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Scientific note

Chemical characteristics in a 22-m ice core on the Belukha Glacier, Russia

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Abstract: To better understand how the chemical composition of a glacier in an inland continental region relates to the local climate, we collected ice core samples from the Belukha Glacier, Russia, in July 2001. We analyzed the samples for pH, anions, and cations. The primary soluble ions were SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, and $HCOO^-$. Moreover, we argue the following. 1) Ca^{2+} and its equivalent $SO_4^{2-}+NO_3^-$ likely originated from terrestrial dust such as soil. 2) $HCOO^-$ and its equivalent NH_4^+ likely originated from vegetation and/or biomass burning. 3) The remaining $SO_4^{2-}+NO_3^-$ and NH_4^+ likely originated from livestock, commercial fertilizers, and natural fertilizers. 4) The NH_4^+ concentration was low when there was no contribution from vegetation and/or biomass burning.

key words: Belukha Glacier, inland continental region, ice core, and chemical characteristics

1. Introduction

Ice-core research is widely conducted to reconstruct paleoclimate conditions on both regional and global scales, especially to better understand the influence of human activity on global climate change. Chemical analysis of the ice is one of the most promising techniques to provide paleoclimate conditions and also to determine the history of the ice's melting. For example, the SO_4^{2-}/Cl^- ratio (Koerner, 1997) and the MG^{2+}/Na^+ ratio (Iizuka *et al.*, 2002) can be used to estimate past climate. Moreover, atmospheric SO_4^{2-} aerosol and some products of biomass burning are known to cause cooling of the atmosphere. Therefore, the chemical properties of glaciers provide important information about the links between past climates and the composition of past atmospheres, which can have important implications for present and future climates.

The Altai mountain region is near the borders of Russia, China, Kazakhstan, and

Mongolia, and thus has an inland continental climate. In the Altai mountain region, there are only a few records of paleoclimate conditions reconstructed from ice cores (Fujii *et al*., 2002; Aizen *et al*., 2003; Olivier *et al*., 2003). The ice core record from the Altai mountain region provides information about Eurasian paleoclimate conditions on the Siberian High and the westerly jet stream. In this paper, we describe our glaciochemical study of a shallow ice core at Belukha Glacier in the Altai mountain region.

2. Study site and analytical procedures

An ice core was obtained in July 2001 from Belukha Glacier (49°48′N, 86°34′E, 4100 m asl), in the Russian Altai Mountain region. (A map of the Belukha Glacier region is in Aizen *et al*. (2003).) The ice core was 22-m deep, and consisted of firn and slight thin ice layers.

The core was transported in a frozen state to a cold laboratory at the National Institute of Polar Research, Japan, and was preserved there at −20°C. For chemical analyses, the core was divided into a continuous sequence of samples, each 4- to 8-cm long. For each sample, we shaved off the surface of the sample with a clean ceramic knife. After the samples are melted, the melt samples were filtered through a pore size of 0.45 μm and then analyzed for pH and the amounts of 11 soluble ions (Na^+, NH_4^+, K^+, MG^{2+}, Ca^{2+}, Cl^-, $HCOO^-$, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, and PO_4^{2-}). The pH was measured using flow-cell-type sensors by the method described in Watanabe *et al*. (1997); uncertainties were estimated to be within ±0.1. The 11 soluble ions were determined using an ion chromatography apparatus with an estimated uncertainty of less than 5% for each ion.

3. Results: Compositions of major soluble ions in the Belukha ice core

Table 1 shows the average values of the 11 soluble ions. The primary anions and cations in the ice core are SO_4^{2-} and NH_4^+, which have average concentrations of 15.2 and 13.2 μeq/*l*, respectively. The secondary components are $HCOO^-$, NO_3^-, and Ca^{2+}, with average concentrations of 6.8, 5.6, and 7.2 μeq/*l*, respectively. These 5 ion concentrations total 88.2% of all 11 ion types measured (79.2%, if we include the concentration of the excess anion). Also, the 6 anion concentrations are 5.8 μeq/*l* higher than those of H^+ plus the 5 cations. Figure 1 shows the depth profiles of SO_4^{2-}, NH_4^+, $HCOO^-$, NO_3^-, and Ca^{2+} concentrations, and also the pH.

Table 1. Measured pH and concentrations of 11 soluble ion species (μeq/l) from the Belukha Glacier ice core.

