Journal of Earth Science, Vol. 22, No. 4, p. 482–489, August 2011 *ISSN 1674-487X*
Printed in China
DOI: 10.1007/s12583-011-0202-9

Chemical Characteristics of Snow-Firn Pack in Altai Mountains and Its Environmental Significance

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ABSTRACT: In order to study the chemical characteristics of snow-firn pack in Altai Mountains and its environmental significance, a 1.5-m deep snow-firn pack was dug in the accumulation zone (3 300 m a.s.l.) of the Kanas Glacier in August 2009. A total of 15 samples were analyzed for major ions. Results show that the concentrations of major ions in the snow-firn pack are NH_4^+>SO_4^{2-}>Ca^{2+}>NO_3^-> Na^+>Cl^->K^+>Mg^{2+}. NH_4^+ is the dominant cation with a medium value of 4.7 ueq·L^{-1}, accounting for 39.8% of the total cations, and SO_4^{2-} is the dominant anion, with a medium value of 4.0 ueq·L^{-1}, which accounts for 33.9% of the total cations. Compared with Belukha Glacier (Altai), Urumqi Glacier No. 1, and the Inilchek Glacier (Tienshan), there is a lower ion concentrations in the Kanas snow-firn pack. Potential sources of these chemical species are explored using correlation and empirical orthogonal function (EOF) analyses. The analyses indicate that major ion concentrations (except NH_4^+) originate from crustal dust. Backward trajectory analysis was applied to get the origin of the air mass to Kanas Glacier. The results suggest that air pollutants emitted by forest fires in Siberia could be transported and influence the NH_4^+, NO_3^-, and SO_4^{2-} concentrations on the Kanas Glacier.

KEY WORDS: Kanas Glacier, snow-firn chemistry, Altai Mountains, backward trajectory, forest fires.

INTRODUCTION

Snow contains a record of the chemistry in the atmosphere during snow crystal formation and subsequent snow pack accumulation (Davis, 1991). Solutes and other contaminants are incorporated into snow during crystal formation in the clouds by scavenging and riming as the particles fall and then by the deposition. Snow and ice core records from midlatitude alpine glaciers have provided unique insights into past atmospheric pollution (e.g., Wagenbach, 1989). For example, enhanced acidity, sulfate, and nitrate concentrations were observed in the 20th century and attributed to SO_2 and NO_x emissions from fossil fuel consumption (e.g., Preunkert et al., 2001;

This study was supported by the Knowledge Innovation Project of the Chinese Academy of Sciences (No. KZCX2-EW-311), the National Basic Research Program of China (No. 2010CB951003), the National Natural Science Foundation of China (Nos. 91025012, 111141001, J0930003/J0109), the Program for New Century Excellent Talents in University (No. NCET-10-0019), and the SKLCS founding (No. SKLCS-ZZ-2010-04).

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Manuscript received December 22, 2010.
Manuscript accepted April 08, 2011.

Schwikowski et al., 1999). Increases in agricultural activity and biomass burning produced elevated concentrations of ammonium during this time period (e.g., Hou et al., 2003; Kreutz et al., 2001; Doscher et al., 1996). Generally, major ions and mineral dust deposited in snow and glacier-covered areas reflect the influence of both atmospheric circulation patterns and the local and regional environment.

Much research on snow pit chemistry and ice core record has been done in Tienshan Mountains, the Qinghai-Tibetan plateau, and Polar regions during recent years (Li et al., 2007, 2006; Wang et al., 2006; Aizen et al., 2004; Hou et al., 1999; Wake et al., 1994). However, little research has been carried out on the Altai Mountains. Here, we present a snow-firn pack record from the Altai Mountain region. This area is located close to major sources of air pollution in Northwest China, East Kazakstan, and South Siberia, as well as the nuclear test site of Semipalatinsk (Fig. 1). It is therefore assumed to be affected by emissions of SO_2, heavy metals, and nuclear fallout. In addition, the Altai region is interesting for climate research, since it is highly continental with pronounced seasonality.

In order to study the chemical characteristics of snow-firn pack in Altai Mountains and its environmental significance in this remote region, a 1.5-m deep snow-firn pack was dug in the accumulation zone (3 300 m a.s.l.) of the Kanas Glacier in August 2009. This glacier is located on a saddle between the two summits of Friendship Peak, the highest mountain in the Altai (4 374 m a.s.l.), and is probably the only site suitable for paleo studies in this region.

Figure 1. Location of the Kanas Glacier in Altai Mountains.

