Characteristics of ion concentrations in snowpits in Longyearbyen, Svalbard, Arctic

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Abstract   Snowpits samples were collected from three glaciers in the Longyearbyen region, Svalbard during March to May, 1996. Among major chemical species (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-}), Cl^- and Na^+, which come mainly from sea-salt aerosol, are the dominant soluble impurities in snowpits. In dirty layers of snowpits (representing autumn), the crustal cation Ca^{2+} has the highest concentration among all species. Thus, snowpits have been dated by high values of Ca^{2+} concentrations and less negative $\delta^{18}O$, which represent autumn and summer layers respectively. Seasonal variations in concentrations of sea-salt ions (Na^+, Mg^{2+} and Cl^-), SO_4^{2-} and NO_3^- have been identified. Results indicate that concentrations of these ions show high value in spring and summer. The spring maximum value likely results from long-range transport of marine aerosol from north Atlantic storms (Na^+, Mg^{2+} and Cl^-) and mid-latitude anthropogenic pollution (SO_4^{2-} and NO_3^-). In summer, high concentrations of the sea-salt species are attributed to local marine aerosol. The summer SO_4^{2-} maximum likely reflects a combination of local marine aerosol, high scavenging ratios, and oxidation of marine biogenic emissions. In comparison, NO_3^- maximum may reflect lightening in the atmosphere and high scavenging ratios. In general, the major ion concentrations in snowpits in Svalbard is high in comparison with those found in snowpits from other remote regions, such as Greenland, Antarctic and Qinghai-Tibetan Plateau, especially for sea-salt species.

Key words   Longyearbyen in Arctic, snowpits, ion concentrations, seasonal variations.

1   Introduction

Studies on chemical characteristics in snowpit are very important in research of modern processes in snow and ice, which is basic content for reconstructing paleoclimatic and environmental records in ice core. In Arctic, these studies were performed mainly in Greenland Ice Sheet, including the characteristics of temporal and special variation of chemical species, source, transport and deposition of impurities in surface snow and ice (Herron 1982; Mayewski *et al*. 1987; Davidson *et al*. 1987, 1989; Heidam 1987; Steffensen 1988; Beer *et al*. 1991; Yang *et al*. 1996).

Svalbard (74° – 81°N, 10° – 35°E), located in Arctic, is close to Greenland. Its area is 6.2×10^4 km^2 and 60% of it is covered by glaciers (ice caps) (Hisdal 1985) (Fig. 1). Glaciological studies in Svalbard have been performed since the beginning of

the 20th century, and major results were limited to physics of glaciers (Kang *et al.* 1996). Though several ice cores were drilled from the northern Spitsbergen (Gordiyenko *et al.* 1980; Fujii *et al.* 1990; Goto-Azuma *et al.* 1995), there were very few evidences to support the reconstruction of paleoclimate and environment recorded in ice cores. Few studies were also made on the modern processes of surface snow and ice (Gjessing 1977; Semb *et al.* 1984; Goto-Azuma *et al.* 1993). In Svalbard, the comparatively mild climate is usually attributed to the North Atlantic Current, which has a branch, the Norwegian Current, flowing towards the west coast of Svalbard. Great temperature fluctuations are characteristic of the weather in Svalbard, primarily due to alternating influences of mild, southerly air streams and the cold Arctic air invading the islands from northerly or easterly directions, and both summer snowing and winter raining can occur (Hisdal 1985). In order to get a better understanding of the climatic and environmental change from ice core records in Svalbard, detailed studies on modern processes of snow and ice should be performed, and also to supplement the research in Greenland Ice Sheet.

In this paper the characteristics of major ion concentrations in 8 snowpits and chemical deposition in key snowpits were analyzed, in order to understand the seasonal variations and sources of major ions in surface snow in Svalbard. Comparison of major ion concentrations was also made between Svalbard and other remote regions, to assess the level of ion concentrations of surface snow in Svalbard.

