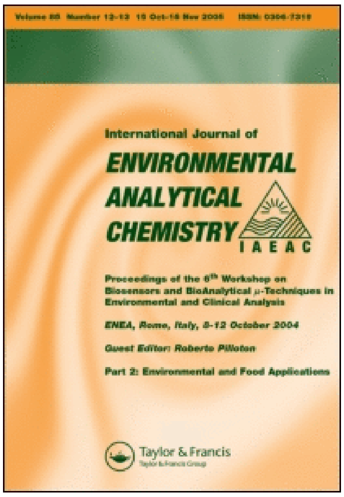

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Ammonium, Alkaline and Alkaline-Earth Element Determination in Antarctic Lake Waters, Flowing Melt Waters, Sea Waters and Snow

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AMMONIUM, ALKALINE AND ALKALINE-EARTH ELEMENT DETERMINATION IN ANTARCTIC LAKE WATERS, FLOWING MELT WATERS, SEA WATERS AND SNOW

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Concentrations of lithium, sodium, potassium, magnesium and calcium were measured by ion-chromatography in samples collected in different sites during the 1989/90 Italian expedition in Antarctica.
Sea waters, lake waters, flowing melt waters and snow were considered. In addition ammonium was determined in all the samples whenever the chromatographic separation of adjacent sodium and ammonium peaks was feasible.
For each element the observed intervals of concentrations (shown in brackets) were:
Snow (concentrations in µM units): Li(not detectable);Na(3–22);NH_4 (0.3–13); K (0.2–1); Mg (0.4–2); Ca (0.3–1).
Lake and melt waters (in mM units): Li ($[0.4–4]\times10^{-3}$); Na (0.1–6); K (0.01–0.3); Mg (0.01–0.6); Ca (0.006–0.6). The lowest concentrations were found in melt waters.
Sea waters (in mM units): Li ($[22–27]\times10^{-3}$); Na (418–472); K (8.7–10); Mg (49–56); Ca (9.2–11).
The above data represent the intervals of variability due to the non-homogeneity of composition among the sampling sites; for sea water, they include the water column depth effect.

Correlations were searched for between relative concentrations of the analytes for the different natures of the samples in order to distinguish the origin of salt content both in snow and meltwater from marine aerosols and other environmental sources.

KEY WORDS: Alkaline, alkaline-earth elements, Antarctic snow and waters

INTRODUCTION

In a previous work[1] the concentrations of some alkaline and alkaline-earth elements in Antarctic sea water were measured to estimate the extent of homogeneity in surface sea water samples collected in different sites during different periods of time (1987/88 and 1988/89 Italian expeditions). In the present paper, an extended area of sea, including in-shore and far off-shore sea waters, was considered (see Figure 1). Samples were collected both at constant depths (0.2 and 20 m) in different sites and at variable depths (from 0.5 to 1300 m)