	$HCOO^-$	Cl^-	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$	PO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	pH
Average value	6.78	1.56	5.61	15.20	0.89	0.25	1.39	13.22	0.77	1.50	7.20	6.0
Standard deviation	5.94	1.18	3.22	10.37	0.71	0.18	1.39	6.84	0.96	1.22	7.91	0.3

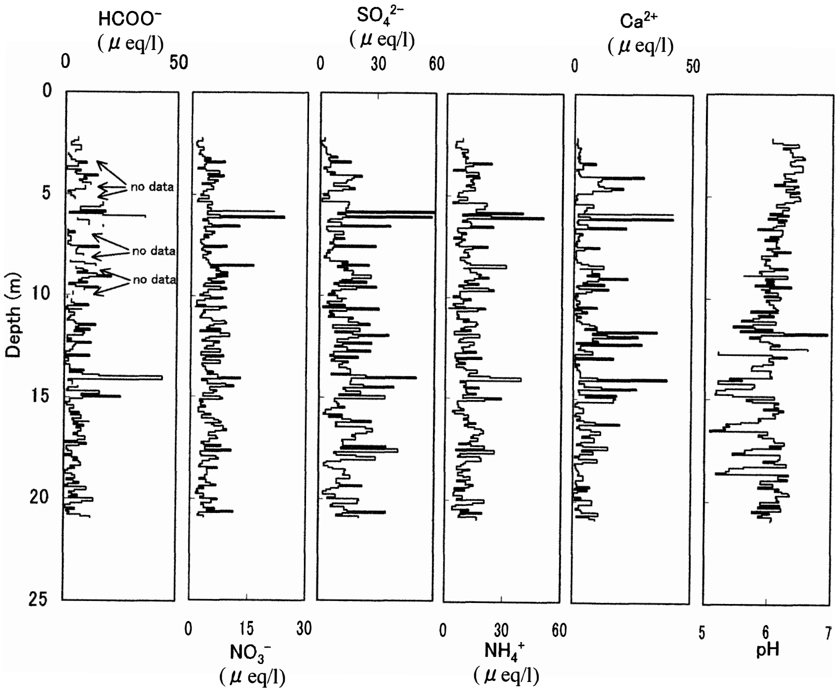

Fig. 1. Depth profiles of pH and five major soluble ions. The ordinate is the depth measured downward from the surface of the glacier.

4. Discussion: Origins of five major soluble ions in the Belukha ice core

Now, we focus on the origins of the five major components (SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, and $HCOO^-$). Table 2 lists the correlation coefficients between the 11 soluble ions. There is good correlation between cations and anions in five major components: 1) NH_4^+ and $HCOO^-$ ($r^2=0.78$), 2) NH_4^+ and NO_3^- ($r^2=0.89$), 3) NH_4^+ and SO_4^{2-} ($r^2=0.84$), 4) Ca^{2+} and NO_3^- ($r^2=0.75$), and 5) Ca^{2+} and SO_4^{2-} ($r^2=0.82$). These correlations suggest that i) NH_4^+ on the Belukha glacier was likely transported together with $HCOO^-$, SO_4^{2-}, and NO_3^-, and ii) Ca^{2+} on the Belukha glacier was likely transported together with SO_4^{2-} and NO_3^-, but not with $HCOO^-$.

Figure 2 shows the ionic diagram of $SO_4^{2-}+NO_3^-$, NH_4^+, and $HCOO^-$. Line 1 in Fig. 2 represents the relation

$$[NH_4^+] : [HCOO^-] = 1 : 1 \ (\text{[ ] means } \mu\text{eq}/l \text{ units}).$$

Each datum satisfies $NH_4^+ > HCOO^-$. This excess of NH_4^+ and the good correlation between NH_4^+ and $HCOO^-$ suggest that almost all $HCOO^-$ on the Belukha glacier was transported together with NH_4^+. Kreutz *et al.* (2001) suggested that $HCOO^-$ was transported together with NH_4^+ on the Inilchek glacier, Tien Shan Mountains. Legrand *et al.* (1992) and Wake *et al.* (1992) suggested that vegetation and/or biomass

Table 2. Correlation coefficients between measured ion species (μeq/l) in Belukha Glacier.