2 Methodology

Snowpits samples were collected from Larsbreen (78°10. 7′N, 15°34. 5′E), Bo-

Fig. 1.   Sketch map of Svalbard and the sampling site.

genbreen (78°08. 0′N, 15°38. 0′E) and Drogbreen (78°09. 7′N, 17°07. 0′E) in Longyearbyen region in Svalbard during March 3 to May 31, 1996 (Fig. 1). Five snowpits (pit1 – pit5), two snowpits (pit6 – pit7) and one snowpit (pit8) samples were collected from Larsbreen, Bogenbreen and Drogbreen, respectively. The date of sampling and elevation of snowpits are showed in Table 1. Each snowpit is located above the average equilibrium line of every glacier. Samples were collected at an interval of 10 cm in the snowpit wall and placed into pre-cleaned plastic bags after sectioning. Each melted sample was transferred to pre-cleaned high density polythylene bottle and kept in the $-20°C$ cold room.

Samples were transported to Lanzhou from Norw and analyzed in the Laboratory of Ice Core and Cold Regions Environment, Chinese Academy of Sciences. Cations analysis (K^+, Na^+, Ca^{2+} and Mg^{2+}) was performed by using PE-2380 Atomic Absorption Spectrophotometer, the prescribed minimum of the system is $(5 - 25) \times 10^{-9}$ (ppb) (relative standard deviation less than 1%). Anions (F^-, Cl^-, NO_3^- and SO_4^{2-}) was measured by using DX-300 Ion Chromatography (relative standard deviation less than 1%). Oxygen isotope analysis was performed by using a Finnigan MAT-252 Spectrometer (accuracy of 0. 5‰).

3   Results and discussion

3. 1   Results of measurement

Measurement results of major ion concentrations in 8 snowpits were shown in Table 1. There are no obvious relationship between ion concentrations and elevation. Due to the short span of elevation, the "elevation effect" of ion concentrations in precipitation may not occur. Among average concentrations of major ions, Cl^- has the highest concentration (2.500×10^{-6}), Na^+ is following (1.256×10^{-6}). It indicates that Cl^- and Na^+ are the dominant soluble impurities in snowpits in this region. "Excessive ion" was calculated to understand the component of sea-salt source for each ion. All of Na^+ is supposed to come from sea salt in the region. According to the ratio of certain ion and Na^+ in Standard Ocean Water (Brewer 1975), the non sea-salt (nss) component of certain ion is calculated by:

$$exA = A_t - Na_t(A_s/Na_s)$$

Here A_t, A_s are certain ion concentrations in the sample and Standard Ocean Water, respectively. Na_t, Na_s are Na^+ concentrations in the sample and Standard Ocean Water.

Except F^- and NO_3^-, percent of nss Ca^{2+} is the highest among nss ions (85%), the following is K^+ (77%). It is agreeable with crustal source of Ca^{2+} and K^+. Valley glacier is major in Longyearbyen region, which is commonly surrounded by rocks (Fig. 1). In summer and autumn, dust is provided by rock and deposited on the glacier. Nss Ca^{2+} > nss K^+ > nss Mg^{2+}, which is shown in Table 1, also agrees with the order of crustal elements: Ca > Na > K > Mg.

For anion concentrations: $Cl^- > SO_4^{2-} > NO_3^- > F^-$, it is mainly due to the influx of sea-salt aerosol. From Table 1, 70% of Cl^- and 49% of SO_4^{2-} come from sea-salt source, while sea-salt contribution of NO_3^- and F^- can be neglected. For nss component of ions, the order is $Cl^- > NO_3^- > SO_4^{2-} > F^-$. The source of anions is more com-

plicated, and detailed discussion will be made later.

