Abstract

The deuterium content of 40 samples of water substances from Antarctica was determined mass spectrometrically.

Snow samples gave -13.4 to -21.2% for δD_{SMOW}. From these and PICCIOTTO's data, -13.4 to -29.9%, as well as a value -32.0% for the 14 meter deep water of Lake Bonney, Victoria Land, the source of which is assumed to be in the snow in the surrounding area, the possible lower extreme of deuterium fractionation on the earth was given.

The value of δD_{SMOW} for continental ice ranged from -15.0 to -23.0%, being similar to those for snow; this fact shows that fallen snow was transformed into glacial ice through no perceptible isotopic fractionation.

The value of δD_{SMOW} for pack ice fluctuates around the sea water value, indicating that the major source of this kind of ice is sea water. The chlorine determination supports the view.

Puddle water was found to be rather uniform in the content of salt, the major source of which was concluded to be sea water spray or air-borne salt. The results of the determination of δD_{SMOW}, -4.3 to -10.9%, indicate that the source of water is partly land water and partly sea ice, but the direct supply of sea water, if any, must be insignificant.

A number of ponds on the East Ongul Island is characterized by a rather high salinity and a ratio Na/Cl smaller than that for sea water. The value of δD_{SMOW} was found to be intermediate between snow water and sea water. From these results it was concluded that the salt of the ponds was transported from the surrounding seas in the form of sea water spray and that the observed value of δD_{SMOW} was caused by fractional concentration of deuterium through evaporation.

Thus, the characteristics of different kinds of water substances from Antarctica were clarified and, at the same time, the history of their formation was elucidated.

INTRODUCTION

The land of Antarctica is assumed to have been well protected from chemical erosion because of prevailing cold climate and ice cover. Furthermore, it has remained little affected by human activity. Naturally the chemistry of the water substances there which have rarely been investigated is expected to be quite specific, reflecting these circumstances. This chemical speciality must be more evident because the material transportation to Antarctica from other continents of the globe is considerably limited by the interposition of the vast circumpolar water, the Antarctic Ocean. The material exchange between this and other continents is only possible through the general atmospheric circulation.

When Japan decided to take part in the Antarctic Research Expedition, the group of Japanese geochemists necessarily planned to take up the chemistry of the Antarctic water substances as one of their most important research projects, and since then they have been successful in contributing many new findings. The present paper deals with the results of the deuterium determination in water substances, as a programme of the general research project of the chemistry of the Antarctic waters.

The author and her co-workers had previously determined the deuterium abundance in nearly 600 samples of the hot spring, subterranean, tap, and sea waters collected from various parts of Japan, and even from abroad[1-4].

The results obtained and those by many other investigators of the world gave the general distribution of deuterium abundance and its range of variations whereby the picture of the role of the isotopic fractionation processes and its effect causing the observed distribution in natural waters can be drawn.

The author's research so far made on the Antarctic waters added not only new data particular to the deuterium chemistry of these waters but also data useful for confirming or checking theories and explanations which were presented from the observation of other chemical elements. Examples are as follows:

1) The values of δD_{SMOW} for Antarctic snow were found to range from -13.4 to -25.6%, values exceedingly low as compared with data from other continents. In fact, the values of δD_{SMOW} for snow in temperate zones are from -9 to -16%. The situation is understandable from KIRSCHENBAUM's old observation[5] of the deuterium abundance in North America and his explanation of

the particular deuterium distribution there. According to him, the deuterium abundance in terrestrial waters of North Ameria such as lake and river waters, tends to decrease with latitudinal increase. This tendency he tried to explain as follows. The general source of the global water is in a warm zone where evaporation is active. The evaporated water gradually moves towards cold temperature zones by repeating condensation and reevaporation. Through these evaporation and condensation the isotopic fractionation occurs with decreasing abundance of deuterium in the evaporated and condensed fractions. In effect, a high latitude water is less enriched with deuterium than a low latitude water. Therefore, the polar water is expected to show the lowest value of δD_{SMOW} as actually shown here. The value is of special importance as it ought to show the low limit of deuterium fractionation possible on the earth. It should be added that the lowest value ever obtained is -32.0% in SMOW for 14 m deep water of Lake Bonney in Victoria Land, the source of which is assumed to be the snow that fell in that area.

