestra de aire, microanálisis.

[1]Micro and Trace Analysis Center, University of Antwerp (U.I.A.), Universiteitsplein 1, B-2610 Wilrijk, Belgium.
[2]Escuela Tecnológica, Universidad de Santiago de Chile, Tabaré 654, Santiago, Chile.

INTRODUCTION

The study of atmospheric aerosols in Antarctica has been a subject of high interest due to its remote geographical location and low anthropogenic influence. More recently, the Antarctic ozone layer has become thinner and this has suscitated a renewed scientific and public interest. Usually, scientific expeditions are scheduled during the Austral summer since meteorological conditions allow the transport of personnel and logistical support to the numerous bases situated on the Antarctic Peninsula. Within this context, seasonal variations of Antarctic aerosols have been reported by Parungo *et al.* (1979). Shaw (1983) reported on composition, size distribution and elemental concentrations of Antarctic aerosol using scanning electron miscroscopy and X-ray spectrometry.

In this work we report on the study of 8 aerosol samples collected during the Austral summer at the Chilean Antarctic Station O'Higgins. This study pertains to the area of bulk and microanalysis and is intended to assess the actual sampling facilities as well as the instrumental techniques to be used in future research.

EXPERIMENTAL

Sampling

During the XXIV Scientific Antarctic Expedition (February 1988), a set of 8 aerosol samples was collected at the Chilean Antarctic Base "Bernardo O'Higgins" (63°19′ S., 57°54′ W.). The sampling station was located upwind, 270 m from the base. The air sampling was carried out using a stacked filter unit (Parker *et al.*, 1977), operated at flow rates varying from 8 to 12 Im^{-1} The sampling period was 40 h, leaving 12 h between 2 consecutive sample collections. Rain and snow showers took place during the whole campaign. The aerosol samples were deposited on Nuclepore membrane filters having a pore-size of 8 μm (coarse fraction) and 0.4 μm (fine fraction).

Analytical Techniques

The samples and the blanks were analyzed for up to 15 elements (Al, Si, P S, K, Ca, Ti, V. Cr, Mn. Fe, Ni, Cu, Zn and Pb) by energy-dispersive X-ray fluorescence (EDXRF) using a X-ray spectrometer Tracor Northern Spectrace 5000 (Tracor Northern, Middleton, Wi., USA), equipped with a Si (Li) detector and a low power X-ray tube with a Rh anode, and controlled by an IBM PC/At microcomputer. The calibration of the X-ray spectrometer was performed using thin film standards from Micromatter Co. (Seattle, Wa., USA). The analysis procedure is given in detail by Rojas *et al.* (1990). The X-ray spectra were analyzed using the AXIL software package developed by Van Espen *et al.* (1986).

Individual particle analysis was performed using a JXA-733 electron probe X-ray microanalyzer (JEOL, Tokyo, Japan), equipped with a Tracor northern TN-2000 energy-dispersive X-ray detector system. Morphological information as average diameter and shape factor is provided, whereas compositional patterns are derived from the X-ray spectrum of each aerosol particle. Details on this instrumental technique can be found elsewhere e.g. Goldstein *et al.* (1981), Heinrich (1981), Storms *et al.* (1987). The aerosol samples were analyzed using an electron beam current of 1 nA, an accelerating voltage of 20 KV and a magnification of 1200 X, which allowed a minimum detectable particle size of 0.26 μm. The X-ray spectrum of each particle was accumulated for 20 sec and then stored on a computer disk for off-line study.

