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A SIMPLE MODEL FOR K AND Ca ENRICHMENT INTERPRETATION IN ANTARCTIC SNOW

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The presence of surface active fluorescent organic matter (SAFOM) in Antarctic snow, similar to the marine matter, suggests that micro components present at the sea surface, capable of interacting with SAFOM, may be transported via marine aerosol. Experimental evidence is given by the enrichment of SAFOM in the smallest marine aerosol particles and by the interaction of K and Ca with SAFOM. The surfactant concentration at the sea surface during large whitecaps coverage is also studied. A hypothesis for the K and Ca excess, evidenced in Antarctic snow at high altitudes, is proposed by means of a spray drop adsorption layer model (SDALM). This model is the result of an improved analysis of the breaking wave process, and of additional experimental findings. It seems to justify the excess concentration of K and Ca with respect to that expected for marine water compositions in high altitude snow in Antarctica. It may also constitute a more general basis for the interpretation of the fine fraction aerosol composition in remote marine areas.

Keywords: Marine aerosol; aerosol transport; Antarctic snow main components; adsorption model; air-sea interaction; Antarctic atmosphere

INTRODUCTION

In 1978 Berg and Winchester^[1] evidenced that the basic problem of the aerosol composition in marine atmosphere is the evaluation of the real marine aerosol contribution with respect to other contributions (continental, anthropogenic, vol-

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canic, gas-to-particle conversion) in view of assessing the total impact due to human activities.

It is important to point out that particles in the aerodynamic range of 0.5–1 μm or smaller are the most important because of their long-life in the atmosphere, and at the same time “they may lead to an improved assessment of the climatic impact of large scale air pollution”. Although much work on this topic has been done, a well defined basis to evaluate the true marine contribution with respect to the total aerosol composition remains an open question. Eventual changes in the composition of marine aerosol itself become determinant. Usually marine aerosol is confined within the 1–150 μm range^[2]. This definition does not agree with the reported data of Blanchard and Woodcock^[3] and Cipriano *et al.*^[4]. The latter authors showed, in an accurate laboratory experiment, that marine aerosol particles in the fine and ultra fine dimensional range (about 0.01 μm in diameter) occur during a breaking wave event. Another important point is that at the beginning of the seventies^[5] field experiments showed that the greatest quantities of organic matter appeared associated to the smallest marine aerosol particles (below 0.5 μm in diameter).

Antarctica represents one of the best remote sites to study the nature of marine aerosol, and at the same time the coastal Antarctic snow appears to be a very good aerosol sampler in those conditions (salt storms) in which all other expected aerosol contributions are minimal. Previous papers^[6–8] showed the presence of surface active fluorescent organic matter (SAFOM) in Antarctic snow which was defined as the organic component associated with the marine aerosol. This organic component showed characteristics similar to marine fulvic acids. On the other hand, some literature reports an excess of K and Ca with respect to their expected concentration as minor marine water components^[1,9–11]. An excess of K and Ca was also recently evidenced in Antarctic snow^[12–14]. One hypothesis to explain this excess is a mixing effect of other aerosols from different origins. Another hypothesis suggests^[5,9] that some components present at the sea surface interact with SAFOM and then are transported into the air together with marine aerosol. Experiments with Bubble Interfacial Microlayer Sampler (BIMS) have verified this last aspect for some elements^[15]. However, Hoffman and Duce^[16] and BIMS experiments seem to exclude this possibility for K and Ca.

In the present work we propose a new approach based principally on an accurate re-examination of the SAFOM adsorption process which takes place during marine aerosol production as microdrops originating from a breaking wave event. The role of a surface concentration wave which occurs in consequence of the adsorption bed constituted by the foam column of whitecaps is considered. An attempt to deduce a spray drop adsorption layer model (SDALM) from the SAFOM data is reported, and applied the excess of some marine aerosol minor components trapped in Antarctic snow.

Laboratory and field Tyrrhenian sea experiments are described to further support the marine origin of the K and Ca excess found in high altitude Antarctic snow. The BIMS^[15] and Hoffman and Duce^[16] experiments are reconsidered in the light of our new results. The generalisation and new aspect emerging from the SDALM application will be discussed.

EXPERIMENTAL

Weather conditions

The air-sea kinetic energy exchange (momentum) is the principal factor in the air-sea exchange of matter. Rough sea conditions with high whitecaps coverage represent the best conditions to study the processes correlated to marine aerosol production. In fact during rough sea events aerosol sampling can be done under the best conditions, viz.:

- a. maximum aerosol production even in the fine and ultra fine fraction^[4],
- b. maximum reduction of interfering phenomena (such as photochemical reactions) and processes (such as mixing with aerosol of different origin).

For our Tyrrhenian coastal sampling site, inland winds with high speed (> 6 m/s) were selected for our studies.

Sampling stations

Coastal Tyrrhenian Sea

Leghorn meteomarine station, near the Inter university Centre of Marine Biology.

Antarctica

McCarthy Ridge (700 m above sea level 74°32'57"S-162°56'29"E) and Styx Glacier Plateau (1700 m above sea level 73°51'56"S-163°41'35"E) stations near Terra Nova Bay (Ross Sea).

Sampling operations

The marine water

Used in the present experiment was taken from a pier in the Tyrrhenian Sea near the Leghorn Meteomarine station^[17] with the procedure described elsewhere^[8]

for calm sea conditions. For rough sea conditions a large mouthed polyethylene bottle lowered into the sea on a nylon wire. In this case, the weather conditions were: wind speed > 6 m/s and wind direction 180° - 270° , i.e. the same at which the marine aerosol was sampled.

The marine aerosol

Was sampled at the meteomarine station of Leghorn, on Tyrrhenian sea coast with a high volume Andersen 1000 sampler fitted with a five stage impactor Sierra-235. The cut-offs of particle diameters were 7.2, 3, 1.5, 0.95 and 0.49 μm . The Andersen preliminary impactor cut off particles > 8 μm . A quartz fibre filter with nominal pore diameter 0.45 μm collected the particles < 0.49 μm . A software-driven meteorological trigger allowed the aerosol sampling in well defined weather conditions^[17]. By means of this trigger, only samples for wind speed > 6 m/s and direction 180° - 270° were collected. The sampling started only after 0.5 hour from the beginning of each event, to ensure the stability of the weather conditions during the sampling. The humidity and the temperature were also taken into account. The selection of particles for Sierra 235 multistage impactor is valid, according to the manufacturer, only for spherical particles of density =1. Therefore the instrument is particularly useful to study marine aerosol as a spray -i.e. immediately after its formation. For these reasons the sampler was placed 8 m above sea level (70 m from the coastal line). To avoid the transition from liquid to solid particles for the most part of the aerosol microdrops, the weather conditions corresponding to a relative humidity $> 85\%$ and temperatures $< 14^{\circ}\text{C}$ were established in the meteorological trigger. Thus limiting the aerosol capture campaigns to the period from November to March.