2) SUGAWARA and others[6,7] found an unusual chemical composition in the water of a number of pools on the East Ongul Island. To explain this, melted snow was assumed as the major source of the water, and sea water spray from adjacent sea as the major source of the salt contained therein. To check this theory, the deuterium abundance determination and some computations based on the obtained data proved to be an effective means by which the proposed theory was positively supported.

3) Another example is the question of the origin of salt lakes in Victoria Land not far from the Base of the American Antarctic Expedition, which were explored by a team of Japanese geochemists headed by Dr. T. TORII. Regarding the origin of the water and salt, the scientists were divided in opinion; some favored marine origin while others volcanic origin. The deuterium determination of the water gave -21.6 to -32.0% in δD_{SMOW}. This is only understandable by assuming that the primary source of the water was the fallen snow, and the melted snow reached some volcanic stratum where it was heated to dissolve the salt components there, then issued from a side wall or the bottom of the lake to fill it. The detail of this investigation will be published as a separate paper.

EXPERIMENTAL

Preparation of hydrogen gas for deuterium determination and the procedure of the analysis employed in this study have been described in earlier papers[1,8,9]. The standard Tokyo Tap Water collected on May 17th, 1957 is used as a working standard in routine analysis by means of the mass spectrometer. The values of deuterium content are represented by deviation (δ) in per cent, from the ratio of a Standard Mean Ocean Water (SMOW), as expressed in the following formula:

$$\delta D_{SMOW}(\%) = \left(\frac{(HD/H_2)_x}{(HD/H_2)_{std.}} - 1\right) \times 100$$

The differences of the deuterium content between working standard and the two reference samples supplied by the U. S. National Bureau of Standards are as follows[10].

N. B. S. reference samples	Deviation from the standard Tokyo Tap Water (%)	
No. 1*	+ 0.21	±0.16
No. 1a	− 13.95	±0.12

* No. 1 : Steam condensate from the Potomac River water.
No. 1a: Snow water from Yellowstone.

RESULTS AND DISCUSSION

All the samples examined were collected from the surroundings of the Syowa Station (69°30′ S; 39°35′ E) by the members of the 1st to the 6th (1956–1962) Japaneses Antarctic Research Expeditions. The forms of the water substances are snow, continental ice, pack ice, puddle water and pond water.

The results of determination are given below.

1) Snow

Samples are of newly fallen snow that fell under a calm condition. As shown in Table 1, the values of δD_{SMOW} of 4 samples range from -13.4 to -21.2%, values a little higher than -25.6% for a snow sample collected at the McMurdo Base. It is also remarkable that the obtained values are considerably low as compared with the data -9 to -16% ever obtained in the temperate zones such as Tokyo and many sites of U. S. A.[11,12] A recent report by PICCIOTTO and his co-workers[13] gave the values of δD_{SMOW} -13.4 to -29.9% for the samples from the Belgian Antarctic Base (70°26′ S; 24°19′ E). These results lead to a conclusion that the deuterium content of the snow in Antarctic region is lower than that in temperate zones.

Table 1. Deuterium content in samples of newly fallen snow and continental ice.

Sample	Date collected	δD_{SMOW} (%)	Cl mg/l
New snow	June 14, 1959	−21.2	1.6
	July 4, 1959	−16.6	1.2
	Jan. 17, 1960	−13.4	
	Sept. 10, 1960	−19.8	
Iceberg	June 30, 1959	−15.0	5.1
Shirase Glacier	May 1, 1960	−18.7	
Glacier lake	May 20, 1960	−16.7	
Honhörbrygga Glacier	Aug. 10, 1960	−20.1	
Iceberg	Sept. 2, 1960	−23.0	

It was already in 1951 that KIRSHENBAUM[5] pointed out the fact that the deuterium content in lake and river waters in North America tends to decrease from the south to the north, and he tried to attribute this tendency to repeated evaporation and condensation followed by the deuterium fractionation. In fact, when evaporation occurs at the surface of a water body, the evaporated vapor is less enriched with deuterium, leaving the mother water body enriched with the isotope. Now, when there occurs condensation to the evaporated water vapor, the condensate is enriched with deuterium, leaving the vapor poorer in deuterium in the air mass. The air mass tends to move from the south towards the north. Naturally, the deuterium content in river and lake waters, the source of which is primarily in precipitation, tends to decrease with latitudinal increase. Later, many other investigators, particularly FRIEDMAN[14], proved a similar decrease of deuterium content with latitudinal increase in the samples of rain and snow collected at various places in North America, differring in latitude. The results by the author and PICCIOTTO are important in that they show the degree of the deuterium decrease in the ice covered cold region of the world.

