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## Soluble species in aerosol and snow and their relationship at Glacier 1, Tien Shan, China

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**Abstract.** Simultaneous sampling of aerosol ( $n = 20$ ) and snow ( $n = 114$ ) was made at Glacier 1, Tien Shan, between May 19 and June 29, 1996. Similar temporal patterns of some major ion (calcium, magnesium, potassium, sodium, chloride, and sulfate) concentrations between snow and aerosol show that snow chemistry basically reflects changes in the chemistry of the atmosphere. This gives us confidence in the reconstruction of past atmospheric change using some snow data. There are no significant correlations between aerosol and snow samples for ammonium and nitrate. This suggests that postdepositional and/or postcollection processes may alter ammonium and nitrate concentrations in snow. The fact that the measured cations in aerosol and snow always exceed the measured anions suggests that the atmosphere is alkaline over Glacier 1, Tien Shan. In aerosol and snow samples, calcium is the dominant cationic species, with sulfate and presumed carbonate being the dominant anions. There is a very good inverse relationship ( $r = 0.96$ ) between the equivalence ratio of calcium to sulfate and the ratio of ammonium to sulfate in aerosols, but this relationship does not hold for snow. This further suggests that postdepositional and/or postcollection processes exert important controls on ammonium concentrations in snow. Although melt-freeze cycles might increase the concentration of all crustal species through progressive dissolution of dust, these cycles seem most important for magnesium and carbonate.

### 1. Introduction

Glaciochemical records have been extensively studied over polar ice sheets and mountain glaciers and have become established as one of the primary archives of atmospheric composition of the past [Mayewski *et al.*, 1990]. However, the interpretation of glaciochemical records is based on the assumption that there is a close relationship between changes in chemical composition of the atmosphere and that in snow [Wolff, 1996]. To fully interpret glaciochemical records of change in the composition of the atmosphere, recent studies have tried to develop transfer functions among air, snow, and ice [Dibb and Jaffrezo, 1997]. Several programs, initiated at Dye 3 (south Greenland) in 1989 and now running at Summit (central Greenland), have started to address these problems [Dibb *et al.*, 1992; Dibb and Jaffrezo, 1997; Davidson *et al.*, 1993]. The Dye 3 Gas and Sampling Program (DGASP), in which a wide variety of constituents were sampled in aerosol and fresh snow [Jaffrezo and Davidson, 1993], was designed as an international effort to study the processes influencing chemical species that eventually reach the deep ice in the south of Greenland. Detailed examination of a 2-week period in April 1989 during the Dye 3 Gas and Aerosol Sampling Program showed that although the overall seasonal pattern in the air was reflected in the snow for a number of species (e.g., MSA, sulfate, sodium,

calcium, aluminum), it was difficult to use snowpit and ice core data to identify specific daily events [Davidson *et al.*, 1993]. Natural radionuclides such as <sup>7</sup>Be and <sup>210</sup>Pb in the atmosphere and snow near Summit, Greenland, indicate the complexity of air-snow transfer processes [Dibb *et al.*, 1992]. For the reversible species, i.e., volatile components of the atmosphere, postdepositional processes modify chemical concentrations in snow [Dibb *et al.*, 1994]. However, little attention has been given to air-snow relationships in mountain glaciers. Only one study conducted at central Asia reported the major ion concentration of aerosol collected by Teflon filter using a low-volume sampling system [Wake *et al.*, 1994].

Although the chemical composition of the snowpack at Glacier 1, Tien Shan, was investigated by Wake *et al.* [1992] and Williams *et al.* [1992], no companion aerosol studies have been conducted to date. Since Glacier 1 is near the Lanzhou Institute of Glaciology and Geocryology (LIGG) Mountain Glaciological Station and Daxigou Meteorological Station, it is relatively easy to carry out daily aerosol and snow sampling and to compare these measurements to meteorological data. Simultaneous aerosol and surface snow samples were collected between May 19 and June 29, 1996, at Glacier 1, Tien Shan, and analyzed for major ions using ion chromatography.

The main purpose of this study is to examine the temporal variation in aerosol composition over Glacier 1, Tien Shan, and investigate air-snow relationships through companion studies of snow composition as an aid to interpreting future ice core data.

### 2. Site Description

All samples used in this study were collected from Glacier 1 (43.05°N latitude, 86.49°E longitude) in the eastern Tien Shan of northwest China (Figure 1). The Tien Shan is bordered by

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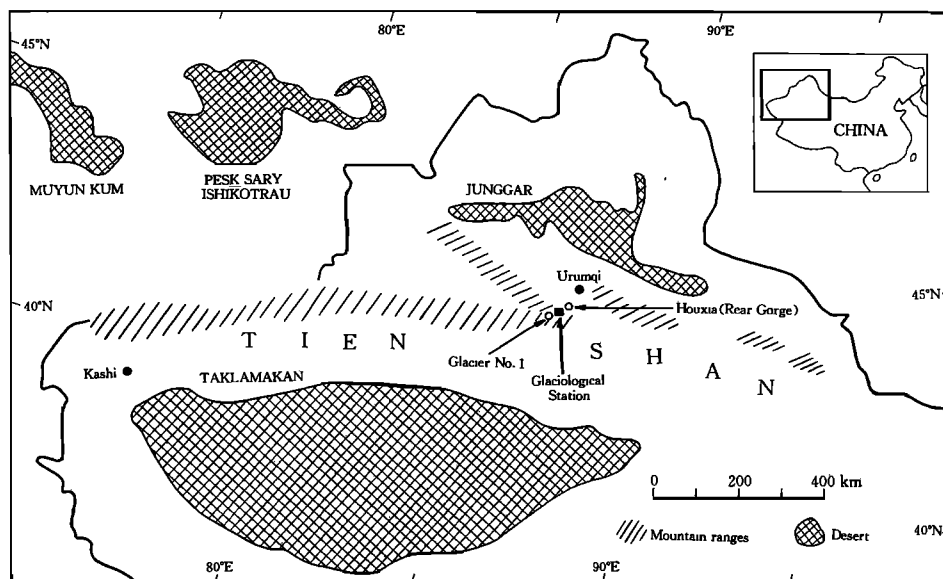


