

A VIEW ON THE FORMATION OF SALINE WATERS IN THE DRY VALLEYS

Tetsuya TORII,

Chiba Institute of Technology, Tsudanuma, Narashino 275

Noboru YAMAGATA,

The Institute of Public Health, Shirokanedai 4-chome, Minato-ku, Tokyo 108

Joyo OSSAKA

Tokyo Institute of Technology, Ookayama 2-chome, Meguro-ku, Tokyo 152

and

Sadao MURATA

Chiba Institute of Technology, Tsudanuma, Narashino 275

Abstract: The previous report by TORII *et al.* (Nankyoku Shiryô, **58**, 116, 1977) on the salt balance in the Don Juan basin pointed out the presence of calcium in excess when the total salt deposits in the basin are assumed to have resulted simply from the evaporation of sea water. Concerning the evolutionary processes of saline waters in the Dry Valleys, sources of the salts other than trapped sea water were not necessarily excluded, and sea spray, ion exchange and rock weathering theories have been suggested by many investigators.

This paper presents the results obtained by further examination of the processes of saline water formation, on the basis of the analytical results of the DVDP cores from the Wright Valley, the information on the chemical characteristics of the water systems in the Dry Valleys, and a recent reconnaissance in the Labyrinth and the Pearse Valley. It is more likely that the chemical composition of waters in these saline lakes is mainly due to the atmospheric salt rather than the modification of trapped sea salt.

1. Introduction

Chemical analyses of the DVDP cores give a valuable information for clarifying the mechanism of formation of the saline waters in the Dry Valleys. At the second DVDP seminar, the authors presented a paper on salt balance in the Don Juan basin to explain the formative processes of saline waters, based principally on the chemical analysis of DVDP 13 core. The results are summarized as follows (Table 1). By assuming that the total salt deposits in the basin have originated entirely from

Table 1. Estimates of the original volume of sea water.

1. Estimated volume from total salt deposit.	$2.6 \times 10^7 \text{ m}^3$
A) Calculation from K, Mg, SO_4 and Cl.	$1.2\text{--}2.2 \times 10^7 \text{ m}^3$
B) Calculation from Ca.	$36.6 \times 10^7 \text{ m}^3$
2. Estimated volume from paleolake shoreline.	$1.2 \times 10^7 \text{ m}^3$

the evaporation of trapped sea water, the original volume of sea water could be estimated as $2.6 \times 10^7 \text{ m}^3$, and when the estimation is made with respect to major chemical elements such as K, Mg, SO_4 and Cl present in the basin, the estimated values range from 1.2 to $2.2 \times 10^7 \text{ m}^3$ (TORII *et al.*, 1977). These estimates were in the same order of magnitude as that based on the paleolake shoreline. However, when the estimation was made on the basis of calcium content, much larger value as high as $36.6 \times 10^7 \text{ m}^3$ was obtained, and we could not explain the presence of excessive calcium in the basin which enforced us to seek other source of salts than trapped sea water.

This paper presents the results obtained by further examination of the processes of saline water formation, on the basis of the analytical data of three DVDP cores from the Wright Valley, the information on the chemical characteristics of the water systems studied so far in the Dry Valleys, and a recent reconnaissance in the Labyrinth and the Pearse Valley.

2. Chemical Characteristics of the DVDP Cores from Wright Valley

The results of the powder X-ray diffractometric identification of three DVDP cores (Lake Vanda, Don Juan Pond and North Fork) obtained from the Wright Valley revealed that calcite was generally predominant in the cores, and the sulfates such as gypsum and mirabilite were concentrated in the upper layers, while there was scarcely any sulfate in the dry basin, *e.g.*, in DVDP 14 core, in comparison with cores from in and around the saline lakes (MORIKAWA *et al.*, 1975; TORII *et al.*, 1977; MURAYAMA *et al.*, 1979).

The core samples of the sediment layers were extracted with water first, and the residue was successively treated with perchloric acid. The total salts in the leachates, that is, the sum of the material extracted with water and perchloric acid, are distributed vertically as shown in Figs. 1, 2 and 3. The concentration of alkaline earth elements largely exceeds that of the alkali elements, and the principal anionic constituent is carbonate.