The deuterium content of snow seems to have seasonal variation. PICCIOTTO pointed out that δD_{SMOW} of snow at the Belgian Antarctic Base is low in winter (May to October) with a mean value -25%, and high in summer (November to April) with a mean value -16%. The author's results appear to support PICCIOTTO's view: the values of δD_{SMOW} for June, July and September being -21.2, -16.6 and -19.8%, respectively, and -13.4% for January.

2) Continental ice

Five continental ice samples were examined, one from a floating ice berg, three from the Shirase Glacier and other glaciers protruding from inland toward the beach line of the Sôya Coast, and one from a glacier lake which is assumed to have been filled with water of glacial origin. All the sample were collected by the fourth Japanese Wintering Team. The values of δD_{SMOW} for these samples range from -15.0 to -23.0%, values being similar to but slightly lower than the values of snow in Antarctica.

FRIEDMAN and his co-workers[12] previously reported that 29 samples from the Greenland ice cap gave values from -21.4 to -31.6% at altitudes of $1,900{\sim}2,560$m, and $-18.3{\sim}-18.5\%$ near the sea level, whereas glacial ice samples collected at altitudes of $1,800 {\sim}3,600$ m of Rocky Mountains gave $-13.8{\sim}-15.6\%$. From these results FRIEDMAN concluded that δD_{SMOW} of glacial ice are comparable to that of snow that falls in the environs. The present author's results in Antarctica endorse this. It is rather natural that the fallen snow and rain are transformed into glacial ice in the environs with no perceptible isotopic fractionation.

3) Pack ice

Pack ice samples were collected at three points in a floating ice area as shown in Table 2. At a point, three samples were collected from three different layers, upper, middle and lower, each being about 50 cm thick sheet ice.

Table 2. Deuterium content and chemical composition of pack ice samples from an area around the East Ongul Island, as determined by Dr. J. OSSAKA.

	I-1	I-2	I-3	I-4	I-5
δDsmow (%)	+1.5	+2.5	−2.6	−0.4	+1.3
Cl mg/l	19.8	134	369	968	1,330
Na mg/l	12.2	77.8	215	510	699
K mg/l	0.4	2.8	7.3	19.2	27.3
Ca mg/l	0.5	3.6	8.2	21.5	28.7
Mg mg/l	1.5	9.3	25.2	64.5	92.1
SO$_4$ mg/l	tr.	21.4	60.9	146	199
(SO$_4$/Cl)$_i$/(SO$_4$/Cl)sea	—	1.1_7	1.2_1	1.0_8	1.0_7
(Na/Cl)$_i$/(Na/Cl)sea	1.1_0	1.0_4	1.0_5	0.9_5	0.9_4
(K/Cl)$_i$/(K/Cl)sea	0.9_8	1.0_5	1.0_5	0.9_9	1.0_2
(Mg/Cl)$_i$/(Mg/Cl)sea	1.1_4	1.0_4	1.0_2	1.0_0	1.0_3
(Ca/Cl)$_i$/(Ca/Cl)sea	1.2_2	1.2_3	1.0_4	1.0_5	1.0_2
Location	67°53'S 37°36'E	67°57'S 36°56'E	67°03'S 40°49'E		

The values of δDsmow of these samples range from −2.6 to +2.5%. As the value of δDsmow of sea water is nearly zero, the deuterium content of pack ice can be said to fluctuate around the sea water value.

The chlorine ion content of these samples is low, with values ranging from 19.8 to 1,330 mg/l [15], and even the highest value does not exceed 1/30 of that of sea water. As shown in Fig. 1, there exists no relationship between deuterium content and chlorine content in general. However it is remarkable that in three layered samples both δDsmow value and chlorine content increase with depth.

The fact that the value of the tested samples is not far from the sea water value indicates that the major source of the samples is sea water; this is particularly so for the samples with values higher than the sea water value.
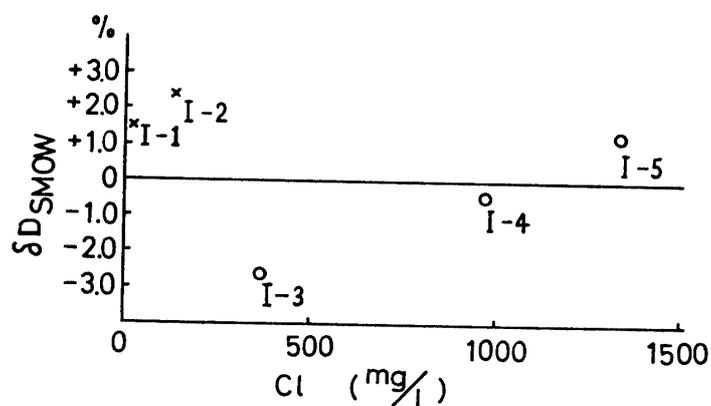

Fig. 1. Deuterium content and chlorine content of pack ice samples.

