Report of the Japanese Summer Parties in Dry Valleys, Victoria Land, 1963–1965

VIII. Occurrence of Antarcticite in Don Juan Pond — Sequential Change and the Conditions of Crystallization

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南極 Victoria Land の Dry Valley 調査報告

VIII. ドンファン池における南極石の産出 —経年変化と晶出の条件

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要　旨

1961年10月に発見された南極ビクトリアランドの不凍池ドンファンについて，数回にわたる観測の結果をのべ，南極石($CaCl_2 \cdot 6H_2O$)の晶出の条件を実験的に確かめた．南極石の産出が発見されたのは1963年12月であるが，それ以前と1968年12月には産出が認められなかった．南極石を産出する池水を実験室に持ち帰り，その母液について種々の温度における晶出時の母液の組成を分析した結果は，純 $CaCl_2 \cdot 6H_2O$ の飽和溶液に関する分献値とほぼ一致した．実験結果から推測すると，結晶が発見されなかった1962年12月および1968年12月の池水も，気温が降下して水温がそれぞれ −7°C および −3°C に達すれば晶出したはずである．

1. History of Don Juan Pond and Its Antarcticite

On October 11, 1961 a field reconnaissance by a U. S. Navy helicopter in the south fork of Wright Valley (Longitude 161°10′E, Latitude 77°34′S), Victoria Land, Antarctica, revealed an unfrozen pond, although the ambient temperature was −24°C. During the following three months several trips were made to the pond, which was named Don Juan Pond after the helicopter pilots.

G. H. MEYER, the microbiologist, and his collaborators reported the occurrence

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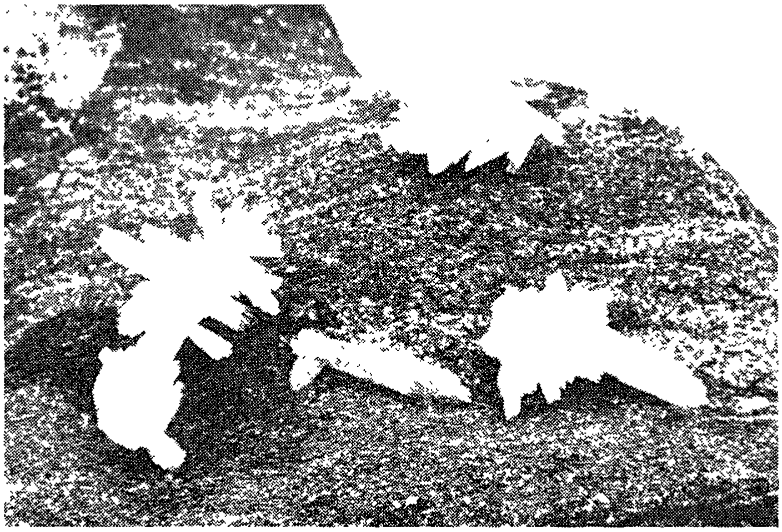

Fig. 1. Crystals of Antarcticite.

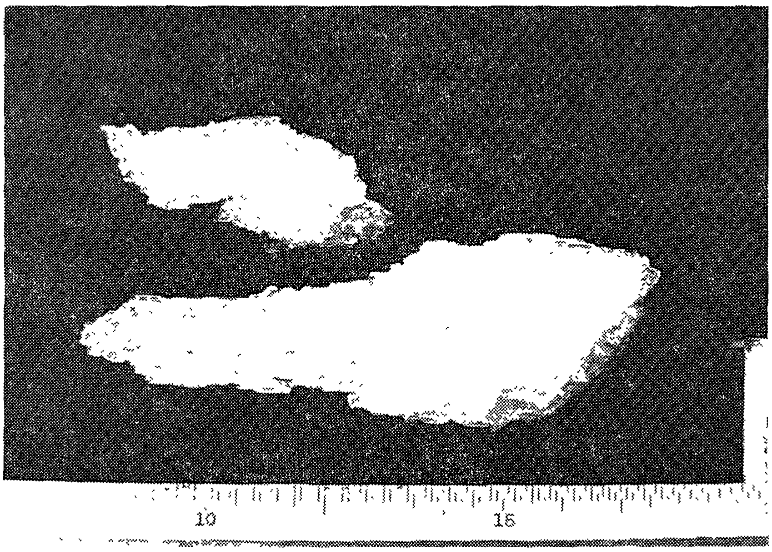

Fig. 2. Large crystals of Antarcticite.

