

Sources of Chemical Constituents in the Salts of the Don Juan Basin

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ドンファン湖盆の塩類の化学成分の起源について

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要旨: 南極, ドライバレーのドンファン湖盆から採取した, 柱状コア7本について, そこに含まれている水溶性の塩類を分析し, 主成分と少量成分の含有量の比から, 過去の湖水の組成を推察した. また, 水不溶性の部分については, 分別溶解法を用いて分析をおこない, 各構成鉱物への, Ca, Mg, Fe, Mn の分配を明らかにした. それらの分析値を用いて, 現在のドンファン湖盆に存在する塩類の総量を見積もった. その結果, ドンファン湖盆の塩類の起源である塩水は, Mg が非常に少ない CaCl₂ 型の水ではないかと考えられる.

Abstract: Water soluble salts in seven sediment cores, which were taken from the Don Juan basin in the Dry Valleys region, Antarctica, were analyzed. The chemical composition of the original pond water was presumed from the contents of minor components as well as major components in the water soluble salts. The partitioning of Ca, Mg, Fe and Mn into each mineral in the water insoluble portion of the sediment was clarified by using a selective chemical leaching technique. The total amounts of salts in the Don Juan basin were estimated from these analytical data.

As a result, the original brine for the salt in the Don Juan basin was supposed to be a calcium chloride type water with a low magnesium content.

1. Introduction

There are many saline lakes and ponds in the Dry Valleys region of south Victoria Land, Antarctica. Don Juan Pond in the south fork of the Wright Valley is famous as a high saline pond of calcium chloride type water. The origin and the formation process of the pond have been discussed very actively because of the quite unique chemical composition of the pond water.

Previously the origin of salts in the Don Juan basin was studied mainly from the present chemical composition of pond water, minerals deposited in the surface of the basin and from the hydrological interest (HARRIS *et al.*, 1979; HARRIS and CARTWRIGHT, 1981; MORIKAWA and OSSAKA, 1975; TORII *et al.*, 1977; TORII and YAMAGATA, 1981). The present authors discuss the origin of a large amount of salts and the formation pro-

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cess of the basin by using analytical data of sediment core samples from the Don Juan basin.

Glacial meltwater flows into the basin in the austral summer, but there occurs no outflow from the pond. Water is lost only by evaporation. Therefore, the chemical composition of the original brine is presumed possibly by estimating the total amount of salts contained both in pond water and in sediment.

Firstly, the authors analyzed water soluble salts in the following sediment core; DVDP 13 taken by using circulating water and DJ 2, 3, 5, 10, 12 and 14 taken without using circulating water. The vertical and horizontal distributions of salts in the sediment were clarified and the total amount of the salts in the basin was estimated. The historical change in the chemical composition of the pond water was discussed through the distribution of minor components contained in water soluble minerals in the core sediments. Secondly, the water insoluble portion in the sediment was analyzed by using a selective chemical leaching technique: Calcium, magnesium, iron and manganese partitioned into the four fractions, which are carbonate, ferro-manganese oxide, acid soluble silicate and the residual stable silicate fractions, were determined by the technique. These results give some information regarding the formation process of the sediment in the Don Juan basin. The amounts of the chemical constituents uptaken into water insoluble minerals through post-depositional processes are estimated.

This paper especially emphasizes the importance of the distribution and behavior of magnesium for the discussion on the origin of salts in the Don Juan basin.

2. Experimental

2.1. Samples

Seven sediment cores, DVDP 13 taken in DVDP phase 4 (1974–1975) and DJ 2, 3, 5, 10, 12 and 14 taken in the 1978–1979 summer season, were used in the present study. Figure 1 shows the locations and the lengths of these cores.

In the selective chemical leaching experiment, samples were dried under vacuum condition, ground slightly in an agate mortar and sieved through a polyethylene sieve (80 mesh). On the dissolution of water soluble salts in the sediment, untreated samples were used.

2.2. Leaching procedures

2.2.1. Leaching with water

(A) Dissolution of water soluble salts in sediment sample for the determination of partitioning of major chemical constituents

As reported in the previous paper on DJ 14 sample (TOMIYAMA and KITANO, 1982), a large amount of water soluble salts such as gypsum and halite exist in the sediment of the Don Juan basin. These salts must be dissolved completely with water before the selective chemical leaching treatment. 0.2 to 1 g of sediment sample was digested in 100 to 200 ml of deionized water and stirred for 12 h. Then the water insoluble portion was filtered off through a 0.45 μ Millipore filter. Ca^{2+} , Mg^{2+} , Na^+ , Cl^- and SO_4^{2-} in the filtrate were determined. After weighing the insoluble portion, the insoluble portion was subjected to the selective chemical leaching procedure.

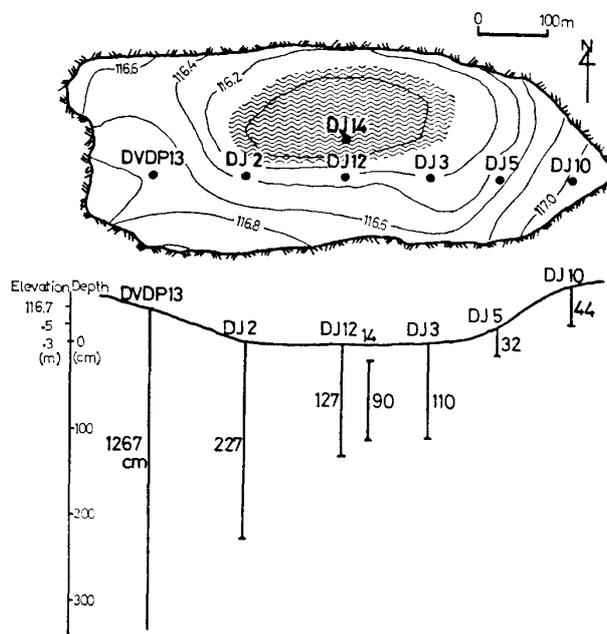


Fig. 1. Sampling stations and lengths of sediment cores in the Don Juan basin.

(B) Partial dissolution of water soluble salts in sediment sample for the determination of partitioning of trace heavy metals

When the dissolution is continued for 12 h according to the procedure shown in (A) for the determination of partitioning of trace heavy metals into water soluble minerals, it is impossible to have exact results because of the readsorption of trace heavy metals on water insoluble materials (TOMIYAMA and KITANO, 1982). Then, the following procedure was used: (1a) About 1 g of sample was put on a 0.45μ Millipore filter, and water soluble salts in the sample were dissolved by dropping deionized water into the sample with a slight suction. About 200 ml of deionized water was dropped through the sample into the receiver containing 2 ml of 1 M HNO_3 to adjust the pH of the filtrate to 2. The residue on the filter was transferred to a polyethylene centrifuge bottle. 50 ml of deionized water was added to the bottle, and it was shaken for 12 h to dissolve the remaining major water soluble salts completely. (1b) Since the heavy metal contents of the water soluble salt were very small, the filtrate had to be concentrated for the determination of heavy metals. 5 g of ion-exchange resin (Dowex 50W \times 12) was taken to a polyethylene syringe (10 ml), and conditioned to H-form. The filtrate mentioned in (1a) was transferred to a separation funnel attached to the top of the syringe, and dropped through the resin. The flow rate was kept at 1 ml/min. (1c) Elution was performed in the following sequence, and chemical constituents in the eluent were determined: Na^+ and K^+ were eluted with about 200 ml of 0.5 M HCl and determined. Then, $\text{Fe}^{2+,3+}$, Mn^{2+} , Cu^{2+} and Zn^{2+} were eluted with 50 ml of 1 M HCl in 92% acetone (FRITZ and RETTING, 1962). The 1 M HCl in 92% acetone eluent (50 ml) was concentrated by evaporating gently to about 10 ml on a hot plate for the determination of trace heavy metals. Finally, Ca^{2+} , Mg^{2+} and Sr^{2+} were eluted with 50 ml of 4 M HCl and determined. (2) The suspension of the residue on the filter after the dissolution procedure for 12 h mentioned in (1a) was filtered off through a 0.45μ Millipore filter,

