

Geochemistry of Ocean Water Bubble Spray

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The salts in rain, snow, and dew are considered to derive from ocean bubble spray. It was shown by laboratory bubble experiments at varying temperatures, humidities, and salt concentrations that the difference in ion ratios between the spray and the bulk of the solution that is sprayed is in agreement with the requirements of the Gibbs adsorption isotherm if the spray is derived from the surface layer of the bulk solution. Inorganic salts dissolved in ocean water are depleted in the surface of the ocean because the surface tension of their solution rises with their concentration. The gradient of this rise has a characteristic value for each salt and is independent of temperature. For sodium chloride this gradient is 1.85 and for potassium chloride it is 1.50. These and other oceanic salts were tested for changes in ion ratio in the bubble spray of their mixtures. Experiments were performed with sea water and artificial solutions at temperatures ranging from 25° to 130°C. The Gibbs theory predicts quantitatively the ratio changes found in bubble spray at equilibrium conditions only (for ocean environment near 100% humidity). When the sprayed surface is evaporated (sub-saturated air, i.e., low humidity), the ratio shift is modified (e.g., enhanced in favor of potassium ions compared with sodium ions). If condensation occurs at the time of bubble spray generation, however, this change in ratio is diminished.

The fact that rain and dew contain small quantities of salts frequently results in increased salt concentration in soil and ground water in arid zones, especially near the sea coast. Desert dew is precipitated and completely evaporated daily, causing erosion and an increase in salt concentration of desert areas. In general, the first precipitation of a rainy period washes the salts deeper into the soil; the following, stronger rains run off without diluting the ground water much. Consequently, we find progressively greater amounts of salt in the ground water; this accumulation can be ignored only in 'humid latitudes,' where the salt is constantly washed away into the sea.

The ocean was recognized as the main source of salt in rain and snow [Rankama and Sahama, 1952, p. 317, quoting Posepny, 1877] when it was discovered that precipitation was more saline near the sea coast. Even weak winds generate ocean waves, which engulf air that

must rise again. The engulfed air rises to the surface in the form of bubbles that create a spray of very fine drops from the apex of their membranes when they burst. The droplets are carried away by the wind. The salts contained in these drops are transported from the oceans to land surfaces on a global scale. The rivers and ground water return these salts to the sea, cycling approximately 10⁹ or more tons per year.

It is peculiar that most analyses of rain, snow, and dew show cation and anion ratios very different from the corresponding ratios in ocean water. This change of ratio (although always in the same direction) is not constant in time or place (Table 1).

Many authors [e.g., Kalle, 1954] believe that the change in the ratio of ions is caused by volcanic, terrestrial, and industrial dust, 'superimposed' on the unchanged oceanic salt aerosol. However, this concept is incompatible with the fact that the quantity of soluble alkali-salts in terrigenous dust is very small. Further, the differences in the ion ratios of rain, snow, and dew are already formed in the spray above the surface of the ocean.

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TABLE 1. Ratios (by Weight) of Ions in the Hydrosphere^a

Ratio	Ocean	Rain	Snow	Dew	Rivers
Na:K	28	~3-10 ^{b,c}	1-5 ^b	1.7-2 ^f	~2-4
Mg:Ca	3.2	0.3-0.7 ^a	1-3 ^d	~0.1 ^e	~0.1-2
Cl:Br	300	~50-100 ^b	~40 ^b		150
Cl:I	380,000	~1000 ^a	200-500 ^e	~1000 ^e	
Cl:SO ₄	7.2	~0.3-3 ^a	9-10 ^d	~0.3 ^e	0.5-0.7

^a Approximate averages or ranges.

^b Bloch *et al.* [1966].

^c Emanuelsson *et al.* [1954].

^d Sugawara [1959].

^e In hoar-frost [Cauer, 1931].

^f Dew of the dry season from Beer-Sheva (Negev), Israel.

^g Yaalon and Ganor [1968].

