

Chemistry of Ice, Snow and Other Water Substances in Antarctica

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南極の雪・プール水・パツクアイスの化学成分

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Introduction

To determine the composition of various types of water substances in Antarctica is not only important from the view-point that it offers materials for drawing a whole scientific picture of this region of the globe but is also of special significance at the point that the obtained information is helpful to complete our knowledge of the transportation of various chemical species on the whole earth and the ways and mechanisms through which such a transportation is actualized. This initiated us to undertake the present research.

All the samples were collected by the members of the Japanese Antarctic Research Expedition Team at locations not far away from Syowa Base, the headquarters of the Japanese Antarctic Research Expedition, 68°30'S, 40°30'E. The following kinds of elements were determined; Na, K, Mg, Ca, Sr, Cl, SO₄, I, P and As**.

Results and characteristics of waters

Pool water of East Ongul Island There are found many fresh-water pools on East Ongul Island some of which remain unfrozen under icecover during the winter

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** Na, K, Ca and Sr. Determined by N. KAWASAKI by using the flame photometric method proposed by K. SUGAWARA, T. KOYAMA and N. KAWASAKI, Bull. Chem. Soc. Japan, 29, 683 (1956).

Mg. Determined by N. KAWASAKI by the usual EDTA titration method.

Cl. Samples rich in Cl were determined by MOHR's method, while samples poor in Cl by K. TERADA in using S. UTSUMI's thiocyanate method, J. Chem. Soc. Japan, 73, 835 (1952).

SO₄. Samples rich in SO₄ were determined by BaSO₄ gravimetric method, while samples poor in SO₄ by E. KAMATA, using the barium chloranilate method by R. J. BERTOLACINI and J. E. BARNEY, Anal. Chem., 29, 281 (1957).

I. Determined by K. TERADA by using the spectrophotometric method proposed by K. SUGAWARA, T. KOYAMA and K. TERADA, Bull. Chem. Soc. Japan, 28, 494 (1955).

P and As. Determined by S. KANAMORI by spectrophotometric methods invented by K. SUGAWARA and S. KANAMORI (unpublished).

Table 1. Chemical composition of pool waters in the Ongul Islands.

	No. 1	No. 2	No. 3	Average
Cl (mg/l)	134.7	136.3	204.2	158.4
Na (mg/l)	74.0	74.0	85.0	77.7
K (mg/l)	2.46	3.3	5.5	3.75
Mg (mg/l)	9.65	13.4	13.7	12.3
Ca (mg/l)	7.7	14.0	11.0	10.9
Sr (mg/l)	0.13	0.36	0.21	0.23
SO ₄ (mg/l)	36.2	16.4	25.2	25.9
I ⁻ (μg/l)	1.9	1.9	0.5	1.4
IO ₃ ⁻ (μg/l)	2.8	2.9	5.0	3.6
It (μg/l)	4.7	4.8	5.5	5.0
Na/Cl (in equiv.)	0.80	0.84	0.64	
K/Cl (in equiv.)	0.017	0.022	0.024	
Mg/Cl (in equiv.)	0.21	0.29	0.19 ₆	
Ca/Cl (in equiv.)	0.10	0.18	0.09 ₅	
Sr/Cl (in equiv.)	0.0007 ₈	0.0018	0.0008 ₃	
SO ₄ /Cl (in equiv.)	0.19 ₈	0.089	0.091	
It/Cl (in equiv.)	0.000009 ₇	0.000009 ₈	0.000007 ₅	

Enrichment Coefficient

Na	(0.9 ₃)	(0.9 ₇)	(0.7 ₄)
K	(0.9 ₃)	1.2	1.3
Mg	1.1	1.5	1.0
Ca	2.7	4.9	2.6
Sr	2.3	5.2	2.5
SO ₄	2.0	(0.8 ₆)	(0.8 ₈)
It	13	13	10

ratio Na/Cl in sample No. 1 is close to but slightly higher than that in sea water, while the ratio in sample No. 2 is evidently higher than that in sea water as usually found in samples of rain and snow which have been collected in other regions of the globe. At this point snow differs clearly from the pool waters.

On the other hand, the ratio SO₄/Cl in snow as in the pool waters is lower than that in sea water.

