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# Geochemistry of airborne particles from the lower troposphere of Terra Nova Bay, Antarctica

By S. GUERZONI, R. LENAZ, G. QUARANTOTTO and M. TAVIANI, *Ist. Geologia Marina/CNR, via Zamboni 65, 40127 Bologna, Italy*, G. RAMPAZZO, *Dip. Sc. Ambientali/Univ. di Venezia, Dorsoduro 2137, 30123 Venezia, Italy*, M. C. FACCHINI and S. FUZZI, *Ist. FISBAT/CNR, via Castagnoli 1, 40126 Bologna, Italy*

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ABSTRACT

Major and trace constituents (soluble + insoluble) of wind-blow particles collected at Terra Nova Bay were studied and the data compared with lacustrine and marine sediments from the same area and the Ross Sea. Compared to the geochemical composition of the other local sediments, the aerosol was found to be slightly enriched in femic minerals and depleted in Si. The Transantarctic Mountains (granitoids and metamorphic rocks) are proposed as the main source of the large ($D > 4$ μm) insoluble particles, with a possible contribution from nearby volcanoes. The soluble fraction accounts for more than 2/3 of the total mass loading and is mainly composed of marine salts. Some traces of contamination due to emissions from human activities were found in the aerosol, with mean Pb enrichment factor ($EF_{crust}$) value of 181. Crustal Pb contribution accounts for less than 10%, marine Pb less than 0.01% and 90% of Pb is unaccounted.

## 1. Introduction

There is increasing interest in the composition of particles in the remote polar atmosphere because its relevance to the overall of the atmospheric energy balance and transport. Particle type and concentration can be a source of information on the state of the atmospheric circulation. Particulate material may also be incorporated into the ice layers, thus recording changes in sea salt or terrestrial dust concentrations in air over the years. Antarctica is a physically remote region and recent work has shown that air reaching it should be well-cleansed of particles after passing through the zone of cyclonic storms and precipitation that surrounds this continent (Shaw, 1988, 1989).

In this paper, we characterize the geochemical composition of wind-blown particles. We compare sediments from different environments (lakes, coastal and offshore seabed) and also discuss the marine and/or crustal components of certain elements. In addition, some data referring to signs of local contamination are reported.

### *1.1. Study area*

The study area is Terra Nova Bay (74°39′S–75°30′S with 162°30′E–164°E). The Bay area is approximately 2400 $km^2$ (80 × 30 km) and is bounded by Mount Melbourne and Cape Washington to the north and the Drygalski Tongue to the South (Fig. 1).

The geographic location results in a predominance of katabatic winds all year round. Parish and Bromwich (1989) have shown that significant channeling of the cold air in the interior of the continent makes the Terra Nova Bay region one of the windiest in all Antarctica. Two years of data collected in the vicinity of the Italian station (ENEA, 1989) show that far more than 60% of the time katabatic winds blow from the Transantarctic Mountains down along the glaciers (average speed: winter 10–15 m $s^{-1}$; summer 5 m $s^{-1}$). Barrier winds from the south are very unusual (5–10%), due to the distance from the Ross Ice Shelf, and calms account for 15–20% of the time. Snow precipitation is of the order of 1.5 m $year^{-1}$,

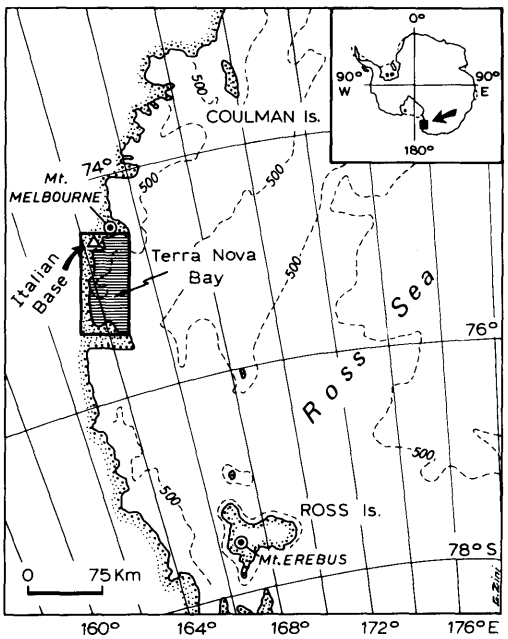


*Fig. 1.* General map of the Ross Sea area: the dashed area is Terra Nova Bay, with the location of the Italian Base (triangle). Two active volcanoes are shown on the map: Mt. Melbourne (2730 m, with fumarolic activity), 70 km N of the Base and Mt. Erebus (3800 m, active), 350 km to the S.

although this parameter is difficult to assess due to the strong winds during winter (blowing snow).

