

# Transport and modification of humic substances present in Antarctic snow and ancient ice

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We performed a study of fulvic acids extracted from fresh and aged snow, and from recent and ancient ice in Antarctica. The fresh snow samples were collected in coastal and inland sites to evaluate the influence of the distance from the sea on organic matter transport. Moreover, in a site (Melbourne Mountain) samples were collected at different heights to study the influence of altitude on transport. The obtained results showed that dissolved fulvic acid concentrations are influenced neither by distance nor by height while particulate fulvic acid concentrations are influenced by both parameters. Moreover, the results showed that fulvic acids transported for a long distance can undergo chemical modifications. Chemical modifications are better evidenced by the analysis of samples taken in trenches at different depth, which showed structural changes attributable to the loss of nitrogen-containing compounds and to an increase in aromatic character of the structures due to reduction and/or condensation processes. With ageing, the humification process proceeds with heavy carbon losses as demonstrated by results obtained from fulvic acids isolated from ice aged between twenty-five thousand and seventy thousand years.

## Introduction

Organic and inorganic substances present in Antarctic snow may provide valuable information for developing transfer models of atmospheric particles to soil and for making a thorough study of the global distribution of chemicals in the atmosphere.<sup>1</sup> In fact, in Antarctica the snow plays a fundamental role in the transfer to soil of both compounds adsorbed on particulates and those present in the gas phase.<sup>2</sup>

Previous studies on humic compounds present in marine aerosol, as well as in Antarctic snow, demonstrated the marine origin of these compounds.<sup>3–5</sup> This confirmed the importance of marine aerosol in the transport of chemical compounds originating from human and natural activities according to the model of adsorption over micro spray (Spray Drops Adsorption Layer Model: SDALM). This model is based on the exchange of materials at the sea water–air interface where the presence of surfactants plays an important role by allowing the formation of the so-called microlayer, a very thin layer (40–80  $\mu\text{m}$ ) over the water surface.

Humic substances, in particular fulvic acids, represent one of the most relevant fractions (50–70%) of natural surfactants dissolved in the water.<sup>6,7</sup> Preliminary studies performed in our laboratory demonstrated that fulvic acids, notwithstanding their presence both in microlayer and in water medium, have in the former a concentration 2.5–8 times higher than in the latter phase. This means that fulvic acids, due to their nature as low molecular weight surfactants highly concentrated in the microlayer, are major players in the formation of marine aerosol.<sup>7</sup> Moreover, fulvic acids, thanks to their high complexing capability, also play a primary role in the transport of heavy metals and organic contaminants.<sup>8,9</sup>

According to the SDALM model, marine spray produced by collapse of gas bubbles in breaking waves and foams is made of very minute drops with a size ranging from a few micrometres to 0.02  $\mu\text{m}$ .<sup>10,11</sup> These drops have a very thin superficial layer where surfactants are highly concentrated and a core with

fulvic acid concentration similar to sea water. During aerosol formation drops become smaller and smaller due the loss of their water core. This implies that while aerosol drops shrink, their organic concentration increases, transforming them into prevalently organic particles when they reach a diameter  $\ll 1 \mu\text{m}$ .<sup>12</sup> These smaller particles have a longer life span in the air that suggests how humic substances present in the sea water can be transported well inside the hinterland.

This study aims to provide qualitative and quantitative data on humic substances in the Antarctic snow in order to have a better understanding of the transport of humic substances *via* marine aerosol.

## Experimental

### Materials

Snow and ice samples analyzed in the study were collected throughout four different Antarctic expeditions (1996–1997; 1998–1999; 2000–2001; 2001–2002) in the context of the Italian research program in the Antarctic.

Sampling stations were located in a very wide area from the coastal area near the Italian base to 400 km inside the continent in the Dome C area. The sampling sites of snow were grouped, on the basis of position characteristics such as distance from the coast and altitude above sea level, into two categories: those relatively close to the coast, such as Mount Melbourne, Hells Gate, Terra Nova Bay, and those far from the coast, such as Dome C, Talos Dome, Rennick Glacier and Rennick Nevè. The ice samples were collected in Hells Gate (recent ice samples) and Frontier Mountain (ancient ice samples) sites. In particular ancient ice samples, aged between twenty five thousand and seventy thousand years, usually flow under the surface but can be collected where they emerge. These samples were collected at 250 km from the coast.