Materials and methods

All reagents were reagent grade. Myristic acid was purchased from the Pfalts & Bauer company.

Laboratory aerosolization process

Was performed in two steps: the first is described elsewhere^[8], in short the seawater sample was submitted directly to the aerosolization process. For the second step we used a special device, similar to that described by Sakai^[18] but with a modified gas-bubble path. Only the first jet drops were collected on a glass plate with this apparatus. These jet drops, whose diameter is about 0.3 μm , are generated by nitrogen bubbles after a path of 1.4 m in marine water. This has been pre-

vously enriched in SOM to simulate the increase in surface concentration, as well as it is occurs during a breaking wave event.

Fluorescence emission spectra

Were measured with a Perkin Elmer LS50B fluorescence spectrometer. For all the samples, we performed a preliminary filtration on 0.45 μm Nuclepore filters. The normalised fluorescence intensity (I_n) is given by:

$$I_n = I_{\text{Max}}/I_{\text{Raman}} \times 100$$

To calculate this value we established an automated procedure (macro) that found both Raman and Emission maximum values and then performed the calculation. The Raman maximum wavelength was first considered as fixed and equal to the theoretical one. This was not always experimentally true in our spectra, because the geometry of the Raman peak can be different in different spectra. In fact, the Raman peak is a scattering peak due to the water structure and so was superimposed onto other peaks and to the background produced by turbidity. This effect was enhanced also by the fact that we used a relatively large slit width because of the low fluorescence efficiency of the natural compounds present in sea water. For this reason we used a second automated procedure, in which the Raman maximum is not considered as fixed, but is found automatically within a range of 20 nm in the spectral region where the Raman peak usually is found^[7].

Na, K, Ca and Mg determinations

Were performed with an ion chromatographic apparatus Dionex 4500i^[19]. Na was used as a total marine aerosol reference.

RESULTS AND DISCUSSION

The role of organic matter in marine aerosol and the aerosol formation process

The results of our previous work^[7] indicated that distribution of SAFOM in Antarctic snow appears to depend on the dimensions of the particles, in agreement with previous findings^[5,20], and encouraged an accurate study of the partition of SAFOM in aerosol particles of different dimensions. Because this study requires rough sea conditions (not feasible in Antarctica), and the general physico-chemical properties of marine humic substances of Tyrrhenian sea and of those of Antarctic seas are relatively similar, this study was carried out at the meteomarine station in Leghorn.

Figure 1 reports the I_n (normalised fluorescence intensity) of the three integrated samples, collected during two campaigns (1994–1995) (each of them refers to 10–12 stormy weather events) vs. the dimensional range of particles. As previously reported [7]. The I_n can be considered, in a first approximation, as an index of the concentration of humic substances (HS), which are an important component of the surfactant organic matter (SOM) [21]. For the three samples the highest absolute quantities of SAFOM are found in the smallest particles. This appears a confirm on similar data previously reported [22].

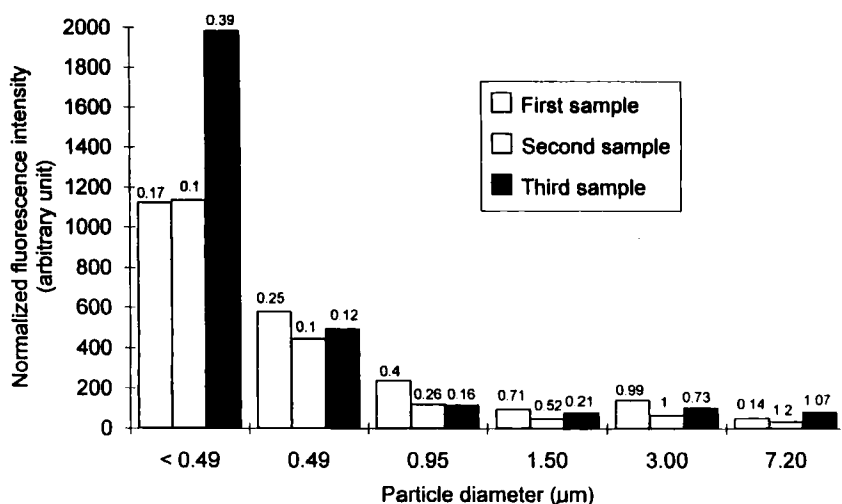


FIGURE 1 Normalized fluorescence intensity in aerosol samples. The first sample was collected from 12/01/94 to 01/27/95 (12700 m³); the second sample was collected from 02/21/95 to 04/05/95 (10864 m³) and the third sample was collected from 01/01/96 to 03/31/96 (9520 m³). For any sample (in every particle diameter) the corresponding Na concentration in μg/m³ is reported. Na concentrations are blank corrected

Figure 2 shows the aerosol (a) to sea water (sw) enrichment ratios $Er = (I_n/Na)_a / (I_n/Na)_{sw}$ vs. the particle diameter. The maximum error for Er is also reported. The I_n values were further corrected with respect to the first presentation [22]. An improvement on the program for the calculation of I_n (evaluation of the Raman maximum intensity) was made. Therefore for the smallest particles in which the ratio $(I_n/Na)_a$ is more affected, this improvement causes a further increase of I_n values. In Figure 2, Er for the three set of data which show a hyperbolic-like trend are reported. A fitting procedure on the data reported in Figure 2 is not feasible because of the low number of data. On the other hand it should be noted that the three large samples were taken over a long time interval and refer

to well selected rough sea perturbations (about twenty two events). This feature reinforces their validity in spite of their limited number.

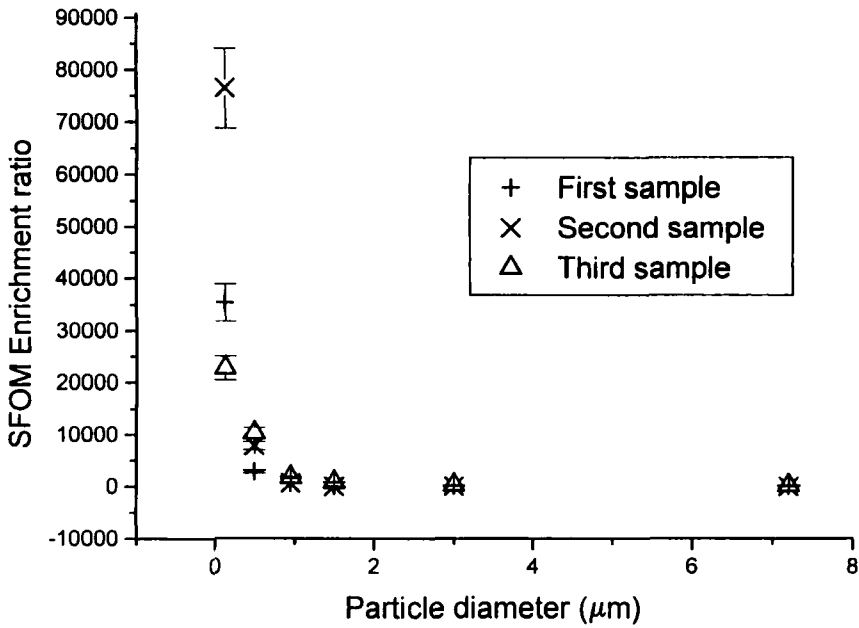


FIGURE 2 Enrichment ratio (Er) of the SFOM in the aerosol samples as obtained from fluorescence data

