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Variations in Ionic Ratios between Reference Sea Water and Marine Aerosols

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Atmospheric particles were collected over the open sea (western Mediterranean, North Atlantic, and Norwegian Sea) by air filtration and cascade impactor sampling. The observed K/Na concentration ratios exhibited marked variation and were greater than the reference ratio in bulk sea water. These concentration ratios can be related to the existence of a chemical fractionation affecting the marine aerosols produced by bubbles bursting at the sea surface. Minute amounts of terrigenous dust are found in northern hemisphere marine air in the same range of concentrations as sea-salt particles and contain sodium and potassium of primary continental origin. The presence of this terrigenous dust in the samples raises questions as to the validity of the fractionation hypothesis. In strong support of this fractionation concept are data from our laboratory based on (a) laboratory and in situ experiments with artificially produced aerosols; (b) high-volume air sampling over the Antarctic Ocean with controlled low loads of hydro-insoluble dust; and (c) coastal region sampling where silicon, aluminum, iron, and potassium provide a corrective index for potassium-rich terrigenous dust concentrations. The Cl/Na ratios measured resemble the sea-water values, which could indicate that an enrichment of potassium takes place rather than a depletion of sodium. The Ca/Na ratios often follow the K/Na ratios and suggest identical enrichment of calcium. The enrichments seem to preferentially affect particles of small size ($\leq 1-2 \mu\text{m}$), and long-range transport of fractionated marine aerosols can be hypothesized. This is supported by K/Na, Ca/Na, and Mg/Na ratios as measured in another laboratory. These ratios, observed in ice from the central part of the East Antarctic Plateau and corrected for a terrigenous influence with the iron index, suggest a geochemical fractionation at the marine source. These data further suggest that fractionated marine aerosols can be transported far from their place of origin.

Attention has been focused on the production of sea-borne salt particles, their inorganic ion chemistry, and their distribution within the framework of an extensive study of the transport and exchange of particulate matter between oceans and continents via the atmosphere.

The data collected and the various geochemical aspects of the processes involved have been published recently [Chesselet *et al.*, 1971]. It was concluded that chemical fractionation processes governing the sodium, potassium, and calcium ratios take place during the formation of marine aerosols. This theory, based on laboratory experiments and oceanic air investigations, constitutes the subject of our present discussion. In this study, the ionic ratios in aerosols will be compared with the following reference sea-water ratios:

Cl/Na	1.8
K/Na	0.037
Ca/Na	0.036
Mg/Na	0.0119

SAMPLE COLLECTION AND ANALYTICAL PROCEDURES

Sampling operations were carried out at sea, under various weather conditions, aboard oceanographic research vessels in the North Atlantic, equatorial Atlantic, Norwegian Sea, and Antarctic Ocean, and on a floating laboratory platform in the western Mediterranean. Some shipboard sampling was undertaken in collaboration with aircraft sampling. Aerosols were filtered on Delbag Microsorban absorption filters and on Millipore membranes (0.45- μm porosity) with controlled $\geq 95\%$ collection efficiency for particles $\geq 0.1 \mu\text{m}$. Filters consisting of 20 sheets of surgical gauze and a high-volume air turbine

(5000 m³/hr) were used over the Antarctic Ocean. In this case, the collection efficiency of 20–50% for the total mass of atmospheric aerosols was computed by utilizing the natural and artificial radioactivity of atmospheric particles. Specific air activities were compared by parallel filtrations for samples obtained on gauzes, on absorption filters, and on blue Poelman-Schneider filters (Atomic Energy standard filters). Norwegian Sea and equatorial Atlantic samples were recently obtained with a six-stage cascade impactor (Scientific Advances Co.). Investigations for samples collected on a high-resolution cascade impactor require great care, because the low flow rate of air (12 l/min) results in very small quantities of material deposited on impactor slides. Filters and slides were dried by infrared heat or kept frozen. The volumes of air sampled were continuously recorded by a gas-volume counter. The filters, folded in half with the collection surfaces facing each other, were sealed in double polyethylene bags to guard against contamination before and after sampling. Two high-sensitivity analytical methods were used:

1. Instrumental neutron activation (NA) analysis was performed on portions of the absorption filter (usually 1/4) without any pre- or post-irradiation chemistry for chlorine, sodium, and potassium; the irradiation was followed either by γ -ray spectrometry associated with β spectrometry for potassium determinations in the presence of sodium [Winchester, 1961; Das *et al.*, 1969] or by high-resolution (GeLi) γ -ray spectrometry. Samples and filter blanks from the same batch and ionic metal standards and flux monitors were irradiated together in a 5×10^{22} n cm⁻² sec⁻¹ thermal neutron flux.

2. Atomic absorption (AA) spectrometry with a Perkin-Elmer 303 instrument was used for sodium, potassium, calcium, and magnesium.

For AA spectrometry, portions of membrane filters, gauzes, and impactor slides were thoroughly washed by repeated immersions and stirring in controlled volumes of quartz twice-distilled water and finally in twice-distilled water to which small amounts of organic detergents were added. Relative recovery yields for the washing processes were checked by measuring the recovered concentration after each stage of the washing procedure. To mini-

mize contamination and loss, all operations were performed in air-filtered laminar flow benches in Teflon vessels. Current precautions against interferences in atomic absorption procedures were taken. Blanks were obtained by washing unused membranes, gauzes, and impactor slides under the conditions outlined above. Some of the more recent atomic absorption analyses were performed with a graphite furnace, Perkin-Elmer HGA 70, at the Laboratoire de Geochimie Nucleaire, Universite de Bruxelles, Belgium.

The validity of the measurements was tested by duplicate analyses of the same portion of filter by both NA and AA procedures.

Results were found to be in close agreement ($\pm 15\%$) [Morelli, 1968]. Using a criterion of 2 standard deviations, the over-all precisions are chlorine, 5%; sodium, 5–10%; low concentrations of potassium, 20–30%. Corrections for blanks were obtained by using identical filters, processed and handled exactly as the sampling filters but without any air passage (see Table 1 for blank Delbag filter corrections). The actual air filters were corrected for the blank for each set of analyses.