Table 1. Chemical composition of Antarcticite.

Component	Weight (%)	Mole (%)	Molar ratio
Ca	17.5	0.437	1.000
Mg	0.41	0.017	0.039
Na	0.34	0.015	0.034
K	0.008	0.002	0.000
Cl	32.7	0.923	2.11
H_2O	49.2	2.730	6.25
Total	100.1		

of small salt deposits in the vicinity of the pond and gave analytical data on the saline water for the first time (MEYER *et al.*, 1962). In the austral summer of 1962-63, Dr. H. FUKUSHIMA of Yokohama City University visited this pond, collected saline water and carried it back for chemical analysis, but he did not observe any peculiar crystals in the pond water.

When two of the present authors (TORII and YAMAGATA) and collaborators visited this same pond in December 1963, they found a peculiar type of large crystal growing in the main pond. The largest crystals, mostly in the form of needles, reached a length of about 10 cm (Figs. 1-2). The optical properties, chemical analysis (Table 1), and powder patterns obtained by X-ray diffraction of the crystals agreed with those of artificial calcium chloride hexahydrate $CaCl_2 \cdot 6H_2O$. TORII proposed the name Antarcticite for the new mineral and the name was approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association (TORII and OSSAKA, 1965).

The succeeding reconnaissance of Don Juan Pond by the Japanese Summer Parties reconfirmed the occurrence of this mineral in the main pond in January 1965 and December 1965. Samples of crystal and saline water were collected each time and were carried back for chemical analysis. Table 2 summarizes the sequential changes in the chemical composition of the water.

Table 2. Sequential changes in chemical composition and specific gravity of the saline water in Don Juan Pond and occurrence of Antarcticite.

Sample No.	1	2	3	4	5	6
Date	11 Oct. 1961	16 Dec. 1962	30 Dec. 1963	5 Jan. 1965	3 Dec. 1965	28 Dec. 1968
Observer	G. H. MEYER	H. FUKUSHIMA	TORII *et al.*	〃	〃	〃
Sp. gr. 24°C	1.251	1.351	1.380	1.386	1.375	1.361
Water temperature (+°C)	—	—	6.45	10.4	3.5	10
Na (g/kg)	11.5	4.11	2.16	1.63	2.66	3.51
K 〃	0.16	0.15	0.23	0.26	0.23	0.20
Ca 〃	114.0	123.9	132.2	137.1	131.7	127.1
Mg 〃	1.20	1.8	2.6	1.8	2.3	1.8
Cl 〃	212.0	229.4	247.1	251.1	243.6	235.5
SO_4 〃	0.011	0.00	0.00	0.00	0.00	0.00
Evaporation residue 〃 (180°C)		361.9	388.8	390.6	384.5	370.7
Occurrence of Antarcticite	Presumably no	no	observed	observed	observed	no

After reconnaissance had been interrupted for two successive austral summers of 1966–67 and 1967–68, TORII and YAMAGATA visited the pond again in December 1968. This time they could not find any of Antarcticite crystals in the main pond, but in small puddles around the main pond the crystals were growing on a small scale. The flat basin of the pond appeared more whitish in color than observed during any of the former visits and suggested that some natural incident had occurred, probably flooding and overflowing of the main pond water during the summer 1966–67 or 1967–68, which resulted in the dilution of the main pond water.

2. Laboratory Experiment on Crystallization

The authors conducted a laboratory experiment on the saline water collected from Don Juan Pond in order to determine the relationships between the temperature and the chemical composition of water in equilibrium with Antarcticite crystals.

A water sample collected from a puddle in which Antarcticite occurred in December 1968 was placed in a thermoregulated bath and the temperature was lowered. When Antarcticite crystals had crystallized out, the mother liquid was drawn and an aliquot was analyzed for chemical composition. The main portion of the mother liquid was then placed in a bath which was adjusted to a lower temperature and after the crystallization occurred the mother liquid was drawn, etc.