BULK ANALYSIS RESULTS

The resulting atmospheric concentrations determined for the 8 samples, are summarized in Table

Table 1
ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATE METTER
COLLECTED AT THE CHILEAN ANTARCTIC STATION "BERNARDO O'HIGGINS"

	Elemental Concentrations (in ng/m^3)							
	Fine Fraction				Coarse Fraction			
ELEM	AF1	AF2	AF3	AF4	AC1	AC2	AC3	AC4
Si	—	53	38	47	90	27	51	59
P	—	30	28	24	34	26	28	31
S	410	410	510	260	730	550	380	220
K	310	90	110	—	280	230	130	45
Ca	160	140	160	8.9	770	250	210	110
Fe	—	—	—	—	80	14	11	21
Ni	—	1.6	—	—	2.2	—	—	—
Cu	—	7.3	11	—	2.8	—	—	—
Zn	3.1	360	710	5	11	14	16	25
Pb	7.1	—	—	—	—	—	—	—

1. In general, the observed values are much higher than those previously reported in the literature for other Antarctic regions (Maenhaut *et al.*, 1979; Cunningham and Zoller, 1981). On the other hand, similar concentrations for Ni, Cu and Pb have been reported by Préndez and Zolezzi (1982), who assigned these elements to local anthropogenic emissions. There are differences from fraction to fraction, e.g. the coarse mode presents higher concentrations for S, K, Ca and Fe. The average Ca/S ratio (0.45) is in satisfactory agreement with that reported by Taback *et al*, (1979) for marine aerosol (0.44). Two samples in the fine mode presented high concentrations of Zn, probably related to local burning waste (Receptor Model Source Composition Library).

SINGLE PARTICLE RESULTS

The abundance of the different particle types was determined by a hierarchical cluster analysis (Storms, 1988). In general, cluster analysis consists of determining the interrelationship of several groups containing common variables. Usually, the criterion to interrelate variables relies on either the correlation coefficient or the Euclidian distance between the data points. In this work, the clustering was performed on the normalized X-ray intensities emitted by each aerosol particle, using the software package (DPP) developed by Van Espen (1984). The study of 2000 particles in each aerosol fraction (500 particles per sample) is represented by a matrix containing morphological data and elemental composition. The results obtained from analyzing the fine mode aerosol, are summarized in Table 2.

It is seen that the most abundant particle types are associated with seaspray, accounting for 85% of the total particles analyzed. NaCl particles containing a considerable amount of S, are often labeled as aged seasalts. $CaSO_4$ particles are thought to have a marine origin. This particle type may be originated from the reaction of atmospheric SO_2 with marine biogenic $CaCO_3$ aerosol particles (coccoliths) (see Andreae *et al.*, 1986) is noticeable that 15% of the particles contained Zn, which confirms the presence of anthropogenic emissions, as shown in the bulk Analysis results. K-rich seasalt has also been found by L. Wouters (personal communication) while studying atmospheric particulate matter collected at King George Island, using the Laser Microprobe Mass Analysis (LAMMA) technique.

Several distribution functions were used to fit the size data in order to obtain an overview of the aerosol contributing to this fraction. The best significance level was obtained for a lognormal size distribution (Seinfeld, 1986). The average aerosol projected diameter was 0.67 μm with a

Table 2
COMPOSITION OF INDIVIDUAL FINE MODE AEROSOL PARTICLES DETERMINED BY CLUSTER ANALYSIS ON THE EPMA DATA

Fine mode particle types			
Abundance (%)	Diameter (μm)	Major X-Ray	Possible origin
46	0.66	Cl, Na	Seasalt
17	0.67	Cl, Na, S, K	Seasalt S, K Rich
15	0.64	Zn	Refuse Burning
13	0.77	S, Ca	$CaSO_4$
9	0.64	K, Cl, Na	Seasalt K Rich

