

Distribution and Origin of Some Trace Metals in Lake Vanda, Antarctica

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南極バンダ湖の微量金属の分布とその起源

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要旨: 1978-79 年のフィールドシーズンに南極バンダ湖 (水深 68 m) で表層から底層まで 10 層の採水を行い, その微量金属 (Al, Fe, Ni, Cu) を定量した. 銅は塩素と同様な分布を示した. アルミニウムは水深によらずほぼ一定の値を示した. 鉄は 55 m 以浅ではほぼ一定の値を示すが, それ以深で急激な濃度増加が認められた. これは 3 価の鉄が底付近で還元され上方に拡散し, この過程をくり返したためと考えられる.

湖水中で大きな除去過程がない (対塩素比が水深によらずほぼ一定) と考えられる銅を微量金属の代表として, その起源を考察した. 湖水の Cu/Na 比は海水に比べ 3 桁以上高い値であり, また Cu/Na 比は南極点などの雪氷の値に近似しており, エーロゾル-降雪-氷河-氷河融水-バンダ湖の径路が微量金属の起源と考えられる.

Abstract: In 1978-79 field season, water samples were collected vertically at Lake Vanda. The concentrations of Al, Fe, Ni, and Cu were determined. The vertical profile of copper is similar to that of chlorinity. Aluminium has constant value from the surface to the bottom. The concentrations of iron are also constant from the surface to 55 m but below this layer iron increases abruptly. In the layer above 55 m, iron should be present as trivalent solid form and precipitated to the bottom where iron is reduced and diffused upward. This process could be repeated to account for the iron distribution of the observed profile.

Copper shows a good correlation with chlorinity which is not removed significantly in the lake. The copper to sodium ratio of sea water is three orders of magnitude smaller than that of deep water of the lake, which has a similar ratio to Antarctic snow. The data supports that the origin of copper is air-borne particles *via* glacier and glacial melt water.

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1. Introduction

A large ice-free area, referred to as the Dry Valleys area, exists in southern Victoria Land on the west side of the McMurdo Sound, Antarctica. The area consists of several east-west trending and glacially eroded valleys and intervening mountains. One of these deglaciated valleys, Wright Valley, remains essentially free of snow and ice all the year round, reflecting the arid climate of the area. This valley is blocked by the Wilson Piedmont Glacier 25 km east and the Upper Wright Glacier 17 km west of Lake Vanda.

Lake Vanda is situated in the west part of the Wright Valley, about 50 km west of the east coast of Victoria Land ($77^{\circ}32'S$, $161^{\circ}32'E$) and occupies the lowest part of the valley 95 m above sea level (Fig. 1). It is approximately 5.6 km long, 1.4 km wide and up to 68 m deep. The lake is permanently covered with 3 m thick ice. During the austral summer season, the lake is supplied with glacial melt water from the east by way of the Onyx River which drains mainly from the Wilson Piedmont Glacier. It has no outflow so that water is lost only by sublimation of the surface ice.

The unique distribution of major elements and nutrients in Antarctic saline lakes, especially for the Dry Valleys area, including Lake Vanda, Bonney, Fryxell and Don Juan Pond, have been reported by ARMITAGE and HOUSE (1962), TORII *et al.* (1975, 1979). They have also discussed the origin of these salts.

There have been few geochemical studies on trace metals in Antarctic saline lakes however. BOSWELL *et al.* (1967a, b) reported some trace metal values of the bottom water in six lakes of the Dry Valleys area and discussed the origin of trace metals. SANO *et al.* (1977) reported the vertical distributions of six metals in Lake Nurume near Syowa Station and discussed the chemical form of trace metals. WEAND *et al.* (1976) reported the short period variation of some trace elements in Lake Bonney. But the origin of trace metals is still not clear. This study presents data on the vertical distributions of Al, Ni, Fe and Cu in Lake Vanda and discusses the reasons for their distributions and the origin of these trace metals.

