# Anthropogenic Sulfate and Nitrate Signals in Snow from Bogda Glacier, Eastern Tianshan

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ABSTRACT: A 1.2 m snow pit was recovered on July 29th, 2009 from the Bogda Glacier, eastern Tianshan (天山). The sample site temperature of -9.6 °C indicates that the unique glaciochemical record was well preserved and suitable for the reconstruction of air pollution levels in this previously unexplored region. Samples were analyzed for major ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, HCOO<sup>-</sup>, and CH<sub>3</sub>COO<sup>-</sup>). NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were characterized by significant high levels of pollution concentration. Most air masses backward trajectories ending in December 2008 have passed the Urumqi City center, while some even traveled across the primary nuclear weapons testing venue of the former Soviet Union (STS). The mean pH value of snow samples is coincident with the average value of Urumqi's aerosol, and the ratio of [NO<sub>3</sub><sup>-</sup>]/[SO<sub>4</sub><sup>2-</sup>] in the snow pit generally agrees with the value of the Urumqi winter aerosols. In addition, the [HCOO<sup>-</sup>]/[CH<sub>3</sub>COO<sup>-</sup>] ratio of snow samples is only 0.7, lower than unity. These analyses indicate that SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-in</sup> the Bogda Glacier are the result of anthropogenic pollutions.

KEY WORDS: anthropogenic pollutions, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>.

### INTRODUCTION

High elevated cold glaciers situated in mid-

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Manuscript received November 15, 2010. Manuscript accepted April 08, 2011. latitude regions are well suited for reconstructing atmospheric concentrations of trace species and for documenting the impact of humans on the environment (Olivier et al., 2003). Ice core records from the glaciers of Tianshan have provided unique insights into past atmospheric pollutions (Lee et al., 2003).

Chemical composition of precipitation in eastern Tianshan, China, is strongly influenced by fossil fuel combustion and agricultural and industrial practices (Wake et al., 1992; Galloway et al., 1987; Zhao and Sun, 1986). The enhanced sulfate and nitrate concentration has already been observed in the twentieth century and was attributed to  $SO_2$  and  $NO_x$  emissions from fossil fuel consumption (Preunkert et al., 2001; Schwikowski et al., 1999; Döscher et al., 1995).

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Tianshan is a remote area of the Eurasian continent. Both aeolian deposits from the arid regions of Central Asia and anthropogenic sulfate and nitrate pollution can be sources of  $SO_4^{2-}$  and  $NO_3^{-}$  on glaciers in this area (Lee et al., 2003; Hou et al., 1999; Wake et al., 1992; Williams et al., 1992).

The results of a snow pit survey for major ions at Bogda Glacier during the 2009 field season are shown in the study. The discussion also exhibits snow pits with the same sampling season from Glacier No. 1, Miaoergou Ice Cap, and Haxilegen Glacier No. 51, respectively, to form a comparative study of different glaciers in the Tianshan area.  $SO_4^{2-}$  and  $NO_3^-$ , the two most disputed chemical species as well as their relationship with  $Ca^{2+}$  and other ions found in dust are discussed in this article. The results attribute the high  $SO_4^{2-}$  and  $NO_3^-$  levels in the Bogda Glacier to anthropogenic pollutions.

# STUDY AREA AND SAMPLE ANALYSES Study Area

Tianshan is bordered on the north by the Gurbantunggut and Muyun Kum deserts, on the south by the Taklimakan desert in the Tarim basin, and on the east by the Gobi desert. Mt. Bogda is located about 2 400 km from the nearest ocean, approximately 69 km west and commonly downwind from Urumqi, a city of one million people and the economical and industrial center of the Xinjiang Uygur Autonomous Region. The mountain is controlled by high atmospheric pressure from Mongolia all the year round, and consequently, glaciers in this area have a typical continental climate. The westerly jet stream prevails across this high mountain. Temperatures are characterized by the large diurnal and annual temperature range and the small amount of precipitation is concentrated in the summer (Wu et al., 1993; Shi and Li, 1991).



Figure 1. Map showing the location of the Bogda Glacier and the surrounding geographic environment.

The glacier where these observations were conducted is located at the head of the Sigong River, 3 km north of the highest peak of Mt. Bogda (5 445 m a.s.l.). The glacier peaks at an altitude of 4 348 m a.s.l., and the glacier tongue goes down to 3 600 m a.s.l.. This glacier is a cirque-valley glacier with an area of 2.96 km<sup>2</sup>; it flows toward the north in the accumulation area and turns to the west in the ablation area. The mean air temperature at the firn line (about 3 800–3 900 m a.s.l.) is about -9  $^{\circ}$ C and the annual precipitation is 670 mm (Okitsugu et al., 1983).

Snow samples were collected during the 2009

field season at the accumulation zone of Bogda Glacier, and no melt-water was observed in the snow pit. Thus, the melt effect can be neglected. This can also be verified by very good chemical record profiles with clear fluctuations as well as a lack of change in the  $\delta^{18}$ O mean value when comparing with results from 1983 and 1992 (Wake et al., 1992; Okitsugu et al., 1983).

## Sample Analyses

A 120 cm (43°49'33"N, 88°19'32"E, 3 997 m a.s.l.) snow pit was successively sampled at the Bogda Glacier on July 29, 2009. The snow pit samples were taken at 10-cm intervals through the entire pit depth and sampling was made by personnel wearing disposable polyethylene gloves and masks to minimize contamination. All samples were transported to the Tianshan Glaciological Station's laboratory in Lanzhou in a frozen state, and then kept in a cold room at -20 °C. The ionic concentration profiles have high correlation between the neighboring samples, indicating that no contamination was introduced into the samples during the preparation and measurement procedures.

