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LASER MICROPROBE MASS ANALYSIS OF INDIVIDUAL ANTARCTIC AEROSOL PARTICLES

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Individual Antarctic aerosol particles in the 0.5–4 μm aerodynamic diameter range were analyzed using laser microprobe mass analysis (LAMMA). As they were sampled near the ocean, the great majority consists of seasalt, transformed to various degrees in the atmosphere. Major alterations include the association of an excess sulfate and methane sulfonate with these particles. Sulfate-rich particles containing little or no chloride were found mostly in the smallest size fraction (0.5–1 μm), where they account for some 5% of all particles: they are most likely highly transformed seasalt. Aluminosilicates, on the other hand, only appear among the coarser particles: they represent 2% of the particulates in the 2–4 μm range. The remainder of the aerosol consists of organic, Fe-rich, K-rich and Zn-rich particles. The latter groups have very low abundances: always less than 1% of the population of the impactor stage(s) onto which they were collected.

KEY WORDS: Aerosol, remote, Antarctic, microanalysis, single particle analysis, LAMMA.

INTRODUCTION

Throughout the years, our laboratory has gained experience in the analysis of individual aerosol particles from various environments: coastal,¹ marine,^{2,3} urban^{4,5} and forests.^{6,7} In the present work, we used laser microprobe mass analysis (LAMMA) for individual particle analysis of aerosol samples collected at the King George Island, Antarctica. The Antarctic continent is the most distant area from the world's predominant pollution sources, so the Antarctic aerosol can be regarded as a "background aerosol".

Earlier single particle analyses (among which are melting point determination, polarizing microscope analysis, electron microscopy, electron diffraction and electron microprobe analysis) of Antarctic aerosol samples from different locations have revealed the following particle types: sulfur-rich particles (which may be formed by gas-to-particle conversion), seasalt particles (formed by the bursting of gas bubbles that arise through wave action), aluminosilicates (earth crustal dust) and particles whose X-ray spectra contain mostly Fe peaks.^{8–11} Naturally, their relative concentrations vary with sampling site, season and meteorological conditions.

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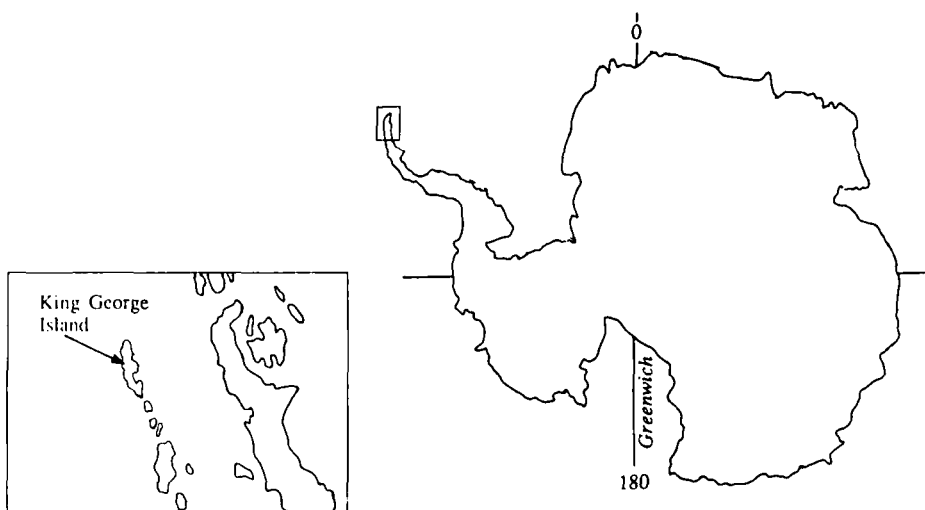


Figure 1 Sampling location.

Due to its special features, LAMMA will allow to perform a further characterization of those particle types. Among its advantages are the capability to provide simultaneously inorganic and some organic information and the favourable detection limits for most elements (ppm range) relative to, e.g., electron microprobe analysis. Its disadvantages lie in its destructive nature, the lack of automation and the difficulties encountered in quantifying the data.