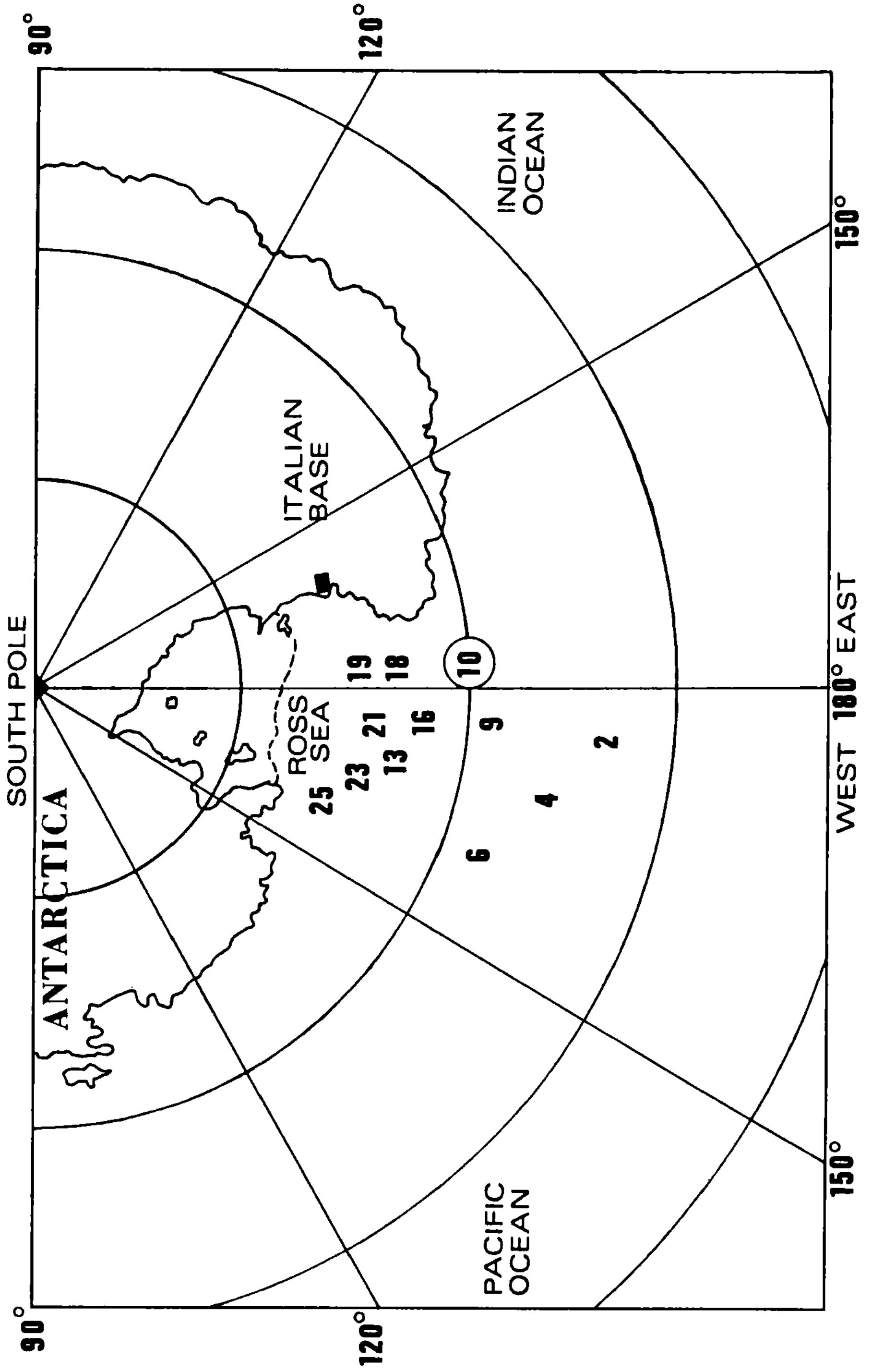

FIGURE 1.

Figure 1 Location of the sampling stations in sea water during the 1989/90 Italian expedition. At station 10 water column samples were gethered.

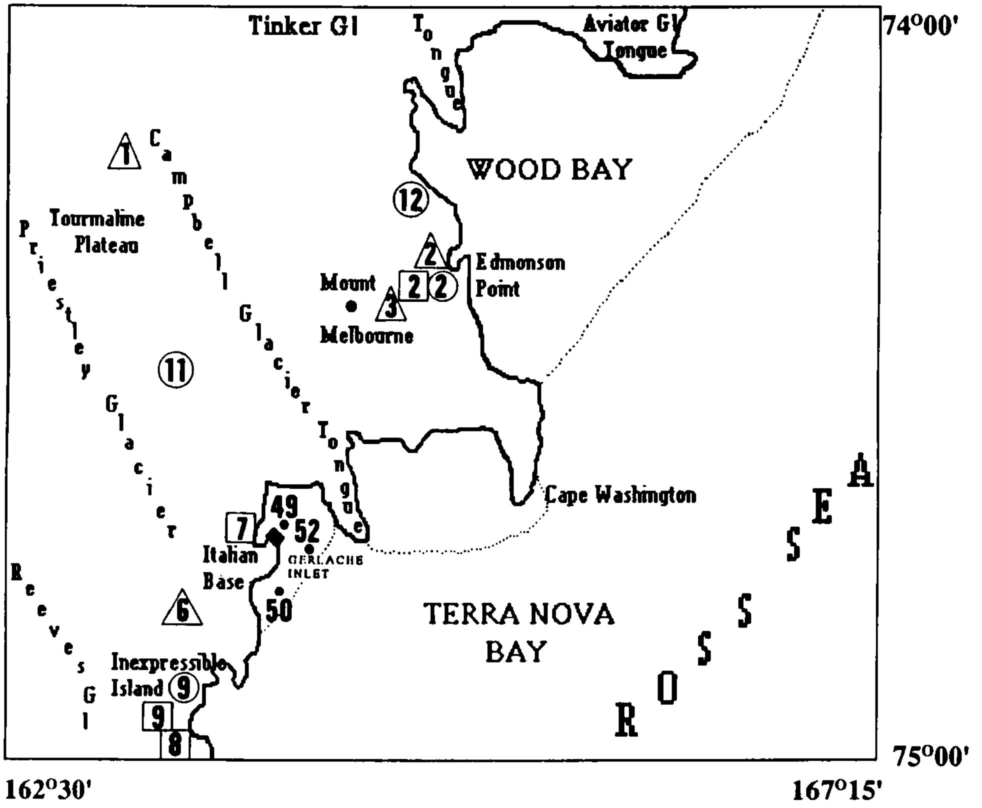

Figure 2 Location of the sampling stations in in-shore sea water (•), lake water (□), meltwater (○) and snow (Δ) during the 1989/90 Italian expedition.

for the same water column. Lake water, melt water and snow samples were also collected (See Figure 2).

By measuring the concentrations of alkaline and alkaline-earth elements in the above matrices, the present research aims to pursue the following tasks: i) estimate the effect of large distances between stations on sample composition, and, in the case of sea water, the effects of depth along the water column; ii) find the origin of any spread in the concentration of the elements.

EXPERIMENTAL

Instrumentation

A Dionex model DX300 Ionic Chromatograph (Dionex, Sunnyvale, Ca, USA) equipped with an injection valve model 9126 Reodyne; a Pulsed Electrochemical Detector (PED) working in conductivity mode; a Dionex Micro Membrane Suppressor (CMMS II:4mm for natural and sea water samples; 2 mm for snow samples) were employed. The separations were carried out on an Ionpac CS11 (250 mm × 2 mm i.d.) for snow samples and on an Ionpac CG12 (50 mm × 4 mm i.d.) and an Ionpac CS12 (250 mm × 4 mm i.d.) for water samples. The loop volume was 50 μL.

A DQP-1 pump (Dionex, Sunnyvale, Ca, USA) was used for the preconcentration of snow samples (2 ml of samples) on an Ionpac CG11 (50 mm × 2 mm i.d.), and an Autolon 450 for data acquisition and processing.

