

CONCENTRATIONS OF TRACE ELEMENTS IN SURFACE SNOW IN THE AREA NEAR SYOWA STATION, ANTARCTICA

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Abstract: Surface snow samples were collected in the area near Syowa Station, Antarctica, with contamination-free technique. Snow samples were melted and filtered with a membrane filter (Nucrepore, 0.4 μm pore size) in a clean room. The filtrates were analyzed for B, Na, Mg, Al, Si, K, Ca, Ti, V, Mn, Fe, Cu, Zn, Sr, Cd and Pb by inductively coupled plasma emission spectrometry (ICP-AES) and Cl^- , NO_3^- and SO_4^{2-} by ion chromatography (I.C.) after evaporation pre-concentration by a rotary evaporator. Particulate matter trapped on the filter was analyzed by ICP-AES after acid digestion with $\text{HNO}_3 + \text{HClO}_4 + \text{HF}$ (10:1:1). From the comparison with those results and average chemical composition of seawater and earth crust, the origin of elements in the snow was estimated; B, Na, Mg, K, Ca, Sr, Cl^- and SO_4^{2-} are derived largely from seawater and Al, Si, Ti, Mn and Fe from earth crust. The origin of other elements could not be clearly specified.

1. Introduction

Because Antarctica is the remotest place from industrialized areas in the world, the concentration of trace elements in snow there is considered an indicator of their global change not directly influenced by human activities.

To establish a representative value in Antarctica, it is important to collect and compare the data on the trace elements in snow from various places of coastal and inland areas of Antarctica. Several studies on trace element contents in snow in Antarctica have been reported (ARISTARAIN *et al.*, 1982; BOUTRON and MARTIN, 1979; BOUTRON and LORIUS, 1979; BOUTRON, 1979, 1982; DELMAS *et al.*, 1982; MUROZUMI *et al.*, 1977, 1978). But, in the area near Syowa Station, the information on trace elements in snow is very scanty (NAKAYA *et al.*, 1985).

The authors determined concentration of trace elements in the surface snow at two points near Syowa Station. By showing the ratio of soluble and insoluble components, the origin of elements is estimated.

2. Experimental

2.1. Samples

Samples of surface snow were taken at two points near Syowa Station as shown

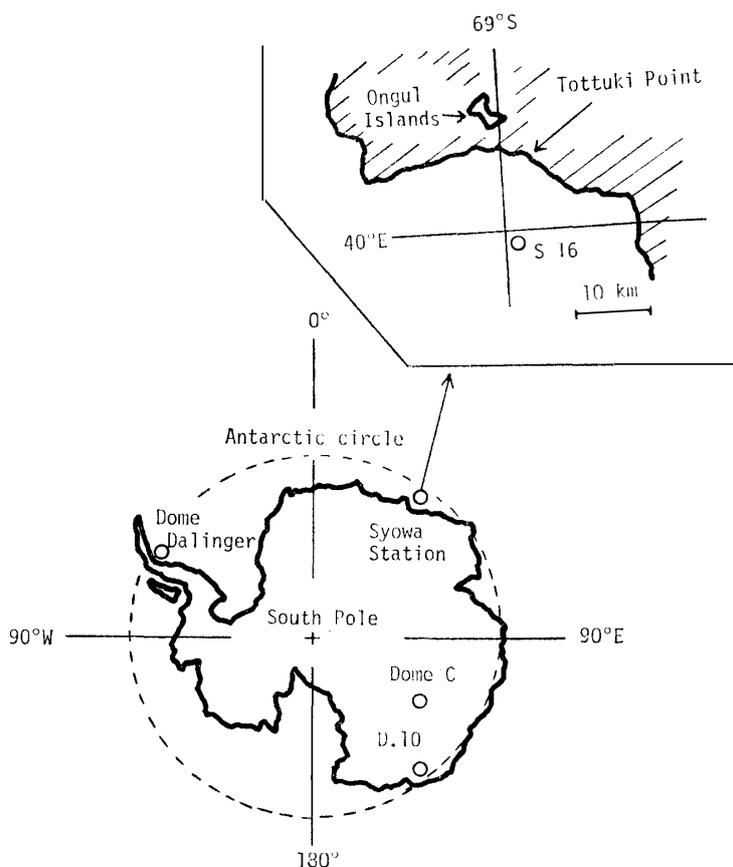


Fig. 1. Map of sampling points.