A theoretical computation supports the above view. The freezing point of HDO is slightly higher than that of H_2O. Thus, when water freezes, HDO must be concentrated in the separated ice. When the freezing is assumed to occur under an equilibrium condition, the freezing must be followed by the isotopic fractionation with a definite fractionation coefficient, the value of which has been theoretically calculated by WESTON as $K = 1.0192$ at $0°C$[16], and determined experimentally by POSEY as $K = 1.021_1 \pm 0.0007$ at $0°C$[17]. Then, the deuterium content in the resulting ice must be by 2% higher than in the original sea water. The positive values of the tested samples are actually in good accordance with this theoretical value. This proves that practically these samples have been formed entirely from sea water, while negative values of samples I-3 and I-4 must have resulted from the addition of terrestrial water from the coastal land area. In other words, the mother sea water had been diluted with inflow of terrestrial water, or the surface of previously formed ice was covered by snow-fall which was mixed with the melt of the surface of the ground sea ice. The repetition of remelting and refreezing may have caused the permeation of the diluent towards deeper layers. The vertical distribution of salt components is in harmony with this explanation.

4) Puddle water

In connection with its formation and origin, the puddle water has been one of the subjects of interest among the Japanese scientists from the beginning of our Antarctic research. In Table 3, the chemical composition are listed as determined by MINAMI, MATSUMOTO and OSSAKA[18] and δD_{SMOW} as determined by the present author on a number of puddle water samples collected from the fast ice

Table 3. Deuterium content and chemical composition of puddle water samples from the area near the East Ongul Island.

	P-1	P-3	P-4	P-6	P-7	P-8	P-9	P-10
$\delta D_{SMOW}(\%)$	-8.2	-5.0	-6.4	-10.3	-9.3	-4.3	-8.1	-10.9
Cl mg/l	43	69	446	209	104	117	48.4	215
Na mg/l	38.8	103.8	244.8	99.8	60.2	69.4	27.7	124
K mg/l	2.0	8.0	13.6	4.4	3.8	3.6	0.8	4.3
Mg mg/l	4.3	9.6	30.4	14.2	8.2	5.7	3.9	14.1
Ca mg/l	8.0	16.0	15.9	6.8	3.9	10.3	1.6	7.0
SO_4 mg/l	tr.	6.3	42.8	28.0	10.2	16.2	5.8	26.8
$(SO_4/Cl)_P/(SO_4/Cl)$ sea	—	0.6_7	0.7_0	0.9_8	0.7_2	1.0_1	0.8_8	0.8_9
$(Na/Cl)_P/(Na/Cl)$ sea	1.6_2	2.7_0	0.9_8	0.8_6	1.0_4	1.0_6	1.0_3	1.0_3
$(K/Cl)_P/(K/Cl)$ sea	2.5_3	6.3_1	1.6_7	1.1_6	2.0_1	1.7_0	0.8_1	0.9_9
$(Mg/Cl)_P/(Mg/Cl)$ sea	1.4_8	2.0_8	1.0_2	1.0_2	1.1_8	0.7_3	1.5_5	0.9_8
$(Ca/Cl)_P/(Ca/Cl)$ sea	8.6_4	10.8	1.6_6	1.5_2	1.7_3	4.1_2	1.2_1	1.5_2
Date collected			Jan. 1957				Jan. 1959	

area between the anchorage of the research ship and the Syowa Station.

As compared with pack ice, puddle water is rather uniform in salt content, with the highest chlorinity being 446 mg/l, but the deviation of the salt composition from sea water is greater. One example is the enrichment coefficient* for calcium which is as large as 1.2_1 to 10.8 in puddle water as compared with 1.0_2 to 1.2_3 in pack ice. This evidently shows that a considerable portion of the salts, even if it is marinogenic, has been transported via air in the form of spray as it will be described in detail in a later section.