Reagents

All reagents were Suprapure reagent grade materials. All standards, samples and reagents were prepared and stored in pre-cleaned polyethylene containers conditioned according to a procedure for trace element determination described elsewhere[2].

Eluent solutions

For water samples 15 mM HCl was used in the isocratic elution mode. For snow samples 40 mM HCl mixed with 2 mM 2,3-Diamminopropionic monohydrochloride acid (DAP HCl, NovaChimica, MI) and 40 mM HCl mixed with 8 mM DAP HCl were used in the step gradient mode. The step gradient mode elution was changed after 5 minutes.

Regenerant solution for the CMMS

The CMMS was continuously regenerated by a 100 mM Tetrabutylammoniumhydroxide solution (TBAOH, Novachimica, MI).

Sampling

Samples of sea water were collected with 30-l Go-Flow teflonated bottles at various depths. The filtration and the storage procedures are described elsewhere[3].

Snow, lake water and melt water samples were collected manually. The sampling stations and the characteristics of these samples are summarized in Table 1. Snow samples were stored in large mouth polyethylene bottles at −10°C without both filtration or addition of acid. Lake and melt waters underwent the same treatment as sea water; since filtration was performed under a mild vacuum, the concentration of ammonia, when found, has no significant meaning.

Procedures

Waters. The procedure previously described[4] was improved in terms of peak separation, numbers of runs required to accomplish the analysis of all the analytes under investigation,

Table 1 Sampling stations and sample characteristics of snow, lake- and melt- waters.

	SAMPLING STATIONS			*SAMPLE TYPE*
Station N°	*Site*	*Altitude m.a.s.l.*	*Code*	
1	Tourmaline Plateau	1650	SN1	*Snow* Soft and dry. Snow thickness about 5–10 cm above the ice.
2	Edmonson Point	190	SN2	*Snow* Icy and dry. Collected after removing the surface layer (about 1 cm).
	"	20	LW2	*Lake water*. Lake N°14. Sampling depth 40 cm. Sampled manually.
	"	20	IW2	*Inland water* Sample collected manually in the water stream.
3	Mt. Melbourne	1130	SN3	*Snow* Soft and dry. Snow thickness about 100 cm.
4	Priestley Plateau	2000	SN4	*Snow* Soft and dry. Collected after removing the surface layer (about 1 cm).
5	Mt. Crummer	650	SN5	*Snow* Snow drifted by wind.
6	Vegetation Island	220	SN6	*Snow* Soft and dry. Collected after removing the surface layer (about 1 cm).
7	Carezza Lake	175	LW7	*Lake water* Lake N°3. Sampling depth 50 cm. Sampled manually.
8	Inexpressible Island	120	LW8	*Lake water* Lake N°9. Sampling depth 60 cm. Sampled manually.
9	"	120	LW9	*Lake water* Lake N°10. Sampling depth 50 cm. Sampled manually.
	"	120	IW9	*Inland water* Stream from lake N° 9 to 10. The flow was on stoney ground.
10	Tarn Flat	−70	LW10	*Lake water* Lake N°20. Sampled manually.
11	Corner Glacier	200	IW11	*Inland water* Glacier melt water.
12	Wood Bay	30	IW12	*Inland water* Glacier melt water flow on vulcanic ground.

equilibration time between runs, and the cost of the eluents. Using the PED detector in the conductometric mode, the amplification of the analogic signal is dynamically adjusted to its best performance during the measurement time. This particular feature allows the off-line measurement of all the peak areas recorded during the same run by considering a suitable amplification of the y (μS) scale, depending on the concentration of the analyte being considered.

Figure 3 shows: i) the chromatogram where the y scale was matched for the sodium area measurement (Figure 3a); ii) the parts of the chromatogram used for area measurements of lithium (Figure 3b), and for magnesium, calcium and potassium (Figure 3c).

Calibration curves were obtained by using synthetic sea water solutions in which the concentration of each element was in turn 0.5, 0.75, 1.00 and 1.25 times the mean concentration found in oceanic sea water[5]. In the case of lithium (a few μg/l), the peak of which is adjacent to the sodium peak (hundreds of mg/l), changes in sodium concentration in the above 0.5–1.25 interval were found not to affect the determination of the lithium area. The CVs on five replicates were: 1.5% for lithium (5 μg/l), 0.07% for sodium (200 mg/l), 0.3% for potassium (6 mg/l), 0.6% for magnesium (15 mg/l) and calcium 6 mg/l). The concentrations in brackets are those found in the standard sample solutions and are comparable with ones in sea water sample solutions with the exception of Li (c.a. two times higher in the standards). The area (A) *vs.* mg/l concentration (C) calibration curves were of the form: $A = aC + b$ for all elements. The r^2 was always 0.9999 or better. The concentrations of the elements in the different sea water samples were estimated by separately comparing the relevant areas to those of two standards solutions prepared as described above, so that the concentration of each element in the sea water sample solutions was within the concentrations of the standards. In this way, the value of the intercept b at $C=O$ can be ignored and errors that might arise are avoided when b is not equal to zero using the standard addition procedure. In fact, the reproducibility between days of the calibration coefficients (which are related to the reproducibility of the instrumental conditions and the daily prepared standard solutions) was better than 1%.

Concentration determinations in lake and melt waters were performed using the same criteria in an appropriate concentration range.

Snow. The different elution mode described above for the snow samples was used to separate ammonium from the adjacent sodium peak at the concentration level present in these matrices.