EXPERIMENTAL

Site Description

The Kanas Glacier is located at the slope south of the Friendship Peak, Altai Mountains of Northwest China, and extends from 4 374 to 2 460 m a.s.l.. The length of the Kanas Glacier is 10.8 km, with an area of 30.1 km^2, and the average altitude of snow line is 3 100 m a.s.l.. This region is dominated by typical continental climate, and the atmospheric circulation of the Altai Mountains is mainly the westerly winds. The precipitation at Kanas Glacier was approximately 600–800 mm w.e., but there are considerable altitudinal differences (Wang et al., 1983). At the highest altitudes, most of the precipitation falls as snow. Based on upper air temperature data, the calculated mean annual temperature was -7 ℃ (Wang et al., 1983).

Sampling

In August 2009, a 1.5 m snow pit (49°07'N, 87°50'E, 3 300 m a.s.l.) was dug in the Kanas Glacier on the southern slope of Friendship Peak. Fifteen samples, each 10 cm long, were collected from this snow pit. A strict protocol was followed during this procedure to prevent contamination, including the use of disposable polyethylene gloves, masks, and pre-cleaned polyethylene sample containers. All the samples were transported in insulated boxes to the Tienshan Glaciological Station (TGS) Laboratory and were kept frozen until analysis.

Analysis

Insoluble particles, insoluble particles, and major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, SO_4^{2-} and NO_3^-), were analyzed in the TGS laboratory. All sample handling was done in a class-100 clean room in order to minimize contamination. The Ca^{2+} and Mg^{2+} concentrations were measured by ion chromatography using a Dionex DX-320 system with a CS12A separation column. The detection limits of Mg^{2+} and Ca^{2+} were 0.8 $ng \cdot g^{-1}$ and 0.75 $ng \cdot g^{-1}$, respectively (Zhao and Li, 2004). Microparticle concentrations and size distributions were measured with an AccuSizer 780A, which uses single particle optical sensing (SPOS) technology and measures in 8 to 512 size channels, with an error of less than 5% in the 0.5–400 μm measuring range. Prior to analysis, samples were melted at room temperature, while the pipeline and AccuSizer system were cleaned with Milli-Q water until the background particle count was below 50 mL^{-1}. The $\delta^{18}O$ values of the samples were determined at the State Key Laboratory of Cryospheric Sciences, Chinese Academy of Sciences, using MAT-252 and DeltaPlus mass spectrometers, with a precision of ±0.2‰.

RESULTS AND DISCUSSION

Characteristics of Major Ion Concentrations

The vertical profiles of the ion concentrations, microparticles contents and oxygen isotopes, are shown in Fig. 2. The median, minimum, and maximum values of analyzed ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-},Cl^-, and NO_3^-) for the Knans snow pit samples are presented in Table 1. We also calculated the sum of measured cations (Σ^+) and anions (Σ^-). The values of Σ^+ and Σ^- are 11.8 and 8.9 $ueq \cdot L^{-1}$, respectively. The ratio of total anions to that of total cations (Σ^-/Σ^+) in this study is 0.75, suggesting at least one major anion was neglected. Since the water from river and snow/glacier around Friendship Peak is calcareous and alkaline (AQ 1), the observed deficiency is most likely due to the exclusion of HCO_3^- from the measurements (Li et al., 2007; Hontoria et al., 2003). Therefore, the HCO_3^- concentration is estimated by the ionic balance of the total cations and anions, assuming that the CO_3^{2-} concentration is negligible.

Table 1 Mean, minimum (Min.), and maximum (Max.) values of analyzed ions for the Knans snow pit samples ($ueq \cdot L^{-1}$)

	Mean	Max.	Min.	Max./Min.
SO_4^{2-}	4.0	12.6	0.7	18.0
Cl^-	1.4	8.4	0.3	28.0
NO_3^-	3.5	13.3	0.9	14.8
Na^+	1.6	12.7	0.1	127.0
NH_4^+	4.7	4.7	0.9	5.2
K^+	0.9	6.4	0.1	64.0
Mg^{2+}	0.7	3.6	0.1	36.0
Ca^{2+}	3.9	20.8	0.2	104.0

According to the percentages in Table 1, the ionic abundance of the Kanas snow pack follows the sequence of $NH_4^+ > SO_4^{2-} > Ca^{2+} > NO_3^- > Na^+ > Cl^- > K^+ > Mg^{2+}$. NH_4^+ concentration contributes the most to the total cation mass (39.8%). SO_4^{2-} is the next most abundant, accounting for 33.9% of the total anion mass. NH_4^+ and SO_4^{2-}, together combined, account for 36.9% of the total ion mass.

