INTERPRETATION OF SALT DEPOSITION IN WRIGHT VALLEY, ANTARCTICA: CHEMICAL ANALYSIS OF DVDP 14 CORE

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***Abstract*:** Powder X-ray diffraction analysis, water and perchloric acid extraction and chemical analysis of extracts were carried out on DVDP 14 core to discuss the past environment in the Wright Valley. From the results of X-ray analysis, quartz and feldspar-group were found as primary minerals, with calcite and halite as secondary minerals. In the results of chemical analysis, the composition of the water soluble part was neary equal to that of ground water and the composition of the perchloric acid soluble part was neary equal to that of DVDP 13 core and soil of the Wright Valley. In general, the sodium content was higher in the upper part, while the calcium ion content increaesd with depth, and sulfate ion was negligibly small through the core. The vertical distribution of the water and perchloric acid soluble matter showed several peaks. This suggests some epochs in sedimentation in the area, such as drying up of or filling up with water.

1. Introduction

Several chemical and mineralogical researches were carried out on the samples obtained in the Dry Valley Drilling Project. For example, WATANUKI and MORI-

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KAWA (1975) studied primary and secondary minerals in core 6 by powder X-ray analysis and showed the geothermal effect in the area. TORII *et al.* (1977) investigated primary and secondary minerals in core 13 by powder X-ray and also carried out chemical analysis of water and perchloric acid extracts, and discussed the salt balance in the Don Juan Basin. HORIUCHI *et al.* (1977) determined the radium content of the sediments from core 13.

In this paper the authors try to discuss the past environment conditions on the basis of the analytical results of extraction and mineral analysis core 14.

2. Description of Samples

Fig. 1 is the locality map of the Dry Valleys area in Victoria Land, which also shows the position of drilling site 14. The Wright Valley runs from east to west between to Olympus Range and the Asgard Range. This valley is blocked by the Wright Lower Glacier at the eastern end and by the Wright Upper Glacier at the western end. Lake Vanda is situated in the western part of the Wright Valley about 50 km west from the Ross Sea coast and occupies the lowest part of the valley. The streams of melt water in the valley flow into Lake Vanda but do not flow into the sea. Drilling site 14 is located on the west side of Lake Vanda. Line AB is drawn by linking the lowest points of Wright Valley between North Fork and the Ross Sea,

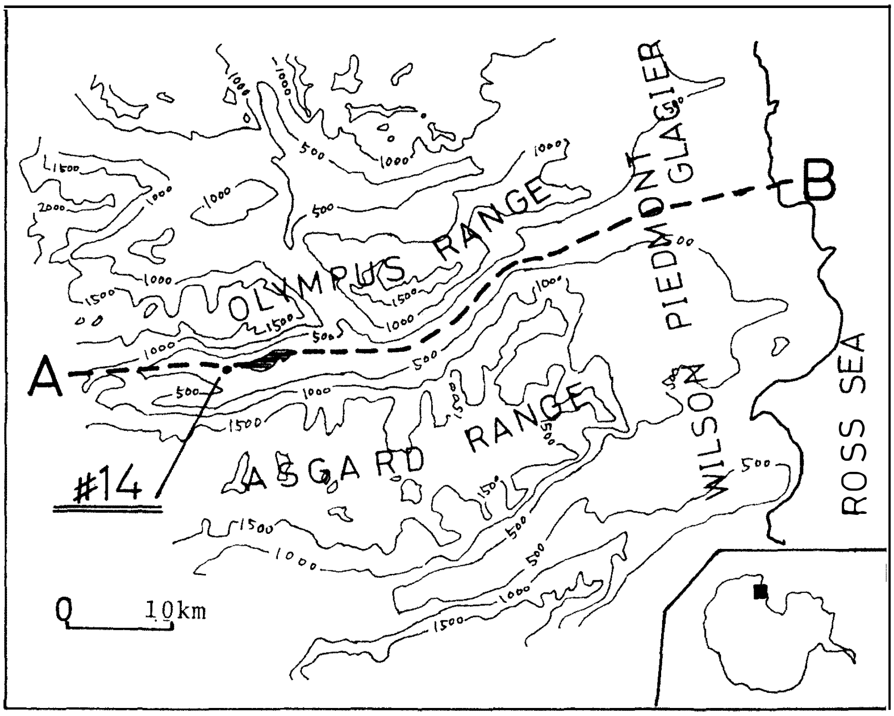

Fig. 1. Locality of DVDP 14 in the Dry Valleys, Victoria Land, Antarctica.

