Atmospheric pollution of a remote area of Tianshan Mountain: Ice core record

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[1] The influence of anthropogenic pollution on the region of Tianshan Mountain, a remote area in arid central Asia, has been debated in the recent years. An ice core, covering the past 43 years, retrieved from Glacier 1 at Urumqi River head in the east Tianshan, northwest China, was analyzed to examine the problem. CH₃COO⁻ (acetate) and HCOO⁻ (formate), the chief tropospheric carboxylates that can originate from anthropogenic pollution, average 389.4 ± 336.3 ng g⁻¹ (N = 489) and 61.1 ± 89.0 ng g⁻¹ (N = 541), respectively, with a mean ratio HCOO⁻/CH₃COO⁻ of 0.21 ± 0.23 (N = 489). SO₄²⁻, the major inorganic anion in the core, averages 232.9 ± 279.9 ng g⁻¹ (N = 542). The organic and inorganic records have covaried in the past four decades. They originate principally from anthropogenic pollution, coal combustion in particular, of the local and regional atmosphere. The pH values in the record range from 6 to 9 with an average of 6.9 ± 0.5 (N = 541). The general trend of the pH data matches that of HCOO⁻, CH₃COO⁻, and SO_4^{2-} , indicating that the anthropogenic pollution has released considerable particulate material along with unsaturated hydrocarbons and SO₂. As a result, the pollution has not been acidifying the environment, but making it alkaline. INDEX TERMS: 0345 Atmospheric Composition and Structure: Pollution-urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1040 Geochemistry: Isotopic composition/chemistry; 1055 Geochemistry: Organic geochemistry; 9320 Information Related to Geographic Region: Asia; KEYWORDS: tropospheric chemistry, carboxylic acid, formate, acetate, sulfate, precipitation

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1. Introduction

[2] Pollution resulting from human activities has affected most of the atmosphere. Usually, the pollution adds acidity to the environment thus contributing to acid precipitation [Likens and Bormann, 1974; Galloway et al., 1982; Zhao and Sun, 1986]. Remote areas, however, have been considered immune from, or less influenced by, the effect of pollution. These areas provide the opportunity to evaluate the natural background levels of chemical species as well as the extent of anthropogenic pollution effect on the chemistry of the atmosphere [Galloway et al., 1982; Likens et al., 1987]. The last two decades saw an increase in the interest in the chemistry of precipitation in remote areas around the world. Precipitation observations have been carried out in America [Galloway et al., 1984; Sanhueza et al., 1989], Australia [Likens et al., 1987]. Indian Ocean [Galloway and

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Gaudry, 1984; *Moody et al.*, 1991], Africa and Atlantic and Pacific Ocean [*Keene and Galloway*, 1986], as well as in the polar regions (see *Legrand and Mayewski* [1997] for a review). Atmospheric chemistry in these remote areas is more or less influenced by human pollution and the acidity of the precipitation is somewhat enhanced with the pH seldom exceeding 5 [*Galloway et al.*, 1982].

[3] Tianshan Mountain is a remote area of the Eurasian continent. The influence of anthropogenic pollution on the remote area was debated in the recent years. Wake et al. [1992], after the chemical species measurement in snow samples from the east Tianshan, proposed that anthropogenic pollution had affected the atmospheric compositions. On the other hand, noting the high correlation of SO_4^{2-} with Ca²⁺ in the snowpacks, Williams et al. [1992] maintained that the high concentration of sulfate in the precipitation was chiefly due to aeolian dust. Like Williams et al. [1992], Hou et al. [1999a], on the basis of positive correlation of pH and electric conductivity measurement with Ca^{2+} , also concluded that the recent atmospheric environment in the area is still controlled by natural processes. In this paper, we present our investigation on formate (HCOO⁻) and acetate (CH₃COO⁻), the chief light carboxylic compounds in the troposphere, and SO_4^{2-} as well as their relationship with pH in an ice core record. Our study demonstrates that human pollution has affected this remote area in the past several decades, that the pollution has not acidified the

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Figure 1. Mean air mass trajectory in 1500 m above the Tianshan Mountain and surrounding area in spring seasons of 1960–1969 (modified from *Li* [1991]). The dot in Tianshan indicates the studying site.

environment as in most areas of the world but otherwise made it alkaline.

