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The pH value and electrical conductivity records of atmospheric environment from three shallow ice cores in the eastern Tianshan Mountains

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Abstract: Electrical Conductivity Measurement (ECM) from ice core is a representative index for atmospheric environmental change. The pH value and ECM from three shallow ice cores (each 3.85 m, 231 ice samples total) on Glacier No.1 at the headwater of Urumqi River, Glacier No.48 in Kuitun area, and Miaoergou Glacier in Hami area in the eastern Tianshan Mountains, western China, were measured and analyzed for atmospheric environment records research. Ice core record shows that the changing trend of pH and ECM in three sites in recent years is different: ECM in Kuitun increases with the ice depth change, but ECM in Hami and Urumqi Glacier No.1 ice cores show a decreasing trend. Average ECM value in Hami is much larger than other two sites, just as the dust concentration and ions concentration are also very high in this site. ECM records in all three sites are mainly affected by aerosol mineral dust of Central Asia, and correlative coefficients of ECM and mineral ions such as Ca^{2+}, Mg^{2+}, Na^{+} are all significantly high. The pH value and ECM are also significantly high correlative coefficients in the eastern Tianshan Mountains. Comparison between the eastern Tianshan Mountains and other sites in western China, and Polar Regions, shows that the difference of ECM can very well reflect the spatial difference of worldwide atmospheric environment.

Keywords: pH and electrical conductivity records; ice cores; atmospheric environment; the eastern Tianshan Mountains

1 Introduction

Electrical Conductivity Measurement (ECM) from ice core is a representative index for at-

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mospheric environmental change, and can also indicate climate change, which mainly depends on its acidity. Research has confirmed that ice formed in cold, dusty periods has a high concentration of alkaline dust, which significantly reduces the conductivity compared to warmer, less dusty periods (IPCC, 2007; Taylor *et al*., 1993). The research from ice core has many advantages in global climate change, such as continuous, high-resolution of climate signal and long time data series. Some researchers have reconstructed the climate incidents since Last Ice Age based on the pH and ECM from ice cores of Polar Regions (Delmas *et al*., 1982; Taylor *et al*., 1993). The similar research has also been done on the Qinghai–Tibet Plateau ice cores (Yao and Sheng, 1995). And much work on pH and ECM about their atmospheric chemistry significance in snow and ice has also been done on the Polar Regions and Qinghai–Tibet Plateau (Moore and Wolff, 1992; Moore *et al*., 1994). The Arctic, Antarctic region and Qinghai–Tibet Plateau are the three largest and most remarkable cold regions in the world. ECM is a good indicator of atmospheric environmental change of these cold regions (Xiao *et al*., 1999). The Tianshan Mountains located in Central Asian region are a major dust source of Asia (Figure 1). However, there is little research about pH and ECM in snow and ice of this region up to now, the relationship between ECM and the atmospheric environment needs to be further studied. And it is very important to study the significance of ECM from snow and ice of this region by providing good understanding to the atmospheric conditions and the effects of dust source to the regions around (Hou *et al*., 1999; Dong *et al*., 2008). Some research has been carried out to discuss the seasonal characteristics of pH and ECM in the snow packs on Urumqi Glacier No.1, suggesting that pH and ECM can still reflect the atmospheric conditions of snow deposition on high mountain glaciers in the inland region of Central Asia (Hou *et al*., 1999; Li *et al*., 2006). However, few researches have been carried out on physical and chemical characteristics of the snow and ice on Miaoergou Glacier in Hami area and Haxilegen Glacier No.48 in Kuitun area. In this study, we mainly discuss the difference of the pH and ECM and its environment significance in the eastern