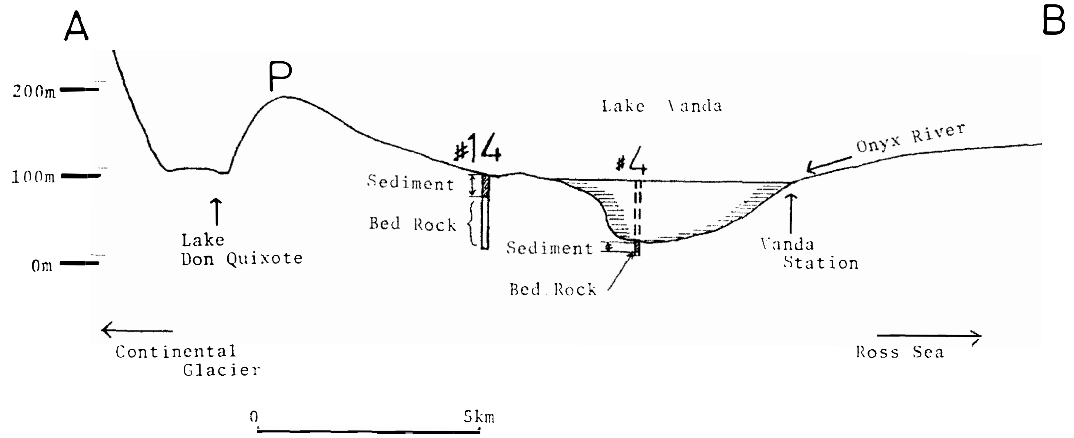

Fig. 2. Schematic cross section along AB line.

and is used for making a sectional diagram of the area as shown in Fig. 2.

As Lake Vanda is the lowest place, with the surface at 83.6 m above the sea level, going westward from the lake the ground level rises gradually. Crossing over a pass P (175 m), there is Don Quixote Pond whose surface elevation is 94 m above the sea level. Farther west in the valley, there is the Upper Wright Glacier

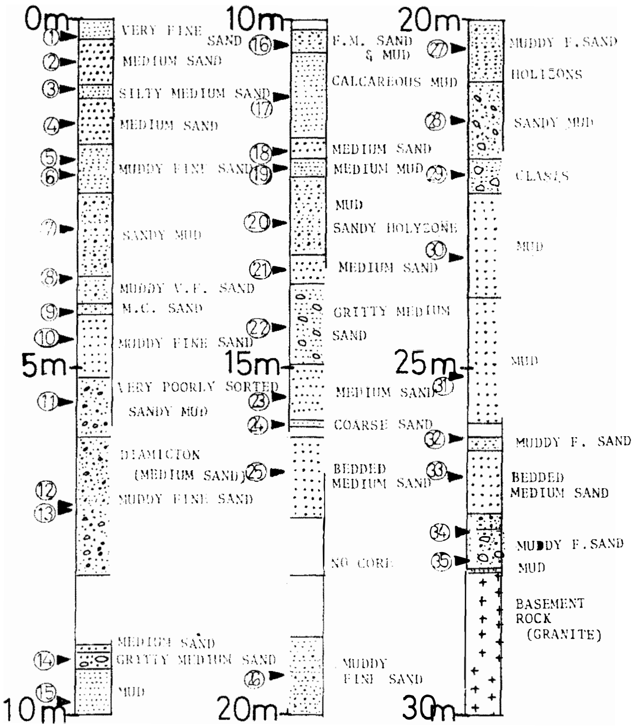

Fig. 3. Description of DVDP 14 core.

which continues to the Continental Glacier. In the summer season the Onyx River flows from the east into Lake Vanda. Going to the east farther, the ground level also rises gradually. The Lower Wright Glacier lies at the east end of the valley. Farther east there is the Wilson Piedmont Glacier at 500 m above the sea level and it extends to the Ross Sea. Along line AB, there are two drilling sites, 4 and 14. Drilling site 4 was set up on the ice of Lake Vanda whose surface is covered with ice sheet all the year round. Drilling core obtained was 17.3 m in length (TORII *et al.*, 1974). Drilling site 14 was set up on the ground 1.4 km from the west side of Lake Vanda across a small hill which is one meter higher than the surface of the lake. The length of drilling core 14 is 78.13 m and the thickness of sediment layer is 27.94 m. Bed rock is gneissic granodiorite or fine-grained granite.

General core description and sampling position of the sediment layer of core 14 are given in Fig. 3, together with classification after CHAPMAN-SMITH (1975). The marks "①▶" indicate sampling position in the core and the numbers correspond to sample number in Tables 1, 2 and 3.