2. Background and the Ice Core

2.1. Tianshan Mountain

[4] Tianshan Mountain is located at the center of the Eurasian continent. The westerly jet prevails high above the mountains. While the mountain topography converts the westerly into cyclonic and anticyclonic circulations up to 4000 m (Figure 1). Near the surface, the local valley wind prevails from March through September of a year [*Zhang et al.*, 1994].

[5] The east Tianshan Mountain is surrounded by vast desert areas (Figure 2). To the south lie the Taklimakan Desert in the Tarim basin and the Qaidam basin desert; to the east, the deserts in eastern Xinjiang and western Gansu province and the Mongolian Gobi Plateau; to the north, the Gurbantunggut Desert in Junggar basin, and Peski Muyunkum and Peski Sary-Ishikotrau deserts to the west. Evergreen vegetation exists between 1600 and 3400 m a.s.l. in the mountains.

[6] The barren geographic background has thwarted the human population. There exist only one large city and a few towns with industrial facilities in the surrounding area. Urumqi, the provincial capital of Xinjiang Uyger Autono-



Figure 2. Geographic environment around the east Tianshan. The stippled areas designate deserts and Gobis that were drawn in the same scale as the surrounding areas.



Figure 3. Glacier 1 and the drilling site. The ice core was recovered near the monitored point H'_2 at the east branch of the glacier.

mous Region, China, with more than a million inhabitants, is 105 km from the studying site. Houxia, a small town where a steel work and a cement plant have been built since 1958, lies 50 km away in the Urumqi River valley. By the criteria of *Galloway et al.* [1982] on a remote place in the world, the east Tianshan is a relatively remote area of an arid geographic background.

2.2. Glacier 1

[7] Located at 43°06'N, 86°49'E in the east Tianshan, Glacier 1 is a valley glacier at Urumqi River head, Xinjiang Uygur Autonomous Region of northwest China (Figure 2). It is composed of east and west branches (Figure 3) and occupies a total area of about 1.84 km² [Liu et al., 1991]. The equilibrium line has averaged around 4000 m a.s.l. in the past two decades [Tianshan Glaciological Station, 1979–1998]. Above the equilibrium line lie the superimposed ice zone and the percolation zone [Xie and Huang, 1989]. The mean annual precipitation at 4050 m a.s.l. in the accumulation area of the east branch is 645.8 mm a^{-1} [Wang and Zhang, 1985; Yang et al., 1988]. The main precipitation period occurs from May to September and accounts for 88% of the annual precipitation [Wang and Zhang, 1985; Yang et al., 1992]. Concurrent with the precipitation, ablation also occurs from May to September.

2.3. Ice Core

[8] The ice core studied here is 14.08 m long and was retrieved in October 1998 at 4040 m a.s.l. in the superimposed ice zone of the east branch of Glacier 1, close to the monitoring point H'_2 at 4042 m a.s.l. (Figure 3). It is composed of clear dense ice with scarce bubbles, which formed in superimposed ice zone, and opaque bubbly ice with spherical bubbles 1-2 mm in diameter, which formed in percolation zone, as well as a few dust layers. In the upper part of the ice core, a crack cut through from 138 to 386 cm affected the ice within 2 to 3 cm of the fracture plane because of introduction of the surface meltwater [*Lee et al.*, 2002a].