## 2. Results

### *2.1. Meteorology and mass loading data*

The dust was collected with two mesh-panels of 1 $m^2$ each, located uphill from the station, on a granitoid bedrock. This sampling method has been previously used in or near the marine environment and, in spite of the cut-off of the finest aerosol fraction (Prospero, 1981; Tomadin et al., 1984; Chester, 1986), the collected dust provides reliable information on the wind-blown aerosol. In the present case, the severe local meteorological conditions emphasize the need for any easy to instal system. This system does not require energy sources and is non-polluting. The mesh-panels consist of 300 $\mu$m terylene threads with a spacing of 800 $\mu$m. A theoretical collection efficiency was calculated, using the Ranz and Wong (1952) equation for cylindrical collectors. These theoretical values are shown in Table 1, as a function of the different classes of wind speed. From the reported values it can be deduced that the collected samples are representative only of the "coarse mode" aerosol fraction, even if the mesh configuration does not exclude a minor contribution of smaller size particles. The sampling site (close to weather station no. 53 of Bromwich and Parish, 1988) has wind speeds that reflect a close coupling between the interior confluence zone and a coastal acceleration of katabatic winds from Priestley Glacier down the lee side of the Northern Foothills.

After each sampling period (ca. 24 h), the mesh-panels were sealed and stored for subsequent study. The panels were extracted in an ultrasonic bath with deionized water, and the solid and liquid fractions were then analysed separately. Mineralogical and chemical analyses of the insoluble fraction of the collected aerosol were performed by X-ray diffraction, Scanning Electron Microscope, Energy Dispersive System and Atomic Absorption Spectrophotometer equipped with graphite furnace. The analytical techniques and precision are discussed in detail elsewhere

Table 1. *Data for each of the three typical wind-types encountered during sampling*

| Wind type | No. samples | Wind direction | Average wind speed ($ms^{-1}$) | 50% collection efficiency[a] ($\mu$m) | Insoluble fraction[b] (%) |
|---|---|---|---|---|---|
| A | 4 | W | >8.0 | 2 | 25 |
| B | 3 | NW | 4.5 | 3 | 24 |
| C | 4 | calm | <2.0 | 4 | 12 |

[a] Collection efficiency calculated according to Ranz and Wong (1952), see text;
[b] Insoluble fraction of the total aerosol.

(Gasparotto et al., 1989). Analysis of the soluble fraction was performed by ion chromatography (anions), AAS (alkaline and alkaline-earth species); $NH_4^+$ was determined by the indophenol colorimetric method (Solorzano, 1967).

The samples considered in the present paper were collected in the period January/February 1988, and are representative of the three typical wind patterns of the Antarctic summer, with different prevailing directions and average wind speeds. Table 1 summarizes the relevant data of each wind-type: (A) ordinary, (B) little katabatic, from W and NW; and (C) calms, for more than a day, with wind velocity $<2\ m\ s^{-1}$, and different directions.

The insoluble fraction represents on average 23% (5–43%) of the total aerosol. This fraction is large with katabatic winds and is minimum with calm wind conditions. This is due to the high marine contribution which can account for more than 90% of the total aerosol mass.

We have tentatively estimated an average total dust loading (coarse mode) of 300 ng $m^{-3}$ in our samples. We recognize that there may be questions about the quantitative aspects of this sampling procedure. This average result might be compared with the values of 170–300 ng $m^{-3}$ for the Antarctic compositional model of Shaw (1979). The Na/Al ratio of approximately 2 in our samples is the same as the value reported by Maenhaut et al. (1979) for the first four stages of their cascade impactor. The cut-off diameter for their impactor (50% efficiency at 1.7 $\mu$m diameter) is also comparable to that of our system.

### 2.2. *Chemistry of particles and soluble fraction*

The average chemical data of the particulate insoluble fraction are listed in Table 2, together with data of surface lacustrine and marine sediments collected in the area.

The comparison with sediments is presented, for the major elements, in the ternary plot (Fig. 2): alkalic feldspars (Al + Na + K, below left), femic minerals (Fe + Ti, below right), and silicates (top) are used to create the diagram. The smaller content of silica, together with femic minerals, allows atmospheric dust to be distinguished from the other samples.