Figure 4 shows the chromatogram of a snow sample after the preconcentration step on the CG11 column. During procedure optimization, using pure water or synthetic snow solutions, it was found that: i) neither ammonia nor other analytes were collected from the laboratory environment; ii) the amounts of each of the analytes present in the sample were completely retained during the preconcentration step and were proportional to the sample volume used.

The probability of ammonia being released from the samples, normally stored at –4°C, during the analysis, seems to be quite low. Further controls in this area are in progress.

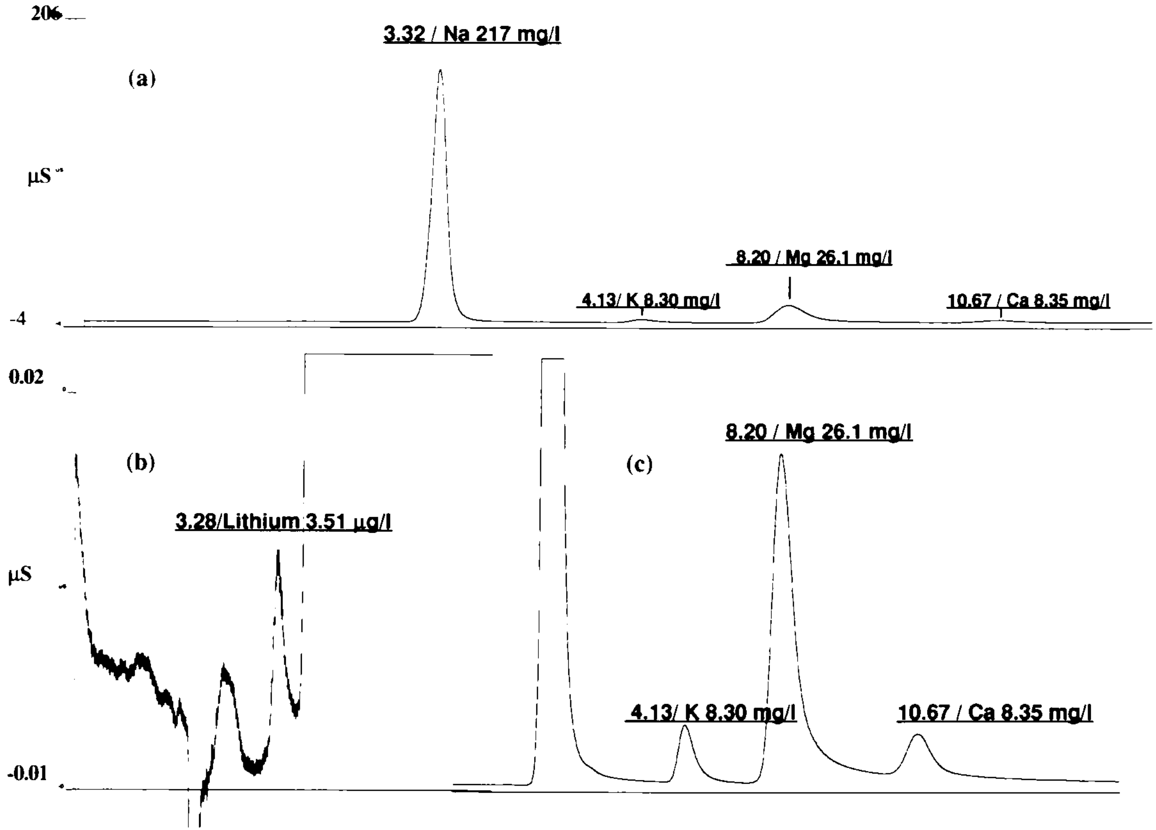

Figure 3 I.C. chromatogram of alkaline and alkaline-earth elements in 1:50 diluted sea water sample. The y scale (µS) was matched to evidence in turn the peak of: Na (Figure a), Li (Figure b), K, Mg and Ca (Figure c).