[9] The core was cross-dated by δ^{18} O, β activity, and variations of Pyruvate and ECM. Basically, temperature from June through to August controls δ^{18} O of the precipitation in Glacier 1. The intensive melting impaired the annual signal of δ^{18} O, the long time correlation between the temperature and δ^{18} O, however, survived [Hou et al., 1999b]. Therefore we dated the core first by comparing δ^{18} O with the temperature in the area thus obtaining four reference dates: 1962, 1966, 1970 and 1976. Measurement of β activity reveals events in 1963, 1967, 1976, 1980 and 1986 as defined by the known global nuclear fallout event in the northern hemisphere (1963) and the local ones in the western China (1967, 1976, 1980) as well as the Chernobyl nuclear accident (1986). Dating via these two series differs by about one year. The whole core was dated by crosscounting peaks of Pyruvate and ECM while consulting the reference dates from δ^{18} O and β activity. It covers a period of 43 years from 1955 to 1998 with an uncertainty of about one year (Figure 4). For more detail regarding the dating, see Lee et al. [2003].

3. Analytical Procedures

[10] Analytical samples were selected every 2 cm from the central part of the ice core using a band saw in the Laboratory of Ice Core and Cold Regions Environment. In the fractured section (FS), however, they were selected to avoid the fracture as much as possible. Around the depth of 260 cm, where the fracture cuts through the center of the core, samples were selected on both sides. In order to avoid the outer 1 cm of the core, which is susceptible to drilling contamination [*Legrand et al.*, 1993], the sampling was compromised by including part of the ice influenced by the crack. The samples were kept frozen in glass vials with airtight covers until analysis.

[11] Since the sample selection has been exposed briefly to air, some minor contamination might have been introduced to the samples. In order to evaluate the possible contamination, blank analysis was carried out. Newly made ultra-pure water (18.2 M Ω cm⁻¹) was frozen quickly into cylindrical ice in glass containers, the artificial ice was then sectioned and analyzed exactly the way the samples were processed. Two species were detected in the blanks, which are CH₃COO⁻ and Cl⁻. The blank value for CH₃COO⁻ is 31.7 ± 23.7 ng g⁻¹ ($\bar{x} \pm 1\sigma$, N = 12, the same for the following statistics).

[12] Organic and inorganic anions were determined by ion chromatography (DX-300) with an AS4A separator using a gradient method and a chemical suppression mode. The procedure can resolve and quantify in a single run of 14 min over 10 analytes from F⁻, CH₃COO⁻, HCOO⁻ to $PO_4^{2^-}$, SO₄²⁻ and finally to (COO)₂²⁻ (Figure 5). Replicate analysis of standard solution prepared from the AcculonTM Reference IC-ACET-1X-1 (for CH₃COO⁻), IC-FORM-1X-1 (for HCOO⁻), and the Certified Reference released by the State Bureau of Technical Supervision of China (for SO₄²⁻) indicated that the relative standard deviation for the three analytes is no more than 4% (Table 1). For more detail of the analysis, see *Lee et al.* [2002b].



Figure 4. Cross-dating for the ice core by δ^{18} O, β activity, ECM and Pyruvate. The thick dark grey lines protruding out of the upper boundary of the graph indicate the reference levels from δ^{18} O and β activity, and represent from right to left 1962, 1966, 1970, 1976 and 1986, respectively.

[13] The pH measurements were completed with a pHS-2 pH meter. For each measurement, the electrode was calibrated with pH 7.0 and pH 4.0 reference buffer. The electrode was rinsed with an aliquot of sample and the temperature-compensated pH determination made on a fresh, quiescent sample after five minutes.

4. Results

4.1. CH₃COO⁻

[14] Acetate is the highest chemical species in the ice core, even allowing for the inorganic species. Leaving out in the whole data set those that are below the triple σ of the blank experiment, CH_3COO^- fluctuates between 72.1 ng g⁻¹ and 2830.7 ng g⁻¹ with an average of 389.4 ± 336.3 ng g⁻¹ (N = 489, not allowing for the concentration in the FS, the same with the following statistics). Variation of acetate in the ice core reveals its first high period from the early 1960s to the middle 1970s followed by another high period from the early 1980s to the middle 1990s (Figure 6). This trend is further corroborated in Figure 7 and Table 2, where the data were averaged in five-year intervals. The occurrence of the crack in the ice core corresponds approximately to the period 1986-1993. The influence of the crack, which has enhanced the concentration [Lee et al., 2002a], however, exists only around 1989 \pm 2 years. Therefore 1985–1989, which includes the time interval, saw the highest CH₃COO⁻ in 648.3 ng g^{-1} (Table 2). On the other hand, acetate still has a high concentration of 404.2 ng g^{-1} in the adjacent part, which corresponds to 1980-1984 and is free from the