Sugawara [1959] was the first to propose that the ratio change is caused by a process unconnected with the accidental admixture of terrigenous dust. He thought of a fractionating mechanism somehow working in the spray of wave-generated bursting air bubbles. Following the lead of Sugawara [1959] and Komabayasi [1962], we investigated the mechanism of ion separation in bubble spray. The mechanism we propose explains not only the fractionation itself but also the seemingly erratic results of this fractionation in nature.

For a possible connection between changes in the ion ratio and bubble formation, various theories have been published. Sugawara [1959] showed that the bubble spray changed its composition ('synfractionation') immediately after formation. He considers a two-step process, the synfractionation and a fractionating crystallization of the salts in the evaporating droplets. Komabayasi [1962] demonstrated that there is a linear relation between enrichment and the atomic weight of the ions; he explains this by a differentiating thermal-diffusion process in the surface of the ocean. This process occurs because the ions of different weight diffuse at a different rate into the surface (which is slightly cooled by evaporation). However, Komabayasi emphasizes that this 'Ludwig-Soret effect' is too slow for a satisfactory solution of the problem.

Wilson [1959] proposed organic, surface-active material as the differentiating factor, explaining that the reactions in the bubble surfaces with absorbed organic compounds enrich ions differentially.

ADSORPTION ISOTHERM OF GIBBS

Laboratory experiments by Komabayasi [1962] on cations and by Bloch *et al.* [1966] on chloride and bromide ions showed that the fractionating effect in bubble breaking occurs in solutions that are carefully kept clean of organic matter. Accordingly, it should be accepted that under artificial bubble breaking conditions a selective fractionation of salts (anions and cations) occurs independently of organic surface-active agents. Hence, it is also probable that under natural conditions fractionation of salts can occur without the assistance of organic surface-active agents.

Rising air bubbles lift the uppermost layer of the ocean and, in doing so, isolate the surface layer from the bulk of the ocean water. The conditions in this surface layer are described (for dilute solutions) by the adsorption isotherm of Gibbs. This theory connects impoverishment or enrichment of solutes in the surface area with the dependence of surface tension on concentration. Soluble inorganic salts in ocean water are depleted in the surface of their solution because the surface tension of their solution rises with their concentration; the gradient of this rise with concentration has a characteristic value for each salt. Consequently, the salts suffer a characteristic impoverishment in the surface of their solution. The depletion Γ of a component i can be expressed in a first approximation as:

$$\Gamma_i = [(cB_i - cS_i)h]/f \quad (1)$$

and, according to Gibbs,

$$\Gamma_i = -(cB_i/R \cdot T) \cdot (\delta\gamma_i/\delta cB_i) \quad (2)$$

where h is the thickness of the surface layer, f is the unit area of the surface, and c is the concentration of solute i in the bulk B of the solution, in the 'uplifted' surface layer S or in its spray S . The surface tension γ in (2) is dependent on temperature T and concentration c . This relationship is illustrated in Figure 1 for the solution of NaCl and KCl (mole/l) at 20° and 0°C.

The surface tension of water and of the solutions decreases with temperature; however, the gradient remains constant, namely $\Delta\gamma = 1.85$ for NaCl and $\Delta\gamma = 1.50$ for KCl. This relationship has been verified for ocean water, in which many salts are dissolved that can, for our purpose, be treated as not influencing each other [Bloch and Luecke, 1970; Fleming and Revelle, 1939].

