

Characteristics of ionic concentration and $\delta^{18}\text{O}$ and their variability in dry-season and wet-season snow on Ürümqi glacier No. 1, eastern Tien Shan, central Asia

Zhongqin LI,^{1,2} Wenbin WANG,¹ Feiteng WANG,¹ Huilin LI,¹ Mingjun ZHANG²

¹National Key Laboratory of Cryospheric Sciences/Tien Shan Glaciological Station, Cold and Arid Regions Environmental and Engineering Research Institute, Chinese Academy of Sciences, Lanzhou 730000, China
E-mail: lizq@lzb.ac.cn

²Northwest Normal University, Lanzhou 730030, China

ABSTRACT. To investigate the environmental and climatic significance of the ice-core records from the Tien Shan, central Asia, the characteristics of ionic concentration and oxygen isotopic ratio ($\delta^{18}\text{O}$) as well as their variability are assessed from surface-snow samples as well as old-snow samples collected year-round at weekly intervals from November 2002 to October 2005 on Ürümqi glacier No. 1, eastern Tien Shan. The results indicate that the $\delta^{18}\text{O}$ in surface-snow samples is reversely coincident with air temperature and insignificantly affected by post-depositional processes. Ionic concentrations in the wet-season (1 November to 31 March) snow are overall higher than those in dry-season (1 April to 31 October) snow, while the variability of relative ionic composition between dry seasons is slightly less than that between wet seasons. During dry seasons, surface-snow chemistry was mostly controlled by the chemical content entrained in some sporadic precipitations. When precipitation is absent, the effect of all post-depositional processes together elevated the ionic concentrations in surface snow. During wet seasons, the snow chemistry is determined mainly by the input of aerosols entrained in precipitation and the elution process from percolation of meltwater.

INTRODUCTION

Precipitation falling as snow to a glacier surface provides natural archives in the form of ice-core records of atmospheric composition. Such conditions exist in the high Tien Shan, central Asia, where the snow and ice cores have yielded invaluable chemical records of changes in environment and climate (e.g. Li and others, 1994; Kreutz and Sholkovitz, 2000; Aizen and others, 2004; Olivier and others, 2006). However, to interpret these records, present-day investigations of the dependency of the snow chemical species on precipitation constituents, as well as of the effect of post-depositional processes on the snowpack records, are essential in many cases. This is because of two major reasons: (1) as the precipitation regime over the Tien Shan is mostly characterized as either a dry or a wet season, the environmental and climatic implications of the chemical records are found to be different between the dry and the wet season, and need to be studied separately; and (2) some post-deposition processes have been observed to alter the chemical records significantly in snowpack. These processes also have a different appearance in dry seasons and wet seasons. During the dry season, the dominant post-depositional processes on snow chemistry are dry deposition, wind erosion and sublimation. During the wet season, as maximum precipitation occurs at the same time as the appearance of the highest temperature, the snow is additionally affected by a meltwater-related elution process. This process can significantly alter the chemical composition of snow (e.g. Ginot and others, 2001; Stichler and others, 2001; Schotterer and others, 2004; Schulz and de Jong, 2004).

To investigate the environmental and climatic significance of the chemical records in snow and ice cores recovered from the high Tien Shan, surface-snow samples and old-snow samples were collected on a weekly basis on Ürümqi glacier

No. 1, eastern Tien Shan. The sampling site was located in a percolation zone of the east branch of the glacier at 4130 m a.s.l. It was named the PGPI site and was established in July 2002 as an observational and experimental site for the Program for Glacier Processes Investigation (PGPI; see Li and others, 2006). Several studies have reported the general features of the chemical composition, elution process and potential source for the elements measured in the snow–firn pack (e.g. Li and others, 2006, 2007; Wang and others, 2006; Zhao and others, 2006). This study focuses on the characteristics of ionic and $\delta^{18}\text{O}$ compositions in the dry-season and wet-season snow during a multi-year period from 1 November 2002 to 31 October 2005, which constitutes a basic research component of the PGPI.

