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Selected Trace Elements in Snowpack on Urumqi Glacier No. 1, Eastern Tianshan, China: As Yielded by Leaching Treatment Representative of Real-World Environmental Conditions

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ABSTRACT: To investigate the seasonal variability and potential environmental significance of trace elements in mountain glaciers, the surface snow and snow pit samples were collected at Urumqi Glacier No. 1 (43º06'N, 86º49'E, 4 130 m a.s.l.), eastern Tianshan (天山), from September 2002 to September 2003, and analyzed for Li, V, Cr, Mn, Co, Cu, and Ba. The samples were acidified (leached) in a manner intended to reasonably approximate the extent to which the natural hydrologic and weathering cycles would liberate elements from mineral grains (dusts) in the ice and snow into the environment. The mean concentrations of Li, V, Cr, Mn, Co, Cu, and Ba are 0.2, 1.1, 0.8, 14.8, 0.1, 0.7, and 3.2 ng/g in surface snow but 1.0, 2.2, 1.8, 92.4, 0.8, 2.9, and 16.2 ng/g in snow pits, respectively. Input varies seasonally: in general, concentrations in the winter are higher than those in the summer. The trace elements are somewhat enriched (relative to expected abundances in material taken directly from the earth's crust) and similar to what is observed in both pre-industrial and modern atmospheric dusts, although some anthropogenic components from nearby industrial cities may be present. Concentration vertical profiles can be redistributed in the post-depositional process, which may cause loss of trace elements in the summer.

KEY WORDS: trace element, snowpack, post-depositional process, Urumqi Glacier No. 1.

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INTRODUCTION

Trace elements in snow/ice records have provided an indication of atmospheric environmental deposition (Fortner et al., 2009; Planchon et al., 2002; Candelone et al., 1996; Lambert et al., 1990). Many researchers have discovered that mountain glaciers at mid/low latitude in high-elevation Asia are sensitive to climatic changes and anthropogenic activities (Aizen et al., 2009; Bajracharya et al., 2008). During recent decades, trace elements in snow/ice have been measured around glaciers in high Asia, such as the Tibetan plateau (including the Himalayas and Karakorum), Tianshan, Pamir, and Altai. Comparing concentrations of selected trace element at several sampling sites along Himalayas-Tianshan, Kaspari et al. (2009) found that concentrations in the South Tibetan plateau are much lower than those in Central Asia, where they may be affected by Asian dust aerosol. However, more scientists have highlighted the anthropogenic factors in snow/ice records. In several previous studies, the Pb and Cd concentrations in the ice cores at both south and north parts of the Tibetan plateau grew during the 20th century as a result of human activities (Xiao et al., 2001; Li et al., 2000; Huo et al., 1999). Later studies have shown that the concentrations have tended to decrease since mid-1990s with controls on pollution sources. For example, analysis of ice cores acquired from East Pamir indicated that Sb, Bi, and Pb concentrations increased from the 1960s to the early 1990s and then decreased in the mid to late 1990s (Li Y F et al., 2006; Li Z et al., 2006). Recently, snow/ice samples collected from the Tibetan plateau and Tianshan were analyzed for more element types, and trace elements were classified as coming from natural and anthropogenic sources (Duan et al., 2009; Lee et al., 2008; Zhang et al., 2008; Kang et al., 2007; Li Z Q et al., 2007).

The eastern Tianshan, with its many mountain glaciers, lies in the center of the Eurasian continent. This region is clearly affected by regional human activities, but scientific research about the human impact on glaciers is still in its early stages, and reports are few on trace elements in the snow/ice from such regions. In order to investigate the depositional and post-depositional processes of chemical substances in snowpack of mountain glaciers, the Program for Glacier Processes Investigation (PGPI) was established at Urumqi Glacier No. 1 (UG1) by the Tianshan Glaciological Station (TGS), Chinese Academy of Sciences (CAS). Based on PGPI, Li Z Q et al. (2007) provided preliminary results from measurements of Pb, Cd, Zn, Al, and Fe in snowpack on UG1, but results were restricted only to that limited suite of elements.

SITE DESCRIPTION

UG1 (43º06'N, 86º49'E) is situated at the headwaters of Urumqi River in Tianshan, Xinjiang Uygur Autonomous Region, Northwest China (Fig. 1a). The air regime of the study area is controlled by the Westerlies in the Northern Hemisphere all year-round (Zhang et al., 1994). Several deserts are distributed near the eastern Tianshan, including the Taklimakan desert to the south and Gurbantunggut desert to the north.