The geographic co-ordinates of these sampling sites are reported in Table 1.

**Table 1** Geographical co-ordinates

Sample	Level/m	Distance from sea/km	Latitude (S)	Longitude (E)
Melbourne 4a	360	10	74° 32'	164° 47'
Melbourne 4c	1280	10	74° 26'	164° 45'
Melbourne 4d/e	2255	10	74° 22'	164° 40'
Hells Gate	0	1	74° 52'	163° 49'
Campo Icaro	57	0.1	74° 42'	164° 06'
BTN	0	0	74° 41'	164° 07'
Talos Dome 1	2350	330	73° 07'	155° 25'
Talos Dome 2	2415	390	73° 56'	150° 08'
Talos Dome 3	2400	370	73° 32'	152° 34'
Rennick Glacier 1	2270	125	73° 19'	162° 29'
Rennick Glacier 2	2042	150	73° 05'	162° 38'
Rennick Glacier 3	1646	200	72° 33'	162° 47'
Rennick Nevè 1	2370	200	73° 14'	160° 14'
Rennick Nevè 2	2373	220	73° 02'	159° 54'
Dome C	2415	400	73° 14'	160° 14'
Frontier Mountain 1	2068	210	72° 57'	160° 26'
Frontier Mountain 2	2068	210	72° 57'	160° 23'
Frontier Mountain 3	1940	210	72° 58'	160° 27'
Frontier Mountain 4	2184	210	72° 58'	160° 17'

In the case of all samples taken from coastal areas and a few samples coming from Dome C, the sampling involved the upper layer of intact fresh snow mantle (about 10 cm deep from surface). In the case of trenches, samples were taken not only from the surface, but also from an intermediate level (generally one metre below the surface, but 3.5 m in the case of the Dome C trench) and a lower level (generally 2 m below the surface, but 6.9 m in the case of the Dome C trench).

In order to evidence time-related composition changes, the sampling in the coastal area was performed every time it snowed.

All the samples were frozen at  $-30\text{ }^{\circ}\text{C}$  immediately after sampling and analysed three months later.

Amberlite XAD-8 resin (Polysciences, INC) was used to extract humic substances (HS) from snow. In order to eliminate organic compounds (*e.g.* hydrolysed acrylic acid) bleeding from XAD 8 columns (36 ml), cleaning by Soxhlet sequential extractions for 24 h were performed with methanol, diethyl ether, acetonitrile and methanol. The resin was then packed in glass columns and rinsed five times with 0.1 N NaOH and 0.1 N HCl, respectively, and then washed with deionised water until DOC concentration was less than  $0.3\text{ mg l}^{-1}$  (deionised water).

Millipore polycarbonate filters (pore sizes  $0.45\text{ }\mu\text{m}$  and diameter 140 mm) were used for filtration.

Millipore cellulose acetate ultrafiltration membranes with molecular weight cut off 500 Dalton (diameter 76 mm) were used for ultrafiltration.

All reagents used were analytical grade.

### Humic substance isolation

The procedure proposed by Thurman and Malcolm<sup>13</sup> was used for HS recovery from melted snow after filtration by means of  $0.45\text{ }\mu\text{m}$  polycarbonate filters (Millipore). Briefly, after acidification to pH 2, the filtered samples (20–30 l) were passed through the Amberlite XAD-8 resin column (36 ml). HS were recovered from the columns with 0.1 M NaOH, and the alkaline extract was then acidified to pH 1 with HCl in order to separate humic acids (HA, precipitate) from fulvic acids (FA, soluble in acid solution). FAs were purified by dialysis by means of ultrafiltration apparatus (diafiltration).<sup>14</sup> HAs were never found.

