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Anthropogenic trace metals in an ice core at Vestfonna, Svalbard, Norway

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Abstract A 211 m depth ice core observation was carried out at the top of the Vestfonna Ice Cap in Nordaustlandet, Svalbard, Norway in 1995. Chronology of the ice core was determined by tritium analysis and comparison to the volcanic eruption of Laki; the resulting accumulation rate is 0.34-0.35 m water eq. $\cdot yr^{-1}$ for the last 400 year. Concentrations of Al, V, Cr, Fe, Cu, Zn, As, Ag, Cd, Pb and U in an ice core have been determined by an inductively coupled plasma mass spectrometry (ICP-MS) with a desolvated micro-concentric nebulizer, which is a recent development and can achieve high sensitivity with low uptake rate of 60 mL/min. The concentrations of Pb, Cu, and Zn had increased from 1940s declined from 1970s to present. However, the profiles of Pb, Cu, and Zn were different and they seem to be influenced by the difference of sources. Since the ratios between Cu, Pb, and Zn in Svalbard is similar to that in French Alps, the source area of these elements is estimated to be Europe.

Key words Ice core, heavy metal, Svalbard, ICP-MS.

1 Introduction

An ice core obtained from polar glaciers or ice sheets is one of the most important archives to reconstruct paleoclimatic and paleoatmospheric condition. Information on paleo-environment can be extracted from ice cores as chemical and/or physical signals. Among the chemical signals, heavy metals are noted as signals of terrestrial environmental change and anthropogenic pollution (e.g. Murozumi *et al*. 1969; Ng and Patterson 1981; Hong *et al*. 1994). Since concentrations of most of the metals in polar snow in central Greenland are at or below the ppt level (Boutron *et al*. 1994; Candelone *et al*. 1996), it is necessary to develop analytical techniques to determine such low concentrations with limited volume of ice core sample for high time resolution analysis, and to employ effective decontamination methods since the ice core exteriors is contaminated during drilling and/or analytical procedure.

Svalbard archipelago is located between lat 77°N and lat 81°N, the same as northern Greenland; nevertheless it has a relative mild climate and an open ocean to its west because of the Gulf Stream. The glaciers in Svalbard archipelago are sub-polar type in

glacier classification and have snow surface melting during the summer even in the summit area. Because this meltwater might disturb both the structures of accumulated snow and chemical profiles in the glaciers, it has been believed that it is difficult to reconstruct the paleoclimate from ice cores in such glaciers. However, in order to evaluate the influences of atmospheric pollution after the industrial revolution and the more recent global warming in the Arctic region, it is necessary to extract the information from not only the Greenland ice sheet, but also the smaller ice caps in the Arctic. Since 1987, the Japanese Arctic Glacier Expedition has carried out several ice core investigations in Svalbard, Norway and in Greenland in order to evaluate the climatic and environmental conditions for the past 100 years in the Arctic (e. g., Watanabe 1996; Fujii *et al*. 1990; Kameda *et al*. 1994). Moreover, recent studies suggest that such ice cores (called "wet" ice cores) could still provide us with important climatic and environmental information (e. g., Thompson *et al*. 1984; Nakawo *et al*. 1990; Goto-Azuma 1998).

In this study, we measured the heavy metals in a 211-m ice core, which was obtained from Vestfonna Ice Cap, Nordaustlandet, Svalbard in 1995, and evaluated the temporal variations of anthropogenic substances in Svalbard.

2 Experimental

2.1 Sample

The Japanese Arctic Glaciological Expedition (JAGE) drilled a 211 m-deep ice core (970 mm diameter) at the summit of the Vestfonna ice cap (79°58′ N, 21°02′ E) in Nordaustlandet, Svalbard, Norway (Figure 1) with an electro-mechanical drill in May and June, 1995. The ice cores were packed in polyethylene bags at the drilling site, were transported to a − 20°C cold room, and were kept frozen until ice core analyses.

Before trace metal analyses, the ice cores have been used for the measurements of electric conductivity of ice, fractionation of oxygen isotope, and concentrations of major chemical species. The age of ice core was determined by the mean annual accumulation rate, which was estimated to be 0.35 m water eq./yr given by the tritium peak in 1963 and the volcanic peak of Laki in 1783 (Matoba 1998; Matoba et al. 2002).

2.2 Instruments and reagents

An ICP/MS (HP4500, Hewlett Packard) was used for the measurement of heavy metals. The nebulizing system adopted for measurement was a desolvated micro-concentric nebulizer (MCN-6000, CETAC). The optimum operating conditions of the ICP/MS and the MCN-6000 were determined by Matoba *et al*. (1998) and are given in Table 1.

