

DETERMINATION OF THE TRACE ELEMENTS IN A MIZUHO ICE CORE SAMPLE BY A COMBINATION OF CONVENTIONAL AND HIGH RESOLUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Abstract: Seventeen elements (Li, Na, Mg, Al, Ca, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Ba, Pb and Bi) in an Antarctic ice core at Mizuho Station collected by the Japanese Antarctic Research Expedition were determined by a combination of conventional and high resolution inductively coupled plasma mass spectrometry (ICP-MS). The ice sample was separated into five fractions from surface to inner core by stepwise melting. All the elements determined decreased from the core surface to the inner core by one to four orders of magnitude. The surface contaminations of Li, Cr, Ni, Co, Cu, Ba, Pb and Bi penetrated into the second fraction, while only the surface fraction was contaminated for Na, Mg, Al, V, Mn, Fe, Ca and Sr. Zn kept decreasing to the innermost fraction. Na, Mg and Ca may be originated from sea water, while V, Cr, Mn, Fe, Cu, Zn and Sr may be supplied from the crust. Significant portions of Co and Ni could be of extraterrestrial origin.

1. Introduction

Global environmental variations are thought to have occurred as results of various natural forces such as the earth's orbital parameters, volcanic activity (GENTHON *et al.*, 1987; BUDYKO *et al.*, 1985) or biological activities (BERKNER and MARSHALL, 1965). Recently, in addition to those natural causes, many anthropogenic sources such as industrial or agricultural emissions of pollutants are considered to be significant causes of environmental changes (MOLINA and ROWLAND, 1974; MANABE and STOUFFER, 1980). To investigate such a problem it is important to know the global circulation of the materials. Chemical composition of the water precipitates is potentially important to trace atmospheric circulation, material transportation or diffusion (BOUTRON, 1979). To use chemical compositions as a tracer it is critically necessary to know the natural background. An ice core sample from Antarctica would be a good candidate as a natural background to avoid the sources of anthropogenic contaminants. It is difficult, however, to obtain ice cores and difficult to determine elemental concentrations of such ice because concentrations of most of the elements are extremely low. Recent development of the ICP-MS enables us to investigate such a low level elemental concentration

(YAMASAKI *et al.*, 1994). We tried to determine the concentrations of 17 elements in an Antarctic ice core by a combination of conventional and high resolution ICP-MS. Though surface contamination of the core is severe, the concentrations of the elements determined inside the core may be representative as a natural background of the water precipitates.

