

Partitioning of Chemical Elements into Mineral Species in Core Sediment from Don Juan Pond Using Selective Chemical Leaching Technique

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分別溶解法によるドンファン池のコア堆積物中の鉱物種への
化学元素の分配について

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要旨: 塩化カルシウム型の塩湖であるドンファン池から採取したコア堆積物を分別溶解法を用いて分析した。堆積物は、1 M 酢酸可溶、1 M 塩酸ヒドロキシルアミン+25%酢酸可溶、1.2 M 塩酸可溶、フッ酸+過塩素酸可溶、の4フラクションに段階的に分別し、それらのフラクション中への Ca, Mg, Fe, Mn, Cu, Zn の分配について、その深度分布を示した。また、堆積物中に含まれる gypsum や calcite への微量元素の分配についても考察した。

この方法は、ドンファン池の堆積物、および塩化カルシウム型の水の起源を議論するうえで、有効であると考えられる。

Abstract: A selective chemical leaching technique has been applied to the sediment core samples from Don Juan Pond in Antarctica, which is known as a very high calcium chloride saline pond. The vertical profiles are shown on the partitioning of Ca, Mg, Fe, Mn, Cu and Zn into the following four fractions of the sediment; 1M CH₃COOH soluble, 1M NH₂OH·HCl+25% CH₃COOH soluble, 1.2M HCl soluble and HClO₄+HF soluble fractions. The partitioning of trace metals into gypsum and calcite found in the sediment has been estimated. This may be helpful for the discussion on the formation processes of the sediment and also of the calcium chloride water in Don Juan Pond.

1. Introduction

A number of investigations about Antarctic saline lakes have been performed (MEYER and MORROW, 1962; NISHIYAMA, 1977; TEDROW and UGOLINI, 1963; TORII *et al.*, 1975; WATANUKI and MORIKAWA, 1975; WATANUKI *et al.*, 1979). Don Juan Pond in the Dry Valleys area of south Victoria Land has been known as an unfrozen pond in which the calcium chloride concentration is very high as shown in Table 1 (TORII *et al.*, 1977).

From the geochemical study of lake waters and sediments, it was proposed that the saline lake waters in this region might be formed through the dissolution of salts, which had been formed from seawater through evaporation, with

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Table 1. Chemical composition of saline water in Don Juan Pond (TORII *et al.*, 1977).

Element	Concentration (g/kg)
Na ⁺	6.73
K ⁺	0.13
Ca ²⁺	105.0
Mg ²⁺	1.6
Cl ⁻	207.5
SO ₄ ²⁻	0.0
Br ⁻	0.098

glacial melt water. On the other hand, it was suggested strongly that the salts in these saline lakes may be attributed to weathering of rock and to sea spray.

In order to obtain information to clarify the salt origin in these lakes, a selective chemical leaching technique has been applied to the sediment core samples taken from Don Juan Pond by TORII in the 1977–1978 summer season.

The present paper deals with minor elements such as Fe, Mn, Cu and Zn as well as major chemical elements. The geochemical behaviors of trace heavy metals in saline lakes such as Don Juan Pond are to be discussed in the present paper.

The selective chemical leaching technique is based on the preferential dissolution of each mineral in sediment with a selected chemical solution. The application of this technique gives the partitioning of elements into each mineral in sediment. This technique was applied already to manganese nodules (CHESTER and HUGHES, 1967; KITANO and FUJIYOSHI, 1980a), various sediments (KITANO and SAKATA, 1978; KITANO *et al.*, 1980; KITANO and FUJIYOSHI, 1980b; KITANO *et al.*, 1981; MALO, 1977) and particulate matters in seawater (GUPTA and CHEN, 1975), and it has proved to be a useful method in obtaining much important information on the formation of the sediment.

2. Experimental

2.1. Sample

The core sample used in the present research is DJ 14 as shown in Fig. 1, which was taken by means of dry drilling technique. Table 2 shows the result of powder X-ray diffraction analysis of this core sample (MURAYAMA, private communication). For the present study No. 2 to No. 14 samples of the core were used.

After the samples had been dried under vacuum condition, they were ground slightly in an agate mortar and sieved through a polyethylene sieve (80 mesh) to remove sand and gravel. And the sieved samples were used for the partitioning study.

2.2. Selective chemical leaching procedure

The leaching procedure employed in the present study is shown schematically in Fig. 2.

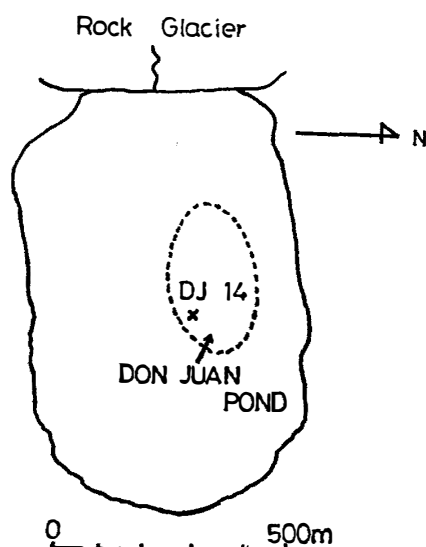


Fig. 1. Sampling station of sediment core in Don Juan Pond.