The relation between the concentration gradients of the surface tension of different salts is independent of temperature. For NaCl and KCl we find, after using (2),

$$\frac{\Gamma_{\text{NaCl}}}{\Gamma_{\text{KCl}}} = \frac{cB_{\text{NaCl}}R \cdot T}{R \cdot T \cdot cB_{\text{KCl}}} \cdot \frac{\delta\gamma_{\text{NaCl}} \cdot \delta cB_{\text{KCl}}}{\delta cB_{\text{NaCl}} \cdot \delta\gamma_{\text{KCl}}} \quad (3)$$

or, using (1) and Figure 1:

$$\begin{aligned} \frac{\Gamma_{\text{NaCl}}}{\Gamma_{\text{KCl}}} &= \frac{cB_{\text{KCl}}}{cB_{\text{NaCl}}} \cdot \frac{(cB_{\text{NaCl}} - cS_{\text{NaCl}})}{(cB_{\text{KCl}} - cS_{\text{KCl}})} \\ &= \frac{\delta\gamma_{\text{NaCl}}}{\delta\gamma_{\text{KCl}}} = \frac{1.85}{1.50} = 1.23 \quad (4) \end{aligned}$$

T has been eliminated. According to (3), one can calculate the concentration of NaCl and

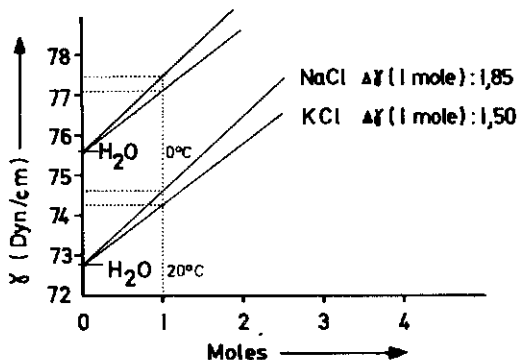


Fig. 1. Surface tension of NaCl and KCl in water at 20° and 0°C in mole/l.

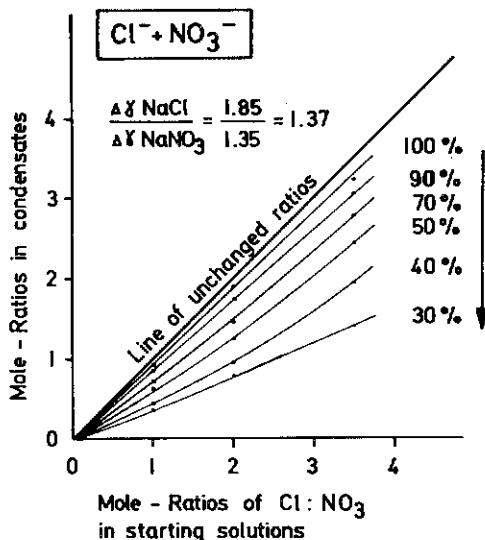


Fig. 2. Mole ratios in starting solutions (NaCl and NaNO_3) against mole ratios in their condensates (and spray). When humidity is at 100%, the liquid and vapor are shown in equilibrium, i.e., saturated water vapor is at boiling temperature (liquid and vapor at 100°C). The solution is also shown under evaporating conditions with subsaturated water vapor, humidity runs from 90% to 30%, i.e., the liquid and vapor are not in equilibrium.

KCl, if the spray is considered as derived from the extremely thin apex of the bubble 'membrane' only. Our experiments (Figure 3) show that the ratio change from KCl in bulk to KCl in spray is $\frac{1}{3}$ the ratio change for NaCl in a 1-molar solution. KCl in the bulk changes to spray containing 0.27 M/l NaCl and 0.40 M/l KCl. It is possible to predict which cation or anion will be more depleted in the ocean surface than other ions, e.g., CaCl_2 will be enriched compared with MgCl_2 , NaBr compared with NaCl [Bloch and Luecke, 1968] and NaNO_3 compared with NaCl (Figure 2).