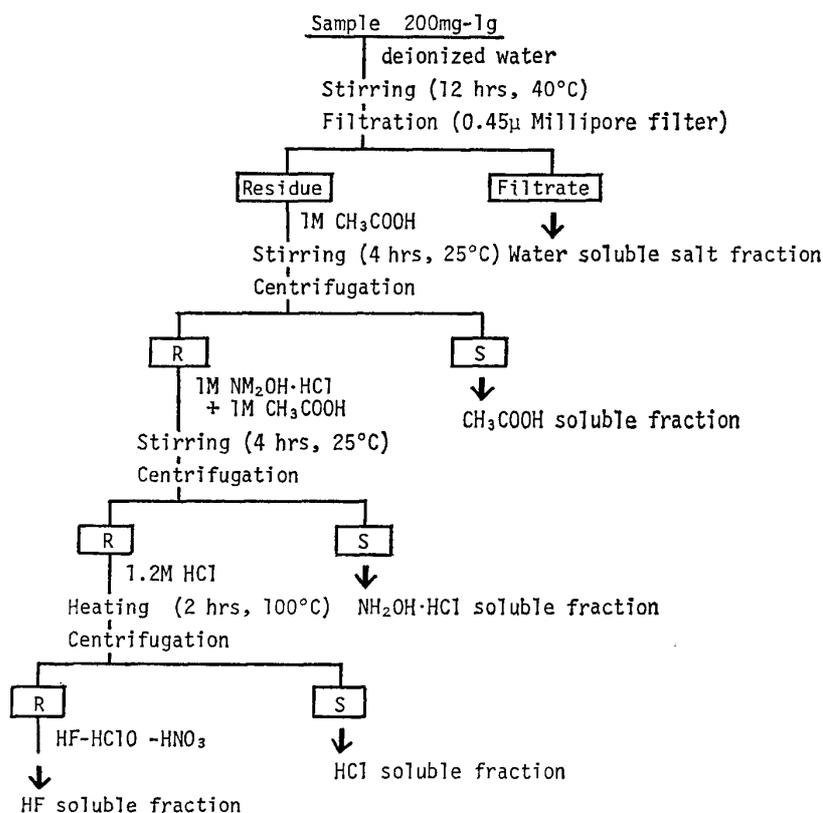


Fig. 2. Analytical procedure for determination of partition of chemical constituents in core sediment samples.

and Na^+ , K^+ , Ca^{2+} , Mg^{2+} and Sr^{2+} in the filtrate were determined.

2.2.2. Selective chemical leaching procedure

The residue from the complete leaching with water as described in 2.2.1. (A) was treated according to the leaching procedure shown in Fig. 2. The detailed description of the scheme was given in the previous paper (TOMIYAMA and KITANO, 1982). Chemical constituents in CH_3COOH soluble fraction, $\text{NH}_2\text{OH}\cdot\text{HCl}$ soluble fraction, HCl soluble fraction and HF soluble fraction are regarded generally as those associated with carbonate, ferro-manganese oxide, acid soluble silicate and residual silicate, respectively.

2.3. Analytical procedure

Na^+ , K^+ , Mg^{2+} , Sr^{2+} , $\text{Fe}^{2+,3+}$, Mn^{2+} , Cu^{2+} and Zn^{2+} were determined by using a Perkin Elmer 503 atomic absorption spectrometer. Sulfate and chloride ions were determined colorimetrically using barium chromate-acid suspension and mercury thiocyanate, respectively.

3. Results and Discussion

3.1. Water soluble fraction

3.1.1. Profiles of major constituents of water soluble salt

Figure 3 shows the content and the chemical composition of water soluble salts in the sediment cores DJ 2, 3, 5, 10, 12, 14 and DVDP 13. The abscissa shows wt% in

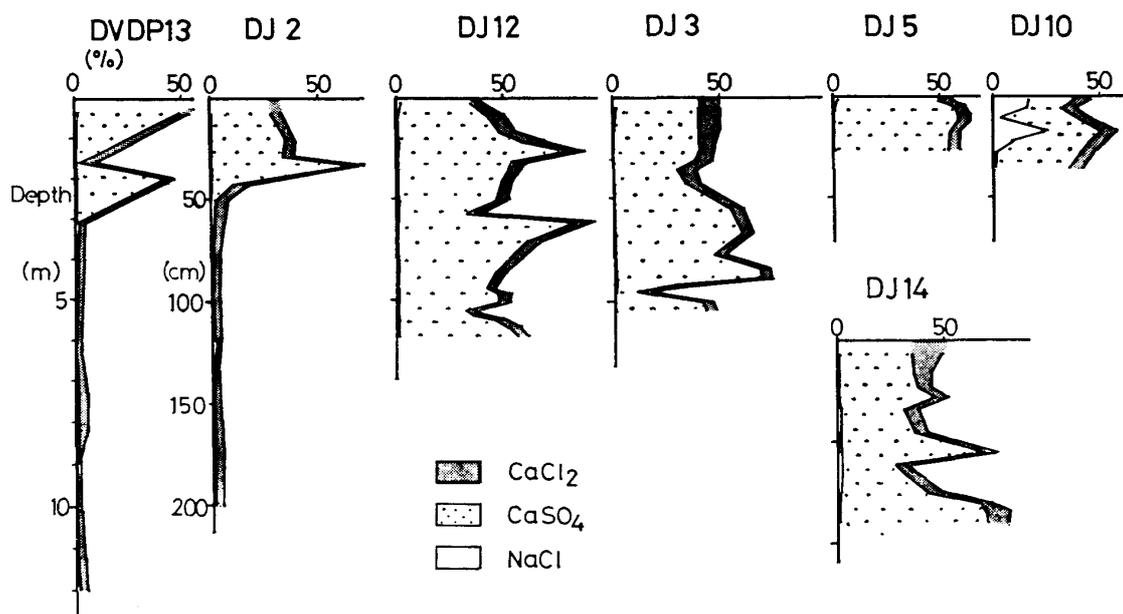


Fig. 3. Vertical distribution of water soluble salts.

dry basis. These profiles show that the water soluble salts in the sediments except for DJ 2 and DVDP 13 are 20 to 90%. The chemical compositions of the water soluble salts in the sediments except for DJ 2, 10 and DVDP 13 are as follows; 84 to 90% CaSO_4 , 10 to 15% CaCl_2 , 1 to 1.5% NaCl . DJ 10 sediment sample taken from the slope at the edge of the basin contains a large amount of NaCl . This agrees with the previous observation that the major component of the surface deposit in the slope of the Don Juan basin was NaCl (TORII *et al.*, 1977).

The sediment layers at 30 cm depth in DJ 2, 12 and 14, at 60 to 70 cm in DJ 3, 12 and 14 and at 90 cm in DJ 3 and 14 are recognized to contain a relatively large amount of water soluble salt. The presence of these salt-rich layers may be correlated to variations of the evaporation rate of pond water, of the sedimentation rate in Don Juan Pond and/or of the input of sulfate ions. It may indicate the climatic variation and the geomorphic history in the Don Juan basin. Through the above discussion, the origin of sulfate ions is thought to be very important. It will be discussed later.

The profiles of water soluble salt in DJ 2 and DVDP 13 are different from those in the other cores. The salt content of DJ 2 core decreases drastically at about 50 cm depth. In DVDP 13, the salt content is observed to be high in shallow layer, to decrease at 1.6 m depth, and to increase again at 2 m. And then, deeper layers of the sediment than 3 m contain only small amounts of salt. These low salt contents of the deeper layers DJ 2 and DVDP 13 are about 3 to 5 wt%. Their chemical compositions (70% CaCl_2 , 20% CaSO_4 , 10% NaCl) are quite different from those of water soluble salts in high contents. The difference in the chemical composition is supposed to be due to the presence of groundwater. HARRIS and CARTWRIGHT (1981) reported that discharge regions of groundwater exist in the Don Juan basin. Table 1 shows the chemical compositions of the groundwater and the pond water. The concentration ratios of Na^+ , K^+ , and Mg^{2+} to Ca^{2+} and SO_4^{2-} to Cl^- in the groundwater are compared with those in the water soluble salt in sediments of DJ 2 and DVDP 13 (Table 2). Table 2 indicates

Table 1. Chemical composition of groundwater and pond water in the Don Juan basin (TORII et al., 1977).