STUDY SITE

Ürümqi glacier No. 1 (43°06' N, 86°49' E) is located at the headwaters of the Ürümqi river in the eastern Tien Shan surrounded by vast desert, arid and semi-arid land in central Asia. With a typical continental climate, the westerly jet stream prevails across these high mountains. The mountain topography converts the westerly into cyclonic and anti-cyclonic circulations up to 4000 m structured regional prevailing winds, which blow from the north and northwest in summer and from the south and southwest in winter (Li, 1991; Zhang and others, 1994; Lee and others, 2003). Near the surface, local winds blow up and down along the valley on a diurnal basis (Wake and others, 1992). Winds from the northeast or north-northeast dominate year-round. This area is situated under the influence of the Siberian anticyclonic circulation during winter, which decreases the quantity of winter precipitation minimally in January (Aizen and others, 2001). Over 95% of the precipitation occurs from April to

Table 1. Temperature, precipitation, $\delta^{18}\text{O}$ and major-ion concentrations in surface-snow samples during dry seasons and wet seasons

Date	Temperature			Total precipitation mm	Major-ionic concentration								
	Mean	Max.	Min.		$\delta^{18}\text{O}$	Mg^{2+}	Ca^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	NO_3^-	NH_4^+
	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$		‰	ng g^{-1}	ng g^{-1}	ng g^{-1}	ng g^{-1}	ng g^{-1}	ng g^{-1}	ng g^{-1}	ng g^{-1}
Dry seasons													
1 Nov 2002 to 31 Mar 2003	-14.9	-28.5	-1.0	33.3	-	67.2	842.9	71.4	34.9	106.1	353.7	345.1	114.1
1 Nov 2003 to 31 Mar 2004	-16.0	-29.0	-1.8	30.8	-25.3	65.4	889.3	64.5	26.4	101.5	309.2	374.1	96.5
1 Nov 2004 to 31 Mar 2005	-15.3	-29.3	-5.3	47.4	-24.9	108.4	1998.1	86.9	47.5	129.4	327.2	316.2	90.4
Wet seasons													
1 Apr 2003 to 31 Oct 2003	-3.4	-18.9	5.3	594.3	-12.8	125.9	1677.7	139.4	30.1	260.2	676.2	371.0	169.8
1 Apr 2004 to 31 Oct 2004	-2.4	-14.2	7.1	579.8	-12.0	202.8	2226.4	316.0	57.3	492.4	778.6	420.3	225.0
1 Apr 2005 to 31 Oct 2005	-2.7	-20.0	6.7	609.8	-	100.5	1356.7	158.0	50.3	264.4	553.7	317.6	249.5

October (wet season), and the maximum precipitation is observed in July and August. Ürümqi glacier No. 1 is a northwest-facing valley glacier composed of east and west branches currently covering 1.68 km². The PGPI site is situated at 4130 m a.s.l., with no direct wintertime exposure to sunshine due to the shadowing effect of the mountain ridges. In situ measurement showed that the mean annual air temperature and precipitation during the sampling period were -9.1°C and 632 mm water equivalent (w.e.), respectively. Maximum precipitation occurs in summer (wet season) at the same time as maximum snowmelt. The depth of the snow-firn layer on the glacier at the sampling site is observed typically ranging from about 1.5 m in the late summer to about 4 m in the late spring. During the late autumn through to winter it remains stable due to snow compaction, snowdrifting and sublimation. In the early summer, as air temperatures rise to ~0°C, the upper part of the snow layer begins to melt. During July and August, melting dominates and affects the entire annual layer and even the accumulation from the previous year.