Humic substances present in the particulate were recovered from  $0.45\text{ }\mu\text{m}$  filters by shaking them with 250 ml of 0.1 M NaOH, for 24 h; filters were removed from this solution which

was then acidified and passed through a column packed with XAD-8 resin. Humic substances taken up by the resin were released by a counter current wash with 0.1 M NaOH solution that was further acidified in order to separate fulvic acids from humic acids. Also in this case humic acids were never found.

The acid solution containing fulvic acids was dialysed, frozen and then lyophilised. Yields of dissolved fulvic acid (DFA) and fulvic acids in particulate (PFA), as well as their total amounts, were calculated by weighing the lyophilised matter.

### Chemical and spectroscopic analyses

The carbon, hydrogen, nitrogen and sulfur elemental content of humic substances was determined with a Carlo Erba model EA11110 CHNS-O Element Analyser. Samples for Fourier Transform InfraRed (FTIR) spectroscopy were prepared by mixing 1 mg of the fulvic acid with 100 mg of oven-dried KBr ( $110\text{ }^{\circ}\text{C}$ ). The spectra were recorded using a Philips model PU9800 FTIR spectrophotometer working in diffuse reflectance conditions. Reflectance spectra were converted to Kubelka Munk units, which are directly proportional to the concentration of the scattering medium. One hundred scans were recorded with a resolution of  $4\text{ cm}^{-1}$  and normal apodization.

<sup>13</sup>C NMR spectra were determined in NaOD 0.5 M by a Varian spectrometer, model XL-300. Samples were prepared by dissolving the dried residue (3.0 mg) in 1 ml of NaOD in an NMR tube (5 mm). The operating conditions were: 75 MHz, pulse  $45^{\circ}$ , acquisition time 0.1 s, delay time 0.5 s. About 1 800 000 scans were accumulated. Spectra were performed in broadband decoupling mode. Under these conditions, a clear spectrum should be obtained with distinct single peaks for each carbon atom; because of the molecular complexity of samples, the spectra show many poorly resolved signals.

## Results and discussion

### Surface snow

The amount of dissolved fulvic acid (DFA) found in fresh superficial snow (Table 2) ranged from  $0.016$  to  $0.397\text{ mg l}^{-1}$  in the sampling sites near to the coast (up to 10 km; BTN, Melbourne and Hells Gate) and from  $0.025$  to  $0.146\text{ mg l}^{-1}$  in the sampling sites far from the coast (200–400 km; Talos Dome, Rennick Glacier, Rennick Nevè and Dome C).

**Table 2** Dissolved fulvic acids (mg l<sup>-1</sup>) in superficial snow<sup>a</sup>

	Dec 96	Nov 98	Dec 98	Jan 99	Dec 00	Dec 01	Jan 02
Melbourne 4a		0.343	0.055	0.129			
			0.052				
Melbourne 4c		0.190	0.087	0.027			
			0.082				
Melbourne 4d/e		0.253	0.041	0.016			
			0.051				
Campo Icaro		0.397		0.069		0.051	0.100
							0.080
BTN						0.054	
						0.263	0.168
						0.096	
Hells Gate						0.059	0.158
							0.105
Talos Dome 1						0.072	
Talos Dome 2						0.115	
Talos Dome 3						0.050	
Rennick Glacier 1	0.027						
Rennick Glacier 2	0.026						
Rennick Glacier 3	0.146						
Rennick Nevè 1					0.025		
Rennick Nevè 2					0.040		
Dome C						0.067	
						0.092	
						0.053	
						0.052	
						0.062	
						0.055	

<sup>a</sup> Relative standard deviations are less than 3%.