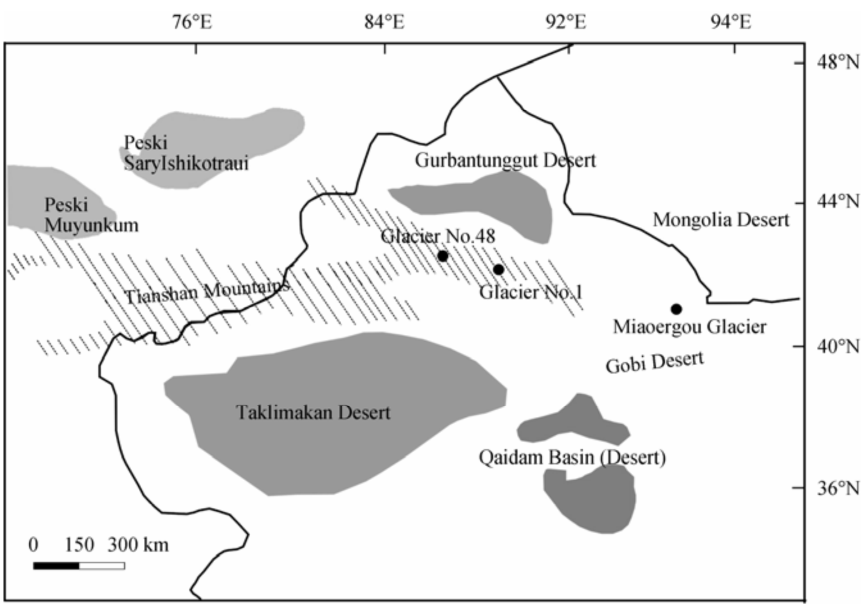

Figure 1 Location of the three study sites in the eastern Tianshan Mountains, Central Asia

Tianshan Mountains based on ice cores from three sites of this region.

2 The study area

The eastern Tianshan is located in an arid and semi-arid region of Central Asia, the source region of Asian dust (Figure 1). Dust storms are an important phenomenon in this region. There are many glaciers in the high mountains of Tianshan. The Haxilegen Glacier No.48 in Kuitun area (43°43′N, 84°24′E) is located in the head water of Haxilegen river in the south of Kuitun city on the northern slope of the Tianshan Mountains. The glacier faces to north-east, with a highest elevation of 4200 m, and the bottom altitude of the glacier is 3400 m, and the snow line altitude is about 3610 m. Urumqi Glacier No.1 (43º05′N, 86º48′E) is the biggest glacier at the water-head of Urumqi River, which is composed of eastern and western branches. The observed data of Tianshan Glaciological Station showed that the length of the glacier is 2.41 km, with an area of 1.73 km^2, elevation of snow line of 4075 m, and the bottom altitude of the glacier of 3777 m. The data of the meteorological station of the river basin since the year 1959 up to now show that the average mean air temperature of glacier region is –5.2℃, precipitation is 441.1 mm which is concentrated in May to September. And Urumqi Glacier No.1 is the longest monitored glacier since 1959 in China. The Miaoergou Glacier (43°03′N, 94°19′E) in Hami area is located in the east of the Tianshan Mountains, and is surrounded by many deserts and Gobi of Central Asia. And there is little precipitation in this area with very dry climate conditions. The glacier faces to southwest, the highest altitude is 4512 m, snow line is about 4100 m above sea level, and the glacier area is 3.45 km^2.

3 Sampling and lab analysis

The samples of this study are mainly from three shallow ice cores of the glaciers in the eastern Tianshan, including Urumqi Glacier No.1, Haxilegen Glacier No.48 in Kuitun area and Miaoergou Glacier in Hami area. We drilled one 60 m ice core from Miaoergou Glacier at the elevation of 4510 m in August 2005, one 20 m ice core on Glacier No.1 at the elevation of 4130 m in October 2006, and one 15 m ice core on Glacier No.48 at the elevation of 4100 m in October 2006. In this study, the environment is suitable for snow deposition as terrain is flat at all three ice core drilling sites and annual wind speed around the sites is small. Atmospheric signals such as mineral dust deposition should be preserved in sequence in the snow and ice layers without redistribution (Osada *et al*., 2004). Ice cores were shipped frozen to the Lab. In this study, we analyzed 3.85 m long ice cores of three sites to study the chemical characteristics and its atmospheric environment significance of this region in recent years. Strict procedures were executed during ice core drilling and transportation to eliminate contamination. We collected samples, typically in 5 cm increments using a pre-cleaned stainless steel hacksaw and polyethylene gloves. The instruments were cleaned between intervals. And thus we obtained 231 ice samples. All ice samples were stored in Whirl-Pak bags and stored at –18℃ until time for analysis. Samples were then melted and aliquots were collected for micro-particle and chemical analysis.

