Polar Meteorol. Glaciol., **17**, 15–24, 2003

Seasonality of isotopic and chemical species and biomass burning signals remaining in wet snow in the accumulation area of Sofiyskiy Glacier, Russian Altai Mountains

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(Received May 1, 2003; Accepted August 20, 2003)

Abstract: Preliminary glaciological investigation was carried out on the accumulation area of Sofiyskiy Glacier, Russian Altai Mountains in July 2000. Analyses of a 12.3 m core and 3 m deep pit samples show that seasonal variations of $\delta^{18}O$, tritium and melt features remained in the wet snow layers. Annual layer thickness determined on the basis of seasonality of these elements for 12.3 m core is 0.99 m of water on average in 1994–1999 with a minimum in 1998 when the minimum mass balance was observed for three other glaciers in the Altai Mountains. High correlations of NH_4^+ concentration with concentrations of K^+, SO_4^{2}, NO_3^- and PO_4^{3-} are found. NH_4^+ and K^+ are considered to be of biomass burning origin, and PO_4^{3-} and NH_4^+ are due to chemical ingredients used for fire extinction in biomass burning.

key words: biomass burning, ice core, Altai, Sofiyskiy

1. Introduction

A glaciological investigation was carried out on the accumulation area of Sofiyskiy Glacier (49°47′N, 87°46′E), one of the major glaciers in the South Chuyskiy Range of the Russian Altai Mountains, during 15–24 July 2000 as a Japan-Russia joint research project prior to the ice core drilling planned in 2001. The purpose of this investigation was to evaluate whether the research site is suitable for ice core drilling from the viewpoint of ice core climate studies (Fujii *et al.,* 2000). As recent climate warming has been remarkable in Siberia (Chapman and Walsh, 1993; Weller, 1998), Sofiyskiy Glacier, which is located on the southern fringe of the Siberian plain, is expected to provide recent records of climate warming and simultaneous environment change.

We obtained an ice core to the depth of 12.3 m and dug a 3 m deep pit at the altitude of 3450 m a.s.l. of the accumulation area. Some of the analytical results from the core (stratigraphy, grain size and density), borehole temperature, stratigraphy of the pit and

meteorological observations have already been published (Fujii *et al.,* 2000). This paper interprets seasonal features of chemical, isotopic and physical properties of the surface wet firn layer and discusses the probable origins of chemical elements.

2. Field work and core analysis

Figure 1 shows the location of Sofiyskiy Glacier. It extends from 3867 to 2450 m a.s.l., is approximately 7 km long and has an average width of 1.7 km facing to the north-east. The head of the glacier is located near Mt. Brat (3867 m a.s.l.), one of the highest peaks of the range.

The camping site was located at 3450 m a.s.l. of the relatively flat accumulation area. Ice core drilling was carried out to a depth of 12.3 m with a hand auger and a 3 m deep pit was excavated about 10 m away from the borehole.

The weather during the research period was mostly clear with wind speed of 0 to 5 m s^{-1}. Minimum and maximum air temperatures were -4 and $+5$°C, respectively. The snow surface height, which was measured using a stake installed in the surface snow

