Separation of the Components of Atmospheric Salt and their Distribution (Continued)

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Introduction

In the previous paper⁽¹⁾ it was shown that due to evaporation, the spray particles of the sea water in the air, separate into at least two kinds of daughter particles; the one, hygroscopic in nature and consisting mainly of sodium chloride, and the other, crystalline in nature and consisting mainly of calcium sulphate*. The latter, being more stable, continues to remain longer in the air and tends to be carried horizontally towards inland or to be raised higher vertically. Thus the distribution of several components of the atmospheric salt are so arranged that the ratios Ca/Cl, Mg/Cl and SO_4/Cl grow larger as we move towards inland or go higher from sea level.

The writers continued the study in a small island "Sugashima" (Fig. 1), located in Ise Bay, about 4 km off Toba, Mie-Prefecture, and the situation in a limited area close to the beach made it possible for them to obtain considerable new information, which will be given below.

The study was carried out as follows: Seven stations were chosen, different in height, starting from the sandy beach "Shirasaki" up to the summit of Mount Ôyama with a height of 236.6 m. At each station except Shirasaki the washings of pine needles were collected according to the procedure which was given in the foregoing paper⁽¹⁾. At Shirasaki, a bare sandy area with no pine trees, a cotton gauze, spanning a metallic frame, was fixed in the calm weather just above the sand so that it was exposed to the sea breeze. After 5 hours exposure the gauze was taken off to rinse with distilled water. In addition to the determination of Na, Mg, Ca, Cl, SO_4 of the washings of pine needles and the cotton gauze, we determined the total carbonic acid of the samples, collected on Dec. 18—19, 1949, where its ratio to chlorine was determined. Also the residual fraction of filtration of a number of the washings left on filter paper, was determined for Ca and Mg and their ratios to Cl were established. The results are given in Tables 1∼4.

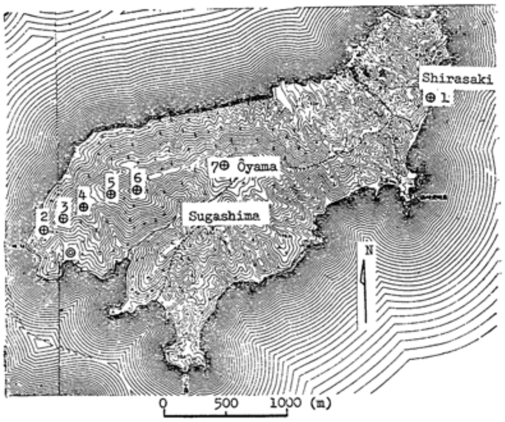

Fig. 1.

⊕…Stations where the samples were collected.
◎…Marine Biological Laboratory attached to Nagoya University.

Results and Discussions

1. What was shown first was that the variation in the composition of the atmospheric salt was very evident already in the samples from the succeeding seven stations (See Table 1). This means that the fractional separation of the components of sea water begins to occur over the

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(1) K. Sugawara, S. Oana, and Tadashiro Koyama: Separation of the Components of Atmospheric Salt and their Distribution, This Bulletin, **22**, No. 2, 47-52 (1949).

* It should be noted that a similar attempt to interpret the variation in the salt composition in rain water by the fractional segregation of the sea salt was already done by H. Matsui who assumed the segregated particles to act as condensation nuclei, thus causing the variation (*J. Meteor. Soc. Japan*, **22**, 2-12 (1944)). In the present paper, the writers deal on the one hand with the problem, and their conclusions are based upon observational and experimental firmer and more definite data, on the other hand they make it clear that the fractionation begins to occur as early as just after the spray is formed from the surface of the sea.

It should also be added that, according to the writers' view, salts are not only supplied to the rain water as condensation nuclei but a considerable amount of them is dissolved in it in its course of falling by washing after the drops are formed.

Table 1

Washings of Cotton Gauze and Pine Needles from 7 Stations, Sugashima, Different in Height and Distance from the Beach. (Nov. 13, 1948)

Ratio in Equivalent	Sea Water	Stations						
		1	2	3	4	5	6	7
SO_4/Cl	0.100_7	0.096_8	0.099_5	0.124_0	0.132_0	0.143_9	0.162_0	0.149_3
Na/Cl	0.860	0.829	0.819	0.848	0.860	0.845	0.845	0.853
Ca/Cl	0.037_9	0.041_2	0.061_6	0.065_5	0.071_8	0.074_6	0.105_6	0.099
Mg/Cl	0.195_1	0.198_6	0.196_9	0.198_4	0.208_4	0.223_9	0.236_6	0.224_7
Ca/SO_4	0.376_2	0.426	0.618	0.528	0.544	0.519	0.652	0.668
$\Sigma+/\Sigma-$	0.98_6	0.97_4	0.98_1	0.98_8	1.00_6	0.99_8	1.02_2	1.02_5