This picture indicates a simplified adsorption model for HS and therefore for SAFOM for all the involved particles. The model considers the adsorption film on the surface of the spherical drop as a thin layer of constant thickness. Therefore the film-volume/drop-volume ratio between the outer layer and the inner sphere can be equated to the surface/volume ratio of a sphere. The variation of this ratio versus the diameter of the sphere can be described by a hyperbolic function and analogous trend can be observed for SAFOM which increases as the dimension of microdrops decrease. To apply this model the adsorption film thickness has to be the same for all the microdrop dimensional ranges (in our case $<8 \mu\text{m}$) considered. This condition requires that the adsorption film should be, in the first instance, saturated.

To confirm this basic condition a more detailed analysis of a breaking wave model is required. Let us consider the marine aerosol coming from a breaking wave: jet drops, film drops, shearing drops. The microdrops with diameters smaller than $10 \mu\text{m}$ (this is exactly the case considered in our experiment as our

preliminary cut-off is 8 μm) originate mainly from film drops and, to a lesser extent, from jet drops. Similarly Cipriano *et al.*^[4] showed microdrops, whose diameter is smaller than 0.1 μm , originate from a breaking wave event. This is in agreement with our findings, i.e. the highest values of I_n are found for particles smaller than 0.49 μm . In our opinion, up to now, an important point that has been underestimated is the role of the foam column which is formed in front of the breaking wave, and moves in the same direction of the wind. For a large coverage of whitecaps the associated foam columns for each wave act as a powerful mobile adsorption bed, which after some times causes an increase of SOM of some order of magnitude in the surface sea water (some times for a depth of some metres).

We therefore studied the increase of typical surfactants during a sea rough condition with abundant formation of whitecaps.

Table I shows the data concerning the traces of anionic synthetic surfactants detected as MBAS, taken as an index of this increase measured in the Tyrrhenian sea. It should be noted that this type of synthetic surfactant is present in trace quantities in the entire Tyrrhenian sea^[23]. For every sea condition we report the I_n behaviour for one event.

TABLE I Surface concentration wave evidenced by means of the increase of MBAS ($Er_{MBAS}=(\text{rough sea/calm sea})$) and the increase of I_n ($Er_{I_n}=(\text{rough sea/calm sea})$) in surface seawater

Sea Condition	MBAS	Er_{MBAS}	I_n	Er_{I_n}
calm	0.01*		7	
rough	0.62**	62	55.1	7.9

* mean value of 4 events.

** mean value of 5 events.

In the foam column the surfactant concentration is so high that it causes the formation of a saturated adsorption film in the film drops, especially in those which come from the "foam head" collapse. These results agree with our previous findings^[24] on the behaviour of surface tension in marine aerosol. This quantity reaches a minimum after some time in steady rough sea conditions. Taking into account the above mentioned generation mechanism, the film saturation condition can be reached, especially near the coast, even by particles up to 10 μm in diameter. A saturated adsorption film for this condition implies that for particles smaller than 10 μm the film thickness is constant and the film is uniformly

distributed on the drop surface. At the same time, the existence of the described "surface concentration wave" well explains other phenomena such as the damage of Tyrrhenian coastal vegetation^[25,26].

The spray-drop adsorption layer model (SDALM)

Figure 3 depicts an ideal aerosol spray-drop with a sphere in which $2R$ represents the whole diameter of the microdrop and Δr the film thickness. The volume of the adsorbed layer Δv is given by:

$$\Delta v = 4/3 \pi R^3 - 4/3 \pi r^3 = 4/3 \pi R^3 - 4/3 \pi (R - \Delta r)^3$$

where the whole volume of the drop is represented by $V = 4/3 \pi R^3$.

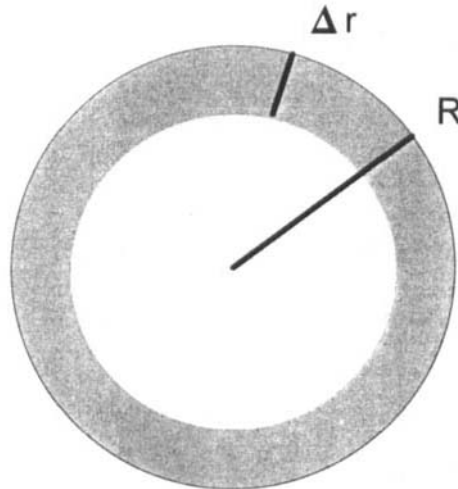


FIGURE 3 Schematic section of a microdrop. Δr is the film thickness

Since the mass of SOM adsorbed on the drop is proportional to Δv the enrichment ratio $Er = (SOM/Na)_a / (SOM/Na)_{sw}$, in which a=aerosol and sw=seawater, and it is proportional to the ratio $\Delta v/V$. The ratio $\Delta v/V$ represents a simplified approximation, taking into account the very high increase of SAFOM concentration with respect to that in the bulk sea water. For this reason we can compare the $\Delta v/V$ vs. $2R$ plots (or better versus the corresponding drop volume V) with the Er vs. particle radius plots. Figure 4 shows three plots of $\Delta v/V$ vs. $2R$ obtained using three different values of Δr , 1×10^{-3} , 5×10^{-3} and $1 \times 10^{-2} \mu m$ respectively. The thickness $1 \times 10^{-3} \mu m$ corresponds to a compressed film of fatty acids, while

$1 \times 10^{-2} \mu\text{m}$ to the thickness of dry adsorption film of HS^[21]. The data show a hyperbolic trend similar to that expected from the known behaviour of the ratio surface/volume of a sphere versus the sphere volume or diameter.