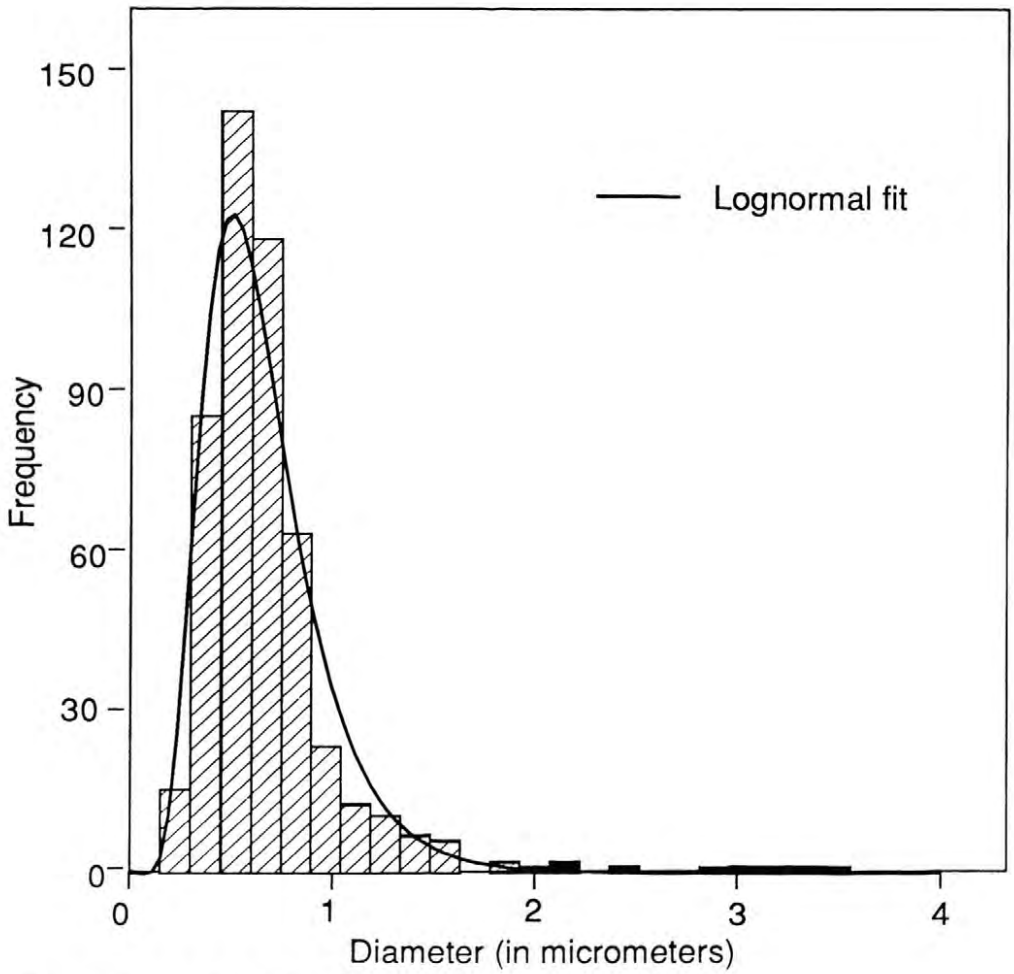

Fig. 1. Size distribution of the fine mode Antarctic aerosol obtained by EPMA.

standard deviation of 0.3. The size distribution as well as the one resulting from the fit, are shown in Fig. 1.

The results of the cluster analysis on the coarse particles, are shown in Table 3. In this aerosol fraction, the major group contains Cl, Mg, S and K, which is thought to have a marine origin. This

Table 3
COMPOSITION OF INDIVIDUAL COARSE MODE PARTICLES
OBTAINED BY CLUSTER ANALYSIS ON EPMA DATA

Coarse mode particle types			
Abundance (%)	Diameter (μm)	Major X-Ray Lines	Possible Origin
60	7.1	Cl, Mg, S, K	Marine
24	5.9	Cl, Na	Seasalt
6	4.8	S, Ca	$CaSO_4$
6	6.6	Si, Al	Aluminosilicate
4	7.5	Si, Al, Fe, Cl, Na	Soil/SeaSALT