Table 1. Concentrations of major ions in snowpits in Longyearbyen region, Svalbard [$\times 10^{-6}$(ppm)]

No. of snowpit	Elevation /m a.s.l.	Sample number	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	F$^-$	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	Sampling date (in 1996)
Pit1	570	9	1.027	0.219	1.036	0.137	0.105	2.142	0.240	0.401	March 5
Pit2	700	11	1.228	0.207	0.066	0.120	0.119	2.419	0.274	0.511	March 5
Pit3	650	9	0.798	0.119	0.141	0.104	0.090	1.505	0.240	0.419	March 26
Pit4	570	12	1.514	0.161	0.305	0.242	0.100	4.019	0.242	0.735	May 10
Pit5	700	12	0.662	0.112	0.660	0.239	0.081	1.484	0.135	0.361	May 10
Pit6	400	12	1.044	0.144	0.421	0.106	0.099	1.373	0.226	0.355	May 14
Pit7	620	15	1.722	0.178	0.268	0.217	0.094	3.532	0.338	0.888	May 14
Pit8	600	22	1.850	0.928	0.222	0.181	0.162	3.282	0.201	0.589	May 31
Average			1.256	0.270	0.381	0.167	0.106	2.500	0.239	0.539	
Non sea-salt				0.208	0.323	0.026	0.106	0.745	0.239	0.272	
Percent of non sea-salt (%)				77	85	16	100	30	100	51	

3.2 Characteristics of major ion deposition and sources

The distribution of ion concentrations and δ^{18}O with depth in snowpit7 (Bogenbreen) is shown in Fig. 2. The dirty layer, which occurred in the depth of 133 – 136 cm, was defined to be formed in 1995 autumn. This is because that: the dust in the dirty layer come from local source in Longyearbyen. In summer and autumn, snow melting and the quantities of dust, which were provided by exposed rock, were transported to the surface of glaciers by wind in short-range. However, in spring the area is covered by snow and the dust source is absent. Thus, in general, dirty layer is formed in autumn in Longyearbyen. It is obvious that the highest concentration of crustal Ca^{2+} occurs in dirty layer, which also happens in other snowpits. Thus Ca^{2+} can be used to date the snowpit (representing autumn). Two autumn layers can be defined by high Ca^{2+} concentration in snowpit8 (in Drogbreen) (Fig. 3). While summer layers can be determined by high value of δ^{18}O in snowpit8.

The distribution of sea-salt species (Na$^+$, Cl$^-$ and Mg^{2+}) is consistent in snowpit (Fig. 3). High concentrations of sea-salt species occur in spring and summer (corresponding the depth of 30 – 40 cm and 110 – 150 cm, respectively). It is agreeable with other studies in Greenland (Mayewski *et al*. 1987; Davidson *et al*. 1989). The spring high concentrations results from long-range transport of marine aerosol from north Atlantic storm during October to March. The summer high value is due to local marine aerosol, such as sea spray from Svalbard coastal regions and local marine precipitation as sea ice retreats and orographic rain prevails.