The vertical distribution of the chemical components in the cores of the Wright Valley suggests that climatic changes might have taken place in the past. For example, in the Don Juan core, the total amount of salts does not change markedly with depth from 3 m to 7 m depth. This may suggest continuous sedimentation

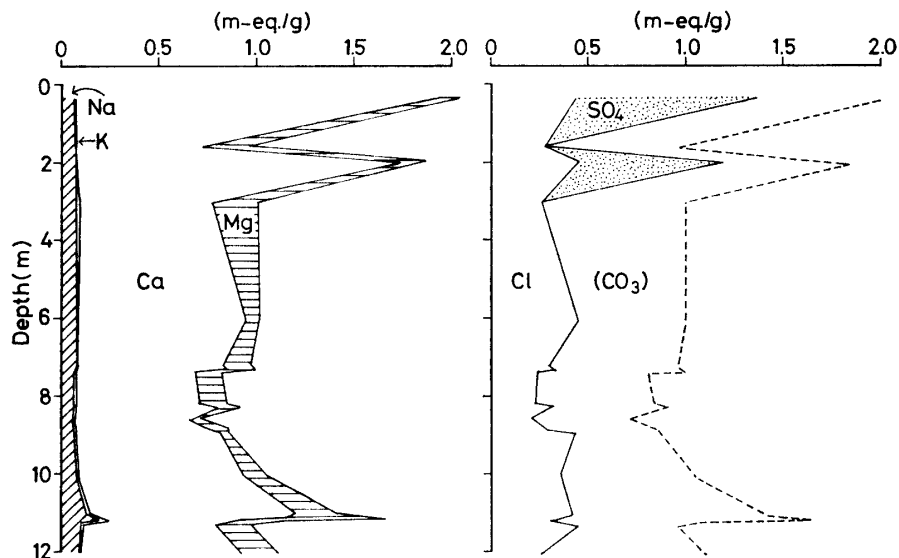


Fig. 1. Vertical distribution of the salts in leachates of DVDP 13 core.

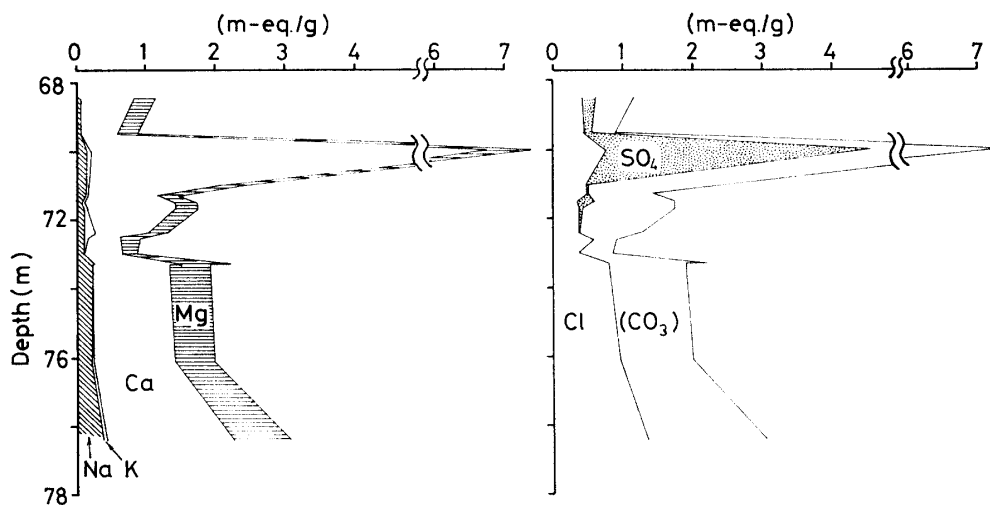


Fig. 2. Vertical distribution of the salts in leachates of DVDP 4 core.

during the concentration–deposition process of the paleolake water in the basin under similar climatic circumstances. The peak at a depth around 2 m in the total salt content may reflect a short water supply during a cold climatic period, while a minimum at around 1.5 m depth may be due to the leaching of salt deposits as a result of a larger water supply during a rather warm climatic period.

