

THE DISTRIBUTION OF SECONDARY MINERALS AND EVAPORITES AT LAKE VANDA, VICTORIA LAND, ANTARCTICA

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Abstract: Secondary minerals and evaporites around Lake Vanda, Wright Valley have been identified by X-ray diffraction techniques in order to investigate the areal distribution of these minerals. Gypsum is the most abundant mineral near the shoreline of Lake Vanda and halite is the most abundant mineral in the elevated areas. Secondary minerals are abundant on the Dais indicating low-grade hydrothermal metamorphism of the dolerite.

Based on the distribution of evaporites, the authors propose that the origin of magnesium and potassium ions in lake water may be clarified by the value of Mg/K, that is, magnesium and potassium ions with Mg/K value less than 4 originated from the weathering of rocks plus sea spray, while those with the value greater than 4 originated from sea water.

1: Introduction

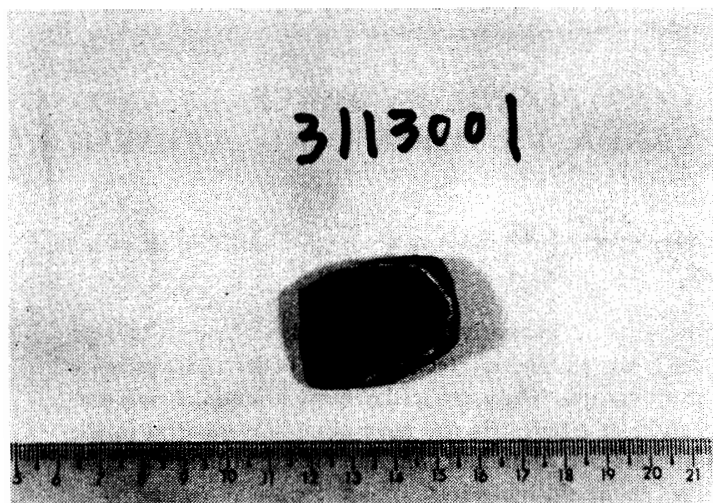
One of the authors (H.M.) joined the phase-3 field operations of Dry Valley Drilling Project (DVDP) in 1973-74 and visited Lake Vanda as the site-geologist of DVDP #4 hole. In cooperation with the Japanese DVDP groups, evaporites, secondary minerals and soil salts around Lake Vanda were collected. Most of the samples were identified at the Thiel Earth Sciences Laboratory of McMurdo Station using a Toshiba powder X-ray diffractometer which was one of the Japanese contributions for DVDP. Some of the samples were further studied by chemical analysis and microscopy in Tokyo. The purpose of the present study is to investigate the areal distribution of minerals in relation to the salinity of Lake Vanda.

2. Occurrences of Evaporites

Evaporites are usually found as efflorescences on the underside of black ventifacts (dolerite) along the shoreline of Lake Vanda, in the elevated areas of moraine heaps and on the Dais. The typical occurrences are reproduced in Fig. 1. Gypsum looks granular with white-yellow to yellowish brown color and sometimes is almost transparent. Thenardite occurs as fine, white powder, and calcite as smooth coating of white to brown color. Calcite often occurs with algae along the shoreline. Halite and gypsum are also found in fissures of rock in the

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1(a) *The typical occurrence of thenardite near the shoreline. Transparent films of gypsum are usually associated with white thenardite.*