Analysis showed the saline water was not a pure saturated solution of calcium chloride, but contained magnesium, sodium and potassium as minor constituents. Table 3 shows the results of chemical analysis and specific gravity measurement at 24°C.

The decreasing concentrations of calcium and chloride with decreasing temperature indicate a temperature gradient in the solubility of calcium chloride as a major component of the saline water, and if the solution were pure calcium chloride, the temperature gradient of calcium ions should coincide with that of chloride ions

Table 3. Chemical composition of the saline water in equilibrium with Antarcticite crystals between 11.4°C and −20°C.

Temperature (°C)	Specific gravity 24°C	Cl	Ca	Mg	Na	K
		g/kg				
11.4	1.388	252.6	136.1	2.03	2.53	0.25
6.3	1.378	246.4	132.4	2.12	2.66	0.27
5.7	1.377	245.6	132.1	2.09	2.66	0.29
−1.5	1.363	239.5	128.2	2.05	2.99	0.30
−6.7	1.347	231.0	121.9	2.72	3.35	0.34
−20.0	1.322	217.3	113.9	2.43	3.75	0.36

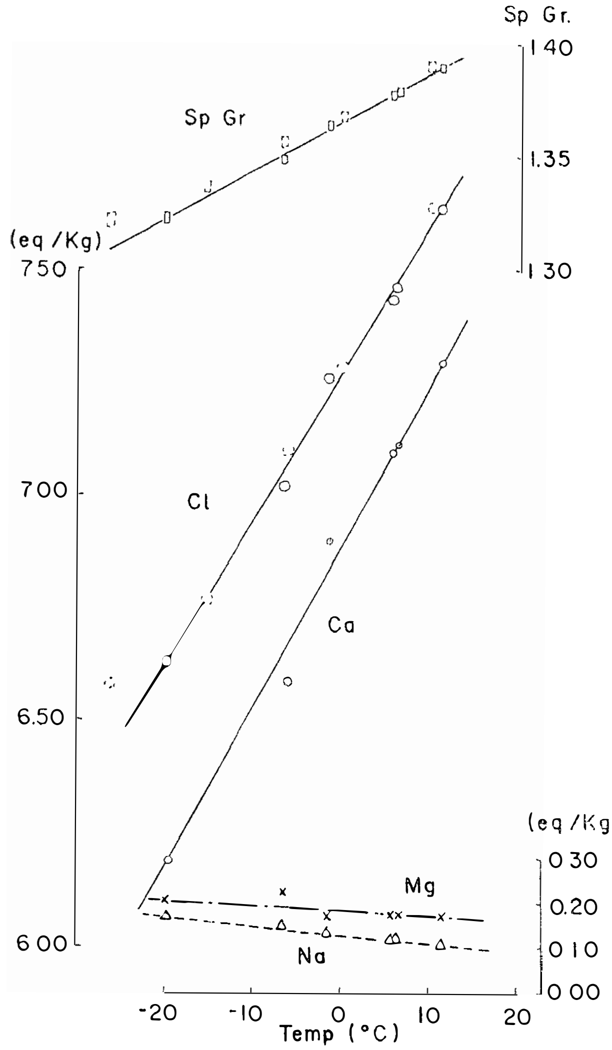

Fig. 3. The concentrations of chloride and calcium and the specific gravity of the saline water in equilibrium with Antarcticite as a function of temperature.

Circles and squares are experimental values for the saline water, and broken circles and squares are literature values for pure $CaCl_2 \cdot 6H_2O$ *solution.*

when the concentration is expressed as equivalent per kilogram. However, this is not the case when the solution contains cations other than calcium even if the content is very small (the content of sulfate ions is practically zero).

The temperature gradients of calcium and chloride in the solution appear as two separate straight lines in Fig. 3. These lines were drawn in order to fit the observed concentration (in equivalent per kilogram) of calcium and chloride ions in the saline water in equilibrium with the crystal, based on the assumption of linear relationships with temperature. The larger values of chloride concentrations as compared with those of calcium concentrations can be interpreted as being caused by the presence of magnesium and sodium in solution. The concentration of magnesium as well as sodium gradually increases with decreasing temperature.