Table 2. Minerals identified in DJ 14 core sample by X-ray diffraction analysis (MURAYAMA, 1980, private communication)

No.	Depth (cm)	Quartz	Feldspar	Mica	Gypsum	Halite	Thenardite	Calcite	Hornblende
1	0—0.5	++	+	?	+	+++	Tr	Tr	Tr
2	0.5—13.5	++	+	Tr	++				Tr
3	13.5—19	+	++	Tr	++		?	Tr	Tr
4	19—27	+++	++		++		?	Tr	Tr
5	27—29	++	+	?	++			+	Tr
6	29—39	+++	++		++		Tr	+	Tr
7	39—52	++	+++	?	++		?	+	Tr
8	52—59	+	+	Tr	+++	Tr	?	Tr	?
9	59—65	++	+	Tr	++	?		?	?
10	65—71	+++	+		++			?	Tr
11	71—79	++	++	?	++				?
12	79—82	++	++	?	+++		?	Tr	Tr
13	82—86	++	+	?	+++	?		?	Tr
14	86—90	++	+	?	+++	?	?		Tr

+++ : abundant, ++ : moderate, + : detected, Tr : trace, ? : dubious.

(a) Since DJ 14 sample contains a large amount of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as seen from the X-ray diffraction result (Table 2), firstly CaSO_4 was dissolved with distilled water. The solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in water is 0.21 g/100 ml (40°C), whereas that of CaCO_3 is 4.4 mg/100 ml (40°C). The sediment sample (about 0.2 g) was digested in distilled water of a sufficient amount (100 ml) at 40°C with stirring for 12 h to dissolve gypsum completely without a significant dissolution of CaCO_3 . The complete dissolution of gypsum was confirmed by the X-ray diffraction analysis. After the dissolution of gypsum, the suspension was filtered through a 0.45μ Millipore filter. The residue on the filter was weighed to know the content of water soluble fraction in the sample.

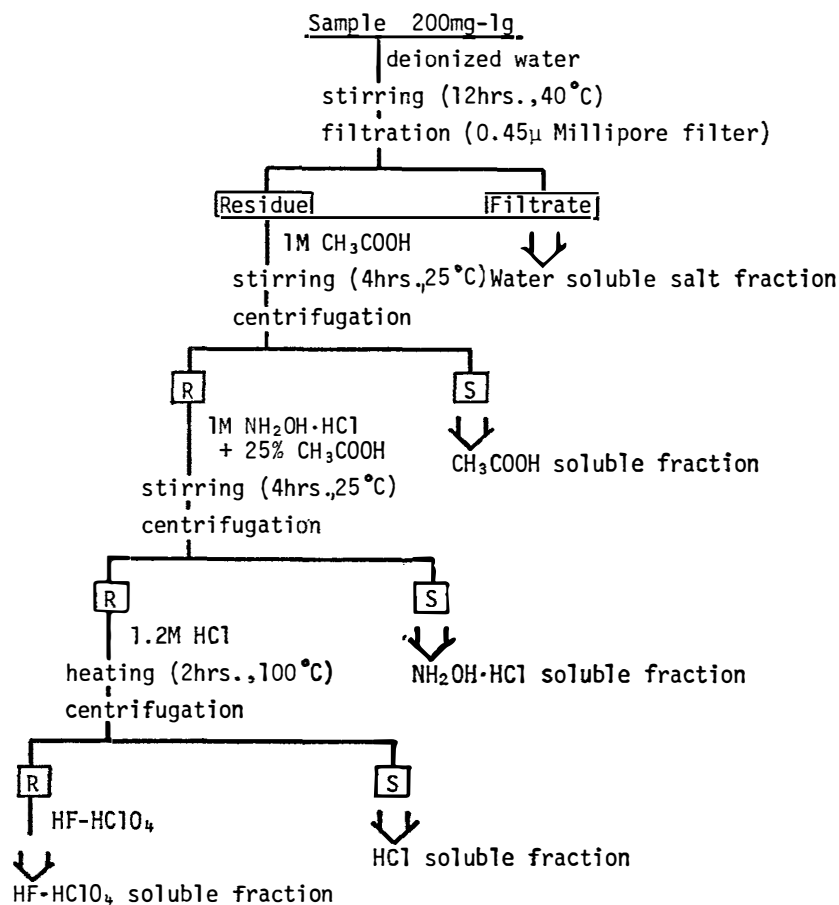


Fig. 2. Analytical procedure for determination of partition of chemical constituents in core sediment samples.

Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- , Fe^{2+} , Fe^{3+} , Mn^{2+} , Cu^{2+} and Zn^{2+} in the filtrate were determined. The chemical constituents in the filtrate are designated as water soluble fraction. Here it must be noted that significant portions of trace heavy metal ions dissolved to distilled water are removed from the water through the adsorption on the remaining water insoluble materials during this water leaching treatment.