2. Experimental

2.1. Samples and sample preparation

Prior to the main experiment, a test experiment was performed to determine

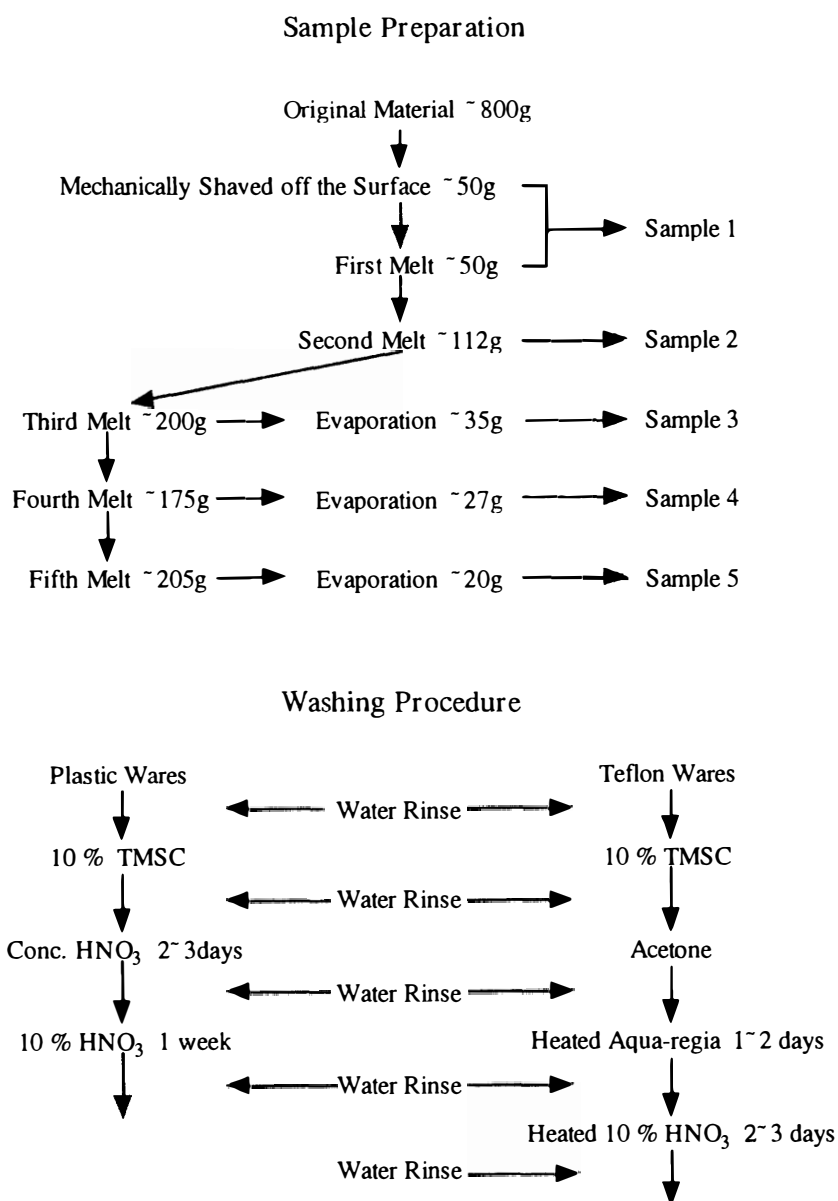


Fig. 1. Flow scheme of sample preparation and washing procedure of ware.

approximate concentrations of the transition metals in Antarctic ice. Commercially available Antarctic ice supplied by Nippon Suisan was obtained. A few tens of blocks of ice with total mass of 1 kg were packed in a plastic bag. The sampling location was unknown. The sample was transferred into acid cleaned plastic ware and melted at room temperature for 2 hours in a class 10 clean bench, then transferred to other plastic ware, and so on. A total of three fractions were obtained. A procedure blank was also prepared with the same conditions using doubly distilled high purity water. Each fraction was stored in a polypropylene bottle.

The ice core sample used for the main experiment was sampled at Mizuho Station, Antarctica, in 1984 (No. 411 JARE-25 depth 370.04–370.11 m). Sample preparation and ware washing procedures are schematized in Fig. 1. The sample had been wrapped with aluminum foil and stored in a -20°C cold room. The sample was then stored in a refrigerator at -10°C for several days to avoid possible cracking during the melting procedure and transferred into a plastic ware. About 50 g of surface material was shaved off using an acid cleaned ceramic knife (zirconia) to prevent contamination from steel tool. After brief washing with semiconductor grade high purity water, the sample was transferred into other plastic ware and melted 50 g at room temperature. This melt and the shaved surface material were combined together as sample 1. Then the ice was transferred into Teflon ware to allow stepwise melting from surface to center. Five fractions, from sample 1 to sample 5, were obtained. Sample 3 to sample 5 were concentrated by simple evaporation. Concentration factors ranged from 5.7 to 10.1. A procedure blank was also prepared. Washing procedures for the plastic ware etc. are as follows. The plastic ware was initially washed with 10% high purity organic alkaline cleaning solvent (TMSC, Tama Chemicals, Japan) followed by soaking in high purity concentrated nitric acid for a few days, then soaked in 10% nitric acid for one week. The Teflon ware was washed with TMSC, then washed with high purity acetone, then soaked in heated aqua-regia for 1 to 2 days, then finally soaked in heated 10% nitric acid for a few days. Rinsing with semiconductor grade water was done between each step. All the acids used were Tamapure AA 10 grade (Tama Chemicals, Japan) that had guaranteed impurity level less than 10 ppt for most of the metallic elements. For TMSC and acetone, impurity levels of less than 1 ppb are also guaranteed by the manufacturer. All the procedures either for the sample or ware washing were done on a class 10 clean bench in a class 1000 clean room. Summaries of the samples are shown in Table 1.

Table 1. Sample weights and concentration factors.

Sample	Original weight(g)	After concentration(g)	Concentration factor
Sample 1	~100	~100	1
Sample 2	112	112	1
Sample 3	199.8	35.0	5.71
Sample 4	175.2	27.2	6.42
Sample 5	205.7	20.4	10.1
Blank	210.2	30.0	7.01

2.2. Instrumentation and measurements

The measurements for Li, Na, Mg, Al, Ca, Sr, Ba, Pb and Bi were made using a conventional quadru-pole based ICP-MS (Q-ICP-MS) (PMS2000 Yokogawa Analytical Systems, Japan). Selected isotopes were ^7Li , ^{23}Na , ^{24}Mg , ^{27}Al , ^{44}Ca , ^{88}Sr , ^{138}Ba , ^{208}Pb and ^{209}Bi , respectively. Typical running conditions are shown in Table 2. Because concentration levels of Na, Mg, Al and Ca were expected to be much less than 0.1 ppm and those of other elements much less than 1 ppb (MUROZUMI *et al.*, 1978; BOUTRON, 1980), instrumental background would be a problem. To reduce background, the sample introduction system, spray chamber, plasma torch, sampling cone, skimmer cone and extraction electrodes were changed to cleaned new ones and introductions of high purity nitric acid (5%) and doubly distilled water were repeated alternatively for one day. Procedure blank contributions of the main experiment were negligible for Na, Mg, Al, Sr and Ba, less than 10% for Li and significant for Ca (20–40%), Pb (10–40%), and Bi (8–67%).

For the first transition metal elements, V, Cr, Mn, Fe, Ni, Co, Cu and Zn, a high

Table 2. Running conditions of the HR-ICP-MS and Q-ICP-MS.