in Fig. 1. The one was collected at Tottuki Point ($68^{\circ}55'S$, $39^{\circ}50'E$) on 28 April 1982 and the other at S16 ($69^{\circ}01'S$, $40^{\circ}02'E$) on 19 August 1982. About 10 cm of the surface layer of the accumulated snow was collected using a teflon scoop into polypropylene bottles (4 liters). Sampling was performed very carefully so as not to get any contamination from snow vehicles and so on. The polypropylene sampling bottles were pre-cleaned as follows; after washing with distilled water, they were filled with 3 N HNO_3 solution and left to stand for one week. After washing first with 3 N HNO_3 solution and then with distilled water ultrasonically, for 10 min respectively, the bottles were rinsed with doubly distilled water.

About 6 kg of snow samples were taken at each point and they were stored in the freezing room at $-20^{\circ}C$ until analyzed in the laboratory.

2.2. Analyses

Analytical procedure is shown in Fig. 2. Snow samples were melted at room temperature in the clean room (class 1000). After the sample bottle was agitated ultrasonically to prevent adsorption of element on the bottle wall, the melted water sample was immediately filtered with a membrane filter (Nuclepore, $0.4 \mu m$ pore size). The filtrate was concentrated using a rotary evaporator (NISHIKAWA *et al.*, 1985) to about 1000-fold and analyzed by inductively coupled plasma emission spectrometry (ICP-AES) (Jarrell-Ash, Model 975 Plasma Atomcomp) for B, Na, Mg, Al, Si, K, Ca, Ti, V, Mn, Fe, Cu, Zn, Sr, Cd and Pb, and by ion chromatography (I.C.) (Dionex,

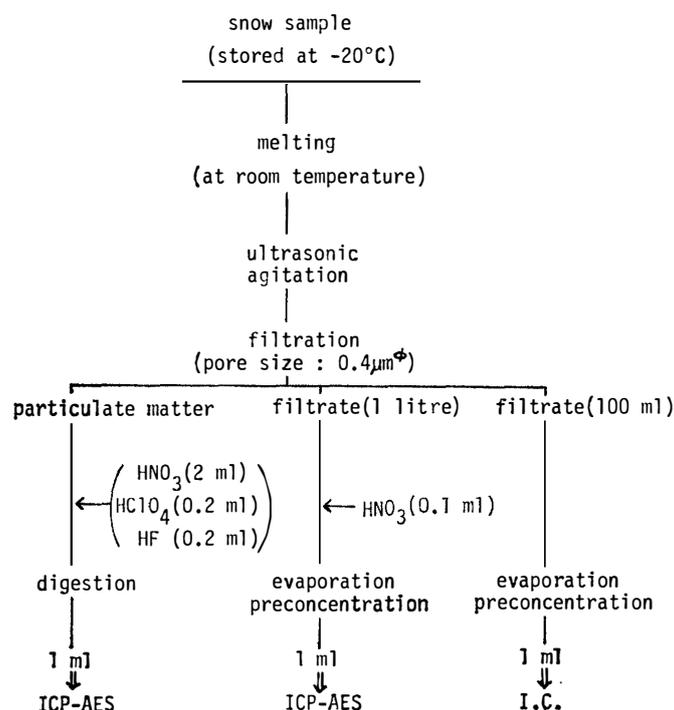


Fig. 2. Analytical procedure.

Table 1. Detection limits of elements after preconcentration.
ICP-AES (Jarrell-Ash, Model 975 Plasma Atomcomp)

Element	d.l.(ng/l)*	Element	d.l.(ng/l)*
B	1	V	3
Na	6	Mn	3
Mg	0.1	Fe	3
Al	10	Cu	2
Si	15	Zn	3
K	30	Sr	0.1
Ca	6	Cd	0.8
Ti	2	Pb	20

I.C. (Dionex, Ion Chromatograph Model 10)

Anion	d.l.(ng/ml)*	Anion	d.l.(ng/ml)*
Cl ⁻	0.8	SO ₄ ²⁻	1
NO ₃ ⁻	1		

*Detection limit (d.l.) is defined as concentration corresponding to twice the deviation of the background noise.

Preconcentration factor: ICP-AES (1000-fold), I.C. (100-fold).