Generally, a selective chemical leaching procedure is started by the treatment of digestion in ammonium acetate or magnesium chloride solution to determine the chemical constituents in an ion exchangeable form. However, it is very difficult in this sample to separate the ion exchangeable fraction from water soluble salts, because this sample contains large amounts of water soluble salts. Therefore, only the overall water soluble fraction was discussed for this sample and the amounts of chemical elements in the ion exchangeable fraction were not estimated. And the ion exchangeable constituents seem to be included in both fractions leached with distilled water and with 1M CH_3COOH in this selective leaching procedure.

(b) The residue from the water treatment was leached with 1M CH_3COOH (30 ml) for 4 h at room temperature. Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Cu^{2+} and Zn^{2+} dissolved in the solution were determined. The chemical constituents in this

fraction are regarded as those associated with carbonate and also partly with the ion exchangeable fraction. Heavy metals once leached with distilled water but adsorbed again on an insoluble residue may be also dissolved in this solution.

(c) The residue from the 1M CH_3COOH treatment was digested in 1M $\text{NH}_2\text{OH}\cdot\text{HCl}+25\% \text{CH}_3\text{COOH}$ solution (30 ml) for 4 h at room temperature to determine the chemical constituents in the ferro-manganese oxide fraction.

(d) The residue from the 1M $\text{NH}_2\text{OH}\cdot\text{HCl}+25\% \text{CH}_3\text{COOH}$ treatment was digested in 1.2M HCl (30 ml) for 2 h at 100°C to determine the chemical constituents in unstable clay minerals. It was reported that 1.2M HCl solution leaches Mg^{2+} and/or Fe^{2+} in rather soluble clays such as vermiculite and chlorite (JACKSON, 1968).

(e) Finally, stable silicates were decomposed with HClO_4+HF solution.

2.3. Analytical procedure

Na^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Cu^{2+} , and Zn^{2+} were determined by using a Perkin Elmer 503 atomic absorption spectrometer, and Fe^{2+} , Fe^{3+} , Mn^{2+} , Cu^{2+} and Zn^{2+} in the water soluble fraction were determined by the spectrometry after concentration with DDDC*- CCl_4 extraction.

Sulfate ions were determined colorimetrically using barium chromate—acid suspension (IWASAKI *et al.*, 1958), by which 20–100 ppm SO_4^{2-} in the solution is determined with a sufficient precision; or gravimetrically. Chloride ions were determined colorimetrically with mercury thiocyanate (TOMONARI, 1962). The carbonate content of the sample was determined by a little modified Conway diffusion method (SARUHASHI, 1953). To complete the dissolution of carbonate in the sample with sulfuric acid, a Conway unit was tightly closed and heated in the air bath at 80°C for 1 h. After cooling, the $\text{Ba}(\text{OH})_2$ standard solution, which had adsorbed CO_2 evolved from carbonate in the sample, was titrated with standard HCl solution.

3. Results and Discussion

3.1. Analysis of overall sample

Table 3 shows the analytical results of overall sample. These values are expressed as the concentration on 105°C dry basis of the sediment sample.

3.2. Selective chemical leaching

3.2.1. Water soluble fraction

(a) Composition: Water soluble salt is considered to repeat a cyclic deposition and dissolution according to environmental changes. Figure 3 shows the vertical profiles of the content and the composition of water soluble salts in the sediment. And the figure shows that the water soluble salt content of the sediment is 30 to 80% in dry basis and most of the salt is gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$).

Since the surface sediment sample in this core (DJ 14–1) was not available, its chemical analysis was not carried out. According to the result of X-ray dif-

* Diethylammonium Diethyldithiocarbamate.

Table 3. Chemical composition of sediment samples in DJ 14 core.

Sample No.	Ca		Mg		Na		Fe		Mn	Cu	Zn	SO ₄		Cl		CO ₃	
	%	meq/g	%	meq/g	%	meq/g	%	meq/g	ppm	ppm	ppm	%	meq/g	%	meq/g	%	meq/g
DJ 14-2	15.6	7.80	1.00	0.82	1.17	0.51	1.92	1.03	420	12	29	25.6	5.33	8.12	2.29	0.66	0.22
3	16.4	8.18	0.70	0.57	1.04	0.45	1.47	0.79	290	16	37	23.9	4.97	4.08	1.15	3.57	1.19
4	14.1	7.05	0.87	0.71	0.92	0.40	1.68	0.90	360	19	27	22.1	4.60	3.23	0.91	2.31	0.77
5	19.9	9.93	0.72	0.59	0.88	0.38	1.56	0.84	560	19	33	31.4	6.54	3.30	0.93	4.74	1.58
6	15.4	7.70	0.92	0.75	1.25	0.54	1.83	0.98	420	22	34	15.8	3.29	3.55	1.00	7.44	2.48
7	15.6	7.78	0.84	0.69	0.93	0.40	1.93	1.04	430	21	36	23.7	4.93	3.76	1.06	2.91	0.97
8	22.5	11.3	2.46	0.38	0.76	0.33	1.06	0.57	340	12	17	46.7	9.72	3.23	0.91	0.72	0.24
9	12.9	6.45	1.37	1.12	1.99	0.87	2.30	1.24	430	24	37	19.8	4.12	3.76	1.06	1.35	0.45
10	13.0	6.48	1.02	0.84	1.33	0.58	2.16	1.16	420	25	41	19.2	4.01	3.90	1.10	0.93	0.31
11	16.6	8.28	1.07	0.88	1.55	0.67	1.75	0.94	390	23	34	28.1	5.86	4.11	1.16	1.02	0.34
12	20.0	10.0	0.47	0.39	0.87	0.38	1.05	0.56	270	11	22	42.5	8.86	2.91	0.82	0.90	0.30
13	24.4	12.2	0.34	0.28	0.59	0.26	0.81	0.44	240	7.8	14	50.0	10.4	4.89	1.38	0.57	0.19
14	22.9	11.5	0.55	0.45	0.51	0.22	0.68	0.37	190	5.7	9.0	47.4	9.88	5.03	1.42	0.45	0.15