This tendency can be seen also in the size frequency distribution determined by granulometric analysis of DVDP core 14 (North Fork) which shows two types corresponding respectively to the aeolian and the lacustrine depositions (NAKAO

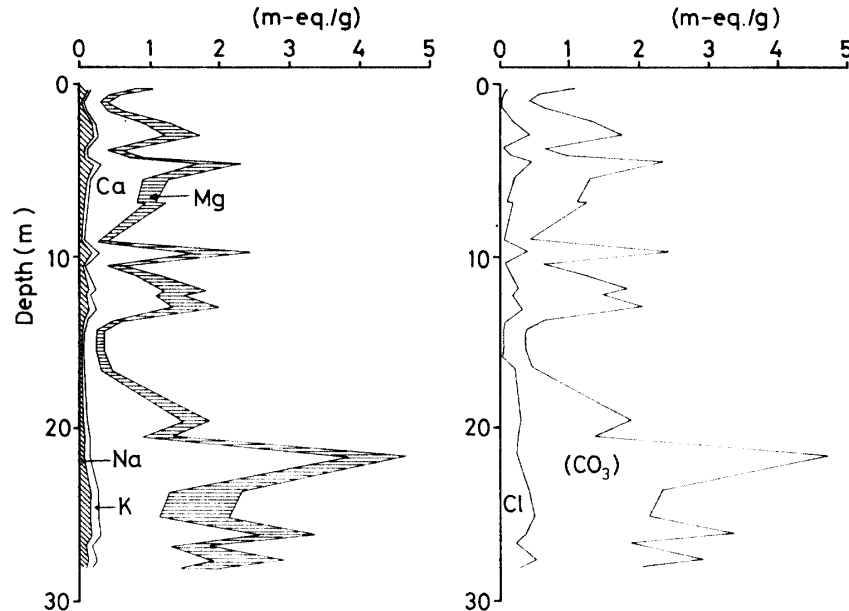


Fig. 3. Vertical distribution of the salts in leachates of DVDP 14 core.

Table 2. Salt contents of water and sediment in lake as the result of climatic change.

Climate	Warm period	Cold period	Coldest period
Melt water supply	Large	Small	Zero
Salt content of lake water	Low	High	(dry up)
Salt content in lake sediment	Low (min.)	High	High (max.)

et al., 1978). This idea is summarized in Table 2. When the water supply decreased to zero in the coldest period, the lake should have been dried up, and the salt content of the sediment may reach the highest value.

Successive drying up and redissolving of Lake Vanda has been suggested by many investigators on the basis of the dating of algal remains on the paleolake shoreline (YOSHIDA *et al.*, 1975) and the chemical analyses of lake water and bottom sediments (WILSON, 1964; SCHIRTCLIFFE, 1964; NAKAI *et al.*, 1975). The authors assume the presence of a "Great Vanda" that once covered a large area extending from around the south of Bull Pass in the east to around the ponds of Don Quixote and Don Juan in the west, on the basis of the DVDP core analysis patterns and the distribution of evaporites in the soils of the Wright Valley studied so far. The above observations lead us to ascribe the origin of the salts to sea spray and/or rock weathering over a long period of time under frigid conditions, in addition to the trapped sea water.

Though the salt content of ice and snow is very small, in the process of advance

and retreat of glaciers during the ice age the salts should remain partly either in concentrated solution or deposited in glacial troughs. The salt thus left behind should have been leached or deposited according to their different solubilities when flooding of the "Great Vanda" occurred. As a result, we often find less soluble sulfate evaporites in the upper layers of the DVDP cores and subsurface soils, while calcium and magnesium prevail in the lower layers.

3. Evolutionary Processes of Saline Waters under Frigid Conditions

3.1. Deposition of salts from sea water under frigid conditions

In connection with the trapped sea water origin theory, the work by THOMPSON and NELSON (1956) on the deposition of salts from sea water under frigid conditions is important (Fig. 4). The process is quite different from our knowledge on the deposition processes of salts during the course of evaporation under normal temperature conditions. When sea water is concentrated under frigid conditions, the order of crystallization is as follows: calcium carbonate crystallizes first, followed by mirabilite at -8.2°C and sodium chloride dihydrate at -22.9°C . The amount of brine remaining at this temperature is only about 2% of the original volume. The magnesium concentration increases successively and at -36°C a