2. Sampling

Samples were taken in the austral summer season (7-9 Jan. 1979) when the Onyx River had already begun flowing into Lake Vanda. They were taken at site R. (Fig. 1) with the 1 litre Kitahara type water sampler made of stainless steel. 1 litre samples were taken at depths of 4, 10, 20, 30, 40, 45, 50, 55, 60 and 64 m for trace metals, another 1 litre for dissolved oxygen, alkalinity, electric conductivity, pH, and hydrogen sulfide. Samples were immediately poured into 1 litre polyethylene bottles for trace metals. Acid-washed polyethylene bottles were used and hydrochloric acid was added

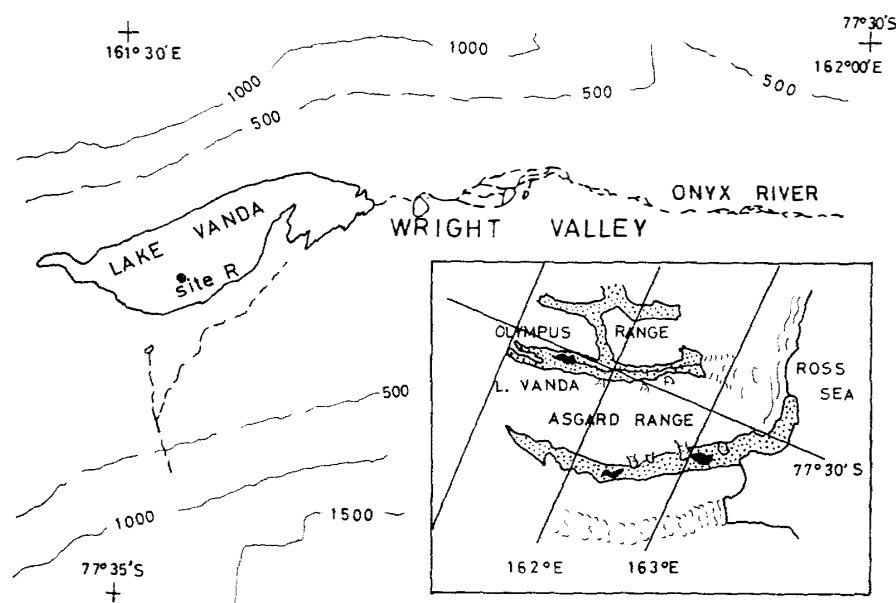


Fig. 1. Location of Lake Vanda and sampling point.

to keep the samples at pH 1.5–1.8. Then the bottles were wrapped in polyethylene bags to prevent contamination from air during transportation and storage.

In situ temperature was measured by a hanging thermister and the conductivity was measured by an electric conductivity meter immediately after sampling.

3. Chemical Analyses

- 1) Dissolved oxygen was determined at the field camp by the Winkler method.
- 2) Alkalinity was measured by titration of 1/10 N hydrochloric acid with an indicator of bromocresol green at pH 4.3.
- 3) Hydrogen sulfide was determined by the cadmium sulfide precipitation method.
- 4) Trace metal concentrations were determined by atomic absorption spectrometry after solvent extraction. Copper, iron, aluminium and nickel were extracted in the laboratory with 8-hydroxyquinoline(Oxine)-1, 2-dichloroethane followed by back extraction with 2 M nitric acid. The extracted metals in nitric acid were determined by flameless atomic absorption spectrometry.

Dissolved oxygen and alkalinity were determined at the field camp, and hydrogen sulfide fixation was made at the sampling site.

4. Results and Discussion

The analytical results of trace metals in Lake Vanda are listed in Table 1 together with chlorinity, temperature, dissolved oxygen, alkalinity, electric conductivity, hydrogen sulfide and pH.

Chlorinity increases abruptly from 45 m to the bottom and the maximum concentration is about four times higher than that of sea water. The distribution of chlorinity (Fig. 2) is considered to be controlled by the diffusion from preconcentrated

Table 1. Analytical results in Lake Vanda.