LABORATORY AND IN SITU EXPERIMENTS

Although it is difficult to ascertain whether laboratory experiments successfully simulate the processes occurring in nature, laboratory experiments with artificially produced aerosols were conducted. According to many workers [Horne, 1969; MacIntyre, 1970], bursting bubbles represent the main mechanism for injecting marine aerosols into the air. Various bubbling experi-

TABLE 1. Delbag Filter Blank Determinations

Impurity	Concentration, $\mu\text{g/g}$	
	Pellicle	Filter
Cl	270 \pm 80	1400 \pm 500
Na	200 \pm 100	6 \pm 3
K	70 \pm 30	2 \pm 1

About 1/4 of the filter was used for each analysis; i.e., ~ 0.15 gram pellicle, ~ 0.5 gram filter. Ten blanks of each were analyzed. The plus and minus values show observed maximum fluctuations in filter blanks originated from same batches. The pellicle, which protects the filter against mechanical erosion by the wind, collects large size fraction (LSF). The filter collects small size fraction (SSF).

ments in the laboratory may produce salt aerosols, and it is possible to observe the variations expected in ionic ratios between the initial solution (sea water) and the phase recovered (Table 2).

Experiments A1, A2, B1, B2, and C duplicate, in many respects, the experiments performed by *Bloch et al.* [1966] and *Bloch and Luecke* [1968]. Our results support their conclusions about the influence of bubbling processes upon the K/Na ratios in marine aerosols. Experiments A1 and A2 show that crystallization is not involved when a shift in the K/Na ratios is observed, because there is no break in the liquid phase during these experiments. We have also used these experiments to confirm gaseous chlorine formation in oceanic air [*Buat-Ménard*, 1970; *Buat-Ménard and Chesselet*, 1971]. It was shown that the Cl/Na ratios in A1 and A2 may be quantitatively explained by a gaseous chlorine phase trapped in the distillate. This does not appear when salt particles are collected on filters. For experiments B1, B2, and C, the gaseous chlorine, which represented only a small release from particulate chlorine (~3%), was not collected on filters.

Experiments D1, D2, D3, and D4 were specifically designed to simulate more realistically the conditions under which marine aerosols are formed in nature. As in experiments B1, B2, and C, no marked change in the Cl/Na ratios were observed. The Cl/Na ratios were always close to the sea-water value, but displacements in the K/Na ratios were constant, showing that ionic chemical fractionation was taking place. The similarity between Cl/Na ratios in particles and the sea-water value would indicate the possibility that increases in K/Na weight ratios were due to enrichments in potassium rather than depletions in sodium. Indeed, it seems unlikely that the chlorine ions would be depleted at exactly the same rate as sodium ions during the fractionation processes.

We shall not attempt to discuss the processes of chemical fractionation-enrichment as illustrated by these experiments, since this is being done elsewhere (Morelli and Chesselet, unpublished data, 1970). Indeed, the intricacy of the great number of variables in those experiments definitely requires a very detailed discussion of the data. However, we should like to point out the particular importance of series D1 to D4

(Table 2). In this series, there is a trend to higher K/Na values with increasing depth, where the bubbles are produced by the immersed fritted glass device.

We still are doing laboratory experiments, but we don't know yet whether this relationship is controlled either (a) by the longer lifetime of the bubbles in the water before bursting or (b) by the change of the bursting bubble sizes, depending on the fact that when you produce bubbles deeper in the water the hydrostatic pressure makes them smaller. The same air flow is then carried to the surface by larger numbers of smaller bubbles. In the latter case, the data could be a clue for an enrichment dependence with the size of the bursting bubbles. We think that hypothesis b is more relevant than a, but one must be aware that, in the two cases, a longer lifetime and more bubble surface are introduced in the system. This could indeed enhance the rate of an enrichment occurring at the surface of the bubbles in the water, before they burst. We cannot yet solve the two hypotheses.

In experiment D4, the added oleic acid film delays the bursting of many small bubbles at the surface, and we observed an enrichment in potassium in comparison with experiment D1 (same depth of the fritted glass device). In fact, probably two primordial effects are superposed in this experiment: one controlling the bubble sizes, the other one scavenging the potassium out of the sea water. This experiment is the most important of the series. Indeed, there is more and more evidence that the enrichment of potassium, if it does exist in nature, would be controlled to a large extent by the presence of organic surfactants at the surface of the sea.

Generally speaking, it can be concluded here that the data from in situ experiments support the fractionation hypothesis. K/Na ratios in marine aerosols injected by bubbles bursting at the sea-air interface may be influenced by the same mechanisms occurring in the laboratory experiments.

NORTHERN HEMISPHERE MARINE AIR SAMPLES

Most of the geochemical importance of fractionated marine aerosols depends upon their capacity to be transported far from their place of origin and to be mixed within the whole troposphere. *Junge* [1963] has demonstrated

TABLE 2. Laboratory and In Situ Experiments

Types of Experiments	Pressure in Flask	Temp. in Flask, °C	Weight Ratios in Original Sea Water		Volumes of Distillate Recovered, ml	Quantities of Elements in Distillate, µg			Wt. Ratio in Distillate	
			Cl/Na	K/Na		Cl	Na	K	Cl/Na	K/Na
Distillation										
A1	Atm.	~100	1.8	0.037	210	240	115	21	2.1	0.183
A2*	80 mb	35	1.8	0.037	260	245	55	29	4.5	0.528
	Filtration Time, hours				Filtered Vol., m ³	Collect. on Millipore 0.1 µ, µg			Wt. Ratio in Particles	
Bursting bubbles										
B1, by filtered air	17	25	1.8	0.037	12	245	140	21	1.7	0.150
B2, by filtered air	27	25	1.8	0.037	19	435	240	25	1.8	0.104
C, by argon	21	25	1.8	0.037	15	322	180	20	1.8	0.111
						Collect. on Millipore 0.45 µ, µg				
In situ production of bursting bubbles at sea surface by filtered air		Temp. of Surface Sea Water, °C								
D1†	1.5	12	1.8	0.037	2	1763	1134	44	1.6	0.039
D2	6	12	1.8	0.037	8	7310	3740	185	2.0	0.049
D3	3.3	12	1.8	0.037	4	930	463	27	2.0	0.058
D4	3	13	1.8	0.037	5	200	97	8	2.1	0.082
			±0.1	±0.001		±5%	±5%	±10%		

Laboratory Experiments. A1, A2: experiments with 2 liters of nonfiltered surface sea water sampled 130 km from the coast, (48°N, 8°E, Occ. Med.) and collected and stored in polyethylene barrels for 2 weeks. B1, B2, C: with 6 liters of sea water of same origin. *In Situ Experiments.* On a laboratory raft moored in Villefranche Bay (French Med. coast). Bursting bubbles produced by an injection of pre-filtered air through a fritted-glass system suspended underwater in a 1 m³ Plexiglas square box suspended above the water and having the open side immersed 20 cm into the water. Before each experiment, air in the box was flushed and entirely replaced by thoroughly filtered air. Exchange with the atmosphere was controlled by a gills-filter system. Except for D4, water from 5-meter depth was continuously stirred slowly by PVC pump to renew surface sea water in box (rate: 20 l/min).