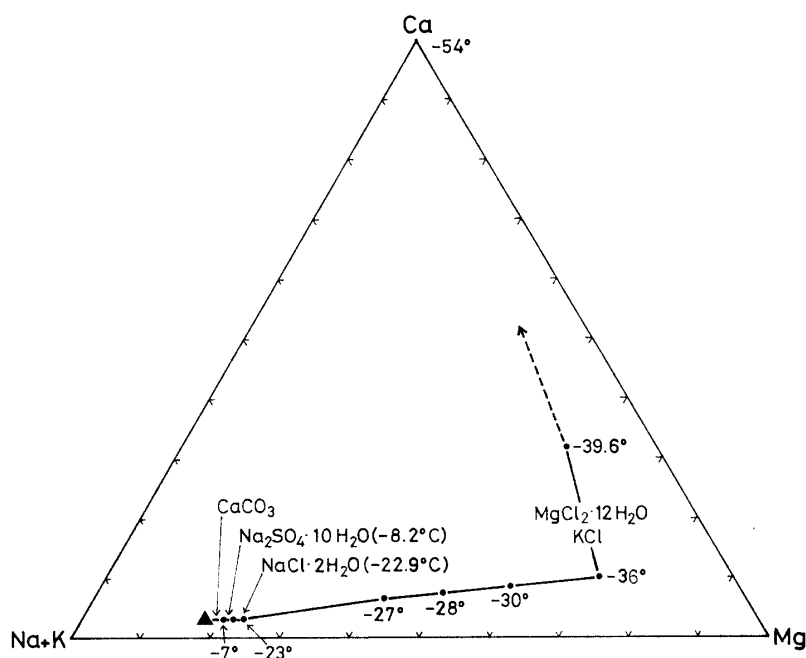


Fig. 4. Chemical composition (in equiv. %) of brines in equilibrium with ice or ice and crystallized salts at different low temperatures ($^{\circ}\text{C}$).

▲: sea water, ●—●: changes of chemical compositions after THOMPSON and NELSON.

mixture of magnesium chloride dodecahydrate and potassium chloride crystallizes. The remaining brine consists principally of calcium chloride and when its saturation point is reached at -54°C , calcium chloride hexahydrate crystallizes. Fig. 4 shows the triangular coordinate diagram representing the relationship among sodium+potassium, magnesium and calcium concentration in equivalent percentages. The small, solid triangle in the diagram represents sea water and the arrow lines show the course of evolution of the brine under frigid conditions.

3.2. Chemical composition of saline waters in the Dry Valleys

Superimposed on the above background, Fig. 5 shows the diagrammatic position of saline waters in the Dry Valleys. The solid triangle indicates sea water, and lies in the circle representing Lake Fryxell, indicating a close resemblance. The west and east lobes of Lake Bonney are in positions corresponding to the formation of brine after successive concentration under the lower temperatures, and Lake Vanda and Don Juan Pond correspond to the residual brine rich in calcium chloride. Small saline ponds such as Don Quixote in the North Fork and Kettle Hole in the South Fork of the Wright Valley have been observed only when the melt water supply was large, otherwise they were usually found dry. As stated before (HENDY *et al.*, 1977; TORII *et al.*, 1975), water in Lake Bonney which formed

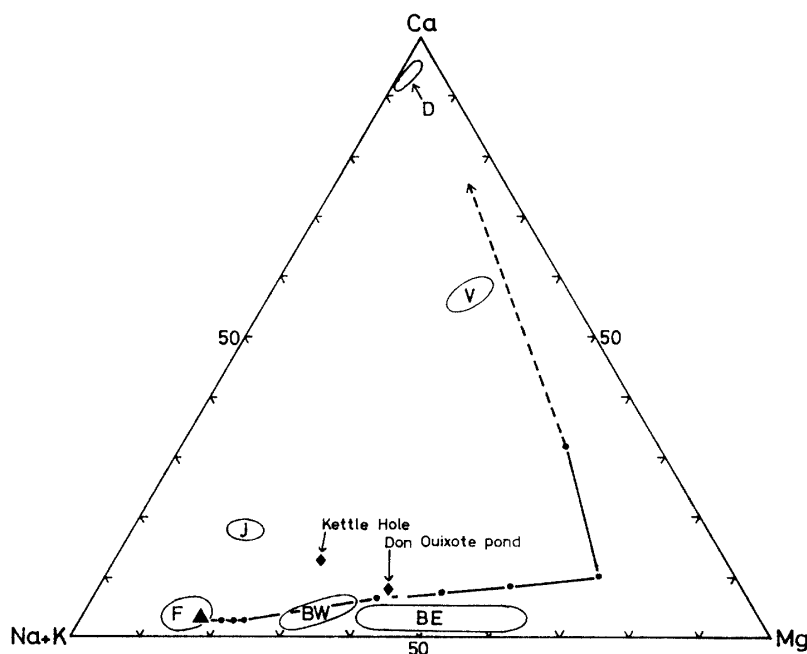


Fig. 5. Chemical composition (in equiv. %) of saline waters in the Dry Valleys. J: L. Joyce, F: L. Frexell, BW: west lobe of L. Bonney, BE: east lobe of L. Bonney, V: L. Vanda, D: Don Juan Pond, \blacklozenge : saline pond, \blacktriangle : sea water, \bullet — \bullet : changes of chemical compositions after THOMPSON and NELSON.