NONEQUILIBRIUM CONDITIONS

The first tests for the validity of the Gibbs theory in dilute solutions of NaCl were performed by MacBain [MacBain and Davis, 1927; MacBain and Dubois, 1929; MacBain and Humphreys, 1932; MacBain and Swain, 1936]. He stripped salt solutions mechanically of their uppermost surface layer for analysis and found the concentration change in the stripped solution compared with the bulk of the

solution, as required by the Gibbs adsorption isotherm. However, he also made certain that *this change occurred only when conditions of equilibrium were carefully maintained during the experiment; any evaporation from the investigated surface (as well as condensation onto the surface) must be rigorously prevented.* However, to evaluate the influence of supersaturation as well as subsaturation, we performed a series of tests. Since bubble experiments are easier to perform near the boiling point of the investigated solution and since *Bloch et al.* [1966] and *Bruyevich and Kulik* [1967] had proved that the effect of interest is not temperature dependent, we performed some of our experiments near 100°C [*Bloch and Luecke, 1970*].

When superheating was desired and, with it, simultaneous evaporation of the breaking bubble-forming surfaces, either we introduced hot air into the vapor phase above the bubbling liquid or we heated the vapor phase with a heating element provided above the liquid level. When undercooling was required and, with it, simultaneous condensation of water onto the bubble surface, we introduced saturated steam into the vapor phase.

According to the model used [*Woodcock et al., 1953; Mason, 1954*] the apex of the bursting bubble is the primary source of the fine spray drops that are carried into the air. This very thin 'membrane' of the bubble apex has, under equilibrium conditions, a composition determined by the Gibbs adsorption isotherm.

In addition, we assume that an internal circulation stream is induced that multiplies the differentially ion depleted layer, bringing increasingly larger amounts of this differentially depleted or enriched solution to the apex of the bubble. In this way the thickness of the layer affected by differential adsorption can become quite considerable. A similar folding mechanism might be expected when wind moves the surface of the solution, bringing one top layer below another, by circulation.

When water condenses or evaporates on the surface and when the system deviates from equilibrium conditions, new differentiation effects are expected. To test this we varied the water vapor pressure systematically over the bubbling surface. The 'starting' solutions were varied in such a way that in the ratio, e.g.,

Na/K, only one portion was changed, the other remaining constant. When the vapor above the bubbling solution was kept subsaturated and when, during the experiment, the temperature in the vapor phase rose, samples were collected for every 10°C temperature interval.

RESULTS

We assume that the ion ratio in the condensates represents the ratio in the apex of the bursting bubbles. Figure 3 represents nearly a hundred experiments distilling KCl-NaCl solutions under equilibrium as well as nonequilibrium conditions. None of our experiments showed unchanged ratios; the estimated extent of experimental error is given by the shaded areas in the graph. The experiments performed under equilibrium conditions show the best reproducibility. At equilibrium the humidity is more easily kept within narrow limits.

The enrichment of K^+ over Na^+ is constant under equilibrium conditions. When condensation occurs during the experiments ($>100\%$ humidity) K^+ is enriched, but it is enriched less than it is under equilibrium conditions. However, if evaporation occurs during spray formation ($<100\%$ humidity) the enrichment of K^+ is much greater than it is under equilibrium conditions. In this way it is probable that the changing ratios between K^+ and Na^+ in natural precipitation are not at all accidental. They can be reproduced by conducting the bubbling experiments under controlled humidity conditions. Ratio changes are, to a first approximation, independent of the absolute concentration of the ions in the bulk of the bubbling solution (e.g., Dead Sea, ocean water, tap water; see Figure 3). Many experiments with Mg^{++} and Ca^{++} (in artificial and natural solutions) show changes of ratios in favor of Ca^{++} in the spray in accordance with the surface tension gradients of Ca and Mg.