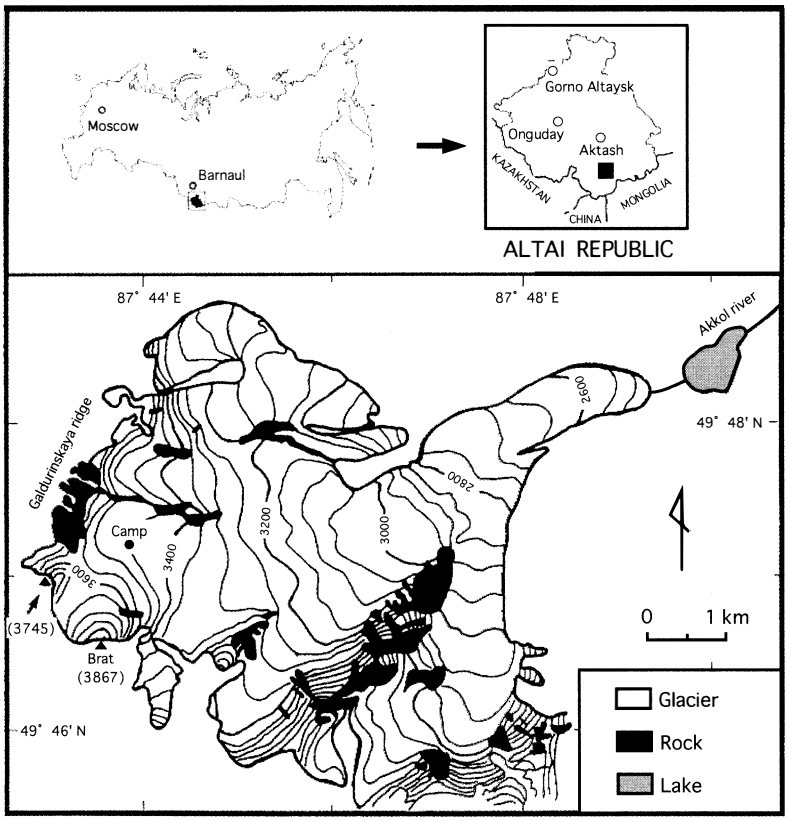

Fig. 1. Sofiyskiy Glacier with 50 m contour lines and its location in Russia. The ice coring site is indicated by solid circle on the map.

from 15 to 24 July, increased from 15 to 17 July due to snow accumulation of 52 mm, and then decreased by 157 mm due to snow melting and sublimation. Due to snow melting and downward melt water percolation, the borehole temperature was 0°C from the surface to 8 m depth with minimum temperature of −0.1°C at 10 m depth (Fujii *et al.,* 2002).

The core consisted of wet firn and ice layers. The core was cut at 10 cm depth intervals and the surface few mm of the core samples was eliminated with a ceramic knife in the core processing trench. These samples were kept in plastic bags and melted in the temperature range from 10 to 20°C. Pit snow samples were collected in plastic bags from the surface to 3 m depth at intervals of 10 cm depth with a pre-cleaned Teflon-coated sampler and were melted. The samples were stored in pre-cleaned plastic bottles (100 cm^3) and sent to Japan for isotope and chemical analyses.

The analyses were carried out in a clean laboratory of the National Institute of Polar Research, Tokyo. The oxygen isotope ratio ($\delta^{18}O$) was measured by a mass spectrometer (Finnigan-MAT, Delta-E). The concentrations of cations and anions were measured by ion chromatographs (Dionex DX-500). The analytical method is described in Watanabe *et al.* (1997).

3. Analytical results and discussion

3.1. Seasonality of $\delta^{18}O$, tritium and melt features

Figure 2 shows the stratigraphy and profiles of $\delta^{18}O$ and tritium for the 3 m deep snow pit together with profiles of the core shown as dashed lines. Remarkable ice layers with thickness more than 1 cm were found at 1.0 and 2.9–3.0 m in depth. Many minor ice layers or ice crusts thinner than this were not found below the depth of 2.0 m, probably due to melting by melt water percolated in the next summer of snow accumulation, suggesting that the depth of 2.0 m is the surface of the previous ablation season.

The $\delta^{18}O$ profile presents two high values at 0.3 and 2.7 m depths and a minimum at 1.2 m depth, both showing isotopic summers and winter. The tritium profile presents high concentration peaks at 0.3–0.6 m and 2.7–2.9 m depths. The tritium concentration in precipitation increases in spring-summer due to breakup of the tropopause between 30 and 60°N latitude in spring and leakage of stratospheric water vapor with a higher tritium content into the troposphere (Gat, 1980). It is, therefore, considered that the two high concentration peaks in the tritium profile show spring-summer seasons. The tritium peak at 1.6 to 1.9 m of the firn core was probably formed by percolation of melt water.

Though Schotterer *et al.* (1997) reported that $\delta^{18}O$ of ice cores in Asian inland regions does not indicate seasonality, the $\delta^{18}O$ and tritium profiles in the surface 3 m deep pit of Sofiyskiy Glacier show clear seasonality.