by a large inflow of water from the Taylor Glacier has almost the same composition with those in these ponds. This suggests that these ponds and the lake were younger than Lake Vanda and Don Juan Pond. Recent reconnaissance in the Labyrinth and the Pearse Valley shows that the chemical composition of the saline pond in the former resembles that in the east lobe of Lake Bonney, while those in Lake Joyce in the latter resembles that in Lake Fryxell, but are richer in calcium.

3.3. Chemical composition of snow and ice, and glacial melt waters

Table 3 gives the chemical composition of snow and ice in Antarctica, and also that of running waters from glaciers in the Dry Valleys that contain small but significant amounts of salt. On the basis of the study of the chemical composition of the water systems in the Dry Valleys in these 15 years, the authors would point out that another important clue to a modification of the simple hypothesis of sea water origin should be the chemical composition of glacial melt waters, which contain much larger relative concentrations of calcium and sulfate than in sea water.

Table 3. Chemical composition of snow and ice, and glacial melt waters in Antarctica (mg/kg).

Sample	Na	K	Ca	Mg	Cl	SO ₄
Snow and ice ^{***} (35)*	17-94 ^{**}	0.9-26 ^{**}	1.9-4.0 ^{**}	1.6-12.8 ^{**}	57-140 ^{**}	—
Onyx River (8)*	5.5-15	0.9-1.8	8.5-21.0	1.4-4.2	7.1-20.1	3.7-14.1
Inflow water from glacier:						
To west lobe of Lake Bonney	12.6	1.2	19.0	4.0	12.0	10.7
To east lobe of Lake Bonney	25.6	3.8	20.0	6.0	25.0	29.1
To Canopus Pond	19.6	1.9	24.2	8.0	20.7	23.6
Lake Brownworth	3.9	0.5	1.9	0.6	4.9	6.2
Lake Bull	9.0	3.3	14.4	3.8	21.5	9.7

*Figures in parentheses indicate the numbers of samples.

**Units: $\mu\text{g}/\text{kg}$.

***Data mainly from BOUTRON *et al.* (1972) and MUROZUMI *et al.* (1969).

This pattern can be shown in a triangular coordinate diagram in Fig. 6. The similarity in the chemical composition of continental snow and ice, denoted by circle S, to that of sea water indicates that the main source of salt in snow and ice is sea spray. However, glacial melt waters, denoted by circle G, are generally richer in calcium than snow and ice. The inflow from the Adams and Miers glaciers to Lake Miers is especially rich in calcium. These observations indicate that during the melting of snow and ice and running through glacier beds, the melt water is enriched with calcium and sulfate. The enrichment in calcium can be explained as resulting from the redissolution of more easily soluble components of deposits