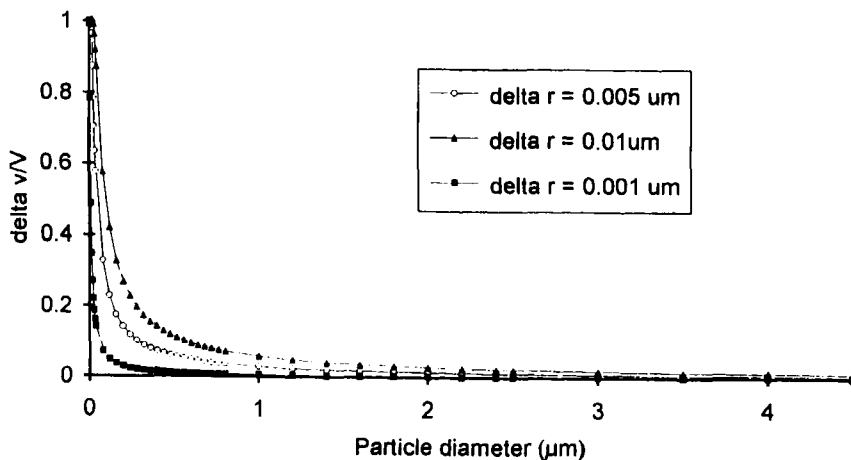


FIGURE 4 Plot of $\Delta v/V$ versus particle diameter for three different film thicknesses

The hyperbolic-like behaviour of I_n reported in Figure 2 agrees with this above reported model. Therefore using the model we can presume that all the elements known to interact with SOM will show a similar behaviour.

The behaviour of K, Mg and Ca. Laboratory experiments

K and Ca, as possible counter ions, are known to interact preferentially with FA which make up a great part of SAFOM^[27]. An increase of surfactant properties of FA caused by K and Ca is expected. The preferential interaction of Ca with fatty acids is well known. On the contrary, the enrichment of Mg by interaction with SAFOM, owing to the very high charge density of Mg and consequently the high electrostrictive effect on water structure, is unlikely to happen. The very high affinity of Mg with water molecules reduces the surfactant properties of its counter ions drastically. The same effect occurs for Na^+ in respect to K^+ . Therefore, notwithstanding the presence of a greater number of ion pairs of humic substances as fulvic acids (FA) with Na and Mg ions in the bulk phase, an enrichment takes place due to the preferential adsorption of FA-K and FA-Ca ion pairs in the aerosolization process. The enrichment is small in consequence of the high concentrations of Ca and K cations in respect to that of FA anions in the bulk phase. For this reason it can be evidenced only for large FA concentrations.

In their study Hoffman and Duce^[16] concluded that it was not possible to evidence any detectable enrichment of K and Ca due to surfactant organic material. It is our opinion that these authors did not take into account, in their experiments, the effect of the breaking waves on surface concentration, which increases of orders of magnitude the initial SOM concentration (in the sea water) that creates the aerosol from high whitecaps.

In Table IIa we report the data of some laboratory aerosolization processes, performed in cases a) and b) with techniques described elsewhere^[8]; process a) was performed on Fleming artificial sea water; process b) on natural sea water. Process c) was carried out on the same sample as b), but with different a procedure. In process c) the natural sea water was previously enriched in SOM by the non-foaming gas-bubble enrichment method^[28] to simulate its SOM increase during an extensive whitecap coverage event. Subsequently the aerosolization process was performed with a modified Sakai technique^[18] which collected only the first jet drops originating by 0.3 mm bubble collapse, after a rising path of 1.4 m. This distance simulates the mean path that a microbubble runs in the sea before the jet drops production. The reported enrichments of K and Ca were obtained with this technique.

TABLE IIA Enrichment of Ca and K in respect to Na in artificial aerosol Experiment performed on: a) artificial seawater b) natural seawater c) natural seawater previously enriched with natural surfactants by the non-foaming gas-bubble process to simulate the wave concentration effect

<i>Experiment</i>	E_{rK}	E_{rCa}	E_{rMg}
a	1.02 ± 0.02	1.01 ± 0.02	1.01 ± 0.02
b	1.11 ± 0.02	1.07 ± 0.02	1.04 ± 0.02
c	1.98 ± 0.02	1.68 ± 0.02	1.02 ± 0.02

In Table IIb we report the results of another aerosolization experiment performed on natural sea water in which a sodium myristate solution was added to reach the final concentration of 2 mg dm⁻³. This fatty acid is a typical marine fatty acid with a high surface activity that is also present in Antarctic snow^[29]. In this case we used two different natural sea water samples and in both cases found an appreciable recovery of the corresponding Ca-Myristate, transferred into aerosolised water, proving the evident Ca enrichment in the aerosol. The surface concentration wave phenomenon could explain the enrichment of K and Ca in the smaller aerosol microdrops, as predicted by SDALM. The higher surface activity of Ca-Myristate and its low molecular weight could favour additional Ca enrich-

ment in the smallest particles. Tables IIa and IIb also show the corresponding maximum errors.

TABLE IIB Experiment performed on Sea Water previously added with 2 mg dm^{-3} of Na Myristate to evidence the Ca enrichment as Ca Myristate in the aerosolised water

Sample	Date	Ca % recovery
1	10/05/1995	85.3 ± 2
2	10/07/1995	65.5 ± 2

The behaviour of K, Mg, Ca in Antarctic snow

The SDALM application can help us to clarify the results of Piccardi *et al.*^[13,14,30] who found K and Ca to be enriched in many Antarctic snow samples collected from a snow pit in two stations at different altitudes.

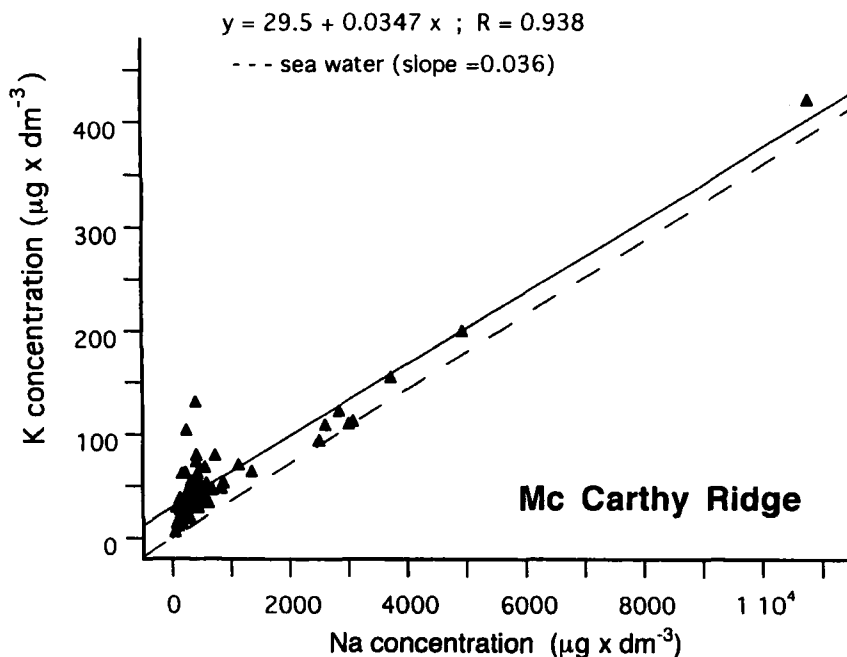


FIGURE 5 Plot of K concentration versus Na concentration in snow of McCarthy Ridge pit. experimental values, continuous line is the best fit linear regression, dotted line is the corresponding function for sea water

By using the same representation used by Duce and Hoffman^[11], Figure 5 and 6 report the K and Ca concentrations vs. Na concentrations in each sample for the McCarthy Ridge sampling station (700 m above sea level) and Figures 7 and 8 report the corresponding values for the Styx Glacier (1700 m above sea level) sampling station.