Sample (depth)	Groundwater No. 1 (548 cm)	Groundwater No. 2 (880 cm)	Pond water
Na (g/kg)	5.04	5.10	9.85
K	0.071	0.072	0.12
Ca	44.4	46.7	91.5
Mg	0.58	0.60	1.2
Cl	87.4	92.6	182
SO ₄	0.367	0.353	0.03

Table 2. Ratios of Na, K, Mg and SO₄ to Ca in groundwater and water soluble salt in Don Juan basin.

Sample	Groundwater	Salt in DJ 2 (deeper than 50 cm)	Salt in DVDP 13	
			(160 cm)	(880 cm)
Na/Ca (mole/mole)	1.94×10^{-1}	1.99×10^{-1}	1.84×10^{-1}	2.12×10^{-1}
K/Ca	1.61×10^{-3}	3.00×10^{-3}	6.10×10^{-3}	4.53×10^{-3}
Mg/Ca	2.14×10^{-2}	2.11×10^{-2}	2.03×10^{-2}	1.94×10^{-2}
SO ₄ /Cl	1.45×10^{-3}	9.62×10^{-2}	4.13×10^{-2}	1.10×10^{-1}

that the ratios of Na⁺ and Mg²⁺ to Ca²⁺ in the water soluble salt are similar to those in the groundwater of the Don Juan basin. However, the SO₄/Cl ratios in the water soluble salt are larger than those in the groundwater. This fact is considered to be attributed to the presence of CaSO₄ in the sediment which was precipitated from the groundwater. The concentration of sulfate ions in the groundwater approximately corresponds to that in a saturated solution of CaSO₄ in calcium chloride solution. Calcium chloride rich salt in deeper layers of DJ 3 and DVDP 13 is supposed to be derived from groundwater soaking into the sediments.

3.1.2. Molar ratios of chemical constituents in water soluble salt

As shown in 3.1.1., the major components of water soluble salt in the Don Juan basin are CaSO₄ and CaCl₂. The NaCl content of the salt is about 1 to 2% except for DJ 10 sample in which it is about 50%. Minor elements such as Mg, K and Sr contained in the water soluble salt are not considered to exist in the forms of their individual single salts, because their concentrations in the present pond water are too low to precipitate their individual single salts. The relationships among Ca in the form of CaCl₂, Ca in the form of CaSO₄, Na, Mg, K and Sr contents of the water soluble salt were examined. The examined results indicated that a positive relation seems to be found between Ca in the form of CaCl₂ and Mg, between Ca in the form of CaCl₂ and K and between Ca in the form of CaCl₂ and Sr (Fig. 4), although any other definite relations were not found. Thus it is presumed that Mg, K and Sr were deposited with CaCl₂.

Figures 5, 6 and 7 show the vertical profiles of the molar ratios of magnesium, strontium and potassium contents to calcium content in the water soluble salt in the Don Juan basin, respectively. In these figures, solid lines denote the results from the dropping dissolution and dashed lines denote the results from the complete dissolution. The concentration ratio tends to decrease with depth except for deeper layers than 50

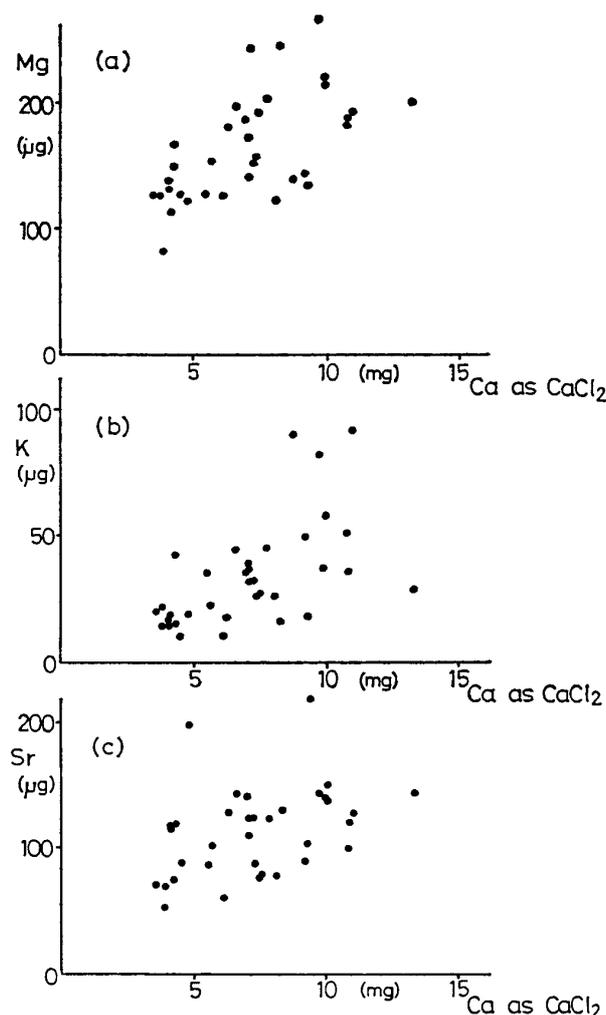


Fig. 4. Correlation between (a) Mg and Ca in the form of CaCl_2 , (b) K and Ca in the form of CaCl_2 and (c) Sr and Ca in the form of CaCl_2 in water soluble salt.

cm in DJ 2 core and several layers in the other cores. The ratio increases drastically at 50 cm in depth of DJ 2 core, and reaches a constant value at deeper layers. These facts are assumed to be ascribed to the presence of salts which originated from groundwater. The decrease in the concentration ratios of magnesium, strontium and potassium to calcium with increasing depth in core sediment suggests that the ratios in the pond water have increased with time. Two reasons for the increase in the ratios are supposed: (a) The calcium concentration in Don Juan Pond water has corresponded to the concentration in the pond water saturated with respect to calcium chloride. And the evaporation of the pond water has resulted in the deposition of calcium salts. Thus the calcium concentration in the pond water has little changed with time. However, the concentrations of minor elements such as magnesium, strontium and potassium have gradually increased through the evaporation of the pond water. (b) About 70% of the pond water is considered to have originated from groundwater (HARRIS and CARTWRIGHT, 1981). The profiles of the concentration ratios in deeper layers of DJ 2 core indicate that the concentration ratios of minor elements to calcium in groundwater are very high.

It is supposed that the concentration ratios of magnesium, strontium and potassium

to calcium in the present Don Juan Pond water became higher owing to the above two processes.

The comparison of the amounts of magnesium and strontium by dropping dissolution with those by complete dissolution (see Figs. 5 and 6) shows that their amounts by complete dissolution mostly are smaller than those by dropping dissolution. However, the profile of potassium (Fig. 7) shows that the amount by dropping dissolution is smaller than that by complete dissolution. By the dropping dissolution procedure,

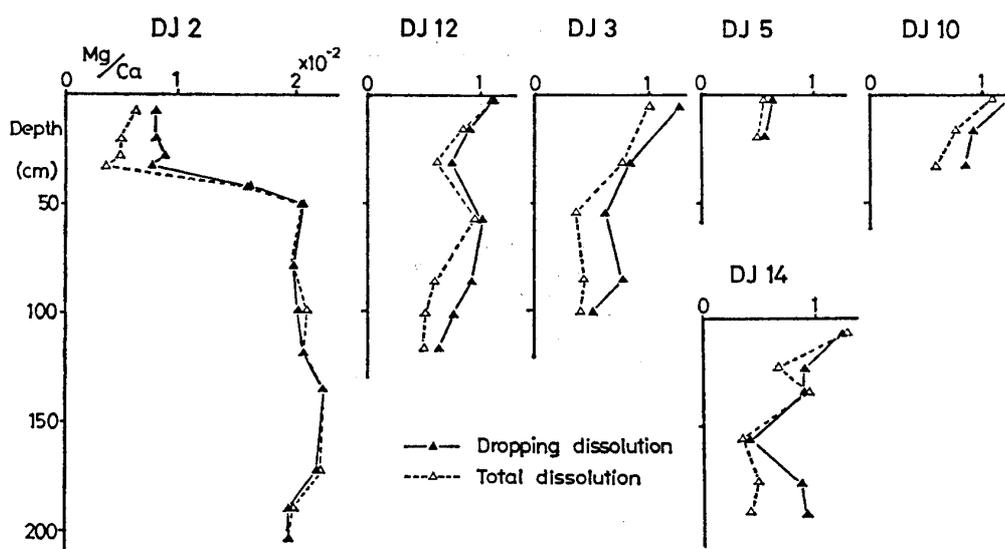


Fig. 5. Vertical profile of the molar ratios of magnesium content to calcium content in water soluble salt.