EXPERIMENTAL

Sampling

During the austral summer of 1985, aerosol particles were collected at the Brazilian Antarctica Station "Commandante Ferraz" (62.1°S , 58.4°W) on King George Island, Admiral Bay, Antarctic Peninsula (Figure 1). Sampling was performed daily from February 13 to 15 and 17 to 19 with a single orifice 6-stage Batelle-type cascade impactor.¹² The 50%-cutoff aerodynamic diameters of the stages 1 through 6 are 8, 4, 2, 1, 0.5 and $0.25\ \mu\text{m}$ respectively. A sampling time of ca. 20 min usually provided a satisfactory loading for LAMMA. Meteorological conditions during sampling were fairly constant: temperatures ranging from -1 to 5°C and wind coming from the west.

LAMMA Instrumentation

In the LAMMA-500[®] instrument (Leybold-Heraeus, Köln, FRG) individual aerosol particles are vaporized by a single high-power laser pulse ($\tau=15\ \text{ns}$) of a Q-switched frequency quadrupled Nd:YAG laser ($\lambda=265\ \text{nm}$; power density:

Table 1 Particle types, detected with LAMMA and approximate particle type abundances

<i>Stage 5</i> (0.5 μm)	<i>Stage 4</i> (1 μm)	<i>Stage 3</i> (2 μm)
seasalt (> 94%)	seasalt (98%)	seasalt (97%)
SO ₄ ²⁻ -rich (5%)	SO ₄ ²⁻ -rich (1%)	aluminosilicate (2%)
organic (< 1%)	Zn-rich (< 1%)	Zn-rich (< 1%)
	K-rich (< 1%)	Fe-rich (< 1%)
		K-rich (< 1%)

10^7 – 10^{11} Wcm⁻²). The induced microplasma contains atomic and molecular ions, as well as electrically neutral fragments. Depending on the spectrum polarity chosen, positive or negative ions are then accelerated and collimated into the drift tube of a time-of-flight mass spectrometer. When ion separation has been achieved, the ions strike an electron multiplier. Thereafter, the signal is fed into a 32 Kbyte memory transient recorder (LeCroy TR8818). Spectra can be stored on an IBM PC-AT for off-line data analysis.

The home-made software package used for data processing includes a baseline correction algorithm, a peak integration routine and spectrum averaging facilities.

Further information about the instrument, its applications and the software package used can be found in the literature.^{13,14}

Reference Aerosol Preparation

In this work, artificial aerosols were used as standards. They were prepared by pneumatic nebulization of aqueous solutions and subsequent collection of the formed aerosol with an impactor.¹⁵ In this way, standard aerosols with the following composition were prepared: NaCH₃SO₃, NaCH₃SO₃:NaCl (1:1), Na₂CO₃, NaOOCCH₃, (COONa)₂, Na₂SO₄ and NaOOCCH₃:Na₂SO₄ (1:1). In the same way, two artificial seawater aerosols were prepared, one using synthetic seawater, the other one using filtered North Sea water. Synthetic seawater was prepared according to the method of Kester *et al.*¹⁶ North Sea water was filtered through a 0.4 μm Nuclepore membrane filter.

RESULTS AND DISCUSSION

For all 6 samples, roughly 100 particles of each of the impactor stages 3, 4 and 5 with 50%-cutoff aerodynamic diameters of 2, 1 and 0.5 μm , respectively, were analyzed. Nearly 2000 individual particles were thus examined. Particles of the stages 1 and 2 were too large to be properly analyzed. Microscopic observation, however, revealed that most of them had a typical seasalt appearance. As for stage 6, the coatings of the grids were always destroyed, making analysis impossible. Peak identification was based on comparison with mass spectra of reference aerosol particles.

Table 1 shows the various particle types, present on the different stages. Since

no significant differences between samples were observed, they were all averaged out for the whole sampling period. The given particle type abundances should be considered as a slightly biased rough estimate of the actual situation, as particles other than the dominating seasalt were sometimes selected on the base of their appearance. For example, particles whose spectra consist of C_n -clusters are often clearly black-coloured. However, the major part (>90%) of the analyzed aerosol clearly consists of seasalt. LAMMA spectra of these particles were compared with spectra of two different artificial seawater aerosols, generated as described in the experimental section.