influence, indicating the onset of the second high period of the species. Between the two high periods is 1975-1979, with a relatively low concentration of 313.9 ng g⁻¹.

4.2. HCOO⁻

[15] Formate varies between 2.1 ng g⁻¹ and 795.5 ng g⁻¹ with an average of 61.1 ± 89.0 ng g⁻¹ (N = 541). In the FS, formate is much more affected by the effects of the crack [*Lee et al.*, 2002a] thus exhibiting a larger peak around 260 cm. However, variations of the formate concentration are consistent with those of acetate in the variation in the past four decades as a whole. From the early 1960s to the middle of the 1970s and from the early 1980s to the middle of the 1970s two high periods are separated by the low interval of 1975–1979 (Figures 6 and 7 and Table 2).

4.3. HCOO⁻/CH₃COO⁻

[16] Formate concentration is lower than that of acetate in the normal section of the ice core. The ratio HCOO⁻/ CH₃COO⁻ varies between 0.0 (below the detection limit for HCOO⁻) and 2.5 and averages 0.21 ± 0.23 (N = 489) with only a few high peaks exceeding unity (Figure 8).

4.4. SO_4^{2-}

[17] SO_4^{2-} is the major inorganic species present in the record. It fluctuates between 11.9 ng g⁻¹ and 1984.3 ng g⁻¹ and averages 232.9 ± 279.9 ng g⁻¹ (N = 542). Variations of SO_4^{2-} in the past four decades are in agreement with those of acetate and formate. Corresponding to the periods when the two organic species have higher concentration, SO_4^{2-}



Figure 5. Chromatogram of the sample: $CH_3COO^{-}(1513.7 \text{ ng g}^{-1})$, $HCOO^{-}(264.9 \text{ ng g}^{-1})$, and $SO_4^{2-}(1267.5 \text{ ng g}^{-1})$. The lower graph is the enlargement of the upper one. The sample volume is 2 mL.

also manifests higher concentration, too (Figures 6 and 7 and Table 2).

4.5. The pH

[18] The pH ranges from 6 to 9 and averages 6.9 ± 0.5 (N = 541). The reference level commonly used to compare acid precipitation to natural precipitation is pH 5.6, which results from the equilibration of atmospheric CO₂ with precipitation [Wang, 1991]. Compared with this value, pH in Glacier 1 is much higher. It is also much higher than pH values in the other remote areas around the world [e.g., Galloway et al., 1982]. Therefore precipitation, as recorded in Glacier 1, has been high in alkalinity. Another point that characterizes the pH lies in its general variation in the record being positively covaried with that of CH_3COO^- , $HCOO^-$ and SO_4^{2-} (Figures 6 and 7), a phenomenon seldom reported in other remote areas of the world. High pH in Glacier 1 is linked to strong input of mineral dust, carbonate in particular [Williams et al., 1992; Hou et al., 1999a]. The correlation of the chemical species with the pH indicates that they are also associated with particulates.