Depth (m)	Conductivity ($\mu\Omega/\text{cm}$ at 18°C)	pH	Temperature ($^\circ\text{C}$)	Dissolved oxygen (ml/l)	Alkalinity (meq/l)	Aluminum ($\mu\text{g/l}$)	Iron ($\mu\text{g/l}$)	Copper ($\mu\text{g/l}$)	Nickel ($\mu\text{g/l}$)
4	6.7×10^2	7.60	4.85	12.5	1.32	6.4	16.4	37.4	20.0
10	5.9×10^2	7.83	5.0	13.2	1.09	7.8	15.6	10.6	8.9
20	1.0×10^3	7.70	7.2	16.5	1.20	9.8	19.2	16.9	8.9
30	1.0×10^3	7.88	7.2	—	1.25	6.0	11.2	24.4	6.7
40	1.0×10^3	7.95	7.2	16.3	1.25	8.1	18.0	29.1	6.7
45	1.8×10^3	7.75	8.8	14.2	1.42	9.9	32.0	30.1	13.3
50	4.3×10^3	7.10	11.8	13.7	1.50	11.2	22.0	74.8	11.1
55	3.8×10^4	5.92	18.3	11.7	2.05	8.1	14.0	650	37.7
60	7.8×10^4	5.81	22.9	0.83	3.54	12.7	196	1040	75.1
64	9.1×10^4	5.72	24.1	0.0	4.63	8.1	540	900	189

H_2S (mg/l): 58.9 m 2.98, 60.8 m 3.11, 61.7 m 21.4, 64.6 m 40.0, after TORII *et al.* (1975).

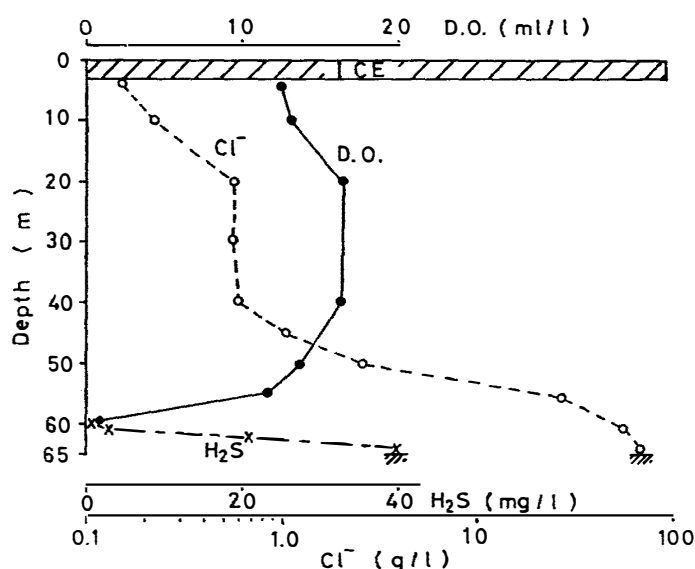


Fig. 2. Vertical distributions of chlorinity, dissolved oxygen and hydrogen sulfide.

bottom water (WILSON, 1964). The temperature profile is similar to the chlorinity profile and the highest value, about 24°C, is observed near the bottom.

The heat source of the lake is believed to be trapped solar energy, not volcanic activity, nor hydrothermal activity (YUSA, 1975). From the surface layer to 55 m, there exists dissolved oxygen but its value is very low at 60 m, and hydrogen sulfide is observed at 60 and 64 m.

4.1. Copper

Data for copper is listed in Table 1 and the vertical profile is presented in Fig. 3. The copper concentration at 4 m (37.4 $\mu\text{g/l}$) is slightly higher than at 10 and 20 m layers. This can be explained as the Onyx River supplies (28.6 $\mu\text{g/l}$) to a zone just below the ice cover, so the copper derived from inflow will contribute to the near surface layer. Another possible effect is related to the sublimation of the ice cover. Ice is sublimated at a rate of about 30 cm/yr and if it is in a steady state, ice is formed beneath the ice cover at the same rate and the copper should be left behind to enrich the water just below the ice. The same phenomenon is observed also on conductivity (Table 1). If the two effects were combined, it would cause the higher concentration.