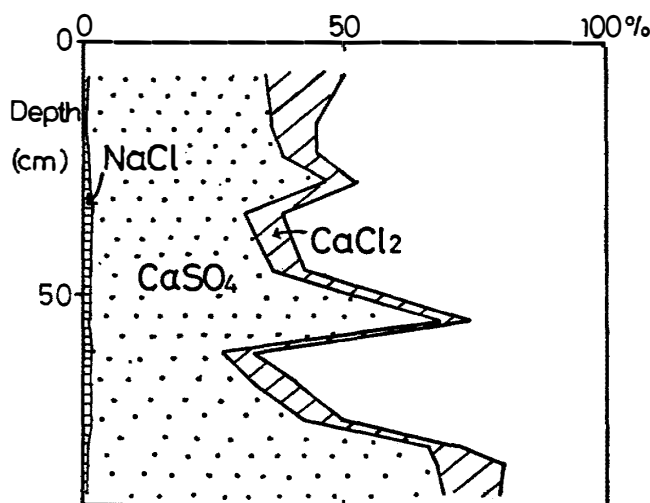


Fig. 3. Vertical distribution of water soluble salts.

fraction analysis shown in Table 2, it is recognized that the surface layer down to 0.5 cm in depth contains a large amount of halite (NaCl) but deeper layers contain no significant amount of halite. Such a fact may suggest that water soluble salts in the surface sediment have repeated dissolution and deposition owing to the supply of land water such as glacial melt water to the pond and also to the evaporation of the pond water. The occurrence of antarcticite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) is regarded as one of these cyclic phenomena (TORII *et al.*, 1970).

The presence of water soluble salts in the surface sediment is considered to suggest a dry climatic condition.

(b) Magnesium in gypsum: Gypsum, a major component in the water soluble salts, is assumed to be formed by the supply of sulfate ions to Don Juan Pond through ground water and glacial melt water. TORII *et al.* (1977) reported that the sulfate concentration of ground water in Don Juan Basin was saturated with calcium sulfate. When magnesium ions in the pond water are incorporated into calcium sulfate as a solid solution, the relative concentration ratio of magnesium ions to calcium ions in the pond water will be expected from the magnesium content of gypsum. The following equation is given for a solid solution at an equilibrium between precipitate and solution: $(A/B)_s = D \cdot (A/B)_l$, where $(A/B)_s$ and $(A/B)_l$ are the concentration ratios of trace component A to major component B in precipitate and solution respectively and D denotes an apparent partition coefficient.

Column (a) in Table 4 shows the molar ratios of magnesium content to calcium content in gypsum of DJ 14 core sample. This calculation was carried out by assuming that all magnesium leached in distilled water was contained in gypsum. DJ 14-2 and DJ 14-14 sample are the sediments at the surface and at a depth of about 88 cm from the surface of the sediment respectively. Therefore, DJ 14-2 and DJ 14-14 are considered to correspond to the sediments formed from the present water and from the past pond water respectively. Thus, the following equation is expected:

$$\frac{([\text{Mg}]/[\text{Ca}]_{\text{pond water in DJ 14-2}})}{([\text{Mg}]/[\text{Ca}]_{\text{pond water in DJ 14-14}})} = \frac{([\text{Mg}]/[\text{Ca}]_{\text{gypsum in DJ 14-2}})}{([\text{Mg}]/[\text{Ca}]_{\text{gypsum in DJ 14-14}})} = \frac{8.1}{2.7} = \frac{3}{1}.$$

Table 4. Ratios of magnesium content to calcium content in gypsum and calcite.

Sample No.	(a)	(b)
	Mg/Ca in gypsum	Mg/Ca in calcite
	$\times 10^{-3}$	$\times 10^{-3}$
DJ 14-2	8.1	35
3	5.5	8.4
4	4.5	13
5	3.9	7.3
6	6.2	3.6
7	5.1	12
8	2.6	26
9	5.0	18
10	5.9	36
11	3.8	23
12	2.2	34
13	2.4	43
14	2.7	42

This value indicates that the concentration ratio of magnesium ions to calcium ions in the present pond water is three times higher than that in the water from which the DJ 14-14 sediment was deposited. The value of D of the present pond is calculated to be 3.2×10^{-1} . The partition coefficient for magnesium in the gypsum-solution system has not been reported because the synthesis of dihydrated salt of calcium sulfate is difficult. And it will be needed to determine the partition coefficient of magnesium ions in the gypsum-solution system in order to discuss the history of the saline water in Don Juan Pond.