Ion Chromatograph Model 10) for Cl⁻, NO₃⁻ and SO₄²⁻. After the particulate matter in the snow trapped on the filter was weighed under the condition of 50% relative humidity and 20°C temperature (NISHIKAWA *et al.*, 1983), it was digested with HNO₃+HClO₄+HF (10 : 1 : 1) at 200°C for 2 hours and analyzed by ICP-AES. Detection limits of the elements by ICP-AES and I.C. methods, both including the preconcentra-

tion process, are shown in Table 1. The precision for the value over 10 times of detection limit was within 5%.

3. Results and Discussion

3.1. Concentration of the elements in surface snow

The results of analyses are shown in Table 2. While Na, Mg, K, Ca, V, Cu, Zn, Sr, Cd and Pb are mostly in soluble form in the snow, a major portion of Al, Ti and Fe is in particulate form. As for Mn, nearly half of it is in soluble form, which resembles those observed for the rain water in Japan (AMBE and NISHIKAWA, 1985). Though no analysis has been performed, Cl^- , NO_3^- and SO_4^{2-} in these samples are considered to be in soluble form, and Si is mainly in particulate form. It is found that at Tottuki Point, the concentration of Na, Mg, Ca, Cl^- and SO_4^{2-} in soluble form shows a higher value than those at S16 point, reflecting the contribution of seasalt.

Table 2. Concentrations of chemical constituents in the surface snow near Syowa Station, Antarctica.

	unit($\mu\text{g}/\text{l}$)			
	Tottuki Point (28 April 1982)		S16 (19 August 1982)	
	Soluble	Insoluble	Soluble	Insoluble
Na	490	<0.2	430	<0.2
Mg	61	0.21	52	0.27
K	26	0.14	26	0.21
Ca	20	0.10	17	0.23
Cl^-	850	—	760	—
NO_3^-	(40)	—	(80)	—
SO_4^{2-}	120	—	95	—
B	0.42	—	0.18	—
Si	0.67	—	1.6	—
Al	0.34	0.57	0.75	0.86
Ti	<0.009	0.19	<0.009	0.13
V	0.031	<0.002	(0.009)	<0.002
Mn	0.023	0.009	0.019	0.012
Fe	0.22	0.70	0.53	1.8
Cu	0.065	(0.004)	0.080	(0.004)
Zn	0.34	0.015	0.90	0.022
Sr	0.35	(0.001)	0.30	(0.002)
Cd*	(0.001)	<0.001	(0.003)	<0.001
Pb*	0.046	<0.02	0.090	<0.02
pH	5.4		5.3	

* Determined by graphite furnace atomic absorption spectrometry.

3.2. Comparison of this work with those done at other places in Antarctica

As the concentration of elements in snow at the other points in Antarctica has been expressed as a total of soluble and insoluble forms, the comparison is performed on the same parameters as shown in Table 3. The concentrations of major elements (Na, Mg, K, Ca, Cl^- and SO_4^{2-}) in the snow in the area near Syowa Station are nearly similar or in the same order with those at Dome Dalinger and at D 10, both situated near the

coast. Trace elements (Al, Mn, Fe, Cu and Pb) are approximately in the same level with those at the South Pole and Dome C, excepting that Zn is higher by 10 times. Thus, the concentrations of major elements in the snow near the coastal area are higher than those in the inland area. Trace elements, on the other hand, show comparatively uniform distribution without much difference in concentration all over the land. As regard the cause of extraordinarily high concentration of Zn in the snow near Syowa Station, some question remains as yet whether it is true or any contamination occurred in the process of analysis or sampling.

Table 3. Comparison of elemental concentrations in the surface snow, Antarctica.

	unit ($\mu\text{g}/\text{kg}$)					
	South Pole ¹⁾	Dome C ²⁾	Dome	D10 ⁴⁾	This work	
	1976	(74°S, 124°E) 1971-74	Dalinger ³⁾ (64°S, 58°W) 1978	(67°S, 138°E) (1974)*, 1978	Tottuki Point 1982	S16
Na	9.1	17.9	397	(439)*	490	430
Mg	1.07	2.77	—	15.5	61	52
K	0.76	1.06	10.2	13.9	26	26
Ca	0.62	1.00	7.6	11.6	20	17
Cl ⁻	—	—	773	(646)*	850	760
SO ₄ ²⁻	—	—	—	92	120	95
Al	0.66	1.14	40.4	—	1.1	1.6
Mn	0.0063	0.018	—	—	0.03	0.03
Fe	0.39	1.24	—	—	0.92	2.3
Cu	0.025	0.062	—	—	0.07	0.08
Zn	0.072	0.047	—	—	0.36	0.92
Cd	0.010	0.019	—	—	(0.001)	(0.003)
Pb	0.028	0.041	—	—	0.05	0.09

¹⁾: BOUTRON (1982), ²⁾: BOUTRON and LORUIS (1979), ³⁾: ARISTARAIN *et al.* (1982), ⁴⁾: DELMAS *et al.* (1982).