Except for 4 m, the concentration increases gradually from 10 m (10.6 $\mu\text{g/l}$) to 40 m (29.1 $\mu\text{g/l}$) and increases abruptly from 45 m (30.1 $\mu\text{g/l}$) to the bottom (900 $\mu\text{g/l}$). The profile is very similar to that of chlorinity. This relationship is shown in Fig. 4, with a good correlation except for the surface layer. This good correlation indicates that copper behaves together with chloride.

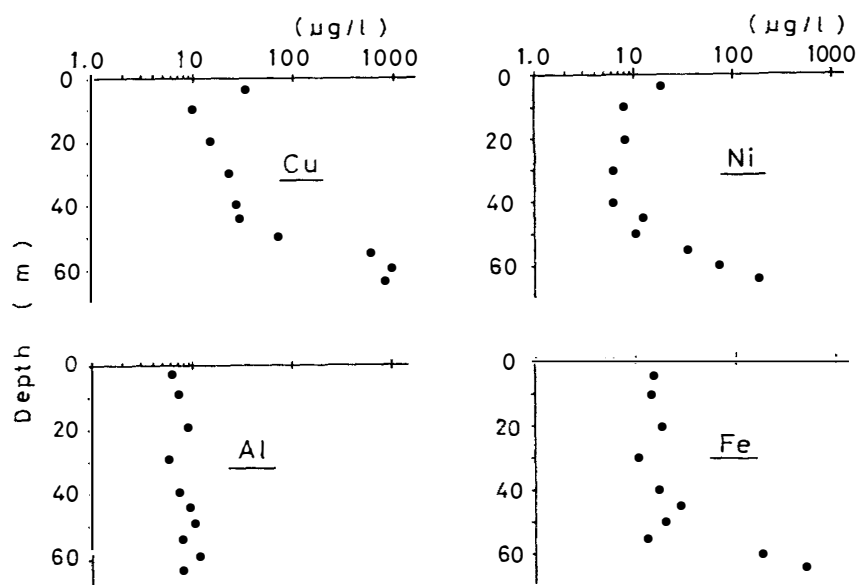


Fig. 3. Vertical distributions of copper, nickel, aluminium and iron.

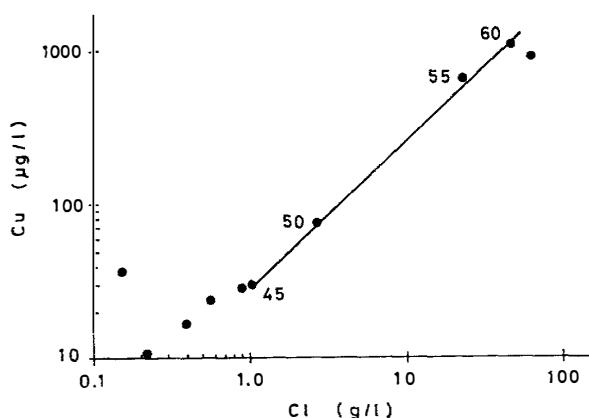


Fig. 4. Relation between copper and chlorinity.

4.2. Nickel

The vertical profile of nickel concentrations is presented in Fig. 3. The nickel concentration at surface 4 m ($20.0 \mu\text{g/l}$) is high. This phenomenon is the same as copper and electric conductivity. The same explanation as that for copper is applicable to this phenomenon. Concentrations are almost constant from 10 to 40 m, but increase abruptly from 45 m ($13.3 \mu\text{g/l}$) to the bottom ($189 \mu\text{g/l}$). The Ni/Cl ratios are presented in Fig. 5. If nickel has been diffused simply from the highly concentrated palaeolake-water (WILSON, 1964) in a same manner as chloride, the plots of the Ni/Cl ratios in deep water should come on the straight line at an angle of 45° (dilution line) in the log-log plot. The dotted line in Fig. 5 indicates an ideal dilution line. The Ni/Cl ratios observed are not linear and there would be a removal process of nickel in Lake Vanda. But the removal mechanism and the rate are not clear.