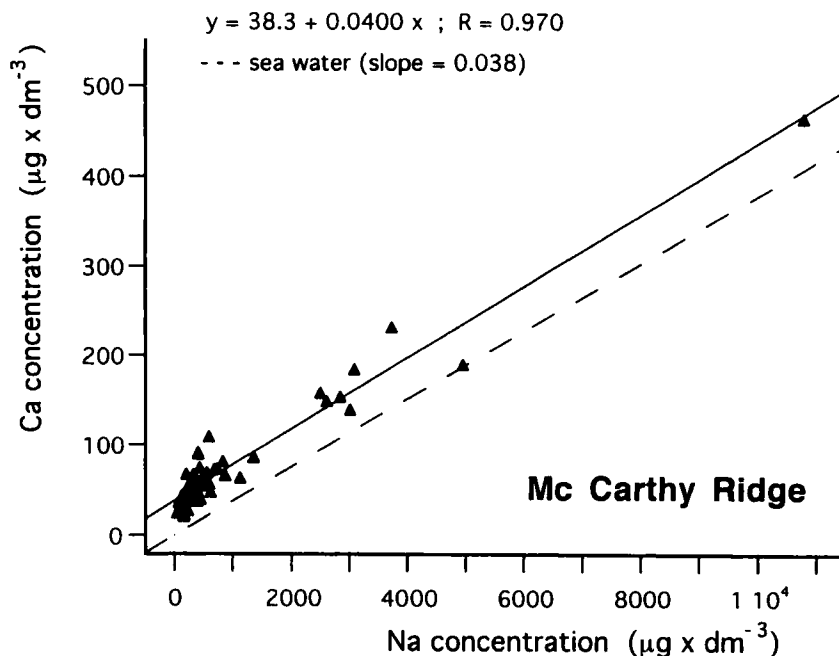


FIGURE 6 Plot of Ca concentration versus Na concentration in snow of McCarthy Ridge pit. experimental values, continuous line is the best fit linear regression, dotted line is the corresponding function for sea water

The values of the linear regression functions that best fit the experimental points (Figures 5–8) represent the average of the experimental K/Na and Ca/Na concentration ratios. It can be noted that while these ratios are constant in sea water, and are represented by lines crossing the vertical axis at zero value, the lines representing K and Ca concentrations in Antarctic snow cross the vertical axis at values greater than zero. In addition, these lines are always above the corresponding lines for sea water. On the other hand, if we consider Mg (not reported here), the corresponding lines cross the vertical axis at zero value and their angular coefficients are slightly smaller than those referring to sea water values.

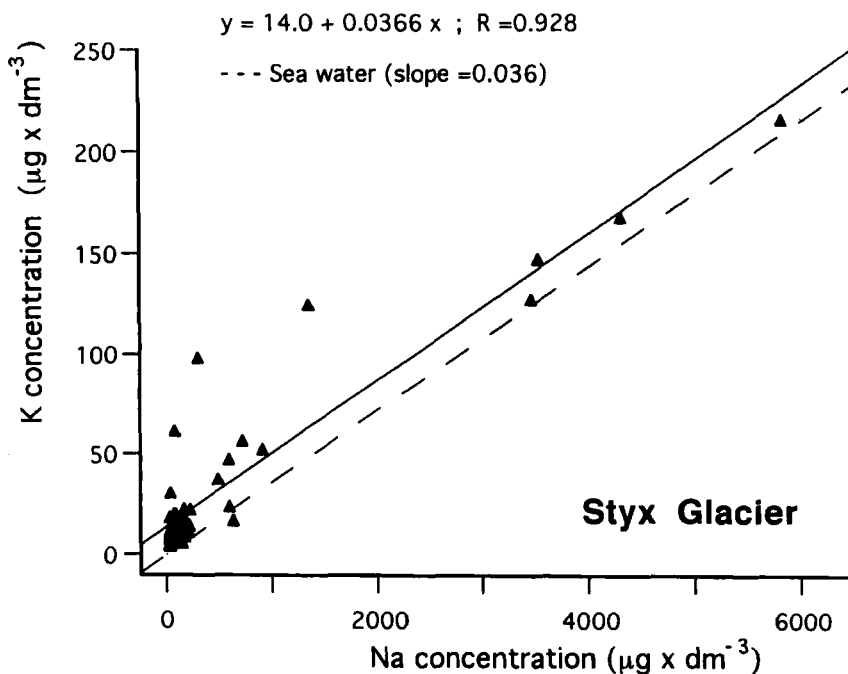


FIGURE 7 Plot of K concentration versus Na concentration in snow of Styx Glacier pit. experimental values, continuous line is the best fit linear regression, dotted line is the corresponding function for sea water

Applications of SDALM to K, Ca, Na data of Antarctic snow samples

We can also represent the experimental data reported in Figures 5–8 by dividing the best fit linear equations ($y=ax+b$) by x , thus obtaining $Y=b/x+a$; where $Y=y/x$. This is the equation of a translate equilateral hyperbole. In our opinion this representation can give additional information on the data. The translation value of these hyperbolas is equal to the angular coefficient of the regression lines reported in Figures 5–8. Figure 9 report as example the Ca/Na ratios vs. Na concentrations for the Mc Carthy Ridge station. The same data treatment for K/Na vs Na for the same station and that one for K/Na and Ca/Na vs Na concentrations for Styx Glacier station show similar behaviour.