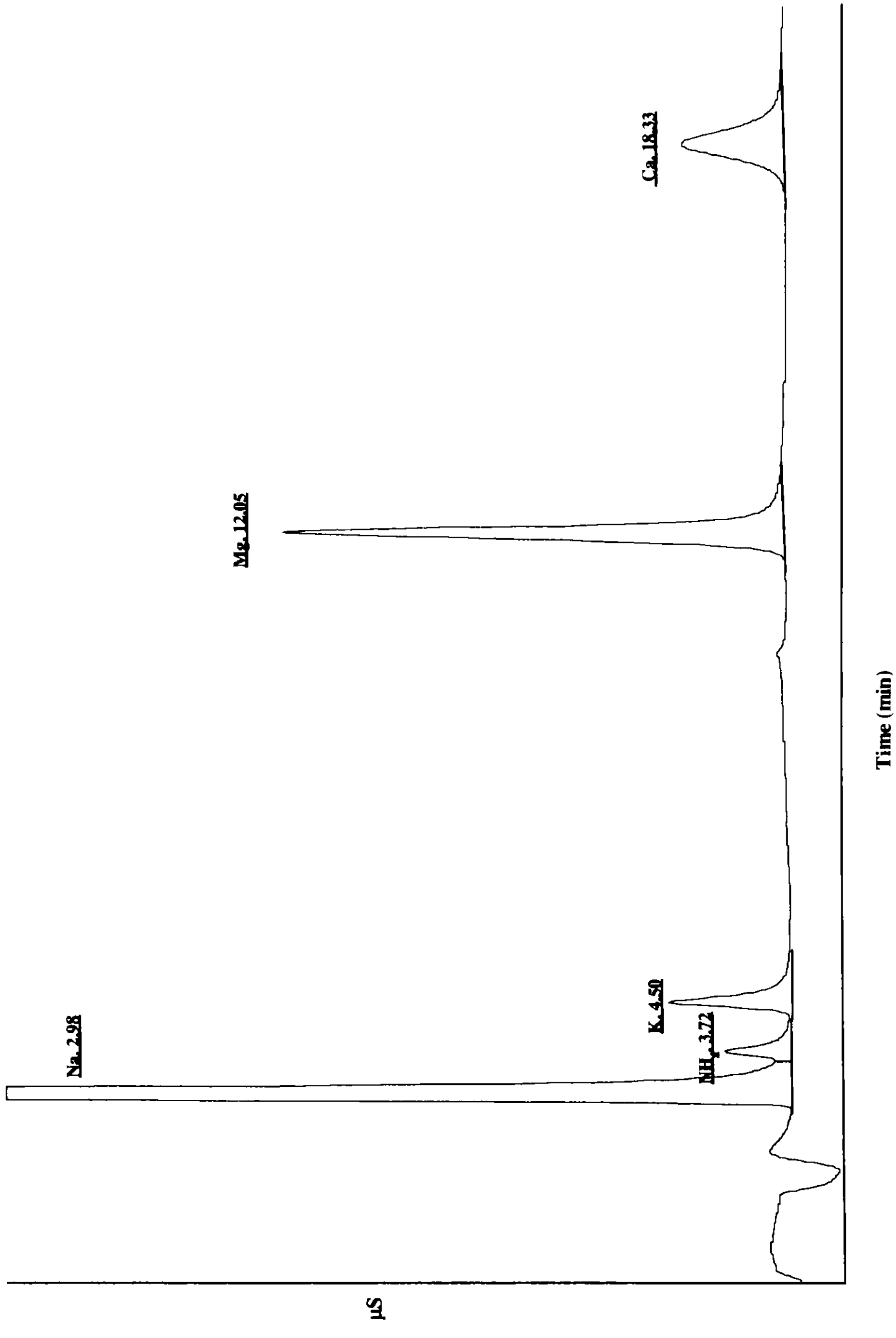

Figure 4 Chromatogram of snow sample after 100 fold preconcentration step. The initial concentration in µM in snow were: Na: 8.3; NH_4: 0.7; K: 0.4; Mg: 0.6; Ca: 0.7.

RESULTS AND DISCUSSION

Seawater

Table 2a shows for each element and each sampling station the mean concentration $[M_i]$, on three replicates, and the coefficient of variation CV. The mean coefficient of variation, estimated by the 17 stations' individual CVs, $\overline{CV} = (\Sigma CV^2/17)^{1/2}$ is also shown. In addition, in order to check the hypothesis H_0 that the spread of concentrations among stations, was purely due to random errors, the pooled mean concentration $[X_i]_p$ and the relevant CV_p were calculated and are shown in Table 2a. It will be shown later that this H_0 hypothesis can be rejected on the grounds of the experimental data seen as a whole. Table 2b shows for each element: i) the $[M_m]/[M_n]$ concentration ratios (R_i) as obtained by dividing the mean concentration $[M_i]$, as estimated for each station *i*, by the average concentration $[M_n]$ of the same element for the *n* stations ii) the $[M_i]/[M_{Na,i}]$ concentration ratios (R_{st}) where $[M_{Na,i}]$ is the concentration of sodium found at the same station *i*. Mean R_i and R_{st} values and related CVs are also shown.

The CVs among stations do not vary significantly for the different elements apart from lithium. In the statistical data treatment, a CV of 0.5% was considered for sodium, potassium, magnesium and calcium, while a CV for lithium is due to the fact that its peak is adjacent to the sodium peak with a Li/Na molar ratio of 5×10^{-5}.

Testing the H_0 null hypothesis. According to the H_0 hypothesis, it is assumed that the set of the $[M_i]$ individual values obtained for the 17 stations belongs to the same population $N(\mu,\sigma)$, and differences between $[M_i]$ values are only due to random errors. Using this assumption, the mean pooled concentration among stations, $[X_{17}]_p$, and the sample standard deviation s_{17} should be considered as a good estimate of μ and σ. According to the central limit theorem s_{17} should be $\sqrt{3}$ lower than $s_{3,i}$ relevant to each station: the closer to $\sqrt{3}$, the more efficient the estimate of s_3 is. In the comparison between s_{17} and s_3 for each element, the mean $\bar{s}_3$ rather than the individual value was used. The mean $\bar{s}_3$ was calculated both from $(\Sigma s_3^2/17)^{1/2}$ and from $(\Sigma CV_i^2/17)^{1/2} \cdot X_{17}$, obtaining practically the same results.

For the sake of comparison among elements, CV_3 instead of s_3 are shown together with CV_p (in brackets) Li:5.16 (4.21); Na: 0.30 (3.04); K: 0.42(3.42); Mg: 0.45 (3.07); Ca: 0.51 (3.48). It is beyond any experimental uncertainty that the CV_p, instead of being lower than $\overline{CV}$ is about one order of magnitude higher for all the elements, except lithium, for which the effect of $\mu_i \neq \mu$ is covered by the irreproducibility of the area determination in the actual experimental conditions (sodium peak adjacent to the lithium peak). Furthermore, the cumulative Kolmogonov test completely rejects H_0 both for sodium and potassium, but not for calcium and magnesium. There is no reason for assuming that, among the stations, samples can be considered belonging to diverse populations for the first two elements and not for the other ones. As matter of fact, a positive Kolmogonov test does not exclude that the H_0 hypothesis is wrong. So H_0 can be rejected.