Figure 1. Location map of Glacier 1, Tienshan, and the surrounding deserts [after Wake *et al.*, 1992].

large deserts on three sides: the Gobi Desert to the east, the Taklamakan Desert to the south, the Junggar, Resk Sary Ishikotran, and Muyum Kum Deserts on the north. These regions experience an inland continental climate. Moisture is derived primarily from the west and north [Li and Xu, 1980]. The study site is located in the Daxigou Valley, at the headwater of the Urumqi River, ~50 km southwest of the town of Houxia (Rear Gorge), which is the site of Yaojin steel mill and a cement plant. Coal and iron are mined in the surrounding hills. Meteorological data from the Daxigou Meteorological Station indicate that up-valley winds predominate in the spring and summer, especially during the afternoon. The weather is usually clear until 1400 (Beijing time), then it is cloudy or snowing during the sampling period (unpublished data).

Glacier 1 (area 1.84 km<sup>2</sup>) consists of two branches, surrounded by extensive ice free areas. The valley floor is covered by sparse vegetation. Glacier 1 is about 2.5 km away from the Daxigou Meteorological Station, which has been in continuous operation for 38 years.

### 3. Experimental Methods

#### 3.1. Aerosol Sampling

Twenty daily aerosol samples were collected during May 19 to June 29, 1996, at 4030 m above sea level (asl) on the eastern branch of Glacier 1. The site is close to the middle of the glacier, just above the equilibrium line and about 150 m away from the steep bedrock slope.

Aerosol samples were recovered on 2  $\mu\text{m}$ , 47 mm diameter Zefluor Teflon filters (Gelman Sciences™) using a 12 V diaphragm pump powered by solar cells. The mean flow rate was 1.27 standard cubic meter per hour (m<sup>3</sup> STP/h), yielding a velocity at the face of the filter of 20.4 cm/s. This velocity is high enough for this kind of filter to have a collection efficiency greater than 97% for aerosol particles larger than 0.035  $\mu\text{m}$  [Liu *et al.*, 1984].

The aerosol sampling period was 3–9 hours based on weather conditions. No aerosol samples were collected during snow events. The air volume through the filter was measured by an in-line meter. Pressure and temperature were recorded

every hour during the collection period, using a barometer and thermometer calibrated at Daxigou Meteorological Station. Therefore sample volume in standard cubic meters can be obtained using the ideal gas equation. The volume ranges from 2.28 to 13.6 m<sup>3</sup> STP and averages 6.87 m<sup>3</sup> STP for all aerosol samples.

Filters were loaded in the field and mounted face down about 1.5 m above the snow surface. After sampling, the filters were removed from the filter holder and put into a cleaned airtight plastic container. They were stored at 4°C before analysis. When loading or unloading the filters, the operator wore plastic gloves and faced upwind in order to minimize contamination.

All sample and laboratory blank filters were wetted with 200  $\mu\text{L}$  UV-spectroscopy pure methanol (Fluka Chemika), then extracted with 25 mL Milli-Q water, shaking for about 10 min.

Soluble ions in aerosol samples were analyzed using a Dionex model™ 4000 ion chromatograph. The chromatography conditions were as follows: for cations, CS12 analytical column, 22 mM MSA eluent, cation self-regenerating suppressor and 25  $\mu\text{L}$  sample loop; for anions, AS11 analytical column, 6.3 mM NaOH eluent, 7.2 mM H<sub>2</sub>SO<sub>4</sub> regenerant and 125  $\mu\text{L}$  sample loop.

Major ions were detected in all aerosol samples. Average concentrations of five laboratory blanks were (in  $\mu\text{eq/L}$ ): Na<sup>+</sup> (0.43), NH<sub>4</sub><sup>+</sup> (0.08), K<sup>+</sup> (0.06), Mg<sup>2+</sup> (0.07), Ca<sup>2+</sup> (0.48), Cl<sup>-</sup> (0.05), NO<sub>3</sub><sup>-</sup> (0.02), and SO<sub>4</sub><sup>2-</sup> (0.03) which were 3–50 times lower than the concentrations detected in aerosol samples. Reported concentrations have the average laboratory blank value subtracted.