These results, together with those of our laboratory experiments, would reinforce the hypothesis that the K and Ca enrichments in marine aerosol are due to the interaction of these elements with SOM. At the same time Figure 9 show how experimental data agree with the SDALM. In fact, this model implies that the

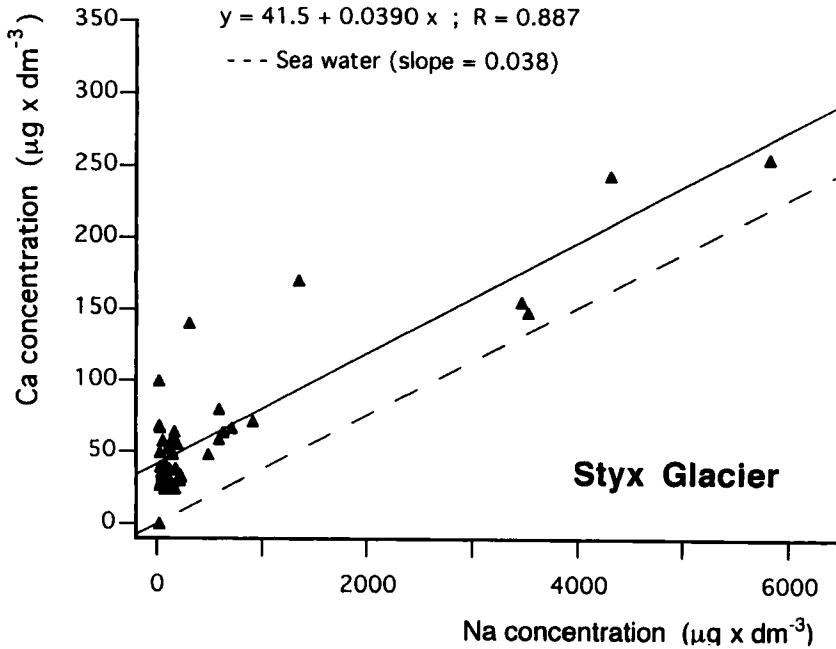


FIGURE 8 Plot of Ca concentration versus Na concentration in snow of Styx Glacier pit. experimental values, continuous line is the best fit linear regression, dotted line is the corresponding function for sea water

intercept values in Figures 5–8 represent the K and Ca excess that is present in the microdrops whose radius is $R=\Delta r$ and whose volume is equivalent to Δv . These microdrops should therefore derive from the saturated adsorption film in its hydrated state.

It must be noted that for the Antarctic snow only the concentrations of the various elements in each snow sample are known, while the particle dimensions or their number per unit volume are not known. For this reason several conditions must be assumed for a correct interpretation of the data. Hence, it is presumed that the sodium concentration in each sample is related to a narrow dimensional range of particles; for each sample corresponding to each snow precipitation event the Na concentration denotes a definite average particle diameter. In addition these particles should show similar concentrations for all events, and comparable time duration. The circumstances that corroborate this hypothesis are the high altitude and the long distance between the sampling site and the aerosol production site, especially during the winter.

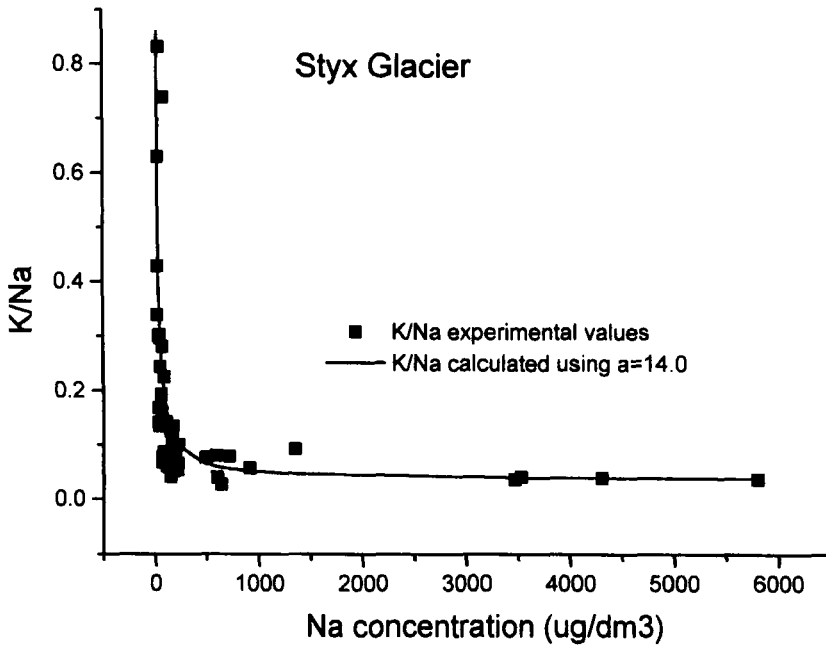


FIGURE 9 Plot of K/Na weight ratio versus Na concentration in snow of McCarthy Ridge pit. The hyperbolic function $y=a+b/x$ is obtained from fig.5 taking $a=29.5$

There have been studies which make it possible to show the selective effect on the particle dimension and number due to kinetic transport conditions. In fact as observed by Cipriano *et al.*^[4] in remote sea areas the number of fine particles which behave like Condensation Nuclei (CN) and Cloud Condensation Nuclei (CCN) appear in almost constant concentrations. However, Blanchard and Woodcocks's data^[3] for the marine aerosol as a function of altitude show that as altitude increases, these concentration values become more and more comparable each other, even at very different wind speeds and different whitecaps coverage.

The data by Dinger *et al.*^[31] show that as altitude increases the aerosol particles progressively decrease in non-volatile marine salt residue. These particles, at high altitudes are almost completely volatile. While the cited authors attribute this fact to the presence of $(\text{NH}_4)_2\text{SO}_4$ and methanesulphonic acid particles, we would like to point out that the expected transition according to SDALM for very small sized particles (from almost entirely saline particles to organic particles) is in agreement with this phenomenon.

If the above mentioned conditions are verified, the enrichments of K and Ca should show a trend following, at least qualitatively, the proposed model. On the other hand, it must be considered that the K and Ca enrichments obtained in our laboratory and field experiments, and the data reported in literature^[5,9-11] are smaller by orders of magnitude than those obtained for the Er_{In} data. On the other hand, the K and Ca concentrations in sea water are greater by orders of magnitude than that of SAFOM. Therefore, in order to correctly apply the model to experimental data we shall assume also that the total quantity of K and Ca in microdrops is contained not only in the external layer whose volume is Δv , but also in the internal volume (denoted as v). Therefore, K and Ca are contained, by rigorous point of view, in the whole volume V . On the other hand we presume that sodium is contained only in the internal volume v . For these reasons the ratio x/Na in ordinate of fig. 9 becomes V/v and Na concentration in abscissa can be expressed by v . Fig. 10 shows the plot of the function that expresses the ratio V/v vs. v . The reported values in abscissa in Figure 10 are evaluated in the dimensional range from $R = 0.01$ to $0.2 \mu m$ (for $\Delta r = 0.01 \mu m$) which is consistent with the expected particle radius for the altitude and distance from the sea.. It must be to remember that

$$\begin{aligned} V/v &= V/(V - \Delta v) = (4/3 \pi R^3) / (4/3\pi (R - \Delta r)^3) = \\ &= \Delta r^3 / (R - \Delta r)^3 + (3 \Delta r^2) / (R - \Delta r)^2 + 3 \Delta r / (R - \Delta r) + 1 \end{aligned}$$