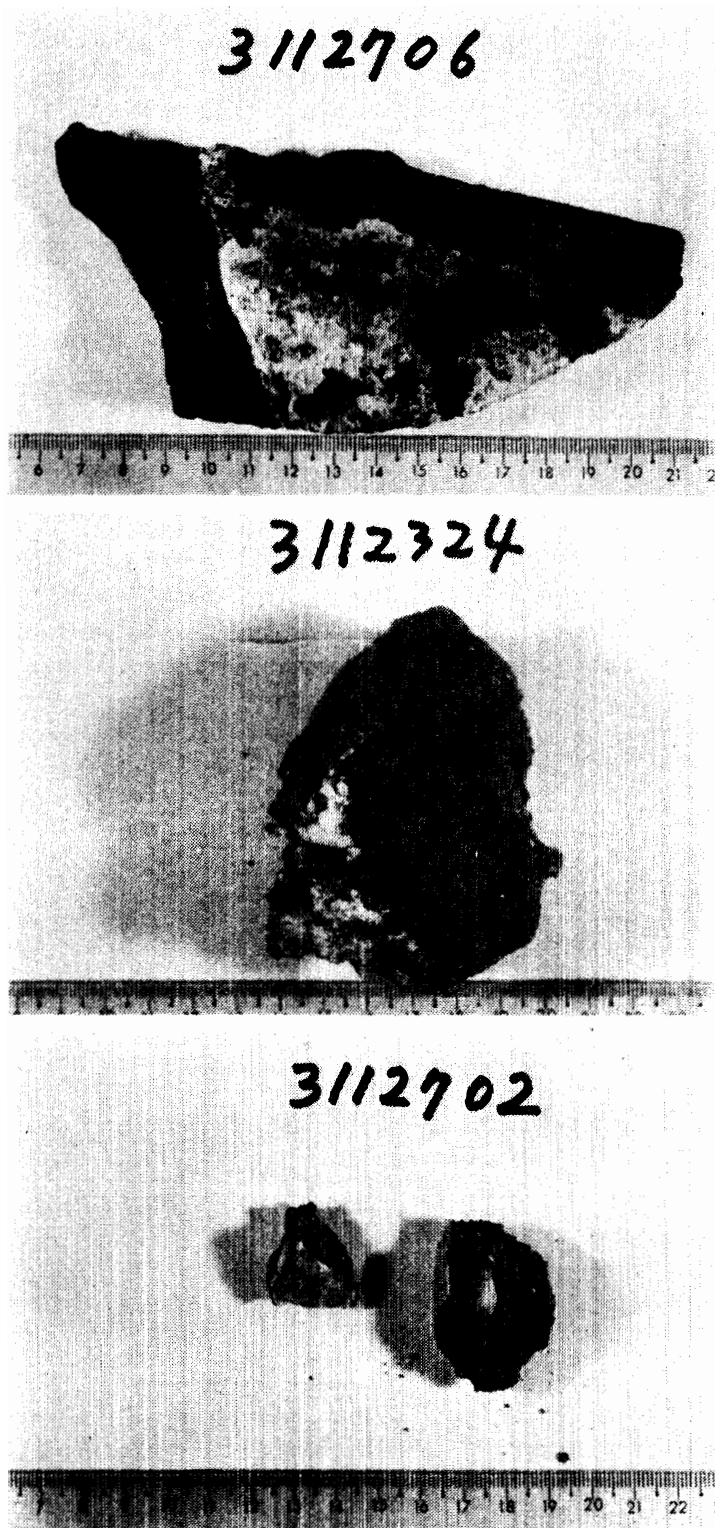


2(b) *The typical occurrence of gypsum near the shoreline, in the elevated areas and on the Dais.*



1(c) *Efflorescence of thenardite and gypsum in the elevated areas and on the Dais. Granular, yellowish brown gypsum is found around fine, white powder of thenardite.*

Fig. 1. *The typical occurrences of evaporites.*



1(d) *Halite found in fissures of rock at the foot of the Bull Pass, indicating salt weathering of rock. No salts are found above the ground level.*

2(a) *The aggregate of halite and thenardite from the Canopus Pond.*

2(b) *Halites from the Bull Pass.*

Fig. 2. *The typical occurrence of soil salts*

elevated areas, and they are related to the physical disintegration of rocks, salt weathering (SELBY, 1971). The typical occurrence is reproduced in Fig. 1 (d).

Soil salts usually occur as aggregates in the soil in the elevated areas and the typical occurrences are reproduced in Fig. 2. Sodium niter is usually found with halite.

3. Distribution of Minerals

3.1. *Evaporites near the shoreline*

The minerals identified were gypsum, thenardite, calcite and halite. Gypsum is the most abundant mineral and thenardite and calcite are less abundant. The occurrence of halite is restricted to the western side of the lake.

3.2. *Minerals from the elevated areas*

The elevated areas investigated are at the Canopus Pond (11/23 and 11/25 in Fig. 3), the front of the Dais (12/2 in Fig. 3) and at the foot of the Bull Pass (11/27 in Fig. 3). The minerals identified were halite, gypsum, thenardite, sodium niter, calcite, epsomite, chlorite and diopside. Halite is the most abundant mineral, and gypsum, thenardite, calcite and sodium niter are less abundant. Bar graphs in Fig. 3 illustrate the distribution of secondary minerals and evapo-