	HR-ICP-MS	Q-ICP-MS
Coolant gas flow rate (l/min)	14	14
Aux. gas flow rate (l/min)	1.1	0.7
Carrier gas flow rate (l/min)	0.86	1.05
RF power (W)	1600	1320
Accelerating voltage (kV)	4.0	—
Mass resolution	3500	—
Sensitivity (cps/ppm)	4×10^7	2×10^7

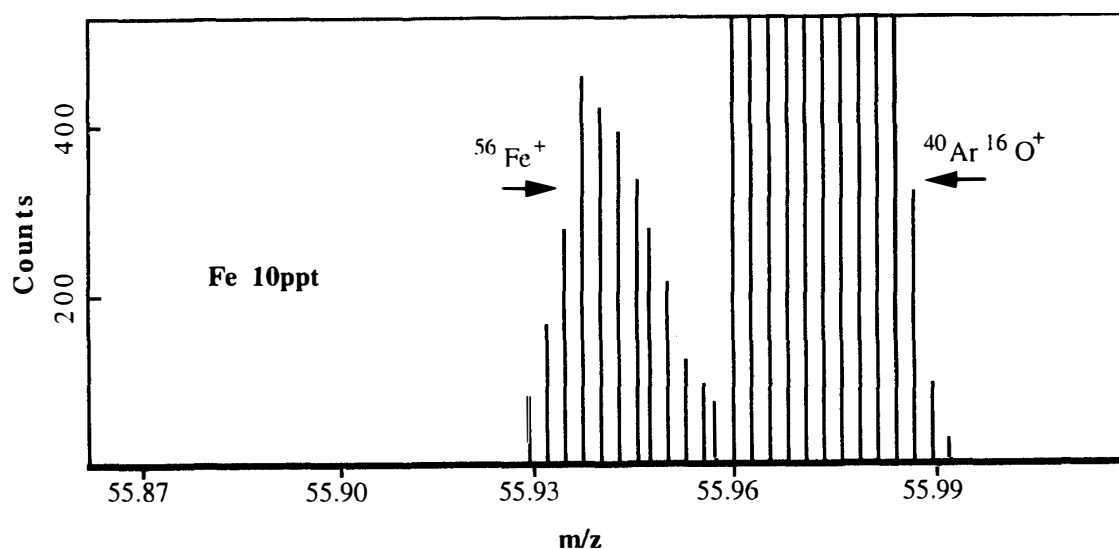


Fig. 2. Mass spectrum of $^{56}\text{Fe}^+$ at nominal $m/z=56$ with 10 ppt Fe solution. $^{56}\text{Fe}^+$ is clearly separated from $^{40}\text{Ar}^{16}\text{O}^+$.

resolution ICP-MS (HR-ICP-MS) (PlasmaTrace, Fison Instruments, UK) was used. This instrument is equipped with a double focusing magnetic sector mass analyzer and thus can be used with mass resolution of up to 10000, enough to resolve the analyte ions from many molecular interferences, *e.g.* $^{56}\text{Fe}^+$ from $^{40}\text{Ar}^{16}\text{O}^+$ etc. (BRADSHAW *et al.*, 1989). In Fig. 2 a typical example of mass spectrum is shown. $^{56}\text{Fe}^+$ is clearly separated from $^{40}\text{Ar}^{16}\text{O}^+$. Typical running conditions of the instrument are summarized together with those of Q-ICP-MS in Table 2. Selected isotopes for the measurement were ^{51}V , ^{52}Cr , ^{55}Mn , ^{56}Fe , ^{59}Co , ^{58}Ni , ^{63}Cu and ^{66}Zn respectively. Molecular ion interferences were observed on $^{51}\text{V}^+$ ($^{35}\text{Cl}^{16}\text{O}^+$), $^{52}\text{Cr}^+$ ($^{40}\text{Ar}^{12}\text{C}^+$), $^{55}\text{Mn}^+$ ($^{40}\text{Ar}^{14}\text{N}^1\text{H}^+$), $^{56}\text{Fe}^+$ ($^{40}\text{Ar}^{16}\text{O}^+$), $^{58}\text{Ni}^+$ ($^{40}\text{Ar}^{18}\text{O}^+$) and $^{63}\text{Cu}^+$ ($^{23}\text{Na}^{40}\text{Ar}^+$). No obvious interference was observed on $^{59}\text{Co}^+$ and $^{66}\text{Zn}^+$. All the molecular interferences were clearly resolved by our running conditions. $^{58}\text{Ni}^+$, however, was interfered by $^{58}\text{Fe}^+$, which could not be resolved. The amount of $^{58}\text{Fe}^+$ was calculated from $^{56}\text{Fe}^+$ and a correction was applied. The contribution of $^{58}\text{Fe}^+$ to $^{58}\text{Ni}^+$ was about 10%. Initially we estimated much lower Fe concentration. This is why we selected ^{58}Ni , but ^{60}Ni was definitely a better selection. An ultrasonic nebulizer (En Vallaire, CH-1024, Ecublens, Applied Research Laboratories, Switzerland) was also used to increase the efficiency of the sample introduction.