Table 2

The Total Carbonic Acid and its Ratio to Cl in the Washings of Pine Needles from Sugashima

	Sea Water	Stations					
		1	2	3	4	5	6
Cl (mg./l.)	184_{30}	215_9	725	733	$376._9$	$341._8$	561
Total carbonic acid (milli-equiv./l.)	3.63	0.56	0.35	0.61	0.38	0.47	0.93
Total carbonic acid/Cl (Ratio in equivalent) $\times 10^2$	0.69_8	0.9_2	1.7	2.9	3.6	4.9	5.9

surface of the sea as early as just after spray is formed. A fuller discussion will be given later.

2. The simultaneous determination of Cl and total carbonic acid (Table 2) shows that carbonates are important components of the atmospheric salt and their relative amount in it grows larger as we recede from the beach, a relation coming in harmony with a general trend of a relative increase of positive components, to negative ones as shown by $\Sigma+/\Sigma-$, the ratio of the sum of the equivalents of the positive components to that of those of the negative ones (Table 1). The increase of $\Sigma+/\Sigma-$ is not only evident in the case of the washings of pine needles on Sugashima, but also in sets of the comparison data of samples of rain water as well as of the pine needles between Sugashima, Nagoya and Matsumoto as given in Tables (Table 3 a, b). The relation is also true in the comparison of the ordinary rain-water, rain from thunderstorms and the rime water from Mt. Fuji (Table 3 c). The whole result tells that in addition to calcium sulphate, we must assume magnesium carbonate and particularly calcium carbonate as members of the stable segregates from the primary spray particle, which remain longer in the air and form predominant components of the atmospheric salt in the air in higher strata and over locations away from the sea beach.

The present view is supported by the determination of Mg and Ca in the residual fraction from filtration of the washings of pine needles which is assumed to consist mainly of carbonates. The result given in Table 4. suggests that actually Mg and Ca are the primary positive components of the carbonate in question and at the same time it shows that between two kinds of carbonates, calcium carbonate is more stable and its

Table 3

(a)

Ratio in Equivalent	Sea Water	Oridinary Rain		
		Sugashima	Nagoya	Matsumoto
SO/Cl	0.1007	0.35	0.368	1.70
Na/Cl	0.860	0.85	0.882	0.91
Ca/Cl	0.0379	0.25	0.298	3.50
Mg/Cl	0.1951	0.23	0.291	0.66
Ca/SO_4	0.376	0.72	0.832	2.06
$\Sigma+/\Sigma-$	0.986	0.98	1.074	1.88

(b)

Ratio in Equivalent	Washings of Pine Needles		
	Sugashima	Nagoya	Matsumoto
SO_4/Cl	0.17	0.72	1.82
Na/Cl	0.83	0.85	1.58
Ca/Cl	0.09	0.55	4.13
Mg/Cl	0.22	0.27	1.26
Ca/SO_4	0.53	0.76	2.27
$\Sigma+/\Sigma-$	0.97	0.97	2.47

(c)

Ratio in Equivalent	Ordinary Rain	Thunderstorm	Rime from the Summit of Mt. Fuji
SO_4/Cl	0.368	3.24	1.00
Na/Cl	0.882	2.43	1.09
Ca/Cl	0.298	2.19	1.90
Mg/Cl	0.291	0.63	0.40
Ca/SO_4	0.832	0.676	1.90
$\Sigma+/\Sigma-$	1.07_4	1.23_6	1.69

relative amount increases rapidly from the beach towards the summit of Mt. Ôyama.

Table 4

Acid Soluble Components in the Residual Fractions of the Washings of Pine Needles from Sugashima

Ratio in Equivalent $\times 10^2$	1	2	3	4	5	6
Ca/Cl	0.002	—	0.746	0.860	1.164	2.65
Mg/Cl	0.357	—	0.221	0.760	0.982	1.174

3. In the previous paper, the writers tried to picture a rough image of the processes of the fractionation of the spray of sea water which occasion the regular distribution of the components of atmospheric salt. The result, reported in the present paper, forces us to modify the picture and elaborate it in its detail to some extent. Namely in the foregoing rough picture the writers assumed that the primary particle of the spray of sea water separates into two kinds of secondary particles; the one, consisting mainly of Ca and SO_4 and more stable, remains longer in the air, and the other, consisting mainly of sodium chloride and less stable, is fated to fall down from the air earlier. The later knowledge, obtained above, affords reason to assume calcium carbonate as well as magnesium carbonate as stable segregates other than sulphates. Secondly the segregation processes must be assumed to begin to occur as early as just after the spray is formed due to wave crushing and while it is suspended in the air unstable segregates fall down back to the sea surface below, leaving a mass of particles whose composition is already quite different from that of the original sea water.