The major ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>,  $SO_4^{2-}$ , NO<sub>3</sub><sup>-</sup>, HCOO<sup>-</sup>, and CH<sub>3</sub>COO<sup>-</sup>) were analyzed by a Dionex DX-320 system with a CS12A separation column. All sample handling was done in a class-100 clean room in order to minimize contamination. Take Ca<sup>2+</sup> and Mg<sup>2+</sup> for example, the detection limits of

these two ions are 0.8 and 0.75 ng·g<sup>-1</sup>, respectively. The pH was analyzed by a pH Meter (PHJS-4A) (uncertainty of less than 1‰ for 0 to 14 measurement range). These methods have been described by Zhao and Li (2004) and Zhu et al. (2006).

## DISCUSSION

#### Overview

To provide a general indication of the chemical characteristics of the snow samples, a summary of equivalent concentrations for the ten measured major water-soluble ions is presented in Table 1. Items like  $\Sigma$ An,  $\Sigma$ Cat and  $\Sigma$ Cat/ $\Sigma$ An are also calculated.

$$\sum An=[Cl^{-}]+[NO_{3}^{-}]+[SO_{4}^{2-}]+[CH_{3}COO^{-}]+$$
[HCOO^{-}]
$$\sum Cat=[Na^{+}]+[NH_{4}^{+}]+[K^{+}]+[Mg^{2+}]+[Ca^{2+}]$$

$$\sum Cat/\sum An=([Na^{+}]+[NH_{4}^{+}]+[K^{+}]+[Mg^{2+}]+$$
[Ca<sup>2+</sup>])/([Cl^{-}]+[NO\_{3}^{-}][SO\_{4}^{2-}]+
[CH<sub>3</sub>COO<sup>-</sup>]+[HCOO<sup>-</sup>])

The sharing percentage indicates that  $Ca^{2+}$  and  $SO_4^{2-}$  are the dominant ions on Bogda Glacier, which account for 32.7% and 15.5% of the total ions in the snow samples, respectively. These two ions account for nearly half of the ten ions, followed in order by Cl<sup>-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>2+</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HCOO<sup>-</sup>, and K<sup>+</sup>.

The fact that measured cations are several times greater than measured anions in the glaciers of Tianshan has already been confirmed many times by previous studies (Kreutz et al., 2001; Wake et al., 1992). While the ratios of measured  $\sum Cat/\sum An$  in the

Table 1 Measured major ion concentrations (µeq·L<sup>-1</sup>) in snow pit samples of Bogda Glacier

Sample	Depth (cm)	Na <sup>+</sup>	$\mathrm{NH_4}^+$	$K^+$	$Mg^{2+}$	Ca <sup>2+</sup>	Cl	NO <sub>3</sub> <sup>-</sup>	$SO_4^{2-}$	HCOO <sup>-</sup>	CH <sub>3</sub> COO <sup>-</sup>
09-6831	0–15	12.4	3.8	1.3	40.2	79.2	13.5	1.8	2.9		
09-6832	15-30	3.1	5.0	0.9	5.4	15.8	3.9	2.9	3.6		
09-6833	30-45	39.0	7.3	22.3	5.5	32.9	36.6	4.8	7.2		
09-6834	45-60	2.2	5.2	0.6	2.9	16.2	1.7	5.9	7.6		
09-6835	60-75	2.3	8.3	0.9	2.2	16.1	2.6	4.6	9.1	0.2	0.3
09-6836	75–90	21.9	21.1	1.9	13.9	104.6	25.2	19.0	44.7	4.3	5.8
09-6837	90-105	23.4	13.5	2.2	16.1	96.0	24.3	21.4	57.0	10.4	13.9
09-6838	105-120	8.8	39.8	4.5	7.7	59.3	10.1	24.5	66.7	9.8	13.1
Mean value	0-120	14.1	13.0	4.3	11.7	52.5	14.7	10.6	24.9	6.2	8.3
Percentage		8.8%	8.1%	2.7%	7.3%	32.7%	9.2%	6.7%	15.5%	5.2%	3.8%
		∑Cat= 95.7			∑An= 64.7						
$\sum Cat / \sum An$							1.5				

Miaoergou Ice Cap, Glacier No. 1, and Haxilegen Glacier No. 51 snow are 3.0, 2.7 and 1.6, respectively, the ratio in Bogda Glacier snow is only 1.5 (Table 2). This low value is not due to a decrease in cation con-

centrations in Bogda Glacier, but rather as a result of the sulfate levels that are four to nine times higher in Bogda Glacier snow than in other glaciers (Fig. 2).

Table 2 Sharing percentage of  $SO_4^{2-}$  and  $Ca^{2+}$  (%) of total ions and  $\sum Cat/\sum An$  ratio in four different glaciers

Glaciers of Tianshan	SO4 <sup>2-</sup>	Ca <sup>2+</sup>	∑Cat	∑An	$\sum Cat / \sum An$	Data source
Miaoergou Ice Cap	8.8%	43.8%	39.5	13.1	3.0	Li X Y et al., 2008
Glacier No. 1	7.5%	44.0%	44.6	16.4	2.7	TGS data*
Bogda Glacier	15.5%	32.7%	95.7	64.7	1.5	This study
Haxilegen Glacier No. 51	3.9%	20.6%	10.3	6.6	1.6	Dong et al., 2010

\*. TGS data, mean value of four snow pits of Glacier No. 1 during 2003-2006.