In two samples of the eight in total, the enrichment coefficient for sodium is less than unity. These two samples are to be interpreted as representing the cases where sea water spray played a leading role in determining the chemical composition, because, as pointed out by SUGAWARA and others[6,7,19], the enrichment coefficient less than unity for sodium is only imaginable for sea water spray that is emitted through the burst of sea bubbles. In conclusion, the source of salt in puddle water seems to be partly in the salt of sea ice and partly in the salt of land ice and snow among which the contribution by sea water spray or airborne sea salt is dominant.

This interpretation comes in quite accordance with the results of the deuterium determination in the water samples. The values of δD_{SMOW} for puddle water ranges from -4.3 to -10.9%. The values are lower than those for sea ice but higher than those for other terrestrial and meteoric waters in Antarctica. This evidences that the water is supplied partly from land water and partly from sea ice, but the direct supply of sea water, if any, must be negligible. Otherwise, the salt concentration must be considerably great. Another particularity in δD_{SMOW} of puddle water is that the value varies greatly from one sample to another. This indicates that the proportion of supply of both kinds of water, sea ice water and land water, is variable. The general idea of this variability can be given by the following calculation.

Let us assume that the value of δD_{SMOW} is -18.3% for land ice and $+2.0\%$ for sea ice. Then, a simple calculation gives the contribution of sea ice as 38 to 65% for producing the observed δD_{SMOW} -4.3 to -10.9% for puddle water. It should be also noted that the result of calculation does not contradict the salinity of puddle water observed.

5) Pond water

The previous research by the group of Japanese chemists revealed that the water of the ponds distributed on the East Ongul Island is generally characteriz-

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* The enrichment coefficient, a term which was originally proposed by SUGAWARA (1959), is

$$(M/Cl)_{sample}/(M/Cl)_{sea\ water}$$

where $(M/Cl)_{sample}$ and $(M/Cl)_{sea\ water}$ are respectively the ratio of an element to chlorine in the sample and sea water. The term shows how much is concentrated an element relative to chlorine in the sample as compared with sea water. If the salt composition of the sample is identical with that of sea water, the enrichment coefficient is unity and if some element is enriched in the sample relative to chlorine in reference to sea water, the coefficient must be larger than unity.

Table 4. Deuterium content in pond water samples from the East Ongul Island.

Sample	Date collected	δD$_{SMOW}$ (%)	Cl mg/l
Pool water No. 1		−13.3	134.7
Pool water No. 3		−12.1	204.2
J−Pond	Jan. 17, 1960	−10.1	
Pond water St. 1	Jan. 25, 1960	−11.0	121
Pond ice	May 2, 1960	−11.0	
Pond water	May 2, 1960	−13.3	
Pond ice No. 1	Aug. 10, 1960	−11.8	
Pond water No. 14	Jan. 22, 1960	−13.8	373
Pond water No. 21	Jan. 23, 1962	− 9.8	1,005
Pond water No. 23	Jan. 23, 1962	−14.7	85.1

Table 5. Chemical composition of samples of pool water and snow from the East Ongul Island, as determined by E. KAMATA, S. KANAMORI, N. KAWASAKI, and K. TERADA, Nagoya University.

	Pool water No. 1	Pool water No. 3	Snow June 14, 1959	Snow July 4, 1959
δD$_{SMOW}$ (%)	−13.3	−12.1	−21.2	−16.6
Cl mg/l	134.7	204.2	1.6	1.2
Na mg/l	74.0	85.0		
K mg/l	2.46	5.5		
Mg mg/l	9.65	13.7		
Ca mg/l	7.7	11.0		
Sr mg/l	0.13	0.21		
SO$_4$ mg/l	36.2	25.2	0.23	0.23
I⁻ μg/l	1.9	0.5		
IO$_3$⁻ μg/l	2.8	5.0		
I total μg/l	4.7	5.5		
Na/Cl (in equiv.)	0.80	0.64		
K/Cl (in equiv.)	0.017	0.024		
Mg/Cl (in equiv.)	0.21	0.19$_6$		
Ca/Cl (in equiv.)	0.10	0.09$_5$		
Sr/Cl (in equiv.)	0.0007$_8$	0.0008$_3$		
SO$_4$/Cl (in equiv.)	0.19$_8$	0.09$_1$		
I$_t$./Cl (in equiv.)	0.000009$_7$	0.000007$_5$		

ed by a rather high salinity, 85.1 to 1,005 mg/l, higher than the values for puddle water, other land waters and meteoric water. Another characteristic of the pond water is that the composition of the salt in the water is considerably different from that of sea water.