4. Further details of the segregation lie still beyond our knowledge; however, the writers may be allowed to try to draw some imaginary picture of it. Thus let us quote the old experiment by Usiglio⁽²⁾ on laying down of salts from the sea water when it is fated to slow evaporation. According to him, at the first stage of concentration, i. e., till the time when 1 l. of sea water is concentrated to 533 cc., about 0.0642 g. of $CaCO_3$ is laid down and at the second stage of concentration to 112 cc., 1.466 g. of $CaSO_4 2H_2O$ with a smaller amount of $CaCO_3$ separates, leaving a brine containing certain amounts of Na, Mg, Ca, Cl and SO_4. Thus we can naturally assume a similar segregation of salts to occur on the spray in suspension, giving rise to the particles of calcium carbonate and gypsum, leaving brine particles. The particles differ in stability and the greater part of the brine particles which are the least stable, will fall down to the sea surface earlier while the particle of $CaCO_3$, probably the most stable, will remain in suspension in the largest proportion. When the composite mass of particles, thus formed, is carried up to the beach and touched by a cotton gauze or pine needles, it is quite natural to assume that a second selective adhesion occurs depending upon the different adhesivity of the individual components. Anyhow we can try to test whether it is possible to obtain the composition of the washings-samples by an appropriate combination of these three kinds of particles, i. e., (a) $CaCO_3$, (b) $CaSO_4 2H_2O$ and (c) the residual brine. For example, let us try to compose the composition of the gauze washings, given in Column 3 of Table 1, by combination of 1 part of the salt in the brine (c), x part of chalk (a) and y part of gypsum (b)*.

Each fraction from 1 l. sea water contains the following amounts of component in equivalent.

	Na	Mg	Ca	Cl	SO_4	CO_3
Fraction (a)	—	—	0.00218	—	—	0.00218
Fraction (b)	—	—	0.0065	—	0.0065	—
Fraction (c)	0.518	0.111	0.003	0.595	0.045	—

Then the amounts of the individual components in the final composite are

Na ·········0.518
Mg ·········0.111
Ca ·········$0.003+0.00218x+0.0065y$
Cl ·········0.595
SO_4·········$0.045+0.0065y$

Then, in order to obtain the value of y, the following equation is set up:

$$\frac{Na}{SO_4}=\frac{Na}{Cl}\text{obs.}\div\frac{SO_4}{Cl}\text{obs.}$$

By introducing the values obtained above and those given in Column 3 of Table 1,

$$\frac{0.518}{0.045+0.0065y}=\frac{0.829}{0.0968}.$$

Thus $y=2.38$ and consequently the amount of SO_4 is determined as 0.0605.

Next x can be evaluated similarly by assuming an equation

$$\frac{Ca}{SO_4}=\left(\frac{0.003+0.0155+0.00218\,x}{0.0605}\right)=(0.426)\text{obs.}$$

Thus $x=3.33$ and consequently $Ca=0.0257$

Summarizing the result, we can compare the values from direct observation of the ratios of individual components of the washings of the cotton gauze to those calculated from the model process here assumed above.

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(2) *Annales chim. phys.*, 3rd Ser., **27**, 92, 172 (1849).

* For convenience the amount of $CaCO_3$, laid down accompanied by gypsum, was added to fraction (a) and Br calculated as an equivalent amount of Cl.

	Sea water	Cotton Gauze Observed	Cotton Gauze Calculated
Na/Cl	0.860	0.829	0.870
Mg/Cl	0.194_4	0.198_6	0.187_6
Ca/Cl	0.037_9	0.041_2	0.043_2
SO_4/Cl	0.100_7	0.096_8	0.101_6
Ca/SO_4	0.376_2	0.42_6	0.42_6
$\Sigma+/\Sigma-$	0.97_4	0.97_4	0.99_9

The conclusion is that the combination of 3.33 parts of fraction (a), 2.38 parts of fraction (b), and 1 part of fraction (c) yields an approximate composition of the washings of the cotton gauze, showing a rough stability sequence of the three fractions which were assumed above, and at the same time it suggests that the fractionation similar to the experiment by Usiglio or something like it, actually occurs on the spray in the air close to the surface of the sea.

No doubt, the treatment above is too easy and arbitrary to explain the supposed complexity of the phenomenon in question. It was simply aimed at building up some concrete broad image along which further studies could be extended. Our knowledge, hitherto obtained, gives a concrete reason to consider magnesium carbonate as another independent fraction and fraction (c) must be divided into several subfractions. Otherwise the variability of the ratio Na/Cl can not be explained. However it will go too far, we believe, for us to discuss the matter further and to try to picture a fuller detail in the process based upon the insufficient knowledge that we now have.

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