Annual mean temperature at the headwaters region of Urumqi River (Fig. 1b) is -5.2 ℃ (meteorological data from 1959 to 2000; Jiao et al., 2004). The monthly mean temperature is below 0 ℃ from October to April. January is the coldest month, and July is the hottest. The annual precipitation at the headwaters region is 440 mm, and precipitation from May to September makes up 90% of the total (Jiao et al., 2004).

UG1 is a northwest-facing valley glacier covering 1.68 km^2 (measured in 2006, Zhou, 2009), which is composed of the east branch (1.09 km^2) and west branch (0.59 km^2) (Fig. 1c). The annual equilibrium line altitude has averaged approximately 4 055 m a.s.l. from 1959 to 2003. The sampling site, which is also known as the PGPI site, is in the percolation zone at the east branch of UG1 at an altitude of 4 130 m a.s.l. (Dong et al., 2010; Li Z Q et al., 2008, 2007, 2006; Wang et al., 2008, 2006; Li X Y et al., 2007; Zhao et al., 2006). There is no direct wintertime exposure to sunshine due to the shadowing effect of the mountain ridges at the sampling site (Li Z Q et al., 2006).

The study area is affected by local or regional anthropogenic activities. Urumqi City, capital of Xinjiang Uygur Autonomous Region, lies 105 km northeast of UG1. Houxia Town is a town with coal-fired power generating plants, a cement factory, and other factories, 50 km away. In this town, fly ash and

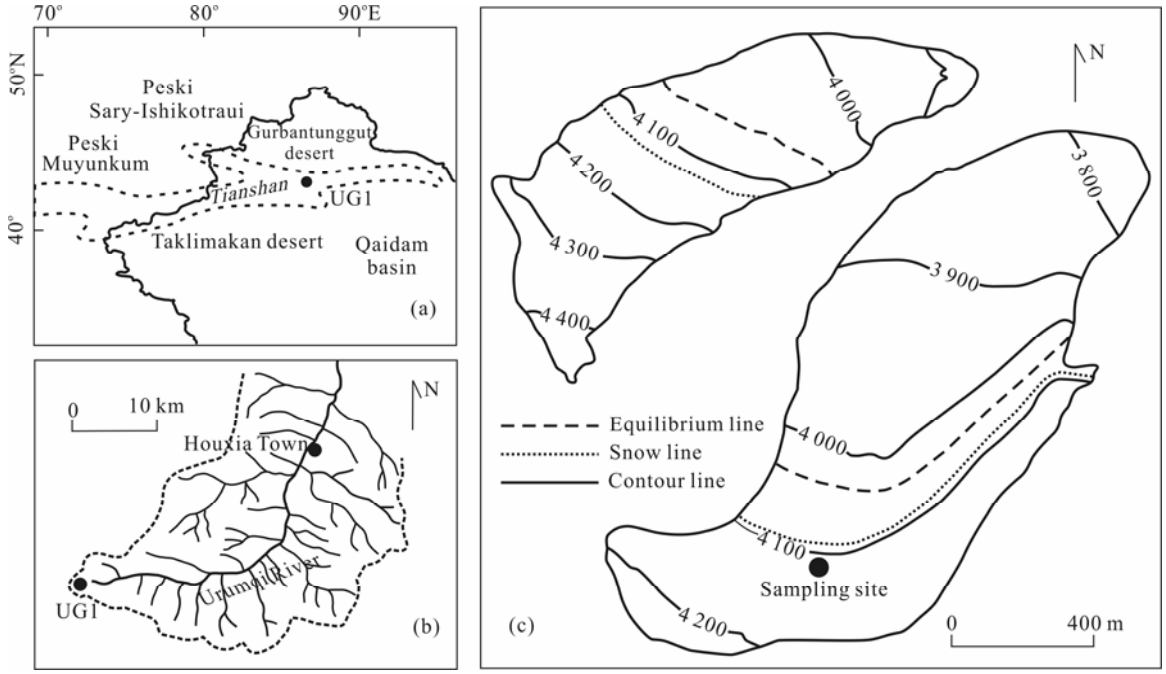

Figure 1. Maps showing locations of the eastern Tianshan (a), the headwaters region of Urumqi River (b), and the sampling site on UG1 (c).

atmospheric emissions are not well treated at most factories. Additionally, local inhabitants use coal for domestic cooking and heating (Zhao et al., 2008).