This fact implies that the concentrations of these ions have not reached the solubility products of the chlorides of magnesium and sodium, and co-crystallization of these salts with the crystals $CaCl_2 \cdot 6H_2O$ should be very small (see Table 1).

Broken circles are values for the pure saturated solution of calcium chloride calculated on the basis of literature values (Nihon Kagakukai, 1956) and the points naturally indicate equivalent values for both chloride and calcium. Broken squares on top indicate literature values for the specific gravity of the saturated calcium chloride solution at each temperature value. Coincidence between the literature values (pure $CaCl_2$ solution) and the temperature gradients for chloride and speific gravity of the saline water from Don Juan Pond seems very good except in the extreme case at the lowest temperature.

3. Discussion

In Fig. 4 are reproduced the three straight lines obtained by the laboratory experiment. The uppermost line indicates the specific gravity (at 24°C) for different temperatures of the saline water in Don Juan Pond in equilibrium with Antarcticite crystals. Open circles on this line indicate the specific gravity of samples collected from the pond at times from December 1962 through December 1968. Numbers in parentheses correspond to the sample numbers shown in Table 2.

Perpendicular broken lines drawn from these points down across the abscissa give the predicted temperatures at which the saline water should have been saturated with calcium chloride (predicted crystallization temperature). The open circles on these broken lines give the observed concentrations of chloride and calcium in each water samples.

The predicted crystallization temperature contrasts with the observed temperature of the saline water in Don Juan Pond at each time of sampling. The comparison of each set of temperatures would reveal that when the observed temperature was lower than or approximately the same as the predicted crystallization temperature, Antarcticite was found in the main pond (Sample Nos. 3, 4 and 5), and when the observed temperature was higher, the mineral did not occur (Sample No. 6).

In the cases of Nos. 2 and 6 (December 1962 and December 1968), it can be predicted that there should have occurred crystallization when the water temperature decreased down to −7 and −3°C respectively, as in early 1963 and 1969.

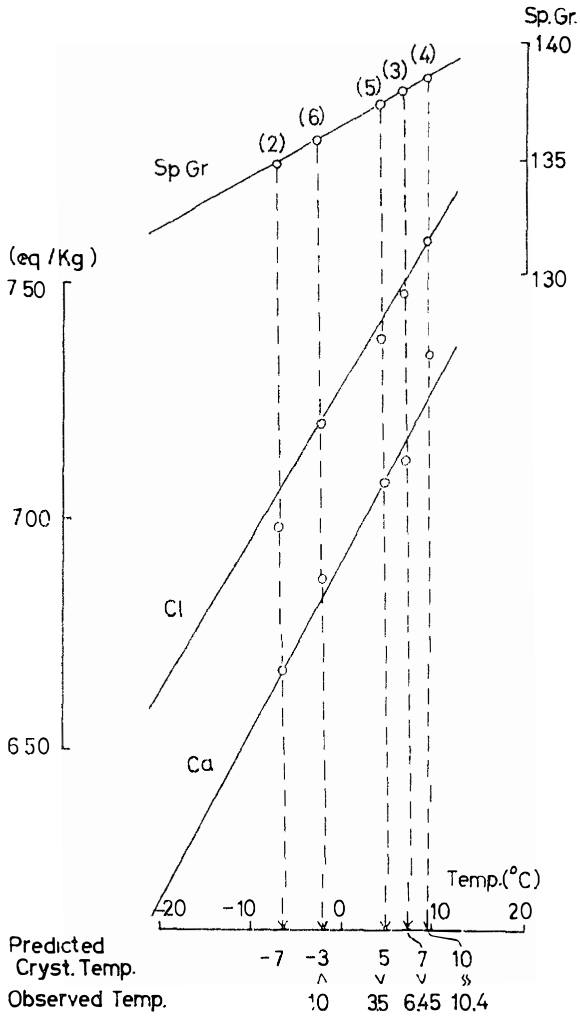

Fig. 4. Schema for the prediction of water temperature of crystallization of Antarcticite in Don Juan Pond. Numbers in parentheses indicate the sample numbers shown in Table 2.

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