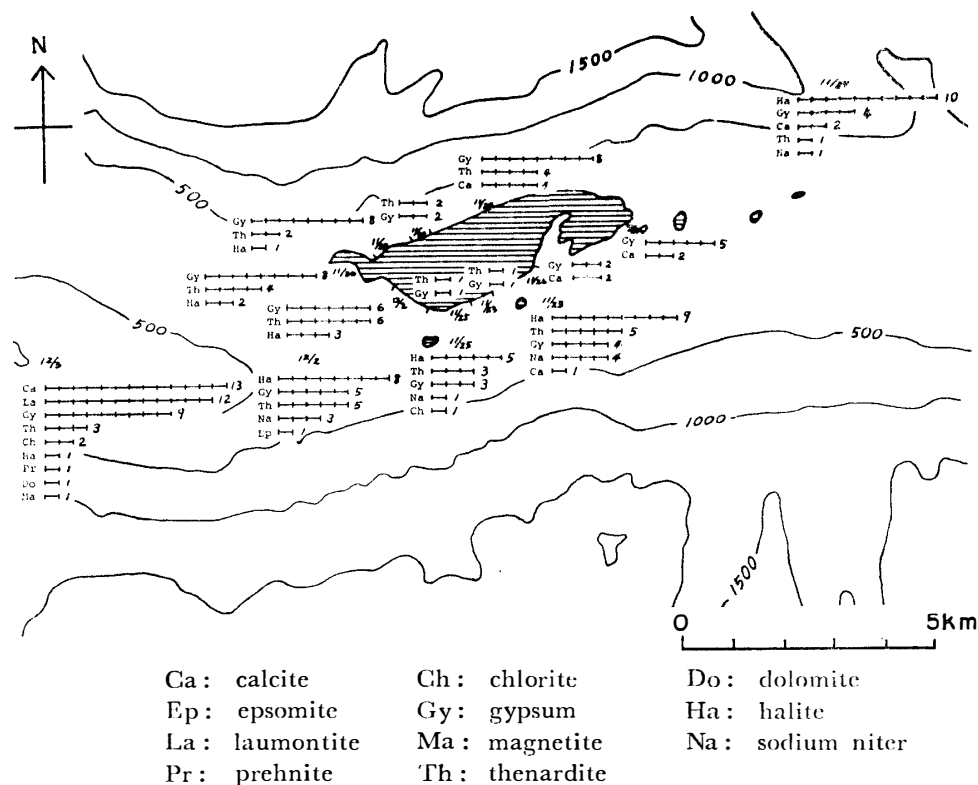


Fig. 3. The distribution of evaporites and secondary minerals at Lake Vanda.

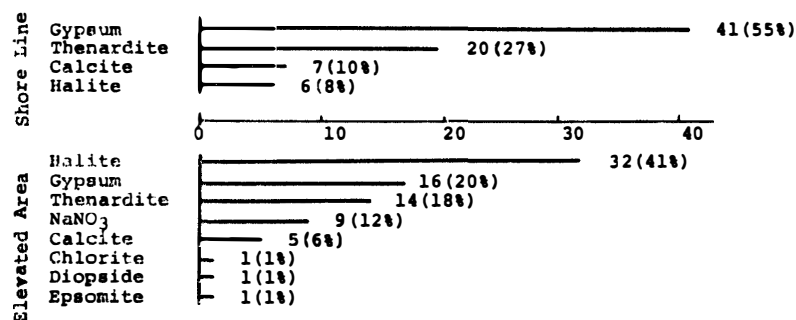


Fig. 4. Comparison of minerals near the shoreline with those in the elevated areas.

rites at Lake Vanda according to the date of the reconnaissance. Number given in the bar graph indicates the frequency of minerals in samples collected for a day. Figure 4 shows the comparison of minerals from the shoreline with those in the elevated areas. Minerals in the elevated areas are highly water-soluble salts, such as halite, sodium niter and epsomite, in contrast to minerals from the shoreline. The occurrence of epsomite in the Wright Valley is very rare but there are some in the Taylor Valley (SMITH, 1965). CLARIDGE and CAMPBELL (1968) reported that nitrate deposits have been accumulated by precipitation from the atmosphere, in the absence of leaching and biological activity. Therefore, the frequent occurrence of sodium niter in this region is worth emphasizing.



Fig. 5. A scanning electron microphotograph of prismatic laumontite from the Dais.

3.3. Secondary minerals from the Dais

The minerals identified were calcite, laumontite, gypsum, thenardite, chlorite, halite, prehnite, dolomite, and magnetite. Laumontite, calcite, chlorite, prehnite and magnetite are found in veins in the dolerite on the eastern side of the Dais. These minerals suggest low grade hydrothermal metamorphism (300°C–3 kb; LIOU, 1971) of the original rock. Prismatic laumontite is shown in Fig. 5 and prehnite under cross nicol is shown in Fig. 6. Laumontite from the Dais is separated using a heavy liquid and its lattice dimensions are calculated by the method of least-squares applying the UNICS program (SAKURAI, 1967), and the results are listed in Table 1 together with previous data. Some differences are

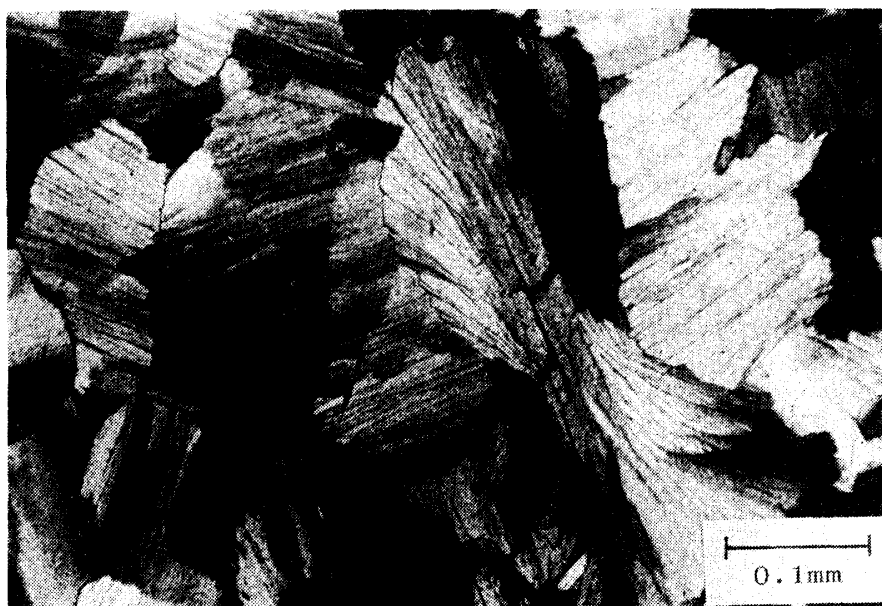


Fig. 6. A microphotograph of prehnite from the Dais (cross nicol).