SAMPLING AND ANALYTICAL PROCEDURES

Two types of samples were collected at the PGPI sampling site: surface-snow and old-snow samples. The surface snow consisted mainly of fresh snow obtained during the wet season and of relatively old snow obtained during the dry season because of sporadic precipitation. During surface-snow sampling, an effort was made to collect the fresh snow to investigate the chemical seasonality in precipitation and dry deposition. Therefore, during the dry season, when there was insufficient snowfall, we usually sampled the topmost 3 cm. However, if an accumulation event occurred prior to the sampling, we collected as thin as 1 cm of the topmost fresh snow. During the wet season, there was usually sufficient fresh snow collected from the top 3–5 cm. Nevertheless, the surface snow was actually subjected to the elution of ions during the wet season. This was because the elution evidently could start right after the deposition, and there was usually a lag time between the deposition and the sampling of the snow. Old-snow samples were recovered underneath surface-snow samples, with a vertical length of 10 cm. They were usually less affected by post-depositional processes during the dry season, but could be significantly altered by meltwater-related post-deposition

processes during the wet season. In this study, 156 surface-snow samples and 156 old-snow samples were investigated. These were collected at 7 day intervals from 1 November 2002 to 31 October 2005.

Strict procedures were followed during sampling and transportation to prevent contamination, including using disposable polyethylene gloves, oronasal masks and pre-cleaned polyethylene sample containers. All samples were transported frozen to the Tien Shan Glaciological Station (TGS) laboratory. Blanks were made at each step in the process to ensure that the cumulative contamination remained below the baseline of each measured chemical species. In the TGS laboratory, samples were analyzed for major ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , Cl^- , SO_4^{2-} and NO_3^-) using a Dionex DX-320 system with a CS12A separation column (Zhao and Li, 2004). The ionic balances ΔC (total cation equivalents minus total anion equivalents) for all samples averaged 40.1 $\mu\text{Eq L}^{-1}$, accounting for 60% of the total anion content. The good linear correlation between calcium and ΔC suggests that the ΔC represents primarily the carbonate/bicarbonate in the snow. The $\delta^{18}\text{O}$ was determined using a Finnigan delta-plus mass spectrometer (accuracy 0.05%).

RESULTS AND DISCUSSION

Variability of ionic concentration and $\delta^{18}\text{O}$ between the dry-season and wet-season snow

Based on the amount of precipitation, the dry season is classified as 1 November–31 March and the wet season as 1 April–31 October. Accordingly, the study period can be divided into three dry seasons and three wet seasons. In situ measurement showed that the average precipitation was 37 mm in the dry seasons and 595 mm in the wet seasons. The diurnal temperature in the dry season averaged -15.4°C, with the maxima occasionally over -3.6°C, while in wet seasons it averaged -2.8°C. The elution of ions in snow resulting from percolation of meltwater occurs commonly in wet seasons but rarely in dry seasons. This is because the elution process initiates when the diurnal mean temperature reaches about -3.6°C (Li and others, 2006).

The measured temperature and precipitation as well as $\delta^{18}\text{O}$ and major-ion concentrations in the surface-snow samples are presented in Table 1. It is noted that $\delta^{18}\text{O}$ has an

