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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  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{HCOO}^-$ . Moreover, we argue the following. 1)  $\text{Ca}^{2+}$  and its equivalent  $\text{SO}_4^{2-} + \text{NO}_3^-$  likely originated from terrestrial dust such as soil. 2)  $\text{HCOO}^-$  and its equivalent  $\text{NH}_4^+$  likely originated from vegetation and/or biomass burning. 3) The remaining  $\text{SO}_4^{2-} + \text{NO}_3^-$  and  $\text{NH}_4^+$  likely originated from livestock, commercial fertilizers, and natural fertilizers. 4) The  $\text{NH}_4^+$  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  $\text{SO}_4^{2-}/\text{Cl}^-$  ratio (Koerner, 1997) and the  $\text{Mg}^{2+}/\text{Na}^+$  ratio (Iizuka *et al.*, 2002) can be used to estimate past climate. Moreover, atmospheric  $\text{SO}_4^{2-}$  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  $-20^{\circ}\text{C}$ . 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  $0.45\ \mu\text{m}$  and then analyzed for pH and the amounts of 11 soluble ions ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCOO}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ , and  $\text{PO}_4^{2-}$ ). The pH was measured using flow-cell-type sensors by the method described in Watanabe *et al.* (1997); uncertainties were estimated to be within  $\pm 0.1$ . 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  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ , which have average concentrations of 15.2 and  $13.2\ \mu\text{eq/l}$ , respectively. The secondary components are  $\text{HCOO}^-$ ,  $\text{NO}_3^-$ , and  $\text{Ca}^{2+}$ , with average concentrations of 6.8, 5.6, and  $7.2\ \mu\text{eq/l}$ , 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  $5.8\ \mu\text{eq/l}$  higher than those of  $\text{H}^+$  plus the 5 cations. Figure 1 shows the depth profiles of  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{HCOO}^-$ ,  $\text{NO}_3^-$ , and  $\text{Ca}^{2+}$  concentrations, and also the pH.

Table 1. Measured pH and concentrations of 11 soluble ion species ( $\mu\text{eq/l}$ ) from the Belukha Glacier ice core.

	$\text{HCOO}^-$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{C}_2\text{O}_4^{2-}$	$\text{PO}_4^{2-}$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	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

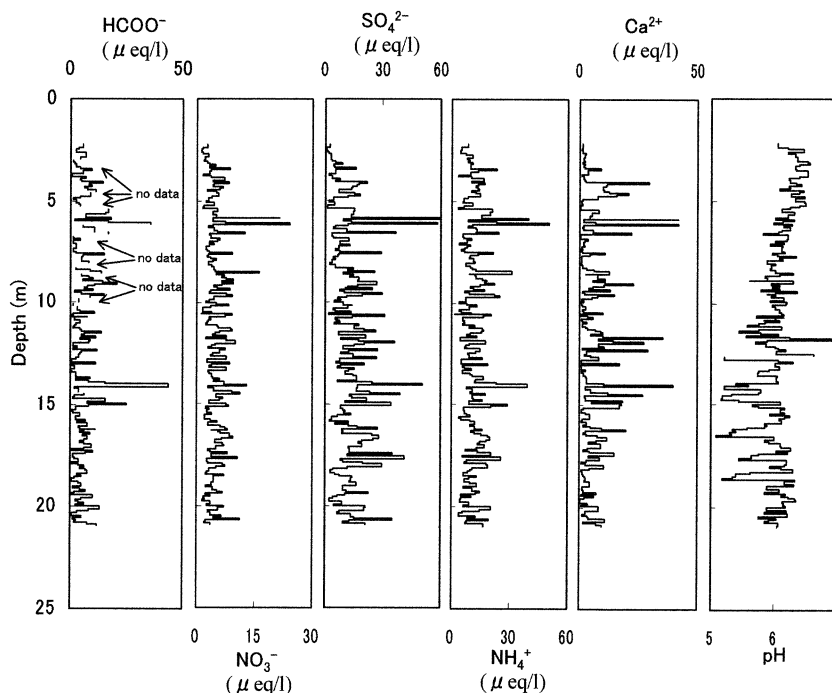


Fig. 1. Depth profiles of pH and five major soluble ions. The ordinate is the depth measured downward from the surface of the glacier.

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

Now, we focus on the origins of the five major components ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{HCOO}^-$ ). Table 2 lists the correlation coefficients between the 11 soluble ions. There is good correlation between cations and anions in five major components: 1)  $\text{NH}_4^+$  and  $\text{HCOO}^-$  ( $r^2=0.78$ ), 2)  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ( $r^2=0.89$ ), 3)  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ( $r^2=0.84$ ), 4)  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  ( $r^2=0.75$ ), and 5)  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ( $r^2=0.82$ ). These correlations suggest that i)  $\text{NH}_4^+$  on the Belukha glacier was likely transported together with  $\text{HCOO}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ , and ii)  $\text{Ca}^{2+}$  on the Belukha glacier was likely transported together with  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , but not with  $\text{HCOO}^-$ .