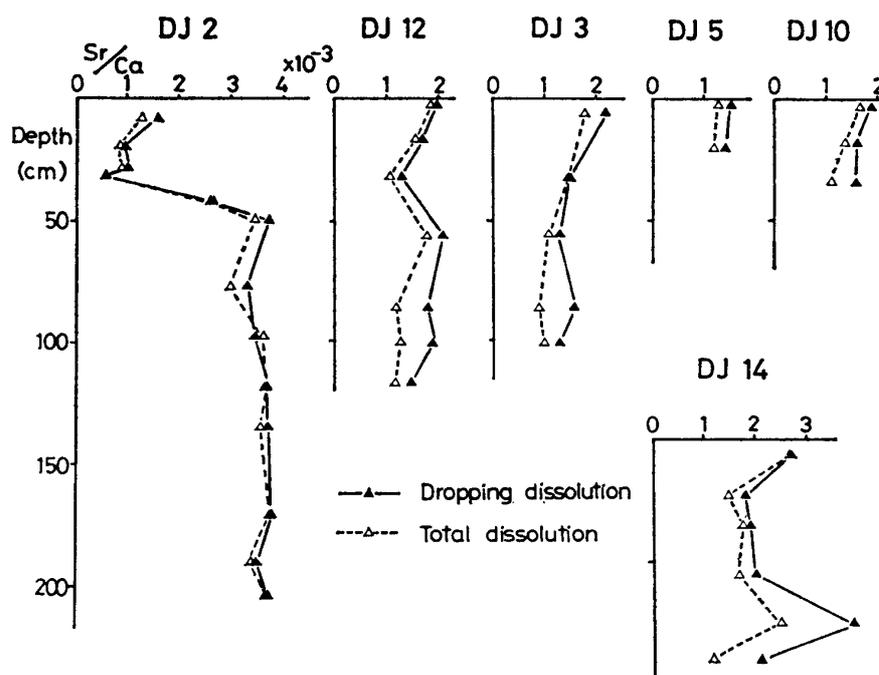


Fig. 6. Vertical profile of the molar ratios of strontium content to calcium content in water soluble salt.

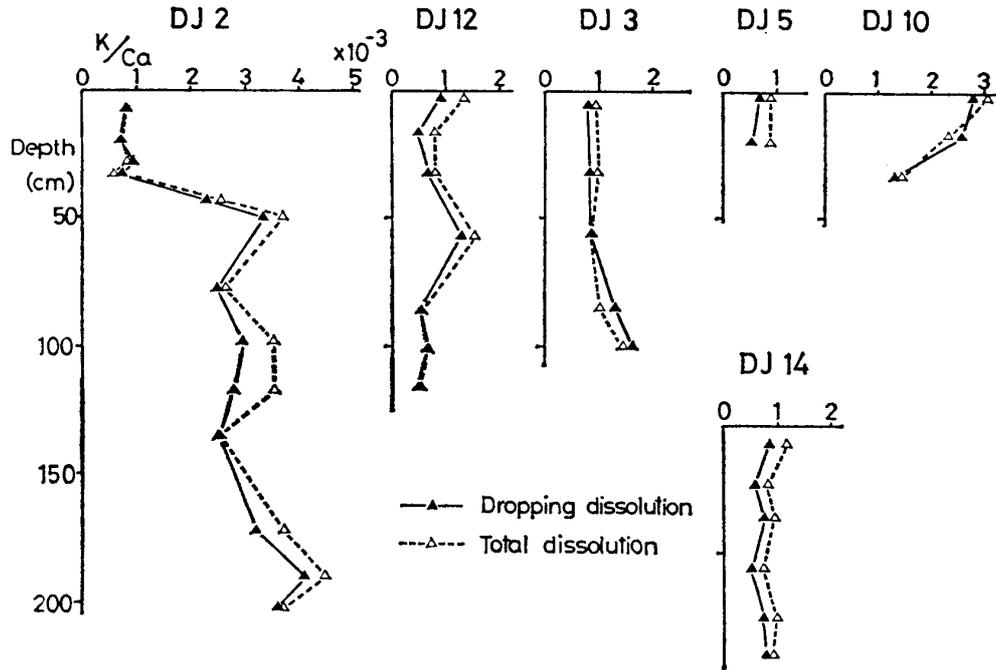


Fig. 7. Vertical profile of the molar ratios of potassium content to calcium content in water soluble salt.

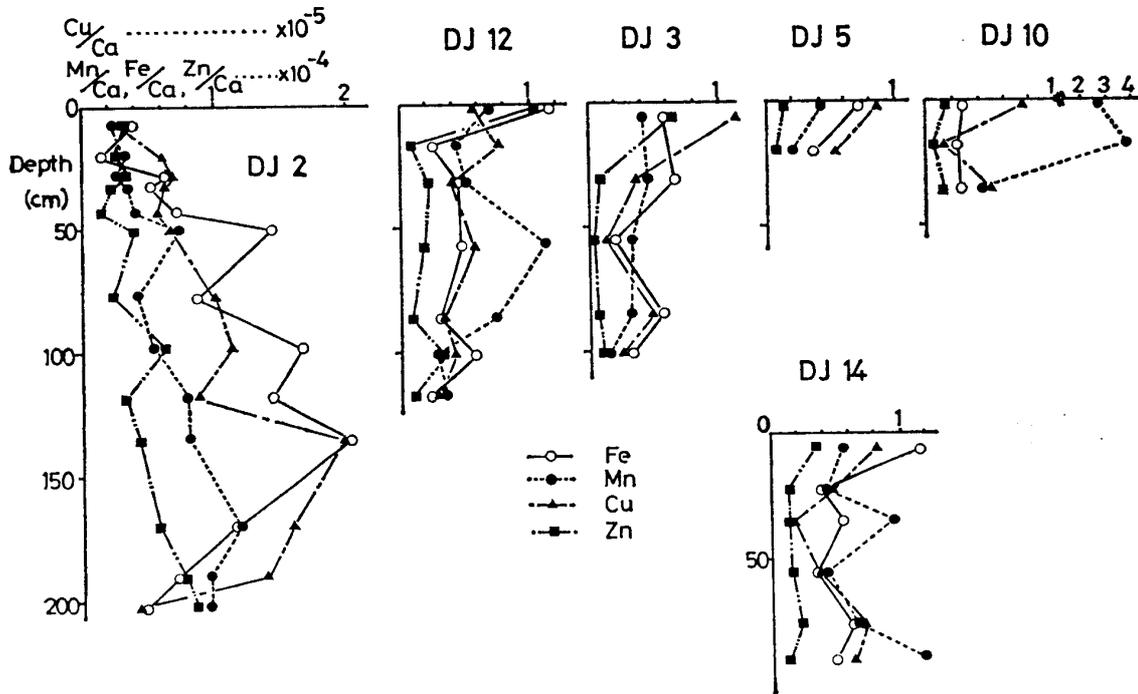


Fig. 8. Vertical profile of the molar ratios of iron, manganese, copper and zinc contents to calcium content in water soluble salt.

about 75% of water soluble calcium and 96% of water soluble sodium were observed to be dissolved. That is, readily soluble salt such as NaCl and CaCl₂ is dissolved almost completely but rather slightly soluble salt such as CaSO₄ tends to remain. The difference between the amounts by dropping dissolution and by complete dissolution

seems to be caused by the difference in the chemical form of individual element in salts. However, here it should be noted that sometimes some elements once dissolved from the salt are readsorbed on clay minerals through ion-exchange reaction. These secondary reactions must be taken into consideration for detailed discussion about the difference.