MATERIALS AND METHODS

Sampling

All the sampling utensils in this study were pre-cleaned by successive soakings in six acid baths in a 100-class clean bench inside a 1000-class clean room in the State Key Laboratory of Cryospheric Sciences (SKLCS, formerly Key Laboratory of Ice Core and Cold Regions Environment), Cold and Arid Regions Environmental and Engineering Research Institute (CAREERI), CAS, Lanzhou, China (Li Y F et al., 2006). All the clean equipments were air-dried in the bench and then sealed in two layers of clean low-density polyethylene (LDPE) bags where they remained until time of sampling.

The samples of surface snow and from snow pits were taken at UG1 with a monthly frequency. There were a total of 113 snow samples collected from 13 snow pits from September 2002 to September 2003. The sampling dates were September 27, October 25, November 29, and December 27, 2002 and January 23, February 27, March 27, April 26, May 29, June 26, July 31, August 30, and September 27, 2003. According to the depth of snowpack, the number of samples collected at each snow pits ranged from 4 to 17. If there was insufficient precipitation (i.e., no recent new snow) prior to sampling dates in the winter months, the top 3 cm of snowpack was sampled; if sufficient new snow had fallen before sampling, the top 1 cm of fresh snow was sampled. In the summer months, if there was sufficient new precipitation, snow samples no more than 2 days old were collected from the top 3 to 5 cm. The snow pit samples were acquired from the top to the bottom at a 10 cm resolution. After each sampling, the site was refilled and marked. During the next sampling, the same pit was re-excavated and the sampling wall was scaled back by at least 50 cm before the new collection. A strict protocol was followed during this procedure to prevent the samples from being contaminated, including using disposable polyethylene gloves, masks, and pre-cleaned polyethylene sample containers. The samples were sealed in two layers of polyethylene bags, transported in insulated boxes to the laboratory, and kept frozen (-15 ℃) until analysis. More details about sampling were described by Li Z Q et al. (2007, 2006).

Experimental Procedures

Ultrapure water (18.2 MΩ Milli-Q) and HNO_3

were applied to clean the laboratory equipment and for preparation of standard solutions. The samples were acidified to make 0.5% solution (1 mL 5% HNO_3 and 9 mL liquid sample were placed together into a 15 mL centrifuge polypropylene bottle, where 5% HNO_3 (v/v) was made by diluting 60% Merck Ultrapur HNO_3 with 18.2 MΩ Milli-Q ultrapure water), just after the snow/ice melted. The acidified samples were refrozen after 3 to 5 hours and melted again just before analysis. These samples are operationally defined as acid-leached rather than digested. Concentrations of Li, V, Cr, Mn, Co, Cu, and Ba in the samples were measured using an inductively coupled plasma mass spectrometer (ICP-SFMS, Element, Bremen, Germany) located in another 1000-class clean room. To avoid introduction of mineral particles (dust) into the plasma, the acidified samples were centrifuged just before analyzing and only the upper part of samples in the tube was introduced into the plasma. We propose that the amount of the elements present in the solutions we analyzed in the instrument are environmentally relevant, in that they include (a) the amounts initially in aqueous solution in the snow and (b) the amounts that would likely be removed by natural leaching from the surfaces of mineral (dust) grains during the typical environmental processes of the water cycle, including the melting and transport of the glacier materials.

The detection limits for Li, V, Cr, Mn, Co, Cu, and Ba were 0.2, 2.0, 1.1, 6.4, 2.2, 8.2, and 3.4 pg/g, respectively. The precision of the measurements in terms of relative standard deviation (RSD) was lower than 10%. The Standard Reference Material SRM-1640 (trace elements in natural water, National Institute of Standards and Technology, USA) was used for assessing the accuracy of the method. The results of selected elements, together with certified values (in parentheses), were (in ng/g): Li, 48.9±0.7 (50.7±1.4); V, 14.1±0.2 (12.99±0.37); Cr, 39.93±0.81 (38.6±1.6); Mn, 126±3 (121.5±1.1); Co, 20.03±0.32 (20.28±0.31); Cu, 88.9±1.1 (85.2±1.2); and Ba, 152.06±1.64 (148.0±2.2), respectively.