Figure 2. Comparison of  $SO_4^{2-}$ ,  $NO_3^-$  concentrations ( $\mu eq \cdot L^{-1}$ ) in snow/ice of Polar regions and High Asia. MG. Li X Y et al., 2008; UG1. TGS (Tianshan Glaciological Station) data, mean value of four snow pits during 2003–2006; IG. Aizen et al., 2004; TP. Kang et al., 2008; Ant. Xiao et al., 2002; Gr. Dibb et al., 2007.

The  $SO_4^{2-}$  and  $NO_3^{-}$  concentrations of the four glaciers in Tianshan (Miaoergou Ice Cap, Bogda Glacier, Glacier No. 1, and Inilchek Glacier) are much higher than those of Antarctica, Greenland, and the Tibetan plateau (Fig. 2). Snow from Bogda Glacier contains two to four times more  $SO_4^{2-}$  and  $NO_3^{-}$  than the three other glaciers in Tianshan. The high values of  $SO_4^{2-}$  and  $NO_3^{-}$  in Bogda Glacier snow compare well with sulfate levels in polluted snow surrounding major industrial regions in the former Soviet Union (Belikova et al., 1984).

 $SO_4^{2-}$  and  $NO_3^{-}$  have more potential sources. Continental dust and sea spray can produce  $SO_4^{2-}$ , thus forming the primary aerosol to the atmosphere (Lee et al., 2003; Legrand and Mayewski, 1997); marine biogenic activity (Saltzman et al., 1983) and sporadic volcanic eruptions are also responsible for the secondary aerosol of  $SO_4^{2-}$  (Zielinski et al., 1994; Herron, 1982). Proposed sources of  $NO_3^{-1}$  in snowpack include marine aerosols; meteoroids; auroral activity, which is related to solar activity; cosmic ray bombardment, which is inversely related to solar activity; and X rays from supernovae (Parker et al., 1978; Wilson and House, 1965).

Researchers hold differing views on the source of  $SO_4^{2-}$  and  $NO_3^{-}$  in glaciers of Central Asia, especially in the Tianshan snow pack. Terrestrial dust is believed to be the main source of  $SO_4^{2-}$  and  $NO_3^{-}$  by many researchers (Kreutz et al., 2001; Sun et al., 1998; Williams et al., 1992); while Wake et al. (1992, 1990) attribute  $SO_4^{2-}$  to anthropogenic pollutions in snow from Bogda Peak. Studies carried out on the former Soviet Union and Kazakhstan also regard it as originating from  $SO_2$  emissions (Olivier et al., 2003; Belikova et al., 1984). The following analysis demonstrates that the high values of  $SO_4^{2-}$  and  $NO_3^{-}$  in the Bogda Glacier mainly come from anthropogenic pollutions.

# **Correlation among the Various Chemical Species**

To connect  $SO_4^{2-}$  and  $NO_3^{-}$  to their sources, correlations among the ions were investigated using factor analysis (Table 3). Factor 1 loadings are highest for  $NO_3^{-}$ ,  $SO_4^{2-}$ ,  $NH_4^{+}$ , and  $Ca^{2+}$ . The conclusion that high concentrations of  $SO_4^{2-}$  can be found in precipi-

tation is derived from many previous studies like Williams et al. (1992) and Hou et al. (1999), which chiefly accepts the factor of aeolian dust, based on the high correlation of  $SO_4^{2-}$  with  $Ca^{2+}$  in the snowpacks. However, the hypothesis that  $SO_4^{2-}$  and  $Ca^{2+}$  origi-

nated from terrestrial dust in the form of CaSO<sub>4</sub> in the snow of Bogda Glacier can be easily overturned by the distinctive feature of their profiles when compared with profiles obtained from the other glaciers in Tianshan (Fig. 3).

Flement	Component							
	Factor 1	Factor 2	Factor 3	Extraction				
Cl	0.68	0.72	0.02	0.99				
NO <sub>3</sub> <sup>-</sup>	0.87	-0.45	-0.18	0.98				
SO <sub>4</sub> <sup>2-</sup>	0.87	-0.46	-0.15	0.98				
Na <sup>+</sup>	0.62	0.78	-0.04	0.99				
$\mathrm{NH_4}^+$	0.71	-0.50	-0.33	0.87				
$K^+$	0.23	0.83	-0.44	0.94				
$Mg^{2+}$	0.19	0.11	0.93	0.91				
Ca <sup>2+</sup>	0.81	-0.06	0.56	0.98				
Fraction of variance (%)	45.0	31.3	19.2					
Cumulative (%)	95.5							

 Table 3
 Factor loading matrix for the ions in snow pit of Bogda Glacier

All snow pits analyzed at Haxilegen Glacier No. 51, Glacier No. 1, and Bogda Glacier were sampled at the same season, and thus they can reflect climate information from last winter to the late spring of each place. Obvious concentration peaks of  $SO_4^{2-}$  and  $NO_3^{-}$ can be seen at the most upper part of the snow pit in Haxilegen Glacier No. 51 and Glacier No. 1, which show the same position and a quite similar pattern with the concentration peaks of  $Ca^{2+}$  (Fig. 3). Profiles in Bogda Glacier were different from the front two glaciers. Cl<sup>-</sup>, Na<sup>+</sup>, and Ca<sup>2+</sup> have the same pattern profiles with Haxilegen Glacier No. 51 and Glacier No. 1, but SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> profiles were characterized by only one concentration peak at the bottom of the snow pit. This special phenomenon cannot be explained by the elution process because Ca<sup>2+</sup> and Na<sup>+</sup> are located in front of  $NO_3^-$  and  $NH_4^+$  in the elution sequence (Li et al., 2006; Eichler et al., 2001; Tranter et al., 1992; Brimblecombe et al., 1987). If the record was influenced by the percolation process, the concentration peak of Ca<sup>2+</sup> and Na<sup>+</sup> at the upper part should be smoother than that of  $NO_3^-$  and  $NH_4^+$ .