After the sample were retrieved, they were immediately analyzed for pH and ECM by a pH Meter (PHJS-4A) (0–14 measurement range with uncertainty less than 1‰) and a Conductivity Meter (DDSJ-308A) (0–999 μs/cm measurement range with uncertainty less than

1‰), respectively, prior to that the ice samples were melted gradually up to 20℃ at room temperature. For each measurement, the electrode was rinsed with deionized water after each sample and the temperature-compensated pH determination was made on a fresh, quiescent sample after 5 minutes. In addition, micro-particle concentrations were measured on an Accusizer 780A counter, which uses the Single Particle Optical Sensing (SPOS) method, equipped with a 120 ~tm orifice (You *et al*., 2006; Zhu *et al*., 2006). The concentrations of major ions (Na^+, Mg^{2+}, Ca^{2+} and Cl^-) were measured at trace levels on a Dionex-600 ion chromatograph using the procedure described by Buck *et al*. (1992). These methods have been described by You and Li (2006) and Zhu *et al*. (2006). Blanks were measured to make sure that cumulative contamination was below the baselines of each measured chemical species. The mean blank value for the whirlpack bags for dust particles number is 444 mL^{-1} in the laboratory measurements of this work. And blank values were subtracted from the sample data. Backward trajectory analysis is also employed to examine the transport processes of the air mass in three sites of eastern Tianshan. The analysis was based on the HYSPLIT4 (hybird single-particle lagrangian integrated trajectory) model, including the vertical motion mode. Backward trajectories up to sampling altitude were calculated for 3 days.

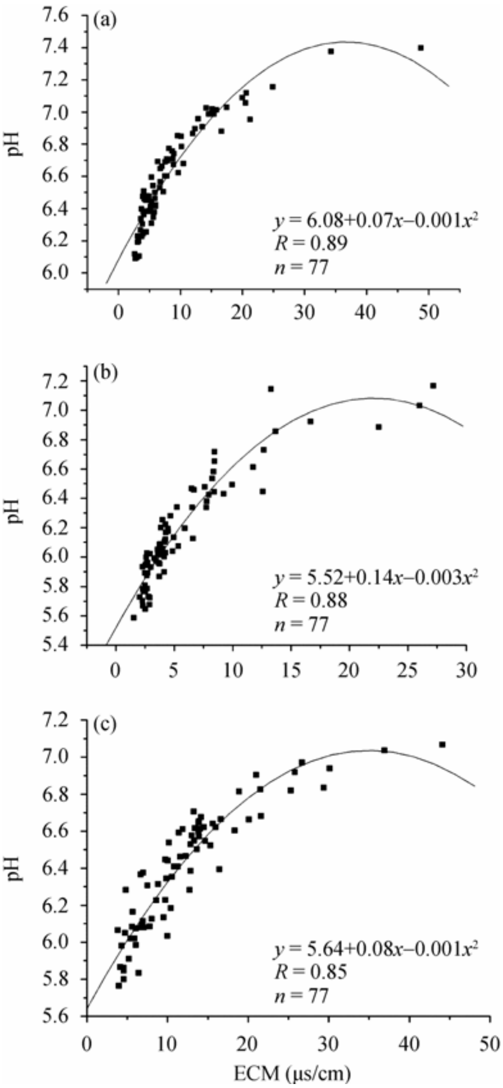

Figure 2 The correlative coefficient between pH and ECM in eastern Tianshan (a stands for Kuitun Glacier No.48, b for Urumqi Glacier No.1, and c for Hami Miaoergou Glacier)

4 Results and discussion

4.1 Correlation of pH and ECM, and ECM annual variation

Figure 2 is the correlation analysis of pH and ECM in the ice cores from the eastern Tianshan. The correlation coefficient is all high in three sites. ECM in Kuitun Glacier No.48 ranges from 2.7–48.7 μs/cm, with a mean value of 9.0 μs/cm; and pH ranges from 6.1–7.4, with a mean value of 6.6. In ice samples of Urumqi Glacier No.1, ECM ranges from 1.546–27.2 μs/cm, with a mean value of 5.9 μs/cm; and pH ranges from 5.587–7.168, with mean of 6.2. And, in the ice samples of Hami Miaoergou Glacier, ECM ranges from 3.84–44.1 μs/cm, with a mean value of 12.5 μs/cm; and pH ranges from 5.764–7.069, with a mean of 6.4. Comparing all these values, we find that the pH is bigger in Glacier No.48 than other two sites; but ECM is of the biggest value in Hami Miaoergou Glacier. The strong spatial distribution of pH and ECM may indicate the spatial difference of atmospheric environment in the eastern Tianshan region.