3. Results and Discussion

3.1. Test experiment

Analytical results on the commercial Antarctic ice are shown in Table 3. The background signal of Ni fluctuated significantly. This was probably because the sampling cone of HR-ICP-MS is made of Ni, and the instrumental background is sensitive to plasma conditions. This is why the procedure blank for Ni showed a rather large negative value. Generally the concentrations of the elements are much higher at the

Table 3. Results of the test experiments (concentration in ppt).

Element	0-2 hours	2-4 hours	4-6 hours	Procedure blank
Li	960	200	76	2.6
Na	3.3×10^6	2.6×10^6	1.5×10^6	360
Mg	2.1×10^6	4.3×10^5	7.6×10^4	60
Al	21	140	40	28
Ca	1.8×10^6	3.6×10^5	9.0×10^4	8.9×10^3
V	20	3	5.1	1.7
Cr	270	32	33	-0.32
Mn	150	20	11	2.5
Fe	2×10^3	410	480	100
Co	5	1.1	0.6	0.4
Ni	150	17	-11	-25
Cu	44	40	12	29
Zn	2.9×10^3	1.1×10^3	170	64
Sr	4.7×10^4	6.5×10^3	1.1×10^3	0.8
Ba	740	170	57	3.8
Pb	210	160	33	5.7
Bi	-0.3	-0.3	-0.3	0.8

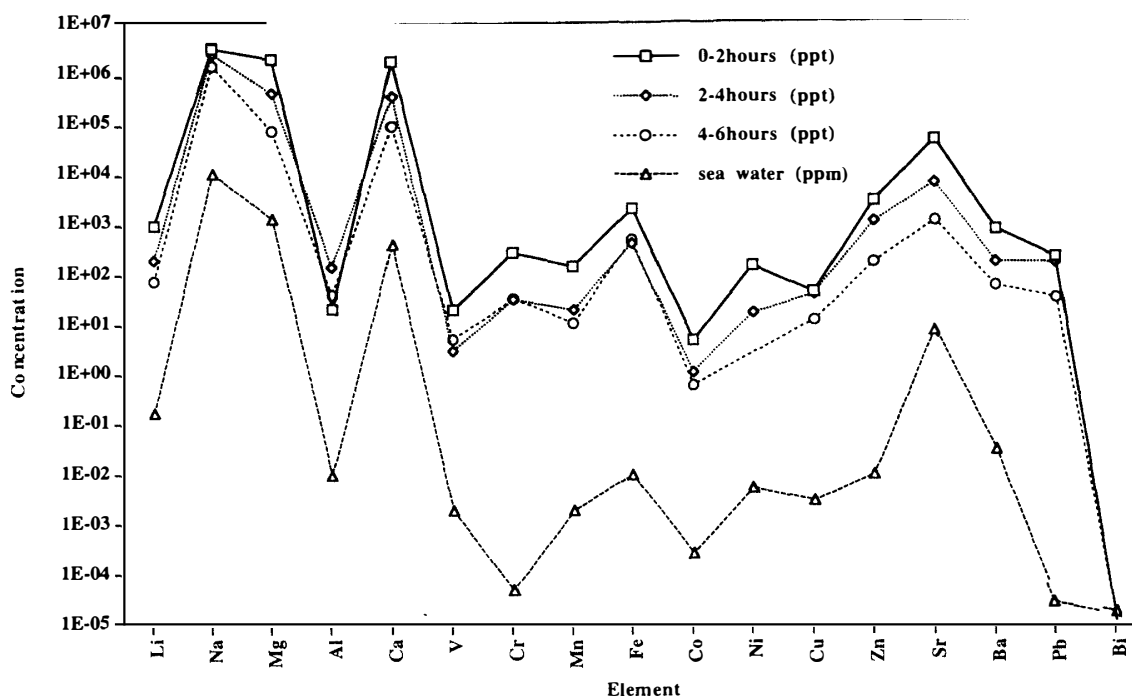


Fig. 3. Comparison of the elemental patterns of the test samples with that of sea water. These patterns are basically identical to that of sea water except for Cr, Pb and Bi.

surface, then decrease rapidly to inner fractions, indicating severe surface contamination of the sample. The concentrations of Na, Mg and Ca of the surface fraction (0–2 hours) are much higher than previously reported (MUROZUMI *et al.*, 1978; BOUTRON, 1980). Even in inner fractions, Na and Cu do not decrease much. It should be noted that the Al concentration is very low and does not show any general trend at all. Figure 3 shows the elemental patterns of individual fractions together with that of sea water (LIDE, 1991). It is obvious that elemental patterns in the test samples are very similar to that of sea water except for Cr, Zn and Pb, suggesting the sea water origin of these samples.