RESULTS AND DISCUSSION

Descriptive Statistics

The mean concentrations of Li, V, Cr, Mn, Co, Cu, and Ba are shown in Table 1. There are large differences in the concentrations of the different elements. The hierarchy of concentrations for the different elements remains similar but not identical from sample to sample. Co, the lowest concentration element in both the surface snow and the snow pit samples, is two orders of magnitude lower than Mn, which has the highest concentration. The concentration order in the surface snow is Mn>Ba>V>Cr>Cu>Li>Co, while that in the snow pits is Mn>Ba>Cu>V>Cr>Li>Co. However, the small differences in the hierarchical order of relative concentrations displayed among V, Cr, and Cu are due to the similarity in the concentrations of those elements.

Another feature is that concentrations in samples from the snow pits are much higher than those in the surface snow by at least a factor of two. This is true especially for Mn, Co, and Ba, where the concentrations of these metals in the snow pits, is 6.2, 5.6, and 5.1 times higher than that in the surface snow, respectively. This contrast is consistent throughout our sample suites. A previous study of UG1 (Wang et al., 2006) found that dust layers in the snowpack contain abundant insoluble microparticles, and the concentration peaks of some inorganic ions often occur near the dust layers. Vertical profiles of Li, V, Cr, Mn, Co, Cu, and Ba concentration on September 27, 2003, as well as dust layers (marked by cross hatched area), are shown in Fig. 2. The concentration peaks coincide with the dust layers (especially for the older dust layers at the bottom section in the snowpack).

Spatial Comparison of Concentration

Prior to this study, for the eastern Tianshan, most elements in this study have not been measured and reported. Compared with other remote regions, mean concentrations of the selected trace elements on UG1 are generally higher than those in Polar Regions and other mountain glaciers (Table 2). The concentrations of element in the snow samples on UG1 are about two to five orders of magnitude higher than reported from Antarctica, depending on the element.

The concentration of trace elements in Tianshan snow may be influenced by Asian dust input and local pollution (Kaspari et al., 2009; Li Z Q et al., 2007; Lee et al., 2003). It is not surprising that the concentration of trace elements on UG1 is higher than that in

Table 1 Mean concentrations and standard deviation of Li, V, Cr, Mn, Co, Cu, and Ba in the surface snow and snow pit samples collected from UG1 from September 2002 to September 2003

Element	Number of samples		Mean concentration (ng/g)		Concentration ratio*	Standard deviation (ng/g)	
	Surface snow	Snow pit	Surface snow	Snow pit		Surface snow	Snow pit
Li	12	110	0.2	1.0	4.8	0.2	0.9
V	12	110	1.1	2.2	2.1	1.8	2.0
Cr	10	90	0.8	1.8	2.2	0.7	1.1
Mn	11	100	14.8	92.4	6.2	16.4	119.9
Co	12	110	0.1	0.8	5.6	0.2	1.0
Cu	12	110	0.7	2.9	4.2	0.9	3.8
Ba	12	110	3.2	16.2	5.1	3.6	20.2

*. Concentration ratio=(concentration in snow pit)/(concentration in surface snow).

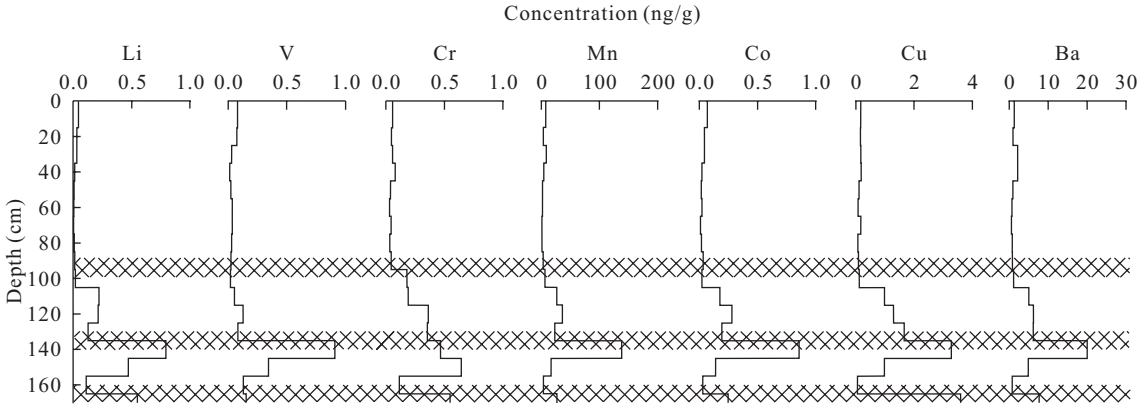

Figure 2. The relationship among Li, V, Cr, Mn, Co, Cu, and Ba concentrations and dust layers (marked by cross-hatched area) in snowpack on UG1 on September 27, 2003.