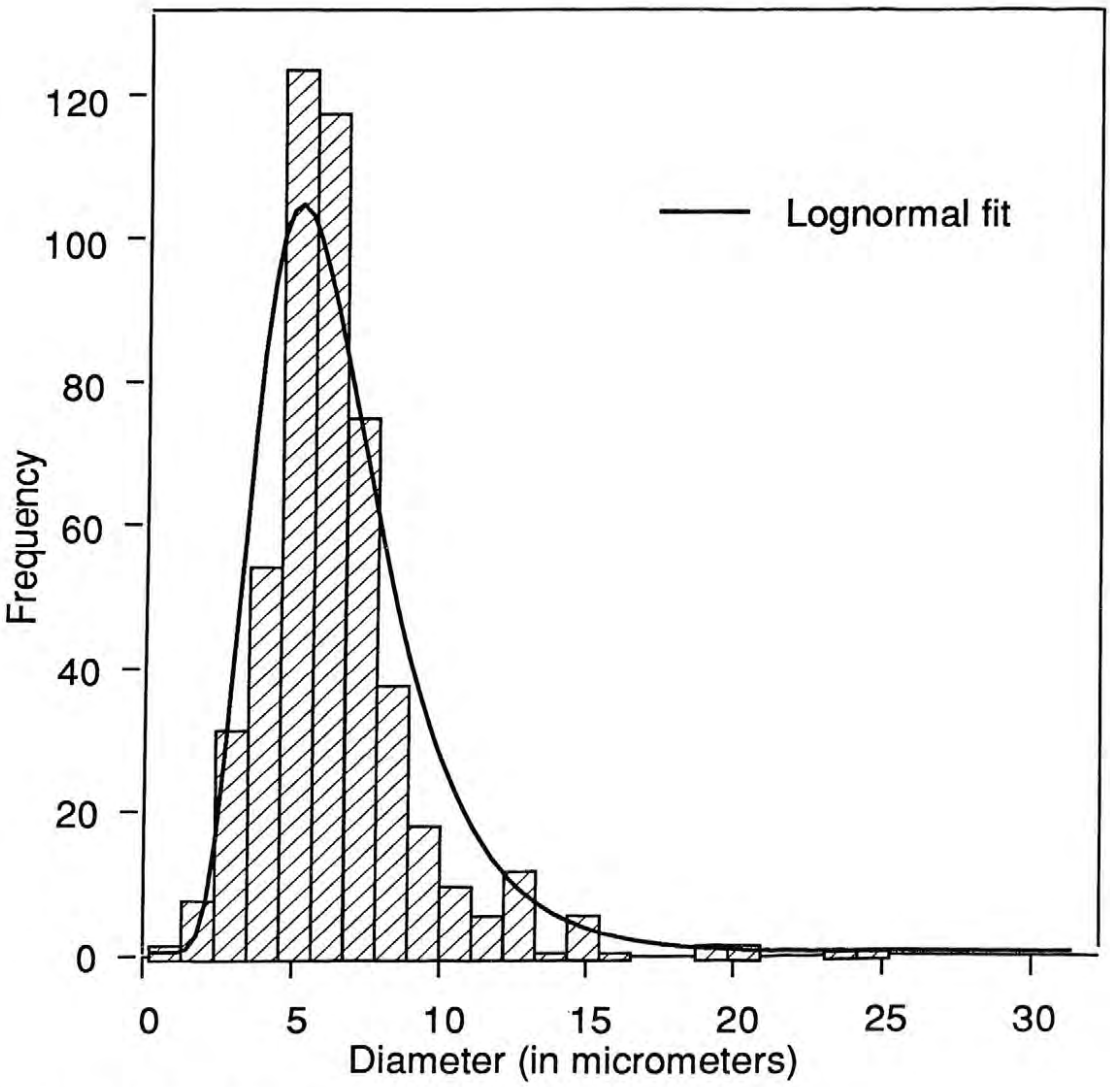

Fig. 2. Coarse mode size distribution obtained by EPMA.