The positive spectra of the synthetic seawater aerosol (Figure 2a) are dominated by mass peaks of Na^+ , K^+ and the $(NaCl)Na^+$ clusters. Mg^+ , Ca^+ and Na/O , $Na/Cl/K$ and $Na/S/O$ clusters are also detected. The negative spectra (Figure 2b) are dominated by the Cl^- isotope peaks and the $(NaCl)_nCl^-$ clusters. We did not detect significant differences between the synthetic seawater aerosol and the aerosols from filtered North Sea water. Obviously, the organic material which is present in the North Sea water does not contribute significantly to these spectra.

It appears that Antarctic seasalt aerosol particles show all mass peaks appearing in the artificial seasalt aerosols (although their relative intensities may sometimes differ) in addition to some entirely new ones. Major differences are discussed below.

Most of the time, the relative intensities of the sulfate peaks in the Antarctic seasalt aerosol are significantly higher than those in the artificial seasalt aerosol. In the positive spectra (Figure 3a) there are mainly the $Na/S/O$, $K/S/O$ and $Na/K/S/O$ clusters, in the negative ones (Figure 3b) S^- , HS^- and SO_n^- mass peaks. A possible explanation for this sulfate enrichment is, e.g., agglomeration of seasalt particles with very small sulfate particles which are very abundant in the South Pole aerosol.^{9,10} Furthermore, the presence of salts derived from methane sulfonic acid (MSA), in or on the particles, can contribute to the sulfate mass peaks in their spectra.

MSA is a reaction product of the photo-oxidation of dimethylsulfide (DMS), which originates from, e.g. the metabolism of certain marine algae and decay processes of dead krill. The emission of DMS from oceanic surfaces contributes significantly to the global sulfur cycle. MSA is produced in the gaseous state; it dissolves into aqueous aerosol droplets and accretes on aerosol particles in the atmosphere.¹⁷ The organosulfur compounds are eventually converted to non-seasalt sulfate ($nss-SO_4^{2-}$).¹⁸ According to Legrand *et al.*,¹⁹ the H_2SO_4 present in Antarctic ice is probably mostly due to the biogenic activity of the surrounding waters. Berresheim²⁰ investigated atmospheric distributions of DMS, SO_2 , MSA and $nss-SO_4^{2-}$ in the surroundings of the Antarctic Peninsula. The local $MSA/nss-SO_4^{2-}$ ratio appeared high compared to values over other oceans. Using LAMMA, Kolaitis *et al.*² also detected MSA-derived compounds in marine aerosol particles, sampled in the Bahamas area.

MSA itself is a volatile acid, and hence cannot be detected by LAMMA. Comparison of spectra of its Na salt ($NaCH_3SO_3$) and Na_2SO_4 revealed that the only mass peaks that give a direct indication of the methane sulfonate structure are the one at $m/z=141$ ($Na_2CH_3SO_3^+$) in the positive mode spectra, and the one

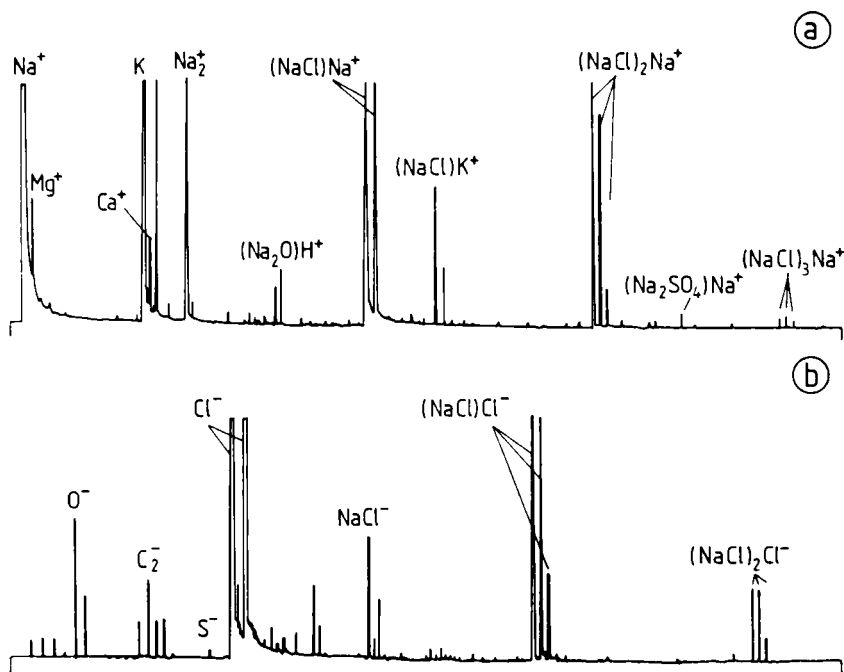


Figure 2 Positive mode (a) and negative mode (b) LAMMA spectra of an artificial seasalt aerosol particle.