The particulate fulvic acid concentrations in fresh superficial snow (Table 3) ranged from 0.019 to 0.440 mg l<sup>-1</sup> in the sampling sites near to the coast and from 0.007 to 0.083 mg l<sup>-1</sup> in the sites far from the coast. The statistical analysis performed on the two groups of data (BTN, Melbourne and Hells Gate are coastal and Talos Dome, Rennick Glacier, Rennick Nevè and Dome C are internal (Table 4)) showed that the coastal DFA and PFA data are not normally distributed (standardised skewness is outside the range -2 to +2). The comparison of medians performed by means of a Kolmogorov-Smirnov test showed that the DFA concentrations are not different at a significance level of 95% while PFA concentrations in coastal samples are significantly ( $p < 0.05$ ) higher than those found in the sites far from the coast. Moreover the percentage of fulvic acids in particulates increases on average going from coastal to inland sites (Table 5). This finding confirms the model of transport "via marine aerosol" for which fine particles ( $\ll 0.49$  mm), having a highly reduced mass ( $10^{-17}$  g) and being mainly composed of organic material, are transported over larger distances from the coast.<sup>12</sup> In aerosol particles the organic matter content increases with decreasing particle size; in turn, these smaller particles have higher mobility and life span leading to deposition of humic substances

**Table 3** Particulate fulvic acids (mg l<sup>-1</sup>) in superficial snow<sup>a</sup>

	Dec 96	Nov 98	Dec 98	Jan 99	Dec 00	Dec 01	Jan 02
Melbourne 4a		0.019	0.059	0.053			
			0.033				
Melbourne 4c		0.030	0.047	0.074			
			0.021				
Melbourne 4d/e		0.200	0.056	n.d.			
			0.034				
Campo Icaro		0.055		0.037		0.262	0.293
							0.098
BTN						0.136	
						0.440	0.144
						0.149	
Hells Gate						0.082	0.231
							0.221
Talos Dome 1						0.083	
Talos Dome 2						0.042	
Talos Dome 3						0.007	
Rennick Glacier 1	0.010						
Rennick Glacier 2	0.026						
Rennick Glacier 3	0.026						
Rennick Nevè 1					0.065		
Rennick Nevè 2					0.022		
Dome C						0.018	
						0.039	
						0.009	
						0.025	
						0.035	
						0.034	

<sup>a</sup> Relative standard deviations are less than 3%.

being directly related with the distance from the coast.<sup>7</sup> On the other hand, the transport process could be influenced by height above sea level.

The only homogeneous series of samples taken at different heights, but in the same area, was that performed in the coastal area of Mount Melbourne. The data evidence that there is a growing percentage of FA in particulate with increasing altitude of sampling area confirming, also in this case, the model of transport "via marine aerosol".

Moreover, it can be observed that the percentages of FA in the particulates of snow samples collected in the area of Mount Melbourne during four successive snowfalls steadily increased (Fig. 1). We attributed this increase to the advancement of summer that induces: 1) the gradual melting of the ice pack so that the sea gradually approaches the sampling sites; 2) the algal bloom that, in turn, increases the exchange of materials at the water-air interface. The gradual melting of the pack ice releases in water the trapped material in the ice which is mainly composed of particulate humified organic material<sup>15</sup> and the algal bloom enriches the particulate organic matter in surface water (algal debris) and then the amount of organic matter exchanged at the water-air interface.<sup>16</sup>