* Specially designed to display expected dependence between fractionation and the lifetime of bubble film at the sea-air interface, before bursting. † Designed to show dependence between fractionation and lifetime of bubbles in the water column before they reach the surface. D4 was with an addition of an oleic acid film at the sea-air interface in the box. Immersion depth of the bubble-producing system: D1, 0.1 m; D2, 0.25 m; D3, 0.4 m; D4, ~0.1 m. Same controlled bubbling rate for D1, D2, D3. Lower rate for D4.

that tropospheric distributions are observed for the aerosols when they have a size range of 1–2 μm radius or smaller. On the other hand, *Komabayasi* [1964] has shown in laboratory experiments that a preferential fractionation may exist for small size particles of 0.4- μm radius for magnesium, calcium, and strontium.

The possibility of troposphere-wide distributions was investigated by studying the occurrence of a relationship between the sizes of the particles and fractionation in samples collected at various open sea locations. We used a characteristic of the Delbag filter in many samplings to discriminate in a very crude way between the ionic ratios existing in the large size fraction from those in the small size fraction. The majority of the large size fraction was supposedly retained on the thin pellicle (100–200 μm porosity) placed in front of the filter to protect the filter against mechanical erosion by wind. The small size fraction was collected, with high efficiency, on the absorption filter itself.

Table 3 shows the data obtained for the absorption filter and the pellicle. These specific examples were selected because they were recently re-examined by interlaboratory comparisons to test the accuracy of previous measurements.

When one considers variations of the ionic ratios that are presumably dependent upon the presence of various populations of particles in the air, a problem arises with droplets of sea water collected on the filters. These sea-water droplets are blown into the air by waves breaking on the hull of the ship. Their quantity increases markedly with high-velocity winds and a fast-moving ship. This artificially produced sea spray can almost completely mask the ionic ratios in naturally occurring aerosol populations. This problem was taken into account in our sampling procedure.

The K/Na weight ratios in the first part of Table 3 for the thin pellicle and absorption filter were observed in the Norwegian Sea, mainly during the periods when the ship was drifting slowly. Under slow drift, a large bubbling zone with no breaking waves exists upwind of the ship. This fact is believed to have influenced the K/Na ratios we observed. These ratios were different from the sea-water value, for both pellicles and filters.

In order to explain these data, one can call

upon the anomalous effect of 'slicks' of organics, leaking from the ship, which could scavenge potassium from sea water in quantities greater than natural sea-water organics would do. It is true that such a film must be present at the sea surface, upwind from the ship, when she slowly drifts. Then we should be close to the conditions occurring in experiment D4 (Table 1) when an added film of oleic acid enhanced the potassium enrichment. This could be a valuable bit of information, but, we have to agree that in this case the natural conditions have been biased.

Chances for shipboard contamination when the ship was stopped are very low, because the stationary samples were taken only when the wind speed was above 10 knots. The samplings were always made upwind from the rest of the ship.

In regard to all these contamination problems, we put much importance on samples taken with aircraft flying at 200 meters above the ship, with no sources of local contamination. They support our shipboard data, as is shown in Table 3 (shipboard contamination is discussed later and in the Appendix).

A floating buoy laboratory platform (FBL), the Cousteau Bouée-Laboratoire, permitted sampling in air at various heights and, occasionally, very close to the sea surface, in an undisturbed marine environment (western Mediterranean, 130 km from the coast of France). Despite the small amount of material recovered on the filters, fractionated K/Na ratios occurred (see Table 3). In every case, the small size fraction collected on the filter itself has K/Na ratios very far from the sea-water value. This was observed even for samples taken very close to the sea surface (11B and 12B), but, for the large size fraction collected on the pellicle, three of the samples do not show much enrichment when the uncertainty of the K/Na ratio is considered.

When we have averaged all our data for a 3-week continuous sampling at FBL, they show the existence of a definite shift in bulk K/Na ratios to higher values as sampling levels rise [Morelli *et al.*, 1971].

An identical trend was observed over the Norwegian Sea when aircraft samples taken at 300-meter altitude were compared with coordinated ship samplings (Table 3).