To determine how the pH and ECM on the eastern Tianshan Mountains are of regional representatives to hemispheric atmosphere, we compared this work with similar measurements from other sites in western China (Table 1). Result shows that in the sites of the eastern Tianshan and Qinghai–Tibet Plateau such as Dongkemadi Glacier and Guliya Glacier, and Yulong Mountains, the correlation coefficients of pH and ECM are very different from each other, as some sites are very similar, but some are not. For example, the correlation coefficients of the sites of the Tianshan Mountains and Qinghai–Tibet Plateau are all of high values ($R \geqslant 0.84$); but are less correlated in the ice samples of the Yulong Mountains (R = 0.34). This may be caused by the difference of atmospheric conditions between these different sites. As the Tianshan Mountains and Qinghai–Tibet Plateau are mainly influenced by dust activities in the Central Asian region since they are located near a major dust source region, while the glaciers on the Yulong Mountains of Southwest China are mainly affected by summer monsoon from eastern Asia and also the monsoon from the Indian Ocean.

Table 1 Correlation coefficient of ECM and major ions in the ice core of the research sites in western China

ECM	Ca^{2+}	Na^{+}	Mg^{2+}	SO_4^{2-}	pH	Ref.
Kuitun Glacier No.48	0.94	0.68	0.73	0.83	0.89	This work
Urumqi Glacier No.1	0.99	0.78	0.54	0.87	0.88	This work
Hami Miaoergou Glacier	0.96	0.82	0.74	0.86	0.85	This work
Guliya ice core	–	–	–	–	0.85	Sheng *et al*.
Tanggula Dongkemadi	0.92	0.70	0.69	0.58	0.85	Xiao *et al*.
Qomolangma Rongbu Glacier	–	–	–	–	0.84	Xiao *et al*.
Yulong ice core	0.89	0.21	0.71	–	0.34	Gu *et al*.

Some research has pointed out that ice formed in cold, dusty periods has a high concentration of alkaline dust, which significantly reduces the conductivity compared to warmer, less dusty periods (Taylor *et al*., 1993). In this study, we obtained the ice-depth relationship of the ice cores based on the annual accumulation of snow in the sites, seasonal variability of dust concentration in the profile and $\delta^{18}O$. The result indicated that the 3.85 m ice core could represent the ice of about recent ten years since 1994. Ice core may be affected by melting, but the ice temperature measured around the drilling site is below 0℃ and obvious seasonal change of chemical characteristics of the snow profiles indicates that the records in the ice core are still well preserved. So, the profiles of the pH and ECM from ice cores in three sites of the Tianshan Mountains can still reflect atmospheric change and regional environment difference of recent years. We can find that there are large differences between the sites: the ECM increases with the increase of the depth in Kuitun ice core, but decreases with the increase of the depth in both Urumqi Glacier No.1 and Hami Miaoergou Glacier ice cores (Figure 3).