	$HCOO^-$	Cl^-	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$	PO_4^{3-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
$HCOO^-$	1.00										
Cl^-	0.48	1.00									
NO_3^-	0.57	0.43	1.00								
SO_4^{2-}	0.56	0.39	0.86	1.00							
$C_2O_4^{2-}$	0.55	0.39	0.59	0.67	1.00						
PO_4^{3-}	0.57	0.44	0.65	0.64	0.77	1.00					
Na^+	0.58	0.88	0.39	0.41	0.49	0.53	1.00				
NH_4^+	0.78	0.44	0.89	0.84	0.59	0.63	0.47	1.00			
K^+	0.27	0.30	0.26	0.24	0.54	0.70	0.45	0.28	1.00		
Mg^{2+}	0.59	0.57	0.69	0.79	0.75	0.68	0.68	0.76	0.43	1.00	
Ca^{2+}	0.53	0.54	0.75	0.82	0.76	0.69	0.61	0.72	0.35	0.90	1.00

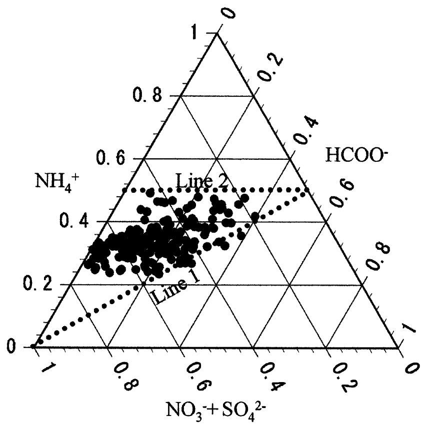

Fig. 2. Diagram of $NO_3^-+SO_4^{2-}$, NH_4^+, and $HCOO^-$. Lines 1 and 2 show $NH_4^+ : HCOO^- = 1:1$ and $NH_4^+ = 0.5$, respectively.

burning is responsible for the correlation seen between NH_4^+ and $HCOO^-$ in snow and ice core records. Thus, $HCOO^-$ and its equivalent in NH_4^+ in Belukha glacier are likely to have originated from vegetation and/or biomass burning.

Line 2 in Fig. 2 represents

$$[NH_4^+] : [HCOO^-]+[SO_4^{2-}]+[NO_3^-]=1:1.$$

Each datum satisfies $NH_4^+ < HCOO^- + SO_4^{2-} + NO_3^-$. The correlation between NH_4^+ and $HCOO^- + SO_4^{2-} + NO_3^-$ is high ($r^2=0.94$). These results suggest that almost all NH_4^+ was transported together with $HCOO^-$, SO_4^{2-}, and NO_3^-. Some NH_4^+ that did not come from vegetation and/or biomass burning probably came from compounds including NH_4HSO_4, $(NH_4)_2SO_4$, and NH_4NO_3, and thus likely originated from livestock, commercial fertilizers, and natural fertilizers (e.g., Kreutz *et al*., 2001).

$SO_4^{2-}+NO_3^-$ transported together with Ca^{2+} is considered to be excess $SO_4^{2-}+NO_3^-$ compared to that of NH_4HSO_4, $(NH_4)_2SO_4$, and NH_4NO_3, that is expressed as $SO_4^{2-}+NO_3^- - (NH_4^+ - HCOO^-)$ in equivalent units. The correlation between Ca^{2+} and $SO_4^{2-}+NO_3^- - (NH_4^+ - HCOO^-)$ is high ($r^2=0.83$). Ca^{2+} and it's equivalent unit $SO_4^{2-}+NO_3^-$ probably originated from terrestrial dust such as soil (*e.g.*, Sun *et al*.,

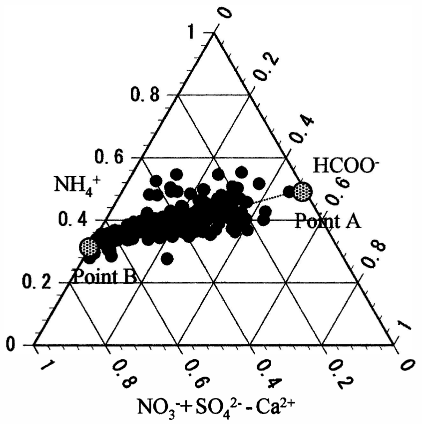

Fig. 3. Diagram of NH_4^+, $HCOO^-$ and $NO_3^- + SO_4^{2-} - Ca^{2+}$. Points A and B indicate NH_4^+ : $HCOO^- = 1 : 1$ and NH_4^+ : $NO_3^- + SO_4^{2-} - Ca^{2+} = 0.3 : 0.7$, respectively.