Table 2 Comparisons of mean concentrations of Li, V, Cr, Mn, Co, Cu, and Ba in the snow samples collected from UG1 with other remote regions

Location	Material	Concentration (pg/g)							Reference
		Li	V	Cr	Mn	Co	Cu	Ba	
Lambert Glacier basin, Antarctica	Snow pit		0.46		3.7		5.3	2.4	Hur et al. (2007)
Atqasuk, Alaska	Surface snow		350		3 320			2 970	Douglas and Sturm (2004)
Summit, Greenland	Surface snow					10.8	13.6		Barbante et al. (2003)
Summit, Greenland	Snow pit					5.8	4.7		Barbante et al. (2003)
Fedchenko Glacier, Pamirs	Firn core		137	146	4 200	60		817	Aizen et al. (2009)
Mt. Qomolangma, Himalaya	Snow pit					7.5	44	73	Duan et al. (2009)
Mt. Qomolangma, Himalaya	Surface snow		139	34	2 000		343		Kang et al. (2007)
Mt. Qomolangma, Himalaya	Snow pit		111	104	1 300	36	76		Lee et al. (2008)
UG1, Tianshan	Surface snow	202	1 070	801	14 800	144	678	3 190	This study
UG1, Tianshan	Snow pit	963	2 230	1 790	92 400	808	2 870	16 200	This study

Antarctica. However, the concentration of trace elements on UG1 is generally higher than most mountain glaciers. It is important to try to gain insight into the causes of the relatively high concentrations of trace elements in snow from UG1.

Seasonality of Input

Surface snow is at the interface between the atmosphere and the snowpack. Trace element inputs vary seasonally, as can be seen by the contrast in concentrations between in surface snow (consistently collected as soon as possible after deposition, before exposure to dry deposition) and snow within the snowpack (which, on average, was exposed to deposition and post-deposition for longer times). Post-depositional process may variably influence redistribution of chemical components in the snowpack (Schotterer et al., 2004). In order to avoid complications from that effect, we sampled from several stratigraphic sequences (snowpacks) from each of a closely spaced linear array of snow pits (Fig. 3).

Generally, concentrations of trace elements in the winter are higher than those in the summer. Most elements peaked in November or December 2002. Due to local meteorological conditions, the concentration of trace elements in the atmosphere of Urumqi City also increases in the winter (Wu et al., 2008). As shown in Fig. 3, during January 2003, the concentration of almost every element dropped suddenly. During the 10 days preceding sampling (January 23, 2003), there was no precipitation and the mean temperature was -9.1 ℃. The upper 10 cm of the snow pit was affected by wind erosion, according to the physical texture of the profile on January 23, 2003. Fresh snow was collected on both the previous sampling day (December 27, 2002) and the following sampling day (February 27, 2003). Following from those facts, wind erosion may be the reason for the observed drop in concentrations.

The low concentrations of January 2003 were followed by an increase over the next months. Li, Mn, Co, Cu, and Ba all peaked in February, and V and Cr peaked in March. Slight peaks occurred in May 2003 for Co, Cu, and Ba and in April 2003 for Mn. Concentrations were high in both May and June 2003 for Li. Data from Daxigou Meteorological Station (3 539 m a.s.l., 3 km from UG1) indicate that the main wind directions are SSE, SSW, WSW, ENE, and NE in the study region, but speed peaks of valley wind occur during the spring (April and May) and early summer (June), so weathered material of rock and soil dust may be transported to UG1 with suitable airflow (Li X Y et al., 2007). With the increase of temperature and decrease of valley wind speed, eluviation is notable in summer, resulting in the low concentration of selected elements in the surface snow.