High concentrations of SO$_4^{2-}$ occur in spring and summer (corresponding to the depth of 30 – 50 cm and 100 – 140 cm, respectively) is agreeable with the study in Ny-Alesund (Semb *et al*. 1984). High concentration of SO$_4^{2-}$ in spring is attributed to mid-latitude anthropogenic pollution transporting to Arctic. The study shows that the maximum concentrations of SO$_4^{2-}$ in the atmospheric aerosol happens in March in Svalbard, is mostly due to low-level transport of polluted air from industrial areas in
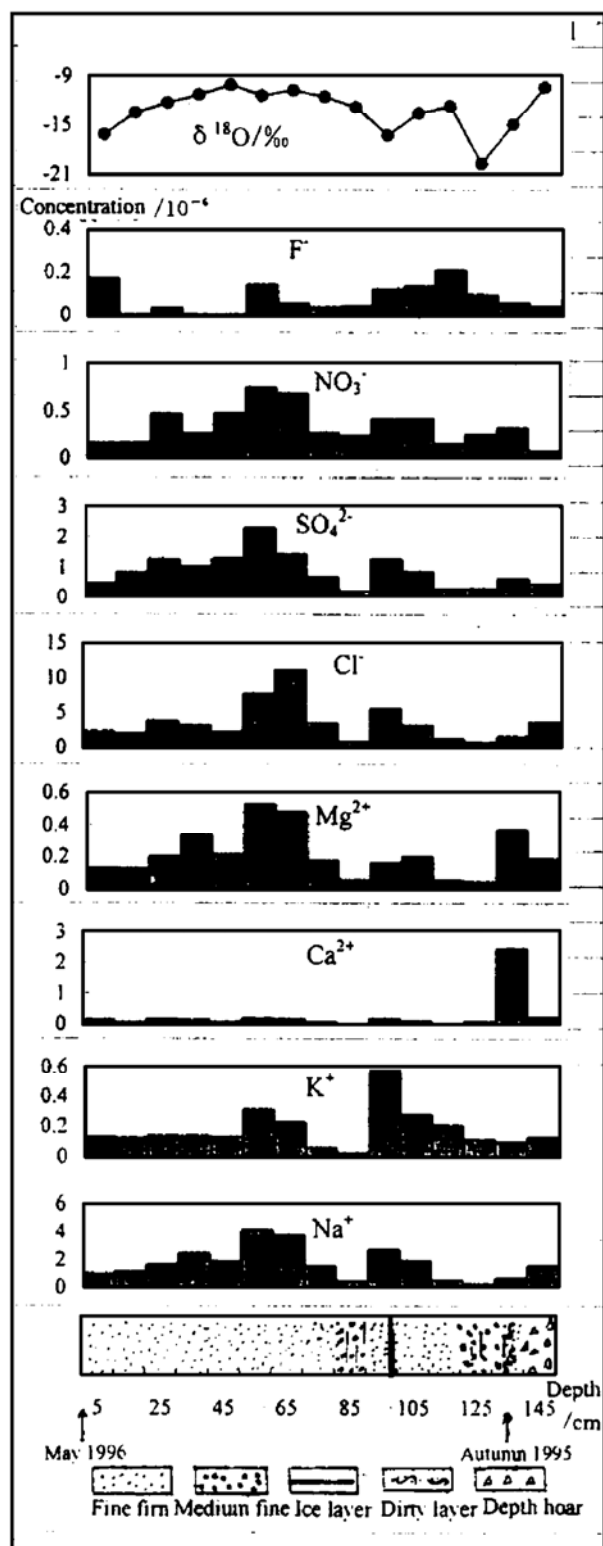
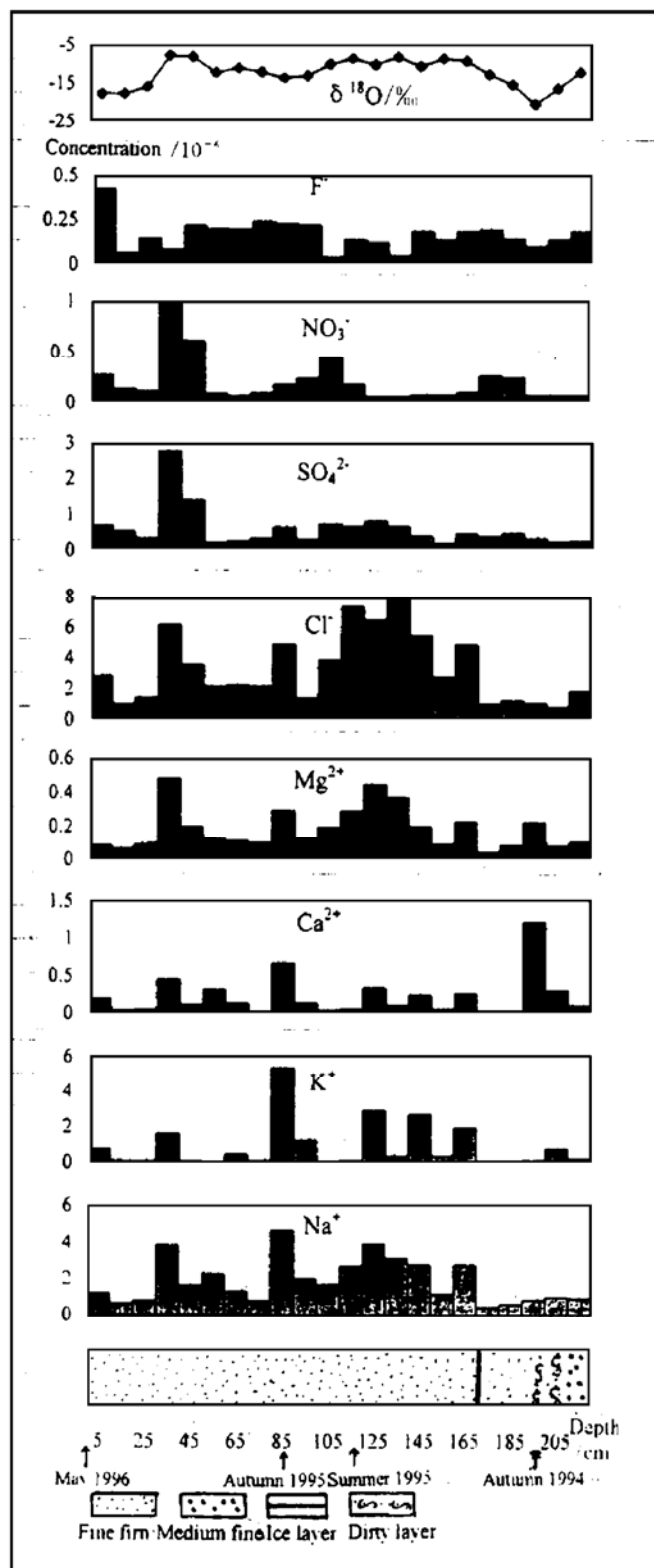Fig. 2.   Concentrations of major ions and $\delta^{18}O$ in snowpit7 in Bogenbreen.