3.2. Main experiment

The results for the Mizuho ice core are shown in Table 4. Errors quoted show only the repeatability of the measurements. It should be noted that procedure blank gave much lower values than test experiment. Even for the difficult elements such as Fe and Zn, blank levels are less than 10 ppt. To achieve this level, a good laboratory environment, careful sample treatment, careful selection of laboratory ware and careful washing procedures for the ware are essential as described earlier. Surface contamination is much higher than that of commercial Antarctic ice except for Na, Mg, Ca and Sr. This may be because drilling devices contaminated the surface of the ice core. Figure 4 shows the depth profiles of the concentration for the measured elements. It is evident that the concentration levels rapidly decrease by one to four orders of magnitude from surface to inner core. There are three patterns of depth profiles. The first pattern (Fig. 4a) is that the only outer layer (sample 1) shows high concentration and inner layers e.g. sample 2 to sample 5 show lower concentration. Na, Mg, Al, Ca, V, Mn, Fe and Sr fall into this pattern. Differences of the concentrations between surface and interior are

Table 4. Element concentrations of Antarctic ice core (concentration in ppt). Errors shown in the table are standard deviations of repeated measurements.

Element	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Procedure blank
Li	779±8	184±2	13±0.5	4.30±0.07	4.7±0.3	0.42±0.02
Na	$(1.15 \pm 0.01) \times 10^5$	$(4.22 \pm 0.02) \times 10^4$	$(4.37 \pm 0.04) \times 10^4$	$(3.94 \pm 0.02) \times 10^4$	$(4.70 \pm 0.03) \times 10^4$	18.6±4.3
Mg	$(1.91 \pm 0.01) \times 10^4$	$(5.53 \pm 0.03) \times 10^3$	$(5.31 \pm 0.05) \times 10^3$	$(4.53 \pm 0.03) \times 10^3$	$(5.05 \pm 0.03) \times 10^3$	5.7±0.6
Al	$(2.57 \pm 0.01) \times 10^5$	$(1.22 \pm 0.06) \times 10^3$	$(1.02 \pm 0.07) \times 10^3$	$(1.14 \pm 0.06) \times 10^3$	$(1.36 \pm 0.05) \times 10^3$	22±6
Ca	$(8.1 \pm 0.2) \times 10^4$	$(2.00 \pm 0.04) \times 10^3$	$(1.04 \pm 0.01) \times 10^3$	987±5	$(1.20 \pm 0.02) \times 10^3$	554±6
V	71.5±1.4	1.2±0.3	1.4±0.2	1.4±0.2	1.9±0.2	0.013±0.011
Cr	636±41	11.4±0.6	1.4±0.1	2.6±0.2	1.9±0.2	0.35±0.10
Mn	$(2.2 \pm 0.3) \times 10^3$	21.3±2.2	21.5±1.8	22.3±1.4	26.8±1.5	0.08±0.35
Fe	$>6 \times 10^4$	556±70	482±76	662±19	820±90	3.4±0.3
Co	80±2	2.9±0.3	0.38±0.06	0.34±0.03	0.33±0.09	0.11±0.02
Ni	$(3.2 \pm 0.3) \times 10^3$	—	10.5±2.7	18.5±4.5	15.3±0.4	8.3±2.5
Cu	$>3 \times 10^4$	39.4±2.4	6.0±0.4	15.3±0.3	3.6±0.2	0.27±0.38
Zn	$>2 \times 10^5$	746±41	25.0±0.7	19.3±3.2	7.2±0.4	7.7±0.7
Sr	360±4	35.6±0.5	37.6±0.3	35.0±0.6	42.4±0.8	0.02±0.01
Ba	$(2.87 \pm 0.03) \times 10^3$	168±3	11.0±0.1	10.8±0.6	8.6±0.3	0.12±0.03
Pb	$(1.66 \pm 0.03) \times 10^4$	45±6	1.7±0.1	10.3±0.3	4.3±0.2	0.86±0.09
Bi	$(4.2 \pm 0.4) \times 10^3$	147±3	6.8±0.4	15±2	1.8±0.2	0.53±0.19