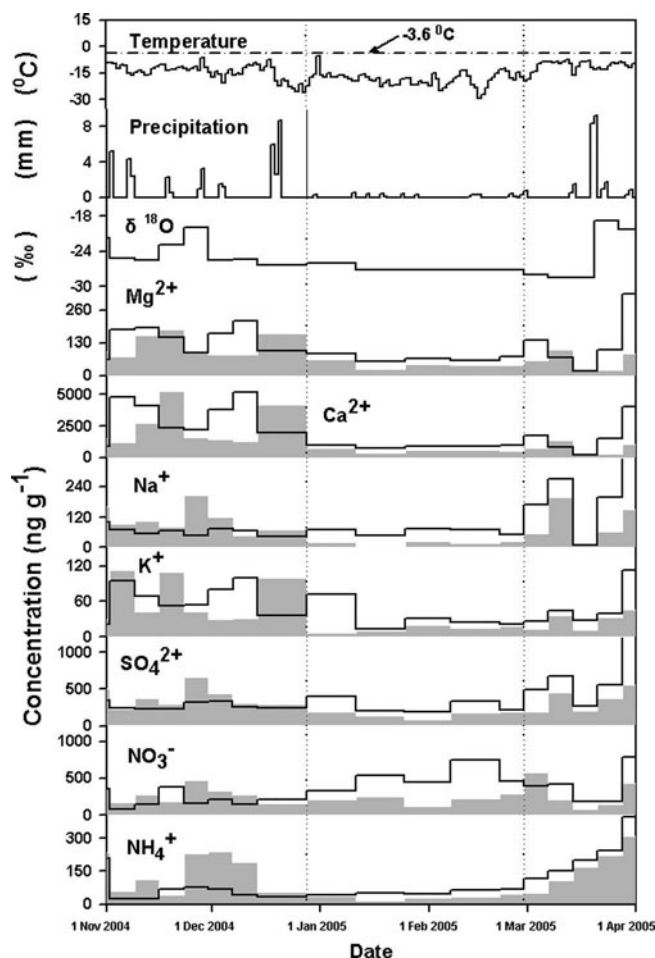


Fig. 3. Temporal variations of temperature, precipitation, $\delta^{18}\text{O}$ and ionic concentrations in surface-snow samples and old-snow samples (shaded portion) during the dry season from 1 November 2004 to 31 March 2005.

and K^+ in precipitation was most likely derived from their potential sources. This includes the local-plus-regional mineral aerosols entrained in moisture mass by the strong winds prevailing during spring, along with a more regional Asian dust flux (Gao and others, 1992; Mori and others, 2003). Elements are found to be better correlated with each other in wet-season snow, indicating the similarities in the wet season with respect not only to their source, but also to the elution that may redistribute the ionic concentrations, particularly for cations, into an analogous pattern. The fact that NH_4^+ and NO_3^- correlate well in wet-season snow and poorly in dry-season snow may be attributed to the discrepancy in the source and the response to the elution process of these species. Despite the fact that both are considered to originate from anthropogenic sources, including emissions from fossil fuel combustion and biomass burning, livestock manure and commercial and natural fertilizers, NO_3^- shows less change between the dry-season and wet-season snow. Therefore, it may have a relatively stable source. This behavior of NO_3^- is also shown in the anion ternary diagram, in which the proportion of NO_3^- with respect to SO_4^{2-} and Cl^- decreases explicitly as dry season changes to wet season. For NH_4^+ , however, the higher concentration in wet-season snow indicates the higher input of NH_4^+ . Compared with NO_3^- , NH_4^+ is more immobile with respect to the percolating meltwater (Li and others, 2006). This may also be a cause for a higher

concentration in wet-season snow. Mg^{2+} and Ca^{2+} exhibit significant correlation in dry-season snow and weak correlation in wet-season snow, probably because Mg^{2+} and Ca^{2+} are affected by similar post-depositional processes during the dry season, but have different sources during the wet season. Previous studies indicate that Mg^{2+} is mainly from a long-distance source derived from mineral dust and evaporite aerosols entrained along the trajectory of the air masses that bring moisture to the region. On the other hand, Ca^{2+} has multiple sources either from local or regional dust aerosols (Li and others, 2006; Wang and others 2006).

Characteristics of ionic concentration and $\delta^{18}\text{O}$ in the dry-season snow

Despite the annual variability between dry seasons and wet seasons, the general behaviors of chemical species in the same seasons are found to be mostly identical. Therefore, one of the dry seasons (from 1 November 2004 to 31 March 2005) is selected as an example to reveal the general characteristics of the ionic concentrations and $\delta^{18}\text{O}$ in dry-season snow. The precipitation during this period was 47.7 mm in total, while the temperature ranged between -29.3 and -5.3°C , with a mean value of -15.3°C . This low temperature excluded any possibility of the elution of ions resulting from melting. Thus, the post-depositional processes mainly included dry deposition, wind erosion and sublimation. Figure 3 presents the temporal variations of temperature and precipitation, as well as $\delta^{18}\text{O}$ and ionic concentrations in surface snow. The data from old-snow samples (shaded portion) are also included for comparison purposes. The figure demonstrates that throughout this period identical temporal variations appeared among Mg^{2+} , Ca^{2+} and K^+ , indicating their similarities in sources and depositional and post-depositional processes, such as are also found between SO_4^{2-} and Na^+ . For detailed analysis, this dry season was further subdivided into three periods according to precipitation volume and appearance of ionic concentrations, as shown in Figure 3: 1 November to 28 December 2004, 29 December 2004 to 30 February 2005 and 1 March to 1 April 2005.