IONIC FRACTIONATION IN MARINE AEROLS

TABLE 3. Samplings from the Norwegian Sea and the Laboratory Buoy

Sample	Place and Type	Collection Period and Duration	Vol. Sampled, 10 ³ × m ³	Sampling Alt. above Sea Level, m	Direction and Wind Speed, knots	Filter	Measured Quantities on 1/4 For P, µg			Atmospheric Conc., µg/m ³			Weight Ratios K/Na*		
							Na	K	Na	Na	K	Na	K	(a)	(b)
D1	JCNS	July 14, 1970, 8 hr	2.3	13	12, NE		119 ± 6	14 ± 2	2.0	0.24	(0.096)	0.117	(0.141)		
D2	JCNS	July 17, 8 hr	2.6	13	20-10, NW		44 ± 4	7 ± 3	0.8	0.12	(0.083)	0.159	(0.250)		
D3	JCNS	July 19, 19 hr	5.8	13	10-20, W		135 ± 6	9 ± 1	2.1	0.14	(0.056)	0.066	(0.077)		
D1	FNS	July 14, 3 hr	0.65	200	12, NE		110 ± 5	13 ± 5	1.7	0.20	(0.069)	0.118	(0.171)		
D2	FNS	July 17, 3 hr	0.63	300	20-10, NW		379 ± 18	38 ± 4	2.6	0.26	(0.085)	0.100	(0.116)		
D3	FNS	July 19, 4 hr	0.95	200	10-20, W		220 ± 7	22 ± 7	1.5	0.15	(0.066)	0.100	(0.136)		
5B	BLMD	June 17, 1967, 14 hr	2.1	1	10, W		40 ± 2	12 ± 1	2.5	0.75	(0.261)	0.300	(0.342)		
5M	BLMD	June 17, 14 hr	2.1	8	10, W		32 ± 2	8 ± 3	1.9	0.50	(0.147)	0.250	(0.366)		
5H	BLMD	June 17, 14 hr	2.1	15	10, W		50 ± 2	7 ± 1	3.1	0.45	(0.115)	0.140	(0.166)		
11B	BLMD	June 24, 15 hr	2.3	0.5	0-1, N		30 ± 3	4 ± 2	1.9	0.25	(0.060)	0.133	(0.222)		
12B	BLMD	June 25, 18 hr	2.7	0.5	0-2, SE		33 ± 2	4 ± 1	1.4	0.17	(0.085)	0.121	(0.161)		
12M	BLMD	June 25, 18 hr	2.7	8	0-2, SE		20 ± 3	8 ± 2	0.8	0.35	(0.260)	0.400	(0.588)		
<i>Laboratory Buoy Samplings</i>															
5B	BLMD	June 17, 1967, 14 hr	2.1	1	10, W		125 ± 8	1 ± 5	2.3	0.02	(<0.008)	0.008	(0.051)		
5M	BLMD	June 17, 14 hr	2.1	8	10, W		17 ± 2	6 ± 3	0.3	0.10	(0.157)	0.352	(0.600)		
5H	BLMD	June 17, 14 hr	2.1	15	10, W		87 ± 8	1 ± 5	1.6	0.02	(<0.011)	0.011	(0.076)		
11B	BLMD	June 24, 15 hr	2.3	0.5	0-1, N		19 ± 2	9 ± 3	0.4	0.17	(0.285)	0.473	(0.705)		
12B	BLMD	June 25, 18 hr	2.7	0.5	0-2, SE		81 ± 8	6 ± 5	1.6	0.12	(0.011)	0.074	(0.150)		
12M	BLMD	June 25, 18 hr	2.7	8	0-2, SE		17 ± 2	7 ± 4	0.3	0.14	(0.157)	0.411	(0.733)		
							298 ± 9	20 ± 8	5.2	0.35	(0.039)	0.067	(0.097)		
							14 ± 2	8 ± 3	0.2	0.14	(0.312)	0.571	(0.916)		
							18 ± 2	6 ± 4	0.3	0.10	(0.100)	0.333	(0.625)		
							16 ± 2	6 ± 4	0.2	0.12	(0.111)	0.375	(0.714)		

Sample identification. JNCS: on board oceanographic ship *Jean Charcot*, Norwegian Sea. FNS: navy survey plane flying above *Jean Charcot*, Norwegian Sea. For JCNS and FNS, positions and meteorological situation: July 14, 63°N, 4°E, high-pressure zone above Greenland, local, 1010 mb; July 14, 66°N, 0°1'E, low-pressure zone above Greenland, local cold front 980 mb; July 19, 68°N, 2°E, low-pressure zone centered on Norwegian Sea, local, 990 mb. BLMD: floating buoy laboratory, 42°47'N, 7°30'E, Western Mediterranean. B, M, and H are different levels of sampling.

P, pellicle; F, filter.
 * (a) Measured K/Na weight ratio. (b and c) Values worked out by making allowance of the maximum inaccuracies on sodium and potassium quantities corrected for blanks. (b) Minimum value defined as K min/Na max. (c) Maximum value defined as K max/Na min.

One can conclude from these data that the surface of the sea acts as the source of various types of salt particles (sea spray and aerosols produced by bubble bursting) that have different K/Na ratios. The variations in this ratio for the filter and the thin pellicle, associated with a shift when sampling altitudes increase, can be related to the influence of the particle settling processes. Small particles more easily escape the washing mechanisms in the first layer of the marine atmosphere. This has been extensively demonstrated by *Toba* [1965] and *Monahan* [1968] for giant salt nuclei. Thus the small size fraction of the particles may penetrate further and remain longer in the marine atmosphere than the larger size fraction. The increasing proportion of this population is indicated by the shifts in the ionic ratios observed when the samples are collected further away from the source or when the local production is falling with a decreasing wind.

The existence of a fractionation versus size relationship was defined more precisely by the use of a 6-stage cascade impactor. The first run with the instrument was performed in the Norwegian Sea and was associated with filtration. We were able to extend our analysis by the AA method to the calcium content on impactor slides (Figure 1). The observed U-shaped enrichment curves look very similar to enrichment curves for iodine and bromine [*Duce et al.*, 1967]. The NSCI2 sample was probably contaminated to some extent by droplets of sea water because of heavy winds and a moving ship.

A trend for enrichments in the small size fraction is observed for both potassium and calcium, which are quasi-identical. This substantiates the data of *Komabayasi's* [1964] laboratory experiments and our Delbag filter data. However, conclusions based on chemical composition versus size, as demonstrated by impactor sampling, must be carefully considered, because chemical fractionation could take place within the instrument itself (D. J. Bressan, personal communication, 1972). Indeed, the kinetics of the capture of salt particles, in moist air, by high-velocity impacts on slides could induce various phase separations followed by different types of recrystallization. The existence of such processes would evenly over-fractionate

the ionic weight ratios in some stages of the impactor.

An alternative explanation can be proposed for enrichments in potassium and calcium in marine aerosols, and this has an essential bearing on the fractionation-enrichment theory. Small dust particles, originating from weathered continental soils, are blown into the air by the action of the wind. These particles have a residence time in the atmosphere sufficient to allow them to be transported over the open ocean [*Junge*, 1968]. Their incorporation in the samples could explain the observed ratios when non-sea-water values are found. This point must be carefully considered. Discrepancies between the measured continental dust concentrations over the oceans exist. These concentrations vary with time and place of collection. However, in the northern hemisphere the range of their concentrations is of the same order of magnitude as the concentrations of the salt particles, i.e. $0.05\text{--}5\ \mu\text{g}/\text{m}^3$ [*Delany et al.*, 1967; *Hwang Chi Trach*, 1969; *Ferguson et al.*, 1970; *Folger*, 1970; *Gillette and Blifford*, 1971; also D. J. Bressan et al., unpublished data]. It has been observed that the potassium and calcium concentrations in the hydro-insoluble phase of this dust are generally 1-2% for potassium and 5% for calcium, in agreement with the average values for continental rocks [*Prospero and Bonatti*, 1969].

Therefore the hydro-insoluble phases of the dust cannot be involved to explain totally the 'excesses' observed in the ionic ratios. However, it can be argued that the small size clay fraction of the dust could be much more enriched in potassium and calcium of continental origin in hydro-soluble form. An incorporation of such potassium and calcium of terrestrial origin could indeed lead to the observed non-sea-water ratios.