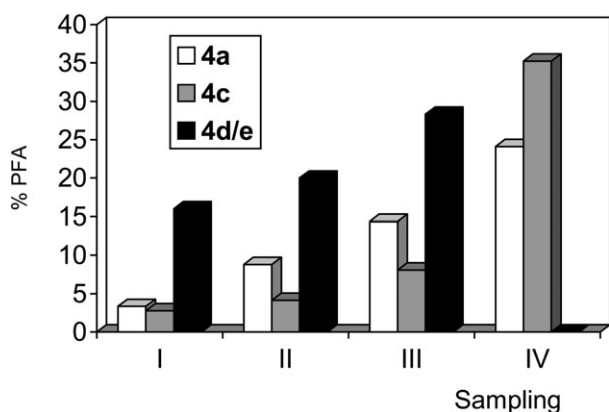
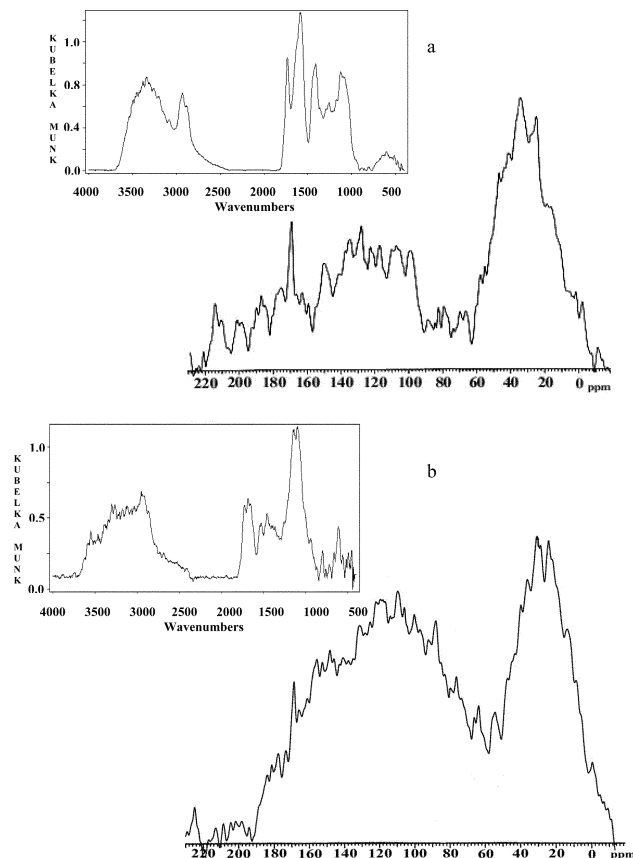
**Table 4** Statistical data of dissolved (DFA, mg l<sup>-1</sup>) and particulate (PFA, mg l<sup>-1</sup>) fulvic acids isolated from fresh snow

	DFA		PFA	
	Coastal sites	Inland sites	Coastal sites	Inland sites
Mean	0.122	0.0630	0.121	0.0315
Median	0.0845	0.0540	0.0740	0.0260
Standard deviation	0.101	0.0347	0.108	0.0213
Variance	0.0104	0.00120	0.0118	0.000454
Standardised skewness	2.998	1.869	2.830	1.925
Standardised kurtosis	1.630	1.043	1.903	1.229

**Table 5** PFA percentage (%) in particulates

	Dec 96	Nov 98	Dec 98	Jan 99	Dec 00	Dec 01	Jan 02
Melbourne 4a		3.3	8.8	24.1			
Melbourne 4c		2.7	4.1	35.3			
Melbourne 4d/e		16.0	20.0	n.d.			
Campo Icaro		4.6		6.1	8.3	6.6	4.4
BTN					10.3	6.1	1.3
Hells Gate					6.2	2.1	4.0
Talos Dome 1							12.1
Talos Dome 2						9.6	
Talos Dome 3						13.3	
Rennick Glacier 1	6.67						
Rennick Glacier 2	17.0						
Rennick Glacier 3	16.2						
Rennick Nevè 1					9.4		
Rennick Nevè 2					16.9		
Dome C						18.9	
						25.2	
						13.8	
						21.0	
						19.1	
						15.3	