Table 1. Lattice dimensions of laumontite.

Locality	a (Å)	b (Å)	c (Å)	beta (°)
Dais No. 6	14.74(2)	13.07(1)	7.53(1)	112.0(1)
Dais No. 27	14.71(2)	13.07(1)	7.52(2)	112.0(2)
Dais No. 1	14.75(3)	13.13(1)	7.50(2)	111.6(2)
Dais No. 22	14.76(3)	13.15(2)	7.49(2)	111.6(2)
Dais No. 3	14.73(2)	13.13(1)	7.48(2)	111.6(2)
Dillsburg, Pa. (LAPHAM, 1963)	14.75(5)	13.08(2)	7.57(5)	112
Hungary (COOMBS, 1952)	14.75(3)	13.10(2)	7.55(1)	112.0(2)
M. SATO	14.795	13.117	7.554	111.37

Table 2. Chemical composition of Mg-chlorite (penninite) found in the matrix of hornblende at the top of the Dais.

Chemical composition (wt %)

	SiO ₂	Al ₂ O ₃	FeO	MgO	Total
No. 1	29.3	22.7	18.4	29.6	100.0
No. 2	19.8	27.4	21.4	31.0	100.0

Chemical formula based on (6-x) (Mg, Fe)O • xAl₂O₃ • (4-x)SiO₂ • 4H₂O

	x	Mg/Fe	Chemical formula
No. 1	1.10	2.9	4.90 (Mg, Fe)O • 1.10 Al ₂ O ₃ • 2.41SiO ₂
No. 2	1.20	2.5	4.80 (Mg, Fe)O • 1.20 Al ₂ O ₃ • 1.48SiO ₂

No. 1: Treatment of Soxhlet's extractor with 6% HCl for 5 hours.

No. 2: Treatment of Soxhlet's extractor with 6% HCl for 24 hours.

observed in the length of the b axis and beta angle, which resulted from shrinkage of unit cell due to slight dehydration of laumontite, leonhardite. The efflorescences of gypsum and thenardite are abundant around the thermometer screen of New Zealand. They are of hydrothermal origin (NAKAI, 1974). On the middle of the Dais, dolomite associated with calcite is found. On the top of the Dais, aggregates of halite are found in the soil and the water soluble halite amounts to 31.6 weight percent. Chlorite associated with hornblende is also found on the top of the Dais. An X-ray powder pattern indicates that the chlorite is Mg-chlorite. Chlorite cannot be separated by a heavy liquid since it is found in the matrix of hornblende. Chlorite is chemically separated using Soxhlet's extractor with 6% HCl solution, because only chlorite is soluble in HCl solution. Since a small amount of calcium ion is detected, the chemical composition is re-calculated eliminating calcium ion and the results are shown in Table 2. Considering the substitution of Mg atom by Fe atom in octahedral site and Si atom by Al atom in tetrahedral site, the chemical formula of chlorite is obtained as listed in Table 2. The amount of silica is smaller because some part of silica is precipitated during extraction. The chemical formula indicates that chlorite is Mg-chlorite and this is compatible with X-ray data.

3.4. Soil salts

Water-soluble elements were leached from the soil samples of which locations are shown in Fig. 7. The results of chemical analyses are tabulated in Table 3 together with the results of chemical analyses of successive treatment with 10% HClO₄ solution. Seven soil samples from the elevated area containing the aggregates of salts were marked with asterisk in the Table and they contain water-soluble elements in the amount of more than 20%. Epsomite is found in sample #3120215. Samples #3112717 from the Bull Pass and #3112316 from the small Canopus

Table 3. Water-soluble and HClO_4 -soluble elements of soil samples at Lake Vanda.

Water-soluble elements

Locality	Sample No.	Na^+	K^+	Ca^{++}	Mg^{++}	Cl^-	NO_3^-	SO_4^{--}	Total
Bull Pass	3112702*	866	0.5	13.6	1.6	1450	1.1	32.1	2364.9
Bull Pass	3112717*	761	2.8	15.8	120.0	868	658	391	2816.6
Dais, vein	3120302	25.8	0.3	7.8	1.1	12.1	8.1	40.4	95.6
Dais, top	3120318	1180	1.0	15.4	1.9	1930	6.1	25.7	3160.1
North, shoreline	3112407	8.0	1.1	21.3	12.1	72.6	3.0	2.1	120.2
North	3112412	2.6	0.3	2.5	0.6	8.2	0.4	1.6	16.2
Front of Dais	3120215*	980	1.8	22.8	89.8	951	803	386	3234.4
Large Canopus Pond	3112504	68.5	2.3	22.6	22.7	160	47.1	50.4	373.6
Small Canopus Pond	3112301	208	6.2	9.7	24.5	229	62.3	206	745.7
Small Canopus Pond	3112302	13.9	1.8	2.2	1.9	17.2	5.4	8.1	50.5
Small Canopus Pond	3112303*	709	2.8	22.0	19.9	283	40.1	1310	2386.8
Small Canopus Pond	3112316*	873	2.6	11.1	82.5	1020	353	381	2723.2
Small Canopus Pond	3112315*	2380	1.3	36.4	6.5	3750	107	101	6382.2
Small Canopus Pond	3112314*	1110	0.6	17.8	8.3	1620	390	64.1	3210.8
East, shoreline	3113003	0.9	1.6	5.1	1.8	10.8	4.4	2.0	26.6