It is clear at this point, because laboratory experiments could be biased by physico-chemical artifacts, that unequivocal arguments must be stressed in order to support the validity of a fractionation theory. This was done by extensively exploring the data presented below.

ANTARCTIC OCEAN SAMPLES

Marine aerosols in oceanic regions with low terrigenous dust concentrations were sampled over the Antarctic Ocean on board the RV *Eltanin*. The terrigenous dust concentrations

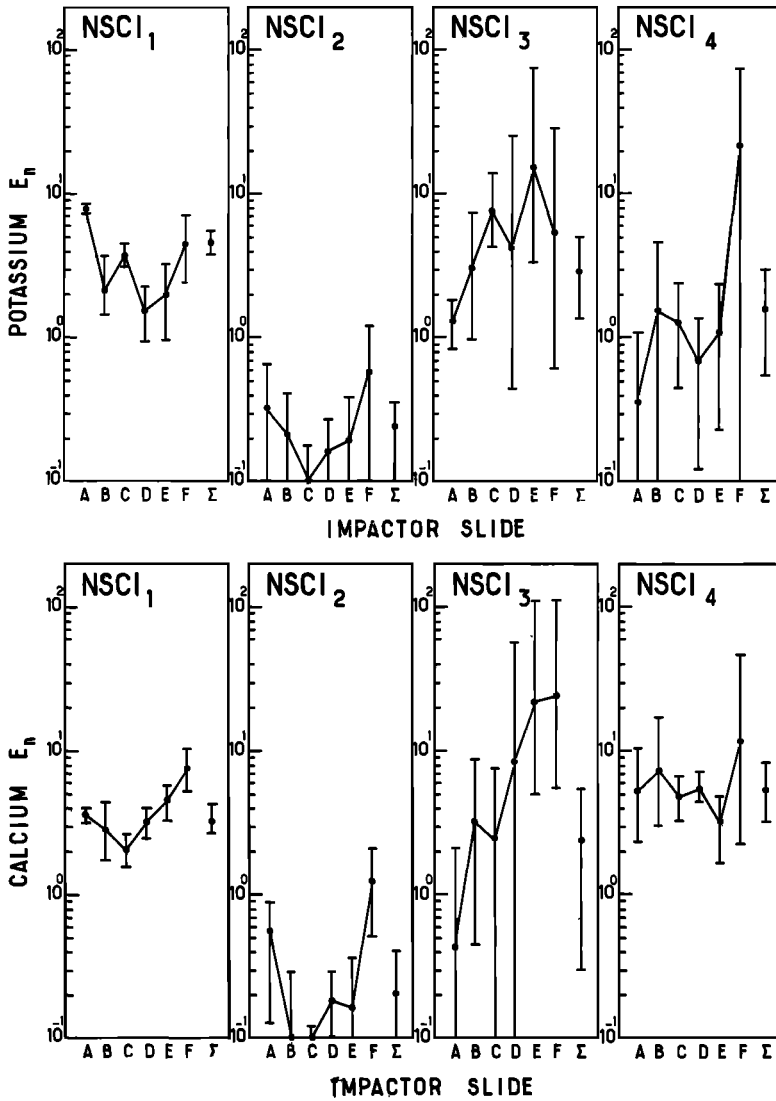


Fig. 1. Potassium and calcium enrichments for ambient marine air particulate samples from Norwegian Sea. Six-stage cascade impactor samplings. NSCI₁: wind speed, 15–20 knots; volume sampled, 13.5 m³; 24 hours; stationary ship (63°N, 4°E). NSCI₂: wind speed, >25 knots; volume sampled, 135 m³; 18 hours; moving ship (66°N, 3°E). NSCI₃: wind speed, 0–5 knots; volume sampled, 90 m³; 120 hours; moving ship (73°N, 4°E). NSCI₄: wind speed, 10–15 knots; volume sampled, 73 m³; 94 hours; moving ship (70°N, 4°E). E_n potassium = $(K/Na \text{ aerosol}) / (K/Na \text{ sea water}) - 1$. E_n calcium = $(Ca/Na \text{ aerosol}) / (Ca/Na \text{ sea water}) - 1$. E_n boundary values are drawn from maximum imprecisions in our measurements: $(E_n)_{min}$ potassium = $[(K/Na)_{min} \text{ aerosol}] / [(K/Na)_{max} \text{ sea water}] - 1$; $(E_n)_{max}$ potassium = $[(K/Na)_{max} \text{ aerosol}] / [(K/Na)_{min} \text{ sea water}] - 1$ (E_n identical for calcium).

were considered to be low because of the concentrations of silica in the air at these latitudes (see Table 4) (J. Servant, personal communication, 1969). Samples of large volumes of air over long time periods and large ocean areas were

filtered. The high quantity of salts recovered on gauze filters permitted an accurate check of the elemental weight ratios. It should be noted that the data deal with the global population of salt particles in marine air without any kind of

TABLE 4. Silica in Marine Air

Latitude	Si, $\mu\text{g}/\text{m}^3$
45°N	0.110
17°N	0.025
14°N	0.640
8°S	<0.014
55°S	<0.014
63°S	0.033

On board SS *Thaladan* from France to Antarctica (French polar expedition), 1967-1968. Precision (2 standard deviations), 20%. Volume sampled, $\sim 7 \times 10^3 \text{ m}^3$.

separation process. For most of the cruise, the ship sailed under heavy weather conditions, and hence the relative proportion of sea spray is important. However, sea-water ratios are not observed (Table 5).

The hydro-soluble fraction of the salts was recovered by repeated thorough washings of portions of the gauze filters. This water was then filtered on preweighed Millipore membranes (0.1- and 0.45- μm porosity) in order to recover non-hydro-soluble dust. For each sample, values of the dust concentration in the air are given. In fact, these levels of dust concentration must be taken as upper limits.

Instrumental neutron activation analyses recently made on those insoluble dust samples have shown the iron to be about 1% (sodium, 1.6%; potassium, 3.3%). The value for iron indicates very little contamination by metallic particles from the ship. Such contamination sources often make the data irrelevant when one looks for trace metals in marine air, but this is not the case when the major alkaline ions are being sought; ships are not built of sodium, potassium, or calcium. However, the occurrences of shipboard contamination for fractionated salt particles is a real problem (see Appendix).