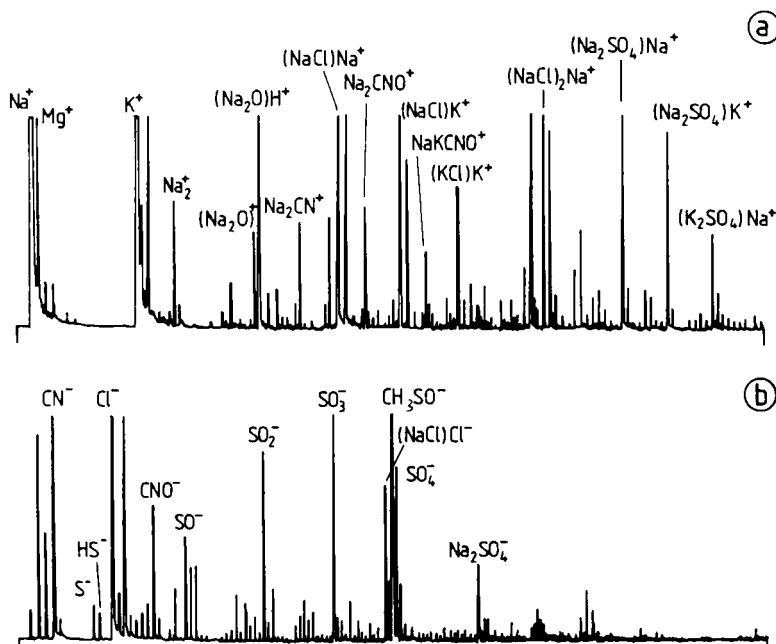


Figure 3 Positive mode (a) and negative mode (b) LAMMA spectra of an Antarctic seasalt particle with a sulfate enrichment.

at $m/z=95$ (CH_3SO_3^-) in the negative mode. As appears from the analysis of an artificial $\text{NaOOCCH}_3/\text{Na}_2\text{SO}_4$ aerosol, those peaks are not likely to be formed by plasma reactions between compounds that do not contain the intact anion (i.e. CH_3SO_3^-). In seasalt spectra, they are not always unambiguously detectable since, within the resolution of the LAMMA, they coincide with the mass peaks of $(\text{Na}^{37}\text{Cl})(\text{Na}^{35}\text{Cl})\text{Na}^+$ and $(\text{Na}^{37}\text{Cl})^{35}\text{Cl}^-$, respectively. Figure 4 shows a positive (a) and a negative (b) LAMMA spectrum where the mass peaks at $m/z=141$ and 95 obviously do not originate merely from the respective Na/Cl-cluster ions. The relative intensities of the "MSA peaks" seem to be the highest for the smallest particle sizes.

Especially on stage 5, particles are found that contain even more sulfate than those on the earlier stages. These particles show no or very little Cl^- in their negative spectra (Figure 5a) and no typical $(\text{NaCl})\text{Na}^+$ clusters in their positive ones. Sometimes, the $m/z=141$ ($\text{Na}_2\text{CH}_3\text{SO}_3^+$) peak in the positive, and the $m/z=95$ (CH_3SO_3^-) one in the negative spectra are rather dominant (Figure 5b). As mentioned earlier, these two peaks are indicative of the presence of methane sulfonic acid (MSA) compounds. From the LAMMA spectra, a significant part of all counter-ions for sulfate seems to be Na^+ . This could mean that the above discussed particulates are in fact highly transformed seasalt.²¹