Five dirt layers were observed at around 0.1, 0.7, 1.5, 1.8 and 2.8 m in depths with thickness of 10 to 30 cm on a 3 m deep pit wall. The most distinct dirt layer was at 2.8 m depth, suggesting deposition in the spring-summer season because dust storms in the windward arid regions mainly occur in spring and early summer (Dolgilevich, 1973). The other light colored dirt layers suggest the occurrence of dust storms even in autumn

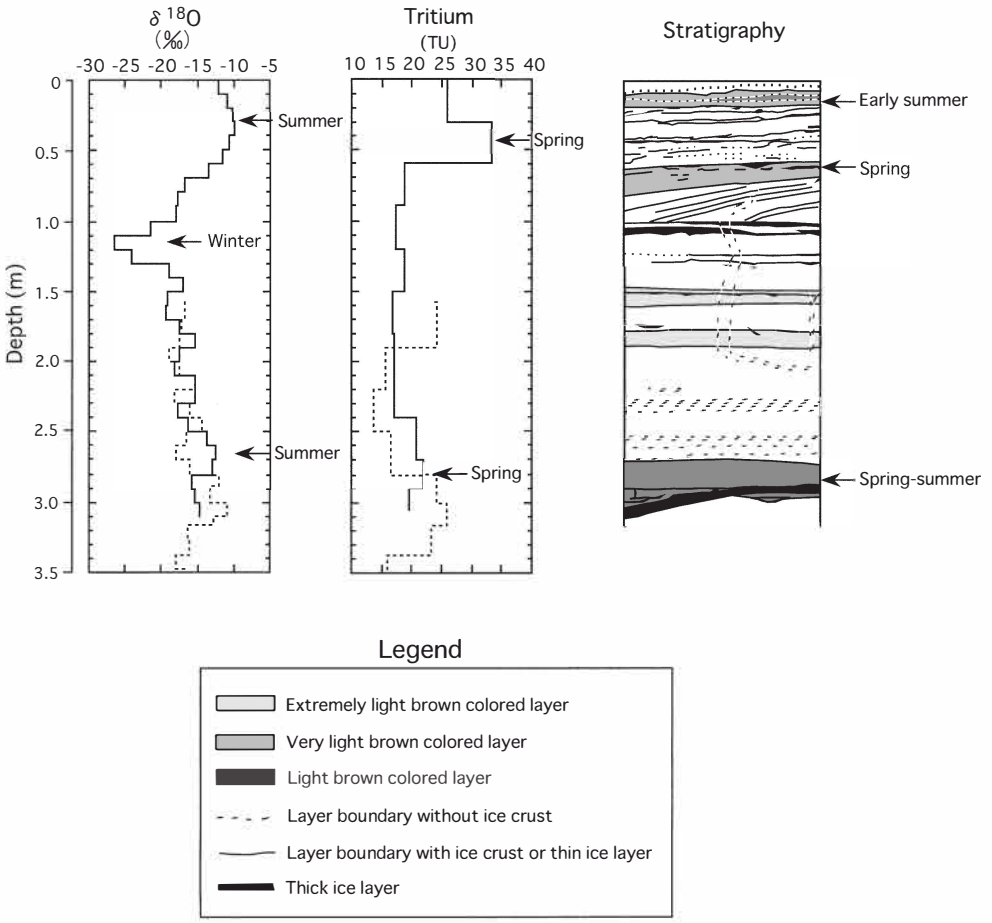

Fig. 2. Stratigraphy and profiles of $\delta^{18}O$ and tritium for surface 3.5 m deep layers. Solid and dashed lines show data obtained from pit and core samples, respectively. Arrows indicate specific season.

and winter (Demshin, 1966).