Another characteristic to Antarctic snow is its high content of phosphorus.

Pack-ice Two examples of the results of analyses of pack-ice samples are listed in Table 2.

Pack-ice is near pool waters in nature and characterized by lower values of both ratio Na/Cl and ratio SO₄/Cl.

time. Three samples of these waters were collected by T. TORII, a member of the Japanese Antarctic Research Expedition Team, in February, 1957, to be transported to the author's laboratory. The results of chemical analyses listed in Table 1 are characterized by two points: 1) Different from ordinary natural waters the ratio Na/Cl in them is lower than that in sea water. 2) The ratio SO₄/Cl in them is also lower than that in sea water.

On these two characteristics discussions will be made later.

Snow Two samples of snow have been examined. As listed in Table 2, the

Table 2. Chemical composition of snow and pack-ice in Antarctica.

	Snow		Pack-ice	
	1	2	1	2
Cl mg/l	413.7	8.3	995.6	3.4
Na mg/l	240	5.3	525	1.5
Mg mg/l	20.4	0.61	65.8	0.15
Ca mg/l	8.9	0.42	21.2	0.19
SO ₄ mg/l	46	0.8	119	1.2
I μg/l	10.5	4.1	8.0	1.4
P μg/l	81	480	250	1500
As μg/l	4.1	2.6	3.2	4.8

Enrichment Coefficient

Na	1.02	1.17	0.95	0.78
Mg	0.72	1.1	0.96	0.67
Ca	1.00	2.4	1.01	2.7
SO ₄	0.80	0.7	0.85	2.6
I	9.5	190	3.0	160
P	53	16,000	63	120,000
As	38	1,200	12	5,400

Discussions on the characteristics of Antarctic water substances

Ratio Na/Cl Among various kinds of natural waters, the sea water is lowest in the ratio Na/Cl, its value being 0.860 as expressed in equivalent. Thus, 1.87 is

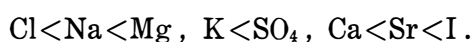
Table 3. Na/Cl in various kinds
of natural waters.

Sea		0.86
River and lake	Japan	1.87
River	World	1.60
Rain and snow	Japan	1.30
Pool	Antarctica	0.76
Snow	Antarctica	0.94
Pack-ice	Antarctica	0.74
Thermal springs	Japan	0.95
Dead Sea	Jordan	0.26

the average of the ratio Na/Cl in 225 representative rivers and lakes in Japan and 1.6 is the average for world rivers, while the average for thermal springs in Japan is 0.95 (*see* Table 3). The ratio in rain and snow stand intermediately between the sea and terrestrial waters. Besides, the ratio in rain gradually changes from sea coast towards inland and from a low level upwards. Thus, the ratio in samples which

were collected at a coastal area is found close to the sea value, and as the point of collection moves away from the coast towards inland and away from sea level to higher levels, the ratio is found to gradually increase. This suggests that the primary source of the atmospheric salt and consequently the salt in rain and snow is sea spray which is constantly emitted into the air through wave breaking. Then the question is: How can we explain the gradual deviation of the composition of the salt in rain mentioned above? A topic of argument. The idea is divided among various experts. The present author accepts that there exist many other sources of salt which are active in modifying to a greater or smaller degree the original composition of the emitted sea salt. At the same time he is convinced that the most important factor causing the deviation of salt composition is the post-wave-breaking fractionation so he termed (1a, b, c). The fundamental of this idea is that the emitted sea spray is subjected to evaporation, while suspended in the air, followed by a successive fractionation and separation of different kinds of salt particles. They differ in composition from one to another and differ in stability in surviving in the air. Some of the particles fall down earlier from the air, others are easily taken in rain and snow and some others are likely to be eliminated by some objects on the path because of their adhesiveness. Thus through the elimination of less stable components the gross composition of the atmospheric salt gradually deviates from the original composition.

The stability of elements is assumed to increase in the following sequence



As seen from this sequence, Cl is the least stable component and it is easily understood that the ratio Na/Cl in rain and snow is greater than the corresponding value in sea water and that the ratio tends to increase horizontally and vertically with distance away from the sea.

Returning to our main subject of the low ratio Na/Cl of the pool waters of East Ongul Island, we must find an explanation to it.