Figure 2 shows the ionic diagram of  $\text{SO}_4^{2-} + \text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{HCOO}^-$ . Line 1 in Fig. 2 represents the relation

$$[\text{NH}_4^+] : [\text{HCOO}^-] = 1 : 1 \quad ([ ] \text{ means } \mu\text{eq/l units}).$$

Each datum satisfies  $\text{NH}_4^+ > \text{HCOO}^-$ . This excess of  $\text{NH}_4^+$  and the good correlation between  $\text{NH}_4^+$  and  $\text{HCOO}^-$  suggest that almost all  $\text{HCOO}^-$  on the Belukha glacier was transported together with  $\text{NH}_4^+$ . Kreutz *et al.* (2001) suggested that  $\text{HCOO}^-$  was transported together with  $\text{NH}_4^+$  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 ( $\mu\text{eq/l}$ ) in Belukha Glacier.

	HCOO <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>
HCOO <sup>-</sup>	1.00										
Cl <sup>-</sup>	0.48	1.00									
NO <sub>3</sub> <sup>-</sup>	0.57	0.43	1.00								
SO <sub>4</sub> <sup>2-</sup>	0.56	0.39	0.86	1.00							
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	0.55	0.39	0.59	0.67	1.00						
PO <sub>4</sub> <sup>3-</sup>	0.57	0.44	0.65	0.64	0.77	1.00					
Na <sup>+</sup>	0.58	0.88	0.39	0.41	0.49	0.53	1.00				
NH <sub>4</sub> <sup>+</sup>	0.78	0.44	0.89	0.84	0.59	0.63	0.47	1.00			
K <sup>+</sup>	0.27	0.30	0.26	0.24	0.54	0.70	0.45	0.28	1.00		
Mg <sup>2+</sup>	0.59	0.57	0.69	0.79	0.75	0.68	0.68	0.76	0.43	1.00	
Ca <sup>2+</sup>	0.53	0.54	0.75	0.82	0.76	0.69	0.61	0.72	0.35	0.90	1.00

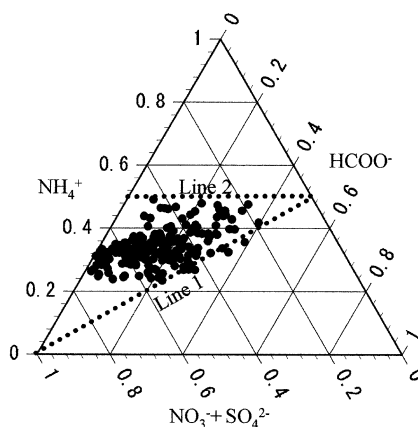


Fig. 2. Diagram of  $\text{NO}_3^- + \text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{HCOO}^-$ . Lines 1 and 2 show  $\text{NH}_4^+ : \text{HCOO}^- = 1 : 1$  and  $\text{NH}_4^+ = 0.5$ , respectively.

burning is responsible for the correlation seen between  $\text{NH}_4^+$  and  $\text{HCOO}^-$  in snow and ice core records. Thus,  $\text{HCOO}^-$  and its equivalent in  $\text{NH}_4^+$  in Belukha glacier are likely to have originated from vegetation and/or biomass burning.

Line 2 in Fig. 2 represents

$$[\text{NH}_4^+] : [\text{HCOO}^-] + [\text{SO}_4^{2-}] + [\text{NO}_3^-] = 1 : 1.$$

Each datum satisfies  $\text{NH}_4^+ < \text{HCOO}^- + \text{SO}_4^{2-} + \text{NO}_3^-$ . The correlation between  $\text{NH}_4^+$  and  $\text{HCOO}^- + \text{SO}_4^{2-} + \text{NO}_3^-$  is high ( $r^2 = 0.94$ ). These results suggest that almost all  $\text{NH}_4^+$  was transported together with  $\text{HCOO}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ . Some  $\text{NH}_4^+$  that did not come from vegetation and/or biomass burning probably came from compounds including  $\text{NH}_4\text{HSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{NH}_4\text{NO}_3$ , and thus likely originated from livestock, commercial fertilizers, and natural fertilizers (e.g., Kreutz *et al.*, 2001).

$\text{SO}_4^{2-} + \text{NO}_3^-$  transported together with  $\text{Ca}^{2+}$  is considered to be excess  $\text{SO}_4^{2-} + \text{NO}_3^-$  compared to that of  $\text{NH}_4\text{HSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{NH}_4\text{NO}_3$ , that is expressed as  $\text{SO}_4^{2-} + \text{NO}_3^- - (\text{NH}_4^+ - \text{HCOO}^-)$  in equivalent units. The correlation between  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-} + \text{NO}_3^- - (\text{NH}_4^+ - \text{HCOO}^-)$  is high ( $r^2 = 0.83$ ).  $\text{Ca}^{2+}$  and its equivalent unit  $\text{SO}_4^{2-} + \text{NO}_3^-$  probably originated from terrestrial dust such as soil (e.g., Sun *et al.*,