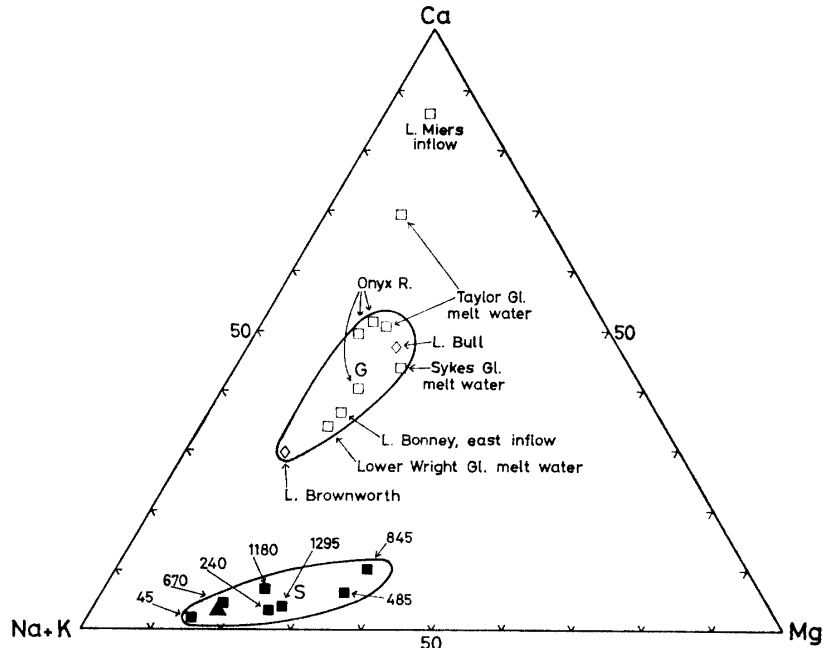


Fig. 6. Chemical composition (in equiv. %) of snow and ice (S), and glacial melt water (G). ■: snow and ice, □: glacial melt water, ◇: fresh pond, ▲: sea water. The figures around circle S indicate the distance from the coast (km).

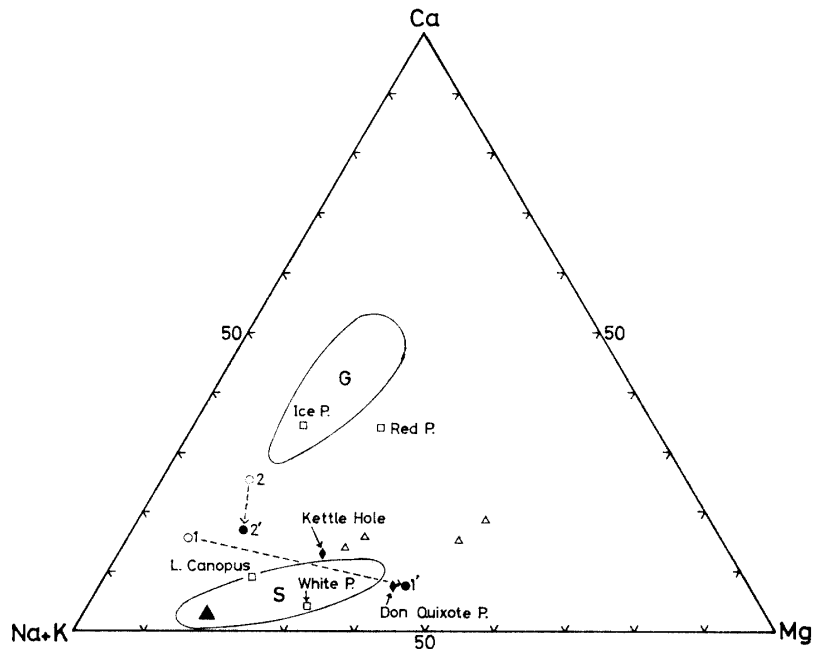


Fig. 7. Chemical composition (in equiv. %) of different types of waters in the Dry Valleys. ○1: fresh pond in the Labyrinth, ●1': saline pond in the Labyrinth, △: fresh pond in North Fork, □: fresh pond in South Fork, ○2: L. Joyce (5 m), ●2': L. Joyce (30 m), ◆: saline pond, ▲: sea water, S: snow and ice, G: glacial melt water.

underneath the ancient ice sheet of the catchment area. It is noted that the fresh water pools in the Wright Valley in Fig. 7 generally lie somewhere between snow and ice, and glacial melt water.

3.4. Evolutionary processes of saline waters

In summer, some 50 pools may form on the ice-free bare basement rock in the Labyrinth of the Wright Upper Valley, where the elevation is almost 900 m above sea level and the trapping of sea water can never be assumed. None of the pools has drainage and some of them are saline. Table 4 shows the chemical compositions of two ponds in the Labyrinth and of Lake Joyce in the Pearse Valley. It is noted that the two ponds in the Labyrinth contain a large amount of sulfate. As can be seen in the triangular coordinate diagram of Fig. 7, the composition of fresh pond (1) in the Labyrinth is between running glacial melt water (G) and snow and ice (S), while the composition of saline pond closely resembles that of Don Quixote Pond, similar in composition to sea water but relatively rich in magnesium. If the fresh pond water (1) is assumed to have undergone concentration under frigid conditions, its chemical composition should approach that of the saline pond water (1') after precipitation of calcium carbonate and sodium sulfate.

Table 4. Chemical composition of some lake waters in the Dry Valleys (mg/l).