3. X-ray Diffraction Analysis

The authors picked up 35 samples from the sediment layer of core 14. Thickness of the each sample was about 5 cm and about 30 g in weight. Homogenizing each sample by hand mixing, about one gram of sample was ground to powder whose size was under 200 mesh. Primary and secondary minerals were studied by powder X-ray diffraction pattern. The measurement conditions are summarized in Fig. 4 and results are shown in Table 1.

X-ray Diffractometer Source -Model DX-GE-E
Goniometer -Model DX-GO-F
Recorder -Model DX-CR-E
(Nihondenki Co., Ltd.)
Conditions Target -Cu
Filter -Ni
Voltage -30kV
Current -15mA
Slit -R-02--S-1°
Scanning Speed -2°/min
Chart Speed -20mm/min

Fig. 4. Instrument and conditions of X-ray measurement.

4. Chemical Analysis

After the extraction of soluble matters from the core, chemical analyses were carried out on the extracts. Every extraction was carried out with distilled water and perchloric acid. Distilled water can leach only the soluble matter, while perchloric acid is used as an extracting agent, to decompose calcite in order to determine chloride or sulfate ions. Extraction methods and chemical analyses are given below:

Extraction method: Weigh about 10 g of air-dried sample. Put the sample in a 200 m*l*-Pyrex beaker and add 100 m*l* of distilled water. Keep the mixture on a hot plate at 80 to 90°C for one hour, and then let it stand for 12 hours at room temperature. Filter the supernatant through an HA-type millipore filter (pore size: 0.45 μm). Wash it three times with about 25 m*l* each of distilled water. Combine the filtrate and washings, then dilute to 200 m*l*. This denotes the water soluble extract.

Transfar the residue on the filter to the 200 m*l*-Pyrex beaker and add 100 m*l* of 10%-perchloric acid. Extract the residue under the same conditions as in the case of water extraction. Then wash and dilute it with distilled water. The final concentration of perchloric acid should be about 5%. This denotes the acid extract.

Analytical method: Sodium, potassium, calcium and magnesium were determined by atomic absorption spectrometry using air-acetylen flame after the dilution of the extract to an adequate concentration with distilled water.

Chloride ion was determined by titration with a mercuric nitrate standard solution at pH 3.1 using bromophenol-blue, xylen cyanol FF and diphenylcarbazone mixed indicator.

Sulfate ion was determined by spectrophotometry with barium chromate at the wave length of 370 nm.

The scheme of extraction and the analytical results are given in Fig. 5 and in Tables 2 and 3, respectively.

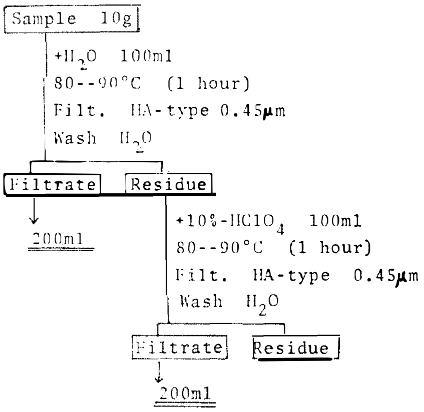

Fig. 5. Extraction of the core with H_2O and $HClO_4$.

5. Results and Discussion

From the results of X-ray diffraction pattern, primary minerals in the sediments

Table 1. Primary and secondary minerals of DVDP 14 core.

Sample No.	Primary minerals	Secondary minerals								
		NaCl		$CaCO_3$		Na_2SO_4			$CaSO_4\cdot 2H_2O$	
		31.7*	45.5*	29.4*	47.5*	19.1*	32.1*	33.8*	11.6*	23.4*
1	Q≧F (H ?)	○	?	○	?	○	?	?	—	—
2	Q≦F (O ?)	?	○	?	—	?	—	—	—	—
3	Q≧F	?	○	—	?	—	?	—	?	—
4	Q=F (H ?) (F ?)	○	○	○	?	○	○	?	?	?
5	Q=F	?	○	○	?	?	○	○	○	?
6	Q≦F	?	?	?	—	—	—	?	?	?
7	Q≧F	?	?	○	○	?	○	○	?	?
8	Q=F	?	—	—	—	—	—	—	?	?
9	Q=F (H ?)	○	?	○	?	○	?	?	?	?
10	Q=F	○	○	○	○	?	?	?	?	?
11	Q≧F	○	?	○	?	—	—	?	○	?
12	Q≧P	○	?	○	?	?	—	—	?	?
13	Q>F	?	?	○	○	—	○	?	○	?
14	Q=F≫M(P ?)	—	—	?	—	?	?	?	○	?
15	Q≧F	○	○	?	—	?	○	○	○	○
16	Q=F≫M(P ?) (H ?)	○	○	○	?	—	?	—	○	?
17	Q=F≫M(P ?)	?	?	?	—	—	—	—	—	?
18	Q>F (P ?)	?	—	○	?	○	?	—	—	?
19	Q=F (P ?)	○	○	○	?	?	—	?	?	?
20	Q=F	—	?	○	○	?	?	—	—	?
21	Q=F	?	—	—	—	?	—	?	?	?
22	Q=F	?	—	?	—	—	—	?	?	?
23	Q≧F	—	—	?	—	—	—	—	?	—
24	Q=F	—	—	?	—	—	—	—	—	—
25	Q=F	—	—	?	—	—	—	—	?	—
26	Q=F	—	—	○	?	?	?	?	—	—
27	Q>F (H ?)	?	—	?	—	?	?	?	○	?
28	Q>F	?	—	◎	◎	—	—	?	?	?
29	Q>F	○	○	◎	◎	?	?	?	?	?
30	Q>F	○	?	?	—	?	?	?	○	?
31	Q=F≫M(P ?) (H ?)	○	○	?	?	?	?	○	?	?
32	Q=F	○	?	◎	◎	○	?	—	—	—
33	Q=F	?	—	◎	○	○	—	?	?	—
34	Q≧F≫M	○	?	◎	○	?	?	?	?	—
35	Q=F (H ?)	?	—	◎	○	?	?	?	?	?