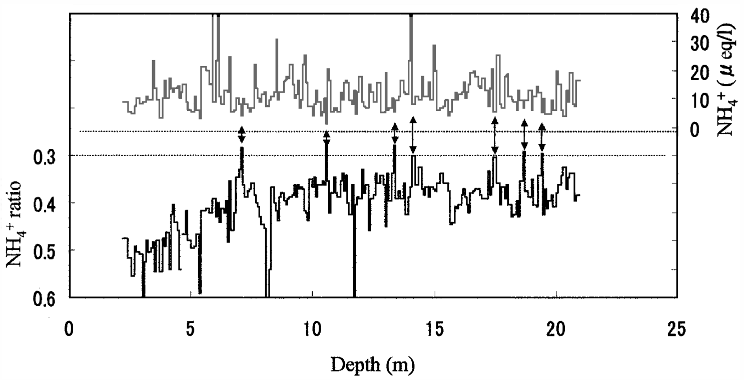

Fig. 4. Depth profiles of the NH_4^+ ratio [specifically, $NH_4^+/(NH_4^+ + HCOO^- + SO_4^{2-} + NO_3^- - Ca^{2+})$] and the NH_4^+ concentration. Arrows indicate regions with an NH_4^+ ratio of about 0.3 or less.

1998).

The above considerations indicate that NH_4^+ was transported in two ways: 1) together with $HCOO^-$ and 2) together with $SO_4^{2-} + NO_3^-$, that is expressed as $SO_4^{2-} + NO_3^- - Ca^{2+}$ in equivalent. As a reference, the correlation between NH_4^+ and $SO_4^{2-} + NO_3^- - Ca^{2+}$ is also high ($r^2 = 0.87$). The diagram of NH_4^+, $HCOO^-$ and $SO_4^{2-} + NO_3^- - Ca^{2+}$ is shown in Fig. 3. The data in Fig. 3 have a linear distribution. The end points of the line are 0.5 : 0.5 : 0 (point A) and 0.3 : 0 : 0.7 (point B) for NH_4^+ : $HCOO^-$: $SO_4^{2-} + NO_3^- - Ca^{2+}$. That point A is about 0.5 for the NH_4^+ ratio indicates that all NH_4^+ at this point came from vegetation and/or biomass burning. Conversely, that point B is about 0.3 for the NH_4^+ ratio indicates that no NH_4^+ at this point came from vegetation and/or biomass burning; instead the NH_4^+ came from livestock, commercial fertilizers, and natural fertilizers. This linear correlation indicates that the NH_4^+ ratio (0.5 to 0.3) determines the relative amount of NH_4^+ that came from vegetation and biomass burning with the rest coming from livestock, commercial fertilizers, and natural fertilizers. Figure 4 has the depth profiles of the NH_4^+ ratio and the NH_4^+ concentration in the 22-m ice core. NH_4^+ ratios at about 0.3 and below coincide with local minima in the NH_4^+ concentration (arrows in Fig. 4). This suggests that the NH_4^+ concentration is low when there is no contribution from vegetation and/or biomass burning.

5. Concluding remarks

We have shown that the primary soluble ions in the Belukha glacier are SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, and $HCOO^-$; together, these 5 ion concentrations equaled 88.2% of all 11 measured ion concentrations. By analyzing the correlations among the various ions, we argued the following. 1) Ca^{2+} and its equivalent $SO_4^{2-}+NO_3^-$ likely originated from terrestrial dust such as soil. 2) $HCOO^-$ and its equivalent NH_4^+ likely originated from vegetation and/or biomass burning. 3) The remaining $SO_4^{2-}+NO_3^-$ and NH_4^+ likely originated from livestock, commercial fertilizers, and natural fertilizers. 4) Within the 22-m ice core, the NH_4^+ concentration was low when there was no contribution from vegetation and/or biomass burning.

The chemical characteristics of the Belukha glacier obtained in this study should aid in the upcoming study of the Belukha glacier paleoclimate, which will be based on the deep ice core that was collected in 2003.

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