3.2. Seasonal signals and the age of the firn core

Summer melt water percolates at least to 8 to 10 m in depth at our research site judging from the borehole temperature of 0°C (Fujii *et al.,* 2002). Due to the melt water percolation into firn, isotopic and chemical concentrations should have changed from the time of deposition. However, seasonal fluctuation patterns seem to persist in the $\delta^{18}O$ and tritium profiles as shown in Fig. 3. The line in the figure of $\delta^{18}O$ shows the [average] − [standard deviation] calculated for snow deeper than 3 m where the seasonal fluctuation becomes indistinct due to the effect of repeated melt water percolation for more than one year. Supposing that melting occurs mainly in summer snow, $\delta^{18}O$ of winter snow does not show much effect of melting compared with $\delta^{18}O$ for

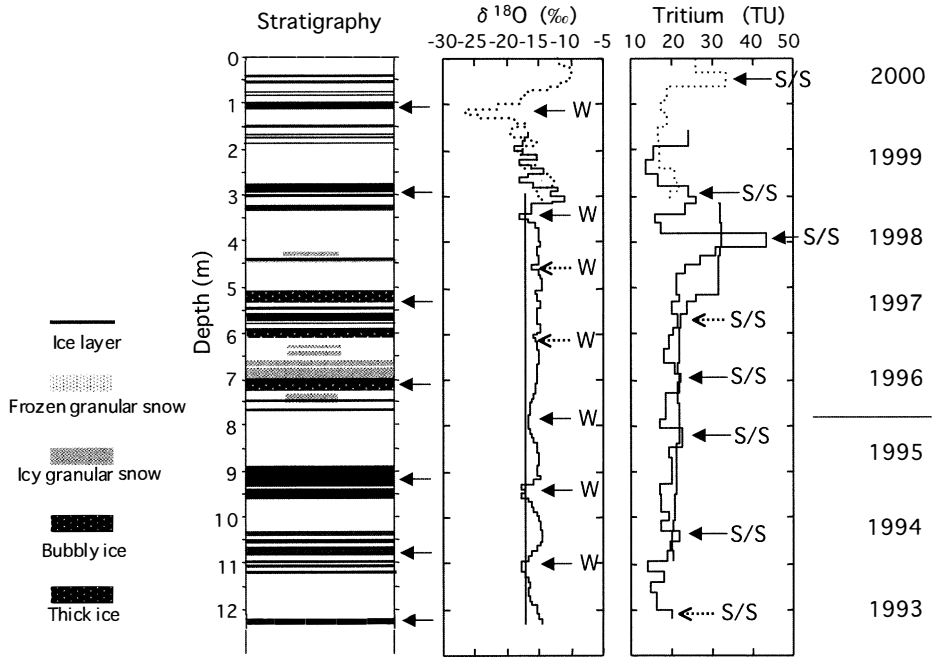

Fig. 3. Stratigraphy and profiles of $\delta^{18}O$ and tritium for 12.3 m firn core (solid line) and 3 m pit samples (dotted line). The solid lines in $\delta^{18}O$ and tritium figures are [average] − [standard deviation] and [2.5 m running mean] + [the standard deviation] to detect isotopic winter and spring/summer tritium peaks. Solid and dashed arrows indicate the definite and probable seasons (W: winter, S/S: spring-summer), respectively. Annual layer boundaries (winter boundaries) are shown on the right side of the figure.

summer snow. We, therefore, consider negative peaks with the value less than the [average] − [standard deviation] as isotopic winter. Indistinct ones are shown as dashed arrows in the figure.

For the tritium signal, which attenuates with a half-life of 12.36 years, we take peaks exceeding the values of [running mean] + [standard deviation] as the spring-summer peaks. Here, we calculated the running mean and the standard deviation for the depth range of around 2.5 m, which corresponds to the annual accumulation rate judging from 3 m deep pit work. Solid and dashed arrows in the figure of the tritium profile show the definite and probable spring-summer peaks, respectively.

The stratigraphy of the core is characterized by thick ice layers at relatively regular intervals of about 2 m as shown by arrows in the figure. These thick ice layers may have been formed in a less permeable layer such as an icy layer, formed at the end of the previous ablation season when summer surface snow may have vanished by strong melting and sublimation (Fujii *et al.,* 2002) and snow deposited in the spring-summer season may have been exposed. Perhaps the thick ice layers were formed at the previous spring-summer surface by percolation of melt water in the next summer.