Successive treatment with HClO_4 of 10%

Sample No.	Na^+	K^+	Ca^{++}	Mg^{++}	Cl^-	NO_3^-	SO_4^{--}	Total
3112702*	2.8	1.2	8.9	5.7	0.61	0.	2.1	21.3
3112717*	9.0	6.6	56.4	61.3	0.55	0.	12.4	146.3
3120302	21.2	8.3	341	14.8	0.56	0.	36.1	422.0
3120318	6.3	6.2	46.1	25.6	0.81	0.	8.2	93.2
3112407	91.7	7.6	92.1	29.8	1.46	0.	2.9	225.6
3112412	8.4	10.2	67.2	22.2	1.28	0.	3.2	113.0
3120215*	7.0	2.9	52.4	34.0	0.72	0.7	48.5	146.2
3112504	1.9	3.2	16.1	15.5	0.	0.	7.9	44.6
3112301	41.8	17.0	44.8	38.9	5.31	3.5	12.3	163.6
3112302	11.8	20.6	75.0	40.6	0.34	0.	6.3	154.6
3112303*	14.8	3.0	45.5	19.7	0.64	1.8	7.4	92.8
3112316*	4.3	1.5	18.5	18.8	0.99	0.5	7.0	51.6
3112315*	4.0	2.8	27.9	8.8	0.99	0.	12.6	57.1
3112314*	4.1	1.0	18.3	5.8	1.41	0.2	2.1	32.9
3113003	3.2	8.2	70.4	33.0	0.10	0.	4.3	119.2

Unit: mg/10g dry soil, Analyst: T. HAYASHI.

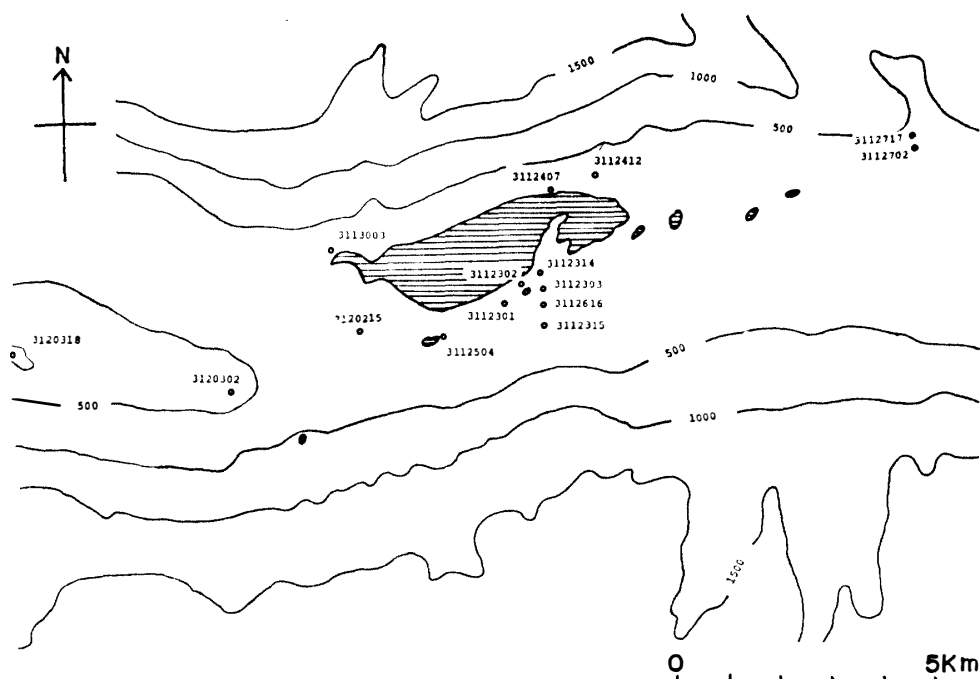


Fig. 7. Soil samples for the analysis of water-soluble elements.