Various authors, having analyzed samples from different locations agree that, especially in summer, sulfate tends to dominate the Antarctic aerosol by number and usually by mass (e.g. refs. 9, 10 and 22). According to Maenhaut *et al.*²³ "sulfate should predominantly exist in the form of H_2SO_4 , $(\text{NH}_4)\text{HSO}_4$, $(\text{NH}_4)_2\text{SO}_4$ or a mixture, possibly including more complex species". Ito¹¹ detected $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 particles. Cadle *et al.*⁸ found possible candidates for the cations of their sulfate particles to be H^+ , NH_4^+ and maybe Na^+ . We never detected NH_4^+ clearly. This can of course be due to the fact that LAMMA is much more sensitive for other cations than for ammonium: Otten *et al.*²⁴ found the relative sensitivity coefficient for Na^+ to NH_4^+ to be 150. The occurrence of the mass peak at $m/z=97$ (HSO_4^-) in the negative spectra can, however, be an indication of the presence of a hydrogen source. In the authors' opinion, the former possibility – i.e. the particles being highly transformed seasalt – seems the most plausible one. Sampling took place in a coastal environment; this explains the fact that seasalt accounts for such a large fraction of the aerosol. Furthermore, since the majority of the sulfate particles are known to be associated with the submicron size fractions, they will definitely be more abundant in the size range beyond the one we measured (0.5–2 μm).

Sometimes, seasalt mass spectra include C_n^- clusters (Figure 6a). These peaks do not appear in Na_2CO_3 and NaCH_3SO_3 standard aerosol spectra. This implies that those C_n clusters are not formed by recombination reactions in the laser-induced microplasm, but originate from compounds having carbon chains within their structures, e.g., black carbon and fatty acids. Negative mass spectra of the artificial North Sea water aerosol do not show those peaks to that extent, so, most probably, an enrichment took place. This alteration can result from atmospheric transformations, although it might just as well (or even more likely)

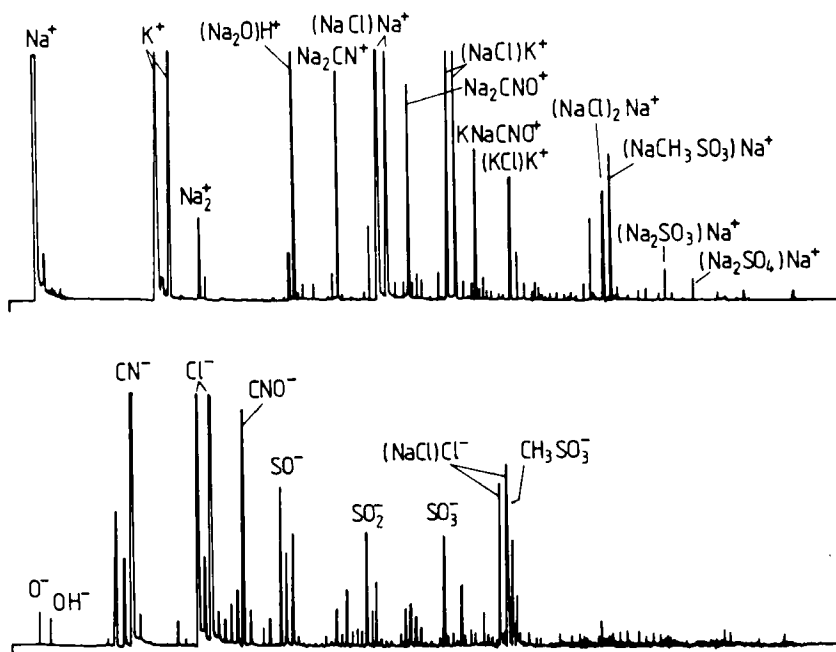


Figure 4 Positive mode (a) and negative mode (b) LAMMA spectra of an Antarctic seasalt particle where the "methane sulfonate peaks" are clearly visible.