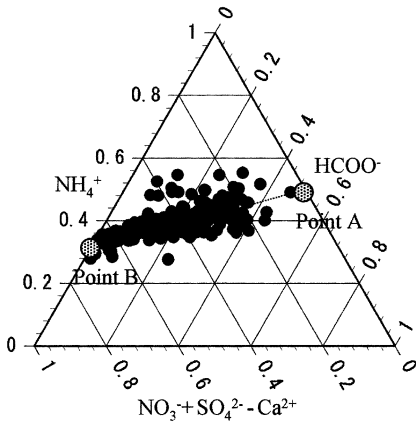


Fig. 3. Diagram of  $\text{NH}_4^+$ ,  $\text{HCOO}^-$  and  $\text{NO}_3^- + \text{SO}_4^{2-} - \text{Ca}^{2+}$ . Points A and B indicate  $\text{NH}_4^+ : \text{HCOO}^- = 1 : 1$  and  $\text{NH}_4^+ : \text{NO}_3^- + \text{SO}_4^{2-} - \text{Ca}^{2+} = 0.3 : 0.7$ , respectively.

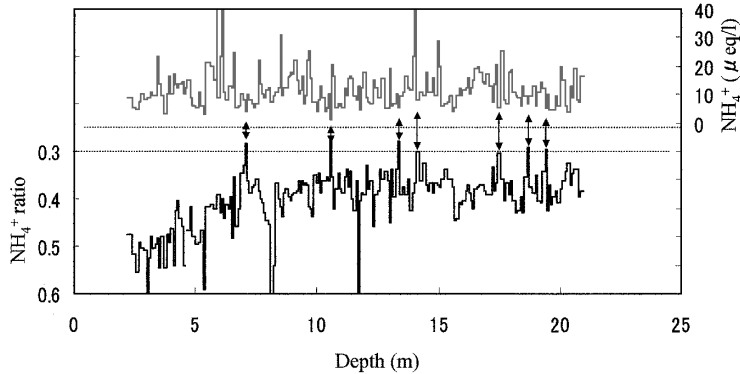


Fig. 4. Depth profiles of the  $\text{NH}_4^+$  ratio [specifically,  $\text{NH}_4^+ / (\text{NH}_4^+ + \text{HCOO}^- + \text{SO}_4^{2-} + \text{NO}_3^- - \text{Ca}^{2+})$ ] and the  $\text{NH}_4^+$  concentration. Arrows indicate regions with an  $\text{NH}_4^+$  ratio of about 0.3 or less.

1998).

The above considerations indicate that  $\text{NH}_4^+$  was transported in two ways: 1) together with  $\text{HCOO}^-$  and 2) together with  $\text{SO}_4^{2-} + \text{NO}_3^-$ , that is expressed as  $\text{SO}_4^{2-} + \text{NO}_3^- - \text{Ca}^{2+}$  in equivalent. As a reference, the correlation between  $\text{NH}_4^+$  and  $\text{SO}_4^{2-} + \text{NO}_3^- - \text{Ca}^{2+}$  is also high ( $r^2 = 0.87$ ). The diagram of  $\text{NH}_4^+$ ,  $\text{HCOO}^-$  and  $\text{SO}_4^{2-} + \text{NO}_3^- - \text{Ca}^{2+}$  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  $\text{NH}_4^+ : \text{HCOO}^- : \text{SO}_4^{2-} + \text{NO}_3^- - \text{Ca}^{2+}$ . That point A is about 0.5 for the  $\text{NH}_4^+$  ratio indicates that all  $\text{NH}_4^+$  at this point came from vegetation and/or biomass burning. Conversely, that point B is about 0.3 for the  $\text{NH}_4^+$  ratio indicates that no  $\text{NH}_4^+$  at this point came from vegetation and/or biomass burning; instead the  $\text{NH}_4^+$  came from livestock, commercial fertilizers, and natural fertilizers. This linear correlation indicates that the  $\text{NH}_4^+$  ratio (0.5 to 0.3) determines the relative amount of  $\text{NH}_4^+$  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  $\text{NH}_4^+$  ratio and the  $\text{NH}_4^+$  concentration in the 22-m ice core.  $\text{NH}_4^+$  ratios at about 0.3 and below coincide with local minima in the  $\text{NH}_4^+$  concentration (arrows in Fig. 4). This suggests that the  $\text{NH}_4^+$  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  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{HCOO}^-$ ; 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)  $\text{Ca}^{2+}$  and its equivalent  $\text{SO}_4^{2-} + \text{NO}_3^-$  likely originated from terrestrial dust such as soil. 2)  $\text{HCOO}^-$  and its equivalent  $\text{NH}_4^+$  likely originated from vegetation and/or biomass burning. 3) The remaining  $\text{SO}_4^{2-} + \text{NO}_3^-$  and  $\text{NH}_4^+$  likely originated from livestock, commercial fertilizers, and natural fertilizers. 4) Within the 22-m ice core, the  $\text{NH}_4^+$  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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