Geochemical Features of Antarctic Lakes

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南極湖沼の地球化学的特徴

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要旨: 南極オアシスの湖沼の多くは氷河，降雪の融氷水によって涵養されているが，大陸沿岸の塩湖には海水と同様の化学組成比を示す海跡湖がある．マクマードオアシスのような山岳オアシスの塩湖では，湖底堆積物および溶存塩類は海水起源であり，涵養水は氷河融氷水である．このような塩湖は地質時代を通じて蒸発乾固に近い状態になり，これが融氷水で抽出され現在の湖沼を形成したものと考えられる．海水より著しく塩分濃度の高い塩湖は，海水が低温下で濃縮されたものを源にしていると推定される．塩湖の硫化水素，栄養塩の分布，有機炭素の含有量，脂肪酸の含有量，メタン，窒素などの気体の存在は，塩湖における微生物の活動を示唆するものであり，昭和オアシスの湖沼中の銅，亜鉛，鉛，カドミウムの存在度とその相対比から，これらの元素は降雪起源であり，人為的寄与も加わっている可能性が示された．

Abstract: Geochemical investigations of Antarctic lakes have been carried out on major components, nutrient matters, stable isotopes and organic substances in waters in order to clarify the geochemical features of the lakes.

The present waters of inland lakes are supplied from the melt water of glacier or snow. But the waters of saline lakes on the coast of the continent have originated mainly from the sea water, for example Lake Nurume, Lake Hunazoko (Syowa Oasis) and Lake Fryxell (McMurdo Oasis). The isotopic compositions of waters in some lakes such as Lake Vanda, are similar to that of the snow or melt water of the glacier, while the isotopic composition of sulfur in the salt deposited or dissolved in the lake is similar to that of the sea origin sulfur compound.

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The water of highly saline lakes should have been produced in the process of concentration of the sea water under a frigid condition. For some of the lakes, it is considered that the water was evaporated once or several times and the residue were extracted with melt water of glacier.

From the contents of organic substances, nutrient matters and gases in the lake, activity of microorganisms is suggested in some of the lakes.

In view of the abundance and relative ratios of some heavy metal elements, such as copper, zinc, lead and cadmium, these elements should have been supplied from snow.

1. Introduction

Geochemical investigations of ponds and lakes have been carried out in the areas around Syowa Station, East and West Ongul Islands, Langhovde, Skallen, etc., since the International Geological Year. On the other hand, limnological surveys of the McMurdo Oasis began in December 1963, and during the successive seasons, many field surveys of the area, especially of the Dry Valleys in the southern part of Victoria Land, were carried out by Japanese summer parties.

Research program of environmental sciences was started in 1974, and the investigations of environmental substances pursued at Syowa Station and at Mizuho Camp. The determinations of minor elements in lakes, ice, and air were carried out in the laboratory at Syowa Station. Determination of the abundance of the elements in Antarctica is to get the background information of the elements on the earth. But lately, the purpose has been expanded to include the surveillance of the environment.

A symposium on the geochemistry in Antarctica was held on 28th and 29th of July, 1976. This report is a summary of the results of limnological surveys on Antarctic lakes. To know the general features of Japanese geochemical activities in Antarctica, one may refer to the work of WATANUKI (1975).

2. Lakes in the Oases

Many small ice-free areas scattered throughout the Antarctic are often called oases. They are of special geological and geochemical interest because of the fact that in contrast with the rest of the white continent they display outcrops of bedrock and sediment through which the geological history of the continent can be examined.

In these oases, there are many ponds and lakes the waters of which contain salt in various amounts ranging from 100 mg/*l* to 390 g/kg. For the interest of the geological history of the lakes, the lakes in the Dry Valleys were investigated by Japanese geochemists (NAKAI, 1975; TORII, 1975). There are many fresh water ponds and saline lakes around Syowa Station, in East and West Ongul Islands, at Skarvsnes, Skallen and Langhovde. These ponds or lakes were investigated by many scientists (WATANUKI, 1963;

SUGIMURA, 1971).

In general, the lakes with waters supplied by large amounts of melt water of continental glacier or snow are fresh water lakes. The waters of those lakes freeze in winter and melt in summer.