On the basis of the above-mentioned interpretations, we estimate the annual layer (winter) boundaries to be consistent with the other seasonal signals shown on the right

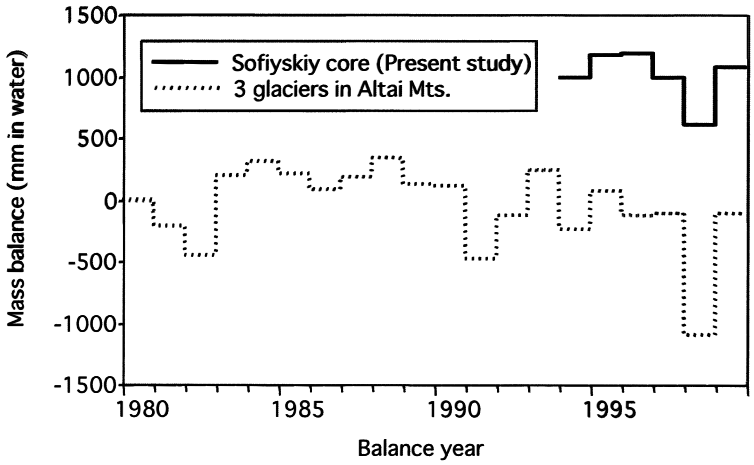

Fig. 4. Change in annual accumulation rates at the drilling site of the Sofiyskiy Glacier in the years from 1994 to 1999 on the basis of 12.3 m core analysis (solid line) and change in mean specific net balance of Maliy Aktru, Leviy Aktru, and No. 125 Glaciers in the North Chuyskiy Range (dashed line), indicating unusual negative balance in the 1997/98 balance year. The latter figures is drawn using data tabulated in IAHS/UNEP/UNESCO/WMO (2001).

side of the figure. The annual accumulation was in the range of 1.1 to 2.1 m, with an average of 1.63 m, from 1994 to 1999. The water equivalent value is calculated to be 0.99 m using detailed density data. The annual accumulation rate in 1998 was about 2/3 of the average; this small accumulation rate is supported by the evidence of the average mass balance of three glaciers in the Russian Altai Mountains (Fig. 4). Figure 4 shows the mean specific net balance of Maliy Aktru, Leviy Aktru, and No. 125 Glaciers in the North Chuyskiy Range, indicating unusual negative balance in the1997/98 balance year due to reduced accumulation, as low as 24% of the average and intensive snow melt as much as 73% less than usual (IAHS/UNEP/UNESCO/WMO, 2001).

3.3. Chemical features of surface snow

3.3.1. Correlation matrix

Figure 5 presents profiles of major anions and cations for surface 3-m deep snow layer together with stratigraphy, $\delta^{18}O$, pH, EC and tritium content. As mentioned in Section 3.1, the seasonal patterns of $\delta^{18}O$ and tritium remain in spite of repeated melt water percolation and the 3-m deep layer covers seasons from spring-summer 1999 to summer 2000. However, initial patterns of snow chemistry should have been disturbed due to flushing of ion species by melt water (Brimblecombe *et al.,* 1985; Iizuka *et al.,* 2000). It is, therefore, difficult to describe seasonal features of major ions.

To consider their sources, we show the correlation coefficient (r) matrix between major chemical species for surface 2 m deep snow, which was deposited after the last ablation season and has less effect of melt water percolation than snow below this depth, in Table 1. Coefficients with values higher than 0.7 are in shaded cells.