3.1.3. Distribution of trace heavy metals in water soluble salt

Figure 8 shows the vertical profiles of the concentration ratios of heavy metals to calcium dissolved by the dropping dissolution technique. The profiles for DJ 3, 5, 10, 12 and 14 show that the ratios decrease mostly with depth. As described earlier for minor elements such as Mg, Sr and K, this trend is caused by the increase with time in the concentration ratios of trace heavy metals to calcium ions in the pond water. It seems that the variation in the ratios for trace heavy metals is larger than that for the minor elements.

The ratios in deeper layers than 50 cm in DJ 2 are appreciably larger than those in the other layers. Since salts contained in these deeper layers of DJ 2 are supposed to be originated from groundwater as described earlier, the present groundwater discharging to the Don Juan basin is expected to contain heavy metals in the relatively high concentration ratios. This should be examined urgently. The results will be very important for the discussion about the origin of heavy metals in the pond water and sediment of the Don Juan basin.

3.2. Water insoluble fraction

The results of selective chemical leaching for the sediment cores, DJ 2, 3, 5, 10, 12, 14 and DVDP 13 from the Don Juan basin, are shown in Figs. 9 to 12.

3.2.1. CH_3COOH soluble fraction

Calcium dissolved with 1 M CH_3COOH solution is considered to be chiefly associated with calcium carbonate. The profiles of calcium dissolved into the CH_3COOH

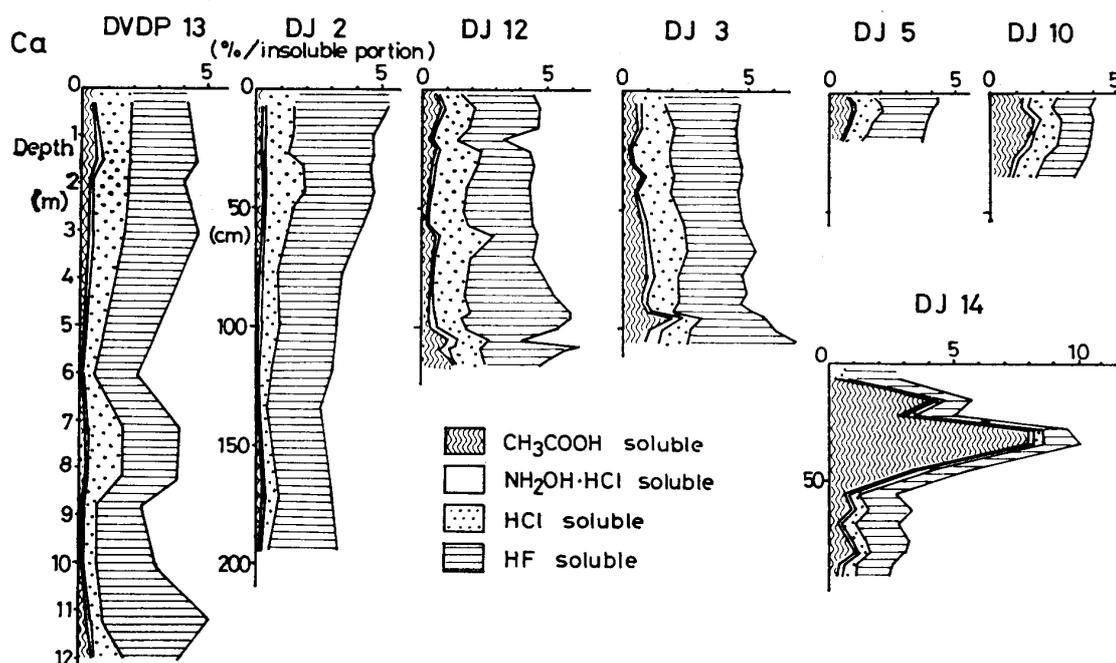


Fig. 9. Vertical distribution of calcium in water insoluble fraction.

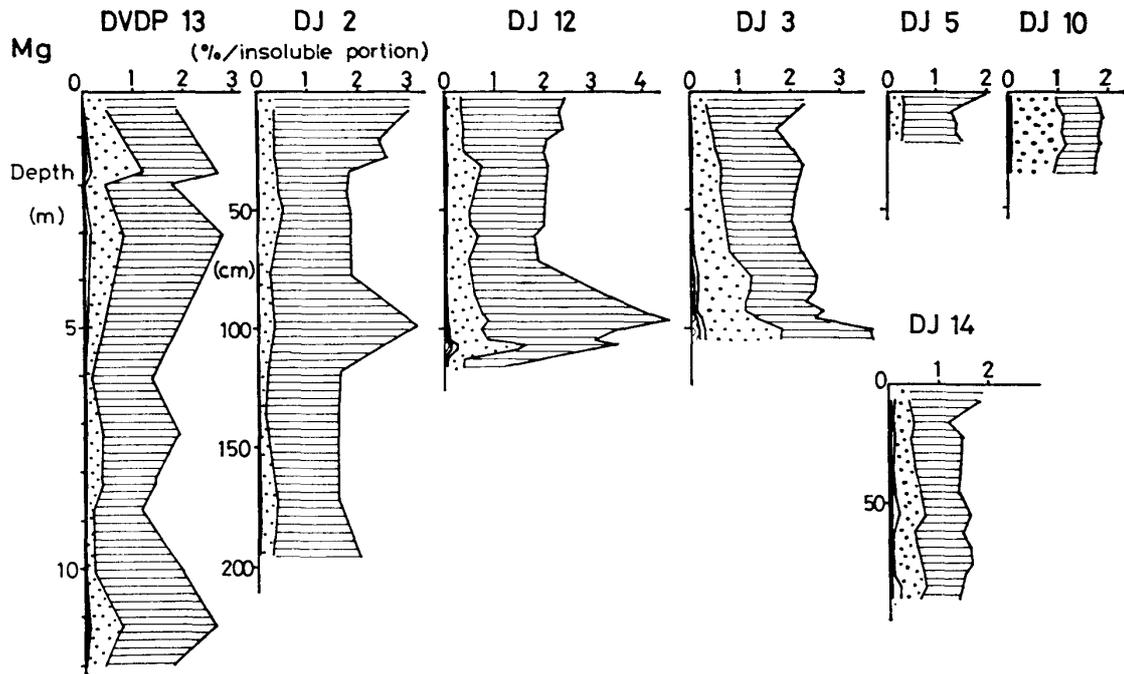


Fig. 10. Vertical distribution of magnesium in water insoluble fraction.

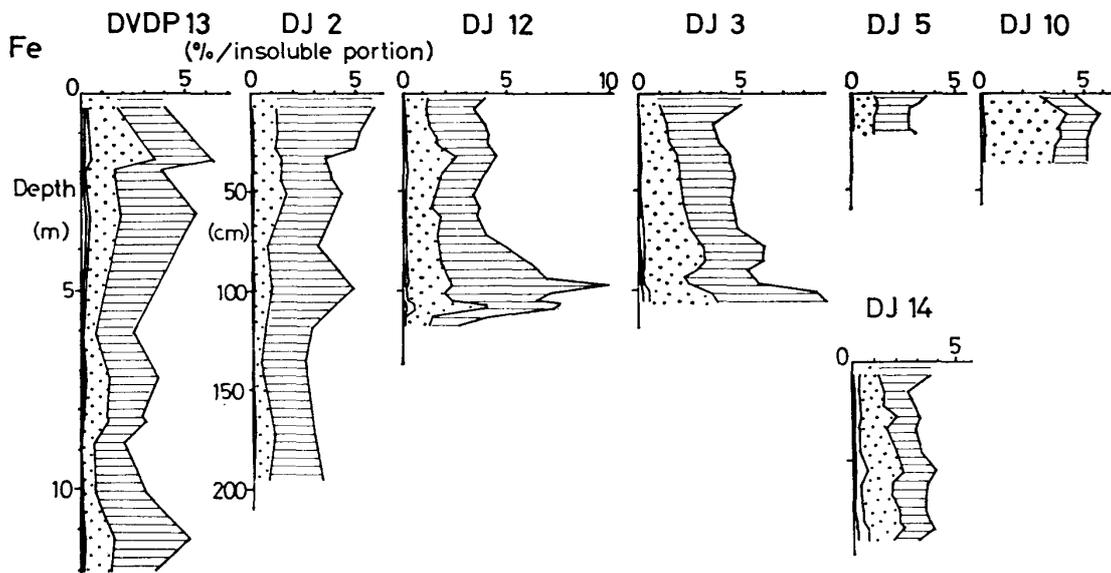


Fig. 11. Vertical distribution of iron in water insoluble fraction.