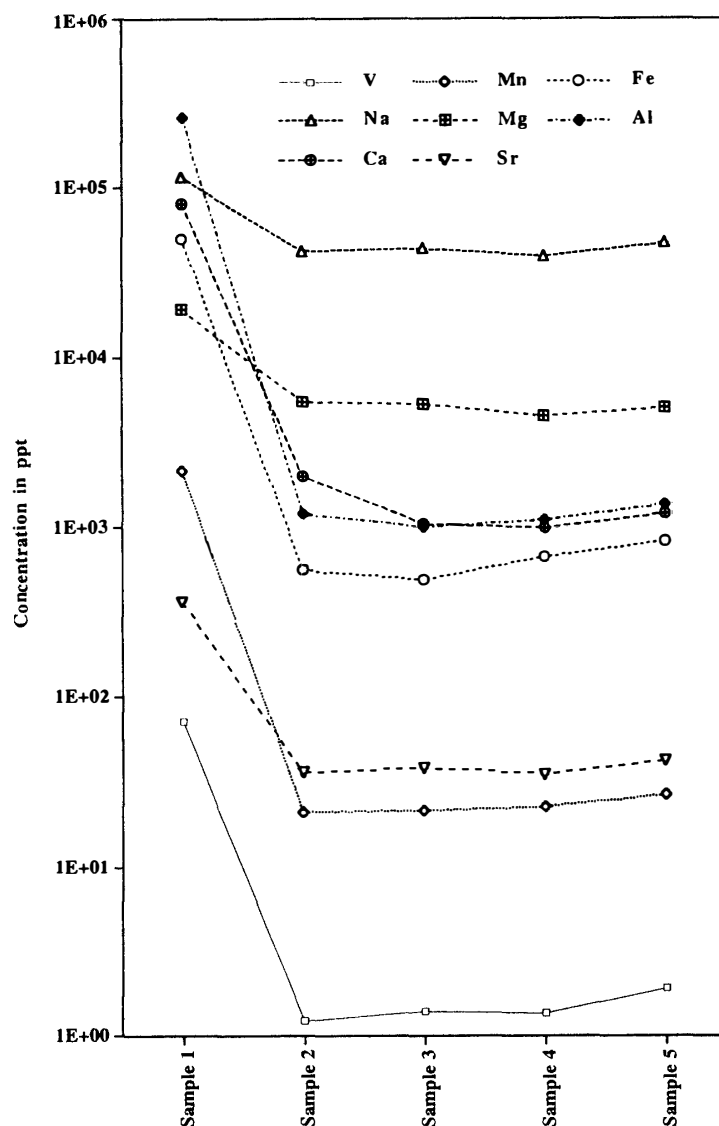


Fig. 4a.

Figs. 4a-c. Depth profiles of individual elements in Mizuho ice core. Three different profiles can be seen (4a, 4b and 4c, see text).

one to two orders of magnitude. The second pattern (Fig. 4b) is that element concentrations decrease to sample 3, then keep almost constant. Concentration differences are two to four orders of magnitude, which are larger than those of the first pattern. Li, Co, Zn and Ba belong to this pattern. Zn keeps decreasing until sample 5, indicating that Zn diffuses easily into the ice even at very low temperature. Cr, Ni, Cu, Pb and Bi behave similarly but somewhat differently as shown in Fig. 4c. Their concentrations are higher in sample 4 than in samples 3 and 5. It may be concluded that the values for sample 3 to sample 5 are typical concentration levels of those elements (except Zn) for the ice core. Let us compare our inner core results with those of Dome C snow data (BOUTRON, 1980) (see Table 5). Na and Mg are generally higher than in the snow data. Ca, Fe and Al are similar to those of the snow (around 1 ppb). Mn is also similar to in the snow

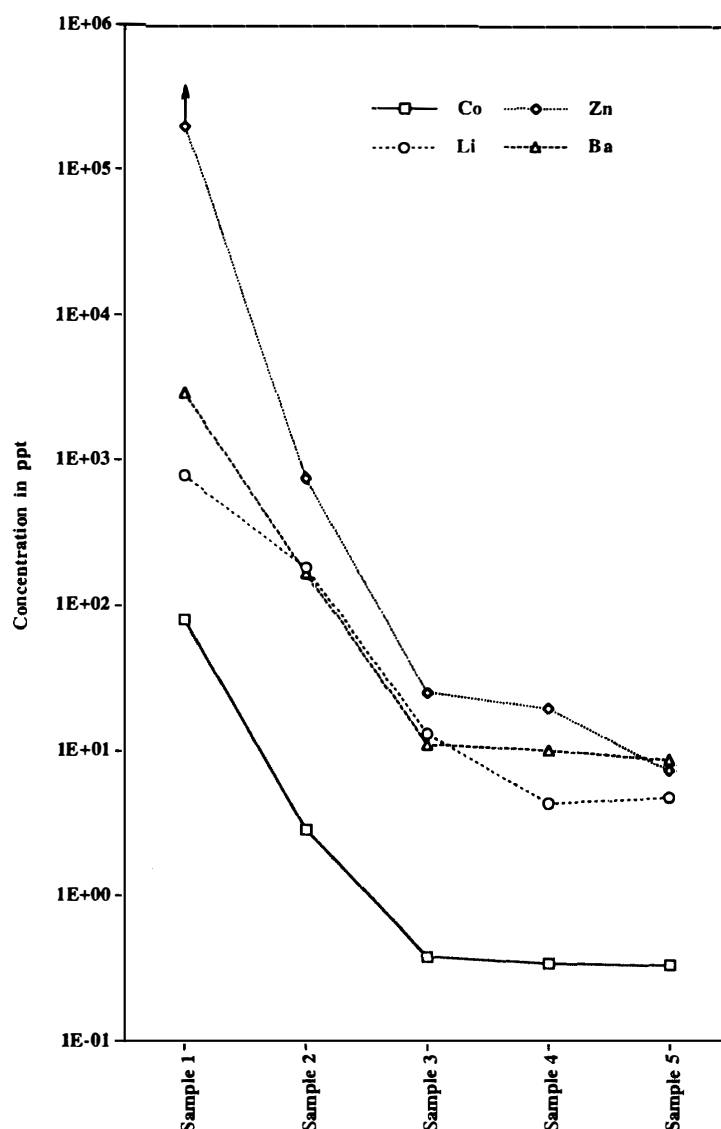


Fig. 4b.