Saline lakes are located in glaciated ice-free valleys or on the coast of the continent. In these lakes, the amount of inflow water is balanced to that of outflow water, or the amount of inflow water is balanced to that of evaporation from the surface.

3. Saline Lakes

Characteristic features of saline lakes in Antarctica are summarized in Table 1. Surface of the lakes located on the coast of the continent is generally below sea level, and mirabilite ($Na_2SO_4 \cdot 10H_2O$) and calcite ($CaCO_3$) were found near the shoreline, and also marine fossils were collected there.

Table 1. Characteristic features of saline lakes in Antarctica.

Type of lake	Geological features		Geochemical features		
	Lake surface	Deposits	M/Cl	Stable isotope	Neutrient
Lakes on the coast of the continent	Below sea level	Mirabilite Calcite Fossil shell	Chloride type similar to sea water	δD $\delta^{18}O$ resemble sea water	Similar to sea water
Saline lakes in the Dry Valleys	$+12\sim122$ m from sea level	Mirabilite Calcite Halite Gypsum Na-niter	Chloride type different from sea water	δD $\delta^{18}O$ enriched light isotope resemble melt water of snow	Rich in N-comp.

From the analytical results of the chemical composition of lake water, the saline lakes near the coast are considered to be of sea origin. The chemical composition of water in these lakes is similar to that of sea water. Correlation numbers calculated by concentration matrix between chemical components of the lake water and those of sea water suggest a high correlation among these water systems. For example, correlation number is 1.00 for Lake Nurume, and 0.67 for Lake Hunazoko. Mirabilite was found at the bottom of Lake Hunazoko, and the correlation number excluding the term concerning sulfate ion, becomes 1.00 for the lake. This result shows that the chemical composition of the lake water deviated from sea water only in sulfate ion due to the deposition of mirabilite.

From the concentration of the salt in water and the correlation between the lakes and sea water stated above, it may be concluded that the water of Lake Hunazoko is older than that of Lake Nurume. In other words, Lake Nurume is the first stage of saline lake originated from sea water and Lake Hunazoko is the second one in the evolution process, and it produces mirabilite at the bottom.

Lake Fryxell in the Dry Valleys is also considered to be of sea origin, but the correlation to sea water is poor because of the influence of inflow water from glacier.

Table 2. Chemical composition of some saline lakes in Antarctica (g/kg).

Locality	Na	K	Ca	Mg	Cl	SO_4
Lake Fryxell	2.84	0.20	0.13	0.34	3.87	0.12
Lake Hunazoko*	58.2	2.40	2.22	7.87	116.6	2.47
Lake Nurume*	10.4	0.46	0.41	1.15	17.14	2.34
Lake Vanda (63 m)	6.5	0.73	22.7	7.17	72.2	0.64
Lake Bonney (west 5 m)	0.38	0.014	0.056	0.068	0.733	0.114
Lake Bonney (east 5 m)	0.29	0.018	0.012	0.067	0.769	0.111
Lake Bonney (west 29.5 m)	32.1	1.47	1.48	8.34	78.12	4.45
Lake Bonney (east 29.5 m)	43.5	2.69	1.11	23.70	141.3	2.85
Don Juan Pond**	2.16	0.23	132.2	2.6	247.1	0.00
Sea water	10.8	0.39	0.41	1.29	19.4	2.7

* Syowa Oasis, ** Collected in 1963.

Surface of the lakes located in the Dry Valleys or glacial trough is above sea level (12~120 m). Mirabilite, calcite, halite (NaCl) and gypsum ($CaSO_4 \cdot 2H_2O$) were found near the lakes. The analytical results of chemical composition of the saline lake waters are shown in Table 2. The composition of chemical components in the lake waters is different from sea water. For example, correlation number calculated between the chemical components of Lake Vanda water and those of sea water is 0. But it does not mean that there is no relation between Lake Vanda and the sea.

The relationships among sodium, magnesium and calcium concentrations in the lake waters in milliequivalent, are shown in Fig. 1. Figures 1, 2, 3, 4, 5, and 6 correspond to Don Juan Pond, saline lakes in West Ongul Island, Lake Fryxell, saline lakes in Syowa Oasis, Lake Bonney and Lake Vanda, respectively. The arrow line shows the evolution of sea water under a frigid condition after THOMPSON and NELSON (1956).