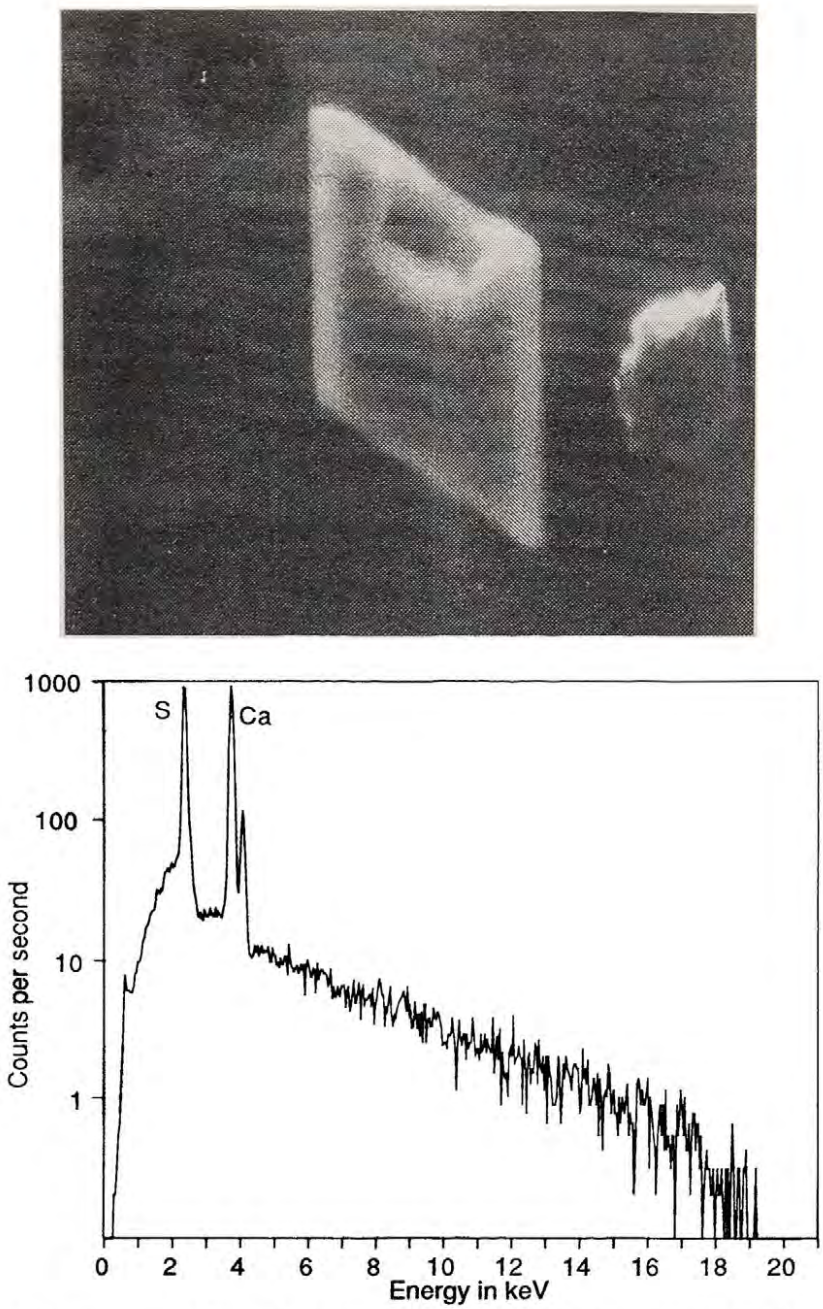

Fig. 3. Secondary electron image photograph of a $CaSo_4^-$ bearing particle, and its corresponding X-ray spectrum.

particle type is produced by the crystallization process that occurs when a droplet of sea water evaporates. The following two groups have also a marine nature. The remaining groups can be attributed to earth's crust particles; however, it is seen that some of the soil related aerosols also contain NaCl; they are probably soil dust coagulated with seasalt.

The size distribution observed for this aerosol fraction is shown in Fig. 2. It was also found that the best fit for this data set was obtained using a lognomal distribution function. The average particle diameter was 5.6 μm with a standard deviation of 2.