In the period 1 November to 28 December 2004, several precipitation events were crucial to the chemical composition of surface snow. The concentrations of Mg^{2+} , Ca^{2+} and K^+ exhibit an identical variation trend characterized by an elevated baseline with sequent peaks. This implies relatively enriched terrestrial aerosols in precipitation. The overlap of concentration peaks reveals their similar transportation and deposition processes. In contrast, Na^+ , SO_4^{2-} and NO_3^- in surface snow show low concentrations and different temporal variations. This indicates that they were relatively less concentrated in precipitations and might have experienced different transportation and deposition processes. The temporal variability of ionic concentrations in surface snow differs clearly from the concentrations in old snow, which also reflects the fact that the surface-snow chemistry is mainly associated with precipitation events.

In the period 29 December 2004 to 30 February 2005, the impact of several small precipitation events (<4 mm w.e. in total) on surface-snow chemistry was negligible. The measurement from a stake network of drifting-snow observation near the PGPI site indicated that the net accumulation at this site was positive during the period. This excluded the possibility that surface snow was blown away by strong winds. Therefore, the dry deposition, drifting snow and

sublimation were attributes of the ionic alterations in surface snow. In this period, all ionic concentrations in surface snow exhibit diverse temporal variations, indicating the discrepancy of the post-depositional effects on different species. However, compared with old snow, the ionic concentrations in surface snow are apparently higher. This indicates that the effects of all post-depositional processes together resulted in an increase in ionic concentrations in the surface snow. The reason for this must be that all of the major post-depositional processes potentially facilitate the elevation of the ionic concentrations: for example, most ions (except for NH_4^+) can be enriched in surface snow by sublimation; mineral dust components such as Ca^{2+} , Mg^{2+} and Na^+ can also be enriched by dry deposition (Ginot and others, 2001; Schotterer and others, 2004); snowdrift that can scavenge particles from the lower levels of the troposphere may lead to an increase in NO_3^- concentration in snow (Wolff and others, 1998).

During the period 1 March to 1 April 2005, as the precipitation began to increase, the ionic concentrations in surface snow were again governed by wet deposition, which elevated the concentration values which rapidly exceeded those in old snow. In addition, during this spring period, cold frontal systems start to sweep across the region, producing Asian dust storms (Gao and others, 1992; Li and others, 1994; Wake and others, 1994). Both the dust storms and precipitation brought terrestrial impurities to the glacier snow, as reflected by the increase of mineral species, especially for Mg^{2+} , Ca^{2+} , Na^+ and SO_4^{2-} . The concentration peaks of NO_3^- and NH_4^+ can also result from mineral dust input because the dust particles commonly act as a carrier for these pollutants (Li and others, 1995, 1999).

Throughout the entire dry season, the oxygen isotopic ratio $\delta^{18}\text{O}$ of surface snow demonstrates a trend that is reversely coincident with temperature. Therefore, the post-depositional processes during this period have little impact on its value. This can be observed clearly during the period 29 December 2004 to 30 February 2005, in which the $\delta^{18}\text{O}$ remained quite stable in spite of the effects of dry deposition, drifting snow and sublimation. NH_4^+ showing a temporal variation differs from any other ion in both surface snow and old snow, indicating that it has different provenance or may be affected by complex depositional and post-depositional mechanisms (e.g. Fuhrer and others, 1996; Andersen and others, 1999).