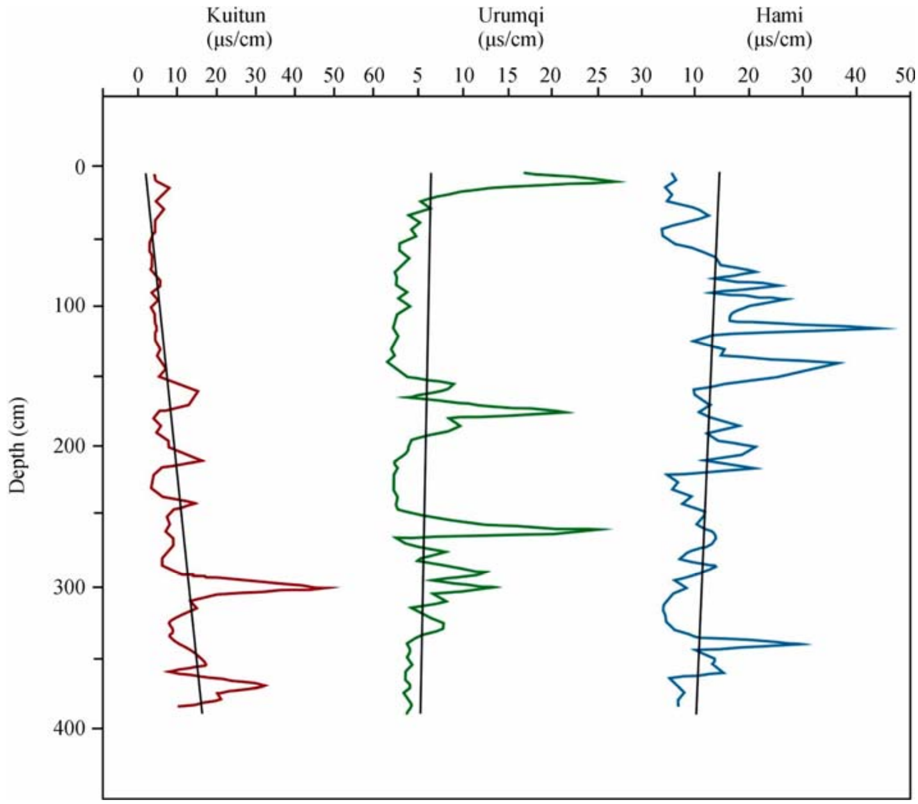

Figure 3 ECM variation as the ice core depth changes in research sites of the eastern Tianshan Mountains

Figure 4 is the comparison of mean dust particle diameter and ECM profiles in Hami glacier ice core. As the study area is mainly affected by Asian dust, the ECM in the snow and ice is also significantly affected by the dust storm. Mean diameter of dust particles has very good coincidence with dust layer in snow and ice, and the peak value can reflect the dust layers in the ice cores. In this work, the ECM and dust profile have very good coincidence with each other as the depth changes (Figure 4). The similar research in the snowpacks of the eastern Tianshan Mountains shows the same result of good correlation between dust and ECM (Dong *et al*., 2008). Dust storm is an important characteristic of atmospheric environment in the Central Asian region. The dust particles can easily reach the glacier of the Tianshan Mountains, and can be preserved in the ice cores. So, we can infer that ECM change could reflect the dust activity change in Central Asia, although there may be other cause of atmosphere to the environmental change besides dust incidents. Moreover, the ECM can reflect the total amount of aerosol ions deposited in the snow and

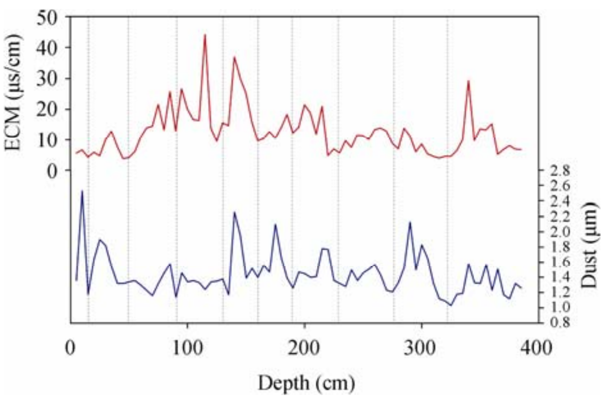

Figure 4 Comparison of dust and ECM profiles in Hami glacier ice core

ice of high mountains, and is a very good representative index of atmospheric environmental change. In Central Asia, during cold and dry periods, as dust activity is strong, the corresponding ECM in ice core shows big value, but during warm and wet periods, as dust activity is weak, the corresponding ECM in ice core shows small value. And thus the ECM stored in snow and ice can reflect the dry and wet change of atmospheric environment.

Some research in the snowpack on Urumqi Glacier No.1 has shown that in Central Asian region, pH and ECM can still reflect the atmospheric condition of snow deposition (Hou *et al*., 1999). In the comparison of the three sites in the eastern Tianshan Mountains, the ECM increases with the change in depth in ice core of west site in Kuitun, or it decreases with the change in time, indicating that the atmospheric environment in the source region and along transport trajectory tend to be wet, with decreased dust activity and increased precipitation; the ECM decreases with the increase of the depth in the ice core of Urumqi Glacier No.1 and Hami Miaoergou Glacier, or it just increases with the change in time, indicating to a certain degree that the atmospheric environment in the source region and along transport trajectory tend to be dry during the past years, with increased dust activities and decreased precipitation. In order to prove this result, we compared results with the data of meteorological stations in these sites (Figure 5). The data showed that in Kuitun site the precipitation has increased since 1994 (Figure 5a); in Urumqi Glacier No.1 the precipitation of head water area of the Urumqi River has decreased since 1994 (Figure 5b); and in Hami the precipitation also showed a slightly decreasing trend during the past years, although it is not very obvious (Figure 5c). These results indicate that there are good correlations between the observed data of meteorological stations and the records of ice cores from the eastern Tianshan Mountains sites, which may also reflect the spatial difference of atmospheric environmental change during the past years in Xinjiang region of