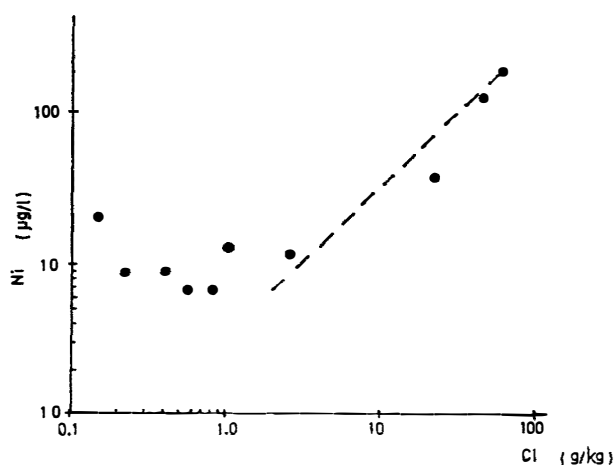


Fig. 5. Relation between nickel and chlorinity.

4.3. Iron

The vertical profile of iron concentration is presented in Fig. 3. From the surface to 55 m, the values show little systematic variation, with an average of $19 \mu\text{g/l}$. But below this layer, concentrations increase abruptly, from 55 m ($14.0 \mu\text{g/l}$) to the bottom ($540 \mu\text{g/l}$). Iron data are plotted against chlorinity in Fig. 6. Above the 55 m depth, the iron concentrations are nearly constant whereas the chlorinity content increases with depth. From the surface to 55 m, the dissolved oxygen is sufficient but in deeper layers, 60 and 64 m, the dissolved oxygen is almost depleted and hydrogen sulfide is found in the layers (Fig. 8). In the layers above 55 m, iron should be present as tri-valent hydroxide or suspended terrestrial particles in the state of insoluble Fe(III) from rock weathering.

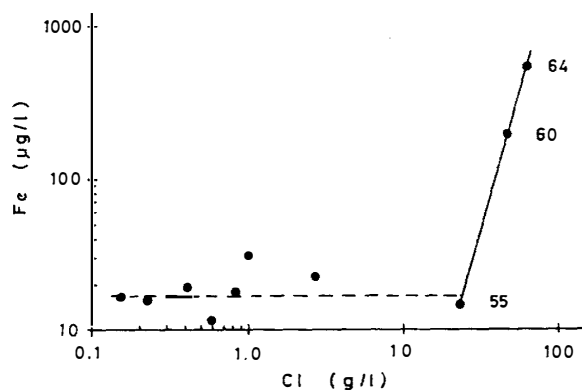


Fig. 6. Relation between iron and chlorinity.

On the other hand, in the layers below 60 m where hydrogen sulfide is found, the environment is so reductive that iron exists as soluble Fe(II). Iron would occur as ferrous ion in those layers. The stable form of iron is discussed thermodynamically based on the data of pH, total iron and hydrogen sulfide contents.

In the 60 m layer, calculated ion products are smaller than the solubility products constant ($[\text{Fe}^{2+}][\text{S}^{2-}] < K_{sp}$), so iron sulfide would not be precipitated. In the 64 m layer, calculated ion products and solubility products constant of iron sulfide are as follows:

$$\text{calculated ion products} \quad ([\text{Fe}^{2+}][\text{S}^{2-}]) = 2.4 \times 10^{-17},$$

solubility products of

FeS

$$K_{sp}(\text{FeS}) = 0.5 - 5.0 \times 10^{-17}.$$

(ionic strength 3.3)

The ionic strength is calculated on the data after TORII *et al.* (1975). No *a priori* theoretical method is available for the calculation of individual ion activities in highly

concentrated saline water. On the calculation of $K_{sp}(\text{FeS})$, the ion activity coefficient of ferrous ion is estimated ($\gamma_{\text{Fe}^{2+}} = 1.1$) by the mean salt method (GARRELS and CHRIST, 1965; LATIMER, 1964). The range of sulfide ion activity coefficient is assumed from 0.1 to 1.0 (STUMM and MORGAN, 1970). The iron concentration is almost saturated and it thus seems that iron concentration would be controlled by the equilibrium with iron sulfide.