If sea water is evaporated by heat, small amounts of hydrous ferric oxide and calcium carbonate appear at first, and successive deposition occurs in the order of gypsum, halite, and complex salt of potasium and magnesium. But on the concentration process of sea water in a frigid condition, the order of salt deposition is quite different.

When the concentration occurs under a frigid condition, a small amount of calcium carbonate appears at first, and mirabilite is formed next at −8.2°C. The content of

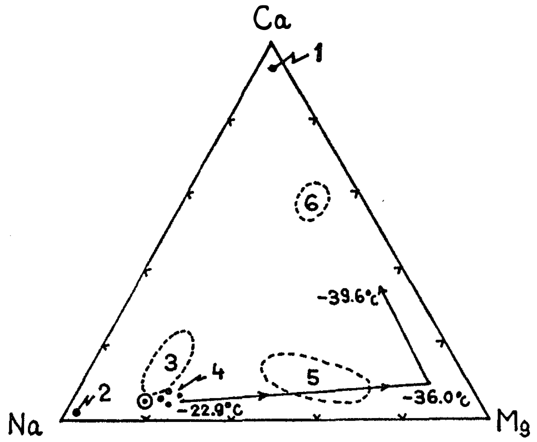

Fig. 1. Na–Ca–Mg diagram of saline lakes in Antarctica in milliequivalent.
1. Don Juan Pond, 2. Saline lakes in West Ongul, 3. Lake Fryxell, 4. Saline lakes in Syowa Oases, 5. Lake Bonney, 6. Lake Vanda, ⊙ Sea water.

sodium ion in sea water is 10.8 g/kg and that of sulfate ion is 2.7 g/kg. And the decrease of sodium ion concentration in sea water is not so large in the stage of the deposition of mirabilite. At −22.9°C sodium chloride dihydrate ($NaCl \cdot 2H_2O$) is formed and the decrease of sodium ion becomes larger, so that the relative increases of calcium, magnesium, potassium and chloride ions occur in the residual solution. At −36°C magnesium chloride dodecahydrate ($MgCl_2 \cdot 12H_2O$) is formed with the coprecipitation of potassium chloride (KCl), and the residual solution becomes rich in calcium and chloride ions. In the process stated above, the calcium-chloride water should be formed as the residual solution.

Calcium chloride concentrated water, such as the water of Don Juan Pond, should have been derived from sea water under a frigid condition with the addition of salt from weathered rocks or leached salt deposit.

The data of correlation revealed that the water of the east lobe of Lake Bonney is different in origin from the water of the west lobe of the lake. The correlation numbers between the lakes and the sea are as follows: 0.60 (W 5 m–E 5 m), 0.20 (W 29.5 m–E 29.5 m), 0.40 (W 29.5 m–seawater) and 0.13 (E 29.5 m–seawater), in which W and E indicate west and east lobes of the lakes respectively and the numerals are the depths where the water was taken.

4. Fresh Water Lakes

There are many fresh water lakes in the Antarctic Oases, and their water is supplied from melt water of glacier or snow. Chemical compositions of these lake waters, as shown in Table 3, are similar to those of the melt water. Correlations of chemical components among the fresh water systems are high, especially within the same area.

Table 3. Chemical composition of some fresh water lakes (mg/l).

Locality	Na	K	Ca	Mg	Cl	SO_4
Lake Ô-ike (West Ongul)	48.5	2.0	5.0	6.2	86.0	15.0
Lake Skallen Ôike	35.5	2.3	7.4	6.1	60.3	—
Skua Lake (Ross Island)	108.0	9.6	7.1	15.4	221.0	41
Blue Lake (Ross Island)	15.5	3.2	1.1	0.9	30.5	—
Lake Miers (Miers Valley)	3.0	2.5	16.6	2.3	14.4	39.5
Onyx Pond (Wright Valley)	9.0	3.3	14.4	3.8	21.6	9.7

At the Syowa Oasis, melt water often makes a stream in summer, and along the stream biological activity is noticed in the summer season at almost the same place every year.

The chemical composition of the fresh water lakes cannot be explained by air-borne salt only, and some contribution from weathering of rock by biological activity must be considered.

Because of the reason stated above, biological researches must be carried out in parallel with geological and geochemical researches.