Q: Quartz, F: Feldsper-group, H: Hornblende, O: Olivine, P: Pyroxene, M: Mica-group.
◎: Clear peak, ○: Exist, ?: May be exist, —: Absent, *: 2θ (X-ray diffraction).

Table 2. Water-soluble salt in DVDP 14 core.

Sample No.	Depth (cm)	Sample Wt. (g)	+H_2O (%)	Sample dry basis (g)	Na mg/g	K mg/g	Ca mg/g	Mg mg/g	Cl mg/g	SO_4 mg/g	No_3 µg/g
1	25- 28	9.630	1.8	9.457	0.81	0.28	0.61	0.14	2.61	0.14	2.20
2	60- 65	10.002	0.4	9.962	0.53	0.20	0.42	0.08	1.65	0.13	1.06
3	100- 105	9.815	0.3	9.476	0.20	0.10	0.24	0.02	0.70	0.08	0.14
4	150- 155	10.825	0.4	10.782	0.45	0.19	0.19	0.08	1.04	0.16	0.68
5	200- 205	10.476	0.5	10.423	0.24	0.13	0.31	0.05	0.96	0.09	1.10
6	220- 225	10.319	3.0	10.009	2.00	0.68	1.15	0.41	6.36	0.10	5.79
7	300- 305	9.690	3.7	9.332	2.85	0.61	3.06	1.14	13.15	0.50	2.34
8	373- 378	9.790	0.7	9.722	0.56	0.21	0.37	0.08	1.55	0.10	3.15
9	420- 425	10.246	0.7	10.174	0.91	0.25	0·93	0.23	3.54	0.31	3.07
10	461- 466	10.312	4.8	9.817	3.48	0.83	2.85	1.28	14.02	0.27	13.9
11	550- 555	9.353	3.0	9.073	1.15	0.38	1.53	0.65	6.54	0.12	8.00
12	695- 700	9.832	1.5	9.685	0.34	0.29	1.09	0.33	3.45	0.05	5.47
13	700- 705	9.816	3.0	9.522	0.60	0.48	1.89	0.66	6.49	0.11	4.81
14	920- 925	10.236	0.5	10.184	0.27	0.17	0.27	0.10	1.20	0.07	2.06
15	970- 975	10.162	5.1	9.644	1.51	0.97	3.32	1.37	13.0	0.12	11.9
16	1040-1045	10.039	0.8	9.959	0.19	0.19	0.42	0.11	1.34	0.07	4.08
17	1110-1115	10.139	2.0	9.937	0.51	0.40	1.41	0.48	4.85	0.05	3.80
18	1190-1195	9.574	3.7	9.220	0.84	0.56	2.40	0.87	8.29	0.09	0.78
19	1210-1215	10.097	1.2	9.976	0.57	0.42	1.51	0.55	5.55	0.05	3.97
20	1290-1295	9.275	3.7	9.028	1.02	0.65	3.02	1.13	10.48	0.09	2.48
21	1357-1362	9.980	0.9	9.890	0.41	0.20	0.36	0.12	1.71	0.02	0.57
22	1440-1445	10.859	0.4	10.815	0.18	0.12	0.40	0.07	0.90	0.03	0.01
23	1540-1545	10.459	0.3	10.428	0.12	0.09	0.11	0.03	0.46	0.01	0.16
24	1580-1585	10.325	0.5	10.273	0.15	0.12	0.29	0.10	1.13	0.01	0.61
25	1647-1652	10.017	0.4	9.977	0.20	0.16	0.26	0.07	1.08	0.01	0.79
26	1946-1951	10.173	2.5	9.919	0.67	0.33	1.95	0.71	6.99	0.03	0.61
27	2039-2142	10.754	3.1	10.421	0.87	0.52	2.60	0.90	8.89	0.05	0.69
28	2145-2150	9.959	3.8	9.580	0.65	0.44	2.69	0.92	8.72	0.07	0.44
29	2220-2225	10.376	3.1	10.054	0.58	0.30	2.28	0.77	7.16	0.07	0.63
30	2340-2345	10.379	5.8	9.777	1.33	0.71	3.80	1.43	13.48	0.08	0.48
31	2512-2517	10.238	7.2	9.500	1.35	0.78	4.52	1.68	15.89	0.05	0.84
32	2600-2605	10.060	4.7	9.588	1.45	0.68	3.22	1.24	12.09	0.10	0.30
33	2657-2662	10.294	1.9	10.098	0.87	0.40	1.50	0.59	6.04	0.04	0.28
34	2738-2743	10.087	5.4	9.542	1.60	0.84	4.93	1.78	16.79	0.05	0.30
35	2781-2786	10.160	3.2	9.835	0.99	0.40	2.41	0.89	8.62	0.03	0.32