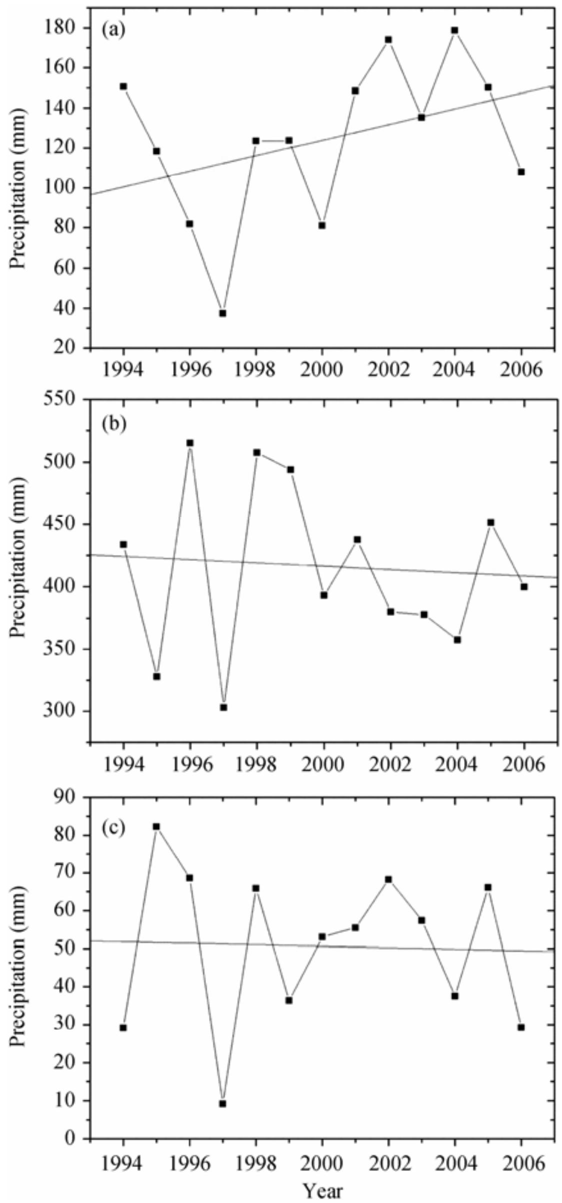

Figure 5 The precipitation in eastern Tianshan sites (a stands for Kuitun Glacier No.48, b for Urumqi Glacier No.1, and c for Hami Miaoergou Glacier)

China.

An example of a 3-day backward trajectory of air mass of the three sites in this work during Asian dust periods is illustrated in Figure 6, which is used to examine the transport processes of the air mass. From the figure we can infer that in some periods the source of air mass transport of the three sites is different. The air mass of Kuitun area originated mainly from the south of the Tianshan Mountains, but that of Urumqi and Hami sites mainly originated from west of Central Asia, just coincident with westerly wind. Such a difference in atmospheric environment may result in different records from high mountain snow and ice. However, the atmospheric environmental change is a very complicated process, and further research is needed to understand the difference in air environments of this region.

4.2 Correlation with major ions of pH and ECM

Table 1 shows the correlation coefficient of pH and ECM with major ions. Results reveal that the glaciers in Hami area are more significantly affected by dust activities of Central Asian region, and ECM has very good correlation coefficient with alkaline Ca^{2+}, Mg^{2+} and Na^{+} from mineral dust. The research of Urumqi and Kuitun Haxilegen glaciers also shows