In the upper layer, weathered particles derived from runoff are precipitated to the bottom where they are reduced and released as divalent iron from the bottom sediment or just above the bottom. Divalent iron (dissolved form) is diffused upward by molecular diffusion like chloride (WILSON, 1964). The concentration of dissolved divalent

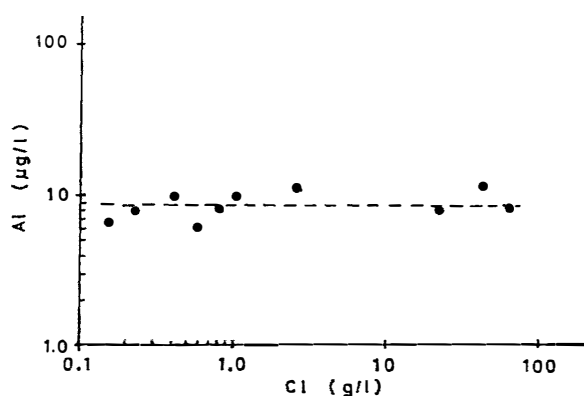


Fig. 7. Relation between aluminium and chlorinity.

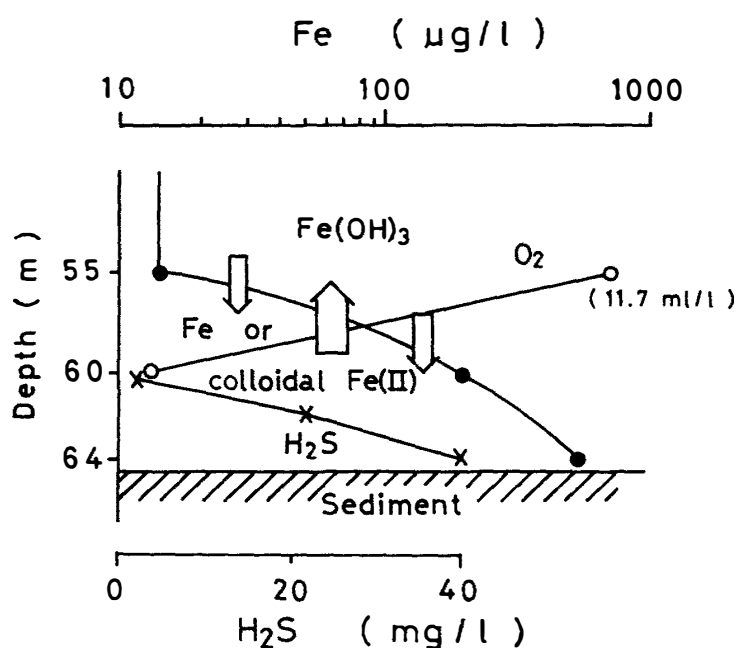


Fig. 8. Possible form of iron in the boundary layer of reduction and oxidation.

iron (Fe^{2+}) is controlled by the equilibrium of pH, S^{2-} and iron sulfide. Diffused divalent iron is re-oxidized in the upper layer, changed to solid form (Fe(III)) and is re-sedimented to the bottom. This process could be repeated to produce the iron distribution of the observed profile.

4.4. Aluminium

The vertical profile of aluminium is presented in Fig. 3 and aluminium against chlorinity is in Fig. 7. The profile is very different from those of copper, nickel and iron. The concentration of aluminium is nearly constant (about $9 \mu\text{g/l}$) at all depths.

Aluminium in the lake water would be derived from the Onyx River in fine weathered particles. Inflow water from the Onyx River spreads just beneath the ice cover and fine weathered particles will constantly be sedimented to the bottom. Aluminium would not be dissolved even under the reducing condition of Lake Vanda's deep water, and could not be diffused upward. Therefore, aluminium has a nearly constant concentration from the surface to the bottom of the lake.

4.5. Origin of trace metals

Three possible origins of trace metals are considered:

- 1) Trapped sea water.
- 2) Inflow of ground water.
- 3) Deposition of air-borne particles.