Table 3. $HClO_4$-soluble salt in DVDP 14 core.

Sample No.	Depth (cm)	Sample Wt. (g)	$+H_2O$ (%)	Sample dry basis (g)	Na mg/g	K mg/g	Ca mg/g	Mg mg/g	Cl mg/g	SO_4 mg/g	NO_3 μg/g
1	25- 28	9.630	1.8	9.457	1.40	1.28	12.26	3.14	nil	nil	nil
2	60- 65	10.002	0.4	9.962	1.00	0.89	6.36	2.22	〃	〃	〃
3	100- 105	9.815	0.3	9.746	0.61	0.43	4.60	1.50	〃	〃	〃
4	150- 155	10.825	0.4	10.782	1.09	0.79	6.29	2.48	〃	〃	〃
5	200- 205	10.476	0.5	10.423	0.88	0.65	6.03	1.96	〃	〃	〃
6	220- 225	10.319	3.0	10.009	1.90	1.89	12.99	4.28	〃	〃	〃
7	300- 305	9.690	3.7	9.332	1.67	2.11	16.38	4.78	〃	〃	〃
8	373- 378	9.790	0.7	9.722	1.23	1.04	5.46	2.59	〃	〃	〃
9	420- 425	10.246	0.7	10.174	0.87	1.11	11.28	2.38	〃	〃	〃
10	461- 466	10.312	4.8	9.817	1.81	2.77	24.90	5.69	〃	〃	〃
11	550- 555	9.353	3.0	9.073	1.46	1.75	13.06	3.91	〃	〃	〃
12	695- 700	9.832	1.5	9.685	1.32	1.18	13.31	2.54	〃	〃	〃
13	700- 705	9.816	3.0	9.522	1.01	1.32	14.61	2.90	〃	〃	〃
14	920- 925	10.236	0.5	10.184	0.59	0.72	4.02	1.39	〃	〃	〃
15	970- 975	10.162	5.1	9.644	2.37	3.11	23.85	7.60	〃	〃	〃
16	1040-1045	10.039	0.8	9.959	0.84	0.83	6.31	2.22	〃	〃	〃
17	1110-1115	10.139	2.0	9.937	1.39	1.45	12.79	3.73	〃	〃	〃
18	1190-1195	9.574	3.7	9.220	2.26	2.41	17.67	5.30	〃	〃	〃
19	1210-1215	10.097	1.2	9.976	1.74	1.48	17.45	3.65	〃	〃	〃
20	1290-1295	9.375	3.7	9.028	2.07	2.74	19.32	6.80	〃	〃	〃
21	1357-1362	9.980	0.9	9.890	0.93	0.80	7.43	1.87	〃	〃	〃
22	1440-1445	10.859	0.4	10.815	0.55	0.38	3.37	1.31	〃	〃	〃
23	1540-1545	10.459	0.3	10.428	0.61	0.44	3.72	1.42	〃	〃	〃
24	1580-1585	10.325	0.5	10.273	0.49	0.50	4.42	1.20	〃	〃	〃
25	1647-1652	10.017	0.4	9.977	0.73	0.64	4.54	1.68	〃	〃	〃
26	1946-1951	10.173	2.5	9.919	0.94	1.48	24.97	3.87	〃	〃	〃
27	2039-2042	10.754	3.1	10.421	0.98	1.69	12.83	4.40	〃	〃	〃
28	2145-2150	9.959	3.8	9.580	0.78	2.45	71.77	8.91	〃	〃	〃
29	2220-2225	10.376	3.1	10.054	0.68	2.29	46.73	9.04	〃	〃	〃
30	2340-2345	10.379	5.8	9.777	2.22	2.69	16.72	11.12	〃	〃	〃
31	2512-2517	10.238	7.2	9.500	2.40	2.82	13.26	10.16	〃	〃	〃
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34	2738-2743	10.087	5.4	9.542	1.15	3.21	28.73	10.20	〃	〃	〃
35	2781-2786	10.160	3.2	9.835	1.05	2.98	22.73	6.02	〃	〃	〃