The weight ratios of *S* (salts) and *D* (dust) indicate clearly that the amounts of dust able to carry associated soluble potassium and calcium of continental origin are definitely too small to have any effect on the ionic ratios shown. Because the gauze filters were not high-efficiency collection filters, one could infer much lower collection efficiency for the very small size dust than for the sea-salt particles. In this case, the *S/D* ratios could have been biased.

This problem was thoroughly examined. Arti-

TABLE 5. Antarctic Ocean Samplings

Sample	Approx. Place	Vol. Sampled, $10^3 \times \text{m}^3$	Sampling Alt. above Sea Level, m	Wind Speed and Direction, knots	Measured Amounts on 1/4 Gauze, * mg				Atmos. Conc., $\mu\text{g}/\text{m}^3$	Weight Ratios			Dust load Recov. from 1/4 Gauze on Millipore 0.45 μ , mg	<i>S/D</i> †
					Na	K	Ca	Mg		K/Na	Ca/Na	Mg/Na		
32/1	48°S-50°S, 170°E	~1300	7	20-30, NW	806	41	41	103	~5	0.051	0.051	0.119	15	65
32/2	50°S-55°S, 170°E	~1200	7	15-25, NW	1653	75	86	213	~10	0.045	0.052	0.128	14	150
32/3	55°S-60°S, 170°E	~1000	7	10-15, NW	401	22	22	49	~3	0.055	0.055	0.122	8	60
32/4	60°S-65°S, 170°E	~1000	7	15-30, N	2322	111	107	295	~8	0.048	0.046	0.127	10	280
32/5	65°S-70°S, 170°E	~2000	7	20-25, N	2316	118	116	322	~9	0.051	0.050	0.139	20	140

Samples taken on board RV *Eltanin*, cruise from Wellington, New Zealand, to Ross Sea, December 1967.

* Precision (2 standard deviations) better or equal to 5%.

† Na concentrations are given only as indications, owing to the sampling procedures.

‡ *S/D*, ratio between total amounts of hydro-soluble cations recovered after filtrations on Millipore of 0.45 μ porosity versus total amounts of non-hydro-soluble dust recovered on 0.45- μ Millipore filters.

ficial and natural radioactivity of the gauze filters and of blue Poelman-Schneider filters having 99% collection efficiency and sampled with volumetric pumps were compared after parallel filtration for each sampling set. The only difference found in air-specific activities was a factor of 2 in favor of the full-efficiency filters. Thus major uncertainty in the validity of the S/D ratios due to dust collection efficiency can be ruled out. Moreover, dust concentrations in the air are in good agreement with the silica concentrations shown in Table 4.

The Antarctic Ocean data support the existence of a fractionation of potassium and calcium, at least for a part of the total aerosol production. The presence of about 5–10% in weight of fractionated marine aerosols incorporated in the total population of salt particles recovered here is sufficient to explain the ratios observed. In various oceanic areas, these percentages appear to be similar. Thus one can assume that the flux of fractionated marine aerosols is very much constant for all the oceans.

COASTAL AND INLAND SAMPLES

When the sampling procedures do not permit accurate weighing for the atmospheric load of dust, elemental silicon, aluminum, and iron concentrations on the filters may serve to describe the presence of a terrigenous fraction. Such data also provide information on the complex mixtures occurring in the atmosphere between sea-source elements and continental-source elements.

Another group of workers (J. Servant, Hoang Chi Trach, and E. Brichet in our laboratory, and D. Cittanova) have looked at the elemental ratios of silicon, aluminum, iron, sodium, potassium, calcium, and magnesium in air samples filtered near the ground at different types of land sites. This was done to study the chemical composition of the continental dust locally blown into the air by the wind. The analyses were performed at Service d'Etudes Analytiques, Centre d'Etudes Nucléaires, Fontenay aux Roses, France. Despite their relatively low precisions (~20%) when compared with the data obtained by the NA or AA method, these data are relevant to this discussion. Insight into the cations and aluminosilicate assemblages col-

lected in air could ascertain whether or not fractionation in marine aerosols occurs.

From Table 6, the following points should be stressed:

First, the average crustal ratios given in Table 7 are generally not observed in the above samples. This probably reflects the existence of mixtures of sea-source elements and aluminosilicates. The Al/Si and Fe/Si ratios are constant in samples 1, 2, 3, and 4. In 5 and 6, these ratios become small, probably reflecting the presence of more pure silica debris occurring in the air at this sandy coastal sampling site. In order to define average continental dust compositions, Al/Si and Fe/Si ratios were referred to values observed in samples 1 and 2 for inland sites, where clay minerals predominate in the soil.

Secondly, for sample 6 at the coastal sampling site in the summertime, with no wind blowing from the sea, the ratios show the presence of a mixture of the pure silica phase, the aluminosilicates, and the sea-source particles. These values do not permit precise interpretation of the chemical composition for the marine aerosol phase.

The data from 5 are important, because the wind was blowing directly from the Atlantic Ocean and much larger quantities of sodium are present with low aluminosilicate concentrations. The ratios between sodium, potassium, calcium, and magnesium are not the sea-water ratios.

An approach to establishing marine versus terrestrial compositions can be tentatively made. The ratios observed inland in 1 and 2 between cations and aluminum or iron concentrations are applied as factors to determine the sodium, potassium, calcium, and magnesium in 5, with aluminum and iron as the alkaline terrigenous contribution, mixed with the sea-source particles. Silicon appears to be enriched too much here to be used in such computation. We then subtract these calculated concentrations from the global concentrations, in order to define the weight ratios in the marine source.

After these corrections, the 'remaining' sodium, potassium, and calcium concentrations exhibit weight ratios close to the values observed in the bulk population of marine aerosols collected on the open sea (see Table 8). In addition, the magnesium appears to be slightly

TABLE 6. Coastal and Inland Station Samplings

Sample No.	Ident.	Concentration in Air, $\mu\text{g}/\text{m}^3$ *										Weight Ratios				
		Si	Al	Fe	Na	K	Ca	Mg	Al/Si	Fe/Si	Na/Si	K/Si	Ca/Si	Mg/Si		
1	HGCFR	2.64	1.43	1.43	1.50	0.70	3.00	0.03	0.541	0.541	0.568	0.265	1.136	0.011		
2	EGCFR	0.35	0.12	0.25	0.15	0.08	0.40	0.07	0.342	0.714	0.428	0.228	1.142	0.200		
3	HJJO	0.44	0.18	0.24	0.06	0.11	0.38	0.10	0.409	0.545	0.136	0.250	0.863	0.227		
4	EJJO	0.43	0.12	0.28	0.04	0.06	0.24	0.02	0.279	0.651	0.093	0.558	0.558	0.046		
5	HSMR	0.35	0.07	0.07	3.50	0.30	0.30	0.12	0.200	0.200	10.000	0.857	0.857	0.342		
6	ESMR	1.70	0.25	0.30	0.80	0.10	0.25	0.20	0.147	0.176	(2.5)†	(2.1)†	0.147	0.117		
											(1.6)†	(0.2)†	(0.5)†	(0.4)†		

* Precision (2 standard deviations), $\sim 20\%$; volume sampled, $5 \times 10^3 \text{ m}^3$.