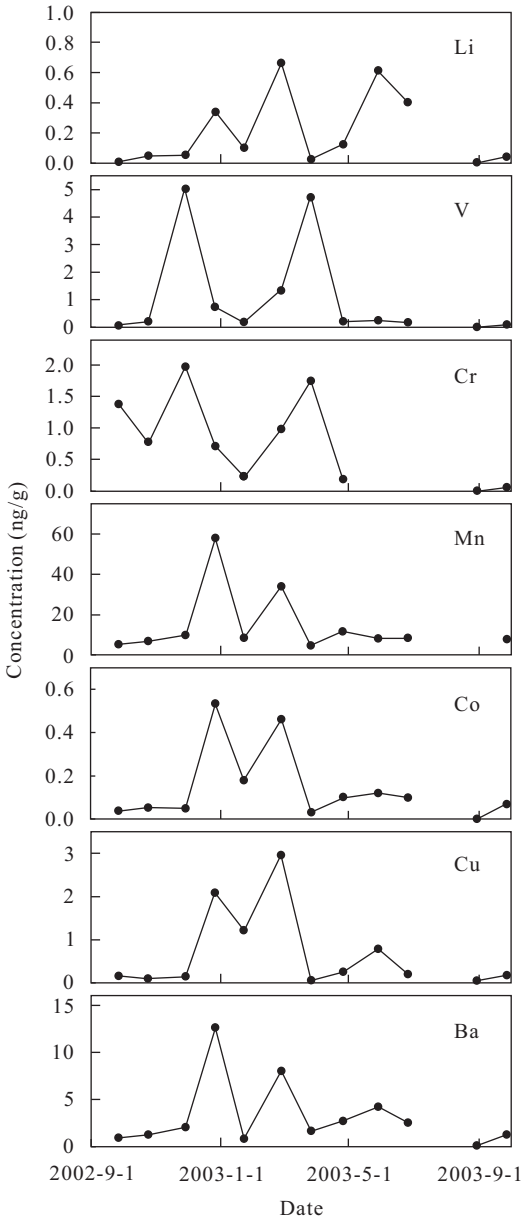

Figure 3. Concentration variations of Li, V, Cr, Mn, Co, Cu, and Ba in the surface snow samples collected from UG1 from September 2002 to September 2003.

Crustal Enrichment Factors

Crustal enrichment factors (EF_c) are used for expressing the degree of enrichment of trace elements in a given material (sample) compared with the earth's crust. The use of the concept of EF_c has been wide in studies of snow/ice samples in different mountain glaciers in Asia (e.g., the Himalayas, Pamir, and Tianshan). Ba is an element that is a geochemically well-understood constituent of many of the minerals that constitute the earth's crust and the soils of the surface of the earth. Anthropogenic contributions of this particular element do not commonly alter its abundance in materials that are transported and deposited by the atmosphere. Therefore, it can be considered to be a stable indicator of crustal material and used as an index in assessing the values of EF_c in samples (Duan et al., 2009; Kaspari et al., 2009; Hong et al., 2004; Rosman et al., 1998). So, in this study, Ba has been chosen as a reference element. For a trace element X, $EF_c(X)=[c_s(X)/c_s(Ba)]/[c_c(X)/c_c(Ba)]$, where c_s is the concentration in the snow samples and c_c is the mean concentration in the upper continental crust. Concentrations in the upper continental crust are calculated based on recent research in Xinjiang by Yang et al. (2009). Presented in Fig. 4, EF_c for the various measured elements on UG1 in the surface snow ranges from 0.2 to 8.2 for seasonal values, with an exception of Cu in the winter (EF_c=14.2).

The main sources of these selected elements may be from the physical environment. Rock with Mn, Li, and other minor and trace elements is widely distributed all around UG1 (Luo, 1983), and the concentrations of these elements in some types of rock near the sampling site may be similar as their concentrations in the dusts. In addition, Hinkley et al. (1997) found that there is a "background" dust that is deposited in central Asia, which has a distinctive composition (for major "rock forming" elements), and this dust is the same as the background dust seen in other parts of the world; this means that it comes from mixed, widely distributed sources around the world. It may be the dominant dust when local atmospheric energy (wind) is low and when dusts from local sources cannot be transported and deposited onto snow surfaces.

