

Ion Separation in Bursting Air Bubbles : an Explanation for the Irregular Ion Ratios in Atmospheric Precipitations

It is well known that a considerable part of the soluble salts present in soil, lakes and rivers is derived from rain-water¹. There is little doubt that the salt content in the rainwater comes mainly from ocean water spray, which is carried into the atmosphere from the surface of the sea, where tiny droplets are formed by air jets shooting out of the top of bursting air bubbles².

The reason why the salts, derived from such action, found in rainwater and snow, have ion ratios incompatible with the ratios found in ocean water has remained obscure. Although the Na^+/K^+ ratio in sea water is 27, it is always lower in precipitation (rain and snow), sometimes being as low as 2. The Cl^-/Br^- ratio in sea water is 302, but is always much lower in rainwater or snow, often less than 50, sometimes less than 20. Examples are given in Tables 1 and 2.

Table 1

Location	Date	Br^- (mg/l.)	$\text{Cl}^- + \text{Br}^-$ (mg/l.)	$(\text{Cl}^- + \text{Br}^-)/\text{Br}^-$
Jerusalem	16.2.1961*	0.105	5.65	53.8
Jerusalem	16.2.1961†	0.122	5.56	45.5
Tel-Aviv	October 1962	0.358	105.95	287.6
Haifa-Hadar	October 1962	0.073	8.88	121.6
Daphna	February 1963	0.061	4.61	75.8
Ein Harod	May 1963	0.201	5.43	27.0
Sde Boker	Winter 1962/63	0.261	3.48	13.3
Nicosia	October 1961	0.18	8.88	49.3
Prodromos	January 1962	0.17	1.78	10.5
Göttingen‡	1-3.11.1951	0.008	0.70	87.5
Bolschewo§ (Moscow District) in snow-water	24.12.1937	0.009	0.35	39.0

* After 12 hours rain.

† After 24 hours rain.

‡ Behne, W. (ref. 6).

§ Selivanoff, L. S. (ref. 7).

Table 2

Location	Na^+/K^+
Southwest Coast, Iceland*	18
Southwest Coast, Norway*	16.5
West Coast, Ireland†	6.3
Rain, Tel-Aviv sea shore‡	35.2
Rain, Jerusalem‡	6.7
Rain, Lodd‡	10.4
Rain, Beer-sheva‡	9.3
Rain, Daphna‡	14.6
Snow from Tasman Glacier	27.4.1958§
Snow from Mt. Egmont	3.5.1958§
Snow from Arthurs Pass	22.8.1958§

* Eriksson, E. (ref. 8).

† Gorham, E. (ref. 1).

‡ Rainy season in Israel 1960/61, analysed by the Geological Department of the Hebrew University.

§ Wilson, A. T. (ref. 9).

Note: All sodium-potassium ratios are given in terms of Na^+/K^+ values although in the literature quoted they are given as K^+/Na^+ .

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Rain, Beer-sheva‡	9.3
Rain, Daphna‡	14.6
Snow from Tasman Glacier § 27.4.1958§	1.11
Snow from Mt. Egmont § 3.5.1958§	2.83
Snow from Arthurs Pass § 22.8.1958§	2.0

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Explanations of these facts have so far not been very satisfactory, including the suggestions that they are brought about by the influence of terrestrial dust, by oxidation of halogens by ozone, by biological absorption of potassium in the ocean surface, or by fractionation crystallization in the atmosphere.

We propose here a mechanism for the separation of ions which becomes effective at the moment and shortly before the bursting of ocean water bubbles: in part this follows the suggestion made by Ken Sugawara and Nobuko Kawasaki³ for $\text{Sr}^{++}/\text{Ca}^{++}$ and Na^+/Cl^- separation. Such a mechanism would lead to a spray of droplets with ion ratios different from those of the ocean water from which it is derived. As the bubbles become thinner and thinner, a solution runs down the wall between the concave inner surface and the convex outside surface. There will be a tendency for the larger and generally heavier ions to stay in the skin⁴, the smaller ones will run off with the solution. When the jet atomizes the bursting skin, the small droplets formed will be relatively rich in the larger ions. It is clear that this mechanism will be influenced by a number of factors, and will probably depend on initial concentrations and the radius of the bubbles. The jet might also disperse solution from the bottom of the bubble, thus admitting varying quantities of original solution to the fine top spray: this may somewhat obscure the effect.

We have carried out some preliminary investigations to test the hypothesis. Distilled water was prepared by boiling sea water, tap water and lake water at atmospheric pressure with and without the conventional spray trap. It can be seen from Table 3 that the spray was reduced through the conventional spray trap by an order of magnitude or more: however, the ratio of the ions, contained in the spray, differed essentially in the same way from the ratio of the ions in the original solution, and was independent of the efficiency of the trap. The variation of ratios caused by artificial distillation was similar to the variation experienced with sea water and rainwater in Nature.

Another series of experiments was undertaken with sea water as well as with artificial salt solutions at ambient temperature (20° C). In these experiments, instead of carrying out distillations, air was bubbled through the various solutions (every bubble was about 5 mm diameter) in a conventional gas washing flask instead of distillation. The air was filtered through cotton wool before and after it was passed through the salt solution. The salts absorbed by the cotton wool from the air were extracted with water, and the resulting solution was analysed. The cotton wool itself contained certain salts, and thus deductions were made for the amounts of Cl^- and Br^- or Na^+ and K^+ respectively—values having been obtained by extraction of the cotton wool with water (see Table 4a).