Characteristics of ionic concentration and $\delta^{18}\text{O}$ in the wet-season snow

We use the samples collected during the wet season from 1 April to 31 October 2004 to explore the general features of ionic concentrations and $\delta^{18}\text{O}$ in wet-season snow. In this period, the total precipitation was 579.8 mm. The temperature fluctuated between -14.2 and 7.1°C , with a mean value of -2.4°C , indicating that the elution of ions resulting from melting was vigorous. The temporal variations of ionic concentrations and $\delta^{18}\text{O}$ in surface snow, as well as the temperature and precipitation, are presented in Figure 4, in which the data from old-snow samples (shaded portion) are also included. During this period, in addition to the deposition, wind erosion and sublimation, the surface snow also experienced the meltwater-related elution process. This was found to significantly alter the chemical composition of surface snow as well as of old snow. Throughout this wet period, the concentrations of Ca^{2+} , Na^+ , K^+ , SO_4^{2-} and Mg^{2+}

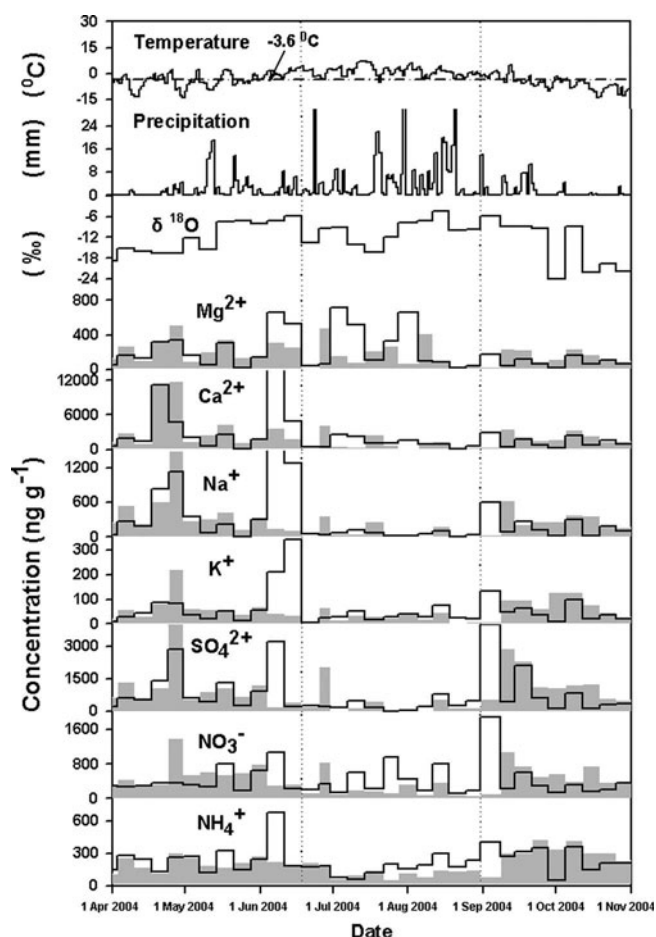


Fig. 4. Temporal variations of temperature, precipitation, $\delta^{18}\text{O}$ and ionic concentrations in surface-snow samples and old-snow samples (shaded portion) during the wet season from 1 April to 31 October 2004.

in surface snow show an analogous variation trend (with the exception of Mg^{2+} for the period 1 July to 11 August), suggesting the similarity in source and transportation, as well as depositional and post-depositional processes, of these terrestrial elements. In contrast, NO_3^- and NH_4^+ exhibit different temporal variations. As in the dry season, $\delta^{18}\text{O}$ shows an overall reverse correlation with temperature, even during the period 19 June to 31 August when snow underwent maximum melting. For a detailed analysis, the wet season was subdivided into two periods according to temperature and ionic concentration profiles as shown in Figure 4.