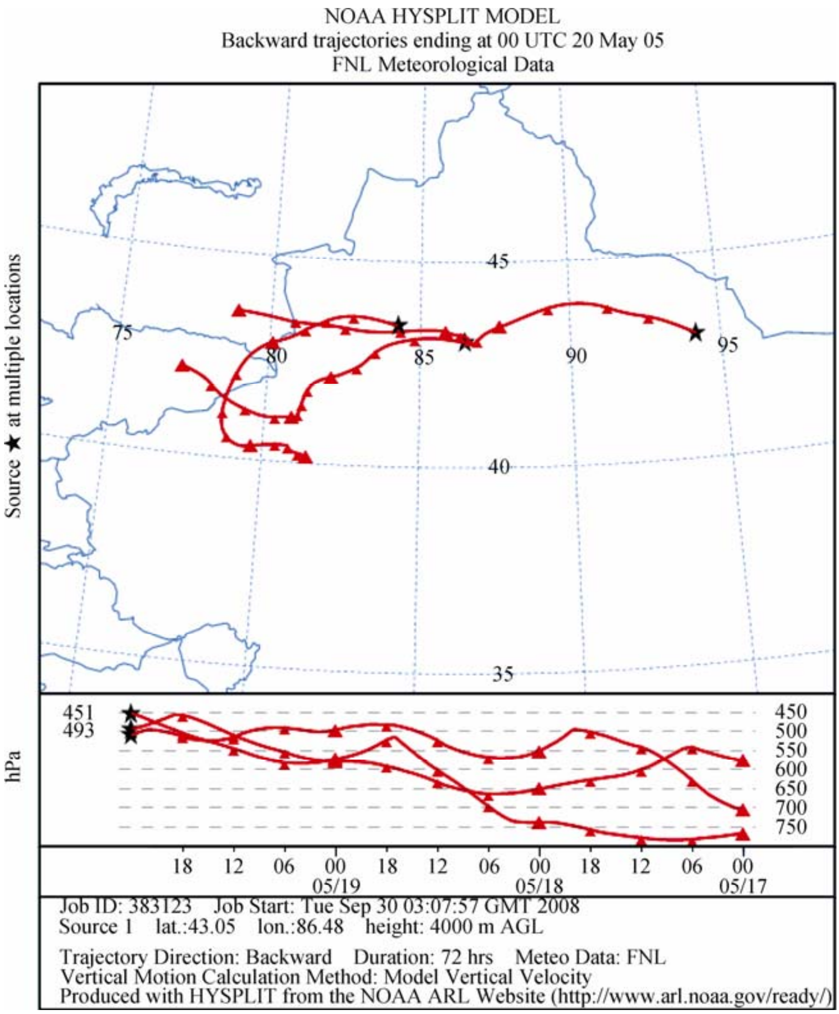

Figure 6 An example of backward trajectory of air mass in research sites of the eastern Tianshan Mountains

similar results, that ECM has good correlation with dust Ca^{2+}, which is also mainly affected by Asian dust, but obviously not as significant as that in Hami Miaoergou Glacier (Table 1). The ECM can reflect the influence of Asian dust activities on the regional atmospheric environment in Central Asia. Moreover, some researches have confirmed that human activities accelerated the dust activity in Xinjiang region during the past years because of unreasonable use of natural resource (Wei *et al*., 2004).

Compared to other researches in western China, we find the Qinghai–Tibet Plateau has the similar results with ECM and major ions correlation, an indication of higher correlation coefficient in eastern Tianshan. However, the result in Yulong Mountains shows very low correlation between ECM and major ions, especially Na^+, which may be caused by the different sources of aerosol ions and is mainly originated from sea source of Indian Ocean, but ECM is mainly controlled by alkaline mineral dust particles originated from land surface sources. These results can also reflect the difference in atmospheric environment in western China.

In order to further understand the influence of the atmospheric environment on ECM record in the eastern Tianshan region, we compared the concentrations of major ions and dust particles here (Table 2). Result shows that major ionic concentrations in Hami ice core are much higher than the other two sites, as the dust concentration is also much higher in Hami than in other sites. And the concentrations of various ions and dust are all low in Urumqi Glacier No.1. The coincidence of major ions concentration, dust concentration with ECM in the ice cores of the eastern Tianshan Mountains indicates a strong correlativity between them. ECM is mainly affected by Asian dust which causes the difference of atmospheric environment between the sites. SO_4^{2-} also shows very high concentration in the ice cores of Hami, which implies that SO_4^{2-} could attach to the dust particles and deposit to the snow of high mountains in Tianshan. Such a coincidence of major ions concentration, dust concentration with ECM in the ice cores of the eastern Tianshan Mountains also confirms that ECM can be the representative index of atmospheric environmental change of this region.

Table 2 Concentration of major ions and ECM in the ice cores of the research sites

Sites	SO_4^{2-} (μg/L)	Na^+ (μg/L)	Mg^{2+} (μg/L)	Ca^{2+} (μg/L)	Dust (#/ml)	ECM (μs/cm)
Kuitun Glacier No.48	479	143	62	1079	312872	9.0
Urumqi Glacier No.1	158	91	46	675	550151	5.9
Hami Miaoergou Glacier	682	243	122	1420	777088	12.5

