

NEUTRON ACTIVATION ANALYSIS OF SNOW AND ICE IN ANTARCTICA

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In order to minimize the possible contamination during storing and pre-treatment of such pure samples as ice and snow collected in Antarctica, trace elements in experimental tools such as bottles, beakers, tubing and filters were determined by neutron activation analysis. By using well certified tools, ice and snow samples from Antarctica and high mountains in China and in Japan were analyzed. Relative concentrations of volatile elements such as Zn, Cd, As, Sb or Ag to Al or Fe which are major components in the earth crust were found to be 10 to 1000 times higher than in the ordinary soil for the samples from Antarctica and Mt. Naimonanyi in China.

Introduction

Antarctica has been one of the most uncontaminated areas with respect to the materials derived from anthropogenic origins as well as those from earth crusts of other continents. The reason is attributed to the geographically and meteorologically unique location of the antarctic continent. From the meteorological point of view, it is said that the transport of materials from the northern hemisphere to the southern or *vice versa* is scarce. Moreover, the major parts of continents which are the main sources of air borne materials from both crustal and anthropogenic origins locate in the northern hemisphere. Therefore, the snow and ice samples in Antarctica are expected to offer a variety of information on the materials from cosmic and marine origins and on the geological, climatical or even anthropogenic events influences of which have spread over in a global scale.

Generally speaking, snow and ice samples taken in the inland part of Antarctica are so clean that any instrumental method of analysis is not sensitive enough to be able to determine trace elements in those samples as kept in a frozen state, although it is desirable not to melt down samples in order to avoid possible losses or contaminations during sample handling.

On dealing with such pure samples, one has to examine and evaluate the extent of contamination arising from impurities in experimental tools such as beakers, filters and even the atmosphere of the laboratory.

The present paper describes the evaluation of impurities in experimental tools commonly used for trace analysis of water samples and of preliminary results obtained for ice samples brought from Antarctica and snow samples from a high mountain in China and from a mountainous region in Japan.

Materials and method

Materials

- 1) Polymer materials of experimental apparatus: Samples of polyethylene, polypropylene, Teflon (TFE and PFA) and acrylate resin were obtained by cutting commercially available beakers, tubings, bottles, etc. These pieces of samples were washed in three different ways so as to find an effective method of cleaning.
- 2) Filters: Nuclepore Filter (pore size: $0.45\mu\text{m}$), Millipore Filter HAWP (pore size: $0.45\mu\text{m}$) and Nalgene Filter cellulose acetate (pore size: $0.22\mu\text{m}$) were examined. The diameter of those filters was 47mm. In one case, those filters were washed by the following manner. Namely, after being soaked in a dilute HNO_3 solution (0.1M) for one night, more than ten sheets of filters were stacked on a filtrating apparatus and washed successively with a newly prepared dilute HNO_3 solution and with pure water by filtration. The top sheet was discarded every time.
- 3) Pure water: Deionized water was distilled in a quartz made distilling apparatus and the obtained distilled water was stored in a specially prepared polyethylene bottle. The distilled water thus obtained was further purified by using a Milli-Q pure water generator before use.
- 4) Mineral acids: HCl and HNO_3 of reagent grade were purified by distilling doubly in a apparatus made of teflon. These were stored in teflon bottles.
- 5) Ice core samples from Antarctica: An ice core stored in the freezing room of the National Institute of Polar Research (NIPR) was used. The core was drilled by the Japanese Research Expedition Group of the NIPR in 1982 at the site JARE-21, z(102.5) locating in Mizuho plateau of the altitude of 2212m. The core of the diameter of about 10cm was cut into appropriate lengths and cleaned by dissolving the surface to the depth of about 1cm by pouring pure water. Pieces of the ice core thus cleaned were melt down slowly in teflon beakers placed on hot plates the surface of which were coated with teflon. In one case, the water sample thus obtained was filtered with a Nuclepore Filter. The filtrate was collected in a teflon beaker and evaporated gently until a spherically shaped droplet of water (1ml) remained on the bottom of the beaker. In another case, water samples were evaporated in a similar way without filtration. The droplets of water samples remaining in teflon beakers were transferred to clean polyethylene dish (diameter: 20mm, height: 5mm) and evaporated off. All the procedures described above were performed in a clean bench in NIPR.