5. Discussion

[19] Numerical studies have been done in recent years on the depositional and post depositional effects on chemical species in snow and firm in the polar regions. Chemical species such as SO_4^{2-} and even HCOO⁻, if present as aerosols, are subjected to post depositional changes very

moderately [Legrand and Delmas, 1988; Silvente and Legrand, 1993; Jaffrezo et al., 1994]. When they are present in acidic gaseous form, however, the chemical species could be changed significantly by the post depositional effects [Neubauer and Heumann, 1988; Mayewski and Legrand, 1990; Staffelback et al., 1991; Sigg et al., 1992; De Angelis and Legrand, 1994, 1995]. The more recent study carried in Greenland by De Angelis and Legrand [1995] revealed that the weak organic acids, HCOOH and CH₃COOH, escape rapidly from firn layers in presence of high strong inorganic acid (H₂SO₄), whose strong acidity causes the exclusion of the weak acids.

[20] Precipitation in Glacier 1 area has had high pH values thus high dust in the past forty years, which leads us to think that SO_4^{2-} , HCOO⁻ and CH₃COO⁻ were probably mainly deposited in aerosol form. Also, because of the very weak acidity of the precipitation, the rapid exclusion of HCOO⁻ and CH₃COO⁻ by strong acidity that was observed in the polar firm may not necessarily occur to

Table 1. Uncertainty of the Analytical Procedure^a

	Ace ⁻	For ⁻	SO_4^{2-}
Added, ng g^{-1}	400	200	375
Found, ng g^{-1}	379	207	398
SD, 1σ	17	4	10
RSD, %	4	2	2

^aThe replicate number is 12.



Figure 6. Variation for acetate, formate, sulfate and pH in the ice core of Glacier 1. The width of the shaded area indicates the core section most affected by the crack.

Glacier 1 snow. Additionally, in the superimposed ice zone in Glacier 1, snow has fallen and melted and is successively refrozen as ice, the firn stage is very brief or does not exist at all during the summer months. Therefore the two-way exchange between air and snow should be limited. However, the chemical species do suffer changes from the melts, resulting in lost of annual signals for most of anions in the precipitation except a select few that are highly volatile. The highly volatile species may quickly reach equilibrium between meltwater and air thus having high temporal resolution [Lee et al., 2003]. In that case, the volatile species is probably still indicative of the atmospheric composition that is equilibrated between air and precipitation because of the concurrence of melting-refreezing and the precipitation in Glacier 1. Nonvolatile species such as SO_4^{2-} may also be retained in the ice although the temporal resolution is decreased. Analysis of the major ions in successive snow pit in Glacier 1 demonstrated that percolation of meltwater can be stopped by ice layers leading to the preservation of the ions in the superimposed ice. Only when very intensive melting occurs, can the ions be leached away in the runoff water [Hou and Qin, 1999]. This is somewhat like the ice caps in the circum-polar regions, where intensive melting affects the climatic proxies, however, they can still give valuable low-resolution climate records for the past [Koerner, 1997]. Because of inability to quantify the influence of post-depositional effects at present, we use the record of formate, acetate and sulfate to infer the atmospheric chemistry in no-less-than five-year intervals.

5.1. Sources for the HCOO⁻ and CH₃COO⁻

[21] General sources for formate and acetate have been identified in the past 3 decades though a satisfactory source attribution is lacking to explain atmospheric observations [*Khare et al.*, 1999]. Direct emission from the biosphere, the vegetation in particular, is a very important source during growing seasons [*Keene and Galloway*, 1986; *Andreae et al.*, 1988a, 1988b; *Talbot et al.*, 1988]. Photooxidation of various alkenes has been observed as another source [*Su et al.*, 1979; *Chameides and Davis*, 1982, 1983; *Atkinson and Lloyd*, 1984; *Keene and Galloway*, 1986; *Talbot et al.*,



Figure 7. Variation for acetate, formate, sulfate and pH in average values of five-year interval. The shaded area indicates the time interval corresponding approximately to the core section influenced by the cracking effect.