Pond may include epsomite from the result of water-soluble elements. In the seven samples, the main cation is Na^+ , and the concentrations of K^+ , Ca^{++} , and Mg^{++} are much lower than that of Na^+ . The maximum concentrations of Na^+ , K^+ , Ca^{++} and Mg^{++} are 238 mg/g-soil from the Canopus Pond, 0.3 from the Canopus Pond and at the foot of the Bull Pass, 3.6 from the Canopus Pond, and 9.0 from the front of the Dais, respectively. The mean concentrations of Na^+ , K^+ , Ca^{++} and Mg^{++} are 110, 0.2, 2.0 and 3.2 mg/g-soil, respectively. The main anion is always Cl^- . The concentrations of NO_3^- , and SO_4^{--} vary from sample to sample. The maximum concentrations of Cl^- , NO_3^- , and SO_4^{--} are 375 mg/g-soil from the Canopus Pond, 80 from the front of the Dais and 120 from the Canopus Pond, respectively. The mean concentrations of Cl^- , NO_3^- , and SO_4^{--} are 142, 28, and 37 mg/g-soil, respectively. Considering the chemical composition of water soluble elements, the most prevalent mineral is halite, which is compatible with the results of X-ray data. Generally, the concentrations of Ca^{++} and SO_4^{--} are low compared with the results of X-ray analysis. This indicates that gypsum and thenardite usually do not occur as aggregates in the soil but as efflorescences. Since the soil sample from the veins of the Dais contains calcite and zeolite, large amounts of calcium ion are leached by HClO_4 treatment.

3.5. DVDP #4 core samples

Salts in DVDP #4 core samples from the sediments of Lake Vanda are also identified by powder X-ray diffraction and the results are listed in Table 4.

Table 4. X-ray identifications of DVDP #4 core samples.

Collected by H. MORIKAWA Earth Sci. Lab. First Drilling only		Collected by N. NAKAI Drilling site	
Depth (m)		Depth (m)	
68.61	gypsum, calcite		
68.63	gypsum, calcite		
68.78	gypsum		
68.83	gypsum	68.83	gypsum, calcite
68.87	calcite, gypsum	68.87	gypsum, calcite
68.92	calcite, gypsum		
69.02	gypsum, calcite		
69.64	calcite	69.56	gypsum, calcite
69.65	gypsum, calcite	69.64	calcite, gypsum
69.71	gypsum, calcite		
69.76	gypsum		
69.81	calcite, gypsum		
70.01	gypsum, calcite		
70.04	gypsum, calcite		
70.09	calcite, gypsum		
70.27	calcite	70.16	calcite, gypsum
70.52	calcite		
72.15	gypsum, calcite	71.09	calcite
72.20	calcite, gypsum		
72.26	gypsum	74.23	calcite

First drilling : bottom=224'10".

Second drilling : bottom=224'.

Silicates are not listed.

Table 5. Water soluble elements of #4 core samples.

(mg/10 g dry soil)

Depth (m)	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻⁻	Total
68.46	12.7	2.2	69.5	21.1	150	0.2	54.5	310.2
69.48	11.9	2.0	56.4	20.3	157	0.1	35.3	283.0
70.41	26.1	3.5	184	37.1	265	0	266	781.7
70.94	19.7	5.2	51.3	21.5	170	0.1	2.9	270.7
71.34	17.5	3.8	49.0	20.3	167	0.1	7.6	265.3
71.45	13.1	3.2	65.3	17.8	124	0.2	75.1	298.7
71.73	15.4	4.0	45.6	16.9	134	0	21.2	237.1
72.20	15.2	3.1	36.0	18.4	126	0	2.2	200.9
72.20	12.0	2.1	59.8	17.8	126	0.2	56.0	273.9
72.46	14.5	3.3	40.3	17.6	129	0.1	2.3	207.1
72.52	21.1	2.5	53.7	23.8	204	0.1	2.0	307.2
72.89	15.3	2.4	34.0	15.7	126	0.1	1.2	194.7
73.28	39.0	7.5	76.1	39.9	283	0.1	5.1	450.7
73.28	39.4	7.3	77.5	34.8	287	0	2.4	448.4
76.05	37.8	6.0	89.8	46.8	340	0	2.0	522.4
78.44	69.0	9.4	130	59.2	486	0.1	2.1	755.8

There remain some uncertainties about the depth of samples because the recovered core is not good. Only calcite and gypsum are found and their solubility in water is very low. They are found above the first gravel layer at a depth of about 72-73 m from the lake surface. Water-soluble elements were also leached from the core samples and the results of the chemical analyses are tabulated in Table 5. They give the almost similar chemical composition as that of bottom water in Lake Vanda.

4. Origin of Potassium and Magnesium Ions in Lake Vanda

The origin of salts in lake water is discussed based on the distribution of evaporites, secondary minerals and soil salts.

At first, marine origin of salts is assumed. This assumption is reasonable for Lake Vanda since the sulfur of thenardite and gypsum along the shoreline, of gypsum in lake sediments, and of SO_4^{--} ion in lake water originate from sea water (NAKAI, 1974). Many workers have analyzed six kinds of ions, Na^+ , K^+ , Ca^{++} , Mg^{++} , Cl^- and SO_4^{--} , in the saline lakes of the Dry Valley areas. These ions are main components in both saline lakes and sea water. Among the six kinds of ions, we searched for some ions whose concentrations are theoretically available to compare with those of sea water.