(c) Manganese in gypsum: When heavy metals of the water soluble fraction were determined according to the procedure shown in Fig. 2, where the dissolution was continued for 12 h, the heavy metal contents of the fraction became negligibly small and blank values. This is assumed to be attributed to that the period of the dissolution treatment was so long that heavy metal ions once leached into the solution were removed again through their coprecipitation with residual materials during the dissolution procedure. Then the period of dissolution treatment was reduced to 1 h, but it was confirmed again that the removal of iron, copper and zinc ions was not negligible even for 1 h of the treatment period. Figure 4 shows the changes in the leached amounts of metals with changing period of dissolution. It was observed very clearly that copper and zinc ions which had been once dissolved, were rapidly removed from the leaching solution. On the other hand, the leached amount of manganese still increased even after the dissolution period of 1 h. These results indicate that the rate of adsorption of copper and zinc ions was very large, whereas that of manganese was small.

Column (a) in Table 5 shows the concentration ratio of manganese to calcium ions in the water soluble fraction when the dissolution period was 1 h. It can be seen from the table that a significant variation is observed in the ratio with

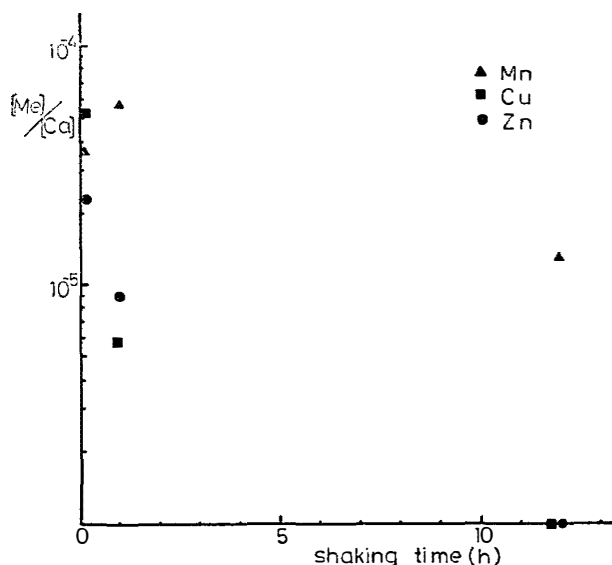


Fig. 4. Relation between leached amount and dissolution period.

Table 5. Ratios of manganese content to calcium content in gypsum and calcite.

Sample No.	(a)	(b)
	Mn/Ca in gypsum	Mn/Ca in calcite
	$\times 10^{-5}$	$\times 10^{-3}$
DJ 14-2	5.4	1.0
4	6.3	0.33
6	8.0	0.87
8	12	15
9	4.1	1.6
11	8.0	3.0
13	33	0*
14	18	1.3

* The amount of manganese leached with distilled water is equal to that leached with acetic acid solution. Thus, it is assumed that manganese is mostly incorporated into gypsum but not into calcite.

depth in the sediment core. If manganese has been incorporated into gypsum as a solid solution under an equilibrium condition, column (a) in Table 5 will indicate that the concentration ratio of manganese to calcium ions in the past pond water was very large as compared with that in the recent pond water. The source and process of manganese entering into Don Juan Pond are an interesting subject to be studied.

3.2.2. Water insoluble fraction

Figures 5 to 10 show the vertical distributions of Ca, Mg, Fe, Mn, Cu and Zn respectively in four fractions except for water soluble fraction, which are given as their concentrations on the basis of water insoluble portion.

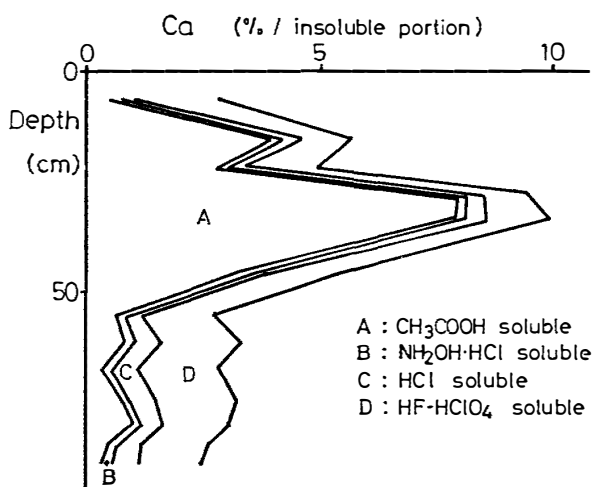


Fig. 5. Vertical distribution of Ca in insoluble fraction of DJ 14 sediment core.