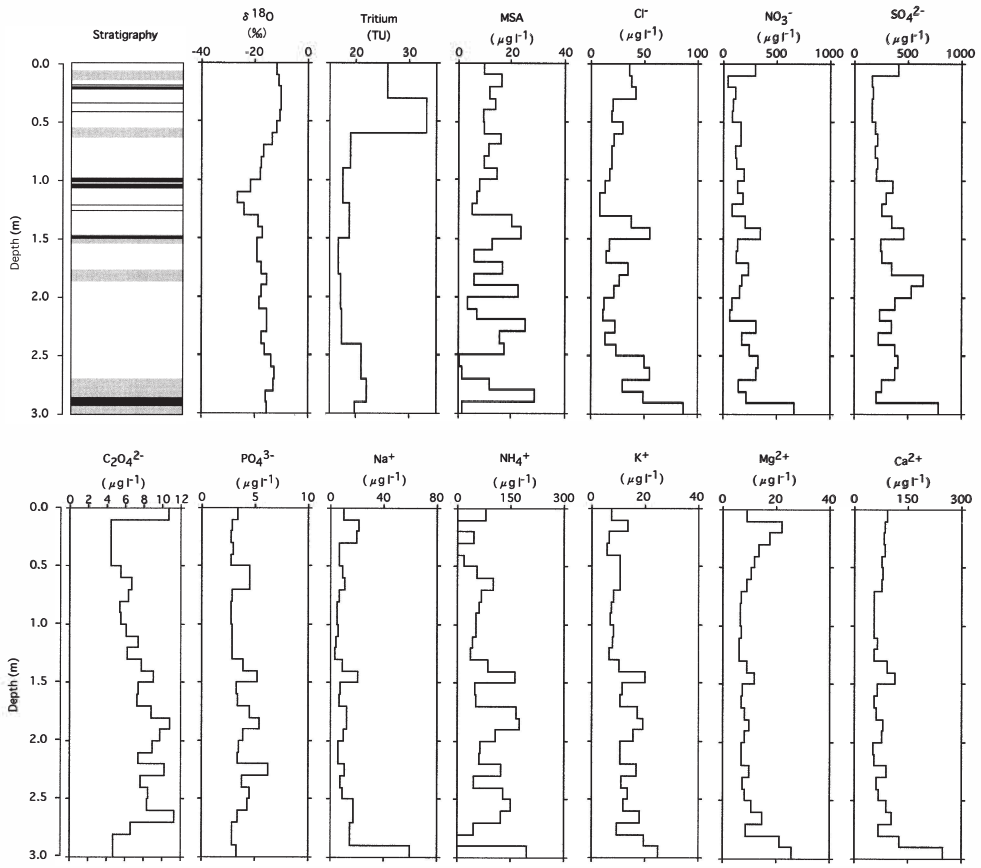

Fig. 5. Stratigraphy and profiles of $\delta^{18}O$, tritium and major chemical components for surface 3 m deep snow layers.

Table 1. Correlation coefficient (r) matrix between major chemical species in surface 2 m snow layers, where less effect of melt water percolation is expected than in snow below this depth. Coefficients with values higher than 0.7 are shown in shaded cells.

	CH_3COO^-	$HCOO^-$	MSA	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
CH_3COO^-	1.00												
$HCOO^-$	0.98	1.00											
MSA	0.50	0.44	1.00										
Cl^-	0.18	0.16	0.30	1.00									
NO_2^-	0.59	0.63	0.21	0.13	1.00								
NO_3^-	0.28	0.35	0.24	0.46	0.44	1.00							
SO_4^{2-}	0.30	0.39	0.37	0.18	0.19	0.56	1.00						
PO_4^{3-}	0.15	0.29	0.05	0.53	0.38	0.48	0.63	1.00					
Na^+	0.40	0.41	0.24	0.87	0.03	0.19	0.18	0.84	1.00				
NH_4^+	0.48	0.59	0.14	0.37	0.25	0.71	0.77	0.92	0.31	1.00			
K^+	0.55	0.59	0.23	0.44	0.21	0.41	0.68	0.82	0.56	0.78	1.00		
Mg^{2+}	0.20	0.34	0.23	0.64	0.37	0.27	0.23	0.81	0.79	0.26	0.16	1.00	
Ca^{2+}	0.12	0.03	0.52	0.79	0.01	0.44	0.27	0.53	0.68	0.24	0.40	0.60	1.00

As seen in Table 1, there are two chemical groups with high correlation between species: the group SO_4^{2-}, NO_3^-, PO_4^{3-}, K^+ and NH_4^+; and the group Na^+, Mg^{2+}, Ca^{2+} and Cl^-. The most probable source of the latter group is terrestrial salts (dust) because the extremely high concentration of Ca^{2+} is undoubtedly due to terrestrial dust deposit and the K/Na of 1.12 is close to the average K/Na of 0.97 of the continental crust (Broecker and Peng, 1982). Next we consider the probable origin for the former group.