Our experiments with Mediterranean and Red Sea water, as well as the experiments of *Bruyevich and Kulik* [1967] with Black Sea water, show the expected enrichment of Br^- against Cl^- . In nature, SO_4^{2-} is enriched compared with Cl^- [*Junge, 1963*]. In laboratory experiments, however, bubble spray is always enriched in Cl^- over SO_4^{2-} according to the surface tension behavior, independently of the kind of cations present; thus the enrichment of SO_4^{2-} over Cl^-

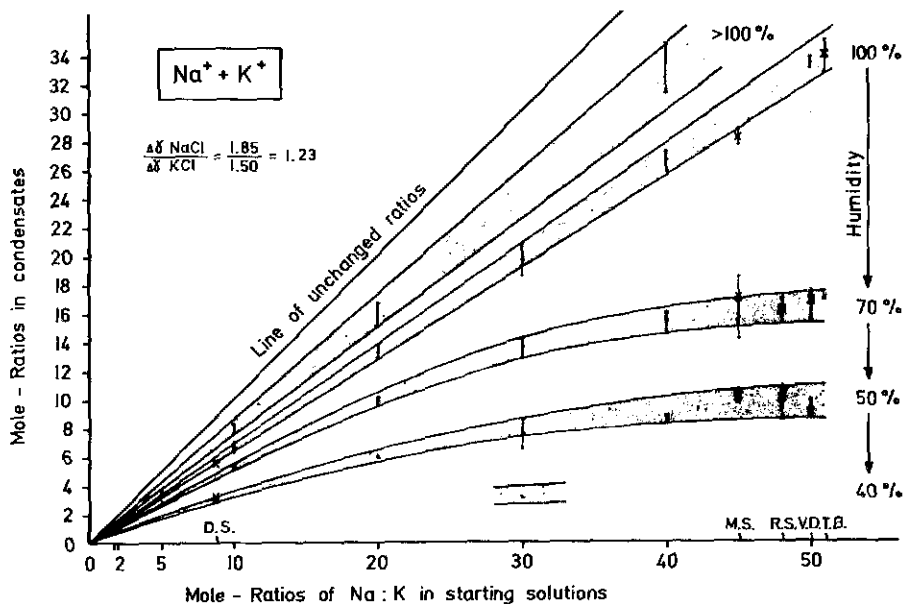


Fig. 3. Mole ratios in starting solutions (NaCl and KCl in natural and artificial liquids) against mole ratios in their condensates (and spray) under different conditions. When humidity is at 100%, the solution is in equilibrium, i.e., saturated water vapor (liquid and vapor at 100°C). When humidity >100%, condensing conditions exist, with supersaturated water vapor (liquid and vapor not in equilibrium). When humidity <100%, evaporating conditions exist, with subsaturated water vapor of different degrees (liquid and vapor are not in equilibrium). Symbols are as follows. D.S. is Dead Sea, at Sodom (37.30 grams Na + 7.21 grams K)/l; R.S. is Red Sea, at Eilat (13.4 grams Na + 0.473 gram K)/l; M.S. is Mediterranean Sea, at Gaza (12.1 grams Na + 0.456 gram K)/l; T.B. is tap water, at Beer-Sheva (0.12 gram Na + 0.004 gram K)/l; and V.D. is vapor dilution by hot, dry air. All artificial starting solutions contained 0.1–0.4 M Na/l.

in natural precipitation must be attributed to causes other than surface tension changes. The ratio changes of isotopes under equilibrium and nonequilibrium conditions (i.e., evaporation) are possibly diffusion controlled; this is shown by isotope separation of sulfur in sprayed SO_4 ions [Luecke and Nielsen, in press, 1972].

Experiments with bubbling air or steam through ammonium chloride solutions gave unexpected results at 30°, 40°, and 100°C. Here the highest ratio change was found to occur under equilibrium conditions, and it was much bigger than was expected from known surface-tension values of NH_4Cl solutions. With decreasing humidity the enrichment effect for NH_4Cl diminished. We attribute the special behavior of these solutions to NH_4Cl hydrolysis, resulting NH_4OH in the spray. NH_4OH decreases the surface tension of water ($\Delta\gamma = -3.35$) and is consequently enriched in the surface of the bubbling solution

over NH_4Cl ($\Delta\gamma = +1.30$). Under evaporative conditions the effect diminishes; the NH_4^+ enrichment in the spray is at a maximum when equilibrium or condensation conditions prevail (as in nature near the Chilean, South African, and Californian coasts [Bloch and Luecke, 1970]).