#### 3.2. Snow Sampling

Fresh snow and surface snow samples were collected near the aerosol-sampling site (about 30 m away from aerosol-sampling site). Almost all snow samples were collected at hourly intervals during the aerosol sampling period. The number of snow samples (3–9) was determined by the aerosol-sampling period, which was largely controlled by the weather. Fresh snow was collected within 24 hours after the end of snow events. Snow samples were collected in plastic bags using a

**Table 1.** Summary of Soluble Species in Aerosol Samples at Glacier 1, Tien Shan, May 19 to June 29, 1996

	All Samples ( <i>n</i> = 20)			May 19–27 ( <i>n</i> = 6)			June 5–19 ( <i>n</i> = 7)			June 24–29 ( <i>n</i> = 7)		
	Average	Median	s.d.	Average	Median	s.d.	Average	Median	s.d.	Average	Median	s.d.
Ca <sup>2+</sup>	68.15	33.95	76.83	156.21	137.69	71.90	42.69	23.72	44.71	8.29	7.96	3.41
NH <sub>4</sub> <sup>+</sup>	14.91	14.54	6.78	12.20	10.82	2.88	16.58	17.82	9.07	15.16	15.80	5.10
Na <sup>+</sup>	10.68	3.37	15.99	28.30	20.16	20.28	3.90	2.39	3.82	1.72	1.46	1.49
Mg <sup>2+</sup>	6.36	3.48	6.24	13.06	12.39	4.70	4.81	3.30	4.99	1.10	1.22	0.36
K <sup>+</sup>	1.47	1.27	1.12	2.62	2.19	1.35	1.02	0.90	0.58	0.89	0.84	0.43
SO <sub>4</sub> <sup>2-</sup>	25.33	24.16	15.31	40.74	38.81	12.78	21.25	22.20	12.89	14.17	14.10	5.27
NO <sub>3</sub> <sup>-</sup>	9.82	9.11	7.44	17.99	18.49	4.52	7.42	6.58	6.12	4.34	2.96	3.39
Cl <sup>-</sup>	9.94	2.07	17.11	28.65	19.56	22.19	2.71	0.67	3.26	0.50	0.51	0.41
ΔC	56.47	28.06	58.33	125.02	109.47	55.27	37.62	19.04	35.73	8.15	9.71	1.37
Σ <sup>+</sup>	101.56	63.39	98.19	212.40	186.33	94.77	69.00	48.49	57.99	27.17	27.28	10.45
Σ <sup>-</sup>	45.09	35.34	39.86	87.38	76.85	39.50	31.38	29.45	22.26	19.01	17.57	9.07

All concentration in neq/m<sup>3</sup> STP.

\*Σ<sup>+</sup> = [Ca<sup>2+</sup>] + [NH<sub>4</sub><sup>+</sup>] + [Na<sup>+</sup>] + [Mg<sup>2+</sup>] + [K<sup>+</sup>]; Σ<sup>-</sup> = [SO<sub>4</sub><sup>2-</sup>] + [NO<sub>3</sub><sup>-</sup>] + [Cl<sup>-</sup>]; ΔC = Σ<sup>+</sup> - Σ<sup>-</sup>.

plastic scraper. The samples were melted in the field and transferred into precleaned containers, which were rinsed 3 times by sample aliquot, for transport to LIGG where they were frozen for storage. Because of logistic constraint, all snow samples melted again during transport to New Hampshire where they were refrozen for the second time. Both aerosol and snow samples were analyzed in the laboratory of the Climate Change Research Center at the University of New Hampshire.

## 4. Results

### 4.1. Soluble Species in Aerosols

A summary of the analytical data for soluble major ions (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) of interest measured in the aerosol samples is presented in Table 1. To show more clearly the temporal variations in the aerosol ionic concentrations, samples are divided into three time periods coinciding with collection times, for example, May 19–27, June 5–19, and June 24–29. Average concentrations during three periods are presented in Table 1.

The average aerosol loading (total cations and anions measured) was 147.8 neq/m<sup>3</sup> STP. The total cations measured (Σ<sup>+</sup> = Na<sup>+</sup> + NH<sub>4</sub><sup>+</sup> + K<sup>+</sup> + Mg<sup>2+</sup> + Ca<sup>2+</sup>) are about twice that of the total measured anions (Σ<sup>-</sup> = Cl<sup>-</sup> + NO<sub>3</sub><sup>-</sup> + SO<sub>4</sub><sup>2-</sup>). Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup> are the dominant ions in the aerosol, accounting for more than 70% of total aerosol loading. It is noteworthy that no measure of H<sup>+</sup> or HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> was made on our samples.

Pairwise correlations among Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> are all significant at the *p* = 0.001 confidence

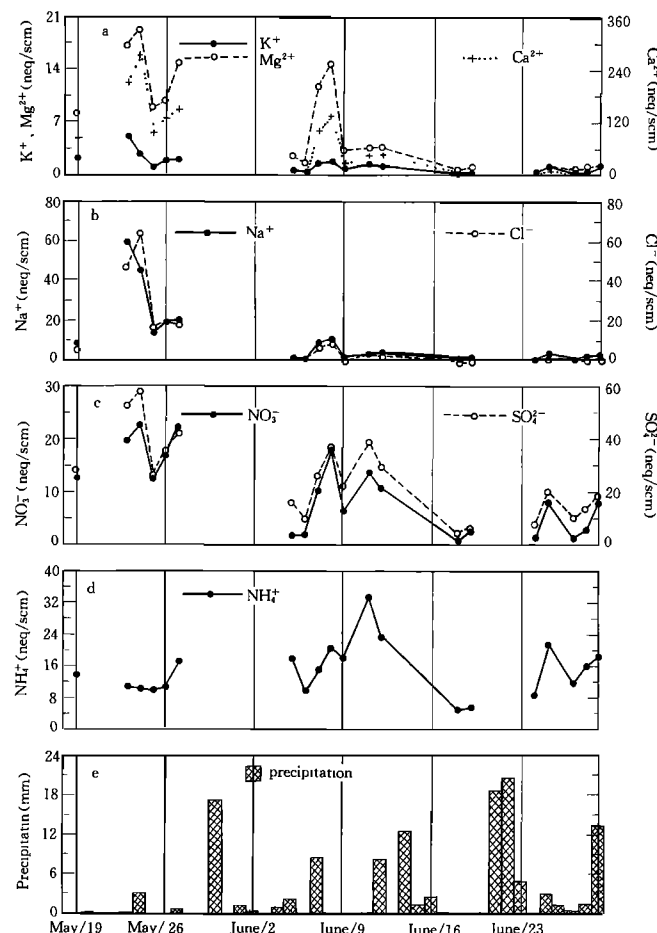
**Table 2.** Correlation Coefficients Between Soluble Species in Aerosol Collected at Glacier 1, Tianshan, May 19 to June 29, 1996