The DVDP (Dry Valleys Drilling Project) studies provide evidence that in the Miocene period there was a fjord in the Wright Valley (BRADY, 1979). NAKAI *et al.* (1975a, b) concluded from isotope study that the sulfate in Lake Vanda was derived directly from the ocean. Results obtained for trace metals do not seem to agree with this because the ratios of trace metals to chlorinity or sodium are so different from those of sea water. For example the Cu/Na ratio in water of Lake Vanda is greater by three orders of magnitude than that of sea water. It can not be possible that sodium has been mostly removed in the lake and trace metals still remain. So, trapped sea water would not be the main origin of trace metals in Lake Vanda.

If the ground water inflow to the lake was sufficiently large and trace metal contents were high enough, the ground water might play a major role on the origin of trace metals in Lake Vanda. NAKAI *et al.* (1975a, b) also studied oxygen isotopes in the lake water and concluded that the present-day lake water is derived from glacial melt water. The ground water also may be derived from glacial melt water. But, there is no available data on the trace metal contents of ground water. Ground water may play some role on the origin of trace metals.

Because air-borne particles are considerably enriched in metals compared with major sea salt (DUCE *et al.*, 1975), such particles could supply metals to the polar ice

either by dry fallout or precipitation. In fact, high ratios of metals to sodium are observed for Antarctic ice and snow (MUROZUMI *et al.*, 1969; BOUTRON, 1979; BOUTRON and LORIUS, 1979).

Glacial melt water flows into the lake *via* the Onyx River, so it is possible that air-borne particles could supply trace metals to Lake Vanda. This source of metals from air-borne particles will then be examined in more detail.

Table 2. Comparison of Cu/Cl and Cu/Na ratios in Lake Vanda bottom water.

	Cl ($\mu\text{g/l}$)	Na ($\mu\text{g/l}$)	Cu ($\mu\text{g/l}$)	Cu/Cl	Cu/Na
Sea water	1.987×10^7	1.105×10^7	0.6	3.02×10^{-8}	5.43×10^{-8}
Antarctic snow					
South Pole ¹⁾		8.0	1.2×10^{-2}		1.6×10^{-8}
Dome C. ²⁾		20.5	5.0×10^{-2}		2.4×10^{-8}
Onyx River at weir	³⁾ 6.9×10^8	³⁾ 6.2×10^8	28.6	4.1×10^{-3}	4.6×10^{-3}
Lake Vanda bottom water	6.97×10^7	³⁾ 6.67×10^8	1.04×10^3	1.4×10^{-5}	1.6×10^{-4}

¹⁾ BOUTRON *et al.* (1977). ²⁾ BOUTRON and LORIUS (1979). ³⁾ TORII *et al.* (1975).

Copper shows a good correlation with chlorinity which is not removed in the lake. Thus, copper can not have been removed significantly. The result also indicates that the ratio of copper to chlorinity in the deep water of the lake should be equal to the original ratio. Concentrations of chlorinity, sodium and copper are listed in Table 2, together with the copper to chlorinity ratio and the copper to sodium ratio. The copper to sodium ratio of sea water ($\text{Cu/Na} = 5.4 \times 10^{-8}$) is three orders of magnitude smaller than that of the hypolimnetic deep water of the lake ($\text{Cu/Na} = 1.6 \times 10^{-4}$), which has a similar ratio to Antarctic snow (South Pole snow $\text{Cu/Na} = 1.6 \times 10^{-8}$, Dome C. $\text{Cu/Na} = 2.4 \times 10^{-8}$). The ratio of copper to sodium, in the lake is also similar to that of the Onyx River. The data therefore support the conclusion that copper came from air-borne particles. Air-borne particles were brought to glacier either by precipitation or by dry fallout, and glacial melt water carried the metal-enriched particles to Lake Vanda *via* the Onyx River.

Major elements such as chloride, sodium, calcium and sulfur could still be derived from trapped sea water. If chloride and sodium concentrations were increased ten times by adding sea salt, the concentration of copper in the lake would increase less than one hundredth. The two origins may thus be independent of each other.

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