Dust storms in the spring and precipitation in the

following summer can bring terrestrial impurities to the glacier surface, which can then be reflected by the ionic concentration profiles (Li et al., 2006, 1999, 1995, 1994; Wake et al., 1994; Gao et al., 1992). The snowpack of Bogda Glacier can reflect climate information from the winter of 2008 to the spring of 2009. This suggests that the concentration peaks of  $Ca^{2+}$ ,  $Na^{+}$ , and  $Cl^{-}$  at the upper part of the Bogda Glacier snow pit resulted from the input of local-to-regional dust aerosols derived by strong winds in the spring of 2009.

Crustal dust in the form of  $CaSO_4$  was the source of sulfate because of the high correlation of  $Ca^{2+}$  with  $SO_4^{2-}$  (Hou et al., 1999; Williams et al., 1992). However, unlike the other three glaciers, the  $SO_4^{2-}$  profile of Bogda Glacier shows very poor similarity with  $Ca^{2+}$ in the upper part of the Bogda Glacier snow pit (Fig. 3). Thus,  $CaSO_4$  is unlikely the main compound through which  $SO_4^{2-}$  travels to the glacier and terrestrial dust is not the source of  $SO_4^{2-}$  on Bogda Glacier.

 $SO_4^{2^-}$ ,  $NO_3^-$ , and  $NH_4^+$  profiles on Bogda Glacier correlated very well with each other, as they were characterized by the only concentration peak at the

bottom of the snow pit, which can be identified as a winter deposition in 2008. According to previous studies done on Glacier No. 1, the Factor 1 in Table 3 that contains  $NO_3^-$ ,  $NH_4^+$ , and  $SO_4^{2-}$  in the snowpack has already been interpreted as an anthropogenic source component, including emissions from fossil

fuel combustion and biomass burning as well as natural fertilizers (Li et al., 2006; Lee et al., 2003). The particular geographical position of Bogda Glacier makes anthropogenic pollutions from Urumqi the most likely source of  $SO_4^{2-}$  and  $NO_3^{-}$ .



Figure 3. Profiles of ion concentration in snow pit on different glaciers in Tianshan. Profiles of Haxilegen Glacier No. 51 modified from Li X Y et al., 2008; profiles of Glacier No. 1 from TGS data, 26th July, 2006.

#### **Backward Trajectory Analysis**

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model of NOAA Air Resources Laboratory has been demonstrated as one of the most effective tools to model the air trajectory (Ming et al., 2007; Marenco et al., 2006; Ramachandran, 2005; Falkovich et al., 2001).

Urumqi (86°37'E–88°58'E, 42°45'N–44°08'N), the capital of Xinjiang Uygur Autonomous Region of China, is in the middle area of Xinjiang, on the north foot of Tianshan and the south edge of the Junggar basin (Fig. 1). For the past two decades, Urumqi has been suffering from heavy air-pollution and was

evaluated as one of the ten heaviest air polluted cities in the world in 1998 (Li J et al., 2008; Mamtimin and Meixner, 2007). Urumqi has been suffering from a very heavy haze that is caused by increasing vehicle exhausts, coal-fired power plants, and domestic heating and cooking for the past several years. The severe haze not only damages health and agriculture, but also changes the earth's radiation balance (Li J et al., 2008; Kaiser and Qian, 2002). The anion concentrations of aerosol from Urumqi were in the order of  $SO_4^{2-}>$  $NO_3^{-}>Cl^{-}>CH_2(COO)_2^{-2-}>F^{-}$ , and the  $SO_4^{-2-}$  and  $NO_3^{-}$ contributed 19.27% and 3.75% to the total aerosol mass, respectively (Li J et al., 2008). Particulate matter, also known as particle pollution or PM, is a complex mixture of extremely small particles and liquid droplets. Particle pollution is made up of a number of components, including acids (such as  $SO_4^{2-}$  and  $NO_3^{-}$ ), organic chemicals, metals, and soil or dust particles. It was reported that the annual average  $PM_{10}$  values in Urumqi were as high as 405  $\mu$ g·m<sup>-3</sup> in the 2002 winter (Feng et al., 2005).

Urumqi air pollution intensity in general is in the order of winter>spring>fall>summer in terms of seasonal variations. Clearly, winter is the most polluted season, as a result of heavy coal combustion in this



Figure 4. Daily backward trajectories arriving at the sampling site. Star. Bogda Glacier; square. Urumqi City; circle. Semipalatinsk test site.



Figure 5. Daily backward trajectories arriving at the sampling site (Continued Fig. 4).

season. Urumqi City has a typical inland climate with a dry-cold winter, so there is a half-year for house heating domestically and industrially from October 15 to April 15 of the next year. Coal combustion for heating in winter is one of the main contaminants found in air pollution. The coal-burning kilns spew out large quantities of sooty waste and chemical compounds compounds such as sulfur dioxide and nitrogen dioxide, which are still being emitted into the atmosphere endlessly. Summer is the least polluted season in Urumqi, because there is more precipitation as well as a lack of heating (Li J et al., 2008).