In this framework, the individual intervals of confidence recover full meaning. Remembering that CV is independent of the concentration in a large range around the concentrations of interest, and that CV_3 was obtained from 51 data, at 95% confidence level one has:

Table 2a Concentrations [M_i] an relative coefficients of variation (CV) of alkaline and alkaline-earth elements in Antarctic sea water samples collected during the 1989/90 Italian expedition. The digits after the slash refer to the sampling depth in the water column. Three replicates per sample.

	Element									
	Lithium		*Sodium*		*Potassium*		*Magnesium*		*Calcium*	
Station	*[Mi]*	*CV*	*[Mi]*	*CV*	*[Mi]*	*CV*	*[Mi]*	*CV*	*[Mi]*	*CV*
10/20	23.6	5.2	455	0.27	9.68	0.56	54.2	0.06	10.0	0.48
10/50	24.0	4.7	459	0.07	9.80	0.19	55.2	0.30	10.2	0.47
10/100	24.5	5.7	463	0.40	9.72	0.48	55.4	0.12	10.3	0.71
10/300	24.9	4.2	468	0.28	9.91	0.28	55.9	0.05	10.1	0.20
10/600	25.3	5.1	469	0.19	9.95	0.21	55.9	0.55	10.3	0.44
10/1000	25.5	3.8	470	0.27	9.87	0.50	56.2	0.27	10.3	0.32
10/1300	26.6	4.3	472	0.08	9.91	0.58	56.3	0.24	10.9	0.50
49/0.5	21.6	6.2	418	0.28	8.70	0.15	49.5	0.53	9.22	0.77
50/0.5	24.4	4.5	449	0.20	9.38	0.40	53.2	0.20	9.91	0.38
52/0.5	24.3	6.1	438	0.30	9.21	0.40	52.4	0.34	9.70	0.46
18/20	25.1	5.2	465	0.36	9.81	0.31	53.7	0.72	10.2	0.45
19/20	24.8	5.8	459	0.16	9.63	0.49	54.2	0.75	10.1	0.31
23/20	25.0	5.1	461	0.68	9.66	0.60	54.7	0.44	10.0	0.47
25/20	24.7	4.2	460	0.31	9.57	0.41	54.6	0.41	10.2	0.43
4/20	25.3	6.5	471	0.26	10.1	0.13	53.6	0.84	10.4	0.54
9/20	24.4	5.3	468	0.07	9.74	0.71	53.5	0.53	9.86	0.43
6/0.5	24.1	4.8	471	0.26	9.93	0.23	53.9	0.33	9.92	0.92
$\overline{CV_3}$		5.16		0.30		0.42		0.45		0.51
Pooled data	24.6	4.21	460	3.04	9.68	3.42	54.3	3.07	10.10	3.48

Table 2b Concentration ratios $[M_i]/[M_n]$ and $[M_i]/[Na_i]$ of alkaline and alkaline-earth elements in Antarctic sea water samples collected during the 1989/90 Italian expedition. The digits after the slash refer to the sampling depth in the water column. Three replicates per sample.

Station	*Element*											
	Lithium		*Sodium*		*Potassium*		*Magnesium*		*Calcium*		*$[M_i]/[M_n]$*	
	$[M_i]/[M_n]$	$[M_i]/[Na_i]$ 10^3	$[M_i]/[M_n]$	$[M_i]/[Na_i]$	$[M_i]/[M_n]$	$[M_i]/[Na_i]$	$[M_i]/[M_n]$	$[M_i]/[Na_i]$	$[M_i]/[M_n]$	$[M_i]/[Na_i]$	Mean	CV
10/20	0.960	0.052	0.989	1.00	1.000	0.0213	0.999	0.119	0.990	0.022	0.988	1.67
10/50	0.976	0.052	0.999	1.00	1.013	0.0213	1.017	0.120	1.007	0.022	1.003	1.63
10/100	0.996	0.053	1.007	1.00	1.004	0.0210	1.021	0.120	1.021	0.022	1.010	1.09
10/300	1.012	0.053	1.019	1.00	1.024	0.0212	1.031	0.119	0.998	0.022	1.017	1.22
10/600	1.029	0.054	1.020	1.00	1.029	0.0212	1.030	0.119	1.025	0.022	1.026	0.40
10/1000	1.037	0.054	1.022	1.00	1.020	0.0210	1.035	0.120	1.018	0.022	1.026	0.88
10/1300	1.082	0.056	1.026	1.00	1.024	0.0210	1.037	0.119	1.078	0.023	1.049	2.68
49/0.5	0.878	0.052	0.909	1.00	0.899	0.0208	0.912	0.118	0.913	0.022	0.902	1.61
50/0.5	0.992	0.054	0.976	1.00	0.969	0.0209	0.980	0.119	0.982	0.022	0.980	0.87
52/0.5	0.988	0.056	0.952	1.00	0.951	0.0210	0.965	0.120	0.960	0.022	0.963	1.55
18/20	1.021	0.054	1.010	1.00	1.014	0.0211	0.990	0.116	1.012	0.022	1.009	1.83
19/20	1.008	0.054	0.998	1.00	0.995	0.0210	0.999	0.118	1.000	0.022	1.000	0.51
23/20	1.017	0.054	1.003	1.00	0.998	0.0209	1.009	0.119	0.993	0.022	1.004	0.92
25/20	1.004	0.054	1.002	1.00	0.989	0.0208	1.006	0.119	1.013	0.022	1.003	0.89
4/20	1.029	0.054	1.024	1.00	1.040	0.0214	0.988	0.114	1.031	0.022	1.022	1.98
9/20	0.992	0.054	1.018	1.00	1.006	0.0208	0.987	0.114	0.976	0.021	0.996	1.65
6/0.5	0.980	0.051	1.026	1.00	1.026	0.0211	0.993	0.114	0.982	0.021	1.001	2.29
Mean		$0.053 \cdot 10^{-3}$		1.00		0.0211		0.118		0.022		