* Measured in 1974.

3.3. Estimation of the origin of each element

In Table 4, ratios of the concentration of each element to Na in the snow samples and in seawater are shown in order to estimate the contribution of seawater. The ratios of soluble form of the elements in the snow above the broken line in Table 4 are nearly close to those of seawater, showing that these elements are derived from seawater through spray or as condensation nuclei. Regarding the elements below the broken line in Table 4, their origins can hardly be estimated by this analysis. From the relative concentration of each element to Al in the snow samples and in the average earth crust indicated in Table 5, it is found that the insoluble form of elements in the snow above the broken line on the table has nearly similar composition to that of earth crust, suggesting that the origin of the insoluble part of these elements is soil or rock on the land surface. However, the ratios of the total (soluble and insoluble) concentration of Na, Mg, K, Ca and Sr to Al show that the contribution of crustal material to the soluble form of these elements is very low.

In order to estimate the origin of each element, enrichment factors of element X are calculated as follows;

Table 4. Comparison of the concentration ratio (X/Na) of the sample with that of seawater.

	Tottuki Point		S16		Seawater*
	Total	Soluble	Total	Soluble	
Mg	0.125	0.124	0.122	0.121	0.12
K	0.053	0.053	0.061	0.060	0.037
Ca	0.041	0.041	0.040	0.040	0.038
Cl ⁻	1.73	1.73	1.77	1.77	1.8
SO ₄ ²⁻	0.24	0.24	0.22	0.22	0.25
B	—	9 × 10 ⁻⁴	—	4 × 10 ⁻⁴	4.1 × 10 ⁻⁴
Sr	7 × 10 ⁻⁴	7 × 10 ⁻⁴	7 × 10 ⁻⁴	7 × 10 ⁻⁴	7.2 × 10 ⁻⁴
NO ₃ ⁻	0.08	0.08	0.2	0.2	3.9 × 10 ⁻⁵
Al	2 × 10 ⁻³	7 × 10 ⁻⁴	4 × 10 ⁻³	2 × 10 ⁻³	9.3 × 10 ⁻⁸
Si	—	1 × 10 ⁻³	—	4 × 10 ⁻³	2.9 × 10 ⁻⁴
Ti	4 × 10 ⁻⁴	< 2 × 10 ⁻⁵	3 × 10 ⁻⁴	< 2 × 10 ⁻⁵	< 8.9 × 10 ⁻¹¹
V	7 × 10 ⁻⁵	6 × 10 ⁻⁵	2 × 10 ⁻⁵	2 × 10 ⁻⁵	1.1 × 10 ⁻⁷
Mn	6 × 10 ⁻⁵	5 × 10 ⁻⁵	7 × 10 ⁻⁵	4 × 10 ⁻⁵	1.0 × 10 ⁻⁹
Fe	2 × 10 ⁻³	5 × 10 ⁻⁴	4 × 10 ⁻³	1 × 10 ⁻³	3.6 × 10 ⁻⁹
Cu	1 × 10 ⁻⁴	1 × 10 ⁻⁴	2 × 10 ⁻⁴	2 × 10 ⁻⁴	1.2 × 10 ⁻⁸
Zn	7 × 10 ⁻⁴	7 × 10 ⁻⁴	2 × 10 ⁻³	2 × 10 ⁻³	3.6 × 10 ⁻⁸
Cd	2 × 10 ⁻⁶	2 × 10 ⁻⁶	7 × 10 ⁻⁶	7 × 10 ⁻⁶	6.6 × 10 ⁻⁹
Pb	1 × 10 ⁻⁴	1 × 10 ⁻⁴	2 × 10 ⁻⁴	2 × 10 ⁻⁴	1.9 × 10 ⁻¹⁰

* Seawater (NOZAKI, 1985).