Furthermore, cluster analysis of the pollution index curves based on the original data of Urumqi in 2004 and 2005 shows that each curve in a calendar year peaked at both sides, and the intermediates were low (Huang, 2006). This distinctive feature indicates that Urumqi had higher levels of pollutions in the winter, especially in December. Ten heavy pollution days in December 2005 had an air pollution index of Grade V (heavy pollution), and took account for 62.5 percent of the total most polluted days in the whole year. Sulfate dioxide and nitrogen dioxide as well as micro-particles were overweight. Increasing air pollution found in Urumqi City during the winter is characterized by successive occurrences of foggy weather in December. These pollutants can then be carried by westward wind on to Bogda Glacier easily, resulting in high concentrations of  $SO_4^{2-}$  and  $NO_3^{-}$ .

Winter air pollution in Urumqi City can be further demonstrated by backward trajectory analysis, which has been applied widely in the field of atmospheric sciences (Ming et al., 2007; Kahl et al., 1997). Five-day-long backward trajectory of air masses arriving at the sampling site (43°49'33"N, 88°19'32"E) in winter 2008 has been obtained from the website (http://ready.arl.noaa.gov/HYSPLIT.php) (Figs. 4 and 5).

The trajectories ending on the 1st, 6th, 8th, 14th, 18th, and 23rd of December originated from the arid regions of west central Asia, and passed the Urumqi city center, suggesting that the high concentrations of  $SO_4^{2-}$ ,  $NO_3^{-}$ , and  $NH_4^{+}$  were caused by coal-burning from Urumqi.

The trajectories ending on the 13th, 14th, and 20th of December originated from the northwest Siberia regions travelling across the Semipalatinsk test site. The Semipalatinsk test site (STS) (50°7'0"N, 78°43'0"E) was the primary nuclear weapons testing venue of the former Soviet Union (Olivier et al., 2003). It is located in Northeast Kazakhstan, at the south valley of the Irtysh River. The nuclear test site was located around 150 km west of the Semipalatinsk town, near the border of the East Kazakhstan Province and Pavlodar Province with most of the nuclear tests taking place at various sites further to the west and south, and some as far as the Karagandy Province. The Bogda Glacier is therefore assumed to be also affected by emissions of SO<sub>2</sub>, heavy metals, and nuclear fallout from the Semipalatinsk test site in winter.

The backward trajectory analysis confirms that anthropogenic emissions from Urumqi and STS are important sources of sulfate and nitrate to the snow of Bogda Glacier downwind from the city and the testing site. Anthropogenic sources of ions in the snow of Bogda Glacier can also be demonstrated by the following supplementary analyses.

## [HCOO<sup>-</sup>]/[CH<sub>3</sub>COO<sup>-</sup>] Mass Ratio Analysis

Talbot et al. (1988) indicated that direct emissions from motor vehicles and biomass combustion processes are important sources of atmospheric acetic acid and these sources have a [HCOO<sup>-</sup>]/[CH<sub>3</sub>COO<sup>-</sup>] ratio of less than 1.0. Those influenced mainly by natural sources on the other hand, vegetation emissions in particular, have the ratio larger than unity. The mean value of [HCOO<sup>-</sup>]/[CH<sub>3</sub>COO<sup>-</sup>] in Bogda Glacier is 0.7, lower than unity and indicating that the main contribution is from anthropogenic sources. This is consistent with previous studies on Glacier No. 1. East Tianshan lies in an arid environment, and therefore the direct emission from vegetation cannot be a major source to the organic species, nor can forest fires (Lee et al., 2003). Thus, the principal source for these two organic species in Bogda Glacier must be motor vehicle exhaust, fossil fuels combustion (coal in particular), and biomass burning in Urumqi. The anthropogenic influence on this investigated glacier has been verified again.

# [NO<sub>3</sub><sup>-</sup>]/ [SO<sub>4</sub><sup>2-</sup>] Mass Ratios Analysis

Coal combustion and mobile motor vehicle exhaust emission (NO<sub>x</sub>) are an important contributor to  $SO_4^{2-}$  and  $NO_3^{-}$  in aerosols. Therefore, the mass ratio of  $[NO_3^{-}]/[SO_4^{2-}]$  has been used as an indicator of the relative importance of stationary versus mobile sources of sulfur and nitrogen in the atmosphere (Shen et al., 2007; Yao et al., 2002). The high  $[NO_3^{-}]/[SO_4^{2-}]$  ratio is usually ascribed to the predominance of mobile sources over stationary sources of pollutants (Xiao and Liu, 2004; Arimoto et al., 1996). In Bogda Glacier, the ratio  $[NO_3^{-}]/[SO_4^{2-}]$  in snow pit samples ranged from 0.37 to 0.77 (averaging 0.43), and was basically consistent with the 0.20 in the Urumqi winter aerosols (Li J et al., 2008). The relatively higher  $[NO_3^{-}]/[SO_4^{2-}]$  ratio in Bogda Glacier than that of

Urumqi winter aerosols can be ascribed to the extreme abundance of  $SO_4^{2^-}$ . This also indicates that the pollution from Urumqi is the principal contributor to the high levels of  $SO_4^{2^-}$  and  $NO_3^-$  in Bogda Glacier snow.

## Low pH Value

Usually, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, HCOO<sup>-</sup>, and CH<sub>3</sub>COO<sup>-</sup> in the air are in an acidic form and contribute significantly to the free acidity of precipitation, especially in remote areas (Lee et al., 2003; Baltensperger and Kern, 1988; Backman and Peden, 1987; Galloway and Gaudry, 1984; Keene and Galloway, 1984). The acidity, however, can be abased in the atmosphere by either directly reacting with mineral dust, carbonates in particular, or being scavenged in water droplets. The process that eventually results in the increase of pH in the atmosphere is a well-known phenomenon (Lee et al., 2003; Mori et al., 1998; Mauptit and Delmas, 1994; Williams et al., 1992).