Locality		Na	K	Ca	Mg	Cl	SO ₄
Wright Upper Valley:							
Labyrinth							
Pond-1 (fresh)		393	6.3	69.5	24.5	456	544
Pond-1' (saline)		4,130	30	530	1,900	7,710	2,130
Pearse Valley:							
Lake Joyce							
	5m	16	2.3	6.3	1.8	33	24
	13m	264	19.4	55.4	23.3	332	265
	20m	1,000	68.5	229	128	1,360	944
	25m	1,050	69.8	237	129	1,375	1,020
	30m	1,060	70.0	248	137	1,448	1,080
	33m	1,090	79.4	251	173	1,475	1,150

If sodium is assumed to be accumulated in the saline pond in the Labyrinth (Table 1) by meteoric precipitation only, the age of the water body can be estimated. Table 5 shows the figures used in this calculation. Assuming an annual snowfall 30 g/cm²/yr and a sodium content of snow 50 ppb, the annual deposition of sodium in 1 cm² water column would be 1.5 μg. As the content of sodium in the saline pond is 4.13 g/kg, the total amount of sodium in 1 cm² water column is estimated to be 84 mg at the present depth of 20 cm. Dividing 84 mg by 1.5 μg, 56000 years

Table 5. Age estimation of saline pond in the Labyrinth.

Assuming pond water originated only from snow and ice.	
1) Annual snowfall	30 g/cm ² /yr
2) Na content of snowfall	50 ppb
3) Annual Na deposition	1.5 μg/cm ² /yr
4) Water depth at present	20 cm
5) Na content of pond water	4.13 g/kg
6) Na in water column	84 mg Na/cm ²
7) Estimated elapse of time	56 × 10 ⁸ yr

should be the highest estimate of the elapse of time, because in this calculation other factors such as water supply from the surrounding catchment area and the contribution by rock weathering and ion exchange between water and weathered rock are neglected. So, the true time of elapse should be much less than the above estimate.

Lake Joyce in the Pearse Valley which is partly covered with thick lake ice of 7.2 m, is chemically stratified like other saline lakes in the Dry Valleys, and the salt in Lake Joyce is principally sodium chloride as shown in Table 4. When comparing the chemical composition of water in Lake Joyce, for example, the uppermost layer (2) and the lower layer (2'), a tendency for downward movement can be seen in the diagram (Fig. 7) from the upper fresh water (2) to the lower saline waters (2').

As to the evolutionary processes of the saline waters in the Dry Valleys, it can be summarized as follows (Fig. 7): starting from glacial melt water and other running waters, the composition of water in the depression should change, approaching that of sea water, as can be seen in Lake Joyce, and then following the Thompson and Nelson model, the composition moves to the right in the diagram as in the case of sea water. In a word, the latter stages of precipitation or concentration of salt should be the same, whether the original water body was glacial melt water or trapped sea water.

3.5. Difference between Lake Bonney and Lake Vanda in chemical characteristics

The major chemical components of water of saline lakes in the Dry Valleys differ greatly from valley to valley and from lake to lake. Water in Lake Bonney contains principally sodium and magnesium chlorides, while water in Lake Vanda is mainly composed of calcium chloride. This difference should be interpreted as follows: The Taylor Glacier melt water contains much calcium and sulfate (Table 3) and in the course of concentration gypsum was precipitated in the west lobe during its formation. The bottom layer of the present west lobe is saturated with calcium sulfate. As a result, waters enriched relatively in sodium and magnesium form the present bottom layers of both west and east lobes. This is confirmed by the

finding of two evaporites at the bottom of the lake, gypsum in the west and hydrohalite ($\text{NaCl}\cdot 2\text{H}_2\text{O}$) in the east. The supply of much calcium and sulfate is still going on through the Taylor Glacier and the formation of gypsum on the bottom of west lobe will continue. However, if the water supply from the glacier were to be decreased by climatic change, Lake Bonney should undergo concentration under frigid conditions and attain nearly the same composition as the Lake Vanda water as already stated. As HENDY *et al.* (1977) and TORII *et al.* (1975) reported, it is believed that the west lobe of Lake Bonney was filled first by melt water from the Taylor Glacier, and the east lobe was formed later by overflow through a narrow channel connecting the two lobes. Standing on these points, it is possible to consider that the age of Lake Bonney is younger than the saline lakes in the Wright Valley.