- 6) Snow samples from Hakuba-Norikura Mountain in Japan: The central part of Japan is a mountainous place. During the winter, it is very common in that region that snow piles up to the depth of several meters. On 24th and 25th, March in 1983, snow samples were collected at several layers of different depths. The altitude of the sampling site in Hakuba-Norikura Mountain was about 1000 meters. These snow samples were stored in 5 liter polyethylene bottles and brought back to the laboratory. The snow samples were already melted down. These samples were treated in a similar manner to the ice core samples described above.
- 7) Snow samples from Naimonanyi Mountain in China (7694m): Snow samples were collected at the base camp (4900m) by the preliminary expedition team of the Japan-China Joint Friendship Expedition in 1984. These samples were treated as described above.

Irradiation and measurement

Polymer samples of 1-2g were doubly wrapped in clean polyethylene sheets and packed together with a set of flux monitors in a pneumatic rabbit made of polyethylene. Monitors used here consist of 10.0 μ g each of Co and Cr and 2.00 μ g Sb spotted on a sheet of Millipore Filter for one hour irradiation. For short irradiation, 10.0 μ g Mn and 200 μ g Na spotted in a similar manner to the above were used. These monitors were sealed in clean polyethylene bags.

Neutron irradiations were performed in a pneumatic facility of Kyoto University Reactor (KUR)(neutron fluxes: $\psi_{th} = 2.2 \times 10^{13} \text{n/cm}^2/\text{s}$, $\psi_{epi} = 8.4 \times 10^{11} \text{n/cm}^2/\text{s}$). γ -ray spectrometry was performed on samples which were irradiated for 30-60 s and cooled for 2-5 min depending on the characters of samples. Al, V, Cl, Ca, Mg, Mn and Na could be determined by this measurement. After cooling short lived nuclides, the same samples were irradiated again for 1 hour and cooled for 7-10 and 21-30 days. Measurements of long lived nuclides were performed for 5-10k and 40-80k seconds, respectively. All the measurements of γ -ray were performed with an intrinsic Ge detector (rel. eff. for 1332keV γ -ray of ^{60}Co to 3 \times 3inch NaI: 20%) coupled to a 4k channel MCA (NAIG). The determination of all the elements detected were carried out by a multi-comparator method in which neutron spectrum was evaluated for every capsule.¹⁾²⁾

Results and discussion

Impurities in materials of experimental apparatus and the effect of washing

Filters and polyethylene dish

In Table 1, are listed impurities in filters and the polyethylene dish which was used for the drying up the last droplet of the water sample obtained by melting the ice core. In the table, rows marked with (washed) denote the filters washed according to the method described in the experimental section. Although the amounts of impurities determined are expressed here for one sheet of filter, these are averaged values obtained by irradiating and measuring several sheets together.

Table 1
Contents of trace impurities in filters and
materials commonly used for preparing water samples

Element	Na	K	Al	Cr	Mn	Zn	Au	Cl	Br	Sc
Filter A	20	15	3	50	0.12	4	0.002	90	20	nd
(washed)	12	9	20	1.0	0.12	6	nd	160	102	0.006
Filter B	600	nd	28	14	2.4	nd	nd	2200	10	nd
(washed)	400	150	200	3	1.0	nd	nd	4300	10	0.07
Filter C	2700	nd	nd	nd	17	nd	nd	1300	7.0	nd
PE-dish	27	nd	27	1.0	0.5	6.5	0.0002	380	2.0	nd

Filter A: Nuclepore Filter, Filter B: Millipore Filter.
 Filter C: Nalgene Filter.
 PE-dish: Polyethylene dish for irradiation of dried up residue.
 nd: not detected.
 Contents are expressed in 10^{-9} g/one sheet of filter or one dishb.