The mean pH value of Bogda Glacier snow is 5.9 with a range of 5.4–6.2, which is much lower than that of Glacier No. 1 (6.9, 6–9, respectively), while the pH value correlates well with the average pH value of 5.80 in Urumqi aerosol (Li J et al., 2008). These results indicate that there are much higher secondary aerosols, mainly  $SO_4^{2-}$  and  $NO_3^{-}$  in the aerosols from Urumqi and this polluted aerosol has been carried on to Bogda Glacier.

# CONCLUSIONS

The snow pit samples in Bogda Glacier provided the record of anthropogenic polluted  $SO_4^{2-}$  and  $NO_3^{-}$ . (1) Most backward trajectories that end in December 2008 passed the Urumqi City center, while some even traveled across STS (the primary testing venue for the former Soviet Union's nuclear weapons), suggesting that the high concentration of  $SO_4^{2-}$ ,  $NO_3^{-}$  in Bogda Glacier undoubtedly came from pollutants. (2) The ratio of  $[NO_3^-]/[SO_4^{2-}]$  in Bogda Glacier agreed with the value of the Urumqi winter aerosols and the [HCOO<sup>-</sup>]/[CH<sub>3</sub>COO<sup>-</sup>] ratio is 0.7, lower than unity. Both of the two mass ratios indicate that  $SO_4^{2-}$  and NO<sub>3</sub><sup>-</sup> in Bogda Glacier mainly came from anthropogenic pollutions. (3) The mean pH value of Bogda Glacier snow is lower than that of Glacier No. 1, and it correlated well with the average pH value of Urumqi aerosol, strengthening support for the hypothesis that  $SO_4^{2-}$  and  $NO_3^{-}$  has been carried on to Bogda Glacier by polluted aerosols from Urumqi.

Future ice core drilling efforts in this region will provide longer glaciochemical records and give a more historical perspective to anthropogenic pollutions.

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#### **REFERENCES CITED**

- Aizen, V. B., Aizen, E. M., Melack, J. M., et al., 2004. Association between Atmospheric Circulation Patterns and Firn-Ice Core Records from the Inilchek Glacierized Area, Central Tien Shan, Asia. *Journal of Geophysical Research*, 109(D08): D08304
- Arimoto, R., Duce, R. A., Savoie, D. L., et al., 1996. Relationships among Aerosol Constituents from Asia and the North Pacific during Pem-West A. *Journal of Geophysical Research*, 101(D1): 2011–2023
- Backman, S. R., Peden, M. E., 1987. Determination of Organic Acid Anions in Precipitation by Ion Chromatography Exclusion. *Water*, Air & Soil Pollution, 33(1–2): 191–198
- Baltensperger, U., Kern, S., 1988. Determination of Mono-Valent and Divalent-Cations and Anions in Small Fog Samples by Ion Chromatography. *Journal of Chromatography*, 439(1): 121–127
- Belikova, T. V., Vasilenko, V. N., Nazarov, I. M., et al., 1984.
  Characteristics of Background Sulfate Pollution of the Snow Cover on the Territory of the USSR. *Meteorologiya i Gidrologiya*, 9: 47–55
- Brimblecombe, P., Clegg, S. L., Davies, T. D., et al., 1987. Observations of the Preferential Loss of Major Ions from Melting Snow and Laboratory Ice. *Water Research*, 21(10): 1279–1286
- Dibb, J. E., Whitlow, S. I., Arsenault, M., 2007. Seasonal Variations in the Soluble Ion Content of Snow at Summit. Greenland: Constraints from Three Years of Daily Surface Snow Samples. *Atmospheric Environment*, 41(24):

5007-5019

- Dong, Z. W., Li, Z. Q., Zhang, M. J., et al., 2010. Chemistry and Environmental Significance of Snow on Haxilegen Glacier No. 51 in Kuytun of Eastern Tianshan Mountains. *Scientia Geographica Sinica*, 30(1): 149–156 (in Chinese with English Abstract)
- Döscher, A., Gäggeler, H. W., Schotterer, U., et al., 1995. A 130 Years Deposition Record of Sulfate, Nitrate and Chloride from a High-Alpine Glacier. *Water Air & Soil Pollution*, 85(2): 603–609
- Eichler, A., Schwikowski, M., Gäggeler, H. W., 2001. Melt-Waterinduced Relocation of Chemical Species in Alpine Firn. *Tellus*, 53B(2): 192–203
- Falkovich, A. H., Ganor, E., Levin, Z., et al., 2001. Chemical and Mineralogical Analysis of Individual Mineral Dust Particles. *Journal of Geophysical Research*, 106(D16): 18029–18036
- Feng, Y. G., Peng, L., Wu, J. H., et al., 2005. Analytical Studies on Source of TSP and PM<sub>10</sub> in Environmental Air of Urumchi City. *China Environment Science*, 25(Suppl.): 30–33 (in Chinese with English Abstract)
- Galloway, J. N., Gaudry, A., 1984. The Composition of Precipitation on Amsterdam-Island, Indian-Ocean. *Atmospheric Environment*, 18(12): 2649–2656
- Galloway, J. N., Zhao, D. W., Xiong, J. L., et al., 1987. Acid Rain: China, United States, and a Remote Area. *Science*, 236(4808): 1559–1562
- Gao, Y., Arimoto, R., Zhou, M. Y., et al., 1992. Relationships between the Dust Concentrations over Eastern Asia and the Remote North Pacific. *Journal of Geophysical Research*, 97(D9): 9867–9872
- Herron, M. M., 1982. Impurity Sources of F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in Greenland and Antarctic Precipitation. *Journal of Geophysical Research*, 87(NC4): 3052–3060
- Hou, S. G., Qin, D. H., Ren, J. W., 1999. The Present Environmental Processes of Ice Core pH and Conductivity Records: A Case Study at the Headwaters of the Ürümqi River. *Journal of Glaciology and Geocryology*, 21(4): 371–379 (in Chinese with English Abstract)
- Huang, G. Q., 2006. Variation Analysis of Air Pollution in Ürümqi City Center. *Gansu Agriculture*, 6: 281 (in Chinese)
- Kahl, J. D. W., Martinez, D. A., Kuhns, H., et al., 1997. Air Mass Trajectories to Summit, Greenland: A 44-Year Climatology and Some Episodic Events. *Journal of Geophysical Research*, 102(C12): 26861–26875