The quotients of maximum and minimum mean concentration of the ions (Max./Min.) are used to describe varying amplitudes of each species. In general, the variability of cations is much bigger than that of anions. Na^+ has the biggest variability (Max./Min.=127) among the ions; Ca^{2+} takes the second place (Max./Min.=104); and their variability exceeds that of other ions by times. Anions (Cl^-, SO_4^{2-}, and NO_3^-) have similar Max./Min., and no significant variability could be distinguished through their Max./Min. values.

Comparisons of Ion Concentrations with Other Regions

To facilitate a discussion of regional variations in snow pack chemistry, the median values of major inorganic ions and relative ionic composition ternary diagrams in snow/ice in different region are listed in Table 2 and Fig. 3.

First, concentrations of major ions in the Kanas snow-firn pack are lower than Belukha Glacier (Altai), Urumqi Glacier No. 1, and the Inilchek Glacier (Tienshan). Second, it is obvious that the data from East Rongbuk (6 450 m a.s.l.) are far lower than that from other places because both the effects of the continental dust are low at such high elevation, and all the ions have experienced heavy depletion (Kang et al., 2002). The observed differences in ion concentrations for these geographic regions can be attributed to differences in source and strength of atmospheric aerosol inputs. Third, the Kanas Glacier and Belukha Glacier show a similar cation composition, especially that the proportions are much higher than other glaciers (see Fig. 3). Those five glaciers have a similar anion composition (see Fig. 3).

Associated Major Ion Sources

Interspecies relationships of ions

In order to investigate the interspecies relationships and the common variability within these major ions of snow pack samples, both linear correlation

Table 2 Median concentrations and percentage of major ions (ueq·L^{-1}) in snow/ice cores from Kanas, Belukha, Inilchek, and East Rongbuk glaciers.

Site	Altai, Kanas Glacier (this study)	Altai, Belukha Glacier (Olivier et al., 2003)	Tien Shan, Urumqi Glacier No.1 (Li et al., 2008)	Tien Shan, Inilchek Glacier (Kreutz et al., 2001)	East Rongbuk, Himalayas (Kang et al., 2002)
Elevation (m a.s.l.)	3 800	4 062	4 130	5 100	6 450
SO_4^{2-}	4.0	11.0	7.4	13.9	1.9
Cl^-	1.4	0.9	3.0	9.7	0.5
NO_3^-	3.5	4.3	5.6	5.5	0.7
Na^+	1.6	1.0	3.1	10.9	0.5
NH_4^+	4.7	11.4	6.3	9.7	3.0
K^+	0.9	0.4	0.9	0.9	0.2
Mg^{2+}	0.7	1.6	5.6	4.7	0.4
Ca^{2+}	3.9	9.4	42.1	66.2	5.3
Total	20.7	40.0	74.0	121.5	12.5

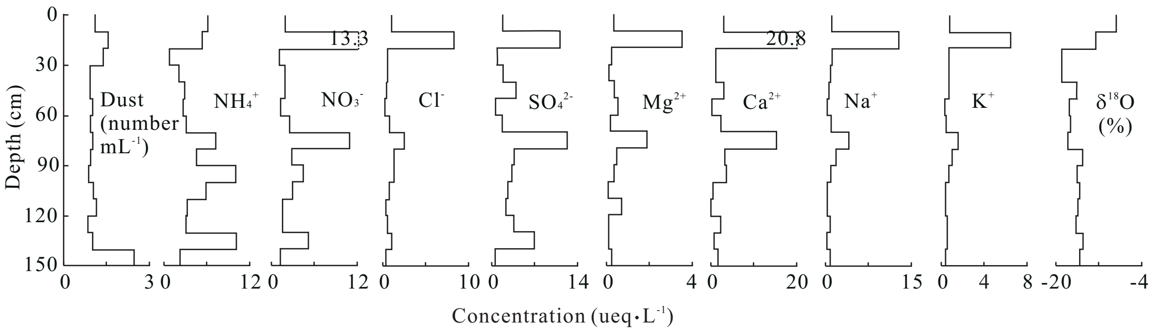

Figure 2. Concentration profiles of the ion concentrations, microparticles contents and oxygen isotopes on Kanas Glacier, August 2009.

analysis (Table 3) and empirical orthogonal function (EOF) (Table 4) are performed. Table 3 presents the matrix of *R* values for the elements measured in the snow pack. The significant correlations ($R \geq 0.7$, 2-tailed, $p=0.01$, $N=15$) are highlighted with bold type. To connect these elements to their sources, correlations among the elements were further investigated using factor analysis (Table 4). EOF decomposition provides objective representations of multivariate data by analyzing the covariance structure of its variates (Meeker et al., 1995), and it has been extensively applied for the analysis of chemical composition in snow/ice cores (Hou et al., 2003; Meeker et al., 1995).