4. Concluding Remarks

In summary, the authors would agree with the trapped sea water theory suggested by many investigators for the Wright and Taylor Valleys. Our studies on trace elements and stable isotopes of saline waters and lake sediments support this view, but the chemical composition of water in saline lakes in the Dry Valleys can not be interpreted only by the trapped sea water hypothesis. The possible accumulation of sea spray supplied by the atmospheric precipitation should be enormous during the long period of an ice age. The authors would point out that the chemical compositions of waters in these saline lakes are derived mainly from the atmospheric salt during the course of accumulation in these areas rather than the modification of trapped sea salt.

Acknowledgments

The authors are grateful to Dr. Y. MIYAKE and our colleagues for their valuable advices, and wish to express their thanks to the Division of Polar Programs of NSF, U.S.A. and the Antarctic Division, New Zealand for supporting their researches in these 15 years. The Ministry of Education, Science and Culture and the Japan Polar Research Association financially supported these works.

References

- BOUTRON, C., ECHEVIN, M. and LORIUS, C. (1972): Chemistry of polar snows. Estimation of rates of deposition in Antarctica. *Geochim. Cosmochim. Acta*, **36**, 1029–1041.
- HENDY, C. H., WILSON, A. T., POPPLEWELL, K. B. and HOUSE, D. A. (1977): Dating of geochemical events in Lake Bonney, Antarctica, and their relation to glacial and climatic changes. *N. Z. J. Geol. Geophys.*, **20**, 1103–1122.
- MORIKAWA, H., MINATO, I., OSSAKA, J. and HAYASHI, T. (1975): The distribution of secondary minerals and evaporites at Lake Vanda, Victoria Land, Antarctica, in geochemical and

- geophysical studies of dry valleys, Victoria Land in Antarctica. *Mem. Natl Inst. Polar Res., Spec. Issue*, **4**, 45–59.
- MURAYAMA, H., NAKAYA, S., MURATA, S., TORII, T. and WATANUKI, K. (1979): Interpretation of salt deposition in Wright Valley, Antarctica: Chemical analysis of DVDP 14 core. *Mem. Natl Inst. Polar Res., Spec. Issue*, **13**, 60–72.
- MUROZUMI, M., CHOW, T. J. and PATTERSON, C. (1969): Chemical concentrations of pollutant lead aerosols, terrestrial dusts and salts in Greenland and Antarctic snow strata. *Geochim. Cosmochim. Acta*, **33**, 1247–1294.
- NAKAI, N., KIYOSU, Y., WADA, H. and TAKIMOTO, M. (1975): Stable isotope studies of salts and water from dry valleys, Antarctica. I. Origin of salts and water, and the geologic history of Lake Vanda, in geochemical and geophysical studies of dry valleys, Victoria Land in Antarctica. *Mem. Natl Inst. Polar Res., Spec. Issue*, **4**, 30–44.
- NAKAO, K., TORII, T. and TANIZAWA, K. (1978): Interpretation of salt deposition in Wright Valley, Antarctica: granulometric analysis of DVDP # 14 core. *DVDP Bull.*, **8**, 68.
- SCHIRTLIFFE, T. G. L. (1964): Lake Bonney, Antarctica: Cause of the elevated temperatures. *J. Geophys. Res.*, **69**, 5257–5268.
- THOMPSON, T. G. and NELSON, K. H. (1956): Concentration of brines and deposition of salts from sea water under frigid conditions. *Am. J. Sci.*, **254**, 227–238.
- TORII, T., YAMAGATA, N., NAKAYA, S., MURATA, S., HASHIMOTO, T., MATSUBAYA, O. and SAKAI, H. (1975): Geochemical aspects of the McMurdo saline lakes with special emphasis on the distribution of nutrient matters, in geochemical and geophysical studies of dry valleys, Victoria Land in Antarctica. *Mem. Natl Inst. Polar Res., Spec. Issue*, **4**, 5–29.
- TORII, T., YAMAGATA, N., OSSAKA, J. and MURATA, S. (1977): Salt balance in the Don Juan basin. *Nankyoku Shiryo* (Antarct. Rec.), **58**, 116–130.
- WILSON, A. T. (1964): Evidence from chemical diffusion of a climatic change in the McMurdo dry valleys 1,200 years ago. *Nature*, **201**, 176–177.
- YOSHIDA, Y., TORII, T., YUSA, Y., NAKAYA, S. and MORIKAWA, K. (1975): A limnological study of some lakes in the Antarctic. *Quaternary Studies*, ed. by R. P. SUGGATE and M. M. CRESSWELL. Wellington, The Royal Society of New Zealand, 311–320.

(Received April, 16, 1979)