† Values in parentheses are Al-corrected.

Si, Al, Fe, and Mg by Jarrell-Ash spectrograph, external standard (SPEX), comparison method. Na, K, and Ca by UV-120 dispersive Huet spectrograph, external standard (SPEX), comparison method.

Sample identification

HGCFR Winter, Gif-sur-Yvette, France, inland station, agriculture soils, 500 km from marine influence, average wind 20 km/hr, westerly.

EGCFR Summer, Gif-sur-Yvette, conditions same as for HGCFR, except there was only a local breeze.

HJJO Winter, Jungfrau Joch Observatory, Switzerland, alt. 3,500 meters, Alpine rocks and snow, north wind 10 km/hr.

EJJO Summer, Jungfrau Joch Observatory, conditions same as for HJJO.

HSMR Winter, Marine Station Roscoff, Northern Brittany, sands, granites, average wind 30-45 km/hr WSW.

ESMR Summer, Marine Station Roscoff, conditions same as for HSMR, except there was only a local breeze of 5 km/hr.

TABLE 7. Average Crustal Weight Ratios*

Ratio	Value
Al/Si	0.295
Fe/Si	0.198
Na/Si	0.084
K/Si	0.074
Ca/Si	0.147
Mg/Si	0.083

* From Taylor [1964].

depleted, which is often observed in marine aerosols [Morelli, 1968].

In samples 3 and 4, at altitudes of 3500 meters, well above the temperature inversions, K/Na and Ca/Na are very high and sodium concentrations are low. This could reflect high-altitude 'background aerosol' compositions, in agreement with data from Junge [1968] and Gillette and Blifford [1971]. To ascertain the extent to which those ratios may be dependent on fractionated sea-source small particles will require more investigations.

In conclusion, the alumino-silicates versus major cations observed inland under varying conditions are not observed in air coming directly from the Atlantic Ocean. The nonterrestrial sodium, potassium, and calcium concentrations can be related to the marine source and show fractionated ratios.

ANTARCTIC ICE DATA

As was stated earlier, fractionated marine aerosols with radii less than 1 μm may have their distribution controlled by long-range transport within the troposphere. Whether associated or not with precipitation, part of these particles fall on the continents, where their influence on the geochemistry of major elements can be hypothesized. However, accurate measurements of the fallout of sea-source salts over the continents are very difficult, because the marine source is often overwhelmed by local terrigenous sources or human pollution. However, the geochemistry of this fallout can be successfully studied in polar ice samples. Recent extensive research on concentrations of impurities in super-pure Antarctic ice has opened the possibility of differentiating between the contributing sources (continental, marine, and extraterrestrial) and their associated chemistry [Hanappe

et al., 1968; Murozimi et al., 1969; Vosters et al., 1970].

Data in Table 9 were kindly provided by M. Vosters, F. Hanappe, and E. Picciotto from Service de Geochimie Nucleaire, Universite de Bruxelles, Belgique. The main purpose of their study was to estimate the influx of extraterrestrial matter (M. Vosters et al., unpublished data). We shall discuss only the data on the terrigenous and marine sources. The ice samples from the central part of the East Antarctic Plateau were collected with extreme precaution against contamination and were brought back to the laboratory in a frozen state. Because of the low concentration of elements, careful analytical procedures were utilized (AA and NA) to measure sodium, potassium, calcium, magnesium, iron, nickel, and manganese [Hanappe, 1970; Vosters, 1971].

In Table 9, the sea-water ratios for the alkaline ions are not observed. The iron concentrations were used to correct these ratios for the terrigenous influence. First, the iron concentrations were corrected for the extraterrestrial iron. This contribution represented only about 20% of the total iron. A value of 5.7% iron in the terrigenous-source crustal rocks [Taylor, 1964] was applied in order to calculate the amount of the terrigenous fraction incorporated in the samples. The rocks uncovered by ice in the Antarctic are the most likely source for large parts of the terrestrial contribution. The values for the cation percentages in the terrigenous source were also considered to be the percentages occurring in the crustal average rocks. It should be noted that the iron concentrations could have been underestimated because of incomplete dissolution by aqua-regia of acid-resistant alumino-silicates, presumably also present in the terrigenous fraction. There are strong indications that this was not the case

TABLE 8. Coastal Sampling 5 (HSMR)

Element	Terrigenous Corrected Conc., $\mu\text{g}/\text{m}^3$	Ratio	Computed Wt. Ratio in Marine Source
Na	2.70	K/Na	0.100
K	0.27	Ca/Na	0.060
Ca	0.16	Mg/Na	0.033
Mg	0.09		

TABLE 9. Antarctic Ice Concentrations

Sampling Zone	Age of Ice	Mean Conc. in Ice,*						Global				Corrected Wt. Ratios for Marine Source†			
		Na	K	Ca	Mg	Fe	Uncorrected Wt. Ratios†	Ca/Na	K/Na	Mg/Na	K/Na	Ca/Na	Mg/Na		
ASS (6)§	1949-1951	11.5	5.1	3.3	2.8	4.1	0.278	0.278	0.156	0.238	0.238	0.135			
PLA-S (12)§	1936-1954	22.0	3.8	5.3	5.0	2.8	0.149	0.172	0.172	0.119	0.091	0.132			
PI (2)§	1950-1951	21.0	2.5	11.0	6.2	6.6	0.119	0.525	0.303	0.044	0.370	0.185			

Precision (2 standard deviations), 10%.

* Averaged concentrations found in samples of about 1-2 kg of ice.

† Average ratios.

‡ Procedure for correction discussed in text.

§ Number of samples for the averaged values.