solution in Fig. 9 show that calcium carbonate is remarkably concentrated in the layer of 30 cm in depth of DJ 14 and its content reaches about 8% of the water insoluble fraction. This was confirmed by X-ray diffraction analysis, too. However, calcium carbonate content in the other cores is only 0.2 to 2%. Here, two possible sources for calcium carbonate are expected: One source is calcium carbonate precipitated inorganically in the pond water, and another source is weathering detritus. The sediment in the Don Juan basin is predominantly derived from glacial detritus. Generally, glacial clay is very homogeneous (GOLDSCHMIDT, 1954; KUNZE *et al.*, 1968). If calcium car-

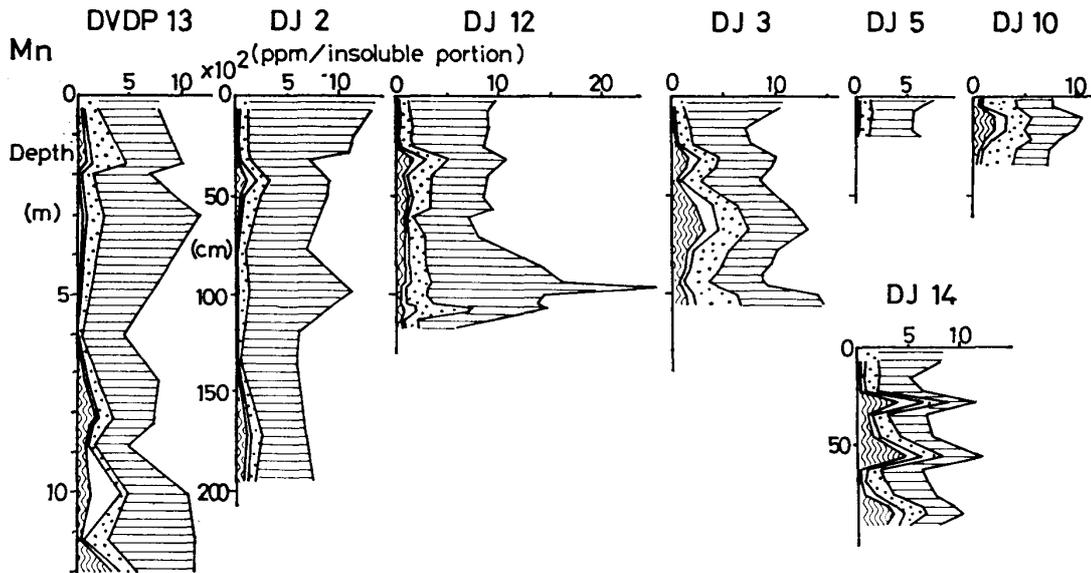


Fig. 12. Vertical distribution of manganese in water insoluble fraction.

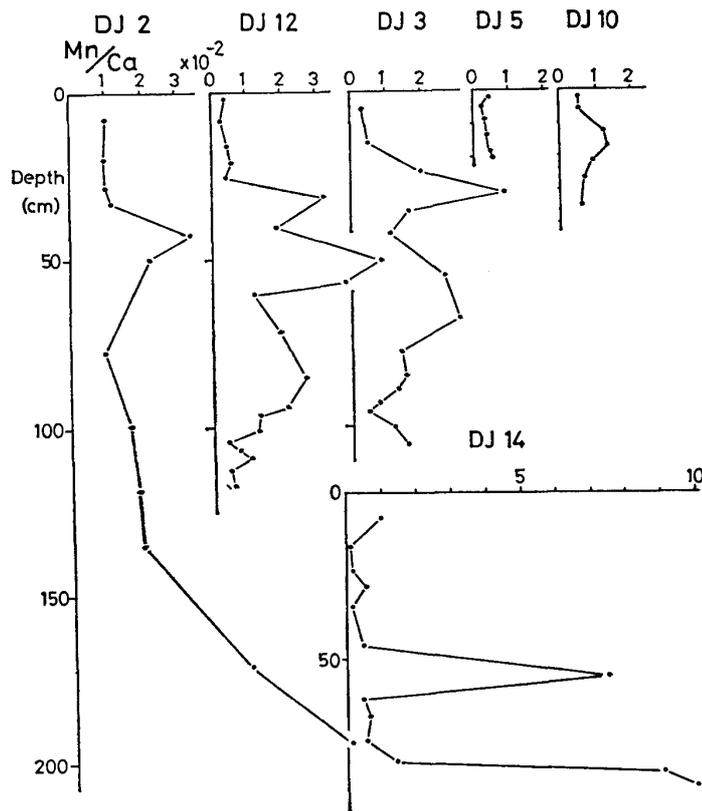


Fig. 13. Vertical profile of the weight ratios of manganese content to calcium content in the CH_3COOH soluble fraction.

bonate in the Don Juan basin is powdered in glacier and transported, the calcium carbonate should have a rather homogeneous composition. Figure 13 shows the weight ratio of manganese content to calcium content in the CH_3COOH soluble fraction. This fraction contains not only chemical constituents associated with carbonate but also

readsorbed chemical constituents which have been once dissolved from water soluble salts and adsorbed again on insoluble portion during the dissolution procedure. Ion-exchangeable manganese in this fraction is considered to be negligible, because ion-exchangeable manganese was reported to be negligibly small in suspended river sediments (GIBBS, 1973) and nearshore sediments (GUPTA and CHEN, 1975). The amount of manganese originating from water soluble salt was estimated and then subtracted from the total amount of manganese in this fraction. And it was found that the estimated value of Mn/Ca in carbonate fraction clearly varies vertically (TOMIYAMA and KITANO, 1982). That is, the chemical composition of the carbonate in the Don Juan basin was known to be heterogeneous. This result makes it possible to expect that calcium carbonate in the Don Juan basin might be precipitated from the pond water, like calcium sulfate.

Here, the source of carbonate ions for the precipitation of calcium carbonate must be discussed. It is imagined that carbonate ions were supplied through groundwater because of the local existence of calcium carbonate in DJ 14 core alone. If carbonate ions were supplied to the Don Juan basin through glacial meltwater, calcium carbonate should be precipitated homogeneously all over the basin. Now, the present authors suppose that groundwater containing a high concentration of carbonate ions was supplied to the pond water near the sampling point of DJ 14 core, and calcium carbonate was precipitated there. This idea may lead to the following consideration: The variation of Mn/Ca in the CH_3COOH soluble fraction shown in Fig. 13 may indicate the change in the Mn/Ca ratio of the pond water. Figure 13 shows that manganese-rich layers in the CH_3COOH soluble fraction are found at 30 cm, 50 to 60 cm and 80 to 90 cm in depth in DJ 3, 12 and 14. Thus, the origin of manganese is considered to be a very interesting subject. KITANO (1980a) reported that heavy metals except for iron and manganese are supplied very significantly to open seawater through aerosol, and iron and manganese are supplied through land water such as river water. The abundance of manganese in aerosol particles is relatively so small (*e. g.*, Fe 620 ± 230 , Al 820 ± 380 , Mn 13.5 ± 3.5 , Cu 29 ± 17 , Zn 33 ± 20 , $\times 10^{-12}$ g/standard cubic metre; BOUTRON and LORIUS, 1979), that only the supply from aerosol seems to be not enough for such enrichment of manganese in the CH_3COOH soluble fraction. The present authors suppose that manganese in the sediment of the Don Juan basin is chiefly supplied through groundwater, although MASUDA *et al.* (1982) reported that the source of trace elements in the Lake Vanda water was aerosol particles. The manganese content of groundwater should be analyzed accurately in order to know the origin of manganese.