The chemical composition of the wind-blown particles indicates that the potential sources may reflect the lithologies of the surrounding area. This includes igneous (Granite Harbour Intrusives) and metamorphic (Wilson Terrane Metamorphics) rocks, together with the young volcanics of the Mt. Melbourne apparatus. The Transantarctic Mountains (granitoids and meta-

Table 2. *Average chemical data of the particulate insoluble fraction (dusts)*

| Sample | Si | Al | Fe | Mg | Ca | Na | K | Ti |
|---|---|---|---|---|---|---|---|---|
| | | | | (%) | | | | |
| dusts | 19 | 5.8 | 5.1 | 1.8 | 1.4 | 1.0 | 2.0 | 0.5 |
| lakes | 33 | 6.3 | 3.2 | 1.0 | 1.5 | 1.6 | 2.7 | 0.4 |
| sea | 34 | 5.0 | 2.5 | 1.0 | 1.6 | 1.4 | 1.5 | 0.3 |

| | Pb | Cd | Cr | Co | Ni | V | $<60\ \mu m$ |
|---|---|---|---|---|---|---|---|
| | | | ($\mu$g/g) | | | | (%) |
| eolian dust | 771 | 3.0 | 419 | 15 | 178 | 146 | 100 |
| lake sedim. | 24 | 0.1 | 67 | 12 | 25 | 71 | 7 |
| marine coast. | 21 | 0.1 | 25 | 78 | 13 | 24 | 23 |
| marine offshore | 12 | <0.04 | 39 | 57 | 30 | 48 | 75 |

Lacustrine data are from Terra Nova Bay and marine samples from the Ross Sea area (Hieke-Merlin et al., 1989a). The data of the major elements (above) were used for the ternary plot of Fig. 2. The data of trace elements in the marine environment are divided into coastal and offshore samples (below).

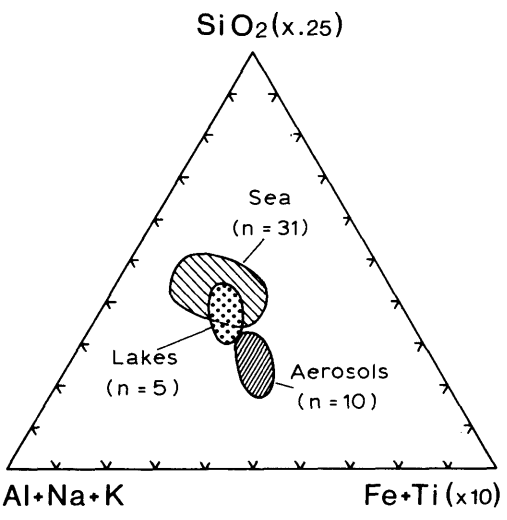


*Fig. 2.* Ternary plot of particulate aerosols, marine and lacustrine sediments. The sum of Al, Na, K (Alkalic feldspars, below left), Fe + Ti (femic minerals, below right) and silicates (top) are used to create the diagram.

morphic rocks) are probably the main sources of large ($D > 4\ \mu m$) particles.

The soluble fraction accounts for more than 2/3 of the total mass loading and is mainly composed of marine salts. The averaged chemical composition is shown in Fig. 3, together with the Na/Cl ratio. The sea salt contribution to the concentration of the species reported in Fig. 3b was calculated using the standard seawater ratios reported by Keene et al. (1986).

The data indicate the following

(a) $Mg^+$ and $K^+$ are all of marine origin: non sea salt (nss) contribution is almost negligible.

(b) nss-$Ca^{2+}$ accounts for more than 80% of the total $Ca^{2+}$ concentration.

(c) nss-$SO_4^{2-}$ represents 1/2 of the total $SO_4^{2-}$. The $SO_4^{2-}$ aerosol mean mass concentration is much lower with respect to data reported by Harvey et al. (1991), obtained from samples collected in the same area of Antarctica. An exceptionally low nss-$SO_4^{2-}/NO_3^-$ ratio is also observed with respect to the data of Harvey et al. (1991). These results can be accounted for by the size cut of our sampling technique (see Table 1). Savoie and Prospero (1982) report that the aerosol sulfate mass mean distribution in the marine atmosphere peaks in the sub-micrometer range, while nitrate is mainly found in the large-particle size range. It is therefore likely that our $SO_4^{2-}$ results are underestimated. Artifact $NO_3^-$ formation can also not be excluded, both during sampling (Savoie and Prospero, 1982) or connected with activities of the nearby Italian Antarctic Station.

