

THE ORIGIN OF FIXED NITROGEN IN THE ATMOSPHERE

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ABSTRACT

It is suggested that low $\text{Na}^+/\text{NH}_4^+$ ratios in the atmosphere be used to explain fixed nitrogen accumulation in places such as Chile and South West Africa. The relatively high ammonia content of oceanic bubble spray is shown, by experimentation, to be a surface tension phenomenon; it is proposed that the ammonia found in droplets of ocean mist is oxidized to nitrate under the influence of light. This mechanism may be responsible for most of the supply of fixed nitrogen to plant life.

INTRODUCTION

"Every drop of rain or dew charged with the smallest amount of fixed nitrogen that reaches the surface of the earth is readily absorbed by the vegetation; consequently direct observation of atmospheric nitrogen supply to plant life is very difficult and the geochemical, or better the bio-geochemical part played by nitrogen has been interpreted very differently by different authors or even overlooked. There are, however, . . . areas where nitrogen-compounds reaching the surface of the Earth are not at all, or not completely used for biological activity and where surface accumulation occurs like in nitrate depots of northern Chile." This observation of W. Wetzel (1969) is connected with a reiteration of the fact that even today nitrate deposits coming from the atmosphere can be seen forming in the arid mountains from which occasional rainstorms transport the nitrates into the Chile-nitrate desert below.

The problem which arises is where it comes from and how much fixed nitrogen is actually in the air feeding the Chilean nitrate deposits. While investigating the origin of the changing Na^+/K^+ and Cl^-/Br^- ratios in rainwater we incidentally established some significant facts concerning the $\text{Na}^+/\text{NH}_4^+$ ratios in the atmosphere; we propose to use these data for an explanation of phenomena leading to the fixed nitrogen accumulation in places such as Chile and south-west Africa.

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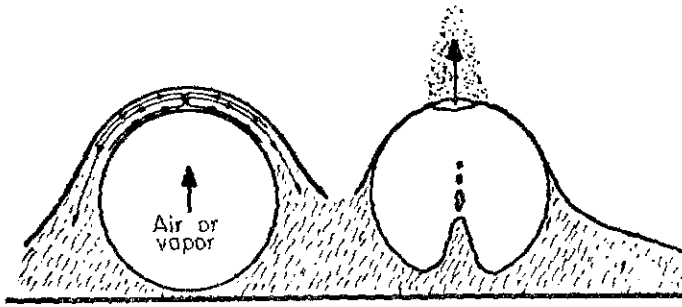


Fig. 1. A rising and a bursting bubble.

It has been shown that the spray generated by air bubbles breaking in ocean waves is the main source of Na^+ , K^+ and Cl^- ions in the atmosphere and consequently in rain and dew (Sugawara & Kawasaki, 1958).

Before the bubbles break (Fig. 1) they lift the uppermost skin of the ocean surface. The membranes formed from this skin become progressively thinner until they break on their apex and release the captured air as vertical jets (Mason, 1954). Every such jet atomizes the adjacent part of the membranes into some 500 droplets of about 1μ diameter.

The droplets so released are carried higher and eventually form the salt nuclei for water condensation in clouds, rain and dew. It was found that these droplets, though originating in the ocean, have ionic ratios other than that of the bulk of ocean water from which they derive.

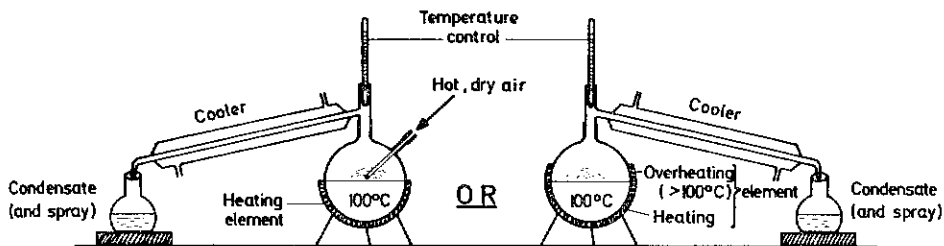
Komabayasi (1964) and Bloch et al. (1966), showed that this phenomenon can be imitated on a laboratory scale with the same results as found in nature. When studying the mechanism more closely we could establish (Bloch & Luecke, 1969) that the change of ion ratios in bubble spray follows the requirements of the Gibbs absorption theorem, according to which the surface of a liquid will suffer impoverishment or enrichment of those ions which increase or decrease the surface tension of the liquid.