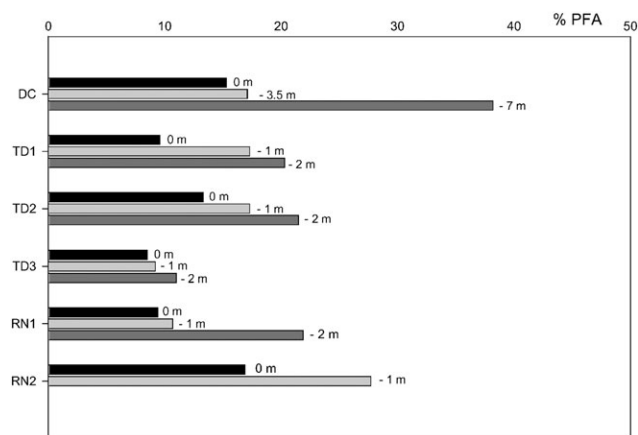
Concerning the structural features of the total fulvic acids (TFA, mixture of dissolved and particulate fulvic acids) in samples taken in the different zones, we did not observe significant differences in atomic C/N, H/C, and S/C ratios calculated by elemental analysis data even if the variability among the data is very high (C/N ranges between 8.13 and 33.4, H/C between 1.41 and 2.22 and S/C between 0.000 and 0.026). Nevertheless, spectroscopic analyses ( $^{13}\text{C}$  NMR and FTIR spectroscopy) showed differences in carboxylic group content which decreased going from coastal to inland samples, and in aromatic character which increased. FTIR and  $^{13}\text{C}$  NMR spectra of both a coastal sample (Campo Icaro) and an inland sample (Dome C) (Fig. 2a, b) are characterised by a band at 168 ppm ( $^{13}\text{C}$  NMR) and a signal at  $1700\text{ cm}^{-1}$  (FTIR) due to the presence of carboxylic groups<sup>17–20</sup> which appear intense in coastal samples and which disappear in inland samples. Moreover, in  $^{13}\text{C}$  NMR of the inland sample we can note increases in signals in the region 120–160 ppm due to an increase in aromatic character of fulvic acids due to progress

**Fig. 1** Percentage of fulvic acids present in particulates in fresh snow sampled in Melbourne Mountain at different heights in four different samplings.**Fig. 2** FTIR and  $^{13}\text{C}$  NMR spectra of both a coastal sample (Campo Icaro, a) and an inland sample (Dome C, b).

of the humification process. These findings lead to the hypothesis that fulvic acids in particles precipitated near their place of origin had not the time to undergo chemical modifications while transported by the marine aerosol. In fact, the greater distance from the coast justifies a longer permanence of particles in the atmosphere and a longer time lapse before their deposition with snowing and the admixture with materials present in the hinterland, eventually moved by katabatic winds.

### Trench snows

The analysis of samples taken in trenches at different depths showed that there was an increasing proportion of FA in particulate with increasing sampling depth (Fig. 3). This was particularly evident in the trench sampled at Dome C where the

**Fig. 3** Percentage of fulvic acids present in particulates in snow collected in trenches from Dome C (DC), Talos Dome (TD) and Rennick Nevè (RN) at different depths.

**Table 6** Elemental analysis (%) and atomic ratios of total fulvic acids extracted from Dome C trench<sup>a</sup>

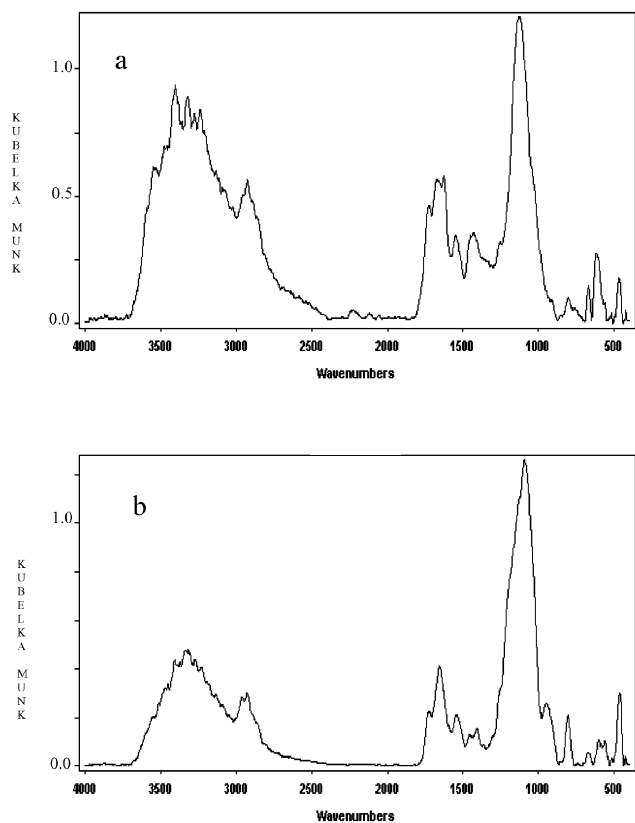
Sampling depth	C	N	H	C/N	H/C
0 m	41.5	5.1	6.9	9.47	2.10
3.1 m	42.3	3.2	4.2	15.26	1.20
7.0 m	43.5	5.1	4.6	9.87	1.27