were found to be quartz and feldspar-group and only a few secondary minerals were found, those were calcite and halite (see Table 1). From the analytical results of extracts (*cf.* Tables 2 and 3), milli-equivalents of chemical species in one gram of air-dried sample were calculated. The total milli-equivalent of cations or anions was calculated respectively by summing up the milli-equivalents of four cations or two anions. The distribution with depth of the water soluble cations and anions is shown in Fig. 6.

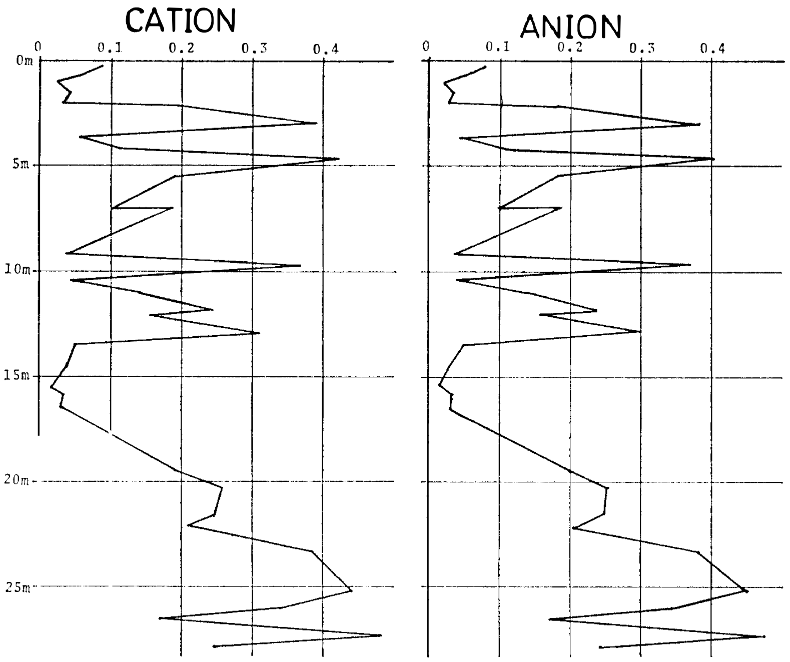


Fig. 6. Distribution with depth of water soluble cations and anions in meq/g.

In Fig. 7, the vertical distribution of the water and perchloric acid soluble matters is shown in equivalent percent. Total water soluble salt ranges from one to 25 mg per one gram of air-dried sediment. Perchloric acid soluble salt ranges from 5 to 80 mg. There are some different features in the distribution patterns for water and perchloric acid extractions. These differences are mainly due to the presence of secondary minerals, for example calcite or halite and so on. There are several peaks in the quantity of soluble matter in the core. This suggests the presence of some epochs in the past sedimentation processes in the area, such as drying up of or filling up with water.

From the equivalent percent of chemical species, the authors tried to make triangular diagrams of calcium, magnesium and potassium plus sodium as shown in Fig. 8. Diagrams for water and perchloric acid soluble portions of DVDP 14 core are shown in Fig. 8a. There is a distinct difference between the two diagrams,