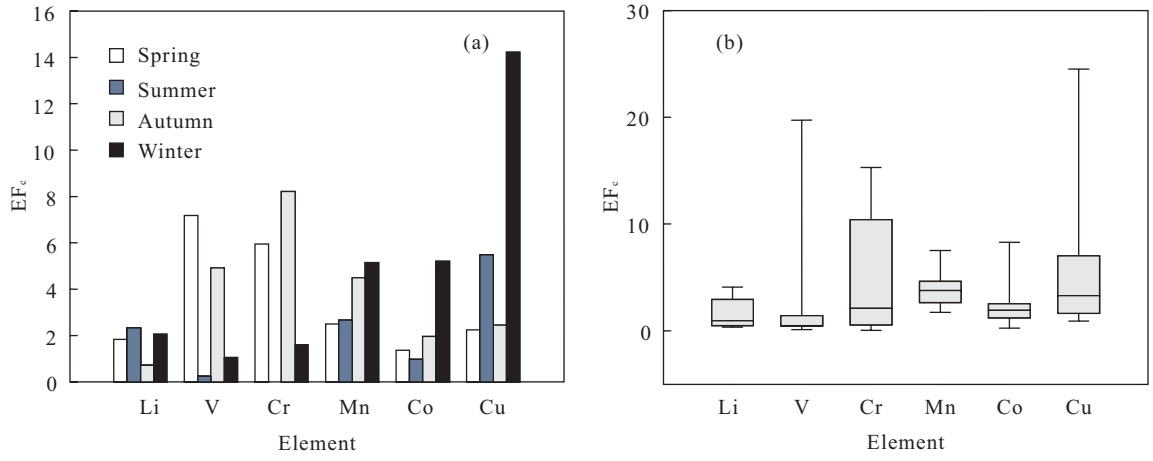

Figure 4. Seasonal variation (a) and box plot (b) of EF_c for Li, V, Cr, Mn, Co, and Cu in the surface snow samples collected from UG1 from September 2002 to September 2003. In Fig. 4b, the boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile; whiskers (error bars) above and below the box indicate the 90th and 10th percentiles.

Many studies suggest that EF_c for Li, V, Cr, Mn, Co, and Cu in the snow samples generally ranges from 0.1 to 10 (Table 3), with exceptional cases of Cu (27) in Mt. Qomolangma region, the Himalayas. The moderate enrichment values for these elements in snow samples may indicate that the dust sources are deposits of sediment and soils, possibly having been enriched in trace elements by natural processes. The worldwide pre-industrial dusts were naturally enriched in several trace elements because of the emissions of quiescently degassing volcanoes (Matsumoto and Hinkley, 2001; Hinkley et al., 1994). Some studies

from peat bogs also show that trace elements were enriched in pre-industrial times (Kylander et al., 2005).

Post-Depositional Process in Snowpack

After undergoing post-depositional processes, seasonality of trace elements in the surface snow may be distorted to some degree in snow/ice records. Variations of mean concentration of selected trace elements in the snow pits with local temperature and precipitation are presented in Fig. 5. Cr is not shown in Fig. 5 because of the absence for several samples.

Mean concentration in snow pit samples is a result of input from dry and wet deposition, combined with output (loss of impurities in the snow) by

Table 3 Comparison of EF_c for Li, V, Cr, Mn, Co, Cu, and Ba in the snow samples on UG1 with other remote regions

Location	Material	Index element	EF_c							Reference
			Li	V	Cr	Mn	Co	Cu	Ba	
Coats land, Antarctic	Snow pit	Al		0.9		2.9	4.9		0.6	Planchon et al. (2002)
Mt. Qomolangma region	Snow pit	Ba					3.6	27		Duan et al. (2009)
Eliot Glacier, Oregon, USA	Fresh snow	Ca^{2+}		0.1				0.6		Fortner et al. (2009)
Sajama ice cap, Bolivia	Firn/ice core	Ba		0.5			0.9	10		Hong et al. (2004)
UG1, Tianshan	Surface snow	Ba	1.6	3.7	5.0	4.0	2.5	5.8		This study
UG1, Tianshan	Snow pit	Ba	2.3	1.1	1.8	3.8	2.4	4.2		This study