<sup>a</sup> Relative standard deviations are less than 5%.

sampling reached its maximum depth (7 m). This finding could suggest that organic substances trapped within the snow undergo further time-related modifications that lead to the observed increase in the FA proportion of particulates. This pattern was not found in all the trenches, probably due to the shallow depth of sampling in some sites and to the different compactness of the lower snow layers.

Moreover, the atomic ratios of the total fulvic acids (TFA) measured in the different samples taken at Dome C (Table 6) showed an increase of C/N and a decrease of the H/C ratios passing from surface to 3.5 m depth, in agreement with the hypothesis of time-related changes. These changes are attributable to the loss of nitrogen-containing compounds and an increase in structural aromatic character due to reduction and/or condensation processes. It is noteworthy that the sample taken in the same trench at a depth of 7 m did not show any further increase in the C/N ratio or decrease in the H/C ratio. This seeming discrepancy is probably due to a different mechanism of carbon loss with the increasing depth and then aging. In samples aged up to a thousand years there is indeed the possibility of a much more massive decarboxylation than in recent surface samples, affecting the reference element for evaluating nitrogen and hydrogen variations.

Confirmation of this transformation process evidenced by elemental analysis was achieved by the comparison of FTIR spectra in samples taken on the surface and 7 m below it (Fig.



**Fig. 4** FTIR spectra of fulvic acids isolated from samples taken on the surface (a) and -7 m (b) in Dome C trench.

**Table 7** Elemental analysis (%) and atomic ratios of the total fulvic acids isolated from ancient ice (Frontier Mountain) samples and from recent ice (Hells Gate)<sup>a</sup>

	C	N	H	C/N	H/C
Frontier Mountain 1	41.5	4.2	5.5	11.6	1.59
Frontier Mountain 2	42.0	4.3	6.1	11.5	1.74
Frontier Mountain 3	40.8	4.3	5.7	11.0	1.68
Frontier Mountain 4	40.5	4.9	5.3	9.54	1.57
Hells Gate 1	42.5	3.5	5.3	14.1	1.52
Hells Gate 2	40.5	5.3	7.5	8.97	2.22
Hells Gate 3	40.2	5.9	8.4	7.98	2.52

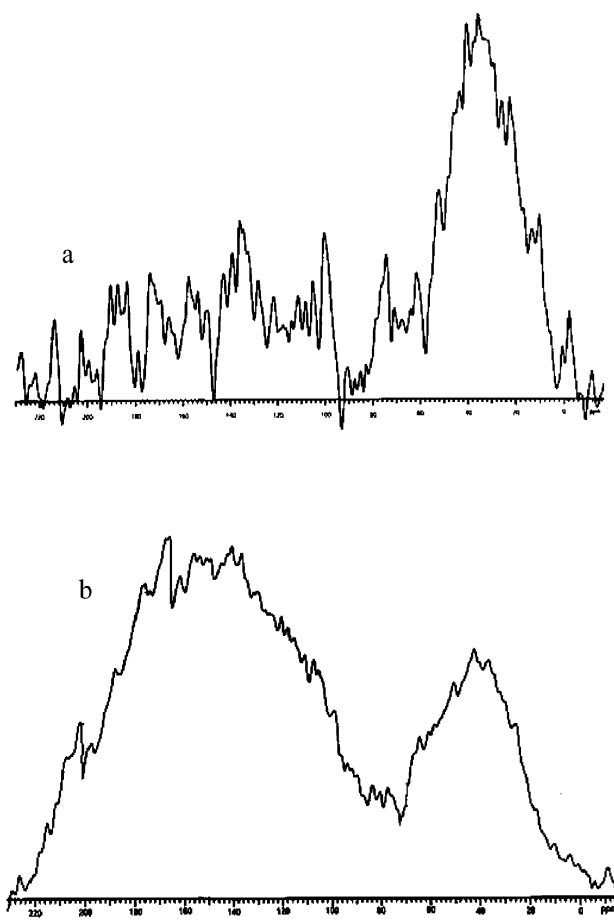
<sup>a</sup> Relative standard deviations are less than 5%.