data. Cu of sample 5 is somewhat lower than the snow data. The Zn level in sample 5 is near the lower limit of the snow. Pb in sample 5 is also lower than in the snow. In Fig. 5, the elemental pattern of sample 5 is shown together with the crustal average and the sea water pattern (LIDE *et al.*, 1991). Comparing the sample 5 pattern to those of the crust and the sea water, the following characteristics can be seen. (1) Na, Mg and Ca (and possibly Li) are parallel to the sea water pattern. (2) V, Cr, Mn, Fe, Cu, Zn and Sr are parallel to the crustal pattern. (3) Al and Ba are intermediate between sea water and the crust, but most of the contribution would be from the crust. (4) Co/Fe and Ni/Fe are slightly higher than in the crust, suggesting the contribution of extraterrestrial matter. (5) Relative concentrations of Pb and Bi are much higher than in either the crust or sea water, indicating selective transportation of these elements. On the other hand, as shown in Fig. 6, sample 1 is parallel to the crust and rich in Cr, Co, Ni, Cu, Zn,

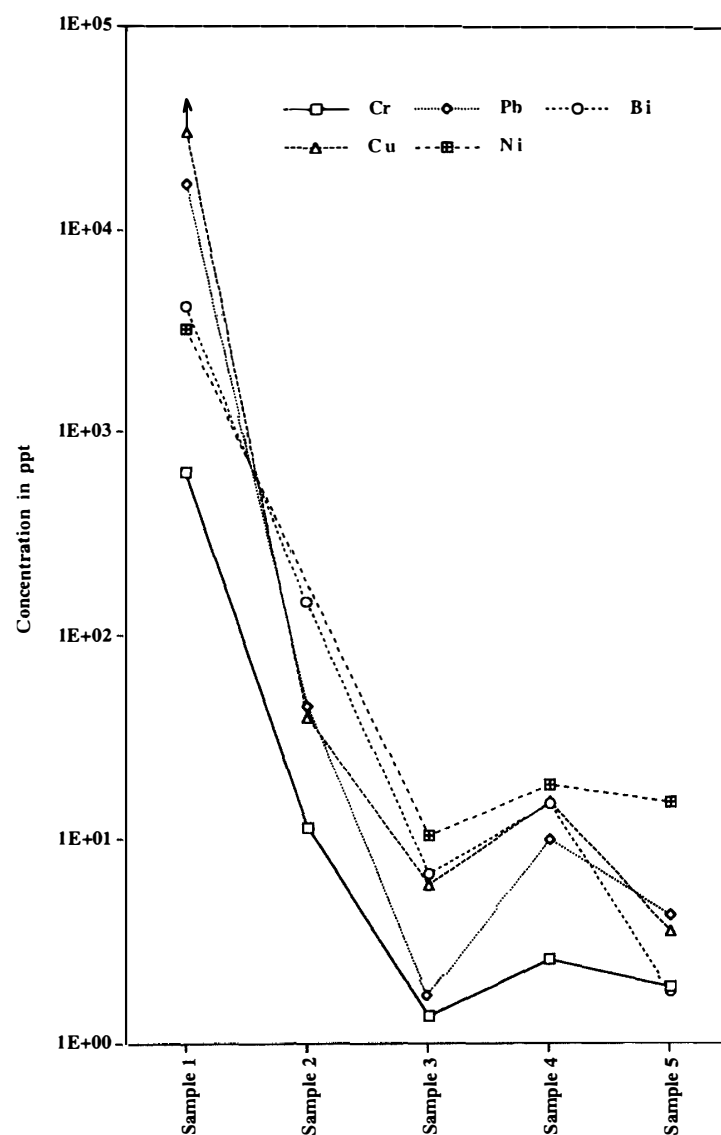


Fig. 4c.

Table 5. Comparison between our results and Dome C snow data (BOUSTRON, 1980).

Element	This work	Dome C snow
Na (ppb)	39 to 47	5.4 to 31.7
Mg (ppb)	4.5 to 5.5	1.23 to 3.97
Al (ppb)	1.0 to 1.4	0.1 to 6.25
Ca (ppb)	0.99 to 2.0	0.46 to 3.98
Mn (ppt)	21 to 27	9 to 78
Fe (ppb)	0.48 to 0.82	0.38 to 6.48
Cu (ppt)	3.6 (sample 5)	2 to 519
Zn (ppt)	7.7 (sample 5)	6.6 to 5014
Pb (ppt)	1.7 to 4.3	8 to 665