Figure 14 shows the vertical profile of the Mg/Ca value in the CH_3COOH soluble fraction. It is seen clearly from this figure that the ratio increased with depth in every core. Figure 5 shows the Mg/Ca value in the water soluble fraction decreased with depth. If calcium carbonate was precipitated from the pond water, the profile in the CH_3COOH soluble fraction should have the same trend as that in the water soluble fraction. But the reverse trend is seen in Fig. 14. The diagenetic behavior of magnesium should be studied. To study the behavior, the states of magnesium in the water soluble and also the CH_3COOH soluble fractions must be clarified urgently. Especially it will have to be clarified whether magnesium is present in carbonate as dolomite or as a solid solution between calcite and magnesite. The crystal form of calcium carbonate taken

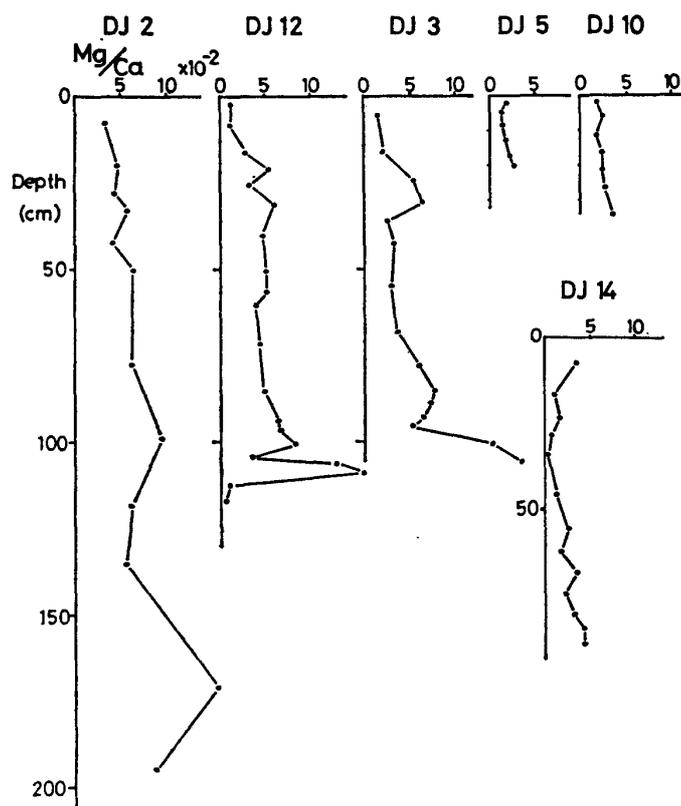


Fig. 14. Vertical profile of the weight ratios of magnesium content to calcium content in the CH_3COOH soluble fraction.

from the Don Juan basin was reported to be calcite by the powdered X-ray diffraction. When calcium carbonate is precipitated inorganically, the presence of magnesium ions in a parent solution generally favors the formation of aragonitic calcium carbonate (KITANO and HOOD, 1962). But, it was confirmed in the laboratory experiment by the authors that calcium-rich brine such as the Don Juan Pond water favors the formation of calcitic calcium carbonate in spite of the presence of magnesium ions in a parent solution (TOMIYAMA and KITANO, 1984). Consequently, magnesium ions are easy to be uptaken in the calcitic calcium carbonate, because calcite incorporates magnesium ions more easily than aragonite. The uptake of magnesium by calcium carbonate seems to be one of the important removal processes of magnesium ions from the original brine in the Don Juan basin, although the small amount of magnesium in the pond water is not explained sufficiently by this process alone.

3.2.2. $\text{NH}_2\text{OH}\cdot\text{HCl}$ soluble fraction

Ferro-manganese oxide is expected to be leached by $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution. The vertical profiles of the ratio of manganese to iron leached to this solution are shown in Fig. 15. This figure indicates that the Mn/Fe ratio in ferro-manganese oxide in the Don Juan basin shows a constant value except for several samples. The ferro-manganese oxide, which has a constant composition, is generally regarded as that derived from weathering detritus. Most peaks in the Mn/Fe profile of the $\text{NH}_2\text{OH}\cdot\text{HCl}$ soluble fraction correspond to peaks in the Mn/Ca profile of the CH_3COOH soluble fraction. The appearance of the Mn/Ca peaks in the CH_3COOH soluble fraction is explained by

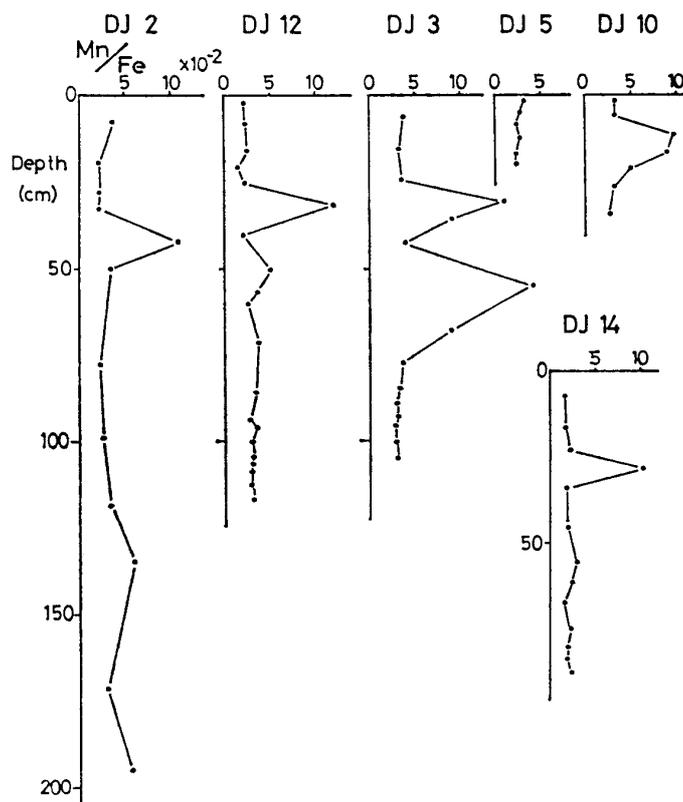


Fig. 15. Vertical profile of the weight ratios of manganese content to iron content in the $\text{NH}_2\text{OH}\cdot\text{HCl}$ soluble fraction.

the consideration that the manganese concentration in the pond water temporarily became high. The ferro-manganese oxide having a remarkably high Mn/Fe value is assumed to have been formed through adsorption of manganese ions on detrital ferro-manganese oxide when the concentration of manganese in the pond water was high.

3.2.3. HCl soluble fraction and HF soluble fraction

The chemical constituents in these fractions are considered to be associated with stable silicate. Less stable clay minerals are dissolved with HCl, and stable silicates are decomposed with HF.

The behavior of magnesium is the most interesting subject for the discussion on the origin of salts in the Don Juan basin. It is considered that globally about 10% of magnesium ions supplied to ocean through rivers is removed from seawater through the formation of $(\text{Ca}, \text{Mg})\text{CO}_3$ and the remaining portion is removed through the formation of chlorite (MACKENZIE and GARRELS, 1966; KITANO, 1980b). If the removal of magnesium through the chlorite formation occurred in the Don Juan basin, a large amount of magnesium should be dissolved with HCl because chlorite is decomposed by HCl. However, the enrichment of magnesium in HCl soluble fraction was not recognized. And also the powdered X-ray diffractometry of certain portions in DJ 10 sample, where the magnesium content was relatively high in HCl soluble fraction, gave only the presence of kaolinite, but no chlorite. Thus, there has not been observed any proof for the removal of magnesium from the original brine through chlorite formation in the Don Juan basin.

3.3. Origin of salts in the Don Juan basin

3.3.1. Estimation of the total amount of salts in the Don Juan basin

A calculation was performed as follows by using the analytical data of DJ samples: Firstly, the amount of water soluble salt in the sediments in the Don Juan basin was calculated by assuming that (a) the water soluble salt content is 40% in the upper 50 cm of the sediment in one-third area of the basin and in the upper 2 m of the sediment in the residual two-third basin, and the salt is composed of CaSO_4 in 85%, CaCl_2 in 13%, NaCl in 1.5% and MgCl_2 in 0.5%; and (b) the salt content is 5% in the other sediment except the above portions of sediment down to 12 m depth and the salt is composed of CaCl_2 in 70%, CaSO_4 in 20%, NaCl in 9% and MgCl_2 in 1%. In the calculation, the area of the pond and the specific gravity of the sediment are assumed to be $400 \text{ m} \times 900 \text{ m}$ and 2, respectively.