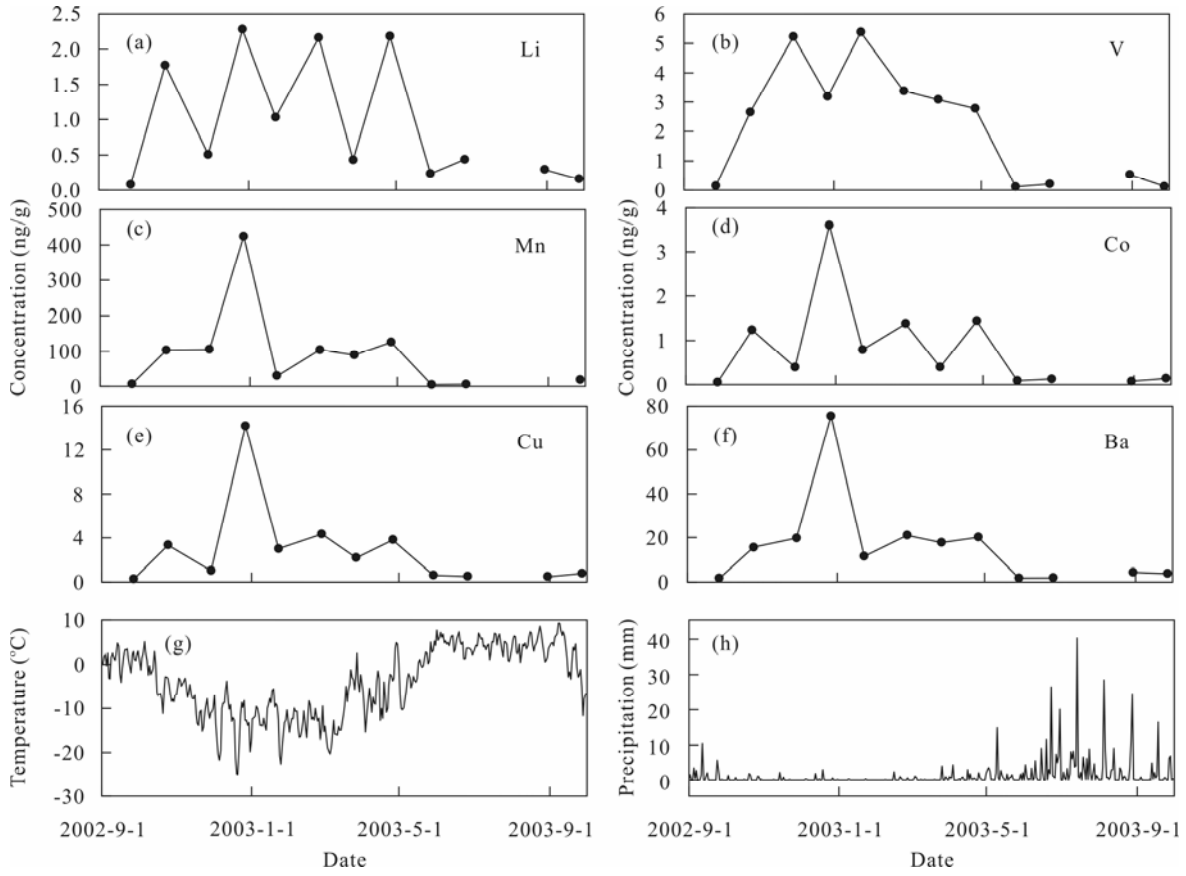

Figure 5. Variations of mean concentrations of Li, V, Mn, Co, Cu, and Ba in the snow pit samples collected from UG1, and local metrological parameters (temperature and precipitation) from September 2002 to September 2003.

eluviation and other post-depositional processes. Because of low temperature, low precipitation, and prominent dry deposition in winter, concentrations of trace elements in the snow pits increase. In the spring and summer of the next year, with the increase of precipitation and temperature, the concentrations drop. On UG1, input of all new ions into snowpack is leached when the temperature is higher than 0.3 ℃ (Li Z Q et al., 2006). This may also be the cause of concentration variations in summer.

Except for Li and V, most elements display a coincident trend. High concentrations were observed from October 2002 to April 2003, with a peak in December 2002 and several slight peaks in October 2002 and February and April 2003, whereas low concentrations occurred from May to September 2003. However, an opposite trend is shown between V and other elements, especially from November 2002 to March 2003.

SUMMARY

Concentrations and variability of Li, V, Cr, Mn, Co, Cu, and Ba in the snow samples on UG1 are discussed. Previous work on UG1 has shown that, for the trace elements Pb, Cd, and Zn, UG1 is affected strongly by human activities, and this may be the case for the samples of the present study. We conclude that trace elements cannot only be indicators of anthropogenic activities but also of natural environment variation. The observed concentrations and variations of Li, V, Cr, Mn, Co, Cu, and Ba may be mainly controlled by local or regional circulation of atmosphere and desertification of central Asia. A full interpretation of the atmospheric and geochemical effects in this part of central Asia will require a longer sampling period and comprehensive analysis of ice cores and snowpacks.

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