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Table 2.	Average	value	101	Acetate,	ronnate,	Sunate,	and p	пш
the 5-yea	r Interval	From	195	5 to 199	98 ^a			
	CH ₃ CC	00-		HCOO-		SO_4^{2-}		pН

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	СН3СОО	нсоо	30_4	рп
1995-98	323.9(283.6)	73.8(40.6)	282.7(263.6)	6.8(0.4)
1990-94	319.8(240.4)	188.1(58.6)	469.4(160.5)	6.7(0.3)
1985-89	648.3(525.2)	331.7(184.4)	896.3(315.6)	7.1(0.4)
1980-84	404.2(305.0)	62.4(90.0)	265.6(240.0)	7.0(0.5)
1975-79	313.9(234.9)	46.0(50.1)	112.9(94.4)	6.6(0.3)
1970 - 74	501.7(423.4)	111.8(65.2)	422.1(271.2)	7.1(0.4)
1965-69	427.8(288.8)	79.0(86.0)	227.1(141.6)	7.0(0.5)
1960-64	389.6(249.5)	38.2(39.2)	154.4(148.0)	6.8(0.5)
1955-59	256.0(137.8)	20.0(9.9)	65.2(41.6)	6.7(0.3)

^aUnits for the former three species are ng g^{-1} . Numbers in parentheses designate the standard deviation (1 σ).

1988; Andreae et al., 1988a, 1988b; Jacob and Wofsy, 1988; Madronich and Calvert, 1990]. Forest fires [Talbot et al., 1988; Hartmann et al., 1990; Lefer et al., 1994], soil emission [Sanhueza and Andreae, 1991] and ants emission [Graedel and Eisner, 1988] in the tropical area represent additional natural sources for the two species. Adding to the natural sources, artificial biomass burning [Talbot et al., 1988] and motor vehicular exhaust [Kawamura et al., 1985; Talbot et al., 1988; Grosjean, 1989] also produce formate and acetate. Moreover, industrial activities emit various unsaturated hydrocarbons [Waldman et al., 1982; Grosjean, 1982; Grosjean and Wright, 1983], which can be subsequently oxidized in the atmosphere to carboxylates. The atmospheric oxidation produces more acetate than formate [Norton, 1985; Talbot et al., 1988]. The importance of anthropogenic emission relative to the natural emission determines formate to acetate ratio in the atmosphere [Arlander et al., 1990]. On the basis of analysis of various sources, Talbot et al. [1988] found that air masses influenced chiefly by anthropogenic emissions have the ratio lower than 1, while those influenced mainly by natural sources, vegetation emissions in particular, have the ratio larger than unity except pollen which has the ratio very close to that of automobile exhaust.

Calendar Year



Figure 8. Weight ratio of formate to acetate in the ice core record. The shaded area indicates the crack-bearing section.

[22] The formate to acetate ratio in Glacier 1 is lower than unity indicating the main contribution from anthropogenic sources. This is consistent with the fact that the east Tianshan region lies in an arid environment; therefore the direct emission from vegetation could not be a major source to the organic species, nor could the forest fires. Furthermore, Tianshan is situated in the midlatitudes, soil and ants emissions could not possibly be the major source either. Compared with the source experiment of Talbot et al. [1988], the mean ratio of formate to acetate in Glacier 1 record is close to emissions from vehicular combustion and biomass burning (Figure 9). Considering the low number of motor vehicles in the surrounding area, automobile combustion should not be the major provenance. Fossil fuels, coal in particular, have been widely used in West China as the energy supply for electricity generation and daily life, it might be the principal source for the organic species in the area.

[23] Formate and acetate were observed to be transported within 200 km of the source before deposition or decomposition [*Keene and Galloway*, 1986, 1988] because of their short retention time in the atmosphere [*Jacob*, 1986; *Keene and Galloway*, 1988; *Jacob and Wofsy*, 1988; *Talbot et al.*, 1988]. Accordingly, atmospheric pollution from cities and industrial towns in the vicinity must be responsible for the organic compounds in the glacier. Atmospheric pollutants from Urumqi, which lies within the range, can be transported to the glacier by the low-level regional atmospheric circulations (Figure 1). Cloud from the factories in the town Houxia drifts in the river valley and can readily reach up to Glacier 1 by the valley wind.