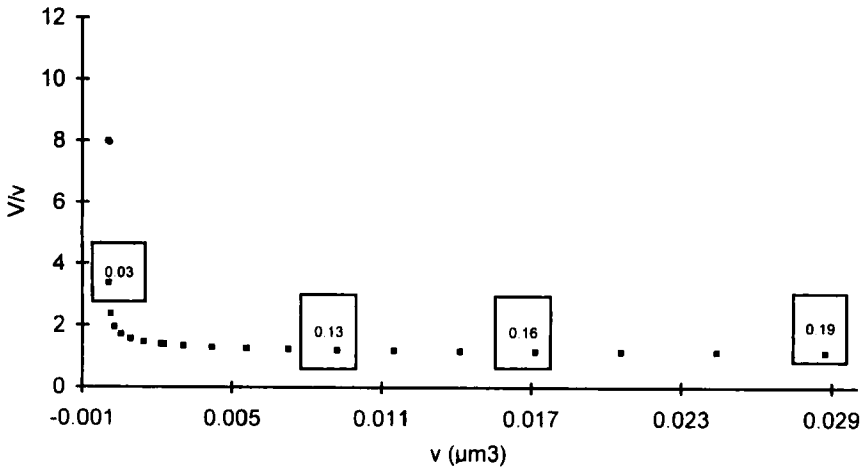


FIGURE 10 Plot of the ratio total volume/inner volume versus inner volume of a microdrop whose adsorption layer is $0.01 \mu m$ thick. The volume is expressed as μm^3 and total radius of the microdrop are indicated in some points

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As v increases, Δv becomes negligible with respect to v and the value of the function tends to be equal to one, as expected for E_r ; whereas as v decreases, it becomes negligible in respect to Δv and the value of the function tends to be infinite.

Figure 9 shows that for great Na concentrations, the ratios tend to be equal to the concentrations of the elements in sea water ($Ca/Na=0.0381$ and $K/Na=0.0362$) for both stations. When the concentration of Na decreases, the ratios increase and this behaviour was also shown by SAFOM.

It must be referred for SAFOM, as reported by Hunter and Liss^[21], that the measured value $\Delta r = 0.01 \mu\text{m}$ refers to dry humic substances (HS). These authors report also that the wet absorption films could be much thicker (up to $1 \mu\text{m}$) and this should be kept in mind when comparing the experimental data with the model.

From the all other data, treated as reported in Figure 9, we can observe the enrichments of K and Ca are smaller by some order of magnitude than that observed for SAFOM. The experiments in Leghorn also showed this as seen in Figure 11. For purposes of a strict comparison with the model, the respective enrichment ratios E_r have been used instead of the X/Na ratios reported in Figure 9.

The data in Figure 11 shows that enrichment is measurable for dimensions less than $1 \mu\text{m}$ in diameter. Therefore, within the limits described above, it could be expected that the initial dimensions of the aerosol present in Antarctic snow should be smaller than $1 \mu\text{m}$. This is plausible, as it has already been noted, considering the distance and altitude of the sampling station from the free marine surface in winter and spring. Keeping in mind that in the marine aerosol microdrops the adsorption film of SAFOM is in a wet state, it is to be expected that this film is much thicker than $0.01 \mu\text{m}$ ^[21]. The sea water fraction in v of microdrops $< 1 \mu\text{m}$ is so small that the K and Ca concentrations in the internal volume of the drops are negligible considering also the other approximations imposed by physical condition of the particle transport.

As a result, the amount of K and Ca in samples containing small quantities of Na can be attributed essentially to the material interacting with SAFOM and present in Δv . As was the case of E_r for SAFOM, the simplified form of the model, that is $\Delta v/V$ vs. V , can be applied to the aerosol particles $< 1 \mu\text{m}$ rather than V/v vs. V . Since the E_r range for K and Ca is considerably reduced, the fitting of the data must be considered using the equilateral hyperbole translated to a value equal to 1, which is the limit value of E_r . This limit value must be considered for small values of E_r . Figure 12 compare for Ca data of Mc Carthy Ridge the fittings of the respective data for the trend of the total volume/internal microdrop volume ratio (dotted line) with the fitting of a translated hyperbole without

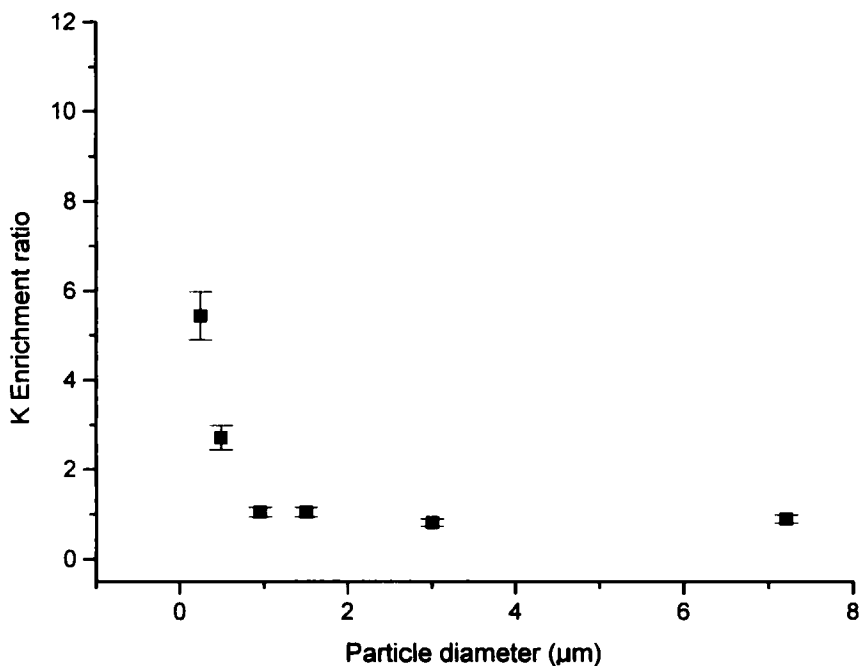


FIGURE 11 Plot of K enrichment ratio (E_r) versus the particle diameter get from the second marine aerosol integrated sample collected in Leghorn station. The vertical bar is referred to the extimed maximum error

established parameters in the translation value (thin continuous line) and with the fitting of a translated hyperbole with the definite value of 1 (thick continuous line). The agreement shown by the graphical presentation of the fitting to the hyperbole translated to a value 1 appears to be the best and the data support the above considerations. In table III is syntetized the parameters comparison of three models for the all collected samples.

The reported values for χ^2 therefore indicate the SDALM validity.

The greatest values of the K and Ca enrichment ratios (E_r) are found at the higher altitude site, i.e. for the samples containing the particles with smaller diameters.

It is interesting to observe how the Ca enrichment is notably greater than of K, especially at higher altitudes. This would agree with the fact that Ca interacts both with fulvic acids (FA) and with fatty acids, and the latter surfactants are preferentially distributed in the smallest particles because of their smaller dimensions and higher surface activity.