Table 3. ION SEPARATION BY DISTILLATION

Sample	In 1 l. original sample			In 1 l. distillate			In 1 l. original sample			In 1 l. distillate		
	Cl ⁻ (mg)	Br ⁻ (mg)	Cl ⁻ /Br ⁻	Cl ⁻ (mg)	Br ⁻ (mg)	Cl ⁻ /Br ⁻	Na ⁺ (mg)	K ⁺ (mg)	Na ⁺ /K ⁺	Na ⁺ (mg)	K ⁺ (mg)	Na ⁺ /K ⁺
Ocean water	22,470	74	304	0.178	0.007	25						
Lake of Kinnereth	369	3.23	114	2.31*	0.191*	12.1*						
Dead Sea water	203,000	4,600	44	0.055	0.0067	8.2						
Tap water, Jerusalem	132	0.427	310	1.017*	0.219*	4.6*	39,900	6,800	6	0.204	0.055	3.7
				0.145	0.013	11.2	83.5	3.7	12.6	0.24	0.064	3.8
				1.528*	0.137*	11.1*						
				0.08	0.006	13						

* Figures received without spray trap.

Another artificial solution, containing magnesium and lead nitrate, was treated in the same way and the spray analysed. The cotton wool used for absorbing the spray contained magnesium to the extent of less than 0.024 mg/g cotton and lead to the extent of less than 0.005 mg/g cotton (see Table 4a).

In another series of experiments, the salts carried over by the air were absorbed in water that had been distilled three times. The original solutions were also prepared by dissolving the various salts in thrice-distilled water (see Table 4b).

It can be seen that an air stream with single bubbles shows the effect almost as markedly as the distillation at 100° C. An air stream where many bubbles coalesce to form a foam has practically no effect of ion separation. The fact that the spray of boiling solutions shows the separation of ions clearly indicates that no solid-phase separations occur during evaporation from droplets as suggested as a 'post-wave breaking fractionation' (Sugawara and Kawasaki³); the separation seems to occur only in the bursting bubble.

Table 4a. ION-SEPARATION BY AIR-BUBBLE BURSTING (ABSORPTION ON COTTON WOOL)

	Bubbling time (h)	Original ion-ratio Cl ⁻ /Br ⁻	Absorbed on 1 g cotton (after deduction of blank value)		
			Cl ⁻ (mg)	Br ⁻ (mg)	Cl ⁻ /Br ⁻
Sea water	51	300	0.484	0.0028	172
"	125	300	0.398	0.0026	153
"	150	300	0.951	0.0079	120
		Na ⁺ /K ⁺	Na ⁺ (mg)	K ⁺ (mg)	Na ⁺ /K ⁺
Sea water	312	27	0.230	0.040	5.7
KBr 0.44 g } KCl 3.0 g } NaCl 143.2 g } 1	50	33	0.362	0.024	15.0
		Mg ⁺⁺ /Pb ⁺⁺	Mg ⁺⁺ (mg)	Pb ⁺⁺ (mg)	Mg ⁺⁺ /Pb ⁺⁺
Mg(NO ₃) ₂ ·6H ₂ O 102.5 g } Pb(NO ₃) ₂ 0.132 g } 1	75	116	0.352	0.049	7.0

Table 4b. ION-SEPARATION BY AIR-BUBBLE BURSTING (ABSORPTION IN TRIPLE-DISTILLED WATER)

	Bubbling time (h)	Original ion-ratio Cl ⁻ /Br ⁻	Absorbed in 1 l. tri-distilled water		
			Cl ⁻ (mg)	Br ⁻ (mg)	Cl ⁻ /Br ⁻
Artificial sea water	316	364	1.775	0.018	98
" " " + NaCl	312	400	3.292	0.0282	117
" " " + NaCl	312	400	4.733	0.0468	101
		Na ⁺ /K ⁺	Na ⁺ (mg)	K ⁺ (mg)	Na ⁺ /K ⁺
Artificial sea water	312	27	3.94	0.55	7.2
		Mg ⁺⁺ /Pb ⁺⁺	Mg ⁺⁺ (mg)	Pb ⁺⁺ (mg)	Mg ⁺⁺ /Pb ⁺⁺
Mg(NO ₃) ₂ ·6H ₂ O 102.5 g } Pb(NO ₃) ₂ 0.132 g } 1	240	116	0.328	0.180	2.0
		Na ⁺ /Ca ⁺⁺	Na ⁺ (mg)	Ca ⁺⁺ (mg)	Na ⁺ /Ca ⁺⁺
NaCl 30 g } CaCl ₂ 3.4 g } 1	312	10	0.243	0.0453	5.4
NaCl 30 g } CaCl ₂ 30 g } 1	312	1.1	0.206	0.382	0.54

The change of ion ratios by 'syn-bubble breaking fractionation', as Sugawara and Kawasaki propose to call it, is probably of considerable importance in the accumulation of the heavy or large ions, such as potassium, found in arid soils in which rainwater has been evaporated to dryness for a long time, without the residue being washed out. The way in which heavy metals accumulate in latterites may also be related to the ion separation in breaking bubbles.

The analytical procedures used in these investigations were as follows:

- Cl⁻ (Br⁻) —mercurimetric method.
Br⁻ —modified Van der Meulen method (Kaplan and Schnerb⁵).
K⁺ and Na⁺—flame-photometric method.
Mg⁺⁺ —complexometric (EDTA) method.
Pb⁺⁺ —colorimetric method, according to *British Pharmacopoeia*.
Ca⁺⁺ —flame-photometric method.

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¹ Gorham, E., *Irish Naturalists' J.*, **12**, 1 (1957).

² Mason, B. T., *Nature*, **174**, 470 (1954).

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⁸ Eriksson, E., *Tellus*, **12**, 63 (1960).

⁹ Wilson, A. T., *Nature*, **184**, 99 (1959).