There exist many amounts of thenardite, halite, sodium niter, calcite, and gypsum around Lake Vanda. However, total amounts of these salts cannot be exactly estimated because of extremely irregular distribution. Therefore, Na^+ , Ca^{++} , Cl^- and SO_4^{--} ions are not suitable for the above purpose. Very close to the western side of Lake Vanda, there exist hydrothermal salts of gypsum, thenardite and calcite on the Dais. Therefore, Na^+ , Ca^{++} and SO_4^{--} ions are not suitable for the above purpose because it is convenient to exclude the salts of different origin. From the above considerations, it is clear that the chemical composition of Na^+ , Ca^{++} , Cl^- and SO_4^{--} ions in lake water has already deviated from that of sea water. However, the ratio of Mg/K in lake water seems to be identical with that in sea water.

The suitability of the Mg/K ratio is supported by the following reason: potassium and magnesium salts are not found around Lake Vanda except rare occurrences of epsomite and dolomite. Another reason is concerned with the kinds of salts formed during the evaporation of sea water. Potassium and magnesium salts formed by the evaporation of sea water under normal temperatures are reported to be magnesium sulphate, magnesium chloride and potassium chloride (USIGLIO, 1849). Under frigid conditions, potassium chloride, magnesium chloride, and/or $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ are formed during the final stage of deposition of salts from sea water (TOMPSON and NELSON, 1956). Since these salts are highly soluble in water, they have a large probability to be carried into Lake Vanda by water, even if they were precipitated near Lake Vanda by the evaporation of sea water. Under the conditions of Antarctica, it would be more reasonable to suppose frigid conditions rather than normal evaporations (YAMAGATA *et al.*, 1967). Under frigid conditions, the concentration of potassium and magnesium

ions increased with decreasing in temperature down -36°C . Below -36°C , there is a marked decrease in the concentration of both potassium and magnesium ions. Magnesium and potassium ions behave in the same way during the deposition of salts from sea water. The value of Mg/K is almost constant, ranging from 3.5 to 4.0. Therefore, the value of Mg/K in lake water remains constant even if magnesium and potassium salts precipitated from some parts of original sea water remained near Lake Vanda. From the above discussions, it is clear that the values of Mg/K are suitable to deduce whether Mg^{++} and K^{+} ions in lake water originated from sea water or not. Based on the chemical composition data of lake water collected from various parts of Lake Vanda reported by YAMAGATA *et al.* (1967), we classified the data according to the values of Mg/K vs. Figure 8 shows the plot of the value of Mg/K vs. total salts (sum of six components) in lake water. There are two groups of brine in lake water according to the values of Mg/K . The boundary value is nearly 4, which is the same value of Mg/K in sea water. Since the value of Mg/K is nearly 1 in the fresh water ponds in the Dry Valley area and in inflow water, magnesium and potassium ions of which ratio is less than 4 originate from the weathering of rocks plus sea spray. These magnesium and potassium ions mainly exist in the shallower parts of lake water, and their concentrations are not denser than that of sea water. However, they still exist at a depth of about 60 m, since the horizontal distribution of dense water is not uniform (YAMAGATA *et al.*, 1967). On the other hand, magnesium and potassium ions of which ratio is greater than 4 originate from sea water. These magnesium and potassium ions mainly exist in the deeper parts of the lake than about 45 m (Fig. 9). The mechanism of enrichment of magnesium ion against potassium ion compared with the chemical composition of sea water is uncertain. However, magnesium ions might be easily carried into Lake Vanda, since magnesium chloride is more soluble in water than potassium chloride.

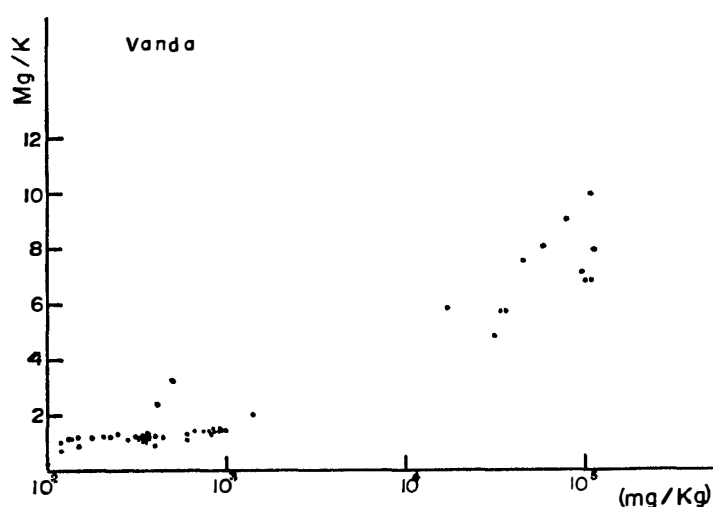


Fig. 8. The value of Mg/K vs. the weight of total amount of salts in lake water of Vanda.