Nitric acid was of ultra-pure grade (Kanto Chemicals). Standard solutions were prepared by diluting a multi-element standard solution (XSTC-13, Spex) with 1% nitric acid. All Teflon containers were cleaned with heated concentrated nitric acid for several hours, followed by washing with hot ultra pure water for several hours. Low density polyethylene (LDPE) containers (Nalgene) for sample preservation were cleaned with 0.2M hot nitric acid and hot pure water, after washing with 5% Extran MA01 (Merck) and 4M nitric acid.

Table 1. Operating conditions for the ICP-MS instrument

RF power		1240 W	
Reflected power		< 10 W	
Coolant gas flow rate		16 L•min^{-1}	
Auxiliary argon gas flow rate		1.1 L•min^{-1}	
Carrier gas flow rate		1.0 L•min^{-1}	
Channel width		3 channel	
Dwell time		500 μsec/ channel	
Number of sweep		100 times	
Replicates		5 times	
Total acquisition time		132 sec/ sample	
Measurement isotopes(m/ z)			
Aluminum	27	Arsenic	75
Vanadium	51	Silver	108
Iron	57, 58	Cadmium	102
Copper	63, 65	Lead	208
Zinc	66, 68	Uranium	238

Table 2. Operating conditions for the MCN-6000

Temperature of spray chamber	70 °C
Temperature of membrane desolvator	160 °C
Carrier gas flow rate	1 L•min^{-1}
Sweep gas flow rate	2.08 L•min^{-1}
Nitrogen gas flow rate	12 mL•min^{-1}
Sample uptake flow rate	0.06 mL•min^{-1}

Table 3. Heavy metal concentrations data published by several investigators for snow deposited around 1975 in Svalbard, Greenland, and French Alps

Sampling site and sample date	Reference	Measured concentrations/ pg•g^{-1}		
		Pb	Cu	Zn
Vestfonna, Svalbard (1980– 1950)	This work	30– 1200	< 6– 370	27– 3400
Dye 3, south Greenland(1978– 1979)	Davidson et al. (1981)	42– 150	28– 65	140– < 580
Central Greenland (1967– 1989)	Boutron et al. (1991)	14– 84	2– 14	70.5
Summit of Mont Blanc(1973)	Batifol and Boutron(1984)	1800– 3600	140– 210	750– 2400

2.3 Procedure

The ice cores were cut horizontally into approximately 0.15-m long sections for trace metal analyses. The weight of each ice core samples was approximately 300 g. Approximately 5 mm of ice core surface was shaved off with a ceramic knife in a clean booth at cold room in order to remove rough contamination and small cracks formed during the ice core drilling. The ice sample was warmed gradually to 0 °C from – 20 °C to prevent the formation of cracks which allow contamination to penetrate into the ice sample during the latter processes. The ice samples washed by ultra pure water (18.3MΩ). Decontamination processes were carried out by stepwise melting processes as described follows; the ice sampls