Among filters, A was found to be relatively clean with respect to the number of trace elements detected and also those quantities, except for Cr. However, the amount of Cr in the filter could be reduced to the level which is allowable to the practical use for naturally occurring samples. Filter B and C contain considerable amounts of Cl which can cause a erroneous result on dealing with the pure water samples. Mn and Al contents in these two filters are relatively high. However, these can be used for the practical use as long as more than one liter of ice or snow samples is treated.

The polyethylene dish in which the water sample was dried up was found to be clean enough to be used in such a purpose except for Cl which sometimes becomes a similar order of magnitude of Cl contents in water samples.

Polymer materials

In Table 2, 3 and 4, impurities in polymer materials commonly used in making beakers and other apparatus are shown. These polymer samples were cut out from the beakers and bottles and washed in different ways described as follows.

Polyethylene, polypropylene and acrylate resin.

- 1) Soaked in 10% Extran(detergent) solution for one night.
- 2) Boiled in 4M HNO₃ solution for one hour.
- 3) Soaked in 4M HNO₃ solution for one night.

Teflon

- 1) Boiled in 10% Extran solution for one hour.
- 2) Boiled in HClO₄ + HNO₃ mixture for one hour.
- 3) Boiled in concentrated HNO₃ for one hour.

Table 2
Impurities in polymer materials and
their removal by different washing methods

Elem.	Acrylate polymer			Polypropylene		
	method 1)	method 2)	method 3)	method 1)	method 2)	method 3)
Al	800(8)	1000(10)	1400(13)	4000(3)	4100(4)	4200(5)
Na	700(3)	630(4)	639(4)	47(6)	50(6)	55(6)
Cl	7200(8)	7800(11)	7000(18)	27000(3)	26800(4)	29000(4)
Br	31(10)	36(9)	31(9)	64(6)	61(9)	70(6)
Zn	36000(1)	44000(3)	36000(1)	360(4)	410(4)	370(4)
Ti	nd	nd	nd	9700(4)	10000(5)	10000(6)
Mn	nd	nd	nd	57(4)	80(4)	60(5)
Cr	nd	nd	nd	27(9)	31(9)	nd
Fe	nd	nd	nd	nd	790(14)	700(16)
Ta	nd	nd	nd	2(11)	3(14)	3(7)

Number in (): Statistical error in %.
Concentration unit: 10^{-9} g/g.

Table 3
Impurities in polymer materials and
their removal by different washing methods

Elem.	Ordinary polyethylene			Special Polyethylene		
	method 1)	method 2)	method 3)	method 1)	method 2)	method 3)
Al	53200(3)	56000(3)	54000(3)	290(7)	290(13)	660(12)
Na	9620(2)	8400(2)	11000(6)	47(6)	50(6)	55(6)
Mg	12000(11)	8200(15)	9600(14)	nd	nd	nd
Ti	14000(5)	14000(5)	16000(6)	nd	nd	nd
Cl	9600(3)	11000(3)	10500(3)	28000(4)	24000(5)	27000(4)
Br	240(10)	220(7)	180(13)	350(4)	390(4)	490(4)
Mn	3(20)	nd	nd	3(5)	3(5)	2(6)
Cr	23(12)	29(8)	27(8)	nd	nd	nd
Sc	0.2(8)	0.2(7)	0.3(7)	0.2(6)	nd	nd
Au	nd	nd	nd	0.1(6)	0.07(8)	nd

Number in (): Statistical error in %.
Concentration unit: 10^{-9} g/g.

In acrylate polymers, the content of Zn which was found to be very high did not seem to decrease by washing.

In ordinary polyethylene and polypropylene, contents of Al, Mg, Ti, Na and Cl were found to be very high and these elements are not removed by washing. Therefore, these are not of the