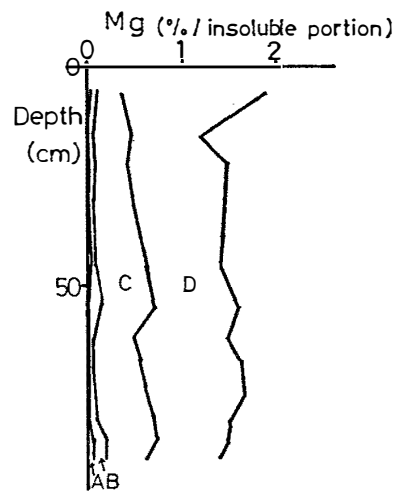


Fig. 6. Vertical distribution of Mg in insoluble fraction of DJ 14 sediment core.

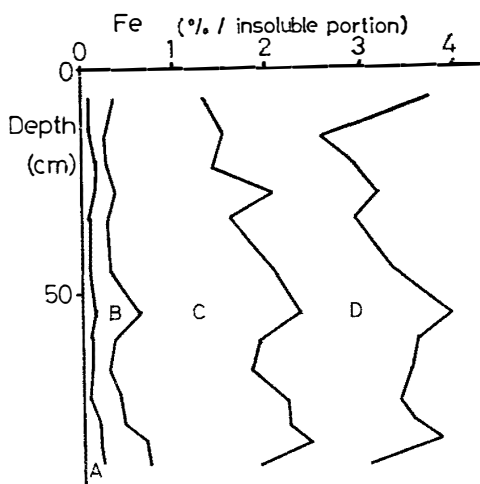


Fig. 7. Vertical distribution of Fe in insoluble fraction of DJ 14 sediment core.

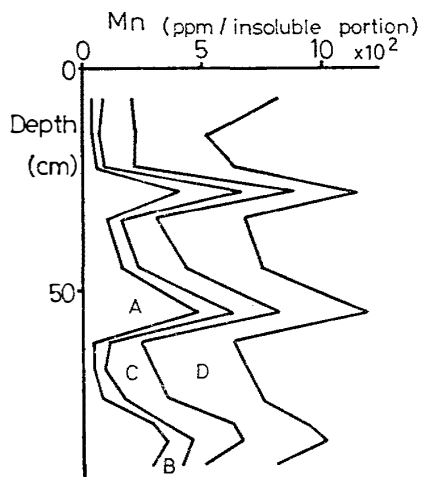


Fig. 8. Vertical distribution of Mn in insoluble fraction of DJ 14 sediment core.

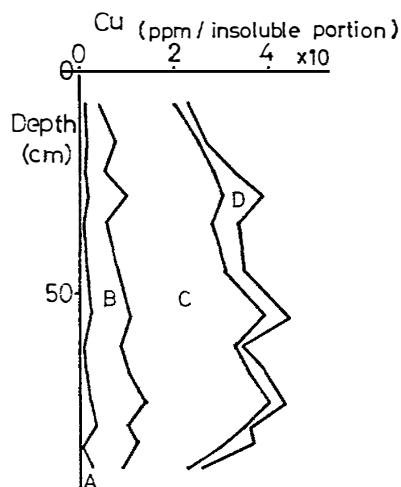


Fig. 9. Vertical distribution of Cu in insoluble fraction of DJ 14 sediment core.

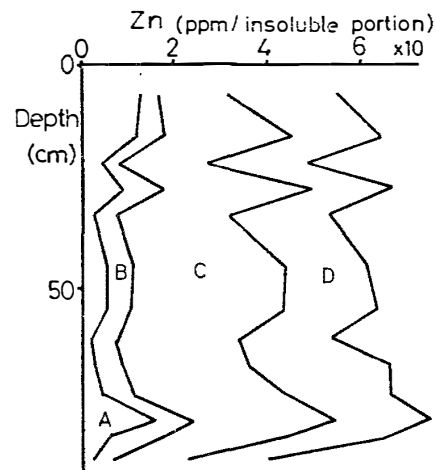


Fig. 10. Vertical distribution of Zn in insoluble fraction of DJ 14 sediment core.

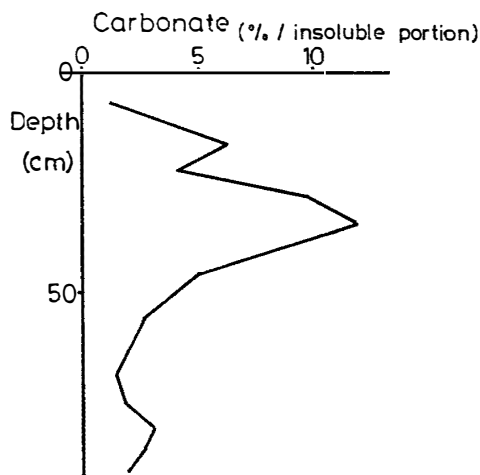


Fig. 11. Vertical distribution of carbonate in insoluble fraction of DJ 14 sediment core.

(a) Calcium and magnesium in CH_3COOH soluble fraction: Figure 5 shows that a large amount of CH_3COOH soluble calcium is contained in the sediment at a depth of 10–50 cm in the core. The distribution profile of the carbonate content in water insoluble part of the sample (Fig. 11) reveals the peak at the depth of 10–50 cm. Further, an equivalent relation 1:1 is observed between the CH_3COOH soluble calcium content and the carbonate content. Therefore, most of calcium leached with 1M CH_3COOH is considered to be derived from calcium carbonate, and the layer rich in calcium carbonate exists at the depth of 10–50 cm in DJ 14 core sample.