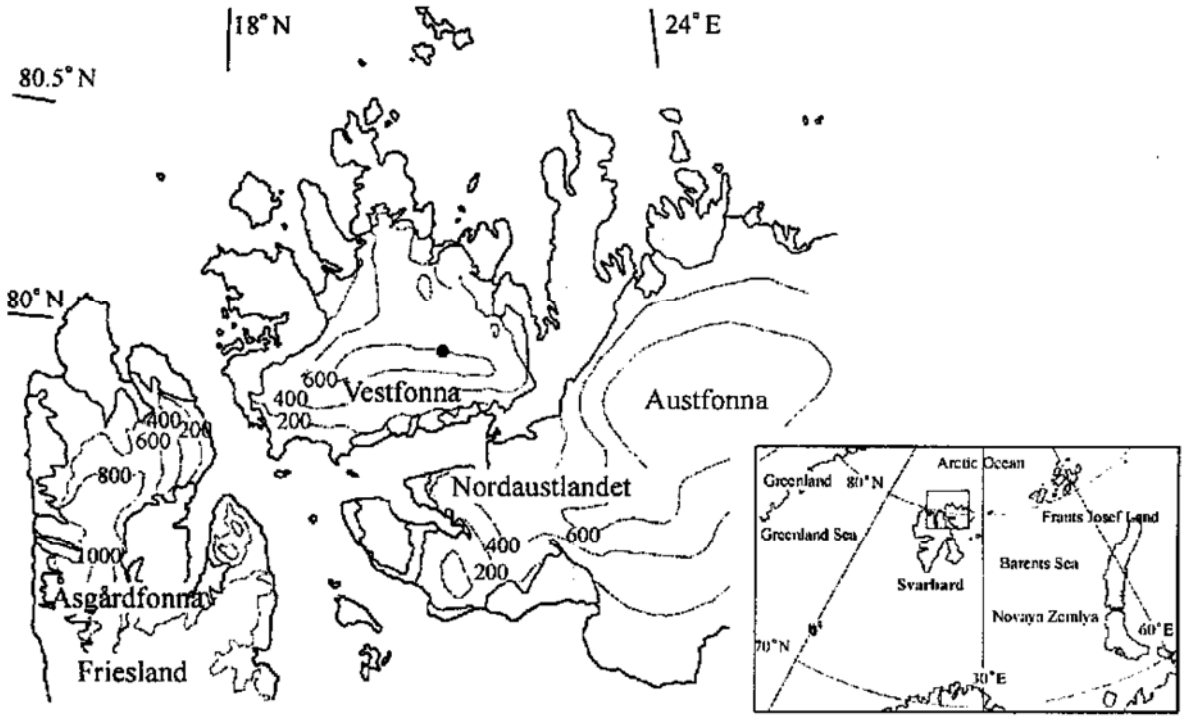

Fig. 1. Location of the ice more drilling site at Vestfonna Ice Cap in Nordaustlandet, Svalbard.

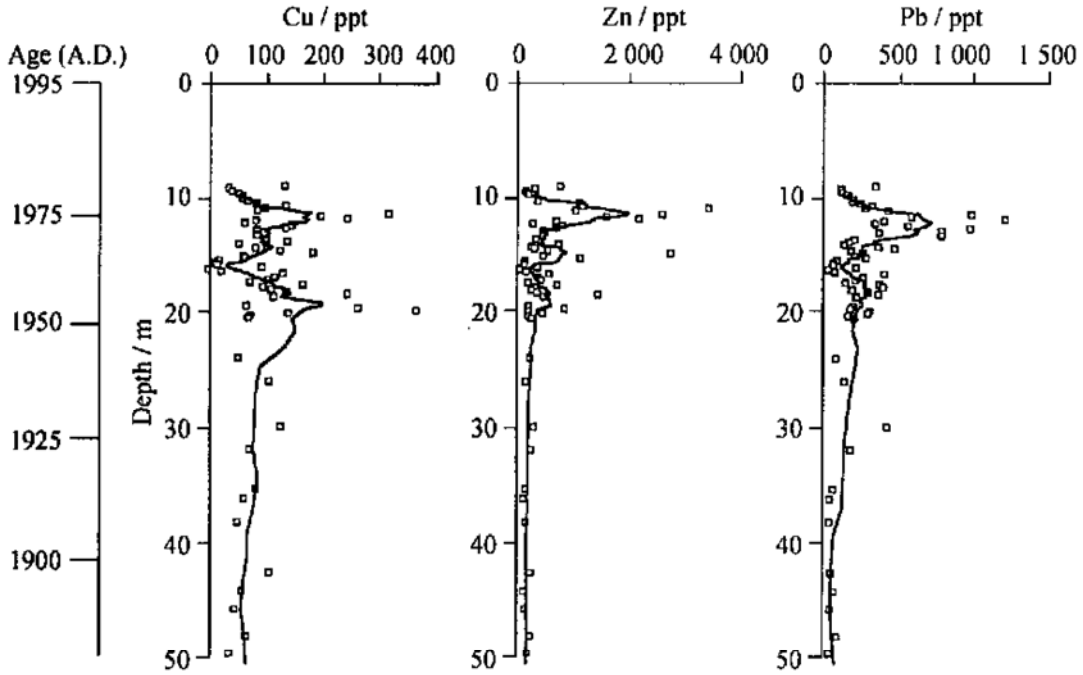

Fig. 2. Depth profiles of Cu, Zn, and Pb with estimated time scale.

were melted by 50g in Teflon containers. The liquid portion was decanted to a LDPE bottle, and was added nitric acid to 1%. The solid portion was transported to next Teflon container and was melted by 50g again. The residue of contamination on the ice surface was check by analyzing the liquid portion.

We measured 53 samples from 9.25 to 20.98 m depth continuously, 13 samples from 20.98 to 50 m depth at 2-3 m intervals, and 13 samples from 50 to 211 m depth at 10-15 m intervals.

3 Results and discussion

The concentrations of these elements in snow/ice around 1975 are shown in Table 1 with that in central and south Greenland and Mont Blanc, French Alps (Boutron *et al*. 1991; Davidson *et al*. 1981; Batifol and Boutron 1984). The concentrations of Cu, Zn, and Pb in Svalbard were close to those in French Alps, and ten times higher than those in Greenland. Such high concentration in Svalbard and French Alps is seems reflected close distance to source area.