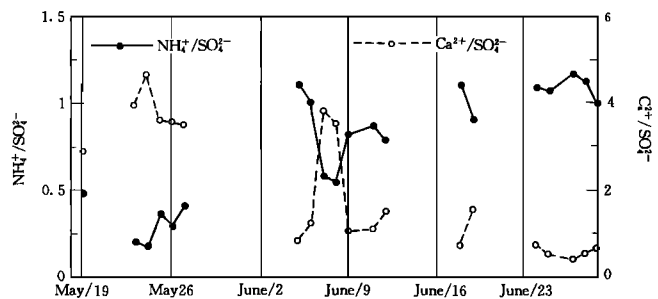
	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>
NH <sub>4</sub> <sup>+</sup>	-0.18						
K <sup>+</sup>	0.92	0.07					
Mg <sup>2+</sup>	0.85	-0.04	0.82				
Ca <sup>2+</sup>	0.91	-0.09	0.84	0.97			
Cl <sup>-</sup>	0.95	-0.21	0.8	0.84	0.94		
NO <sub>3</sub> <sup>-</sup>	0.76	0.24	0.81	0.91	0.9	0.76	
SO <sub>4</sub> <sup>2-</sup>	0.83	0.3	0.86	0.89	0.91	0.82	0.96

Sample number is 20, if *r* > 0.679, the correlation is significant at *p* = 0.001.

level. There is no correlation among these species and NH<sub>4</sub><sup>+</sup>. All correlation coefficients are shown in Table 2.

The statistical data presented in Tables 1 and 2 provide only a general indication of the chemical characteristics of the aerosol samples collected during May–June 1996. Significant differences in chemical composition were detected over the 6-week sampling period. Figures 2a–d show atmospheric concentrations of soluble ionic species from filters collected at

**Figure 2.** Concentrations of soluble species in aerosol samples collected at Glacier 1, Tien Shan: (a) K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>; (b) Na<sup>+</sup>, Cl<sup>-</sup>; (c) NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>; (d) NH<sub>4</sub><sup>+</sup>; (e) precipitation.



**Figure 3.** Relationship between  $\text{NH}_4^+/\text{SO}_4^{2-}$ , and  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  in aerosol samples collected at Glacier 1, Tien Shan.

Glacier 1. For comparison, precipitation amount is presented in Figure 2e. On the basis of their similar patterns we grouped chemical species into three categories: (1)  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  (Figure 2a),  $\text{Na}^+$ ,  $\text{Cl}^-$  (Figure 2b); (2)  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  (Figure 2c); (3)  $\text{NH}_4^+$  (Figure 2d). Despite the slight increase of  $\text{NH}_4^+$  the concentration of all species in aerosol decreased from May to June (Figure 2). The concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$  decreased faster from May 19–27 to June 5–19 than from June 5–19 to June 24–29. Compared to the rapid decrease of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ , the decrease was slower for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . However, year-round sampling is needed in this region to characterize temporal trends.

It is interesting that the equivalence ratio of ammonium to sulfate shows a very good inverse relationship to the equivalence ratio of calcium to sulfate (Figure 3). The correlation coefficient between the two ratios is 0.96 ( $p = 0.001$ ). Average equivalence ratios of ammonium to sulfate are 0.33, 0.86, 1.08 in May 19–27, June 5–19, June 24–29, respectively, while the corresponding values for the equivalence ratio of calcium to sulfate are 3.71, 1.72, 0.59, respectively.

#### 4.2. Soluble Species in Snow

Fresh and surface snow samples collected during the aerosol sampling period were analyzed for major ions. All snow samples were collected near the aerosol sampling site. The concentration of surface snow presented here is a mean value of the snow samples collected on any particular day.

It is noteworthy that snow samples were melted twice before analysis. It has been suggested that melt-freeze cycles can increase the concentration of calcium, magnesium, and acid-neutralizing capacity (ANC) in the samples because of the dissolution of dust [Williams *et al.*, 1992]. Ammonium concentrations are questionable when samples have been melted before analysis. So, it is possible that postcollection processes altered the ionic concentrations in the snow samples.

Table 3 compares the mean concentration of the major ions

**Table 4.** Coefficient Between Soluble Species in Surface Snow Collected at Glacier 1, TienShan, May 19 to June 29, 1996

	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{NO}_3^-$
$\text{Na}^+$							
$\text{NH}_4^+$	-0.21						
$\text{K}^+$	0.75	-0.34					
$\text{Mg}^{2+}$	0.59	-0.44	0.89				
$\text{Ca}^{2+}$	0.72	-0.42	0.96	0.92			
$\text{Cl}^-$	0.99	-0.22	0.73	0.59	0.73		
$\text{NO}_3^-$	-0.25	0.77	-0.41	-0.42	-0.41	-0.23	
$\text{SO}_4^{2-}$	0.89	0.13	0.63	0.42	0.56	0.87	0.07

Sample number is 20,  $r > 0.561$ , the correlation is significant at  $p = 0.01$ .

in our samples with snowpack samples from Glacier 1 [Wake *et al.*, 1992; Williams *et al.*, 1992]. The concentrations of magnesium and calcium in our samples are higher than those reported in previous studies. However, the concentration of other major ion species are comparable to those in previous studies. This may be explained by the fact that our samples are surface snow from the spring to summer period, while the comparison data are snowpits that include winter to spring snow. During the study period, especially in May, there are a lot of visible particles in the surface snow. Compared to previous studies, magnesium seems much more enriched than other species in our snow samples. Perhaps melt-freeze cycles have a greater influence on magnesium dissolution than other species. However, high values of magnesium and calcium do reflect high-dust flux to the snow surface.