REFERENCES

- Bloch, M. R., and W. Luecke, Uneinheitliche Verschiebungen der Ionenverhältnisse zwischen Meerwasser und Niederschlägen durch Gischbildung, *Naturwissenschaften*, **9**, 441, 1968.
- Bloch, M. R., and W. Luecke, The origin of fixed nitrogen in the atmosphere, *Israel J. Earth Sci.*, **19**(2), 41–49, 1970.
- Bloch, M. R., D. Kaplan, V. Kertes, and J. Schnerb, Ion separation in bursting air bubbles: An explanation for the irregular ion ratios in atmospheric precipitations, *Nature*, **209**, 802–803, 1966.
- Bruevich, S. V., and Z. Kulik, Chemical interaction between the ocean and the atmosphere

- (salt exchange), *Oceanology USSR*, 7(3), 279-293, 1967.
- Cauer, H., *Das Jod der Luft im Hochgebirge*, *J. Sonnenblickverein*, 11, 20-27, 1931.
- Emanuelsson, A., E. Eriksson, and H. Egner, Composition of atmospheric precipitation in Sweden, *Tellus*, 6, 261-267, 1954.
- Fleming, R. H., and R. Revelle, Physical processes in the ocean, in *Proceedings of the American Association of Petroleum Geologists Symposium*, 736 pp., American Association of Petroleum Geologists, Tulsa, Okla., 1939.
- Junge, C., *Air Chemistry and Radioactivity*, 382 pp., Academic, New York, 1963.
- Kalle, K., Zur Frage des 'Cyklischen Salzes,' *Ann. Meteorol.*, 6, 305-314, 1954.
- Komabayasi, M., Enrichment of inorganic ions with increasing atomic weight in aerosol, rain-water and snow in comparison with sea water, *J. Meteorol. Soc. Jap. Ser. 11*(40), 25-38, 1962.
- Luecke, W., and H. Nielsen, Isotopen fraktionierung des Schwefels in Blasenprüh, *Fortschr. Mineral.*, 50, in press, 1972.
- MacBain, J., and G. Davies, An experimental test of the Gibbs adsorption theorem, A study of the structure of the surface of ordinary solutions, *J. Amer. Chem. Soc.*, 49, 2230-2257, 1927.
- MacBain, J., and R. Dubois, Further experimental tests of the Gibbs adsorption theorem: The structure of the surface of ordinary solutions, *J. Amer. Chem. Soc.*, 51, 3534-3549, 1929.
- MacBain, J., and C. Humphreys, The microtome method of the determination of the absolute amount of adsorption, *J. Phys. Chem.*, 36, 300-311, 1932.
- MacBain, J., and R. Swain, Measurements of adsorption at the air-water interface by the microtome method, *Proc. Roy. Soc. London A254*(882), 608-623, 1936.
- Mason, B., Bursting of air bubbles at the surface of sea water, *Nature*, 174, 470-471, 1954.
- Rankama, K., and T. G. Sahama, *Geochemistry*, University of Chicago Press, Chicago, Ill., 1952.
- Sugawara, K., Synfractionation of sea salt components at the burst of bubbles, paper presented at International Oceanographic Congress, New York, 1959.
- Sugawara K., and N. Kawasaki, Records of oceanographic works in Japan, *Spec. Rep. 2*, 227 pp., Ministry of Education, Tokyo, 1958.
- Wilson, A. T., Surface of the ocean as a source of airborne nitrogenous material and other plant nutrients, *Nature*, 184, 99-101, 1959.
- Woodcock, A. H., C. F. Kientzler, A. B. Arons, and D. C. Blanchard, Giant condensation nuclei from bursting bubbles, *Nature*, 172, 1144-1145, 1953.
- Yaalon, D. H., and E. Ganor, Chemical composition of dew and dry fallout in Jerusalem, Israel, *Nature*, 217, 1139-1140, 1968.

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