In Table 4, the first two EOFs account for 94.5% of the total variance. EOF 1, which represents 79.9% of the total variance in the major ion series, is heavily loaded by Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, Na^+, K^+, and SO_4^{2-}. Good correlations are also observed between these ions (Table 3). This indicates that EOF1 represents variations in the main crustal species (Ca^{2+}, Mg^{2+}, Cl^-, Na^+, K^+, and SO_4^{2-}), which are mainly derived from crustal dust and evaporation of saline lakes. The study of snow chemistry from the same region also highlights the contribution of the local environment to the source of chemical ion in snow (Olivier et al., 2003). EOF2 accounts for 14.6% of the total variability in the snow pack (Table 4), with highest loadings for NH_4^+ (91.2%), and there is no significant linear correlation between NH_4^+ with other elements, suggesting that this specie originates from a different source that is independent from the crustal ion source (EOF1). Evidently from the Table 4, NO_3^- and SO_4^{2-} have more potential sources than other species, because these two elements had very high loading (34.7 and 21.8, respectively) on factor 2, indicating that there is an additional source.

Table 3 The correlation matrix for the elements in the Kanas snow-firn pack

	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Cl^-	1							
NO_3^-	0.88	1						
$SO4^{2-}$	0.73	0.94	1					
Na^+	0.99	0.86	0.71	1				
NH_4^+	0.24	0.48	0.51	0.11	1			
K^+	0.99	0.82	0.68	0.99	0.12	1		
Mg^{2+}	0.93	0.90	0.79	0.96	0.15	0.93	1	
Ca^{2+}	0.90	0.94	0.87	0.92	0.24	0.88	0.95	1

The underlined type indicates that the correlation is significant ($R \geq 0.7$) at the 0.01 level (2-tailed).

Table 4 EOF associations among major ion concentrations in the Kanas snow-firn pack

	Factor loadings	
	1	2
Cl^-	96.4	-13.9
NO_3^-	96.3	21.8
SO_4^{2-}	86.9	34.7
Na^+	96.0	-25.1
NH_4^+	32.0	91.2
K^+	94.1	-25.0
Mg^{2+}	96.6	-15.1
Ca^{2+}	97.0	-3.8
% of variation	79.9	14.6

* The numbers in the table represent the percent of variance associated with each major ion. Negative values indicate an inverse relationship. The underlined type indicates the highest factor loading.

Higher EOF2 loading for NH_4^+, NO_3^-, and SO_4^{2-} as compared to other ions suggests additional inputs.

Relationship with air mass transport

Backward trajectory analysis has been applied widely in the field of atmospheric sciences (e.g., Kahl et al., 1997). Moreover, the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Resources Laboratory) is one of the useful tools to model the air trajectory among the models and has been credibly used in some previous studies (e.g., Ramachandran, 2005; Falkovich et al., 2001). To determine the transport pathway of air mass to Kanas Glacier, we use a compromised method of six-days-long backward trajectory with a daily resolution to simulate the moving routes of air masses arriving at the sampling site after setting our ending location at the sampling site and ending time at 12:00 of Beijing time in the middle of each day for the period July 2008 to August 2009. The results of backward trajectory analysis are presented in Fig. 3. Biomass burning is now recognized as an important source of many atmospheric components at global scale (Andreae and Merlet, 2001; Crutzen et al., 1979). For instance, forest fires are one of the major sources of nitrogen oxides (NO_x), sulfate dioxide (SO_2), and ammonia (NH_3).

Figure 4 shows that a number of forest fires which occurred in Siberia during July 2008 to August 2009, which came from satellite data by ESA (European Space Agency). It can be seen that most of the air masses come from the Siberia (from the North/Northwest direction), which passed over the forest-fire and agricultural region in Siberia. Therefore, we speculate that most of the NH_4^+ and part of NO_3^-, SO_4^{2-} come from biomass burning. In addition, biogenic emissions, bacterial decomposition of livestock wastes, and fertilizer applications also contribute to atmospheric NH_4^+, NO_3^-, and SO_4^{2-} and are likely influencing the associated ion budgets in the Kanas Glacier snow pack (Olivier et al., 2003).