4.3 Comparison with the researches of the Polar Regions and Qinghai–Tibet Plateau

ECM is significantly affected by mineral dust particles in the eastern Tianshan Mountains (such as Ca^{2+}, Mg^{2+}, SO_4^{2-}), which are mainly originated from Asian dust source (Figure 4). And pH and ECM have very high correlation coefficient in this region. Much research on ECM in worldwide snow and ice has been carried out. Many reports on ECM in Antarctic Ice Cap and Greenland Ice Cap reveal that pH and ECM have good correlation. And based on this conclusion, the volcanic eruptions were resumed in historic periods. In Antarctic ice core the ECM and H^+, SO_4^{2-}, NO_3^-, Cl^- also have very good correlation (Legrand *et al*., 1987), while silicate, which mainly comes from the earth's crust, is negatively correlated with ECM, indicating that the mass of Antarctic ice is mainly originated from the ocean source. This is different from the results of the Tianshan Mountains of this work. In the whole Arctic including Canadian Arctic and Greenland regions, ECM reflected the regional atmospheric environment difference (Xiao *et al.*, 1999). The Canadian Arctic and Greenland Ice Cap snow and ice ECM also indicated that the major ions (such as Cl^- and SO_4^{2-}) are originated from the ocean source just like the result of the Antarctic. The research in the Qinghai–Tibet Plateau showed very different result from the Polar Regions. Acidity is not the dominated factor for ECM in this region, for example, in the ice core of Dongkemadi Glacier, the alkaline soluble (Ca^{2+}, Mg^{2+}) ions and ECM have good correlativity in the Qinghai-Tibet Plateau, which mainly come from the earth's crust (Xiao *et al.*, 1999). The relationship of various kinds of ions, pH and ECM is very different from that of polar ice sheet. In this study, pH and ECM are positively correlated with high correlation coefficient ($R \geqslant 0.85$). And ECM has good correlativity with ions (for example, Ca^{2+} and Mg^{2+}) which mainly come from the earth's crust. The cations are the dominated factor for ECM in the eastern Tianshan region, which is similar to the result of the Qinghai–Tibet Plateau, but different from that of Polar Regions. Moreover, among ions of Ca^{2+}, Mg^{2+}, Na^+ and SO_4^{2-}, Ca^{2+} has the best correlativity with ECM. So we can infer that Ca^{2+} can indicate the atmospheric process more sensitively than other ions in the eastern Tianshan Mountains.

5 Conclusions

The key point of this study is to research the atmospheric environment records of pH and ECM from three shallow ice cores of the eastern Tianshan Mountains in Central Asian region, including the sites of Haxilegen Glacier No.48 in Kuitun area, Glacier No.1 in Urumqi area and Miaoergou Glacier in Hami area. And the following conclusions can be drawn from the above analysis:

(1) The annual changing trend of pH and ECM of ice cores in the three sites is different: the ECM increases with the change in depth in Kuitun ice core, but decreases with the change in depth in Urumqi Glacier No.1 and Hami Miaoergou Glacier ice cores. The ECM increases with the change in depth in ice core of west site in Kuitun, or it just decreases with the change in time, indicating that the atmospheric environment in the source region and along transport trajectory was turning wet, with decreased dust activity and increased precipitation; the ECM decreases with the increase of the depth in ice core of the middle site of Urumqi Glacier No.1 and east site of Hami Miaoergou Glacier, or it just increases with the change in time, indicating that the atmospheric environment in the source region and along transport trajectory was turning dry, with increased dust activity and decreased precipitation. The results indicate that there are good correlations between the observed data of meteorological stations and the records of ice cores from the eastern Tianshan sites, which may also reflect the spatial distribution of atmospheric environmental change during the past years in Central Asian region.

(2) Results reveal that the glacier in Hami area is significantly affected by dust activities of the Central Asian region, and ECM has very good correlation coefficient with mineral dust Ca^{2+}, Mg^{2+} and Na^+. ECM (12.5 μs/cm) and major ions concentrations (1420 μg/L of Ca^{2+} concentration) in Hami ice core are much higher than that of the other two sites, as the mean dust concentration (777×10^3 mL^{-1}) is also much higher in Hami than in other sites, which also confirms that ECM can be the representative index of atmospheric environmental change of this region.

(3) Comparison of ECM among the Tianshan Mountains, Yulong Mountains, Qinghai–Tibet Plateau, and Polar Regions indicates that, there exist different ECMs between different places of the worldwide range because of different atmospheric environments. ECM

in the eastern Tianshan region, which is similar to the result of the Qinghai–Tibet Plateau, is mainly affected by mineral dust from the earth's crust, while in Polar Regions such as Arctic and Antarctic, and Yulong Mountains of south China ECM is mainly affected by the ions originated from the oceans.

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