Linear regression analysis between water soluble species from the snow samples shows that sodium and chloride are highly correlated ( $r = 0.99$ ). Calcium is correlated very well with magnesium and potassium ( $r = 0.92, 0.96$ ). All of the coefficients are shown in Table 4. The strong inverse relationship seen in the aerosol samples between the equivalence ratios of ammonium to sulfate and of calcium to sulfate does not show up in snow samples. This suggests that postdeposition and/or postcollection processes may alter ammonium concentrations in the snow samples.

## 5. Discussion and Conclusions

### 5.1. Potential Artifacts in Aerosol Samples

Earlier studies [Pierson *et al.*, 1976; Lipfert, 1994] have reported artifacts during aerosol sampling using either filter pack or denuder methods. Because of advantage in handling and costs, the filter pack is more frequently used than denuders. In the filter pack, the air is drawn through an assemblage of filter

**Table 3.** Mean Ion Concentrations and Standard Deviation in Snow Samples Collected at Glacier 1, Tianshan

	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\Delta\text{C}$	Reference
Mean s.d.	45.7	nd	1.2	9.3	86.9	13.9	4.0	31.9	93.4	Wake <i>et al.</i> [1992]
	85.9	nd	1.3	11.1	98.4	21.2	3.5	53.0	141.3	
Mean s.d.	9.7	nd	1.2	5.9	52.5	9.9	5.7	16.2	50.2	Williams <i>et al.</i> [1992]
	4.1	nd	0.8	1.8	15.8	3.6	1.7	5.0	14.6	
Mean s.d.	12.4	4.4	3.4	53.4	147.5	12.3	2.3	9.8	196.8	this work
	21.0	4.2	3.4	73.7	183.7	22.1	2.2	10.0	249.6	

All concentration in  $\mu\text{eq/L}$ .

\*nd, no data available.

in series. The particulate material is collected on the first filter (usually Teflon) and gaseous components on subsequent filters (e.g.,  $\text{HNO}_3$  on nylon,  $\text{NH}_3$  on acid-impregnated filters). However, the denuder method, which is to collect gaseous components of interest first and then the particles, is believed to give the best separation of the gas and particles.

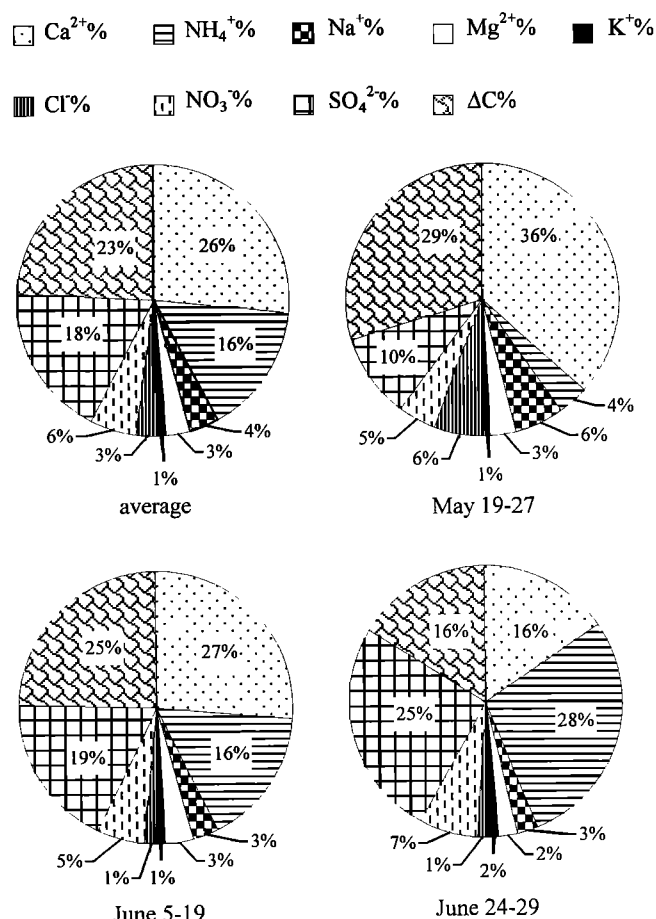
**5.1.1. Ammonium artifacts.** Anderson *et al.* [1994] conducted measurements of gaseous ammonia ( $\text{NH}_3$ ) and particulate ammonium ( $\text{NH}_4^+$ ) by denuder and filter pack methods at five locations in Denmark. The  $\text{NH}_4^+$  determination by the two methods was, in general, found to be in good agreement. Anlauf *et al.* [1985] reported there were no significant difference between the tungstic acid denuder and the filter pack methods in measuring particulate ammonium in southwestern Ontario during June 1–14, 1982.