METHODS

We consider the spray droplets as deriving entirely from the surface of the ocean and define its concentration as C_s of ions y . We use concentration rather than activity in a first approximation. The concentration of ions y in the bulk of the liquid is C_{by} . The impoverishment or enrichment Γ_y of ions y in the droplets is then:

$$\Gamma_y = \frac{(C_{by} - C_{sy}) \cdot h}{F} = - \frac{C_{by}}{RT} \cdot \frac{\delta_{yy}}{\delta C_{by}},$$

i. Bubbling under equilibrium or evaporating condition



ii. Bubbling under condensing conditions

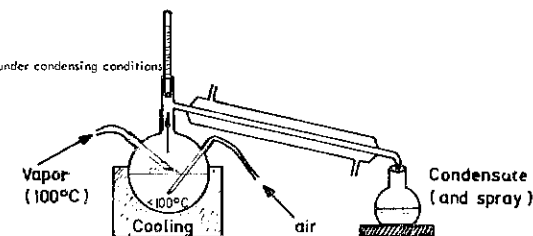


Fig. 2. Bubbling arrangement.

where R denotes the gas constant, T the absolute temperature, F the area of the atomized part of the bubble surface and h the thickness of this atomized area. Some of our experiments to test the Gibbs theorem on bubble spray were performed in the apparatus shown in Fig. 2. It consists of a simple distillation and condensation device where the distilling solution and the resulting vapor can each be heated separately; an air and steam inlet above and below the surface of the distilling solution make it possible to have supersaturated (wet) or superheated (dry) steam above the distilling (bubbling) solution.

We worked with temperatures close to 100°C since the results of our experiments were shown to be independent of temperature and since this simplified experimental procedure.

Most of the ions dissolved in ocean water increase the surface tension of water proportionally to their concentration, as can be seen in Fig. 3: different salts have different slopes $\delta\gamma_y/\delta C_y$ of the lines showing the influence of concentration C_y on γ_y . As mentioned above these slopes are not dependent on the temperature of the solution (Fig. 4); for ocean water this is shown in Fig. 5.

The impoverishment for KCl and NaCl was calculated from the known values of $\delta\gamma_{KCl}/\delta C_{KCl}$ and $\delta\gamma_{NaCl}/\delta C_{NaCl}$ in water and our experiments determined the ratio NaCl/KCl in the bulk of their solution and in the spray of bubbles generated in these solutions.

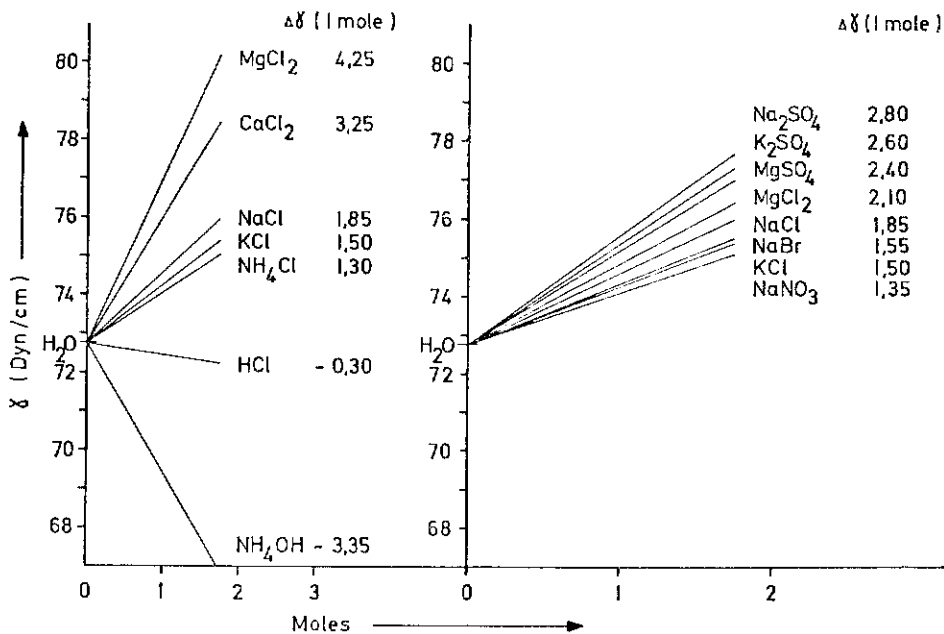


Fig. 3. Surface tension of different salts in water at 20°C in mole/l.