Table 5. Comparison of the concentration ratio (X/Al) of the sample with that of earth crust.

	Tottuki Point		S16		Earth crust*
	Total	Insoluble	Total	Insoluble	
Na	450	< 0.2	270	< 0.2	0.35
Mg	56	0.28	33	0.27	0.26
K	24	0.19	16	0.24	0.32
Ca	19	0.14	10	0.27	0.45
Ti	0.17	0.25	0.81	0.15	0.054
Mn	0.03	0.01	0.02	0.01	0.012
Fe	0.84	0.93	1.5	2.1	0.62
Sr	0.32	0.002	0.19	0.003	0.0046
V	0.029	—	0.006	—	0.0017
Cu	0.0063	6 × 10 ⁻³	0.052	5 × 10 ⁻³	6.8 × 10 ⁻⁴
Zn	0.33	0.02	0.57	0.03	8.6 × 10 ⁻⁴
Cd	1 × 10 ⁻³	—	2 × 10 ⁻³	—	2.5 × 10 ⁻⁶
Pb	0.046	—	0.056	—	16 × 10 ⁻⁴

* Earth crust (Rika Nenpyō, 1980).

$$EF_{\text{sea}} = (X/Na)_{\text{snow}} / (X/Na)_{\text{seawater}},$$

$$EF_{\text{crust}} = (X/Al)_{\text{snow}} / (X/Al)_{\text{crust}},$$

where $(X/Na)_{\text{snow}}$, $(X/Na)_{\text{seawater}}$, $(X/Al)_{\text{snow}}$, $(X/Al)_{\text{crust}}$, are ratios of total concentration of element X to Na and Al in snow, seawater and crust, respectively. Na and Al are reference elements for seawater and materials derived from earth crust, respectively. Based on the magnitude of these enrichment factors, each element is

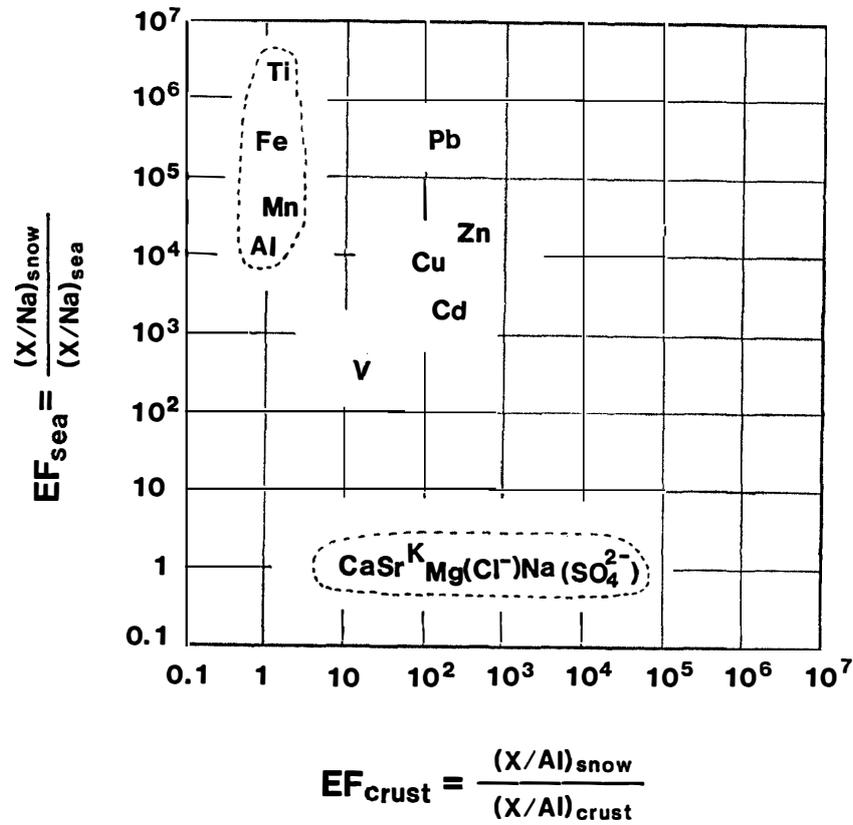


Fig. 3. Classification of elements in the surface snow at Tottuki Point.

plotted on a diagram as shown in Figs. 3 and 4. Both figures show a similar pattern of the distribution of elements. Three groups of elements are distinguished. The one consists of Na, Mg, K, Ca, Sr, Cl⁻ and SO₄²⁻ which lies on the line of $EF_{\text{sea}}=1$ showing their similarity to seawater. The second group is Fe, Al, Ti and Mn on the line of $EF_{\text{crust}}=1$ and these elements are considered to originate from crustal materials. Heavy metals like V, Cu, Pb, Cd and Zn have high values of both enrichment factors in the order of $10-10^6$.