The crystal form of the calcium carbonate was identified as calcite by a powdered X-ray diffractometry. Two possible sources for this calcium carbonate are expected (KITANO and HOOD, 1962): One source is calcium carbonate precipitated inorganically from the pond water, and another source is fine carbonate particles which are transported into the pond from the land area where limestone exists. The source of calcium carbonate in Don Juan Pond remains an important subject for future study.

Column (b) in Table 4 shows the magnesium content of the calcite. In this calculation, all CH_3COOH soluble magnesium was considered to be contained in calcitic calcium carbonate. These values show that the deeper layer sediment contains the higher magnesium content of calcium carbonate except for the surface sediment sample (DJ 14-2). This result seems to agree with the fact that the older calcium carbonate contains the higher magnesium content (FRIEDMAN and SANDERS, 1967). That is, concentration of magnesium into calcium carbonate is assumed to have occurred in the Don Juan Pond sediment.

Figure 12 shows the relation between gypsum and calcite in the concentration ratio of magnesium to calcium. These plots indicate an inverse correlation in the ratio between the two minerals except for two layers (DJ 14-2, -10). The mechanism for the appearance of the inverse relationship is not clarified, because the factors controlling the magnesium contents of calcite and gypsum in these samples are complex. Analysis of the interstitial water in this sediment and dat-

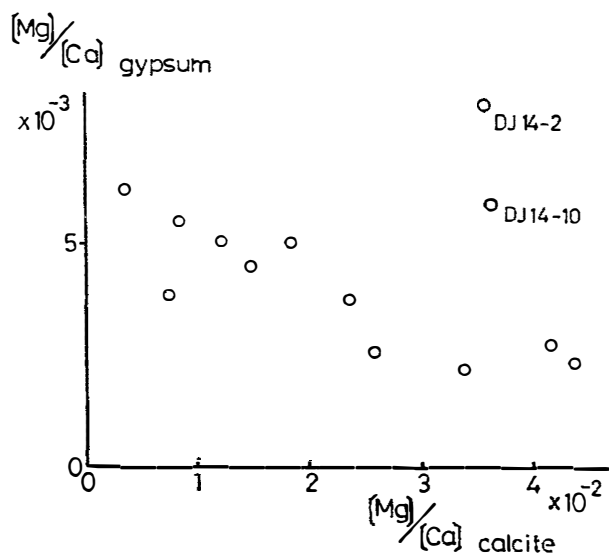


Fig. 12. Relation between gypsum and calcite in ratios of magnesium content to calcium content.

ing of the sediment core will be helpful for this subject.

(b) Manganese in CH_3COOH soluble fraction: Heavy metals leached with CH_3COOH seem to be contained mainly in calcium carbonate as a solid solution. But, as described earlier, the following must be taken into consideration: Even when heavy metals were contained in water soluble salts in the sediment, they might change to be incorporated into the CH_3COOH fraction, because heavy metals once dissolved might return to a solid phase in the dissolution process with distilled water.

The amount of manganese contained in gypsum was calculated by extrapolation from the column (a) values of Table 5. And the amount of manganese to have been contained originally in calcium carbonate was estimated by subtracting the calculated amount of manganese in gypsum, mentioned above, from the amount of manganese leached with CH_3COOH solution. These corrected values are given in column (b) of Table 5, where * mark indicates that the amount of manganese considered to exist in gypsum is nearly equal to that leached with CH_3COOH solution. Therefore, manganese is considered to be mostly incorporated into gypsum but not into calcite.

Figure 8 shows that CH_3COOH soluble manganese is enriched in the sediment layers at 30 cm, 55 cm and 85 cm from the surface of the sediment core. However, the values in column (b) of Table 5 obviously show that the CH_3COOH soluble manganese at a depth of 55 cm (DJ 14-8) exists in calcite, whereas that at 85 cm (DJ 14-13) exists in gypsum, that is, manganese in DJ 14-13 sample is concentrated considerably in gypsum and hardly in calcite. Generally manganese is considered to be greatly concentrated in calcite as compared with gypsum. These observations seem to be important for the discussion on the source of calcite in the pond.

(c) Iron, manganese, copper and zinc in $\text{NH}_2\text{OH}\cdot\text{HCl}$ soluble fraction: In the leaching treatment with $\text{NH}_2\text{OH}\cdot\text{HCl} + \text{CH}_3\text{COOH}$ solution, ferro-manganese