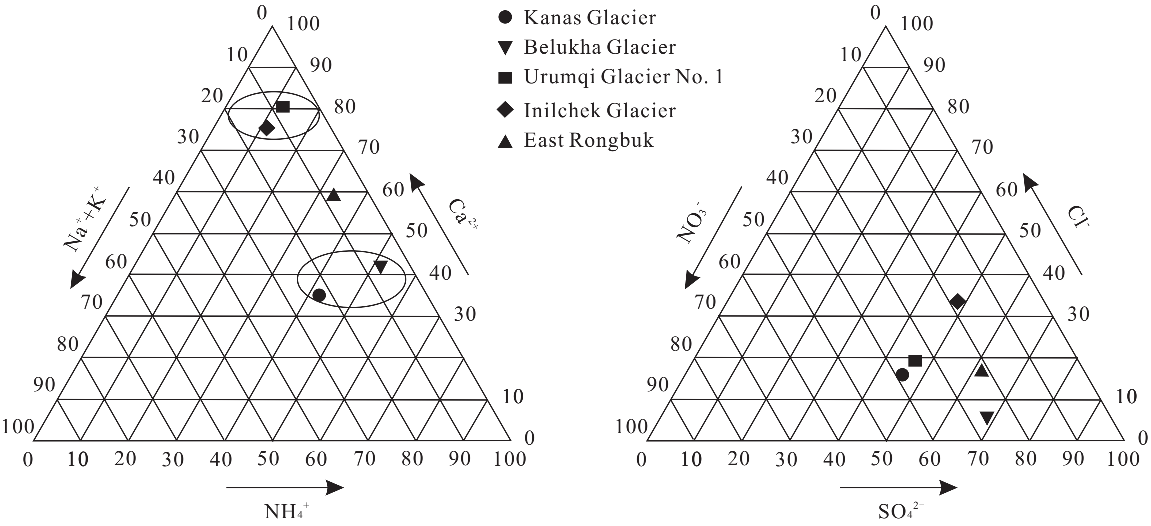

Figure 3. Relative cationic and anionic composition of snow/ice samples.

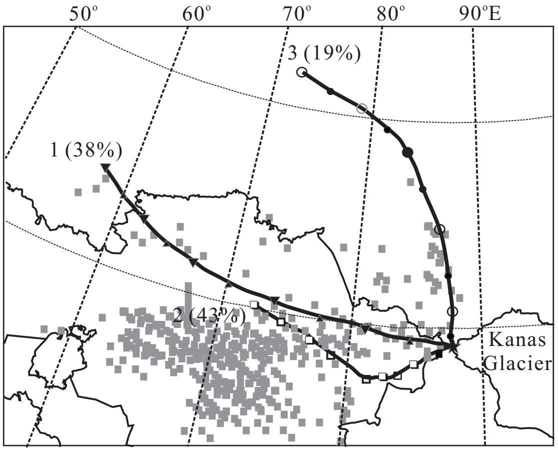

Figure 4. Frequency plot of six-day back trajectories and the fire spots for the period July 2008 to August 2009 using HYSPLIT.

In summary, local and regional mineral dust (crustal and evaporate sources), which contribute to Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, Na^+, K^+, and SO_4^{2-}, are the predominant ion sources in the Kanas Glacier. Significant contributions from biomass burning, biogenic emissions, and anthropogenic sources also contribute to most of NH_4^+ and part of NO_3^- and SO_4^{2-}.

CONCLUSIONS

The investigations of snow-firn pack chemistry are scarce at remote glacier sites in Altai Mountains. This work studies the chemical characteristics of the Kanas snow-firn pack in Altai Mountains and its environmental significance. Results show that the NH_4^+ is the dominant cation, and SO_4^{2-} is the dominant anion. Concentrations of major ions in the Kanas snow-firn pack are lower than Belukha Glacier (Altai), Urumqi Glacier No. 1, and the Inilchek Glacier (Tienshan). EOF associations and correlation analysis show that major ion concentrations (except NH_4^+) in the Kanas Glacier are mainly controlled by regional crustal dust. Backward trajectory analysis suggests that air pollutants emitted by forest fires in Siberia could be transported and influence the NH_4^+, NO_3^-, and SO_4^{2-} concentrations on the Kanas Glacier. In short, the glaciochemical data presented here indicate that the Kanas Glacier provides a probably unique archive of atmospheric and environmental information in Central Asia.

ACKNOWLEDGMENTS

We would like to thank the anonymous reviewers for their valuable comments which were greatly helpful for improving the manuscript. We would like to thank Li Zhongqin, Zhao Jingdong, Li Huilin and Sun Jizhou for assistance in the field.

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