5.2. Sources for the SO_4^{2-}

[24] Anthropogenic pollution is a principal source for atmospheric SO_4^{2-} . Fossil fuel combustion, for example, releases SO_2 to the air, which is then converted in the



Figure 9. Formate to acetate ratios of various sources. The cross located between vehicular and biomass burning sources designates the mean ratio in Glacier 1 record. Other ratios together with their error bars are digitized from Figure 10 of *Talbot et al.* [1988]. Ratios that lie in the shaded area indicate sources relating to anthropogenic influences.

atmosphere to the secondary aerosol SO_4^{2-} [Baird, 2001]. The SO_4^{2-} is in acidic form thus contributing to the acidity of precipitation [Delmas, 1992]; Continental dust and sea spray also produce SO_4^{2-} thus forming the primary aerosol to the atmosphere [Herron, 1982; Legrand and Mayewski, 1997]. This fraction of SO_4^{2-} is in form of salt and does not contribute to the acidity of precipitation. Besides, marine biogenic activity [Saltzman et al., 1983] and sporadic volcanic eruptions are also responsible for the secondary aerosol SO_4^{2-} in the atmosphere [Legrand and Delmas, 1987; Zielinski et al., 1994]. Atmospheric SO_4^{2-} in east China is mainly from anthropogenic pollutions, particularly coal combustion [Zhao and Sun, 1986; Galloway et al., 1987; Huebert et al., 1988]. This is also the case in northwest China. The general covariation of SO_4^{2-} with $HCOO^{-}$ and CH_3COO^{-} in the record (Figures 6 and 7) suggests that they have been controlled by the same primary source(s) in the past four decades. As an additional proof, Meikuang Glacier, which is located at 35°40'N, 94°11'E in the east Kunlun mountains in the northeast of Oinghai-Tibetan Plateau, is 692 km west of the nearest city, Xining, the 0.8 million inhabitant city of Qinghai province. Whereas Dunde Ice Cap is located at 38°06'N, 96°25'E in Qilian Mountains in the northeast edge of the Plateau and is 500 km northwest Xining. Besides, 200 km northeast to the ice cap lies Yumen, a large town of 0.1 million people and a transportation as well as processing center in a region with productive petroleum fields. Corresponding to the geographic difference, SO_4^{2-} in precipitation at Dunde Ice Cap is over two-fold higher than at Meikuang Glacier. Furthermore, Glacier 1 is 100 km from Urumqi and thus higher than Dunde Ice Cap in SO_4^{2-} concentration. Bogda Feng is approximately 60 km from Urumqi, and has the highest SO_4^{2-} in precipitation [*Wake*, 1993]. The spatial variation of SO₄²⁻ concentration suggests its anthropogenic contribution in the west China. On the other hand, we tried to think that SO_4^{2-} in the precipitation is mainly from dust of the surrounding arid areas. This scenario, however, contradicts the evidence that SO_4^{2-} in the core record covaries with HCOO⁻ and CH₃COO⁻ for which continental dust has not been observed as a potential source up to now.

5.3. Effect of Anthropogenic Pollution to the Environment

[25] SO_4^{2-} was deemed a better indicator than H⁺ for tracing anthropogenic effect in remote areas [Galloway et al., 1984]. However, because of the potential source of SO_4^{2-} from evaporites in the arid area, pH should be a better indicator in this environment. Usually, HCOO⁻ and CH₃COO⁻ in the air are in acidic form and contribute significantly to the free acidity of precipitation, especially in the remote areas [Keene and Galloway, 1984; Galloway and Gaudry, 1984; Backman and Peden, 1987; Baltensperger and Kern, 1988]. SO_4^{2-} , if from oxidation of SO_2 in the air, also contributes to the acidity hence to the low pH of the environment as mentioned above. 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. This process that eventually results in the increase of pH in the atmosphere has been a well-known phenomenon [Mauptit and Delmas, 1994a, 1994b; Mori et