The origin of these elements is not simple. BOUTRON and LORUS (1979) suggested some relationship between these elements and volcanic activity from the observation that the fluctuation of volcanic aerosol approximately corresponded to the fluctuation of EF_{crust} value of these elements in snow. Some reports (BOUTRON, 1979, 1982; GOLDBERG, 1976; KOIDE *et al.*, 1981; MAENHAUT *et al.*, 1979; NAKAYA, 1982; NAKAYA *et al.*, 1985; ZOLLER *et al.*, 1974) showed that EF_{crust} values of heavy metals such as Cu, Zn, Cd and Pb in aerosols in Antarctica were in the order of $10-10^4$ like those in the snow. Because the oxides of these elements have a high volatility, a certain fraction of the original source materials might escape into atmosphere as aerosols during emission process in the volcanic activity, resulting in some enrichment of these elements from crustal rock. Another possible source of these elements in the atmosphere may be human activity like combustion of fossil fuel, but no evidence has been obtained at present. Many further studies will be necessary to solve this problem.

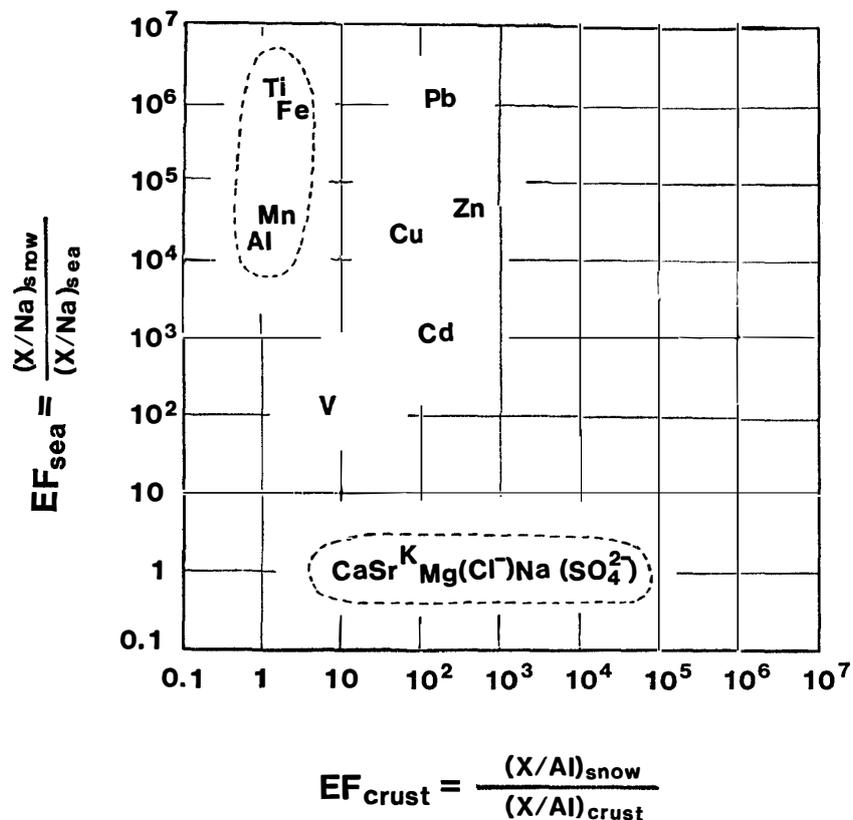


Fig. 4. Classification of elements in the surface snow at S16.

4. Conclusion

It is concluded that the major components in the surface snow in the area near Syowa Station are heavily affected by seawater. The concentrations of trace elements such as Al, Ti, V, Mn, Fe, Cu, Sr, Cd and Pb are nearly in the same level with those at the South Pole except for Zn. It is revealed that Al, Ti, Mn and Fe are derived mainly from earth crustal materials or soil. As to the origin of heavy metals in the snow, volcanic activity and fractionation process, human activity and other causes should be studied as a future problem.

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