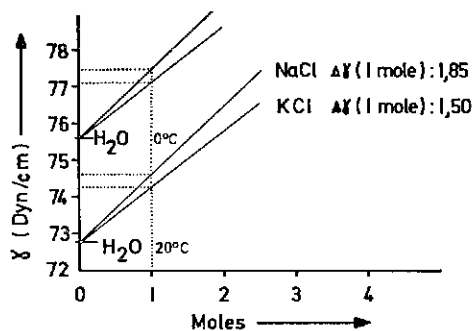


Fig. 4. Surface tension of NaCl and KCl in water at 20° and 0°C in mole/l.

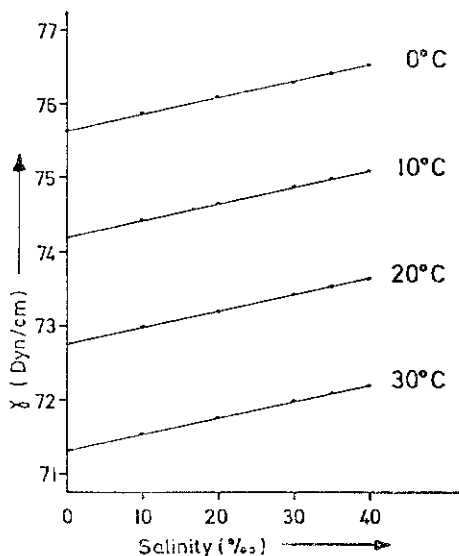


Fig. 5. Dependence of surface tension on salinity of sea water at different temperatures.

RESULTS AND DISCUSSION

Bubble experiments made under equilibrium conditions yield results closely following the Gibbs absorption theorem.

NaCl is impoverished by 73% in the spray and KCl by 60%. This leads to essentially the same relative enrichment of KCl against NaCl in the spray at all temperatures investigated (20°C, 80°C and 100°C).

$$\frac{\Gamma_{NaCl}}{\Gamma_{KCl}} = \frac{\delta\gamma_{NaCl}}{\delta\gamma_{KCl}} = \frac{1 - C_{spray NaCl}}{1 - C_{spray KCl}} = 1.23 \quad (\text{from literature; Fig. 4})$$

$$\frac{C_{spray NaCl}}{C_{spray KCl}} = 0.66 \quad (\text{our experiments; Fig. 6; 100% humidity})$$

However the ratio changes do not conform with the Gibbs theorem when equilibrium conditions are not carefully maintained, i.e., when the surface of the bubble is either evaporating or water condenses on it (McBain & Swain, 1936). We have investigated this at different temperatures and found that under evaporating conditions the ratio $C_s NaCl / C_s KCl$ in the bubble spray is reduced considerably. The resulting relative enrichment in KCl is shown in Fig. 6 for different relative humidities in the gas phase above the breaking bubbles. One can consequently expect that in nature, rain and dew are especially KCl enriched, as opposed to NaCl, when the salts originate from the ocean surface under conditions of low relative humidity in the air.