al., 1998; Galy-Lacaux, 1998; Khare et al., 1998; Schwikowski et al., 1999]. Since the HCOO⁻, CH₃COO⁻ and SO_4^{2-} have been primarily caused by anthropogenic pollution, they should be acidic on generated. To form the covariation with pH, their inputs to the atmospheric environment should be compensated by dust of alkali or alkaline-earth metals. The latter should be strong enough that, after neutralizing the acidity brought by the organic and inorganic acids, it still has the capacity to raise the alkalinity of precipitation. The key point for the explanation rests on the synchronism of the two processes, a convenient way leading to which is the two inputs are from the same sources. If they were controlled otherwise by different sources, i.e., if the chemical species were anthropogenic while the alkalinity were natural-dust derivative, it is too coincidental to be true that in the two periods when anthropogenic emission of HCOO⁻, CH₃COO⁻ and SO²₄ is high, the input of continental dust is also strong. We tried to consider alternatively that the input of continental dust to the regional atmosphere has been keeping strong in the past four decades thus resulting in the high pH in the record, then pH in the periods when the acidic form HCOO⁻, CH_3COO^- and SO_4^{2-} are high should be lowered relative to the rest of the record rather than the opposite. Finally, pH variations in the ice core are the result of the man-made alkalinity added to the natural pH background. Therefore, when the anthropogenic HCOO⁻, CH_3COO^- and SO_4^{2-} are strong, so are the artificial alkaline particles. This is similar to the precipitation that has been observed in Tennessee in the United States in the early twentieth century, where high anthropogenic SO₄²⁻ concentrations were accompanied by nearly equivalent amounts of anthropogenic bases from the atmospheric emission of fossil fuel combustion [MacIntire and Young, 1923]. In China, because of the lack of particulate emission controls, coal combustion releases alkaline particles to the local and regional atmosphere is well observed. In Guiyang, a provincial capital city in Guizhou province, southwest China, where vegetation cover is very high, for example, high SO_4^{2-} in precipitation was observed to correlate with high anthropogenic Ca^{2+} [e.g., Galloway et al., 1987]. Coal combustion in the industrial facilities in Urumqi city and particularly in the nearby cement plant and steel work in the Urumqi River valley emits to the atmosphere considerable particulate material along with SO₂ and unsaturated hydrocarbons [Editorial Board of Chinese Chronicle of Environment, 1991]. The gaseous material is then oxidized in the air to SO_4^{2-} , HCOO⁻ and CH₃COO⁻, respectively. The acidity of the secondary aerosol, however, has been exceedingly neutralized by the man-made particles. As a result, the anthropogenic pollution did not acidify the environment but rather made it alkaline.

6. Conclusions

[26] Located in the central Asia, the east Tianshan Mountain is a relatively remote area in the arid background. The ice core from Glacier 1 in the mountain recorded the atmospheric chemistry for the past 43 years. HCOO⁻ and CH₃COO⁻, the main carboxylic compounds in the troposphere, average 61.1 ± 89.0 ng g⁻¹ and 389.4 ± 336.3 ng g⁻¹, respectively, with a mean ratio HCOO⁻/CH₃COO⁻ of $0.21 \pm$ 0.23 (N = 489). SO_4^{2-} , the major inorganic species in the record, averages 232.9 ± 279.9 ng g⁻¹. The organic and inorganic species covaried in the past four decades and were mainly caused by the anthropogenic pollution, coal combustion in particular, to the atmosphere. The pH ranges from 6 to 9 and averages 6.9 ± 0.5 which is much higher than precipitation in other remote areas in the world. Its variations in the past decades agree with those of HCOO⁻, CH₃COO⁻ and SO_4^{2-} , suggesting that the anthropogenic pollution has released large amount of alkaline particulate material along with unsaturated hydrocarbons and SO₂. The particles exceedingly neutralize the acidic chemical derivatives and bring alkalinity to the environment.

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