Figure 2 shows profiles of Cu, Zn, and Pb concentrations with the time scale from 9.25 m to 50 m depth. The profiles of three elements show a significant increasing until beginning of 1970s, followed by a significant decreasing trend. This trend was also shown in Greenland snow/ice (Candelone *et al*. 1995). These variations do not result from changes in emissions from natural sources to the atmosphere, such as terrestrial dust, sea salt spray, and volcanoes (Niagu 1989). The contribution due to the crustal source was calculated using Al as crustal reference element and using the mean metal to Al ratios in rocks given by Taylor (1964). The average crustal contribution was always negligible for Zn and Pb (< 1.0%), but for Zn it reached values as high as 5% in several samples. The crustal contribution for Cu was 3.6% on average with a maximum around 10%. The contribution of sea salt was calculated using Na as a reference element and using the mean metal to Na ratios given by Bowen (1979). The contribution for three elements was negligible (< 0.01%). Consequently, these profiles of three elements reflected the changes of the emission from anthropogenic activities. The decreasing trend of Cu and Zn results from decreasing of emission from non ferrous smelting which was affected by anti-pollution measure taken in various countries (e.g. Pacyna 1989; 1991). The decreasing trend of Pb results mainly from the decreasing use of leaded gasoline (e.g. Loranger and Zared 1994).

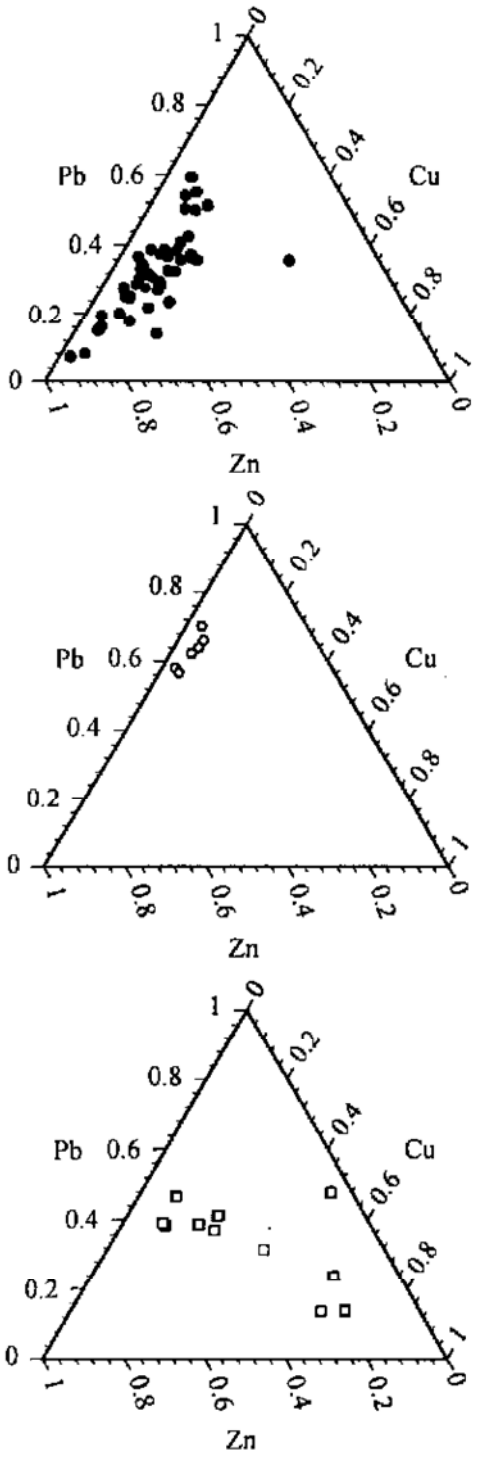

Fig. 3. The ratio of Cu, Zn, and Pb in Svalbard (a), French Alps (b) (Batifol and Boutron 1984), and Geenland Dye 3 (c) (Boutron *et al*. 1993).

The details of profiles of three elements are different from that in Greenland. Especially, the profile of Cu showed pronounced two peaks from 1950s to 1970s in Svalbard while that in Greenland snow showed two peaks in 1800s and 1970s (Candelon *et al*. 1995). Figure 3 shows the ratio of Cu, Zn, and Pb in Svalbard, French Alps (Batifol

and Boutron 1984), and Greenland (Boutron *et al*. 1993). The ratio in Svalbard is similar to that in French Alps, and not similar to that in Greenland. It is reported that anthropogenic substances in French Alps are originated from Europe, and ones in Greenland are originated from North America and Europe. The ratio in Svalbard reflects the emission from rather Europe than North America. However, the ration in Svalbard is not completely correspond with that in French Alps. The difference might reveal that Svalbard and French Alps are affected by small regions in Europe each. If the future study identifies the source regions which affects Svalbard, the history of the impact on environment by human activities in the small region will be revealed.

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