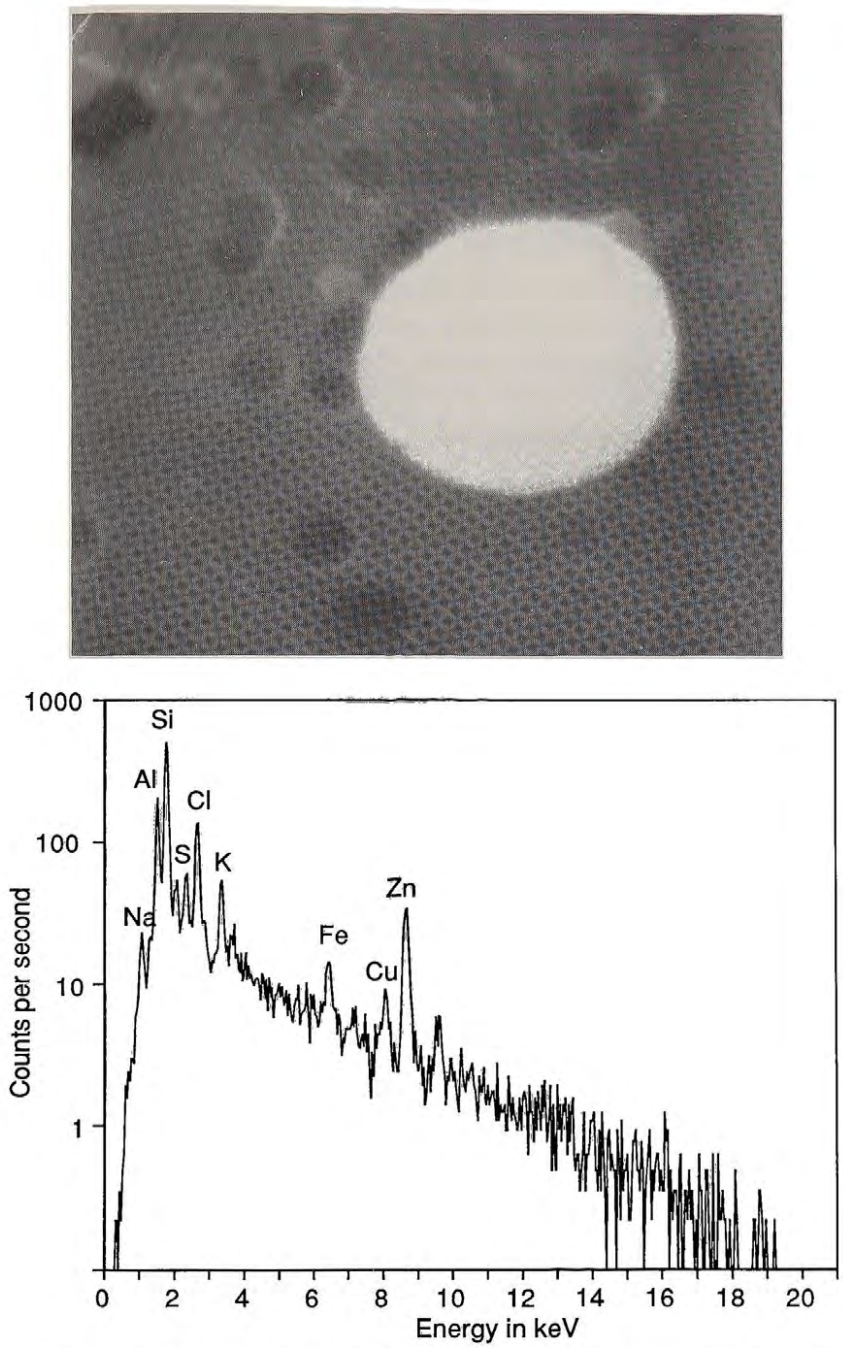

Fig. 4. Secondary electron image photograph of a Zn-bearing particle, and its corresponding X-ray spectrum.

Secondary electron image photographs are shown in Fig. 3 and 4 pertaining to particles thought to be representative of the Antarctic aerosol collected during this compaign. The corresponding X-ray spectrum, on which the particle identification and classification has been made, is also shown. It is seen that the marine related aerosol presents a phyhedral shape; combustion release particles, on the contrary, are almost spherical in shape, like the Zn - bearing particle in Fig. 4 which could be originated from incineration waste.

CONCLUSIONS

The bulk X-ray analysis results presented much higher values than those reported in the literature for other Antarctic locations. It has been possible to detect mainly two aerosol sources, namely marine and anthropogenic; we think that the latter has a local origin and it is responsible for high concentrations of Zn found in the fine mode aerosol. The same type of contamination has been previously reported by Préndez and Zolezzi (1982). Zn has an episodic nature, and it can be associated with sporadic local burning waste.