- Kaiser, D. P., Qian, Y., 2002. Decreasing Trends in Sunshine Duration over China for 1954–1998: Indication of Increased Haze Pollution? *Geophysical Research Letters*, 29: 2042–2045
- Kang, S. C., Huang, J., Xu, Y. W., 2008. Changes in Ionic Concentrations and  $\delta^{18}$ O in the Snowpack of Zhadang Glacier, Nyainqentanglha Mountain, Southern Tibetan Plateau. *Annals of Glaciology*, 49(1): 127–134
- Keene, W. C., Galloway, J. N., 1984. Organic Acidity in Precipitation of North America. *Atmospheric Environment*, 18(11): 2491–2497
- Kreutz, K. J., Aizen, V. B., Cecil, L. D., et al., 2001. Oxygen Isotopic and Soluble Ionic Composition of a Shallow Firn Core, Inilchek Glacier, Central Tien Shan. *Journal of Glaciology*, 47(159): 548–554
- Lee, X. Q., Qin, D. H., Jiang, G. B., et al., 2003. Atmospheric Pollution of a Remote Area of Tianshan Mountain: Ice Core Record. *Journal of Geophysical Research*, 108(D14): 4406
- Legrand, M., Delmas, R. J., 1987. A 220-Year Continuous Record of Volcanic H<sub>2</sub>SO<sub>4</sub> in the Antarctic Ice-Sheet. *Nature*, 327(6124): 671–676
- Legrand, M., Mayewski, P., 1997. Glaciochemistry of Polar Ice Cores: A Review. *Reviews of Geophysics*, 35(3): 219–243
- Li, J., Zhuang, G. S., Huang, K., et al., 2008. Characteristics and Sources of Air-Borne Particulate in Urumqi, China, the Upstream Area of Asia Dust. *Atmospheric Environment*, 42(4): 776–787
- Li, X. Y., Liu, S. Y., Han, T. D., et al., 2008. Ion Concentration in Snow Pits on Glaciers in Eastern Tianshan Mountain— Take Haxilegen Glacier No. 51 of Kuitun River and Hami Miaoergou Flat-Topped Glacier as an Example. *Advances in Earth Science*, 23(12): 1268–1276 (in Chinese with English Abstract)
- Li, Z. Q., Edwards, R., Mosley-Thompson, E., et al., 2006. Seasonal Variability of Ionic Concentrations in Surface Snow and Elution Processes in Snow-Firn Packs at the PGPI Site on Ürümqi Glacier No. 1, Eastern Tien Shan, China. Annals of Glaciology, 43: 250–256
- Li, Z. Q., Lu, G. X., Liu, B. Z., et al., 1999. Ice Core Dust Particulate by XPS-SEM/EDAX—Impact of Dust Particulate on SO<sub>4</sub> <sup>2-</sup> Record in Ice Cores. *Chinese Science Bulletin*, 44(15): 1424–1427
- Li, Z. Q., Yao, T. D., Xie, Z. C., 1995. The Studies of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in Aerosol. *Advance in Earth Sciences*, 10(3): 289–295 (in Chinese with English Abstract)

- Li, Z. Q., Yao, T. D., Xie, Z. C., et al., 1994. Modern Atmospheric Environmental Records in Guliya Ice-Cap of Qinghai-Xizang Plateau. *Chinese Science Bulletin*, 40(10): 874–876
- Mamtimin, B., Meixner, F. X., 2007. The Characteristics of Airpollution in the Semi-Arid City of Urumqi (NW China) and Its Relation to Climatological Process. *Geophysical Research Abstracts*, 9: 06537
- Marenco, F., Bonasoni, P., Calzolari, F., et al., 2006. Characterization of Atmospheric Aerosols at Monte Cimone, Italy, during Summer 2004: Source Apportionment and Transport Mechanisms. *Journal of Geophysical Research*, 111(D24): D24202
- Maupetit, F., Delmas, R. J., 1994. Snow Chemistry of High-Altitude Glaciers in the French Alps. *Tellus*, 46(4): 304–324
- Ming, J., Zhang, D. Q., Kang, S. C., et al., 2007. Aerosol and Fresh Snow Chemistry in the East Rongbuk Glacier on the Northern Slope of Mt. Qomolangma (Everest). *Journal of Geophysical Research*, 112(D15): D15307
- Mori, I., Nishikawa, M., Iwasaka, Y., et al., 1998. Chemical Reaction during the Coagulation of Ammonium Sulphate and Mineral Particles in the Atmosphere. *Science of the Total Environment*, 224(1–3): 87–91
- Okitsugu, W., Nobuko, K., Yutaka, A., et al., 1983. A Preliminary Report on the Chemical Composition of Glaciers in the Eastern Tian Shan Mountains. *Journal of Glaciology* and Cryopedology, 5(3): 91–100
- Olivier, S., Schwikowski, M., Brutsch, S., et al., 2003. Glaciochemical Investigation of an Ice Core from Belukha Glacier, Siberian Altai. *Geophysical Research Letters*, 30(19): 2019
- Parker, B. C., Heiskill, L. E., Thompson, W. J., et al., 1978. Non-Biogenic Fixed Nitrogen in Antarctica and Some Ecological Implications. *Nature*, 271(5646): 651–652
- Preunkert, S., Legrand, M., Wagenbach, D., 2001. Sulfate Trends in a Col du Dome (French Alps) Ice Core: A Record of Anthropogenic Sulfate Levels in the European Midtroposphere over the Twentieth Century. *Journal of Geophysical Research*, 106(D23): 31991–32004
- Ramachandran, S., 2005. PM<sub>2.5</sub> Mass Concentrations in Comparison with Aerosol Optical Depths over the Arabian Sea and Indian Ocean during Winter Monsoon. *Atmospheric Environment*, 39(10): 1879–1890
- Saltzman, E. S., Savoie, D. L., Zika, R. G., et al., 1983. Methane Sulfonic Acid in the Marine Atmosphere. *Journal of*