Table 4
Impurities in teflon and their removal by different washing methods

Elem.	Teflon (PFA)			Teflon (TFE)		
	method 1)	method 2)	method 3)	method 1)	method 2)	method 3)
Al	100(11)	240(8)	nd	485(5)	294(8)	690(10)
Na	147(5)	124(8)	160(5)	100(5)	110(6)	140(14)
K	nd	nd	nd	210(17)	280(13)	nd
Cl	820(9)	670(7)	360(10)	680(7)	380(9)	700(7)
Br	nd	nd	nd	0.9(15)	nd	nd
Mn	5(6)	9(9)	25(7)	4.7(9)	2.2(7)	6(7)
Cu	1810(5)	1850(4)	830(8)	nd	nd	nd
Cr	nd	nd	nd	66(4)	22(7)	6(7)
Sb	nd	nd	nd	0.2(32)	nd	1.5(30)
Au	nd	nd	0.0(20)	0.17(2)	0.03(8)	0.02(12)

Number in (): Statistical error in %.
Concentration unit: 10^{-9} g/g.

surface contamination but are derived from the Ziegler-Natta type catalyst incorporated in the polymer matrices.

If these elements are homogeneously dispersed in the polyethylene matrices, atomic ratios Al:C and Ti:C would become 1:40000 and 1:200000, respectively.

If these elements are present on the surface as corresponding oxides, i. e., Al-O and Ti-O, these can be sites adsorbing trace elements from solutions. A similar argument holds for polypropylene materials. The specially prepared polyethylene listed in Table 3 is far cleaner than ordinary polyethylene and polypropylene except for Cl which can not be removed by washing. This material is essentially of the similar quality to that of polyethylene dish shown in Table 1.

Among polymer materials examined here, teflon is the cleanest material if judged from the total quantity of impurities contained. However, a considerable amount of Cu was found in PFA and Cr in TFE. In case of Cu in PFA, amount of the element can be reduced to a certain extent by washing with 4M HNO₃.

In conclusion, bottles and beakers made of the specially prepared polyethylene and Teflon (PFA and TFE) can be used as containers which have the least risk of becoming the source of contamination for storing highly pure water samples.

Snow and ice samples

Snow collected in Hakuba-Norikura, Nagano Pref., Japan

The collection of snow samples was performed on 25th, March 1983 at the site (alt. 1000m) of the Mt. Hakuba-Norikura where snow piled up more than 10m. On digging a big hole in the snow, four different layers were observable from the top to the bottom of the hole. Snow samples were

collected from each layer with a shovel made of polyethylene. After one month, particulates in the water were filtered with Millipore Filter and analyzed by neutron activation analysis. The result is presented in Table 5.

From February to May, it is common in Japan to have the precipitation of loess (fine clay particles) transported from the Asian continent by the strong westerlies.

In Table 5, are listed the elemental compositions of the particulates in those four layers of snow. Concentrations of elements are expressed on the bases of weights of particulates collected by filtration of water samples. Volumes of water samples are listed together for the reference sake.

Samples 1 and 2 are close to one another in elemental composition. They seem to consist of well weathered clay or soil particles of the mother rocks of granitic nature, based on the low content of Na and high contents of Al, Fe, rare earth elements, Sc and Th. Samples 3 and 4 are a little different from other two in the contents of Cl and Br which are considered to be derived from marine origin.

Table 5
Elemental compositions of particulates in snow fallen in
the Hakuba-Norikura mountainous region, Nagano Prefecture, Japan

sample	weight	Na	K	Rb	Cs	Mg	Ba	Al	Sc	La	Ce	Sm	Nd	Eu	Tb	Yb
	(volume)	%	%	μg/g	μg/g	μg/g	μg/g	%	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
No.1	0.0710g (1300ml)	0.881	22.8	150	10.1	2.56	680	12.9	14.8	45.1	92.2	7.50	68.3	1.41	0.844	2.02
No.2	0.0467g (3000ml)	0.834	22.9	130	11.6	3.11	593	14.1	15.8	45.1	88.4	7.90	51.7	1.59	0.960	2.56
No.3	0.0113g (4000ml)	0.475	nd	nd	8.17	nd	nd	15.9	8.17	67.7	113	6.69	nd	1.35	nd	3.36
No.4	0.0323g (5000ml)	0.522	nd	51	5.81	2.40	35	15.8	15.8	29.8	74.9	6.71	nd	1.57	0.714	2.22
		Lu	Hf	Th	U	V	Cr	Mn	Fe	Co	Zn	As	Sb	Cl	Br	
		μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	%	μg/g	μg/g	μg/g	μg/g	%	μg/g	
No.1		0.58	4.87	15.8	4.07	149	89.2	481	4.61	15.2	303	33.4	7.94	nd	4.24	
No.2		0.59	5.33	15.5	4.42	162	102	546	4.69	17.5	322	30.0	3.95	nd	6.18	
Na.3		0.49	5.65	10.7	5.62	227	147	656	4.77	12.8	231	39.4	2.70	0.143	24.0	
No.4		0.50	7.11	9.6	3.00	188	98.6	627	4.99	15.1	239	14.0	5.35	0.205	19.0	