Sample identification. ASS, Amundsen-Scott station; PLA-S, Plateau station (East Antarctica); PI, Pole of Relative Inaccessibility station.

and that there were no losses in the recovery of iron during the analytical procedure. This is also confirmed by recent data of *Boutron et al.* [1972] and R. A. Duce (personal communication, 1972). They showed that the quantities of iron recovered in snow samples collected in a similar area in East Antarctica are not changed by an attack by HF after dissolution by aqua-regia.

Table 9 also gives the values for the ratios after a terrigenous correction for each sample. The sea-water ratios are still not observed.

The ice samples integrate a longer span of time than locally filtered air. Thus, they provide good statistical values and are probably representative of a situation occurring on a large geochemical scale. The existence of chemical fractionation globally affecting the marine source on the East Antarctic Plateau is shown by the data of *Vosters et al.* [1970].

In this area, very low rates of snow accumulations are observed: $\sim 3 \text{ g cm}^{-2} \text{ yr}^{-1}$ [*Picciotto et al.*, 1964]. Such low accumulation rates are currently explained by a meteorological shielding effect against direct penetration of oceanic air. In this specific zone, the marine source appears to be more fractionated than in zones such as coastal regions [*Vosters*, 1971; *Boutron et al.*, 1972] and presumably West Antarctica [*Murozimi et al.*, 1969]. These regions are more directly under the influence of intrusion of marine air, as is shown by a higher snow accumulation rate.

We feel that such a relationship between fractionation in the marine source and the 'ages' of the oceanic air could be related to a size-fractionation relationship that was used to explain variations in ratios in marine air particles. Indeed, a sorting process from large to smaller particles could control the trends observed in fractionated ratios; i.e., the fractionation is more marked when the distance and time between the sampling location and the oceanic source increase.

SUMMARY AND CONCLUSION

It has been tentatively demonstrated by laboratory experiments that, at the very beginning of their history in the atmosphere, part of the aerosols produced by bursting bubbles at the surface of the sea do not have the elemental K/Na weight ratio that exists in the bulk sea water.

This ratio shows large variations over time and space for particles sampled in open sea marine air under various conditions. This situation probably reflects the presence of a complex population of atmospheric particles, with proportions largely controlled by settling processes. These particles are: (a) sea-spray particles, presumably with the sea-water ratios; (b) terrigenous dust of small size, probably enriched with cations of primary continental origin in a hydro-soluble phase; and (c) ionic fractionated marine aerosols.

The existence of this last category of sea-source particles is shown by data obtained where the amounts of dust of any elemental composition is much too small to have an influence when non-sea-water weight ratios are observed. This was the case for our samples from the Antarctic Ocean and for coastal samples.

When scrutinized, the open sea data seem to demonstrate that the smaller size categories of marine aerosols are probably the more fractionated. In upper layers of the marine atmosphere, their concentrations may compete with the terrigenous dust load to govern the cations ratios.

The K/Na and Ca/Na weight ratios appear to depend upon the same processes and same proportions of fractionated aerosols in the marine atmosphere. The Cl/Na ratios remain close to the sea-water value. Thus, when compared with the sodium concentrations, potassium and calcium concentrations in particles appear to be essentially controlled by a process of enrichment at the sea-air interface. Many aspects of the chemistry of such an enrichment are not yet fully explained and will receive further investigation.

If part of the enriched marine aerosols have sizes small enough to be transported far from their place of origin, their influence on elemental ratios in precipitation can be traced. This was done by looking at the major element ratios in ultrapure Antarctic ice. After a correction for the influence of terrigenous impurities the remaining K/Na, Ca/Na, and Mg/Na ratios are fractionated in comparison to the sea-water values.

In conclusion, bubbles bursting at the sea surface seem to inject into the atmosphere quantities of ionic fractionated aerosols large enough to affect the geochemistry of atmospheric particles.

APPENDIX

On board a ship, there are many sources and processes that could introduce into the filtered air ions having ratios unlike those in sea water. One source of shipboard contamination could be the smoke. Despite all precautions that were taken, many of our filters have been darkened by smoke constituents. In regard to the effect of this kind of contamination for sodium, potassium, and calcium, our arguments are as follows:

a. We have never found any kind of correlation between the degree of darkness of the filters and variations in ionic ratios.

b. Two important parameters are the weight of ashes produced by a given volume of fuel and their average compositions in alkaline ions. The average ash concentration produced by the fuel is at maximum 0.01% [*Battelle Memorial Institute*, 1959]. The concentration of ashes is as follows: Na₂O, 0.8 to 12.5%; K₂O, 0 to 1.8%; CaO, 1 to 11% [*Sürü*, cited in *Zul'Fugarly*, 1964], and it is probably much less than these values [*Bertine and Goldberg*, 1971]. Using these data, we see that 1 ton of fuel will produce about 10 grams of sodium, 1 gram of potassium, and so on. The average consumption in fuel of our research vessels is about 10 tons per 24 hours. Then, 100 grams of sodium is injected for about the duration of our average sampling. The dilution coefficients that were studied for many years for radioactive smoke released from nuclear reactors at Saclay Nuclear Center for the same geometry between the exhaustor and sampler, same wind conditions, and for about the same flow rate of exhausted vapor, are 10⁷ to 10⁸. Then one can reasonably predict that, for 24 hours of sampling, the average amount of sodium that could have the smoke as its origin is about 10 to 1 μg on our filters. Quantities of ashes 10 times higher may darken the filters, but the associated sodium and potassium quantities cannot influence the weight ratios we observed, which are based on 100 to 1000 μg of sodium per filter.

c. An additional source of contamination by the exhaustor could be small quantities of sea water vaporized in the exhaustor. From technical discussions with engineers and measurements we made on board research vessels, an escape of less than 1 liter of sea water per hour can be assumed. Taking the same dilution parameter,

this again gives an amount of salt far less than the amount of salt collected on filters.

Another source of shipboard contamination could be worse: drying of sea-water droplets on the surface structure of the ship could introduce, during crystallization, a chemical fractionation between the cations. Blown again in the air after drying, these secondary fractionated sea-salt particles could in fact contaminate the samples. However, we do not know yet whether these processes really occur and how to measure this effect. The only argument we have on this aspect of the question is that, whenever our samples have been taken, the rate of rainfall was extremely high, repeatedly washing the superstructure of the ship, and that all samples were collected upwind from the ship. Again, the arguments for the existence of a true fractionation derived from low-altitude aircraft samplings are of extreme importance in this discussion.

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