Fig. 3.   Concentrations of major ions and $\delta^{18}O$ in snowpit8 in Drogbreen.

northern former USSR (Joranger and Ottar 1984). The study on sulfur cycle near the top of the marine boundary layer over Spitsbergen indicates that nss SO_4^{2-} concentrations in atmospheric aerosol is high in spring, while methansulphonate (MSA) is high in summer (Heintzenberg and Caroline 1994), also high scavenging ratio occurs in summer in Greenland (Davidson *et al.* 1989). Thus, the summer SO_4^{2-} maximum reflects a combination of local marine aerosol, oxidation of marine biogenic emissions

(MSA), and high scavenging ratios from atmosphere.

High NO_3^- concentrations occurs in spring and summer (corresponding to the depth of $30-50$ cm and $90-110$ cm, respectively). It is also agreeable with other studies in Greenland(Beer *et al.* 1991). The spring NO_3^- maximum results from long-range transport of mid-latitude anthropogenic pollution. Finkel *et al.* (1986) offered two hypotheses for the summer airborne concentrations at Dye 3. The first is that local phenomena, such as photochemical NO_3^- aerosol production, may be prevalent in summer. The second is that NO_3^- may reflect high altitude transport from the stratosphere. The latter is for the high elevation of Dye 3. Considering the low elevation of Longyearbyen region, the stratospheric transport of NO_3^- is not important. While enhanced scavenging by riming is likely to be significant, as in May 1985 the Dye 3 measurements show $0.380 \times 10^{-6} NO_3^-$ in rime but only 0.180×10^{-6} in snow (Davidson *et al.* 1989).

Seasonal variation of F^- is not distinct in snowpit (Fig. 3). Study shows that in the precipitation of high latitude the natural background of F^- comes from non-volcanic dust, and the contribution of sea-salt aerosol is not significant (Herron 1982). Thus, for short time (e. g. 2 a) because of no volcanic dust import, the F^- concentrations only show background value which has no obvious seasonal variations.