The first period is from 1 April to 18 June and 1 September to 1 November. During this period, the temperature fluctuated about -3.6°C . Therefore, the snow was partially affected by elution. The chemical composition of surface snow is determined by both precipitation chemistry and the elution process. Figure 4 shows that the ionic concentrations in a number of old-snow samples are higher than those in surface-snow samples, which may indicate that the chemical species in surface snow have been partially eluted downwards to underlying old snow. However, the high concentration peaks in surface snow at the beginnings of June and September apparently resulted from fresh accumulations that were not yet affected by the elution process. Throughout the period, the ionic concentrations are characterized by successional peaks and troughs, illustrating

that, in spite of the elution, general information on atmospheric depositions is preserved in both surface- and old-snow samples. In addition, the terrestrial elements, especially Mg^{2+} , Ca^{2+} , Na^+ and K^+ , exhibit high concentration peaks from 1 April to 18 June, which coincide with the Asian dust-storm period. These peaks apparently resulted from dust-storm-derived mineral aerosols that entrained in precipitation events. The low ionic concentrations in snow samples collected during the period 1 September to 1 November indicate a higher purity of the precipitation.

The second period investigated was 19 June to 31 August. In this period, the diurnal temperature was above -3.6°C , indicative of elution occurring every day. The ionic concentrations in both surface snow and old snow were found to be controlled mainly by the elution process and elution sequence of ions, and the ionic information from precipitation was mostly lost. The low concentrations of mineral elements Ca^{2+} , Na^+ , K^+ and SO_4^{2-} show that these elements are mostly leached from snow by meltwater. In contrast, the occurrence of concentration peaks of Mg^{2+} in this period is interesting. An interpretation is that Mg^{2+} is bound to the surface of insoluble dust particles. Therefore, it is less susceptible to leaching during elution compared with the other cation species that are located at ice-grain boundaries and thus are more easily washed out by meltwater. The concurrence of Mg^{2+} and insoluble microparticle peaks in the snow samples also supports this interpretation (Wang and others, 2006). NO_3^- is found to be relatively enriched in surface snow. Note that NO_3^- deposited as HNO_3 , and gas-phase HNO_3 within the snow, undergo reversible exchanges with the atmosphere and eventually equilibrate to atmospheric levels (Zhao and others, 2006). As the NO_3^- washed out from surface snow, the snow became more facilitating for atmospheric sources, which led to an increase of NO_3^- in the surface snow. The relatively high concentration of NH_4^+ in snow may be explained by the fact that NH_4^+ is relatively immobile with respect to the percolating meltwater because it is incorporated into the ice lattice (it is highly soluble in ice), as noted by Eichler and others (2001).

CONCLUSIONS

Despite the fact that the chemical species in snowpack on glaciers originate from wet depositions (precipitation) and dry depositions, our investigation shows the interannual-scale variability in snow chemistry resulting from multiple factors. To reconstruct atmospheric composition by the chemical records, those factors have to be studied and discussed. This study indicates that wet deposition is a primary input for the Tien Shan snow impurities, and the ionic stratigraphies in snow are characterized not only by precipitation composition, but also by the temporal distribution of precipitation: the dry season and wet season. The concentrations in wet-season snow are overall higher than those in dry-season snow, while the variability of relative ionic composition between dry seasons is slightly less than that between wet seasons. During dry seasons, snow chemistry is still largely controlled by the chemical content in those sporadic precipitations.

The effect of the post-depositional processes on snow chemistry is observed to be significant in both seasons. When precipitation is absent during the dry season, the effect of all post-depositional processes elevates the ionic concentrations in surface snow. During wet seasons, the

following observations are made: if the diurnal temperature is lower than -3.6°C , the snow chemistry is determined mainly by precipitation composition; if the diurnal temperature fluctuates around -3.6°C , the snow chemistry is determined by both precipitation composition and the elution process from the percolation of meltwater; and if the diurnal mean temperature rises above -3.6°C , the ionic concentrations in both surface snow and old snow are found to be controlled mainly by the elution process and the elution sequence of ions, and the ionic information from precipitation is mostly lost.

It is also observed from the investigation that $\delta^{18}\text{O}$ in surface-snow samples is reversely coincident with air temperature and relatively insignificantly affected by post-depositional processes in both dry seasons and wet seasons. This makes it a good proxy of air temperature in Tien Shan snow.

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