It is natural to assume that the major source of the pond water is in the melted snow and ice of the surrounding areas, while a major source of the salt in the water has been transported from the surrounding seas laden on the spray. The geology and geography of the environs deny an additional supply of salt through direct invasion of sea water or supply from other kinds of salt water such as thermal springs.

An explanation must be given for the deviation of the composition of the salt from that of sea water. An idea came to SUGAWARA that the salt composition of spray might differ from that of sea water and this difference might be caused when sea bubbles are broken and the individual ions escape laden on spray, thus causing the observed difference in salt composition. SUGAWARA and his group were later successful in proving this idea by a series of experiments. Among their results it is particularly significant that chlorine escapes more easily than sodium, resulting the enrichment coefficient of sodium smaller than unity, the most significant feature of the composition of the pond water salt which cannot be explained otherwise.

The deuterium determination proved to be another effective approach to the history of the pond water for checking the explanation given above.

In fact, δD_{SMOW} for pond water was found to range from -9.8 to -14.7%, the values being higher than those of the meteoric or usual terrestrial waters and lower than those of sea waters. This indicates that the pond water was supplied partly from the melted snow and partly from the sea.

A further computation, however, proves that a simple addition of sea water is not sufficient to explain the elevation in δD_{SMOW} of the pond water from the level of the snow value. The added amount of sea water computed from the chlorine concentration of the pond water is not enough to increase δD_{SMOW} to the pond water value.

Let us take two ponds having the chlorine content 134.7 and 204.2 mg/l, respectively, and imagine that the chlorine was transported from the sea in the form of spray. Further, let us assume that the chlorine concentration in the spray was identical with that in sea water. Then, the transported sea water fraction of the pond water can be calculated. From the calculated fraction and snow water fraction, the resultant δD_{SMOW} is computed as -17.4 and -17.7%. The values are still far below the actually observed pond water values.

Naturally, we must consider another active factor which brought about an additional increase of δD_{SMOW} of the pond water. The fractional concentration of deuterium is such a possible factor, and the calculation substantiates the role of this factor.

The calculation is made in two steps.

1) Computation of the evaporation from the surface of the ponds in question.

The evaporation, F (mm), can be calculated by using the equation

$$F = 0.216\mu(1 - t/273)(E-e)$$

where wind velocity μ(m/sec.), tension of water vapor in the air over the surface of the pond e(mb), air temperature on the spot t($^\circ$C) respectively are given from

Table 6.   Evaporation from the surface of the pond on the East Ongul Island.

month	1957										1958	
	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov	Dec.	Jan.	Feb.
F mm/day	1.18	0.35	0.16	0.40	0	0	0	0.33	1.10	2.01	2.51	1.56

the observation data of MURAKOSHI[20], while the vapor tension of the surface water is theoretically calculated. The result of calculation is given in Table 6. The values obtained are in accordance with the value for December in Victoria Land as observed by RAGOTZKIE and others[21]. Based on these data a value 288 mm/yr. is given as the annual evaporation from the pond.

2) Computation of the rise of δD_{SMOW} of the pond water accompanied by the evaporation.

Assume that evaporation proceeds according to Rayleigh's equation

$$R/R_o = f^{\frac{1}{\alpha}-1} \qquad\qquad\qquad (2)$$

where R_o and R are the deuterium concentrations in the water before and after the evaporation, and α is the fractionation constant with a value 1.12 at 0°C.

Let us take the average δD_{SMOW} −17.8% for snow as the value for R_o. This means that we take the pond water when the pond was filled only with melted snow as the initial state. We also assume that the average depth of the pond is 3 m. Then, calculation of δD_{SMOW} after one year evaporation is nothing but computation of the fractionation that occurs in 3,000 mm original water to be subjected evaporation to 288 mm water. The calculation gives −15.9% as δD_{SMOW}. If the loss by evaporation was compensated by an equivalent amount of melted snow, the final δD_{SMOW} would be −16.1%.

If evaporation and addition of snow water are repeated yearly, a period of 9 years is sufficient to raise δD_{SMOW} level from the snow water value to the present day value of the pond water. Nine years is quite a short period as compared with the time during which the ponds in question have continued to exist with the prevailing conditions unchanged over the surrounding areas. Thus, it is concluded that the deuterium approach has proved successful in substantiating the proposed explanation of the history of the pond water, as well as in giving an additional interpretation to the problem on the δD_{SMOW} of the water.

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