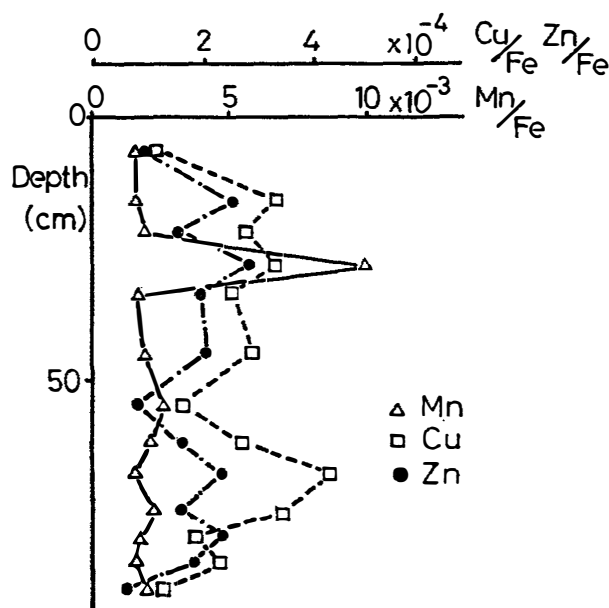


Fig. 13. Vertical profile of ratios of Mn, Cu and Zn to Fe in $\text{NH}_2\text{OH}\cdot\text{HCl}$ soluble fraction.

oxide is dissolved. The amounts of manganese, copper and zinc leached in this digestion treatment are shown as ratios of their amounts to the amount of iron leached. Figure 13 shows plots of the ratios against the depth in the sediment core. It is apparent that the ratios of the leached amount of manganese to that of iron are surprisingly constant except for only one point, as seen from Fig. 13. This constancy could be interpreted in the following two ways: The ratio of manganese ions to iron ions supplied into Don Juan Pond has been constant, and ferro-manganese oxide has been precipitated in the pond. Or, iron and manganese oxides were not precipitated from the pond water but were supplied to the pond as particles with a constant ratio of manganese to iron.

If the oxides were precipitated from the pond water, the heavy metal contents of $\text{NH}_2\text{OH}\cdot\text{HCl}$ fraction will reflect their concentrations in the pond water. From the assumption that the heavy metal concentrations of the pond water were recorded in the water soluble salts, the heavy metal contents of $\text{NH}_2\text{OH}\cdot\text{HCl}$ soluble fraction should be considered to have some relation with those of water soluble fraction. That is, the manganese content of $\text{NH}_2\text{OH}\cdot\text{HCl}$ soluble fraction in DJ 14-13 sample should be high, because the manganese content of the water soluble fraction is large and the concentration in the pond water is supposed to be high. But Fig. 8 does not show such a trend. Then, it seems difficult to consider that ferro-manganese oxide was formed in the pond water. It should be studied how ferro-manganese oxide has been supplied as particles to the pond water.

3.3. Consideration on the origin of salts in Don Juan Pond

The discussion on the origin of heavy metals in Don Juan Pond is considered to be useful for the discussion on the origin of major salts.

NAKAI *et al.* (1975) reported about stable isotope in the lake water and sediment of Lake Vanda, which is also situated in the Dry Valleys area. They re-

ported that ^{34}S of gypsum from the Lake Vanda sediment was equal to that of the present seawater, and they suggested that the salts in Lake Vanda were derived from seawater. And they concluded that the salts in Lake Vanda were derived not from sea spray but from seawater concentrated through evaporation (NAKAI and JENSEN, 1967). Similarly it has been proposed that the origin of salts in Don Juan Pond is seawater, that is, seawater was concentrated under frigid conditions and finally CaCl_2 type brine was formed. The experimental result by THOMPSON and NELSON (1956) on the concentration of seawater under frigid conditions shows the following order for the deposition of salts: CaCO_3 , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{NaCl} \cdot 2\text{H}_2\text{O}$, KCl and MgCl_2 . That is, the deposition of magnesium salt occurred at the final stage in the concentration process of seawater, and calcium chloride remained to be dissolved in water. When calcium chloride type brine in Don Juan Pond is thought to have been formed through such a process, the traces of the deposited magnesium salts should be searched and clarified, because magnesium salts have not been found in the surface sediment of Don Juan Pond, the magnesium concentration of the pond water is quite low, and further, the analytical results of DVDP core down to a depth of 1200 cm in the Don Juan Basin showed the absence of the sediment layer with concentrated magnesium (TORII *et al.*, 1977).

Calcium chloride type brine is found in oil-field brine, in the deep water of the Red Sea (CRAIG, 1969) and in the ground water of the Matushiro swarm earthquake region (Nagano Prefect., Japan) (KITANO *et al.*, 1967, 1968; YOSHIOKA *et al.*, 1970). The formation of this type water seems to be connected with connate water in sediments, although the exact mechanism and process for the formation of the calcium chloride type water remain to be clarified.

The present authors will study the distribution and geochemical behavior of magnesium in the areas where calcium chloride type water exists. They are conducting the partitioning experiments for many sediment core samples taken by TORII's group in the Dry Valleys areas of Victoria Land, Antarctica.

4. Summary

The partitioning of major and minor chemical elements into mineral species in core sediment samples taken from the Dry Valleys area has been determined with a selective chemical leaching technique. In the Dry Valleys area many high saline ponds are found, one of which is the well-known Don Juan Pond, with the water having the chemical composition of calcium chloride.

The present study has shown the partitioning of the chemical elements such as Ca, Mg, Fe, Mn, Cu and Zn into mineral species for the core sediment of Don Juan Pond with a selective chemical leaching technique. This line of study seems to be useful to clarify the formation and evolution of the calcium chloride brine water in Don Juan Pond.

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