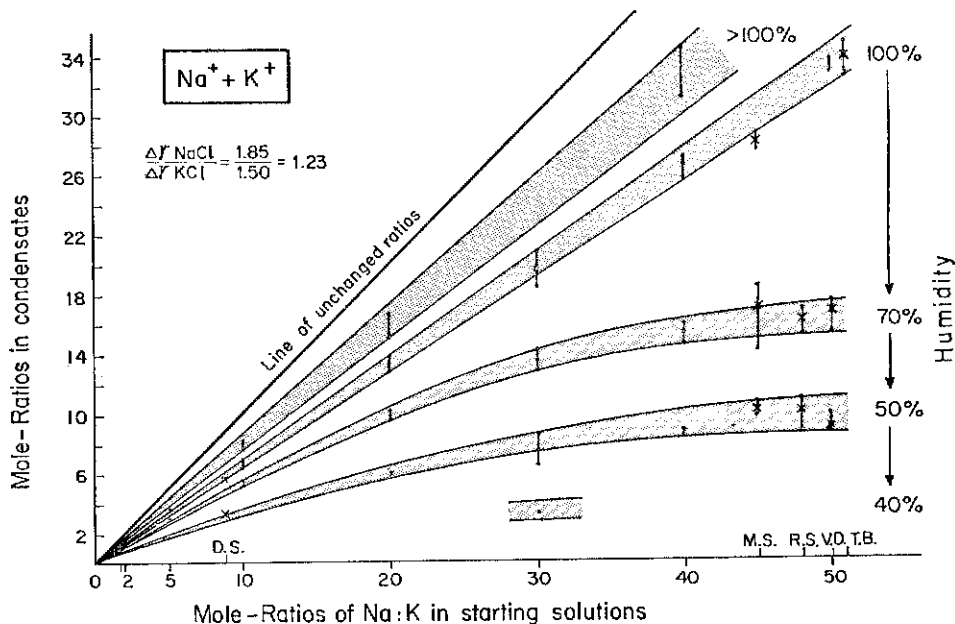


Fig. 6. Mole ratios in starting solutions (NaCl + KCl in natural and artificial liquids) against mole ratios in their condensates (and spray) under different conditions:

> 100%: condensing condition with supersaturated water vapor (liquid and vapor not in equilibrium).

100%: equilibrium, i.e., saturated water vapor (liquid and vapor at 100°C).

< 100%: evaporating condition with undersaturated water vapor of different degree (liquid and vapor not in equilibrium).

D.S.: Dead Sea, Sedom (37.30 g Na + 7.21 g K/liter.)

R.S.: Red Sea, Elat (13.4 g Na + 0.473 g K/liter.)

T.B.: Tap water, Be'er Sheva' (0.12 g Na + 0.004 g K/liter.)

M.S.: Mediterranean Sea, Gaza (12.1 g Na + 0.456 g K/liter.)

V.D.: Vapor dilution by hot, dry air (all artificial starting solutions contained 0.1–0.2 m Na).

When investigating how salts, other than NaCl and KCl, follow the Gibbs absorption theorem we found that NH_4Cl is apparently a significant exception. The enrichment of NH_4Cl as compared to NaCl and the other salts is considerably greater than can be expected from its surface tension-concentration gradients; in Fig. 3 it can be seen that δ_{ν}/δ_C of NH_4Cl is 1.3. Although this leads us to expect a smaller impoverishment in the surface of its solution than that of all other salts, it does not predict an enrichment of three orders of magnitude as we found under apparent equilibrium conditions (Fig. 7). However if we decrease the humidity and introduce evaporating conditions during bubble breaking we are reducing the enrichment of NH_4^+ , as can also be seen in Fig. 7. Salt solutions other than that of NH_4Cl have their salt ratio change enhanced by evaporation;

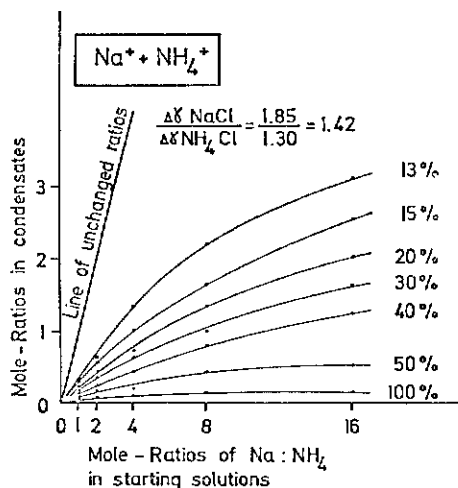


Fig. 7. Mole ratios in starting solutions (NaCl + NH₄Cl) against mole ratios in their condensates (and spray) at boiling temperature (liquid and vapor in equilibrium = 100% saturated water vapor) and under evaporating conditions with undersaturated water vapor (liquid and vapor not in equilibrium).

evaporation before bubble breaking causes a continuous renewal of the skin by solution which has already undergone salt ratio changes according to the Gibbs theorem.

Of all the salts we investigated, only NH₄Cl showed the reverse behavior; the relative enrichment of this salt diminishes under evaporative conditions compared with NaCl; this happens although with higher concentration, NH₄Cl increases the surface tension of water less than NaCl.

The explanation for this extraordinary phenomenon is the hydrolysis which it undergoes when forming NH₄OH and HCl, both products reducing the surface tension of water with rising concentration (Fig. 3). This means that the products of hydrolysis are not only less impoverished compared with NaCl but are actually absorbed and enriched at the surface.