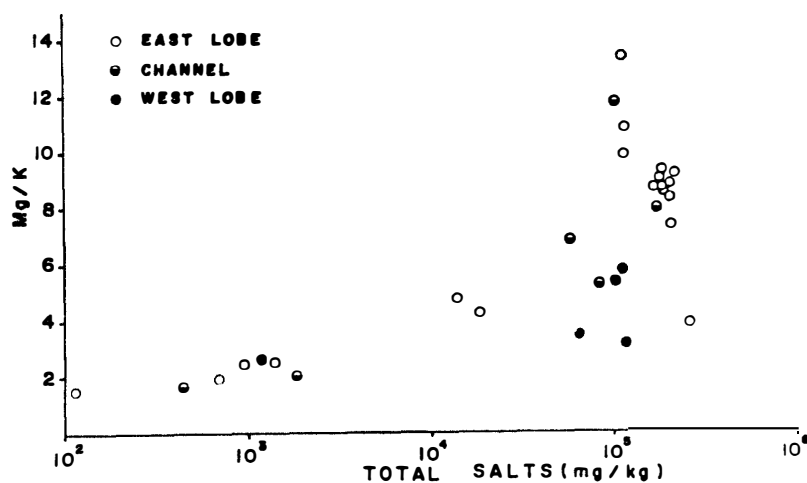
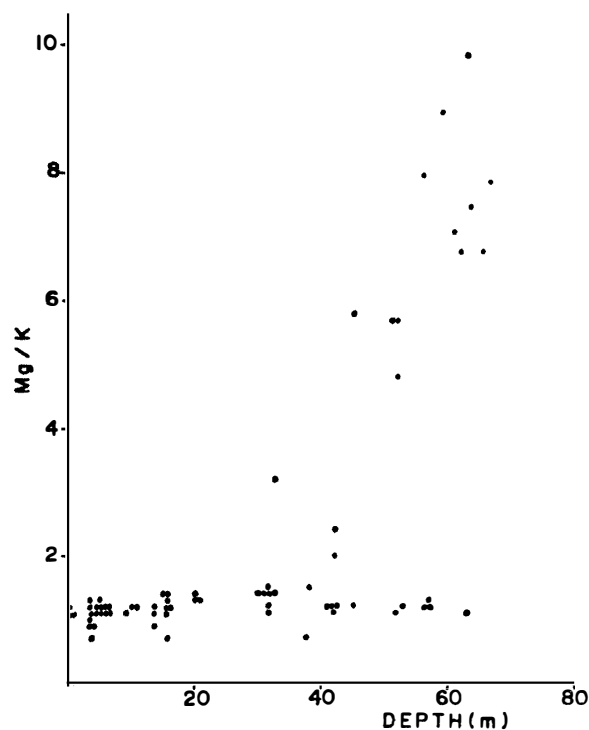


Figure 10 shows the plot of the value of Mg/K vs. total salts in lake water of Bonney, Taylor Valley, based on the chemical data reported by YAMAGATA *et al.* (1967). Although small amounts of magnesium salts (epsomite) are found

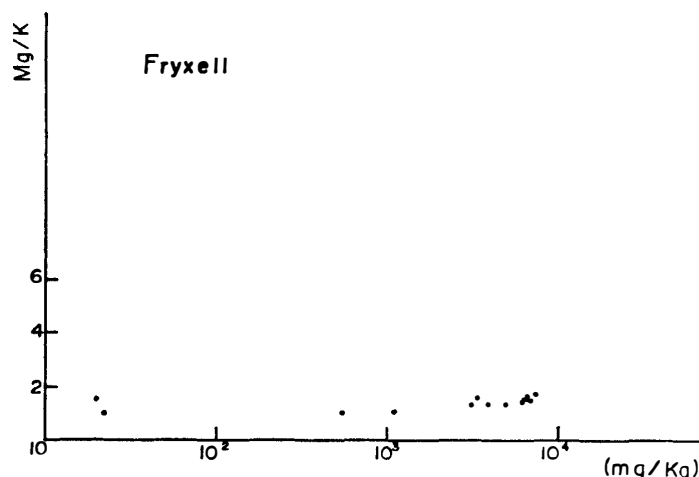


Fig. 11. The value of Mg/K vs. the weight of total amount of salts in lake water of Fryxell.

in Taylor Valley, the value of Mg/K in lake water of Bonney can be classified into two groups like those in lake water of Vanda. However, a slight difference of the value of Mg/K is observed in dense water of the west lobe as compared with that in dense water of Lake Vanda. The values of Mg/K in dense water of the west lobe are smaller than those in dense water of the east lobe and Lake Vanda. TORII *et al.* (1974) and HENDY *et al.* (1974) pointed out the different chemical characters between the west lobe and the east lobe. The smaller value of Mg/K indicates that some parts of magnesium and potassium ions in dense water of the west lobe originate from rock weathering and sea spray salts, and it is also suggested that the west lobe is more influenced by inflow water than the east lobe.

Figure 11 shows the plot of the value of Mg/K vs. total salts in the lake water of Fryxell, Taylor Valley, based on the chemical data reported by YAMAGATA *et al.* (1967). The value of Mg/K is always smaller than 4, indicating that magnesium and potassium ions in the lake water originate from rock weathering and sea spray salts. Since Lake Fryxell is located near the McMurdo Sound, invaded marine water is not concentrated *in situ* but turned back to the sea.

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