Weight: Weight of particulates in snow melt water. (volume) : Volume of snow melt water
Concentrations of elements are given on the bases of weights of particulates.

Elements enclosed by broken lines are volatile ones which tend to be injected to the atmosphere by volcanic activities, natural fires and industrial activities. Since the contents of these volatile elements in the samples are much higher than those of the average soil, particulates in the snow layers can be concluded to consist of mainly loess from the Asian continent in which volatile elements and those of marine origin, i.e., Cl and Br, are mixed.

Ice core samples of Antarctica

Trace elements in ice cores taken in the vicinity of the Mizuho station (JARE-21, Z102.5) are compiled in Table 6. Concentration given here are based on the water volumes of ice samples, because the quantity of the particulate accumulated on the filter was too minute to be accurately weighed.

Table 6
Trace elements in ice cores taken in
the vicinity of the Mizuho Station in Antarctica

sample	Na	Al	Fe	Cr	Mn	Sc	As	Sb	Zn	Cd	Ag
	$\mu\text{g}/1$	$\mu\text{g}/1$	$\mu\text{g}/1$	$\mu\text{g}/1$	$\mu\text{g}/1$	$\mu\text{g}/1$	$\mu\text{g}/1$	$\mu\text{g}/1$	$\mu\text{g}/1$	$\mu\text{g}/1$	$\mu\text{g}/1$
14-P	0.41	1.5	nd	0.093	0.014	4.1×10^{-4}	0.21	3.1×10^{-3}	0.19	nd	0.032
17-P	1.2	1.0	2.3	0.15	0.014	1.7×10^{-4}	0.19	4.2×10^{-3}	0.21	nd	0.058
3-P	1.9	4.0	nd	0.015	6.8×10^{-4}	nd	nd	0.019	12.8	nd	nd
6-P	1.1	3.2	12	0.048	6.8×10^{-4}	3.2×10^{-4}	nd	4.0×10^{-3}	17.7	nd	nd
9-P	1.7	3.5	1.7	nd	nd	3.6×10^{-4}	nd	7.0×10^{-3}	5.6	nd	nd
3-F	95	1.8	nd	0.74	0.16	6.9×10^{-4}	nd	nd	0.84	0.23	nd
6-F	64	nd	nd	0.14	0.19	5.5×10^{-4}	nd	nd	0.84	0.23	nd
9-F	36	0.01	2.1	0.05	0.06	nd	nd	nd	nd	0.07	nd

Concentrations are based on the weights of elements in one liter of ice melt.
-P denotes particulates collected on a sheet of filter. -F denotes filtrate.

If we take the weight ratios of volatile elements such as Zn, As and Sb to those of non volatile Al and Fe which are supposed to be of fine particles of crustal origin, ratios become far greater than those in ordinary soils, that is, for Zn/Al: 100 times, for As/Al or Fe: 100-1000 times, for Sb/Al or Fe: 10 times as much as those in soil.

There have been several reports on Ag concentrations in ice sheets in Greenland and in Antarctica³⁾⁴⁾⁵⁾. The concentration range of Ag presented in Table 6 is of the same order of magnitude found in the literatures.