(d) The molar ratio $R_{Na/Cl}$ is higher (avg. 1.18) than the expected $R_{sea\ water} = 0.86$, thus indicating a significant $Cl^-$ loss.

Several studies have dealt with the estimation of $Cl^-$ loss in marine aerosols due to the overall reaction (Keene et al., 1986; Möller, 1990):

$$NaCl_p + H_p^+ \rightleftharpoons Na_p^+ + HCl_g,$$

where "p" and "g" denote the particulate and gas phases, respectively.

The atmospheric acids $HNO_3$ and $H_2SO_4$ have been proposed as source of protons,

$$HX_g \rightleftharpoons H_p^+ + X_p^-.$$

Bodhaine et al. (1987) found increasing $Cl^-$ depletion with increasing $Na^+$ concentration and particle size and decreasing nss-sulfur. This could be the case of our "C"-type samples, collected in calm wind conditions, and having a smaller contribution of accumulation-mode particles than the "A"- and "B"-types.

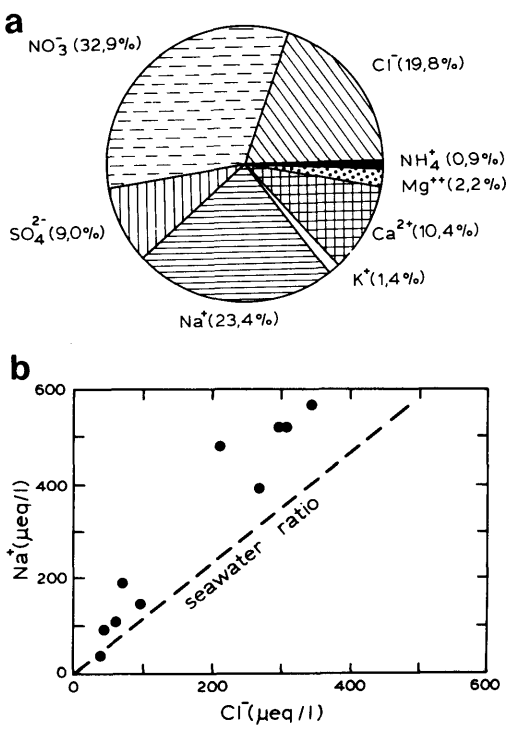


*Fig. 3.* Average chemical composition of the soluble fraction (above) and Na/Cl plot (below) with standard seawater ratio (dotted line, from Keene et al., 1986).

### *2.3. Crustal and marine sources*

The major natural sources previously identified as contributing to the total atmospheric particulate concentrations are the earth's crust and the ocean. The chemical composition of particles originating from other potential important natural sources such as volcanoes and extraterrestrial material are not well-known.

Enrichment factors with respect to Al were calculated for each sample.

$$EF = (X/Al)_{sample}/(X/Al)_{crust},$$

where X and Al refer to the concentration of the trace element of interest and of Al, respectively.

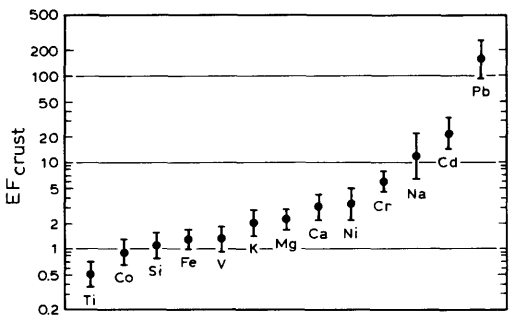


*Fig. 4.* Crustal enrichment factors for non-enriched (EF < 10) and enriched elements (Na, Cd, Pb) on atmosphere aerosols collected at Terra Nova Bay. The vertical extent of the error bars represents the range of $EF_{crust}$ values for all of the samples.

Crustal values are taken from Taylor (1964). The average enrichment factors are plotted in Fig. 4.

All major elements with EF values around one are of crustal origin. Among the trace metals, the enrichment in Cr, Ni and V is associated with femic minerals (EF values between 1 and 5). The high enrichment factor for Na is obviously due to the fact that this element has an oceanic rather than crustal origin, whilst lead and cadmium data indicate some anthropogenic contribution (EF values >20).