4). This comparison shows the “ageing” of FA isolated from the deeper sample by the decrease in the band centred at 3300  $\text{cm}^{-1}$  (stretching of O–H and N–H bonds) and in peaks centred at 1670 and 1625  $\text{cm}^{-1}$  whose decrease is related to the loss of nitrogen compounds. Contemporaneously, a decrease in the peak at 1720  $\text{cm}^{-1}$  characteristic of carboxyl groups was observed that supports the hypothesis of carbon loss as a consequence of decarboxylation processes.

#### Ancient and recent ice matrices

The analysis of ancient ice samples (Frontier Mountain) and recent ones (Hells Gate) did not show differences in total fulvic acid (TFA) concentrations. They ranged from 0.138  $\text{mg l}^{-1}$  to 0.223  $\text{mg l}^{-1}$  in ancient ice samples and from 0.080  $\text{mg l}^{-1}$  to 0.225  $\text{mg l}^{-1}$  in recent ones.

In order to confirm the heavy carbon losses in the long term we determined the atomic ratios in TFA isolated from ice aged



**Fig. 5** <sup>13</sup>C NMR spectra from a recent ice sample (a) and an ancient ice sample (b).

between twenty-five thousand and seventy thousand years. Table 7 shows that C/N atomic ratios of Frontier Mountain samples are slightly higher than those of FA extracted from Hells Gate 2 and 3 samples, in spite of the great difference in age. Conversely, Hells Gate 1 fulvic acids, despite the fact that they are surely younger than those of Frontier Mountain showed a high C/N atomic ratio. In effect the Hells Gate 1 ice sample was collected at 1 m depth while Hells Gate 2 and 3 were superficial samples, so surely characterised by more recent formation with respect to Hells Gate 1. Nevertheless, all Hells Gate samples were characterised by a great difference in age compared to those of Frontier Mountain. The differences between C/N atomic ratios, if they are put in relation to the age of samples, showed that the humification process occurs at the beginning with the loss of peptide fragments and after with the loss of aliphatic carbon fragments. On the other hand, the comparison of  $^{13}\text{C}$  NMR spectra from a recent ice sample (Fig. 5a) and an ancient ice sample (Fig. 5b) demonstrates that this technique may show the increased humification in the older sample. In fact, the ancient ice samples are characterised by a higher content of aromatic structures that are evidenced by strong signals between 120 and 160 ppm. At the same time it is possible to evidence the decrease in the aliphatic character, passing from young to old ice, by the decrease in the signals between 30–40 ppm that characterise the resonance of aliphatic carbon atoms. These signs of an increased humification are paralleled by a strong decrease of the signal centred at 168 ppm that confirms the heavy decarboxylation in the long term. Therefore,  $^{13}\text{C}$  NMR spectra show differences in the humification process occurring over a very long time lapse that are not evidenced by atomic ratios due to the carbon atom loss caused by decarboxylation processes.

## Conclusions

The study of fresh snow samples provided evidence for the validity of the model of transport “via marine aerosol” for which fine particles having a highly reduced mass and being mainly composed of organic material, are transported at larger distances from the coast. The structural differences shown by organic matter found at greater distances from the coast, can be justified by a longer permanence of particles in the atmosphere where they can undergo chemical modifications. The chemical modifications to which fulvic acids can be subjected are better evidenced by results obtained from snow sampled in the trenches. In the aged samples time-related transformations leading to loss of nitrogen-containing groups and an enrichment of aromatic character of structures were shown. These transformations were confirmed by the analysis of ancient and recent ice samples.

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