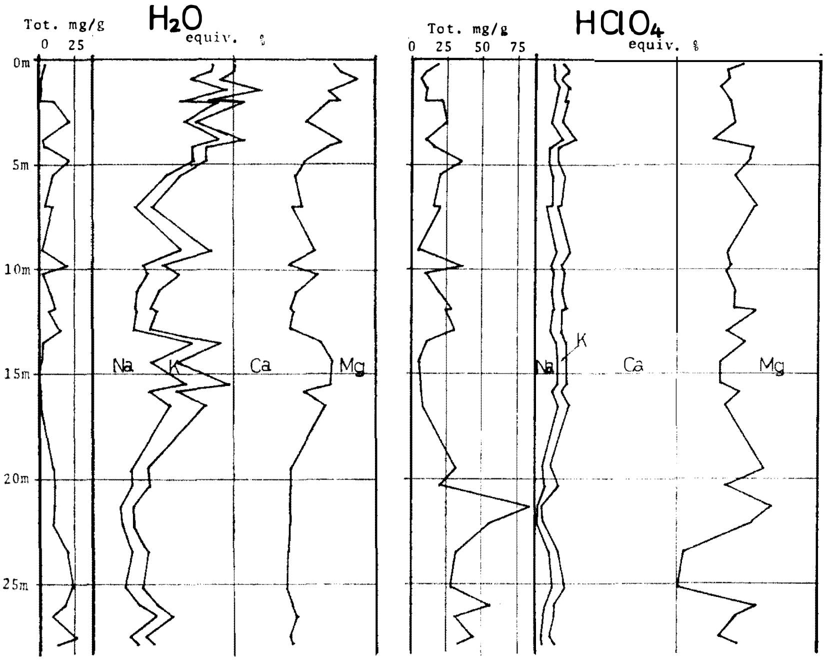
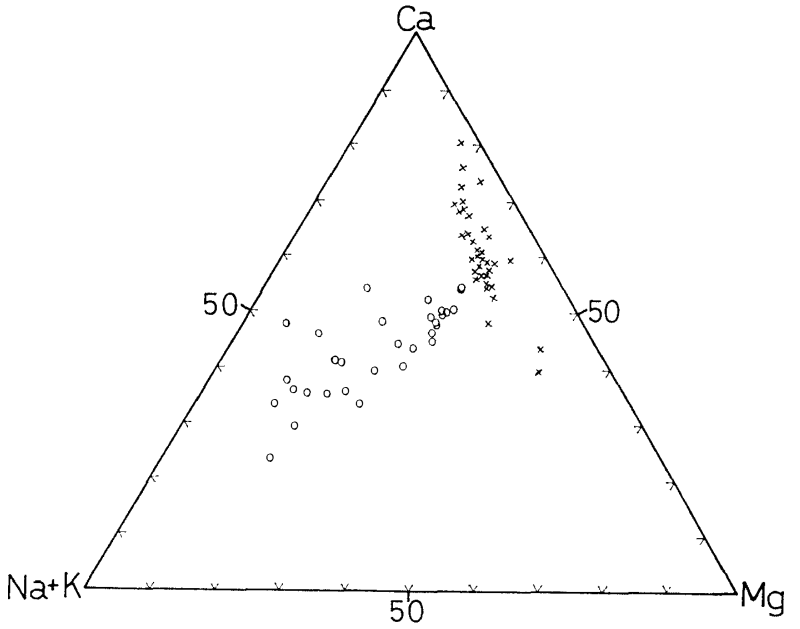


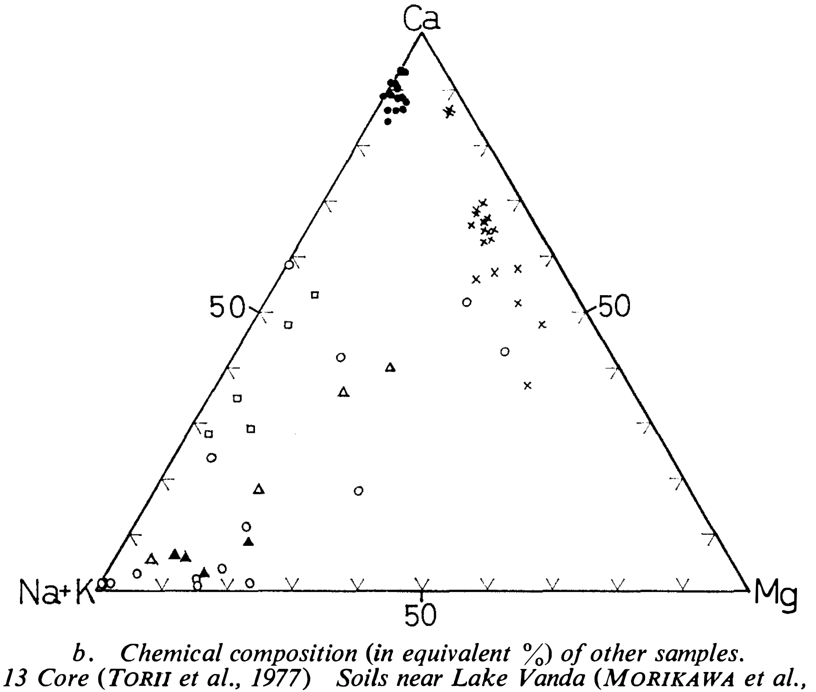
Fig. 7. Distribution of H_2O and $HClO_4$ soluble matters in equivalent %.