Geophysical Research, 88(NC15): 897–902

- Schwikowski, M., Döscher, A., Gäggeler, H. W., et al., 1999. Anthropogenic versus Natural Sources of Atmospheric Sulphate from an Alpine Ice Core. *Tellus*, 51(5): 938–951
- Shen, Z. X., Li, L. Z., Du, N., et al., 2007. Mass Concentration and Water-Soluble Ions in Spring Aerosol (PM<sub>2.5</sub>) at Xi'an. *Ecology and Environment*, 16(4): 1193–1198 (in Chinese with English Abstract)
- Shi, Y. F., Li, J. J., 1991. Glaciological research of the Qinghai-Xizang Plateau in China. In Proceedings of Symposium on Qinghai-Xizang (Tibet) Plateau. Science Press, Beijing. 1589–1597 (in Chinese)
- Sun, J. Y., Qin, D. H., Mayewski, P. A., et al., 1998. Soluble Species in Aerosol and Snow and Their Relationship at Glacier 1, Tien Shan, China, *Journal of Geophysical Research*, 103(D21): 28021–28028
- Talbot, R. W., Beecher, K. M., Harriss, R. C., et al., 1988. Atmospheric Geochemistry of Formic and Acetic Acids at a Mid-Latitude Temperate Site, *Journal of Geophysical Research*, 93(D2): 1638–1652
- Tranter, M., Tsiouris, S., Davies, T. D., et al., 1992. A Laboratory Investigation of the Leaching of Solute from Snowpack by Rainfall. *Hydrological Processes*, 6(2): 169–178
- Wake, C. P., Mayewski, P. A., Li, Z., 1994. Modern Eolian Dust Deposition in Central Asia. *Tellus*, 46(3): 220–233
- Wake, C. P., Mayewski, P. A., Spencer, M. J., 1990. A Review of Central Asian Glaciochemical Data. *Annals of Glaciol*ogy, 14: 301–306
- Wake, C. P., Mayewski, P. A., Wang, P., et al., 1992. Anthropogenic Sulfate and Asian Dust Signals in Snow from Tien Shan, Northwest China. *Annals of Glaciology*, 16: 45–52
- Williams, M. A., Tonnessen, K. A., Melack, J. M., et al., 1992. Sources and Spatial Variation of the Chemical Composition of Snow in the Tien Shan, China. *Annals of Glaciol*ogy, 16: 25–32
- Wilson, A. T., House, D. A., 1965. Fixation of Nitrogen by Aurora and Its Contribution to the Nitrogen Balance of the Earth. *Nature*, 205: 793–794
- Wu, G. H., Yutaka, A., Qiu, J. Q., 1983. Physical Geographic Features and Climatic Conditions of Glacial Development in Bogda Area, Tianshan. *Journal of Glaciology and Cryopedology*, 5(3): 5–16 (in Chinese with English Abstract)
- Xiao, C. D., Qin, D. H., Ren, J. W., et al., 2002. Glaciochemistry Distribution in the Surface Snow/Ice in Some Key Re-

gions of the Cryosphere: The Environmental Significance. *Journal of Glaciology and Geocryology*, 24(5): 492–499 (in Chinese with English Abstract)

- Xiao, H. Y., Liu, C. Q., 2004. Chemical Characteristics of Water Soluble Components in TSP over Guiyang, SW China, 2003. Atmospheric Environment, 38(37): 6297–6306
- Yao, X. H., Chan, C. K., Fang, M., et al., 2002. The Water-Soluble Ionic Composition of PM<sub>2.5</sub> in Shanghai and Beijing, China. *Atmospheric Environment*, 36(26): 4223–4234
- Zhao, D., Sun, B., 1986. Air Pollution and Acid Rain in China. *Ambio*, 15(1): 2–5

- Zhao, Z. P., Li, Z. Q., 2004. Determination of Soluble Ions in Atmospheric Aerosol by Ion Chromatography. *Modern Scientific Instruments*, 5: 46–49 (in Chinese with English Abstract)
- Zhu, Y. M., Li, Z. Q., You, X. N., 2006. Application in Glacier by Accusizer 780A Optical Particle Sizer. *Modern Scientific Instruments*, 3: 81–84 (in Chinese with English Abstract)
- Zielinski, G. A., Mayewski, P. A., Meeker, L. D., et al., 1994.
  Record of Volcanism since 7000 B.C. from the GISP2
  Greenland Ice Core and Implications for the Volcano-Climate System. *Science*, 264(5161): 948–952