**5.1.2. Sulfate artifacts.** Only positive artifacts have been reported resulting from the conversion of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  [Pierson *et al.*, 1976; Lipfert *et al.*, 1994]. Pierson *et al.* recommended the Teflon filter and pH-neutral quartz fiber which yielded substantially less  $\text{SO}_4^{2-}$  artifacts. Appel *et al.* [1984] reported that quartz and Teflon filters collected very low levels of  $\text{SO}_2$ . Harrison and Kitto [1990] reported, for particulate sulfate, that the denuder and filter pack method correlated very well.

**5.1.3. Nitrate artifacts.** Unlike sulfate, nitrate artifacts can be positive and negative in the filter pack methods. Appel *et al.* [1979, 1980] compared nitrate collection on different types of filters and concluded that Teflon filters minimize artifact nitrate formation. Mulawa and Cadle [1985] compared the denuder penetration method, denuder difference method, and filter pack for nitric acid and particulate nitrate. Both the denuder difference and the penetration method show significant reductions in  $\text{HNO}_3$  and particulate nitrate artifacts compared to the filter pack technique. However, Harrison and Kitto [1990] reported that the filter pack gives a lower measure of particulate  $\text{NO}_3^-$  compared to the denuder method, but the differences are small. So the use of the filter pack method and its restrictions demand an individual investigation of the sampling site. Wake *et al.* [1994] collected aerosol at central Asia using the same low-volume sampling system as this study. The atmospheric environment at Mount Geladandong and Meikuang Glacier (two of their sampling sites) is similar to that in the study area. They suggest that the  $\text{HNO}_3$  deposition did not influence nitrate concentrations for 47 mm Teflon filters, while nitrate may be lost from 90 mm Teflon filters. In our aerosol samples, 47 mm Teflon filters were used through the sampling period. Although Teflon filters have low blank and minimal retention of gaseous species such as  $\text{SO}_2$  and  $\text{HNO}_3$  [Appel *et al.*, 1984], there might have been some loss of nitrate by decomposition of  $\text{NH}_4\text{NO}_3$ ; therefore the nitrate concentration reported here should be regarded as lower limit of true atmospheric concentration [Shrestha *et al.*, 1997], and sulfate and ammonium concentrations were not subject to any significant artifacts.

## 5.2. Relationship Between Aerosol Ionic Concentration and Precipitation

Weather conditions had an effect on the aerosol ionic concentration in the study area during the sampling period. Generally, the weather at the study site is clear until 1400, then it is cloudy or snowing. Wet deposition is an effective mechanism for the removal of aerosols, especially in the size range of 0.1–10  $\mu\text{m}$  [Barrie, 1985]. Therefore it is expected that low aerosol ionic concentrations will be measured following snow



**Figure 4.** Relative contribution of soluble species to total ionic charge in aerosols collected during May 19 to June 29, Tien Shan.

events, as is the case for May 24 and June 5 but not for June 27 (Figure 2). Concentrations were lower on June 27, then increased on the following two days although there was little snow, because of less scavenging of atmospheric constituents. Therefore it seems that precipitation events must exceed an intensity threshold in order to exert an important influence on the temporal variation in the aerosol ionic concentrations. Aerosol ionic concentrations appear to steadily increase on the following clear days such as May 25, 26, and June 6. Unfortunately, the data set is too small to make a definitive conclusion. In addition, aerosol ionic concentrations are affected by many processes, including upwind chemical processes, removal of wet and dry deposition, and variability in source regions. To understand which process is important for aerosol ionic concentration in the study area, year-round meteorological data and more detailed aerosol sampling, such as daily or weather dependent sampling, is necessary.

## 5.3. Soluble Species in Aerosols and Their Sources

To compare the relative contribution of each species to the aerosol loading, the percentage of total ionic charge ( $=2\Sigma+$ ) was calculated on a sample-by-sample basis, then averaged (Figure 4).  $\Delta\text{C}$  is the excess of cations relative to anions (Table 1). In general,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\Delta\text{C}$ , and  $\text{SO}_4^{2-}$  are the dominant ions in aerosol samples.  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\Delta\text{C}$ , and  $\text{SO}_4^{2-}$  accounted for 27, 16, 23, and 18% of the total ionic charge in the aerosols, respectively. In the May 19–27 period,  $\text{Ca}^{2+}$  comprised 37% of

the total ionic charge, and the next major cation was  $\text{Na}^+$  (6%), while  $\Delta\text{C}$  and  $\text{SO}_4^{2-}$  comprised 29 and 10% of the total ionic charge. In the June 5–19 period,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\Delta\text{C}$ , and  $\text{SO}_4^{2-}$  represented almost the same percentage (about 20%) of the total ionic charge. In the June 24–29 period,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\Delta\text{C}$  accounted for 28, 26, 15, and 14% of the total ionic charge, respectively. *Wake et al.* [1992] suggested that  $\Delta\text{C}$  was primarily carbonate/bicarbonate. Therefore aerosols were dominated by  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-/\text{CO}_3^{2-}$  (dust) in May and by  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-/\text{CO}_3^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  (dust and secondary aerosol) in June. Dust storm activity occurs in China from mid-February to late May with a strong maximum in late April to early May [*Merrill et al.*, 1989]. Thus concentration changes in our aerosol samples appear to reflect changes in the atmospheric dust loading.