3. 3   Comparison of ion concentrations between Longyearbyen and other remote regions

The latest data of ion concentrations from Arctic, Antarctic and Qinghai-Tibetan (Q-T) Plateau are shown in Table 2. Except Zepu Glacier, all ion concentrations are average value in snowpit so that these data can be comparable. Concentrations of sea-salt species (Na^+, Cl^- and Mg^{2+}) are similar in Longyearbyen and Ny-Alesund in Svalbard, while crustal Ca^{2+} concentration is 5-fold in Longyearbyen as much as that in Ny-Alesund. Located in the northwestern Spitsbergen, Ny-Alesund is covered by snow and ice in the whole year, and low Ca^{2+} concentration is because of very few local crustal dust. SO_4^{2-} concentration is comparable between two regions, while NO_3^- is different, which needs to be further studied.

Concentrations of all major ions are higher in Longyearbyen region than those in Greenland, and the concentrations of Na^+, Cl^- and Mg^{2+} is 314-,147- and 167-fold in Longyearbyen as much as those in Greenland, respectively. Longyearbyen is located in the coastal region, while the central Greenland is far from the coast. The huge difference of concentrations results from the depletion of sea-salt aerosol transporting from the coast to the central Greenland. The concentrations of Ca^{2+} and K^+ are 47. 6- and 135-fold in Longyearbyen as much as those in Greenland. The reason is obvious: central Greenland is covered by huge ice sheet, and very low concentrations of Ca^{2+} and K^+ are due to few influx of local crustal dust. The concentrations of NO_3^- is slightly higher in Longyearbyen than in Greenland, while SO_4^{2-} is 5. 8-fold in Longyearbyen as much as that in Greenland. The possible reason is that the air temperature is higher in Longyearbyen than that in Greenland, and it is favorable to accelerate chemical reaction in the atmosphere, such as oxidation of MSA and SO_2 to SO_4^{2-}. In addition, as mentioned above, sea-salt SO_4^{2-} is also higher in the coastal regions than that in central Greenland.

Table 2. Comparison of ion concentrations between Longyearbyen and other regions (×10⁻⁶)

	Region	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}	References
Svalbard	Longyearbyen	1.256	0.270	0.381	0.167	2.500	0.239	0.539	This paper
	Ny-Alesund	1.873		0.077	0.126		0.080	0.468	Semb et al. (1984)
	Central Greenland	0.004	0.002	0.008	0.001	0.017	0.143	0.093	Yang et al. (1996)
Antarctic	South Polar	0.013		0.002	0.001	0.030	0.094	0.039	Qin(1995)
	Larsen Ice Shelf	1.054		0.049	0.127	1.872	0.046	0.210	Qin(1995)
Qinghai-Tibetan Plateau	Guliya Ice Cap	0.450		1.030	0.150	0.290	0.240	0.310	Li et al. (1995b)
	Dongkemadi Gl.	0.050		0.230	0.050	0.080	0.040	0.080	Xiao et al. [1] (1997)
	Zhazigou No. 29 Gl.	0.195	0.242	1.879	1.419	0.323	0.154	0.213	Ren [2] (1997)
	Kangwure Gl.	0.020		0.260	0.010	0.030	0.110	0.090	Li [3] (1994)
	Mushitage Gl.	0.100		1.040	0.110	0.150	0.300	0.370	Li [3] (1994)
	Zepu Gl.	0.440		0.150	0.530	0.430	0.000	0.150	Yao et al. (1993)

(1)Xiao CD, Qin DH and Ren JW et al. (1997): The major transport processes of natural aerosol over High Asia revealed by glaciochemistry. Annual report of Laboratory of Ice Core and Cold Regions Environment，3：104 – 113. (2)Ren JW(1997): A tentative study of the Glacier No. 29 in Danghe Nanshan，Qilian Mountains and chemical characteristics of snow，precipitation and the surface water in the area. Annual report of Laboratory of Ice Core and Cold Regions Environment，3：37 – 43. (3)Li ZQ(1994):A study on aerosol recorded in glacier in the Qinghai-Tibetan Plateau. dissertation of Lanzhou Institute of Glaciology and Geocryology，CAS，66 – 73.