It is evident that the primary source of the water of the pools is the snow which fell on the surrounding region. At the same time it is quite probable that an additional source of salt is the sea spray which was directly transported from the sea in the vicinity.

Now, let us imagine that the author's theory of post-wave-breaking fractionation is valid and that the first fraction of elimination enriched by Cl constitutes the transported spray.

Then it appears rather natural to find the composition of the pool water is sufficiently affected by this transported spray so that its Na/Cl becomes low as actually observed. The situation, however, is not so simple. Some other components which stand higher in the stability sequence are found already enriched in the pool water. In fact, as seen in Table 1, the enrichment coefficient, $(\text{Mg}/\text{Cl})_{\text{pool water}}/(\text{Mg}/\text{Cl})_{\text{sea water}}$, is found to be greater than unity for components such as Mg, Ca, Sr, and I.

Then it is only after this complicacy is solved that the validity of the proposed explanation can be positively accepted.

Aside from this explanation, the process of synfractionation of sea salt is another important factor causing the observed low ratio Na/Cl²⁾.

Synfractionation of sea salt is an experimentally established fact which the author reported in detail at the International Oceanographic Congress in New York, last September. The fundamental is that when droplets are formed through collapse of sea foam to be emitted in to the air, the composition of salt in the droplet differs already from that of the sea water from which the spray came. This shows that different salt components escape with different eases at the burst of bubbles to become the components of the emitted spray. The relative ease can be expressed in terms of enrichment coefficient, $(\text{Mg}/\text{Cl})_{\text{spray}}/(\text{Mg}/\text{Cl})_{\text{sea water}}$, where $(\text{Mg}/\text{Cl})_{\text{spray}}$ and $(\text{Mg}/\text{Cl})_{\text{sea water}}$ stand for the ratios of one component to Cl in spray and sea water respectively. The enrichment coefficient was experimentally proved to increase in the following sequence



Most remarkable is that the ease of escape is greater for Cl than for Na with resultant spray more enriched by Cl than Na.

Then the transportation of spray from such synfractional process is quite probable to considerably contribute to the observed low ratio Na/Cl in the pool water.

The low ratio Na/Cl in pack-ice samples is also understandable when we consider that while the ice was floating and growing on the sea, it must have been exposed to the effect of the sea spray which was produced by synfractionation process.

Ratio SO₄/Cl The SO₄ problem regarding the Antarctic water substances in which the ratio SO₄/Cl is nearly always lower than the corresponding value in sea water is more difficult to solve.

Table 4. SO_4/Cl in various kinds of natural waters.

		Cl mg/l	SO_4 mg/l	SO_4/Cl in equivalent
Mist	Hallde, Norway	3.56	0.57	0.115
Fog	Coast of Nova Scotia and Massachusetts	—	—	0.37-1.23
Rain	Japan			0.37
Snow	Japan			3.2
River	Japan	5.8	10.6	1.35
Sea water		19,000	2,650	0.1007
Pool water	1.	134.7	36.2	0.19 ₈
	Antarctica 2.	136.3	16.4	0.089
	3.	204.2	11.0	0.091
Newly fallen snow	1.	413.7	4.6	0.082
	Antarctica 2.	8.3	0.8	0.07
Pack-ice	Antarctica 1.	995.6	119	0.088
	2.	3.4	1.2	0.26

All possible factors which modify this ratio in waters work to increase it. Thus starting with the ratio in sea water, 0.1007, the ratio ranges 0.115-3.2 in meteoritic waters and the average in 220 representative rivers and lakes in Japan is 1.35 (see Table 4). One example of exception is Dead Sea with a value 0.0019 in which the preferential precipitation of CaSO_4 by evaporation is the cause of the low value. Even synfractionation process acts to increase the ratio. The only one conceivable idea is of the first elimination fraction of the post-wave-breaking fractionation, in which the ratio SO_4/Cl is likely to be lower than in sea water. However, we must face a similar difficulty again to that which we met in the previous section in the discussion on the Na-Cl relation. How can we explain that except SO_4 the whole picture of the composition of salt is rather to be taken for indicating a later stage of fractionation? Especially important is that the SO_4 shortage is to every kinds of land and meteoritic waters in Antarctica so far tested. The final solution of this problem can be given only through an exhaustive investigation.

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