As seen from Figures 2a and 2b,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$  have very similar patterns during the study period suggesting that they may have common source areas.  $\text{Na}^+$  and  $\text{Cl}^-$  in the Tien Shan represent an input of Na and Cl rich dust originating from the extensive evaporite deposits in the arid regions surrounding these mountain ranges [*Wake et al.*, 1990]. Potassium is probably also derived from these evaporites, because it is chemically similar to sodium. Further, sodium, chloride and potassium show very high correlations with calcium and magnesium (Table 2). Calcium and magnesium are accepted proxies for dust [*Wolff*, 1996; *Mayewski et al.*, 1993]. As for the sources of nitrate and sulfate, both *Wake et al.* [1990] and *Williams et al.* [1992] reported that terrestrial dusts, originating from the extensive arid regions of central Asia, are a source of nitrate and sulfate in Tien Shan snow. Anthropogenic emissions contribute in part to the observed high levels of sulfate in Tien Shan snow because of the location of Glacier 1 adjacent to the industrial city of Urumqi.

As seen in Figures 2a–2c, although the general variability for the first two categories are similar, the relative amplitudes are different. If nitrate and sulfate were derived from dust, they would probably have similar patterns to calcium, and magnesium, especially during periods with high dust. However, the amplitudes of nitrate and sulfate concentration variation are much smaller than those of the first group. This suggests that anthropogenic emissions are a more important source for both nitrate and sulfate than crustal dust during spring and early summer. Under an alkaline atmospheric environment, gaseous  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  can be absorbed on the surface of mineral particles and react to form salts [*Mamane and Gottlieb*, 1992; *Mamane et al.*, 1992]. This may be the reason that sulfate and nitrate have a significant correlation with calcium, magnesium, potassium, sodium, and chloride. In some cases the equivalence ratio of ammonium to sulfate exceeds 1 (Figure 3), perhaps resulting from the presence of  $\text{NH}_4\text{NO}_3$  [*Warneck*, 1988].

Variation in ammonium (Figure 2d) is different from those of other species in Figures 2a–2c. It does not show clear trends during the study period. Large-scale transport of ammonium seems unlikely because ammonia has a relatively short lifetime due to its heterogeneous conversion and atmospheric deposition processes [*Siedman and Shetter*, 1983]. The potential sources for ammonia which exist in this region are biomass burning, livestock, and soil emissions resulting from the use of nitrogen fertilizers (e.g.,  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $(\text{NH}_2)_2\text{CO}$ ).

The equivalence ratio of ammonium to sulfate shows a strong inverse relationship to that of calcium to sulfate. The inverse relationship between the equivalence ratio of ammonium to sulfate and of calcium to sulfate also appears in the

Hidden Valley aerosols [*Shrestha et al.*, 1997]. This may be explained by the fact that some of the sulfate is associated with mineral particles and another part with ammonium. When dust is the dominant aerosol, the sulfate associated with dust has a large contribution to the total sulfate in aerosol. Hence the equivalence ratio of ammonium to sulfate is lower with an increase of dust or a higher ratio of calcium to sulfate. When secondary aerosol and dust are both dominant in aerosols, sulfate associated with ammonium is much more important to the total sulfate in the aerosol, thus the ratio of calcium to sulfate decreases with the increase of secondary aerosol.

Since ammonium and sulfate are the major soluble components of tropospheric aerosols [*Gorzelska et al.*, 1994; *Warneck*, 1988], more attention has been paid to these species and their ratio. *Warneck* [1988] suggests that ammonium and sulfate exist mainly as  $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  in the continental aerosol, based on the equivalence ratio of ammonium to non-sea-salt sulfate (range from 0.5 to 1). *Barrie et al.* [1990] demonstrated that Arctic airborne sulfates are mainly associated with  $\text{NH}_4\text{HSO}_4$  and  $\text{H}_2\text{SO}_4$ . *Shrestha et al.* [1997] suggest that ammonium exists mainly as  $\text{NH}_4\text{HSO}_4$ , based on the mean equivalence ratio of ammonium to sulfate of 0.69 found in the generally basic or slightly acidic aerosols collected in Hidden Valley, Nepal. Ammonium was well correlated with sulfate in that study.

Extreme care should be taken in explaining the association between ammonium and sulfate using the ratio of these two species. For our aerosol samples, the equivalence ratio of ammonium to sulfate is different in the samples collected in May 19–27 (0.33), June 5–19 (0.86), and June 24–29 (1.08). It has been suggested that ammonia is the dominant atmospheric gaseous base available for neutralizing  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  [*Whitlow et al.*, 1994]. Besides ammonia, continental-source calcium carbonate and marine-source sea salt are believed to be able to neutralize the acidity of the atmosphere [*Silvente and Legrand*, 1993]. It seems unlikely that  $\text{H}_2\text{SO}_4$  would be an important constituent in our aerosol samples because the samples are alkaline. However, the equivalence ratio of ammonium to sulfate does not allow us to discriminate between  $\text{NH}_4\text{HSO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  as the dominant ammonium species in the aerosol. As mentioned above, the aerosol is dominated by dust in May, with more even distribution between dust and secondary aerosol in June. The ratio is only an estimate for the relative contribution of secondary aerosol to the aerosol loading.

#### 5.4. Aerosol-Snow Relationship

Scavenging ratios were calculated using snow and aerosol data according to the relationship  $w = \rho_a C_s / C_a$ , where  $C_s$  is concentration in snow ( $\text{ng g}^{-1}$ ),  $C_a$  is concentration in air ( $\text{ng m}^{-3}$ ), and  $\rho_a$  is density of air ( $\text{g m}^{-3}$ ). Large values of  $w$  suggest efficient scavenging of this species by snow [*Davidson et al.*, 1985]. Because no aerosol samples were collected during the snow events, we use the aerosol sample from the day before each snow event and the first snow sample collected after the event to calculate the scavenging ratio. Because the ammonium concentration in snow is questionable, nitrate concentration in aerosol may be lower than the true value, ammonium and nitrate data were excluded from the analysis. Mean values of scavenging ratios at Tien Shan are compared to results from previous studies in Table 5.