Single particle analysis combined with a statistical classification approach such as cluster analysis, also revealed the presence of anthropogenic emissions forming part of the fine mode aerosol. The results for the coarse mode are mainly characterized by sea and soil related particles. Both fine and coarse fractions presented a lognormal size distribution.

In order to avoid the excessive collection of sea aerosol, and anthropogenic influences due to human activities near the sampling site, it is necessary to conduct future research in a sampling station located far inland. Also, sampling periods must be long enough to ensure the collection of representative samples of Antarctic aerosol. In order to reach lower detection limits, proton induced X-ray emission (Pixe) should be used instead.

ACKNOWLEDGEMENT

We thank the Instituto Antártico Chileno for financial support.

REFERENCES

ANDREAE, M.O., R.J. CHARLSON, F BRUYNSEELS, H. STORMS, R. VAN GRIEKEN and W MAENHAUT. 1986. Internal mixture of sea salt, silicates and excess sulfate in marine aerosols. Science 232:1620-1623.

CUNNINGHAM, W and W. ZOLLER. 1981. The chemical composition of remote aerosols. J. Aerosol Sci. 12: 367-384.

GOLDSTEIN, J.I., D.E. NEWBURY, P. ECHLIN, D.C. JOY, CH. FIORI and E. LIFSHIN. 1981. Scanning Electron Microscopy and X-Ray Analysis. Plenum Press, New York.

HEINRICH, K.F.J. 1981. Electron Beam X-Ray Microanalysis. Van Nostrand Reinhold, New York.

MAENHAUT, W., W.H. ZOLLER, R.A. DUCE and G.L. HOFFMAN, 1979. Concentration and size distribution of particulate trace elements in the South Polar atmosphere. J. Geophys. Res. 84: 2421-2431.

PARKER, R.D., G.H. BUZZARD, T. DZUBAY and J.P BELL. 1977. A two stage respirable aerosol sampler using Nuclepore filters in series. Atmos. Environ. 11: 617-621.

PARUNGO, F., B. BODHAINE and J. BORTNIAK. 1981. Seasonal variation in Antarctic aerosol. J. Aerosol Sci. 12: 491-504.

PRÉNDEZ, M. and S. ZOLEZZI. 1982. Composición elemental de aerosoles subantárticos en función de tamaño de partícula. Ser. Cient. INACH 29:17-30.

RECEPTOR MODEL Source Composition Library. 1984. U.S. Environmental Protection Agency EPA-450/4-85-002.

ROJAS, C.M., P. ARTAXO and R. VAN GRIEKEN. 1990. Aerosols in Santiago de Chile: A study using receptor modeling with X-ray fluorescence and single particle analysis. Atmos. Environ. 24V: 227-241.

SEINFELD, J. 1986. Atmospheric Chemistry and Physics of Air Pollution. Plenum Press, New York.

SHAW, G., 1983. X-Ray spectrometry of polar aerosols. Atmos. Environ. 17: 329-339.

STORMS, H., ARTAZO, F BRYSNSEELS and R. VAN GRIEKEN. 1987 Individual particle analysis by automated EPMA for the improvement of source apportionment studies for remote aerosols. Microbeam Anal. 18: 343-345.

STORMS, H. 1988. Quantification of Automated Electron Microprobe X-Ray Analysis and Application in Aerosol Research. Ph. dissertation, University of Antwerp, U.I.A.

TABACK, H.J., A.R. BRIENZA, J. MACKO and N. BRUNETZ. 1979. Fine particle emissions from stationary and miscellaneous sources in the south coast air basin. Report N° KVB 5809-7 83. KVB Inc. Tustin, Ca. USA.

VAN ESPEN, P 1984. A program for the processing of analytical data (DPP). Anal. Chim. Acta 165:31.

VAN ESPEN, P., K. JANSSENS and J. NOBELS. 1986. Axil-PC, Software for the analysis of complex X-ray spectra. Chemometrics and Intelligent Lab. Sys. 1: 109-114.

Recibido: 04.03.91. Aprobado: 12.08.91.