Snow sample collected at Mt. Naimonanyi in China

IN Table 7, the elemental compositions of freshly piled up snow collected at the base camp (alt.:

Table 7
Neutron activation analysis of snow fallen at Mt. Naimonanyi in China

sample	Na	K	Rb	Cs	Mg	Ca	Sr	Ba	Al	Sc
Nam-1	45.5	153	1.76	0.31	106	100	0.50	0.30	370	0.04
Nam-2	41.4	32	0.08	0.02	64	194	1.1	0.13	40	3.1×10^{-5}
Nam-3	31.8	nd	0.10	0.03	61	226	nd	0.25	40	9.3×10^{-5}
sample	Ce	Sm	Hf	Th	U	V	Cr	Mu	Fe	Co
Nam-1	0.29	0.026	0.006	0.05	0.06	0.2	0.27	3.4	134	0.040
Nam-2	0.02	2.8×10^{-4}	nd	nd	nd	nd	0.01	0.04	nd	nd
Nam-3	0.02	4.2×10^{-4}	nd	nd	nd	nd	0.01	0.03	nd	nd
sample	Zn	Ag	As	Sb	Ta	Cl	Br	Se		
Nam-1	125	nd	0.14	0.12	0.014	7.0	0.02	0.42		
Nam-2	0.04	0.008	0.04	0.002	nd	176	1.2	0.01		
Nam-3	nd	0.011	0.03	0.003	nd	162	1.6	0.10		

Concentration unit: 10^{-6} g/one liter snow melt water.

Nam-1: Particulates collected on a sheet of Nuclpore filter by filtering 1.25 liter snow melt water.

Nam-2: The dried up residue by evaporating. 5 liter filtrate of the snow melt water from the same sample as Nam-1.

Nam-3: The dried up residue by evaporating. 5 liter of snow melt water without filtering.

5000m) are compiled. In the table, sample Nam-1, is the particulates collected by filtering 1.25 liter of snow melt with Nuclepore Filter, Nam-2 is the dried up residue of the filtrate of the same sample as Nam-1 and Nam-3 is the dried up residue of the snow melt other than samples Nam-1 and Nam-2.

One of the characteristic features of the particulates in these samples is that the high contents of Ca and Sr relative to that of Na which is the same order of magnitude as in ordinary soil. This holds for the dissolved fractions of those ions contained in samples Nam-2 and Nam-3 in which the relative concentration of Ca to Na is much higher than in sea water. Since the Na concentrations of sample Nam-2 and Nam-3 are the similar order to those in ice sheets in inland parts of Antarctica where the influence of sea water is minimal, the high concentrations of alkali earth elements in these snow samples are attributed to the surrounding of the mountain. It should be pointed out that the concentration of Se is extremely high in this snow. It is not clear whether the high concentration of Se is a phenomenon peculiar to the snow around the sampling site or common to the precipitation in the northern hemisphere since data points are so scarce. However, the latter seems to be probable in view of the fact that the chemical behavior of selenium is more or less similar to that of sulfur and the injection of large quantity of sulfur oxides to the troposphere is taking place in the northern hemisphere where the human activity has been much more prevailing than in the southern.

Again, a relatively high concentration of Ag was observable. It means that the relatively high concentration of Ag to other trace elements in precipitations is not a characteristic phenomenon in

Antarctica or Greenland but the phenomenon commonly observable in polar regions including high mountains where precipitation of particles of crustal origins such as clay minerals or loess are scarce.

Conclusion

An appropriate method of pre-treatment of extremely pure water samples for activation analysis was established by choosing the most uncontaminated experimental tools such as bottles, filters, beakers and tubings.

It was concluded that the concentrations of volatile elements such as Zn, Cd, As, Sb, Ag or Se are relatively high in ice cores and snow samples as compared to the non volatile elements such as Al and Fe in all the samples analyzed. This tendency is much more clearly demonstrated by samples from polar regions such as Antarctica and Mt. Naimonanyi in China where the influence of Aeolian dusts is not significant.

Since the presence of silver in the snow samples from Mt. Naimonanyi in China, the relatively high concentration of silver in ice core or snow seems to be not peculiar to the samples from Greenland or Antarctica. In the case of selenium, however, the relatively high concentrations of the element in snow and in other precipitations might be characteristic of the northern hemisphere where the injection of sulfur in a large quantity is taking place, as is typically indicated by acid rain problems. Much more studies should be made from the point of view mentioned above.

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