Sea-salt ion concentrations （Na^+, Cl^- and Mg^{2+}） in Longyearbyen are much higher than those in inland of Antarctic and Q-T Plateau，while similar to those in coastal Antarctic (Larsen Ice Shelf) and margin of Q-T Plateau which are influenced by marine climate. In Longyearbyen，Ca^{2+} concentration is higher than that in Antarctic and central and southern Q-T Plateau，but lower than that in western and northern Q-T Plateau，where there are the vast arid and semi-arid desert regions providing quantities of crustal dust (Li et al. 1995a). In Longyearbyen，NO_3^- and SO_4^{2-} concentrations are roughly as much as those in western and northern Q-T Plateau，while higher than those in other regions. NO_3^- has multiple sources，for example，stratosphere-troposphere interaction，anthropogenic，biologic and volcanic source. In Longyearbyen，NO_3^- may reflect the combination of these sources (especially atmospheric and anthropogenic sources). While in western and northern Q-T Plateau (e. g. Guliya Ice Cap)，at least 66% of NO_3^- comes from dust imput in the dust storm season (Li et al. 1995b). In Longyearbyen about half of SO_4^{2-} comes from sea-salt aerosol，while 76% of SO_4^{2-} results from dust influx in the dust storm season in Guliya Ice Cap.

3. 4 Seasonal variation of $\delta^{18}O$

Studies in Greenland snowpits suggest that $\delta^{18}O$ has a positive correlation with air temperature，and the seasonal variation of $\delta^{18}O$ is higher in summer and lower in winter (Beer et al. 1991). In Svalbard，the source of precipitation is complicated，and raining in winter or snowing in summer may happen sometimes. Thus，though the higher $\delta^{18}O$ value occurs in summer，the lower value doesn't occur in winter but in autumn (Fig. 3). Autumn is a dry season in Longyearbyen (Hisdal 1985)，whether low $\delta^{18}O$ value in autumn is related to the minimum precipitation needs further studies. Also $\delta^{18}O$ is related to the concentrations of sea-salt ions，NO_3^-，and SO_4^{2-}，i. e.

high $\delta^{18}O$ value is corresponding to high concentrations of these ions (Fig. 3). It suggests that $\delta^{18}O$ value are high in precipitation origins from local marine air mass in summer and mid-latitude marine air mass in spring. Though Longyearbyen is located in the Arctic, the seasonal variation of $\delta^{18}O$ is complicated for complicated source of precipitation. Further works need to investigate the relationship between $\delta^{18}O$ and air temperature as well as the seasonal variation of $\delta^{18}O$, which is significant to reconstruct paleoclimate from ice core records in Svalbard.

4 Conclusion

(1) Cl^- and Na^+, which mainly come from sea-salt aerosol, are the dominant soluble impurities in snowpits in Longyearbyen region. It also suggests that the precipitation is mainly controlled by marine air mass in the region.

(2) Crustal Ca^{2+} can be a mark of autumn to date snowpit in Longyearbyen region. Ca^{2+} concentration is highest in dirty layer that is formed in autumn. Ca^{2+} mainly comes from local exposed rock.

(3) Concentrations of sea-salt species (Mg^{2+}, Cl^- and Na^+), NO_3^-, and SO_4^{2-} show high value in spring and summer. The spring maximum may result from long-range transport of marine aerosol from north Atlantic storm (Mg^{2+}, Cl^- and Na^+) and mid-latitude anthropogenic pollution (NO_3^- and SO_4^{2-}). For sea-salt species, high concentration in summer are attributed to local marine aerosol. The summer SO_4^{2-} maximum reflects a combination of local marine aerosol, high scavenging ratios, and oxidation of marine biogenic emission. For NO_3^-, high concentration in summer may reflect lightening in the atmosphere and high scavenging ratios.

(4) The concentrations of sea-salt ions in snowpits in Svalbard are higher than those found in snowpits from other remote regions, such as Greenland, Antarctic, and Q-T Plateau. Also in Svalbard, Ca^{2+} concentration is higher than that in central Greenland, Antarctic, and Q-T Plateau; however lower than that in central, northern, and western Q-T Plateau. Concentrations of NO_3^- and SO_4^{2-} in Svalbard are similar to those in the western and northern Q-T Plateau, and are higher than those in other regions.

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