5. Stable Isotopes in Lake Water

As shown in Table 1, the stable isotopic compositions of water, δD or $\delta^{18}O$, in the saline lakes located near the coast resemble those of sea water. The main portion of the saline water is considered to be of marine origin. And δD and $\delta^{18}O$ of fresh water collected on the coast of the continent or around Syowa Station are similar to those of snow. The fresh lake water should be supplied from precipitation.

The $\delta^{18}O$ values of the water of Lake Vanda in the Dry Valleys are small, ranging from -30.3 to -31.9‰ in SMOW scale, while $\delta^{18}O$ value of snow collected on the ice shelf near McMurdo Station is $-32\sim-34$‰. The very small values for the lake suggest that the lake water is not marine origin because the $\delta^{18}O$ of the ocean water is almost constantly 0‰.

The $\delta^{34}S$ value of sulfate ion in the lake is $20.4\sim20.9$‰, and this approximates the value of marine origin sulfate. The difference of $\delta^{34}S$ between sulfate ion and coexisting hydrogen sulfide in the lakes is $34.4\sim33.5$‰. Such large fractionation cannot be explained by high-temperature products of volcanic activity, and hydrogen sulfide should have been produced by activity of bacteria. Considering the above results it can be concluded that the present-day lake water is neither marine nor volcanic origin in spite of the high salt concentration, but the melt water of snow or glacial ice. And the following history is being considered: After the isolation of the original lake from the sea, evaporation of lake water in cold climate and supply of glacial melt water in warm climate have alternately taken place several times, until the formation of the present lake (NAKAI, 1975).

6. Nutrient and Organic Matters in Lake Water

As the data on nutrient and organic matters in the lakes around Syowa Station are scanty, any detailed discussion is not possible here. But the distributions of nutrient matter in the lakes suggest the contribution not only of airborne salt but also biological activity in coupled with disintegration of rocks.

Distributions of nutrients in the saline lakes in the Dry Valleys can be summarized as follows. Vertical profile of the SiO_2–Si content in the lake water shows an ordinary pattern. In the bottom layer SiO_2–Si becomes 200 μg-at/l, suggesting a supply from the bottom sediment. Distribution curve of NO_3–N or NO_2–N has a maximum in the middle layer, and the content of NH_4–N increases in the bottom layer. The presence of nitrate maximum in the middle layer may be ascribed to nitrification from ammonia by biological activity. And the nitrate is reduced to ammonia in the bottom layer (TORII, 1975).

Nitrogen, oxygen, carbon dioxide and argon gases were detected in the deeper layers of Lake Vanda, Lake Bonney and Lake Fryxell, and methane was identified in the west lobe of Lake Bonney and Lake Vanda. In the water of Lake Vanda, the content of total organic carbon was 63.8 mg/l which is considerably high compared with the content in ordinary lakes. Saturated fatty acids having 8∼32 carbon atoms, and unsaturateded fatty acids having 16∼18 carbon atoms were detected in the water. These results suggest microorganism activity in the lake. Recently some bacteria living in saline water were identified at Lake Fryxell.

7. Heavy Metals, Copper, Iron, Zinc, and Manganese

Available data on the distribution of heavy metals in the lakes are scanty. But at Lake Nurume, characteristic features of distribution of heavy metals were observed. Lake Nurume can be divided into two layers, the upper one is 0 to 10 m, and the lower one is 10 to 15 m. In the upper layer the salt content is the same as in the sea water, but the heavy metals are more abundant. This layer is in an oxidizing environment. Abundance ratios of the heavy metals in the lake are almost the same as those in snow. So these heavy metals are considered to have been supplied from snow which includes dust of artificial origin.

In the lower layer, the salt content is 1.5 times that of sea water, and the content of iron increases with depth. Manganese shows a maximum concentration at the interface of the two layers. This means that the manganese ion in the reducing lower layer is diffused upwards and is oxidized at the interface, to accumulate in this layer.

Acknowledgments

The authors express their hearty thanks to the National Science Foundation of the United States, to the Division of Science and Industrial Research of New Zealand, to the National Institute of Polar Research, Japan, for supporting their researches in Antarctica.

The authors are grateful to their colleagues for their kind cooperation and encouragements during the studies.

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