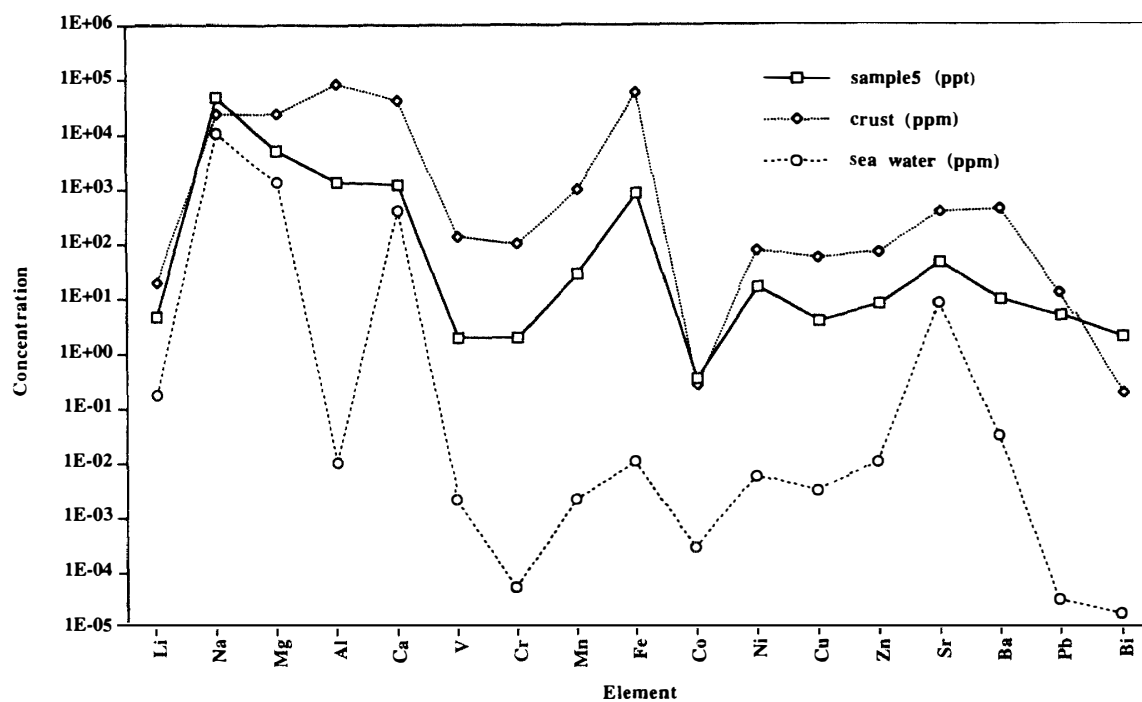


Fig. 5. Comparison of the elemental pattern of sample 5 with mean value of the earth's crust and sea water. Note large enrichment of Pb and Bi, small enrichment of Co and Ni. Al is intermediate between the crust and sea water.

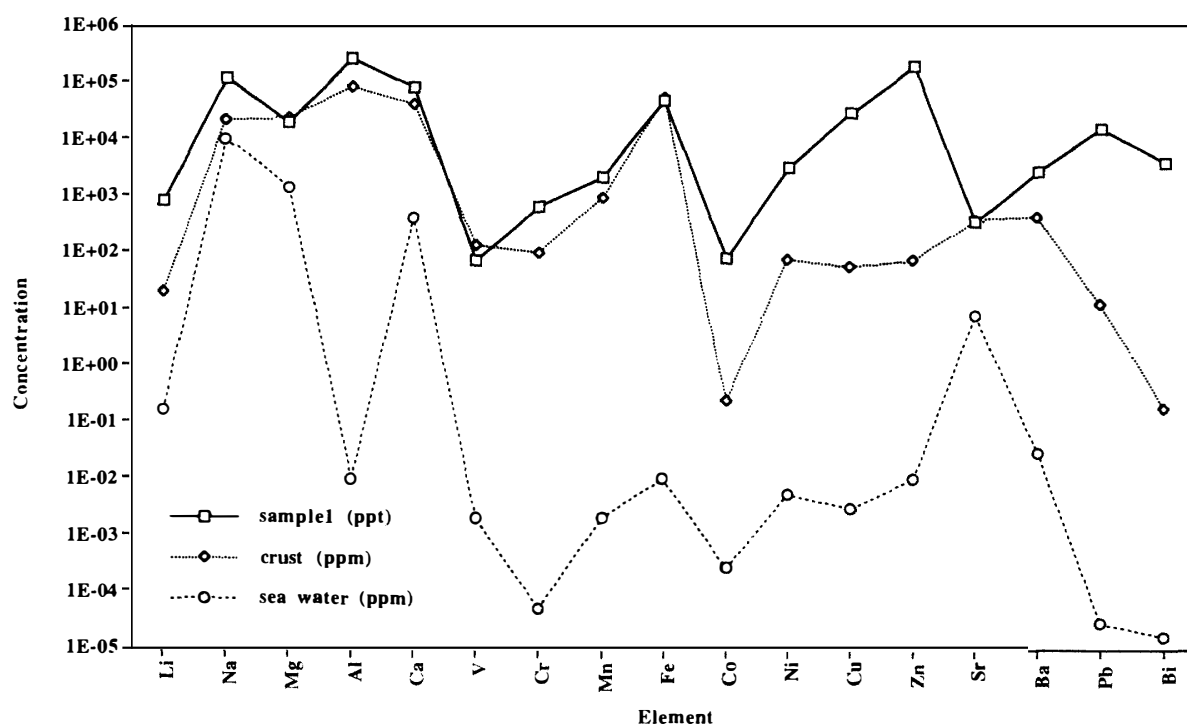


Fig. 6. Same comparison for sample 1. Large enrichment of Cr, Co, Ni, Cu, Zn, Pb and Bi can be seen.

Pb and Bi. Those enriched elements might be from contamination by drilling devices.

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