3.3.2. Signals of biomass burning and fire extinction

The main ice core signals for biomass burning are NH_4^+ and black carbon (Peel, 1993; Chýlek *et al.,* 1995; Holdworth *et al.,* 1996; Taylor *et al.,* 1996; Legrand and Angelis, 1996; Jaffrezo *et al.,* 1998). Furthermore, there are reports that give the concentrations of K^+, formate ($HCOO^-$), acetate (CH_3COO^-), glycolate ($C_2H_3O_3^-$) and oxalate ($C_2O_4^{2-}$) in ice cores. These values are elevated during biomass burning events (Legrand and Angelis, 1996; Jaffrezo *et al.,* 1998).

High correlations with NH_4^+ in 2 m surface snow of Sofiyskiy Glacier are seen for PO_4^{3-} ($r=0.92$), K^+ ($r=0.78$) and SO_4^{2-} ($r=0.77$) as shown in Table 1. As the concentration of K^+ is not well correlated with that of Ca^{2+} ($r=0.40$), the K^+ is considered to be not of soil dust origin. The content of K^+ in Summit snow layers in Greenland shows peaks mostly corresponding to biomass burning events (Legrand and Angelis, 1996).

Recent satellite images have clearly revealed that boreal fires in Siberia, Mongolia and China have occurred over large areas (Cahoon *et al.,* 1994; Kasischke, 1999; Tanimoto *et al.,* 2000). According to the fire spot map over Siberia in August 1998 (Tanimoto *et al.,* 2000), an extreme fire year (Kasischke, 1999), forest fires occurred at some places in southwestern Siberia. Occurrences of forest fires in southwestern Siberia in 1999 and 2000 are unknown, but forest fires should have occurred in these years judging from the statistic of report of forest fires in Russia in 1970–1998 (Kasischke, 1999).

On the basis of these considerations, the major source of NH_4^+ and K^+ is likely to be biomass burning.

The concentration of PO_4^{3-} is extremely well correlated with the concentration of NH_4^+ ($r=0.92$). PO_4^{3-} is not a chemical species emitted by biomass burning. The most probable source is a chemical ingredient, monoammonium phosphate ($NH_4H_2PO_4$), of the dry chemical fire extinguisher known as "ABC" extinguisher, which is most commonly used for fire extinction (*e.g.* SEJIN T&E, 2003).

It is, therefore, explained that the high correlations of NH_4^+ concentration with concentrations of K^+ and PO_4^{3-} in surface snow of Sofiyskiy Glacier are due to chemical species emitted by biomass burning and chemical ingredients used for fire extinction.

4. Conclusions

Analyses of 3 m deep pit snow and a 12.3 m firn core in the accumulation area of Sofiyskiy Glacier in the South Chuyskiy Range of the Russian Altai Mountains reveal the following:

1) Seasonality persists in $\delta^{18}O$ and tritium profiles even in the surface wet snow layer.

2) The average annual snow accumulation rate during 6 years from 1994 to 1999 was estimated to be 0.99 m of water on the basis of seasonality of $\delta^{18}O$, tritium and melt features.

3) Annual net accumulation was extremely low, about half of the average, in 1998, being consistent with the extremely low mass balance of glaciers in the North Chuyskiy Range of the Altai Mountains.

4) The high correlations of NH_4^+ concentration with concentrations of K^+ and PO_4^{3-} are due to chemical species emitted by biomass burning and a chemical ingredient used for fire extinction.

5) The present study shows that the research site is considered to be suitable for ice core drilling to study past climate.

Acknowledgments

We would like to thank Prof. Okitsugu Watanabe and Prof. Kokichi Kamiyama of the National Institute of Polar Research (NIPR) for their support of our research project and Prof. Hugo Decleir and Dr. Frank Pattyn of Vrije Universiteit Brussel (VUB) for providing valuable information on the research site. Thanks are extended to Mses. Tomoko Kobayashi, Maki Nakata and Tomoko Naka for their sample analyses. This research was supported by a Grant-in-Aid of the International Scientific Research Program of the Ministry of Education, Culture, Sports, Science and Technology, Japan (Principal investigator of the Grant: Prof. K. Kamiyama of NIPR, Grant No. 11208202).

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