$$95\%\ \text{I.C.} = [M_i] \pm \bar{s}_3 \times 1.96/\sqrt{3}$$

and in terms of relative I.C.:

$$95\%\ \text{R.I.C.} = 1 \pm 0.01\ \overline{CV} \times 1.96/\sqrt{3} = 1 \pm 0.0113\ \overline{CV}$$

In the case of Lithium ($\overline{CV}_3 = 5.2\%$) and of the other elements considered ($\overline{CV}_3 = 0.5\%$), the R.I.C. is respectively 1± 0.058 or 1±0.0056.

A convenient way of comparing stations for effective no-random variations was to use relative concentrations. Among different criteria, the mean concentration $[M_n]$ was considered as the reference level even though the actual $[M_i]$ values do not belong to the same population tested previously. By comparing the $[M_i]/[M_n]$ values among stations, (vertical columns of Table 2b) dependable information on the extent of variation is rapidly obtained: in this case the level of the reference concentration does not affect the quality of the information. An effect on the quality of the information could be expected whenever comparison of relative concentrations is proposed among elements at the same station, (horizontal line in Table 2b), due to the lack of correlation between the $[M_n]$ values of the metals. Actually, in the present case, while relative values of concentration of the elements may vary among stations to up to about 10% of their $[X_m]$ values, they are fairly constant among elements at the same station. In general, the agreement between $[M_i]/[M_n]$ values, calculated at each station for the different elements, except lithium, was inside a CV range of 0.5–2.5%, typically 1.3%. This interval includes the effects of all the random error sources such as peak area measurement and calibration, detector sensitivity and eluent flow-rate.

The circumstance in which the concentrations of all the elements for any pair of stations *a* and *b* are higher (or lower) by the same factor is further sound proof that the observed differences in composition of the sea water, as a function of distance and water column depth, are effective and, in addition, that these differences, as far as Antarctica is concerned, are merely due to dilution with melt-ice.

The mixing of melt-ice with sea water can be unambiguously proved by comparing for each element (vertical columns in Table 2b) to sodium concentration $[M_i]/[Na_i]$ both measured at the same station. Whenever mixing concerns water at different dilutions, we should find that the relative concentration values do not depend on the station and sampling depth and only depend on the nature of the metal M. Actually, as shown in Table 2b $[M_i]/[Na_i]$ was found to be constant with a CV between 1 and 2%, which includes the effect of among days irreproducibility.

On these bases, some conclusions can be drawn: i) the absolute concentrations of all the elements increase as the depth of the water column (station 10) increases; ii) at constant depth (20 m), station 10 presents the lowest concentrations for most elements, even though these concentrations are close to the interval of random error. In this extreme case the frequency of R_i among elements, which are lower (or higher) than 1, provides an additional criterion for data interpretation; iii) stations 10/1300 and 49/05 present the highest and the lowest R_i values, respectively, for all the elements; iv) regardless of the sampling site location and depth, the maximum variation in concentration observed for all elements considered was around 12%.

Snow

The chemical composition of Antarctic snow impurities depends on several factors such as: source intensity, transport or deposition phenomena, and atmospheric transformations. Antarctic background aerosol has three main sources: continental dust, sea salt and gas-derived species. The relative importance of these sources very much depends on climatic conditions[6].

By using different approaches glaciologists are able to estimate the amounts of sodium, potassium, magnesium and calcium of marine origin in the snow.

Using data reported in literature[7], we were able to answer the preliminary question as to whether or not sea salts in Antarctic aerosol maintain the same molecular ratios R as in sea water. The calculated R values with reference to sodium were: K=0.022, Mg=0.10, Ca=0.05. They are in perfect agreement with the R_{st} of sea water for the first two elements (0.021, 0.12 respectively), and about two times higher for calcium (0.022). Rs of the same magnitude were also obtained by using the data given by Legrand[6]. Whenever the calcium disagreement is an artefact, we may conclude that the sea salt content in Antarctic snow maintains the same molecular ratios for alkaline and alkaline-earth elements as in sea water.

By further considering that the marine concentration and total concentrations of sodium practically coincide with the data found in the surface layer of Antarctic snow[6], one should expect the R_{st} values for the snow relevant to the Italian 1989–90 expedition, to be near the R_{st} values for the sea.

The airborne particulate matter were measured in several Terranova Bay stations during the 1989/90 expedition[8]. From their data we have found that the average molar ratio K/Na is 0.26, more than ten times higher than in sea water. These findings agree with the conclusions of recent studies which assume that continental and marine impacts are relatively modest compared to gas-derived sulphuric aerosol in present-day central Antarctica.