NH₄OH reduces the surface tension of water more than HCl (Fig. 3) and should consequently be of a higher concentration at the surface than is HCl and thus raise its pH. We have found that this is indeed the case. Figure 8 shows how the salt ratio and the pH changes in the course of a distillation experiment when air is bubbled through a NH₄Cl-NaCl-solution at 20°-40°C. The experiments were conducted under condensing conditions by constantly adding supersaturated, hot steam to the surface of the bubbling solutions (Fig. 2, II).

The pH of the condensates is very high at the beginning of the experiments and that of the starting solutions rather low; as the distillation continues the condensate becomes more acidic because of increasing HCl- quantities (hydrolysis) in the starting liquid.

The mole ratios of Na⁺ : NH₄⁺ in bubbling solutions > 5000 change in the condensates to < 10. The grey areas in the diagram (Fig. 8) represent the extent

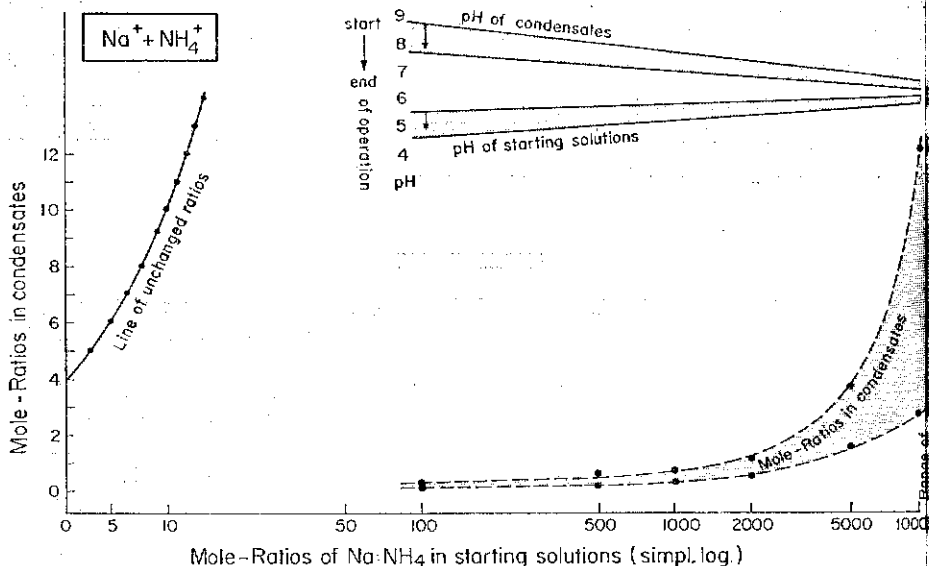


Fig. 8. Mole ratios in starting solutions ($\text{NaCl} + \text{NH}_4\text{Cl}$) against mole ratios in the condensates (and spray) under condensing condition with supersaturated water vapor. Liquid ($20\text{--}40^\circ\text{C}$) and vapor (100°C) in equilibrium.

of the experimental error; any change caused by temperature variations in our experiments ($20\text{--}40^\circ\text{C}$ and $70\text{--}90^\circ\text{C}$ in the starting solutions) are well inside these areas. This means that the hydrodynamic behavior of bubbles at different temperatures does not influence the effect in a significant way.

According to our experiments we have to expect that ocean water spray which is formed under conditions of high humidity, of water-saturated air, should contain three orders of magnitude more NH_4^+ ions than ocean water from which it derives. Ocean water contains 10^{-1} ppm NH_4^+ and, correspondingly, spray will have 10^2 ppm NH_4^+ which explains the values found in snow and rain.

Conditions of condensation rather than evaporation prevail at the Chilean and South West African coasts where cold polar ocean water wells up; there the humid air is cooled by the cold ocean water below dew point, thus forming cloud droplets, i.e., a dense mist, which is driven inland by the prevailing westerlies. This mist contains the salt water spray from the sea and it carries the salts contained in this spray to the high ridges inland where they are deposited as salty dew.

It is well known that this salty deposit contains nitrates which are finally transported by seasonal rains into the nitrate deserts. We propose that the ammonia which we suppose according to our experiments is in the mist droplet is oxidized to nitrate under the influence of light and ozone previously formed

in the atmosphere. Since a deficit of anions should result from the hydrolysis before bubble breaking the finally formed nitrates might well be neutral.

The formation of nitrate deposits seems to be the most spectacular result of the ammonium chloride separation mechanism which we propose; a more important aspect of it is that this mechanism might be generally responsible for most of the supply of fixed nitrogen to plant life.

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