The amounts of chemical constituents in water soluble salts existing in the basin are as follows: Ca $2.4_6 \times 10^5 \text{ t}$, Na $1.5_9 \times 10^4 \text{ t}$, Mg $1.5_4 \times 10^3 \text{ t}$, Cl $2.3_4 \times 10^5 \text{ t}$ and SO_4 $3.1_2 \times 10^5 \text{ t}$. The total amounts of individual chemical constituents in the present Don Juan Pond water were estimated by TORII *et al.* (1977) as follows: Ca 760 t, Na 82 t, Mg 10 t, Cl 1500 t and SO_4 0.25 t. The amounts of Ca and Mg existing in carbonate were calculated as follows: By assuming the carbonate content of the sediment to be 0.25% in one-third of the basin and 0.8% in two-third, the Ca amount in carbonate was calculated to be $2.3 \times 10^4 \text{ t}$. And the Mg amount in carbonate was estimated to be 1140 t by assuming that the Mg/Ca value in carbonate is $5 \times 10^{-2} \text{ (g/g)}$.

Thus, the total amounts of chemical constituents in the Don Juan basin are estimated as follows (Table 3): Ca $2.7 \times 10^5 \text{ t}$, Na $1.6 \times 10^4 \text{ t}$, Mg $2.7 \times 10^3 \text{ t}$, Cl $2.4 \times 10^5 \text{ t}$ and SO_4 $3.1 \times 10^5 \text{ t}$. In the above calculation, halite in the surface and the slope of the Don Juan basin was not taken into consideration. It is difficult to estimate the amount of the halite because of the lack of data. However, if it is assumed that halite is deposited on the surface of the basin with a thickness of 1 cm, the amounts of Na and Cl are estimated to be $4.3 \times 10^3 \text{ t}$ and $6.6 \times 10^3 \text{ t}$, respectively. When these values are added to the above total values, the amounts of Na and Cl reach $2.0 \times 10^4 \text{ t}$ and $2.5 \times 10^5 \text{ t}$, respectively. These values indicate that the major chemical constituents of salts in the Don Juan basin are Ca, SO_4 and Cl with a rather small amount of Na and only a small amount of Mg. In reality, larger amounts of salts than the estimated amounts may exist in the basin, because the estimation was performed chiefly from the distribution of salts in the surface 1 to 2 m layer of sediment. However, it is clear that the magnesium amount in the basin is very small as compared with the Na and Ca amounts.

Table 3. Estimation of total amount of salt in the Don Juan basin.

	Water soluble salt	Pond water	Carbonate	Total
Ca (t)	2.46×10^5	760	2.27×10^4	2.70×10^5
Na	1.59×10^4	82		1.60×10^4
Mg	1.54×10^3	10	1.14×10^3	2.69×10^3
Cl	2.34×10^5	1500		2.36×10^5
SO_4	3.12×10^5	0.25		3.12×10^5

3.3.2. Discussion on the origin of sulfate, chloride, calcium, sodium and magnesium

The origin of a large amount of sulfate is a very interesting subject. NAKAI *et al.* reported that the $\delta^{34}\text{S}$ in gypsum from the sediment of Don Juan Pond was about 31.8 to 37.5‰ (a personal communication). Generally, the sulfur with such a high value of $\delta^{34}\text{S}$ is regarded to be derived from seawater (HOLSER and KAPLAN, 1966; NAKAI *et al.*, 1975). However, the high $\delta^{34}\text{S}$ value does not always indicate that the salts were deposited from seawater itself in the Don Juan basin through concentration, because there may be a possibility that groundwater flows into the pond through evaporite layers with a high value of $\delta^{34}\text{S}$, and also magnesium is never balanced geochemically in this basin. Of course, there may be a possibility that the origin of the groundwater is seawater. DORT and DORT (1970) reported that mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) up to 4 m thick exists in front of the Hobbs Glacier and in the Miers Valley in southern Victoria Land. When the original brine contained a large amount of sulfate ions like seawater, the deposition of sulfate salt would occur as thick layers. However, in the Don Juan basin such a salt layer is not found. The authors suppose that CaSO_4 in the Don Juan basin has been deposited through the gradual inflow of sulfate ions with high $\delta^{34}\text{S}$ value into the pond water containing Ca ions in a high concentration. This should be confirmed urgently.

Two sources of water entering the pond are important; groundwater and glacial meltwater. The concentration of sulfate ions in the groundwater approximately corresponds to that in a saturated solution of CaSO_4 in calcium chloride solution and is 360 ppm as seen in Table 1. Since the concentration of sulfate ions in the pond water is about 30 ppm, it is supposed that a large portion of sulfate ions supplied to the pond through groundwater has been removed through the CaSO_4 precipitation. However, the concentration ratio of sulfate to chloride ions in the groundwater is 4×10^{-3} (weight ratio), whereas the estimated ratio of the salt existing in the basin was 0.9 as shown earlier. Therefore, it cannot be accepted that the source of sulfate ions in this basin is only groundwater. The sulfate concentration in glacial meltwater is about 60 ppm and the

Table 4. Mg/Ca values of salt and water in the Don Juan basin and of various natural waters.

Type of water (and salt)	Mg/Ca (g/g)	Content order	Reference
Don Juan Pond water	1.3×10^{-2}	Ca > Na > Mg	
Groundwater in Don Juan basin	1.4×10^{-2}	Ca > Na > Mg	
Total salt in Don Juan basin	1.0×10^{-2}	Ca > Na > Mg	
Past pond water	7.3×10^{-3}	Ca > Na > Mg	
Seawater	3.14	Na > Mg > Ca	
River water	0.27	Ca > Na > Mg	LIVINGSTONE (1963)
Glacier ice (Antarctica)	0.85–2.3	Na > Mg, Ca	BOUTRON <i>et al.</i> (1972)
Sea spray (Matsumoto)	0.12	Ca > Na > Mg	SUGAWARA <i>et al.</i> (1949)
Oil field water (U.S.A.)	3.2×10^{-4} – 3.4×10^{-2}	Ca > Na > Mg	GRAF (1978)
Groundwater (Canadian Shield)	1.9×10^{-4} – 5.6×10^{-2}	Ca > Na > Mg	FRITZ and FRAPE (1982)
Geothermal brine (Salton Sea)	3.6×10^{-4} – 1.8×10^{-3}	Ca > Na > Mg	SKINNER <i>et al.</i> (1967)

concentration ratio of sulfate to chloride ions is 0.4 (HARRIS and CARTWRIGHT, 1981). Thus, glacial meltwater also is supposed to be the source of sulfate ions in this basin. The exact sources of sulfate and also chloride ions remain still unsolved.

For the study on the sources of salts in the Don Juan basin, the magnesium amount is one of the most important problems to be solved. Table 4 shows the Mg/Ca values in the Don Juan basin. From this table, it is apparent that seawater, sea spray, water participating in rock-weathering and glacial meltwater as the sources of the salt are not sufficient to explain such a low Mg/Ca value (1.0×10^{-2}) in the Don Juan basin. Here, groundwater in the basin should be considered as one important source for the salts. If the discharge of groundwater to the basin is $30 \text{ m}^3/\text{day}$ (HARRIS and CARTWRIGHT, 1981), the amount of chemical constituents supplied to the basin is calculated to be about 1400 t/year (Table 1). It may take about 500 years to accumulate salts existing in the Don Juan basin, if this groundwater has been the source of the salts. The sources and the formation processes of the groundwater in this basin should be investigated very urgently.

The very small value of Mg/Ca in this basin remains unexplained. The very small value was reported in certain deep groundwaters, oil field waters and some geothermal waters as given in Table 4. Their major chemical constituents are calcium chloride. These calcium chloride type waters have been supposed to be formed through an active water-rock interaction for a long period underground (CHAVE, 1960; WHITE, 1965; GRAF *et al.*, 1966; YOSHIOKA *et al.*, 1970). The present authors are thinking that the information of these calcium chloride type waters should be helpful for the interpretation of the formation process of calcium chloride water in the Don Juan basin. This will be discussed elsewhere.

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