Elements with significant marine components are listed in Table 3 along with elements partially associated with crustal sources or others which remain unknown.

Sea salt is the major source of Na, Mg and K at Terra Nova Bay, a partial source of Ca and a negligible source of Pb.

Table 3. *Fractional contribution of elements associated with more than one component, in the ambient samples*

| | Mg | K | Ca | Na | Pb |
|---|---|---|---|---|---|
| | | (%) | | | ppm |
| insoluble | 0.4 | 0.5 | 0.3 | 0.2 | 217 |
| soluble sea | 1.7 | 1.6 | 1.5 | 12.4 | <0.1 |
| nss-soluble | — | — | 5.0 | — | 502 |
| total | 2.1 | 2.1 | 6.8 | 12.6 | 719 |
| crustal % | 20 | 20 | 4 | 2 | <10 |
| marine % | 80 | 80 | 22 | 98 | <0.01 |
| unaccounted | — | — | 74 | — | 90 |

### 2.4. *Signals of pollution (lead) in the Antarctic area*

From Table 3, it is evident that more than 90% of the total Pb in aerosols is not accounted for by crustal and marine sources. Whether this enrichment at Terra Nova Bay is natural or anthropogenic is still unknown. Boutron (1980) interpreted data on excess lead in ice cores as natural, originating partially from volcanoes and from the lead-enriched surface microlayer of the oceans. On the other hand, an inventory of metal emission from human activity in Antarctica resulted in 1800 kg/year, mostly deposited at coastal stations. This is 20% of the total fallout of Pb to snow in Antarctica each year (Boutron and Wolff, 1989).

The high enrichment factors of atmospheric aerosols are usually considered to be a contamination signal (Wolff and Peel, 1985). Therefore, the aerosol Pb EF data from Fig. 4 (mean value of 181) may indicate some evidence of anthropogenic contamination. Our Pb values can be compared with other measurements at the South Pole: Duce et al. (1975) and Maenhaut et al. (1979) found some "anomalously enriched" elements, among which the mean Pb EF values ranged from 200 up to 2200.

2/3 of the unaccounted lead in the aerosols are soluble in form, probably originating partially from the lead-enriched surface microlayer of the

Table 4. *Average Pb concentrations (range in parentheses) of different samples collected in Terra Nova Bay and Ross Sea, Antarctica*

| Sample | Average (range) | (unit) |
|---|---|---|
| *aerosol* | | EF[a] |
| total | 181 (94–318) | |
| particulate | 63 (54–79) | |
| *surface seawater*[b] | | |
| coastal | 17 (12–24) | ($ngl^{-1}$) |
| open sea | 6 (5–8) | |
| *seabottom sediment*[c] | | |
| coastal | 21 (14–26) | ($\mu gg^{-1}$) |
| offshore | 12 (10–16) | |
| *lake sediments* | | |
| | 24 (22–25) | ($\mu gg^{-1}$) |

[a] $EF = (X/Al)_{sample}/(X/Al)_{crust}$.
[b] Capodaglio et al. (1980).
[c] Hieke-Merlin et al. (1989b).

ocean. Also, increasing coastal seawater Pb values in the Terra Nova Bay area (Table 4) were found and have been interpreted as possible local impact (Capodaglio et al., 1989).

## 3. Conclusions

The geochemical composition of wind-blown dust is very similar to other local sediment samples (marine and lacustrine), with a slight enrichment in femic minerals (Fe + Ti) and depletion in Si. The Transantarctic Mountains (granitoids and metamorphic rocks) are probably the main sources of the large ($D > 4\ \mu m$) particles, with a possible contribution from nearby volcanoes (Lenaz et al., 1989; Taviani et al., 1992).

Si, Al, Fe, Ti (Cr, Ni and V) are derived from the crustal source. Na and Cl are almost completely derived from a marine source, whilst Mg and K are common to both sources (80% marine and 20% crustal).

Some evidence of anthropogenic contamination was found in the aerosols, with a mean Pb enrichment factor ($EF_{crust}$) value of 181. Pb data of samples from different environments collected at Terra Nova Bay and in the Ross Sea during the last three years of activity (Table 4) confirm that in Antarctica the atmospheric input from local human activity is still mainly confined to small areas near the station (Wolff, 1990).

Several problems remain open. In particular: examination of Mt. Erebus as a possible source of the particles we are collecting, identification of other nearby natural sources and determination of the extent of anthropogenic impact on the area.

## 4. Acknowledgements

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