Table 3 shows the results obtained in terms of mean concentrations, CV and R. Note that in this case, owing to the preconcentration step, large CV values and large CV oscillations were found. By taking this effect on confidence intervals into account, some considerations can be drawn:

— the highest concentrations for the elements were found at station SN6, while the lowest were generally found at SN3;
— station SN5 (not shown in Figure 2) is the only one where the R values are in the range of the corresponding R_{st} values for sea water. In the other cases, Rs oscillate significantly. These values should further increase whenever the marine concentration of sodium in snow is only a part of the total concentration. Moreover one should expect K/Na molar ratios around 0.25 if the impurities are due to airborne particulate aerosol.

By considering the $[M_i]/[Na_i]$ values in Table 3, the following median R_{st} values were obtained: K=0.05; Mg=0.09; Ca=0.07. These values, quite similar to those obtained for lake and melt waters (see below) are far from the sea water R_{st} values.

These findings show that impurities of different origins contribute to the total concentration values and that the distance from the sea is not the most important parameter. This is in agreement with Legrand's observations (1988).

Table 3 Mean concentration (μM), coefficient of variation CV and concentration ratio $[M_i]/[Na_i]$ values for sodium, ammonium, potassium, magnesium and calcium in superficial snow samples collected during 1989/90 Italian expedition in Antarctica. Three replicates per sample.

	Element														
Station	*Sodium*			*Ammonium*			*Potassium*			*Magnesium*			*Calcium*		
	conc.	CV	$[M_i]/[Na_i]$	conc.	CV	$[M_i]/[Na_i]$	conc.	CV	$[M_i]/[Na_i]$	conc.	CV	$[M_i]/[Na_i]$	conc.	CV	$[M_i]/[Na_i]$
SN1	5.1	0.1	1.00	1.7	8.7	0.34	0.61	7.0	0.12	0.71	20	0.14	0.84	18	0.16
SN2	16.6	0.1	1.00	2.1	1.5	0.13	0.47	2.2	0.03	0.38	31	0.02	0.40	24	0.02
SN3	4.0	0.1	1.00	1.3	3.5	0.32	0.19	12	0.05	0.36	21	0.09	0.34	41	0.09
SN4	3.1	2.0	1.00	0.26	13	0.08	0.27	25	0.09	0.46	6.7	0.15	0.91	12	0.29
SN5	15.4	0.3	1.00	13.3	0.1	0.86	0.36	7.5	0.02	1.29	6.7	0.08	0.43	19	0.03
SN6	21.8	0.2	1.00	9.0	0.6	0.41	1.02	1.7	0.05	1.90	3.9	0.09	1.01	22	0.05

Table 4 Mean concentration and variation coefficient (CV) values for lithium, sodium, potassium, magnesium and calcium in filtered and acidified water samples (Lakes and Meltwaters) collected during the 1989/90 Italian Expedition in Antarctica. All the concentrations are expressed in mM with the exception of lithium the values of which are in μM units. Three replicates per sample.

Station	*Element*									
	Lithium		*Sodium*		*Potassium*		*Magnesium*		*Calcium*	
	conc.	CV	conc.	CV	conc.	CV	conc.	CV	conc.	CV
LW2	n.d.		1.49	0.3	0.061	0.3	0.124	0.4	0.066	0.4
LW7	0.36	22	1.10	0.2	0.059	0.2	0.098	0.2	0.265	0.2
LW8	1.58	5.7	5.02	0.3	0.210	0.1	0.404	0.2	0.271	0.5
LW9	1.87	5.7	6.06	0.5	0.245	0.3	0.509	0.4	0.375	0.5
LW10	3.89	0.5	2.67	0.5	0.116	0.1	0.426	0.4	0.634	0.1
IW9	1.58	0.4	5.29	0.1	0.211	0.2	0.434	0.2	0.308	0.6
IW2	n.d.		0.519	0.7	0.021	0.2	0.044	0.2	0.033	0.3
IW11	n.d.		0.074	0.3	0.003	0.4	0.011	0.4	0.012	0.3
IW12	n.d.		0.186	0.4	0.007	0.1	0.011	0.1	0.006	0.1

Lake and meltwaters

Table 4 shows the results obtained for lake (LW) and flowing melted waters (IW). The good similarity among R_{st} values, which was generally observed, (not shown in Table 4) leads to the conclusion that the salt content in these waters has the same origin, although it is not marine.

This assumption was further supported by using the IW2 water as a reference. In fact a comparison of $[M_i]/[M_{IW2}]$ ratios at constant station shows that most stations present generally constant values for the different analytes if the uncertainty which is due to the size of the actual random errors is considered.

Ammonium concentrations, which were also measured along with the other analytes, are not shown in Table 4 due to their lower reliability. In fact, because ammonia in the samples was not to be determined initially, they were filtered on field before acidification under a mild vacuum with a consequent loss of an unknown amount of ammonia. The melt water enrichment factors, *f*, with reference to sea water, were estimated by averaging homogeneous R_{st} values. These average values and the relevant enrichment factors (in brackets) were:

$$Li=3\times10^{-4}\ (f=10);\ K=0.04\ (f=2);\ Mg=0.08\ (f=0.7);\ Ca=0.05\ (f=2.5).$$

With reference to the IW2, station LW9 presents the highest ratios (11.6±0.1) for sodium, potassium, magnesium and calcium while station IW11 represents the lowest ones (0.21±0.07), thus confirming that impurities of the same origin are present in melt waters.

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