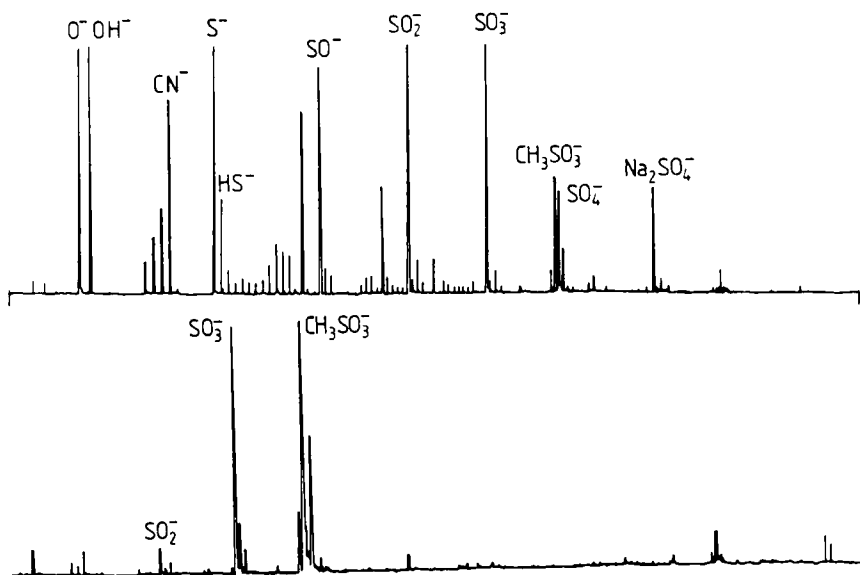


Figure 5 Negative mode LAMMA spectra of sulfate-rich particles where (a) SO_n^- mass peaks dominate the spectrum, and (b) the $CH_3SO_3^-$ mass peak dominates the spectrum.

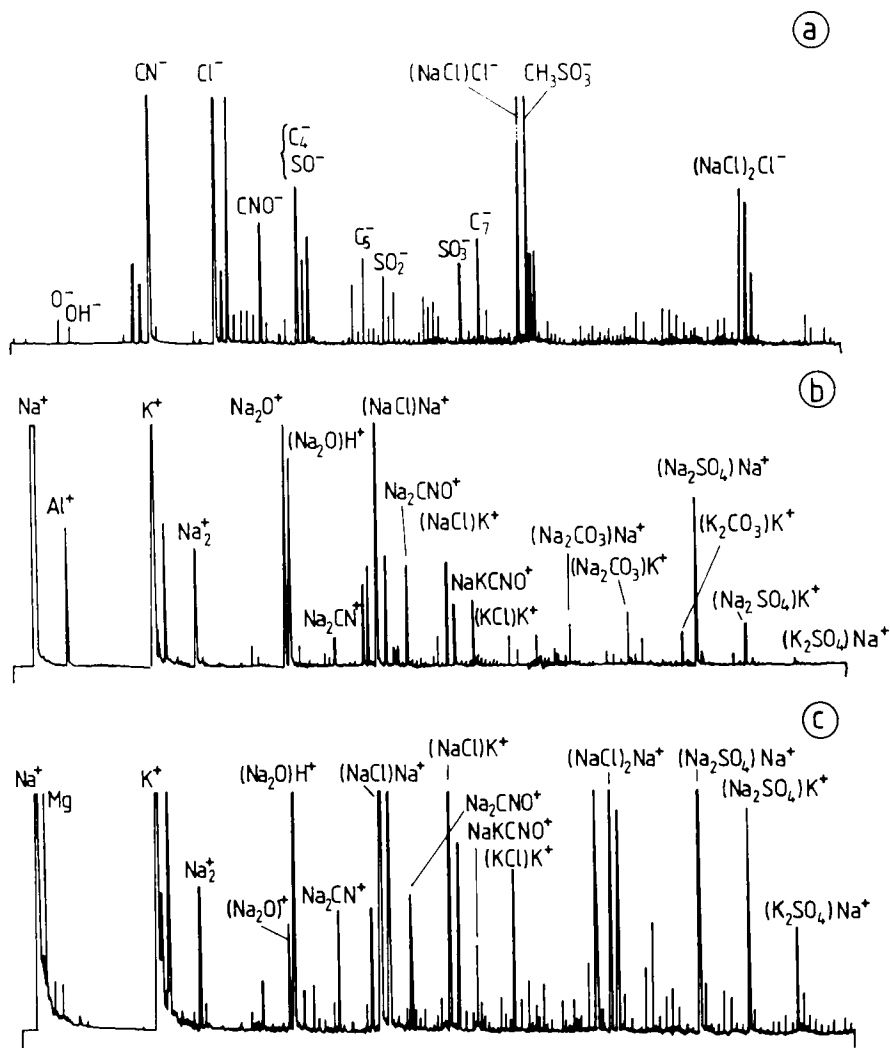


Figure 6 LAMMA spectrum of an Antarctic seasalt aerosol particle containing (a) C_n^- clusters (b) carbonate clusters and (c) Na_2CN^+ , Na_2CNO^+ and NaKCNO^+ mass peaks.