i.e. water soluble portion is rich in alkali metals—sodium and potassium, and perchloric acid soluble portion is rich in alkaline-earth metals—calcium and magnesium. Chemical compositions of DVDP 13 core (Torii *et al.*, 1977), Onyx River water (Lois and Faure, 1969), soils near Lake Vanda (Morikawa *et al.*, 1975), and soils from Mt. Jason and Mt. Odin (Hendy, 1973) are characteristically shown in Fig. 8b by plotting their positions. The chemical compositions of water soluble portion of soils near Lake Vanda, soils from Mt. Jason and Mt. Odin and of Onyx River water are similar to that of DVDP 14 core. Those are rich in sodium and sodium salt such as halite found in the core samples. Fig. 7 shows that the layer near the surface of the ground is rich in alkali metals. Chemical compositions of perchloric acid soluble portion in soil and DVDP 13 core are similar to that of DVDP 14 core. Those are rich in alkaline-earth metals. Conclusively, the authors consider that river water is originated from the glacier melt water and that the origin of soluble salt is re-dissolution of salt presented on the soil surface. In general, because of their solubilities, alkali metals remain on the soil surface as chloride on evaporation or concentration and then are easily redissolved with water by washing out. But alkaline-earth metals precipitated as carbonate or sulfate can not be easily re-dissolved by washing out.

The total soluble matters in the core are summarized in Fig. 9, in which the carbonate profile was estimated by the subtraction of the chloride ion content from the total cation content, on the assumption that the total cation content is equal to



a. Chemical composition (in equivalent %) of DVDP 14 core.
○: H_2O soluble portion, ×: $HClO_4$ soluble portion



b. Chemical composition (in equivalent %) of other samples.

DVDP 13 Core (TORII et al., 1977)	*Soils near Lake Vanda (MORIKAWA et al., 1975)*
●: *H_2O soluble portion*	○: *H_2O soluble portion*
×: *$HClO_4$ soluble portion*	*Soils from Mt. Jason and Mt. Odin (HENDY, 1973)*
Onyx River Water (LOIS and FAURE, 1969)	△: *Mt. Jason,* ▲: *Mt. Odin*
□: *River water*	

Fig. 8. Triangular diagram of cations in extracts.

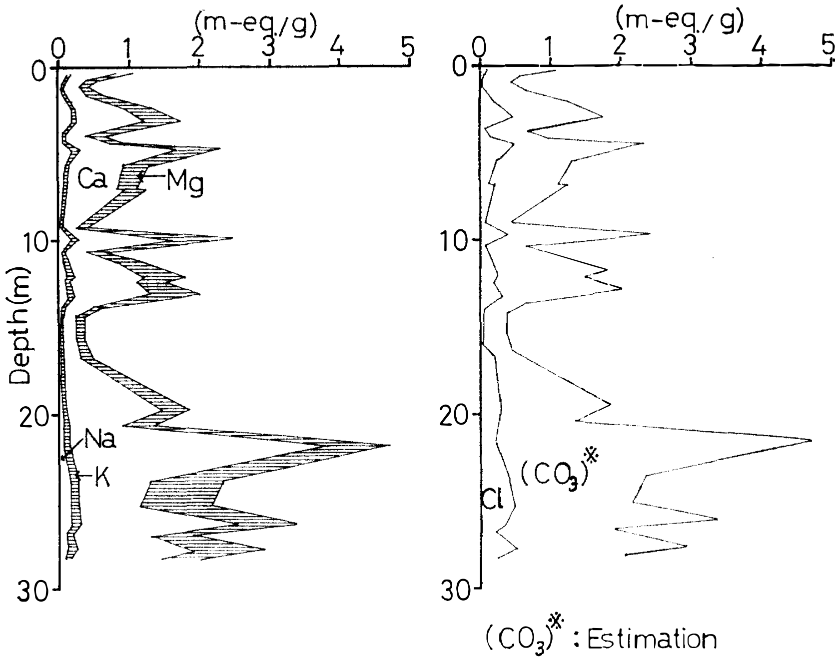


Fig. 9. Distribution of total soluble matters in meq/g.

the total anion content, because the sulfate ion was negligibly small in the core. In general, the content of calcium ion increases with increasing depth. It means that calcium ion remained in solution when lake water was concentrated under a frigid condition. Sodium ion should be deposited first as mirabilite from the solution in the concentration stage. And these salts should be re-extracted when the volume of lake water increased, and deposited again when the concentration process began. Therefore, the peaks of soluble matter may indicate the number of times of drying up of the lake water since the first appearance of the lake in this basin. This interpretation is supported also by granulometric analysis of the sediment (NAKAO *et al.*, 1979).

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