Values of scavenging ratios for sodium, potassium, magnesium, calcium, chloride, and sulfate are consistent with values



**Table 5.** Comparison of Scavenging Ratios From Different Locations

Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	Location	Reference
2000 ± 1200	1200 ± 620	1800 ± 1100	2400	180 ± 120	Dye 3, Greenland	<i>Davidson et al.</i> [1985]
				1000	Dye 3, Greenland	<i>Davidson et al.</i> [1993]
				500	Summit, Greenland	<i>Silvente et al.</i> [1993]
1880 ± 2200	1270 ± 930	2680 ± 2400	2150 ± 2170	550 ± 140	Tien Shan	this work

from previous studies. The high standard deviation of scavenging ratios shows that these ratios vary widely, which is consistent with the results based on <sup>7</sup>Be and <sup>210</sup>Pb over the Dye 3 Gas and Aerosol Sampling Program year [Dibb *et al.*, 1992].

Although it is difficult to interpret these scavenging ratios quantitatively, some order-of-magnitude comparisons may offer useful information about scavenging mechanisms [Davidson *et al.*, 1993]. Compared with the scavenging ratio of sulfate, the higher ratios for sodium, potassium, magnesium, and calcium suggest higher scavenging efficiency in snow. The lower scavenging ratio of sulfate seems to suggest that most of sulfate is in smaller particles.

The soluble species in simultaneous aerosol and surface snow samples show similar patterns (Figure 5). Their corre-

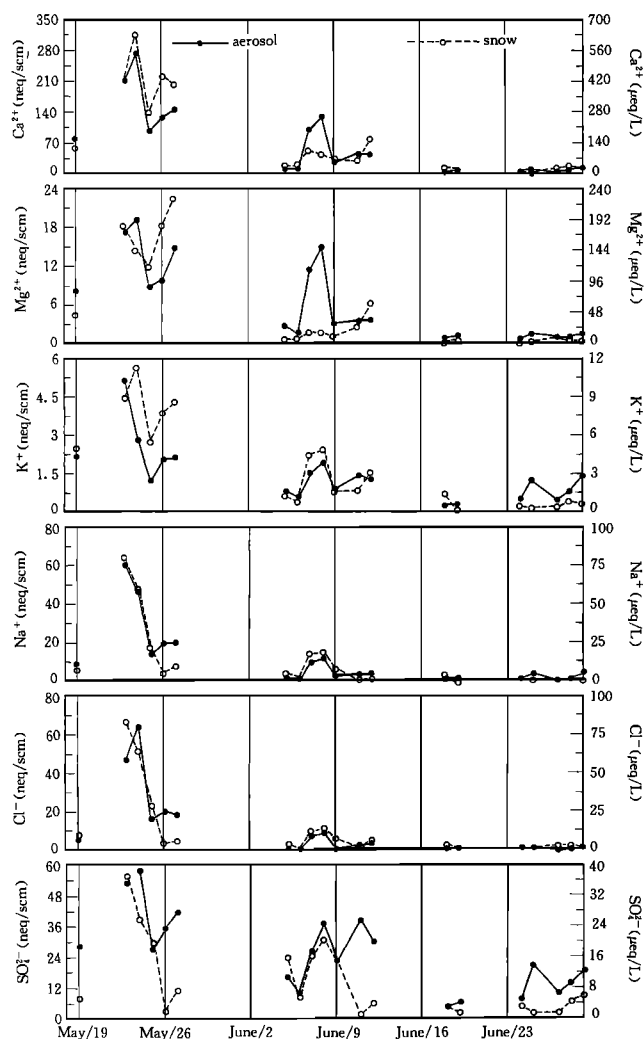
sponding correlation coefficients between aerosol and snow samples are 0.91, 0.95, 0.91, 0.79, 0.76, and 0.63 for calcium, sodium, chloride, potassium, magnesium, and sulfate, respectively, which are significant at the 95% confidence level. This suggests that the concentrations of most species, especially calcium, sodium, and chloride, in snow reflect changes in atmospheric composition. This finding gives us confidence in the reconstruction of past atmosphere change using some snow data, although postdepositional processes can alter the records of snow to some extent.

For ammonium and nitrate the concentration in the atmosphere is composed of gaseous ammonia and particulate ammonium, and gaseous HNO<sub>3</sub> and particulate nitrate. Legrand and Mayewski [1997] pointed out that the situation is more complex for the species present in the gas phase in the atmosphere than for particulates because they sometimes interact strongly with ice. Postdepositional processes have been observed in studies of HNO<sub>3</sub> [Mayewski and Legrand, 1990; Yang *et al.*, 1995] and HCl [De Angelis and Legrand, 1995]. Concentrations in snow for these species may not clearly reflect atmospheric signals [Legrand *et al.*, 1996]. Postdepositional processes maybe exert an important control on the concentration of nitrate in snow. So future long-term investigation should collect gas, aerosol, fresh snow simultaneously, and take some measure to guarantee the quality to make studies more valuable, including employing different sampling methods, minimizing the contamination, keeping the snow sample frozen, using meteorological data, etc.

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**Figure 5.** Temporal variations of soluble species in aerosol samples and snow samples.

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