be inherent to the seasalt aerosol formation process: rising bubbles can pick up surfactants and transport them to the surface. Furthermore, the surface microlayer itself is known to be enriched in organic material. Thus, total organic matter in the spray droplets may be very much concentrated compared to the bulk seawater.²⁵

Na/CO₃ and Na/K/CO₃ cluster ions were also rather regularly detected (Figure 6b). The most intense peak is the one at $m/z=129$ (Na₃CO₃⁺). This ion is detected in spectra of Na₂CO₃, NaOOCCH₃ and (COONa)₂ standard aerosols but not in those of, e.g., NaCH₃SO₃. That is the carbonyl group is not formed in the microplasm. The origin of these cluster ions is not clear; just as in the case of the C_n⁻ clusters, the "bubble bursting" process can be responsible.

The last obvious difference with the artificial seasalt aerosol spectra is the frequent appearance of a set of 3 mass peaks in the positive spectra: $m/z=72$, 88 and 104 (Figure 6c). Considering the (most of the time) intense peaks at $m/z=26$ (CN⁻) and 42 (CNO⁻) in the negative spectra, they may be assigned to Na₂CN⁺, NaKCN⁺ and/or Na₂CNO⁺ and K₂CN⁺ and/or NaKCNO⁺, respectively, originating from nitrogen-containing organic compounds.

Because of its significantly lower abundance, the non-seasalt particulate fraction could not be studied as exhaustively. Still, some general remarks are given below.

Aluminosilicates (Figure 7a), probably earth crustal dust, were detected exclusively among particles of stage 3 (2 μm), where they account for roughly 2% of all particles. They always seem to contain Ba as a trace component. This does not necessarily imply that Ba has the greatest bulk concentration: it can merely be due to the fact that LAMMA is particularly sensitive for this element.

Sporadically, particles whose spectra are dominated by C_n clusters are found on stage 2 (Figure 7b). They generally have a black appearance. Therefore, we assign them as graphitic or "black" carbon particles: they can act as a tracer for combustion emissions. Hansen *et al.*²⁶ showed that concentrations of this pollutant at the South Pole range from 50 pg.m⁻³ to 5 ng.m⁻³. Although local source contamination events certainly contribute to some extent, part of them may have been carried over a long distance from their source regions.

Just like the aluminosilicates, Fe-rich particles (Figure 7c) were exclusively detected on stage 3 (2 μm); they always seem to contain Pb. Using an X-ray energy spectrometer interfaced with a scanning electron microscope, Parungo *et al.*⁹ also detected such particles in their Antarctic aerosol, and stated that they could be meteoric dust.

On comparison with spectra of a metallic Zn standard, we could identify the particles whose positive spectra contain mainly Zn⁺, Zn₂⁺ and Pb⁺ mass peaks (Figure 7d). The origin of this kind of particles is not clear. They may originate from the galvanized material, extensively used in the base station, which can be altered to some extent by the marine aerosol.

The final group includes particles whose positive spectra show enormous K peaks and much less intense, but nevertheless obvious, Pb-isotope patterns (Figure 7e). They could originate from biogenic aerosol emissions. According to their size (≥ 1 μm), however, long-range transport does not seem so obvious. Another possibility, of course, is local contamination.