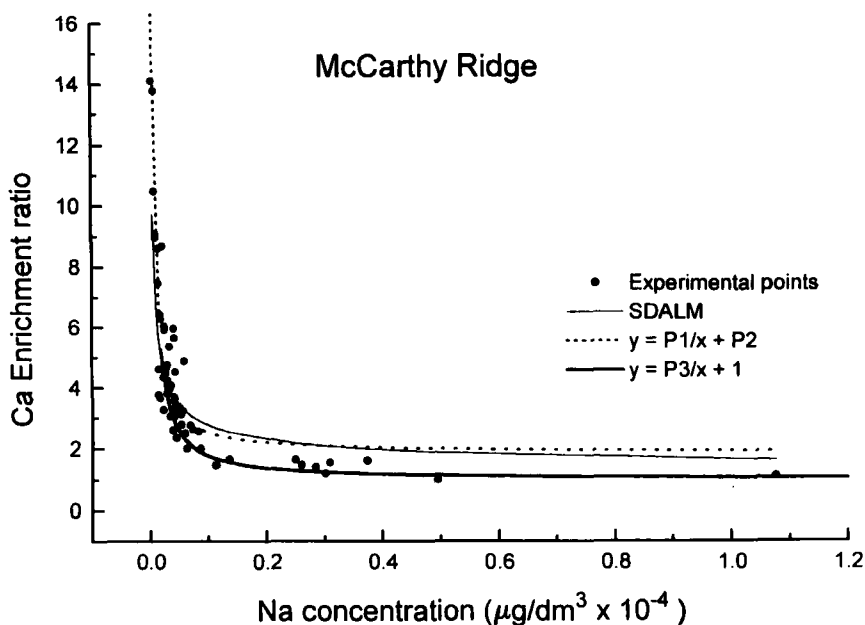


FIGURE 12 Plot of Ca enrichment ratio versus Na concentration in snow of McCarthy Ridge (Antarctica). Experimental points are fitted with three different models: SDALM ($\Delta r = 1.2E-01 \mu m$) $\chi^2 = 1.3E+01$, Standard Deviation = $3.1E-01$, $y = P1/x + P2$ (floating translated hyperbola with $P1 = 664.9E+00 \pm 39.8E+00$, $P2 = 1.9E+00 \pm 0.2E+00$) $\chi^2 = 1.4E+00$, and $y = P3/x + 1$ (constrained translated hyperbola with $P3 = 778E+00 \pm 32.5E+00$, translation parameter = 1) $\chi^2 = 1.8E+00$

Looking the Figures 5, 6, 7, 8 and considering the adopted model, we can observe that even for high Na concentrations the K and Ca concentrations are always greater than those in sea water (denoted by the dotted lines).

Taking into account the whole transport conditions that must be present for the aerosol particles to have a good applicability of SDALM, it is possible that two extreme cases can arise. In the first case, in transport by very strong winds, large particles reach even high altitudes and these particles will have an elevated quantity of Na with practically the same composition as sea water, in agreement with the model for great Na values for large-sized particles. In the second case, in transport during a weak but long weather event, the snow samples have a considerable quantity of Na but, on the opposite to the previous case, an appreciable enrichment of K and Ca. Samples corresponding to these last case have greater Er K and Er Ca values to the ones for sea water even for high quantities of Na. Practically, there may be an unexpected excess of K and Ca not predicted by the model. We should observe, on the other hand, that a unusual excess of Ca in Ant-

arctic snow can also be due to a possible local crustal contribution produced by partial solubilization by the effect of atmospheric acidity on dry deposition of larger local crustal particles.

As a final remark, the study of the transition from saline to organic for the smallest particles of aerosol, opens new perspectives in the study of long range transport of micro components via marine aerosol. It could be applied to all micro components capable of interaction with SOM everywhere^[22,32,33]. Perhaps a new interpretation of the AEE (anomalous enriched elements) origin could also be proposed.

TABLE III Fitting parameters for the investigated models. χ^2 is referred to about 40 experimental data for each sample

<i>SDALM</i>				
<i>Sample</i>	<i>element</i>	$\Delta r/\mu m$	χ^2	<i>St. dev.</i>
Mc Carthy Ridge	K	0.10	1.4	2.0
Mc Carthy Ridge	Ca	0.12	13.0	0.3
Styx Glacier	K	0.09	9.8	3.8
Styx Glacier	Ca	0.20	20.0	9.1
<i>Floating Translated Hyperbola $y = P1/x + P2$</i>				
<i>Sample</i>	<i>element</i>	<i>P1</i>	<i>P2</i>	χ^2
Mc Carthy Ridge	K	292.8 ± 71.1	2.3 ± 0.4	4.4
Mc Carthy Ridge	Ca	664.9 ± 39.8	1.9 ± 0.2	1.4
Styx Glacier	K	258.9 ± 48.9	1.3 ± 0.8	13.8
Styx Glacier	Ca	1189.3 ± 102.1	-0.5 ± 1.7	60.4
<i>Constrained Translated Hyperbola $y = P3/x + 1$</i>				
<i>Sample</i>	<i>element</i>	<i>P3</i>	<i>translation parameter</i>	χ^2
Mc Carthy Ridge	K	459.3 ± 56	1	5.2
Mc Carthy Ridge	Ca	778 ± 32.5	1	1.8
Styx Glacier	K	270.3 ± 32.9	1	13.5
Styx Glacier	Ca	1122.5 ± 69.8	1	60.1

CONCLUSIONS

- The K and Ca excess in marine aerosol trapped in Antarctic snow appears well explained by the hypothesis of the interaction of these elements with SOM.
- Field and laboratory experiments support SDALM. This model is apparently able to give a semi-quantitative interpretation of the behaviour of Ca and K concentration in the Antarctic snow samples taken at higher altitudes i.e. for particles whose diameter is probably smaller than 0.5 μm .
- SDALM appears particularly interesting for the smallest particles that originate in marine aerosol, in agreement with the findings of Cipriano *et al.*^[4] i.e. for particles of 10^{-17} g of mass.
- The validity of the SDALM model also leads to a new interpretation of BIMS results^[34] which now refer only to the element enrichments of a mean dimensional range of particles. In particular K (which does not show any enrichment in the BIMS experiments^[2]) is to be reconsidered in the light of our new laboratory experiments and field results.

LIST OF ACRONYMS

SAFOM : Surface active fluorescent organic matter

SDALM : Spray drop adsorption layer model

BIMS : Bubble interfacial microlayer sampler

SOM : Surfactant organic matter

MBAS : Methylene blue active substances

CN : Condensation nuclei

CCN : Clouds condensation nuclei

FA : Fulvic acids

Er : Enrichment ratio (see text)

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