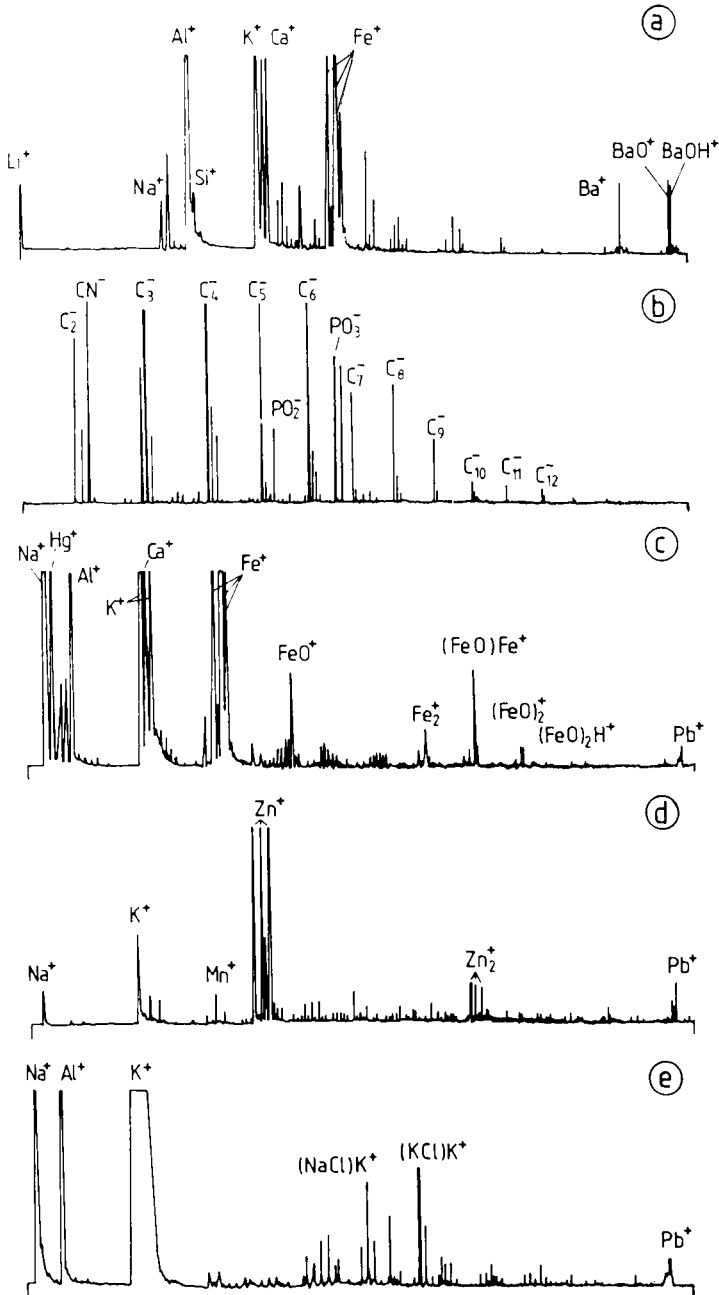


Figure 7 LAMMA spectrum of a(n) (a) aluminosilicate particle, (b) organic particle, (c) Fe-rich particle, (d) Zn-rich particle, and (e) K-rich particle.

COMPARISON WITH SEASALT AEROSOL PARTICLES, SAMPLED OVER A LESS REMOTE AREA (NORTH SEA)

The North Sea (Western Europe) is surrounded by several highly industrialized regions. LAMMA spectra of marine particulates from this location show all mass peaks that appear in the Antarctic ones. That is, all transformations that take place on the Antarctic particles, also seem to occur with the North Sea aerosols. In addition to the previous "background" mass peaks, we also found some clearly pollution-derived peaks in the North Sea marine particulates, e.g., nitrate, ammonium and some heavy metal ion peaks (V^+ , Ni^+ , Cu^+ and Pb^+).

CONCLUSION

As sampling took place in a coastal environment, most particles we analyzed have a marine origin: they are generated by "bubble bursting" and subsequently transformed in the atmosphere. Association of excess sulfate and methane sulfonate with those particles are the most striking alterations. Furthermore, the typical seasalt spectra sometimes show molecular ions containing CO_3^{2-} or C_n^- clusters. The extent of transformation depends on both the age of the particles and meteorological conditions. The remaining part of the aerosol consists of sulfate-rich, aluminosilicate, Fe-rich, organic, K-rich and Zn-rich particles. The sulfate-rich particles are most likely highly transformed seasalt while the aluminosilicates and Fe-rich particles, solely appearing in the coarse fraction, seem to be earth crustal dust. K- and Zn-rich particulates might be derived from local contamination events. Typical ions often found in LAMMA spectra of marine aerosol particles from less remote areas (e.g. ammonium, nitrate and some trace element ions), are not present in detectable concentrations in Antarctica.

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